

Carnot Engines and the Principle of Increase of Entropy

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Abstract

On the basis of an axiomatization of classical thermodynamics given in a previous paper, the existence of Carnot engines is established, and used to prove rigorously the principle of increase of entropy and Clausius' inequality for compound systems.

1. Introduction

In an earlier paper (Boyling, 1972) hereafter referred to as I, an axiomatic formulation of classical thermodynamics was proposed, which was essentially a rigorous version of that of Carathéodory (Carathéodory, 1909). On the basis of the postulates laid down in I, we shall here prove the existence of Carnot engines, and hence deduce the principle of increase of entropy for compound systems in full generality (i.e. without the restrictions imposed in I).

Carnot engines are constructed in Section 2, the procedure being to start with simple Carnot engines capable of executing small Carnot cycles between pairs of almost equal temperatures, and then to build up out of these compound Carnot engines of arbitrary power working between arbitrary pairs of temperatures.

In Section 3 the principle of increase of entropy for compound systems is proved with the aid of two further assumptions about the relation of adiabatic accessibility. An indirect method of proof is used, in which it is assumed that the compound system M can undergo an adiabatic transition from a state x to a state y , which is accompanied by a decrease in entropy. A contradiction is established by imagining M to pass from x to y via a sequence of small quasi-static transitions, during each of which a particular simple component of M can be in thermal equilibrium with some thermometer (I). The resulting transition of the product system consisting of M and all of these thermometers is adiabatically impossible, but can nevertheless be achieved by making M perform the postulated adiabatic transition from x to y while the thermometers undergo a transition which is shown to be adiabatically possible by considering an associated transition in which they are thermally coupled with a number of Carnot engines.

In Section 4 the principle of increase of entropy is used to prove a form of Clausius' inequality.

The definitions and notations of I are employed throughout.

2. The Existence of Carnot Engines

The existence of entropy and absolute temperature as differentiable functions was established in I on the basis of postulates I-V of that paper. Explicitly, if M is a simple system, whose (equilibrium) states form a connected C^∞ differentiable manifold (also denoted by the symbol M), then the entropy S_M and absolute temperature T_M are C^∞ functions on the C^∞ manifold M .

If the simple system M is of the special type known in I as a thermometer, then postulate V(e) of I implies that every point (i.e. state) x of M may be surrounded by a standard coordinate neighbourhood V , i.e. an open rectangular coordinate neighbourhood on which S_M and T_M are two of the local coordinates. It is therefore clear that in this case M can be taken round a small Carnot cycle within V by keeping the coordinates other than S_M and T_M fixed and making it describe a rectangle in the (S_M, T_M) plane. However, our postulates do not guarantee that M can perform a Carnot cycle whose isothermals have widely separated temperatures. To obtain a Carnot engine to work between an arbitrary pair of temperatures, it is necessary to consider a compound system consisting of a whole 'battery' of infinitesimal Carnot engines of the above type.

Let T' and T'' be any two absolute temperatures satisfying $0 < T' < T''$. Given a point T^* of the closed interval $[T', T'']$, there exists a thermometer M^* , a state x^* of M^* such that $T_{M^*}(x^*) = T^*$, and a standard neighbourhood V^* of x^* in M^* . The open intervals $I^* = T_{M^*}(V^*)$ for varying T^* constitute an open covering of the topological space $[T', T'']$. Since $[T', T'']$ is compact, it can be covered by a finite number of these intervals, and we may assume without loss of generality (by eliminating some of the intervals if necessary) that this finite covering consists of a finite sequence of intervals $I_1^*, I_2^*, \dots, I_n^*$ satisfying

$$\begin{aligned} T' &\in I_1^*, & T'' &\in I_n^* \\ T_j^* &\in I_j^* \cap I_{j+1}^* & \text{for } j &= 1, 2, \dots, n-1 \end{aligned}$$

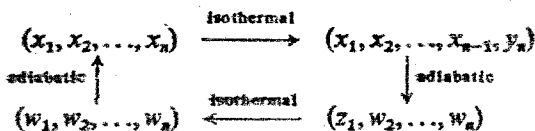
where

$$T' = T_0^* < T_1^* < \dots < T_{n-1}^* < T_n^* = T''$$

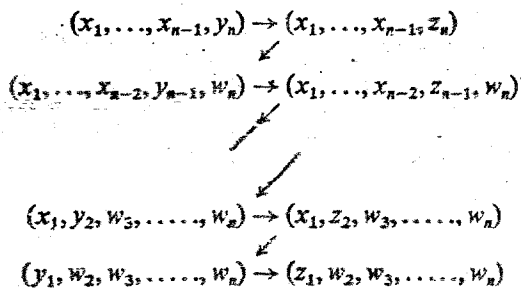
Let M_j be the thermometer corresponding to the interval I_j^* , V_j the corresponding standard neighbourhood, and let ΔS be any positive number smaller than the length of the smallest of the open intervals $S_j(V_j)$ for $j = 1, \dots, n$, where S_j is the entropy of M_j . Then clearly M_j can perform quasi-statically a small Carnot cycle between the temperatures T_{j-1}^* and T_j^* in which the entropy difference between the two adiabatics is ΔS . All that is necessary is to send M_j round the rectangle $x_j y_j z_j w_j$ in the

(S_j, T_j) plane, keeping the other standard local coordinates on V_j all fixed, where the states x_j, y_j, z_j and w_j correspond to the points $(S_j^*, T_j^*), (S_j^* + \Delta S, T_j^*), (S_j^* + \Delta S, T_{j-1}^*)$ and (S_j^*, T_{j-1}^*) of the (S_j, T_j) plane. By suitably combining these cycles for the M_j , we can now make the product system $M = M_1 \times M_2 \times \dots \times M_n$ (i.e. the system consisting of the M_j separated by adiabatic partitions) perform a Carnot cycle between the temperatures T' and T'' .

The Carnot cycle for the compound system M begins and ends with the state (x_1, x_2, \dots, x_n) and proceeds quasi-statically as follows:



The two isothermal transitions each involve only one of the subsystems M_j . In one the subsystem M_n , which we call the *head* of the Carnot engine M , proceeds isothermally from the state x_n to the state y_n at temperature T'' , absorbing heat $T'' \Delta S$ in the process. In the other the subsystem M_1 , which we call the *foot*, proceeds isothermally from the state z_1 to the state w_1 at temperature T' , giving out heat $T' \Delta S$ in the process. The adiabatic transition from (w_1, \dots, w_n) to (x_1, \dots, x_n) is the transition in which each M_j passes quasi-statically and adiabatically from w_j to x_j in the obvious way. The other adiabatic transition is more complicated, and consists of the following sequence of quasi-static adiabatic transitions:



The horizontal arrows here represent adiabatic transitions in which only one of the M_j takes part. The oblique arrows represent transitions in which two of the M_j exchange heat quasi-statically and isothermally, while the rest of the M_j remain unchanged. These transitions are also adiabatic since they proceed at a constant entropy value for the simple system which is the sum (I) of the two M_j involved. This is also physically obvious, since the transitions involve no heat exchange between M and the outside world.

Thus we have built up a cycle for M consisting of two isothermal transitions at temperatures T' and T'' separated by two adiabatic transitions, i.e. a Carnot cycle between the temperatures T' and T'' . In the course of this cycle, the Carnot engine M absorbs a net amount of heat $(T'' - T') \Delta S$

and performs an equivalent amount of useful external work. We can increase the power of the engine by a factor k by replacing each M_j by the sum of M_j with itself k times, i.e. the simple system consisting of k copies of M_j separated by diathermic partitions. For this has the effect of multiplying ΔS by a factor k . Since the original ΔS can be as small as we please, this means in effect that we can achieve any desired value of ΔS , i.e. construct a Carnot engine of arbitrary power operating between the temperatures T' and T'' .

Since the whole cycle is quasi-static and therefore reversible, we can put it into reverse and so make M act as a refrigerator, in which the work $(T'' - T')\Delta S$ is used to extract heat $T'\Delta S$ from a body at temperature T' and supply heat $T''\Delta S$ to a body at the higher temperature T'' .

It is perhaps unnecessary to add that the Carnot cycle constructed above is by no means unique, nor is the engine M that performs it.

3. The Principle of Increase of Entropy

Before we proceed any further, we must introduce two further assumptions about the relation \leq of adiabatic accessibility:

- (i) Let M and N be any two thermodynamic systems, x and y any two states of M , and z any state of N . Then $(x, z) \leq (y, z)$ for the product system $M \times N$ if and only if $x \leq y$ for M .
- (ii) Let M_1, M_2, \dots, M_n be mutually compatible simple systems (i.e. simple systems capable of coexisting at the same temperature), x_i and y_i states of M_i such that $x_1 \sim x_2 \sim \dots \sim x_n$ and $y_1 \sim y_2 \sim \dots \sim y_n$ (where \sim denotes the equality of temperature, as in I). Then $(x_1, \dots, x_n) \leq (y_1, \dots, y_n)$ for the product system $\prod_{i=1}^n M_i$ (in which the M_i are separated by adiabatic partitions) if and only if $(x_1, \dots, x_n) \leq (y_1, \dots, y_n)$ for the sum $\sum_{i=1}^n M_i$ (in which the M_i are separated by diathermic partitions).

The 'if' parts of both of these assumptions were already made in I. The 'only if' part of (i) seems physically reasonable, and has already been used by Cooper (1967). The 'only if' part of (ii) amounts to allowing the temporary insertion of internal adiabatic partitions in the course of an adiabatic transition, provided the insertion and subsequent removal occur while the temperature of the system is uniform. Since the insertion and removal processes are purely 'mechanical', this is evidently in accordance with the usual interpretation of the word, 'adiabatic' (Buchdahl, 1966).

We now define a new relation $<$ on the states of an arbitrary thermodynamic system M in terms of the relation \leq as follows:

$$x < y \quad \text{if and only if} \quad x \leq y \quad \text{and} \quad y \not\leq x$$

Clearly $<$ is transitive. For suppose $x < y$ and $y < z$. Then $x \leq z$ by the transitivity of \leq . On the other hand $z \not\leq x$. For suppose on the contrary

that $z \leq x$. Then, since $x \leq y$, we should have $z \leq y$, contradicting $y < z$. Thus $x < z$.

We now deduce, as an immediate consequence of assumption (i), the following lemma and its corollary:

Lemma 1

Let M and N be any two thermodynamic systems, x and y any two states of M , and z any state of N . Then $(x, z) < (y, z)$ for $M \times N$ if and only if $x < y$ for M .

Corollary

Let M_1, \dots, M_n be thermodynamic systems, x_i and y_i states of M_i satisfying $x_i < y_i$ ($i = 1, \dots, n$). Then the states $x = (x_1, \dots, x_n)$ and $y = (y_1, \dots, y_n)$ of the product system $M = \prod_{i=1}^n M_i$ satisfy $x < y$.

The corollary follows from the lemma via the sequence of inequalities:

$$(x_1, \dots, x_n) < (y_1, x_2, \dots, x_n) < (y_1, y_2, x_3, \dots, x_n) < \dots < (y_1, \dots, y_{n-1}, x_n) < (y_1, \dots, y_n)$$

We likewise deduce from assumption (ii) the following lemma:

Lemma 2

Let M_1 be a simple system, M_2, \dots, M_n thermometers such that M_1, M_2, \dots, M_n are mutually compatible, x_i and y_i states of M_i such that $x_1 \sim x_2 \sim \dots \sim x_n$ and $y_1 \sim y_2 \sim \dots \sim y_n$. Then $(x_1, \dots, x_n) < (y_1, \dots, y_n)$ for $\prod_{i=1}^n M_i$ if and only if $\sum_{i=1}^n S_i(x_i) < \sum_{i=1}^n S_i(y_i)$, where S_i is the entropy of M_i .

To prove this, one has merely to observe that the entropy of the simple system $\sum_{i=1}^n M_i$ is an empirical entropy (Buchdahl, 1966) for that system.

It is evident that lemma 2 would still hold if assumption (ii) were taken to apply only to the special case where M_2, \dots, M_n are all thermometers (so that $\sum_{i=1}^n M_i$ is a simple system). However, there seems to be no good physical reason for weakening (and thereby complicating) assumption (ii) in this way.

We are now in a position to prove the principle of increase of entropy in the following form:

Theorem

Let M be a compound system, i.e. a system of the form $M = \prod_i M_i$, where the M_i are all simple. Then, if x and y are states of M satisfying $x \leq y$, the entropies of these two states must satisfy $S(x) \leq S(y)$.

Proof

Suppose on the contrary that $x \leq y$ but that $S(y) < S(x)$, i.e. that

$$\sum_i S_i(y_i) < \sum_i S_i(x_i)$$

where S_i is the entropy of M_i , and x_i and y_i are the states of M_i corresponding to the states x and y of M . Then

$$\Delta S = \sum_i \Delta S_i < 0$$

where

$$\begin{aligned} \Delta S &= S(y) - S(x) \\ \Delta S_i &= S_i(y_i) - S_i(x_i) \end{aligned}$$

We shall prove the theorem by showing that the above supposition leads to a contradiction.

First we observe that, as M_i is connected, there exists (see e.g. Hocking & Young, 1961, Theorem 3-4, p. 108) a finite family of open sets V_{ij} and points p_{ij} in M_i such that $x_i \in V_{i1}$, $y_i \in V_{im}$, $p_{ij} \in V_{ij} \cap V_{i,j+1}$ ($j = 1, \dots, m_i - 1$), where within each V_{ij} the absolute temperature T_i of M_i lies in the temperature range of a standard neighbourhood W_{ij} of some thermometer M_{ij} .

Now, by hypothesis,

$$\sum_{ij} \Delta S_{ij} = \sum_i \Delta S_i < 0$$

where

$$\begin{aligned} \Delta S_{ij} &= S_i(p_{ij}) - S_i(p_{i,j-1}) \quad (j = 1, \dots, m_i) \\ p_{i0} &= x_i, \quad p_{im_i} = y_i \end{aligned}$$

We can therefore choose quantities $\Delta S'_{ij}$ satisfying

$$\sum_{ij} \Delta S'_{ij} = 0$$

and

$$\Delta S_{ij} + \Delta S'_{ij} < 0 \quad \text{for all } i \text{ and } j$$

e.g. we could take

$$\Delta S'_{ij} = -\Delta S_{ij} + m^{-1} \sum_{ij} \Delta S_{ij}$$

where

$$m = \sum_i m_i$$

By replacing M_{ij} by the sum of several copies of itself, we can widen the standard neighbourhood W_{ij} in the entropy direction to any desired extent. We may therefore assume without loss of generality that M_{ij} possesses three states x_{ij} , y_{ij} and z_{ij} in W_{ij} satisfying

$$\begin{aligned} T_{ij}(x_{ij}) &= T_{ij}(z_{ij}) = T_i(p_{i,j-1}) \\ T_{ij}(y_{ij}) &= T_i(p_{ij}) \\ S_{ij}(y_{ij}) &= S_{ij}(z_{ij}) = S_{ij}(x_{ij}) + \Delta S'_{ij} \end{aligned}$$

Thus

$$x_{ij} \sim p_{i,j-1}, \quad y_{ij} \sim p_{ij}$$

and

$$\begin{aligned} S_i(p_{ij}) + S_{ij}(y_{ij}) &= S_i(p_{i,j-1}) + S_{ij}(x_{ij}) + \Delta S_{ij} + \Delta S'_{ij} \\ &< S_i(p_{i,j-1}) + S_{ij}(x_{ij}) \end{aligned}$$

Therefore, by lemma 2, $(p_{ij}, y_{ij}) < (p_{i, j-1}, x_{ij})$ for the system $M_i \times M_{ij}$, and hence, by lemma 1,

$$(p_{ij}, y_{ij}, \dots, y_{ij}, x_{i, j+1}, \dots, x_{im_i}) < (p_{i, j-1}, y_{ij}, \dots, y_{i, j-1}, x_{ij}, \dots, x_{im_i})$$

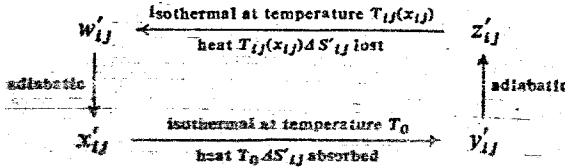
for $M_i \times \prod_j M_{ij}$. Since this holds for $j = 1, \dots, m_i$, we may use the transitivity of the relation $<$ to deduce that

$$(y_i, y_{i1}, \dots, y_{im_i}) < (x_i, x_{i1}, \dots, x_{im_i})$$

for $M_i \times \prod_j M_{ij}$. It then follows by the corollary to lemma 1 that $(y, \bar{y}) < (x, \bar{x})$ for $M \times \bar{M}$, where $\bar{M} = \prod_{ij} M_{ij}$, and \bar{x} and \bar{y} are the states of \bar{M} for which M_{ij} is in the state x_{ij} and y_{ij} respectively (for all i and j).

We shall now obtain a contradiction, by showing that in fact $(x, \bar{x}) \leq (y, \bar{y})$. Since $x \leq y$ for M by hypothesis, it will suffice to show that $\bar{x} \leq \bar{y}$ for \bar{M} .

To do this we introduce for each i and j a Carnot engine M'_{ij} capable of executing a Carnot cycle between the temperature $T_{ij}(x_{ij})$ and some fixed temperature T_0 less than all of the $T_{ij}(x_{ij})$, the entropy difference between the adiabatics of the cycle being precisely $\Delta S'_{ij}$. Explicitly, we assume that the cycle proceeds as follows:



(with an obvious change of wording in the event that $\Delta S'_{ij}$ is negative).

We now prove that $(\bar{x}, z) \leq (\bar{y}, z)$ for the system $\bar{M} \times M'$, where $M' = \prod_{ij} M'_{ij}$ and z' is the state of M' for which M'_{ij} is in the state z'_{ij} .

Firstly, $(\bar{x}, z') \leq (\bar{z}, w')$ (in an obvious notation), since the product (or sum) of M_{ij} with the head of M'_{ij} has the same entropy in these two states. Physically, an adiabatic transition between these two states may be realised by allowing transfer of heat between each M_{ij} and the head of the corresponding M'_{ij} (the other simple components of M'_{ij} remaining unchanged).

Secondly, $(\bar{z}, w') \leq (\bar{z}, x')$, since $w'_{ij} \leq x'_{ij}$ for each M'_{ij} .

Thirdly, $(\bar{z}, x') \leq (\bar{z}, y')$, since $x' \leq y'$ for M' . To see this, note that only the feet of the M'_{ij} change state in the transition from x' to y' , that these are all at temperature T_0 in both states, and that the net entropy difference between the two states is $\sum_{ij} \Delta S'_{ij} = 0$. Thus the transition can be achieved adiabatically for the sum, and therefore also (by assumption (ii)) for the product of the feet, and hence for the whole system M' . Physically, we could arrange that the Carnot engines performed their $T = T_0$ isothermals simultaneously with their feet in thermal contact, their individual rates being mutually adjusted in such a way that no heat ever passed between M' and the outside world. This is possible since the net absorption of heat in the transition is $T_0 \sum_{ij} \Delta S'_{ij} = 0$.

Fourthly, $(\bar{z}, y') \leq (\bar{y}, z)$, since $z_{ij} \leq y_{ij}$ for M_{ij} and $y'_{ij} \leq z'_{ij}$ for M'_{ij} .

By the transitivity of \leq , it therefore follows that $(\bar{x}, z) \leq (\bar{y}, z)$ for $\bar{M} \times M'$. We deduce at once from assumption (i) that $\bar{x} \leq \bar{y}$ for \bar{M} , and hence that $(x, \bar{x}) \leq (y, \bar{y})$ for $M \times \bar{M}$, contradicting $(y, \bar{y}) < (x, \bar{x})$.

Thus the assumption that $S(y) < S(x)$ has led to a contradiction, and we can only conclude that $S(x) \leq S(y)$, as in the theorem.

4. Clausius' Inequality

Consider a cyclic transition of a compound system M in which it begins and ends in a certain definite state x . The transition is not necessarily quasi-static, so the state of M will not in general be well-defined at intermediate stages. However, we assume that the transition may be parametrised by a real parameter t running from 0 at the start to 1 at the finish, in such a way that the rate of heat intake dQ/dt is well-defined and continuous for $0 \leq t \leq 1$ (except possibly for a finite number of exceptional values of t).

We further assume that this heat is at any given stage being absorbed from or given out to some simple component of an auxiliary compound system M_1 , which executes in the process a *quasi-static* (but in general non-cyclic) transition, represented by a piece-wise smooth curve γ_1 in M_1 . This assumption is physically reasonable if M_1 consists of a number of heat reservoirs whose thermal capacity greatly exceeds that of M . The transition of the product system $M \times M_1$ may then be too rapid for M to be always in thermodynamic equilibrium but nevertheless slow enough for the equilibrium of the large heat reservoirs of M_1 never to be seriously disturbed.

Since M exchanges all of its heat with M_1 , the combined transition of $M \times M_1$ will be adiabatic, and will therefore result in a net increase in entropy (in the wide sense). As the entropy of M is the same at start and finish, the entropy S_1 of M_1 must therefore have increased in the course of the transition, i.e. $\Delta S_1 \geq 0$.

Since the combined transition of $M \times M_1$ is adiabatic, we must have

$$\frac{dQ}{dt} + T_1 \frac{dS_1}{dt} = 0$$

at (almost) any instant, where T_1 is the absolute temperature of the simple component of M_1 with which M is exchanging heat at that instant. Thus

$$\frac{1}{T_1} \frac{dQ}{dt} = - \frac{dS_1}{dt}$$

and

$$\int_0^1 \frac{1}{T_1} \frac{dQ}{dt} dt = -\Delta S_1 \leq 0$$

which is a form of Clausius' inequality.

It is important to realise that T_1 is not the instantaneous temperature of M (which is not in general well-defined for $0 < t < 1$, even when M is simple), but that of the simple system with which it is instantaneously exchanging heat.

We also remark that the inequality does not automatically reduce to an equality when the cyclic transition of M is quasi-static, and therefore (according to our assumptions) reversible. In this case the transition is represented by a (piece-wise smooth) closed curve γ in M , and we may write $dQ/dt = \psi(\dot{\gamma})$ almost everywhere, where ψ is the heat form (I) of M , so that Clausius' inequality takes the form

$$\oint_{\gamma} \frac{\psi}{T_1} < 0$$

It is now tempting to conclude that the left-hand side must vanish, since the same inequality may be applied to the reverse of the transition γ . This argument fails because the reversal of γ is in general accompanied by a change in the function T_1 , which is not a function of state of M but a function depending on the path γ and only defined on γ .

As an example, consider an isometric (Buchdahl, 1966) quasi-static cyclic transition $\gamma(t)$ of a simple system M , in which its absolute temperature rises monotonically from T' to T'' as t increases from 0 to $\frac{1}{2}$, and then falls monotonically from T'' back to T' as t increases from $\frac{1}{2}$ to 1. For the transition γ , we must have $T_1 > T$ for $0 < t < \frac{1}{2}$ (when M is absorbing heat) but $T_1 < T$ for $\frac{1}{2} < t < 1$ (when M is losing heat); where T is the instantaneous absolute temperature of M . On the other hand, for the reverse transition $\dot{\gamma}$ defined by $\dot{\gamma}(t) = \gamma(1-t)$, we must have $T_1 > T$ for $0 < t < \frac{1}{2}$ (corresponding to the part of γ on which $\frac{1}{2} < t < 1$) and $T_1 < T$ for $\frac{1}{2} < t < 1$ (corresponding to the part of γ on which $0 < t < \frac{1}{2}$). Thus $T_1(t)$ is not the same function as $T_1(1-t)$,

$$\oint_{\gamma} \frac{\psi}{T_1} + \oint_{-\dot{\gamma}} \frac{\psi}{T_1} \neq 0$$

and there is no contradiction in having both integrals negative.

Thus Clausius' inequality cannot in general be reversed, even when the transition of M is quasi-static. This is because, although the associated transition of the combined system $M \times M_1$ is then quasi-static and therefore reversible, its reverse is not in general adiabatic (since it may involve a decrease in entropy).

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