

# A New Statement of the Second Law of Thermodynamics

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A new statement of the second law of thermodynamics is given. The law leads almost effortlessly, for very general closed systems, to a definition of absolute entropy  $S$ , a demonstration that  $\Delta S \geq 0$  in adiabatic processes, a definition of temperature, and a demonstration that  $dS \geq \delta Q/T$  along quasistatic processes. Entropy is given a clear physical meaning.

"One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity."

J. W. Gibbs

**1. Introduction.** The second law is at the center of thermodynamics. The law has many formulations.<sup>1</sup> It is usually expressed in physical terms. The most common forms are those of Kelvin, Clausius, and Carathéodory. Kelvin's form  $\Pi_K$  states:

It is impossible for a cyclic process of a thermodynamic system to transfer positive heat from a heat source, deliver positive work, and produce no other effect.  $(\Pi_K)$

The existence of entropy  $S$  as a function of state is deduced from this law. Entropy has two fundamental properties:  $\Delta S \geq 0$  for adiabatic processes and  $dS \geq \delta Q/T$  for quasistatic processes. The existence and two properties of entropy are indispensable, for they, and not the second law directly, are used to obtain the results of thermodynamics.

Another approach is that of Tisza and of Callen, who *postulate* the existence of an entropy with certain properties.<sup>2</sup>

This paper offers a new statement of the second law, proves the existence and fundamental properties of entropy from it, and compares the development here with those of others. I see these positive features of the present approach:

- It is general. We discuss here the *equilibrium* thermodynamics of *closed* systems. Every other approach to this thermodynamics of which I am aware makes, in addition to some statement of the second law, auxiliary assumptions which *restrict* the generality of the systems to which it applies. Sometimes the assumptions are made explicitly and sometimes implicitly. Examples are given in §4. With auxiliary assumptions present, one wonders the extent to which results obtained about entropy are dependent on these assumptions. We show that the results are independent of the assumptions.

- It is simple. The proofs of the existence and fundamental properties of entropy take only a few lines in total. Often generality and simplicity are a trade-off; here they occur together.

- It is independent of the notion of empirical or absolute temperature. In fact, we are able to *define* absolute temperature in terms of entropy and dispense entirely with empirical temperatures.

- It gives entropy a simple and direct physical meaning.
- It defines an absolute entropy, rather than only entropy differences.

Our second law has a weakness compared to Kelvin's: Kelvin's can be *directly* supported by pointing out that if it were violated, we could, for example, run a steamship with the ocean as a heat source or build a perpetual motion machine of the second kind, contrary to experience. (Callen's approach shares this weakness.) While this is a *weakness*, it is not a *flaw*: neither Einstein's field equation of general relativity nor the Schrödinger equation of quantum theory have been *directly* supported by experience. Their credibility is based on the correct predictions they make.

Our second law incorporates part of the conventional third law of thermodynamics. This is what makes possible the simplicity and generality of our results about entropy. This indicates that part of the essence of the entropy concept is contained in the third law.

In §2 we give our statement of the second law. The existence and two fundamental properties of entropy follow from it. In §3 we obtain further consequences of the second law. In §4 we explore the relationship between conventional thermodynamics and the approach taken here. We show that our entropy coincides with the entropy based on Kelvin's law  $\Pi_K$ . We also show that conventional thermodynamics implies our second law. Thus the thermodynamics developed here is as secure as conventional thermodynamics. In §5 we discuss the extent to which our approach is more general than others.

**2. The Second Law.** We take as primitive the terms heat, work, state, process, quasistatic process, and reversible process. *State* will always mean *thermodynamic equilibrium state*. *Process* is short for *thermodynamic process*. In a *quasistatic process*, the thermodynamic system moves through a linear continuum of equilibrium states. (This definition is elaborated in §5, under "Coordinates".) A quasistatic process is carried out *reversibly* if a slight change in the forces (thermal and mechanical) driving the process can reverse it. (Slow heating of water by a resistor is an example of a quasistatic *irreversible* process.) Whatever ambiguity these terms suffer, they are commonly used, and it is not the purpose of this paper to clarify them.<sup>3</sup> Note that there has been no mention of temperature – empirical or Kelvin. We will not use any notion of temperature when defining entropy. Instead, we will use entropy to define temperature.

Let  $Z$  be a *closed* (with respect to the transfer of matter) thermodynamical system. In the *most general* thermodynamical process  $P$  of system  $Z$ , heat is transferred to  $Z$ , work is done on  $Z$ , and/or internal constraints of  $Z$  are manipulated. As a result of  $P$ ,  $Z$ 's (equilibrium) state changes from  $A$  to  $B$ . All such thermodynamical processes can be achieved with the arrangement of Fig. 1. The curve for  $P$  is dashed to indicate that  $Z$  need not be in equilibrium during  $P$ , i.e.,  $P$  need not be quasistatic. It is essential to our analysis that there is only one heat source external to  $Z$  for all processes. We use a standard heat source of triple point water. This does not restrict  $P$  in any way: the heat  $Q_P$  transferred to  $Z$  during  $P$  is transferred by the heat transfer device, which also transfers heat  $H_P$  from the heat source and work from a work source as needed. We take it as an empirical fact that there exist heat transfer devices which can so transfer heat, and in fact do so reversibly. The heat transfer device must be returned to its original state at the end of  $P$ . Different devices can be used for different  $P$ 's. Our analysis does not require any bookkeeping of the work delivered to the device or to  $Z$ .

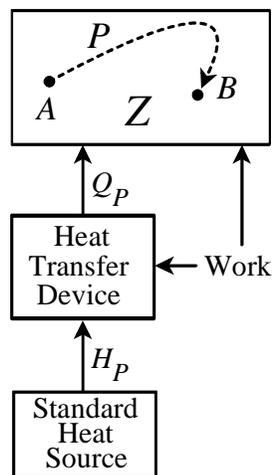


Fig. 1. The most general thermodynamical process  $P$  of  $Z$ .

We give an example.  $Z$  is a cylinder of gas with a piston. The heat transfer device is a Carnot engine operating between the standard heat source and the gas (or perhaps two engines operating independently).  $Q_p$  might alternate between positive and negative values during  $P$ . Work is done on  $Z$  by moving the piston, and/or by dissipating mechanical energy to internal energy, as in Joule's paddle wheel experiment. The cylinder might be separated into two chambers by an internal diathermic wall which is moved or removed during the process.

Before proceeding, we must acknowledge that Kelvin's second law  $\Pi_K$  is not universally true: it fails for negative absolute temperature states. Most thermodynamic systems do not have such states, but nuclear spin systems do.<sup>4</sup> Positive temperature states are characterized (as we shall see) by the property that work can be dissipated in them, as in Joule's paddle wheel experiment, i.e.,

$$\text{A change of state made by delivering positive heat to } Z \text{ can also be made by delivering positive work to } Z. \quad (1)$$

Thus Kelvin's law should read  $(1) \Rightarrow \Pi_K$ , or, more loosely: If mechanical energy can be dissipated to internal energy, then heat cannot be completely converted to mechanical energy. Our second law is also restricted to states satisfying (1).

We now state our version of the second law of thermodynamics:

$$\text{It is impossible to transfer an arbitrarily large amount of heat from a standard heat source with processes terminating at a fixed state of } Z. \quad (\text{II})$$

In other words, for every state  $B$  of  $Z$ ,

$$\text{Sup}\{ H_p : P \text{ terminates at } B \} < \infty. \quad (\text{II})$$

Since (II) holds, we can define the *entropy*  $S(B)$  of state  $B$ :

$$S(B) = \text{Sup}\{ H_p/T_o : P \text{ terminates at } B \}, \quad (2)$$

where  $T_o = 273.16$ . (The temperature of triple point water is defined to be  $T_o$  in the Kelvin temperature scale. But for us, for now,  $T_o$  is just a number, not a temperature. The only reason for introducing  $T_o$  is so our units of entropy and temperature will agree with those of conventional thermodynamics; the entire development below could be made without it.)

Entropy is clearly a function of state.  $S(B)$  has a simple physical meaning: it is the most heat (divided by  $T_o$ ) that can be transferred from a standard heat source in processes terminating at  $B$ . Note that we assign an absolute entropy to a state, not just an entropy difference between states.

Consider a particular process  $P$  from state  $A$  to state  $B$ . Precede  $P$  with any process  $P'$  which terminates at  $A$ . See Fig. 2. Since  $P' + P$  terminates at  $B$ , we see from (2) that

$$H_{p'}/T_o + H_p/T_o \leq S(B). \quad (3)$$

If we take the supremum of (3) over all processes  $P'$  terminating at  $A$ , then by (2) we obtain

$$S(A) + H_p/T_o \leq S(B). \quad (4)$$

If  $H_p = 0$ , then

$$S(A) \leq S(B). \quad (H_p = 0) \quad (5)$$

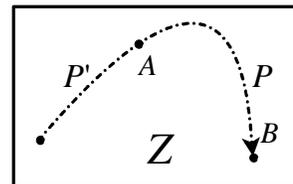


Fig. 2. If  $P$  is adiabatic, then  $S(A) \leq S(B)$ .

If  $P$  is adiabatic, then no heat is transferred to  $Z$ . Thus the heat transfer device need do nothing,  $H_p = 0$ , and (5) holds. We have a simple proof of the first fundamental property of entropy: it does not decrease in an adiabatic process. If  $P$  is a reversible adiabatic process, then also from (5),  $S(B) \leq S(A)$ , and so  $S(A) = S(B)$ .

Our definition of  $S$  did not use a notion of temperature. Intuitively, this was possible because we used the standard heat source as a "common medium of exchange" for the different temperatures of  $Z$  during a process. We now define temperature using  $S$ . Consider an infinitesimal reversible process which transfers heat  $\delta Q$  and no work to  $Z$ . Define the *temperature*  $T$  of  $Z$  by

$$1/T = dS/\delta Q. \quad (6)$$

According to (1), if  $\delta Q > 0$ , then the same state change can be made in an adiabatic process which delivers work to  $Z$ . Since this process is adiabatic,  $dS \geq 0$ . So from (6),  $T > 0$ .

Let  $P'$  be an infinitesimal quasistatic process from state  $C$  to state  $B$  with entropy change  $dS$ . Let  $P''$  be the reversible process from state  $C$  to state  $A$  with the same heat  $\delta Q$  as  $P'$  but with no work done on  $Z$ . See Fig. 3. Consider the process  $P = -P'' + P'$ . During  $-P''$ , heat  $-\delta Q$  is transferred to  $Z$ . During  $P'$ , these transfers are reversed. Thus we may take  $H_p = 0$ , and (5) applies. Using (5) in the form  $S(B) - S(C) \geq S(A) - S(C)$ , and using (6) for  $P''$ ,

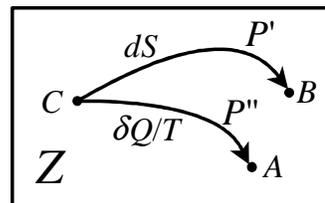


Fig. 3.  $dS \geq \delta Q/T$ .

$$dS \geq \delta Q/T,$$

which is the second fundamental property of entropy. If  $P'$  is reversible, then  $dS = \delta Q/T$ . For a finite reversible quasistatic process,  $\Delta S = \int \delta Q/T$ .

This completes our statement of the second law, definition of entropy and temperature, and derivation of the two fundamental properties of entropy.

**3. Further Consequences of the Second Law.** It is natural to ask: What processes terminating at  $B$  give large  $H$ 's in the definition (2) of  $S(B)$ ? We give two answers.

(i) Let  $P$  and  $R$  be two processes from  $A$  to  $B$ , with  $R$  reversible. Suppose  $H_R < H_P$ . Then for the cyclic process  $-R + P$ ,  $H_{-R+P} = -H_R + H_P > 0$ . Repeating this process over and over, we can make  $H$  as large as we like in processes terminating at  $B$ . This contradicts II. Thus  $H_R \geq H_P$ . If  $P$  is itself reversible, then also  $H_P \geq H_R$ , and so  $H_P = H_R$ . Thus reversible processes from  $A$  to  $B$  (if they exist) all have the same  $H$ , which is the largest  $H$  for processes from  $A$  to  $B$ .

(ii) Let  $P$  be a process from state  $A$  to state  $B$ . Let  $P'$  be a reversible process starting at  $A$  in which the heat transfer device transfers positive heat from  $Z$  to the standard heat source. Then  $-P' + P$  terminates at  $B$ . We have  $H_{-P'+P} = H_{-P'} + H_P$  and  $H_{-P'} = -H_{P'} > 0$ . Thus

$$H_{-P'+P} > H_P. \quad (7)$$

According to (7), we obtain a larger  $H$  (i.e.,  $H_{-P'+P}$ ) than  $H_P$  if we reversibly transfer positive heat from  $Z$  before starting.

If absolute zero is unattainable in the sense that from every state of  $Z$  (no matter how cold) there is a reversible process  $P'$  which transfers positive heat from  $Z$ , then (7) shows that the Sup in the definition (2) of  $S(B)$  is not attained.<sup>5</sup> (Analogously,  $\text{Sup}\{x: 0 \leq x < 1\}$  exists, but it is not attained.)

A *compound system*  $Z = (Z_1, Z_2)$  is a thermodynamic system composed of *subsystems*  $Z_1$  and  $Z_2$ , separated by a wall. The subsystems must themselves be thermodynamic systems in the sense of this paper. In particular, they must be closed. Thus the wall must not allow the transfer of matter. During a process of  $Z$ , the wall can be adiabatic or diathermic, or alternate between the two. The wall can, e.g., divide a container of gas into two parts. During a process it can be fixed or movable, or alternate.

States of  $Z$  are of the form  $B = (B_1, B_2)$  where  $B_i$  is a state of  $Z_i$ . These states have an entropy,  $S(B_1, B_2)$ . In addition,  $Z_1$  and  $Z_2$  have their own entropies,  $S_1(B_1)$  and  $S_2(B_2)$ .

We now show that entropy is additive over subsystems:

$$S(B_1, B_2) = S_1(B_1) + S_2(B_2), \quad (\text{Rev}) \text{ assumed}, \quad (8)$$

where the statement (Rev) is:

There is a reversible process between every pair of states of a thermodynamic system. (Rev)

This assumption is commonly made: Authors who define the entropy difference between two states as  $\int \delta Q/T$  along a *reversible* process between the states assume, explicitly or implicitly, (Rev). But it is desirable to find a proof of (8) without (Rev).

Now let  $(A_1, A_2)$  be any state of the compound system  $Z$ . According to (Rev), there are reversible processes  $R_i$  of  $Z_i$  from  $A_i$  to  $B_i$ . If  $R_1$  is followed by  $R_2$ , then  $(R_1, R_2)$  is a reversible process of  $Z$  from  $(A_1, A_2)$  to  $(B_1, B_2)$ , and

$$H_{(R_1, R_2)} = H_{R_1} + H_{R_2}. \quad (9)$$

We noted above that all reversible processes between two given states have the same, and largest,  $H$  for processes between the states. It follows that in determining the Sup in the definition (2) of  $S(B)$ , we need not use *all* processes terminating at  $B$ : we need use only a single reversible process from each starting state  $A$  to  $B$ . Use  $(R_1, R_2)$  as the reversible process from  $(A_1, A_2)$  to  $(B_1, B_2)$  in the definition (2) of  $S(B_1, B_2)$ , and use  $R_i$  as the reversible process from  $A_i$  to  $B_i$  in the definition of  $S(B_i)$ . Then take the Sup over all  $(R_1, R_2)$  in (9) to obtain (8).

Now suppose that  $Z_1$  and  $Z_2$ , with temperatures  $T_1$  and  $T_2 = T_1 + dT > T_1$ , have an adiabatic wall between them. Make the wall momentarily diathermic, and suppose heat  $\delta Q$  transfers spontaneously from  $Z_2$  to  $Z_1$ . We suppose that this transfer is reversible. From (5),  $dS \geq 0$ , as this is an adiabatic process of  $Z$ . From (6),  $dS_1 = \delta Q/T_1$  and  $dS_2 = -\delta Q/T_2$ . And from (8),  $dS = dS_1 + dS_2$ . Putting all this together,  $\delta Q/T_1 - \delta Q/T_2 \geq 0$ . Thus  $\delta Q > 0$ ; positive heat transfers from the system at the higher temperature to that at the lower, in accord with our intuitive understanding of temperature. Note that since (8) was used, this is proved only under the assumption (Rev).

**4. Relationship to Conventional Thermodynamics.** Intuitively, our second law states that there is a limit to how cold  $Z$  can be. We formalized this in II by assuming a limit on  $H$  for processes terminating at a given state  $B$ . We might have instead tried to assume a limit on  $Q$  for processes terminating at  $B$ . But this does not work. To see this, let a Carnot cycle  $R$  of  $Z$  starting and terminating at  $B$  have net heat  $Q_R > 0$ . Repeating  $R$   $n$  times, we have a process with  $Q = nQ_R$ , which can be made arbitrarily large.

We now show that the entropy and temperature based on II are the same as those based on II<sub>K</sub>. Let  $R$  be a reversible process from  $A$  to  $B$ . Applying (4) separately to  $R$  and  $-R$  gives

$$\Delta S_R = S(B) - S(A) = H_R/T_o. \quad (R \text{ reversible}) \quad (10)$$

Considered as a reversible process of  $Z$  + heat transfer device + heat source in Fig. 1,  $R$  is adiabatic. Thus the  $S$  based on  $\Pi_K$  also gives (10). (Remember that we require the heat transfer device to be returned to its original state after  $R$ .) This shows that the entropies based on  $\Pi$  and  $\Pi_K$  have the same entropy differences, which is all that  $\Pi_K$  defines. Note that in the analysis of (10) via our second law,  $T_o$  is, as we have emphasized, just a number, whereas in the analysis of (10) via Kelvin's second law,  $T_o$  is the Kelvin temperature of the standard heat source. The numerical equality of the two  $T_o$ 's ensures the numerical equality of our and Kelvin's entropy.

The definition (6) of  $T$  agrees with the Kelvin temperature scale. For (6) is valid in conventional thermodynamics with the same meanings on the right side for  $dS$  (as we have just seen) and  $\delta Q$ . In particular, we assign temperature  $T_o$  to the standard heat source, in accord with the Kelvin temperature scale.

**Theorem.**  $\Pi \Leftrightarrow (\Pi_K + (S \geq 0))$ . The proof has three parts.

(i)  $\Pi \Rightarrow \Pi_K$ . We obtain the result by showing that  $\neg\Pi_K$  contradicts consequences of  $\Pi$ . Suppose then that a thermodynamic system  $Z_o$  violates  $\Pi_K$ :  $Z_o$  goes through a cycle, transferring positive heat  $Q$  from a heat source  $HS$  at temperature  $T$  and delivering positive work. ( $HS$  is not the standard heat source of Fig. 1. For in general,  $T \neq T_o$ .) Consider this process  $P$  as a process of  $Z_o + HS$ . Then  $P$  is adiabatic, and so  $\Delta S_p \geq 0$ . Assume (Rev).<sup>6</sup> Then as shown above,  $S$  is additive. Thus  $\Delta S_p$  is the sum of the entropy changes of  $Z_o$  and  $HS$ . The entropy change of  $Z_o$  is zero, since it goes through a cycle. The entropy change of  $HS$  is  $-Q/T$ . Thus  $\Delta S_p = 0 + (-Q/T) < 0$ . This contradiction to  $\Delta S_p \geq 0$  establishes  $\Pi_K$ .

(ii)  $\Pi \Rightarrow (S \geq 0)$ . One process in (2) terminating at  $B$  starts at  $B$  and immediately stops, doing nothing. For this process  $H_p = 0$ . Thus  $S(B) \geq 0$  in (2).

(iii)  $(\Pi_K + (S \geq 0)) \Rightarrow \Pi$ . Let  $S_K$  be Kelvin's entropy. Let  $P$  be a process terminating at state  $B$ . Considered as a process of  $Z$  + heat transfer device + heat source,  $P$  is adiabatic. Thus an analysis based on  $\Pi_K$  gives

$$S_K(B) - S_K(A) - H_p/T_o \geq 0,$$

where  $A$  is the starting state of  $P$ . Since  $S_K(A) \geq 0$ ,  $H_p \leq T_o S_K(B)$ . Since this is true for all  $P$  terminating at  $B$ ,  $\text{Sup}\{ H_p: P \text{ terminates at } B \} < \infty$ , which is  $\Pi$ . This completes the proof.

We now discuss the relationship between  $\Pi$  and the third law of thermodynamics.<sup>7</sup> It is convenient to divide the third law into two parts:

$$S \geq 0. \tag{IIIi}$$

$$S(0K) = 0. \tag{IIIii}$$

(As 0K is unattainable,  $S(0K) = 0$  is only an abbreviation for  $S \rightarrow 0$  as  $T \rightarrow 0K$ .)

With this terminology, we can restate our theorem:  $\Pi \Leftrightarrow (\Pi_K + \text{IIIi})$ .

**$\Pi_K$  does not imply IIIi.** For a monatomic ideal gas satisfies  $\Pi_K$ , but violates IIIi: its entropy  $S \rightarrow -\infty$  as  $T \rightarrow 0K$ .<sup>8</sup> In view of our theorem, this means that our second law is stronger than Kelvin's.

**$\Pi$  does not imply IIIii.** To see this, consider glycerol, whose liquid form freezes to a crystalline form at 291K. Liquid glycerol can also be supercooled to a glassy form near 0K. In process  $C$ , start with the crystalline form near 0K and reversibly heat it to the liquid form, arriving at state  $B$ . In process  $G$ , start with the same sample in the glassy form near 0K, and

reversibly heat to state  $B$ . The entropy changes for these processes have been *measured* using  $\Delta S = \int \delta Q/T$ . The result is  $\Delta S_C > \Delta S_G$ .<sup>9</sup>

From (10),  $\Delta S_C > \Delta S_G$  implies that  $H_C > H_G$ . Thus processes which start with crystalline glycerol near 0K contribute larger  $H$ 's to the supremum in the definition (2) of  $S(B)$  than processes which start with glassy glycerol near 0K. This is not a problem for II.

But there is a problem for IIIi. For if  $S(0K, \text{crystalline}) = 0$ , then  $\Delta S_C > \Delta S_G$  implies that  $S(0K, \text{glassy}) > 0$ , violating IIIi. The usual explanation is that since a frozen in atomic disorder in glassy glycerol persists to 0K, glassy glycerol is not "really" in equilibrium, and so one cannot speak of its entropy.<sup>10</sup> I am not entirely happy with the explanation in view of the remarks about equilibrium in Ref. 3. And if glassy glycerol is not in equilibrium, can one speak of its Kelvin temperature, which is defined only for equilibrium states?

Be that as it may, it is entirely consistent with II that there be a substance like glycerol whose glassy form *is* in equilibrium (in the sense of the remarks in Ref. 3) and has  $S(0K, \text{glassy}) > 0$ , violating IIIi. This shows that II does not imply IIIi.

We have seen that a full discussion of IIIi involves the atomic structure of the system, whereas IIIi is independent of microscopic considerations. We might call IIIi the *thermodynamical* part of the third law, and IIIi the *statistical mechanical* part. We can then restate the theorem above by saying that our second law strengthens Kelvin's by incorporating the thermodynamical part of the third law. Our purely thermodynamical second law needs no help from an atomic picture of matter to establish the existence of an absolute entropy and its properties in a simple and general manner. This leaves the delicate  $S(0K) = 0$  statistical mechanical part of the third law as a separate matter.

**5. Auxiliary Assumptions.** As stated in §1, other treatments of entropy use auxiliary assumptions which restrict their generality. We give several examples.

**Coordinates.** Boyling<sup>11</sup> gives the example of two containers of water equipped with pistons and separated by a diathermal wall. Usually three coordinates suffice to specify the state of this system (e.g., the volumes of the two containers and their common temperature), but if the water in both containers is at a triple point, then four coordinates are needed (e.g., the volumes and energies of the two containers, which can be varied independently over a limited range without changing the common temperature of the containers). All definitions of an entropy function using coordinates of which I am aware require a *fixed* number of coordinates to describe the states of the system. These definitions do not assign an entropy to Boyling's system. We do not use coordinates.

Mathematically speaking, a state space with a fixed number of continuous coordinates is a *manifold*. Boyling, and also Cooper,<sup>12</sup> use the more general structure of a *topological space*. Boyling points out that the state space of his example is not a manifold, but is a topological space. Our definition assigns an entropy to his system.

In defining a quasistatic process as a *linear continuum* of states, we have implicitly assumed that our thermodynamical state spaces are topological spaces. For a topological space is the minimal structure necessary to give this meaning: a *linear continuum* of states is a continuous image of a closed interval of the real line (thought of as an interval of time) in the state space.

**Carnot Cycles.** Thomsen and Hartka give the example of water near its temperature of maximum density, where there are "strange" Carnot cycles.<sup>13</sup> For example, there are cycles with one adiabat and one isothermal. Most definitions of absolute temperature use "normal" Carnot cycles, with two adiabats and two isothermals, and tacitly assume that normal, and only normal,

cycles exist. These definitions do not establish that water has an absolute temperature under the conditions of the example. A discussion of entropy based on an absolute temperature restricted in generality is similarly restricted in generality. We do not use Carnot cycles.

**Homogeneity.** Callen assumes that entropy is *homogeneous*, i.e., if (in Callen's terminology)  $X$  is a set of extensive coordinates defining the state of  $Z$ , then for  $\lambda > 0$ ,  $S(\lambda X) = \lambda S(X)$ .<sup>14</sup> Homogeneity is an *approximation*, which is obtained by ignoring "surface effects". We do not make this approximation.

There are two other conditions often discussed in relation to entropy. One is *concavity*:

$$S(\lambda X + (1-\lambda)Y) \geq \lambda S(X) + (1-\lambda)S(Y), \quad 0 \leq \lambda \leq 1.$$

The other is *superadditivity*:

$$S(X + Y) \geq S(X) + S(Y).$$

The idea of superadditivity is that if systems with coordinates  $X$  and  $Y$  are combined, then the total entropy is nondecreasing. Note that this is a different situation than additivity over subsystems (8). In (8), the subsystems retain a separate identity. For superadditivity, the subsystems are combined, destroying the subsystems.

We now show that, assuming (Rev), our entropy is superadditive without using coordinates. Let system  $Z_i$  be in state  $B_i$ ,  $i = 1, 2$ . Let the  $Z_i$  be separated by an adiabatic unmovable wall, forming composite system  $Z$ . Then by the additivity of entropy over subsystems (8),  $Z$  has entropy  $S(B_1, B_2) = S(B_1) + S(B_2)$ . Now remove the wall, allowing the systems to combine. This is an adiabatic process of  $Z$  (which destroys the subsystems), terminating in a state of  $Z$ , which we denote  $B_1 + B_2$ . Since the process is adiabatic,

$$S(B_1 + B_2) \geq S(B_1, B_2) = S(B_1) + S(B_2). \quad (\text{Rev}) \text{ assumed.}$$

This proves superadditivity under the assumption (Rev).

One relationship between superadditivity, concavity, and homogeneity is:<sup>15</sup>

$$(\text{Superadditivity} + \text{Concavity}) \rightarrow \text{Homogeneity.} \quad (11)$$

Since homogeneity is only an approximation and superadditivity holds, it follows from (11) that concavity fails. (Of course entropy is usually approximately concave.)

Note added 1/18/08: H. Touchette has given examples of spin models in which entropy is not concave. ("Simple spin models with non-concave entropies", Am. J. Phys. **76**, 26-30 (2008).)

All this has bearing on the debate as to whether superadditivity or concavity is the key property of entropy.<sup>16</sup> In particular, the claim that "The essence of the second law is concavity"<sup>17</sup> seems too strong.

**Adiabatic Accessibility.** Carathéodory's version of the second law states that in every neighborhood of a state  $A$ , there are states  $B$  not adiabatically accessible from  $A$ . Buchdahl's very elegant development of thermodynamics is explicitly based on the additional assumption that  $A$  must then be adiabatically accessible from  $B$ .<sup>18</sup> Both Boyling and Cooper also make this assumption.<sup>19</sup> But König gives this example:<sup>20</sup> Consider a mixture of hydrogen and oxygen enclosed in a rigid adiabatic chamber. Explode the mixture. Then cool it, reducing its entropy *part* of the way to that of the original mixture. Then neither the original nor final state is adiabatically accessible from the other. And Thomsen has given the example of a cylinder enclosing a gas<sup>21</sup>. The cylinder has a piston which moves with sliding friction. States of the same entropy but with different positions of the piston are not adiabatically connected. We make no

assumptions about adiabatic accessibility. (Landsberg<sup>22</sup> discusses other implicit assumptions of several authors – including Carathéodory – who base their thermodynamics on Carathéodory's axiom.)

Buchdahl's<sup>23</sup> and Zemansky and Dittman's<sup>24</sup> approach are based on the existence of reversible adiabatic surfaces, in which two states are on the same surface if and only if they have the same entropy. Such surfaces do not exist in König's or Thomsen's example.

I thank an anonymous referee for pointing out an error in an earlier version of this paper and for several valuable suggestions.

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<sup>1</sup>See the following for a discussion of the second law. Joseph Kestin, Ed., *The Second Law of Thermodynamics* (Dowden, Hutchinson, and Ross, Stroudsburg, Pennsylvania, 1976). S. R. Montgomery, *Second Law of Thermodynamics* (Pergamon Press, Oxford, 1966). M. Zemansky and R. Dittman, *Heat and Thermodynamics* (McGraw-Hill, New York, 1981), 6th ed. F. O. König, "On the various statements of the second law of thermodynamics", *Surv. Prog. Chem.* **7**, 149-251 (1976). P. T. Landsberg, *Thermodynamics with Quantum Statistical Illustrations* (Interscience, New York, 1961). Landsberg's book is based on Carathéodory's form of the second law.

<sup>2</sup>L. Tisza, *Generalized Thermodynamics* (M. I. T. Press, Cambridge Massachusetts, 1966). H. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, New York 1985), 2nd ed.

<sup>3</sup>See the following for discussions of the primitive terms. O. Redlich, "Fundamental thermodynamics since Carathéodory", *Rev. Mod. Phys.* **40**, 556-563 (1968). H. Erlichson, "Internal energy in the first law of thermodynamics", *Am. J. Phys.* **52**, 623-625 (1984). D. Kivelson and I. Oppenheim, "Work in irreversible expansions", *J. Chem. Ed.* **43**, 233-235 (1966). The notion of equilibrium is particularly difficult. See the following references. H. Callen, Ref. 2, p. 15: "In practice the criterion for equilibrium is circular. *Operationally, a system is in an equilibrium state if its properties are consistently described by thermodynamic theory!*" (Emphasis Callen's.) H. A. Buchdahl, *Concepts of Classical Thermodynamics* (Cambridge University Press, Cambridge, 1966), p. 8: "One may sometimes – strictly speaking, perhaps always – have to assume that a given terminal condition is one of equilibrium, even when the possibility of a direct verification of this assumption is not at hand. In that case subsequent empirical verification of falsification of certain theoretical conclusions, based in part on the assumption, must serve instead." O. Costa de Beauregard and M. Tribus, "Information theory and thermodynamics", *Helv. Phys. Acta*, **47**, 238-247 (1974), p. 243: "Geological samples from the earth's interior have been found to be in thermodynamic disequilibrium. If substances that have been around for times comparable to the life of the Earth are not in equilibrium, surely 'waiting' does not guarantee equilibrium. There is no way out of the dilemma that equilibrium is defined via thermodynamic constructs which were in turn defined for the equilibrium state. We have no way of telling if a system is 'at equilibrium' except by making experiments which rely on the constructs which are defined by the theory of equilibrium." R. O. Davies and G. O. Jones, "Thermodynamic and kinetic properties of glasses", *Adv. Physics* **2**, 370-410 (1953), p. 395. Davies and Jones have interesting comments about the concept of equilibrium. In particular, they claim that a glassy phase is as much in equilibrium as a mixture of hydrogen and oxygen, which is unstable with respect to chemical reactions. And they point out that even an atom can be unstable with respect to spontaneous nuclear reactions.

<sup>4</sup>Norman F. Ramsey, "Thermodynamics and statistical mechanics at negative absolute temperatures", *Phys. Rev.* **103**, 20-28 (1956), reviews the arguments in favor of considering nuclear spins systems as equilibrium systems at negative absolute temperatures. Ramsey points out that in a pure LiF crystal, the spin lattice relaxation time is as large as 5 minutes, whereas the spin-spin relaxation time is less than  $10^{-5}$  sec. For a period of the order of minutes, the spin system obeys the (slightly modified) laws of thermodynamics. See also the comments on equilibrium in Ref. 3. The texts by M. Zemansky and R. Dittman, Ref. 1, and G. Weinreich, *Fundamental Thermodynamics* (Addison-Wesley, Reading MA, 1968), use negative absolute temperature states. See also comments on negative absolute temperatures in Ralph Baierlein, *Atoms and Information Theory: An Introduction to Statistical Mechanics* (Freeman, San Francisco, 1971), pp. 405-408. However, H. Callen, Ref. 2, p. 29, states that "Such states are not equilibrium states ... [because] they spontaneously decay away." It is difficult for me to reconcile this statement of Callen's with his comments on equilibrium cited in Ref. 3 and Ramsey's observations.

<sup>5</sup>Many authors take (some form of) the unattainability of absolute zero to be equivalent to (some form of) the third law of thermodynamics. See, e.g., M. Zemansky and R. Dittman, Ref. 1, pp. 514-518; H. Callen, Ref. 2, p. 281; E. G. Guggenheim *Thermodynamics* (North-Holland, Amsterdam, 1959), 4th ed., p. 192; and J. Wilks, *The Third Law of Thermodynamics* (Oxford University Press, London, 1961), p. 113. Other authors disagree. See, e.g., John C. Wheeler, "Nonequivalence of the Nernst-Simon and the unattainability statements of the third law of thermodynamics", *Phys. Rev. A* **43**, 5289-5295 (1991); John C. Wheeler, "Addendum to 'Nonequivalence of the Nernst-Simon and the unattainability statements of the third law of thermodynamics'", *Phys. Rev. A* **45**, 2637-2640 (1992); P. T. Landsberg, "The third law of thermodynamics" in *Satyendrana Bose 70th Birthday Commemoration Volume* (Satyendrana Bose 70th Birthday Celebration Committee, Calcutta, 1965-66), vol. 2, pp. 209-220; and P. T. Landsberg, Ref. 1, pp. 100-115.

<sup>6</sup>If we are willing to do a bit more work, we can finish the proof without (Rev), as follows. Let  $Z = Z_0 + HS$  be as in Fig. 1, (So now we have two heat sources:  $HS$  and the standard heat source of Fig. 1.) We know that  $\Delta S_P \geq 0$ . Let process  $P'$  of  $Z$  start in the same state as  $P$ , reversibly transfer positive heat  $Q$  from  $HS$ , and leave  $Z_0$  alone. From (10),  $\Delta S_{P'} = H_P/T_0$ . Also, since  $P'$  and  $P$  have the same initial and final states of  $Z$ ,  $\Delta S_{P'} = \Delta S_P$ . Now let  $P''$  be the process  $P'$  considered as a process of  $HS$  alone. Then  $H_{P''} = H_{P'}$ . Again from (10),  $\Delta S_{P''} = H_{P'}/T_0$ . Putting all this together,  $\Delta S_{P''} = H_{P'}/T_0 = H_P/T_0 = \Delta S_P = \Delta S_P \geq 0$ . But also  $\Delta S_{P''} = -Q/T < 0$ . This contradiction establishes  $\Pi_K$ .

<sup>7</sup>J. Wilks, Ref. 5, provides an extensive discussion of the third law.

<sup>8</sup>H. Callen, Ref. 2, p. 68.

<sup>9</sup>J. Wilks, Ref. 5, p. 58.

<sup>10</sup>J. Wilks, Ref. 5, p. 59.

<sup>11</sup>J. B. Boyling, "Thermodynamics of non-differentiable systems", *Int. J. Th. Phys.* **9**, 379-392 (1974).

<sup>12</sup>J. L. B. Cooper, "The foundations of thermodynamics", *J. Math. Anal. Appl.* **17**, 172-193 (1967).

<sup>13</sup>J. Thomsen and T. Hartka, "Strange Carnot cycles; thermodynamics of a system with density extremum", *Am. J. Phys.* **30**, 26-33 and 388 (1962). See their Fig. 5e. They also point out that "this system does not seem to meet the basic assumptions used in the Carathéodory approach. For those who feel that Carathéodory's formulation is the only rigorous approach to thermodynamics, this point would certainly seem to require further investigation."

<sup>14</sup>H. Callen, Ref. 2, p. 28.

<sup>15</sup>P. T. Landsberg and D. Tranah, "Entropies need not be concave", *Phys. Lett.* **78A**, 219-220 (1980). Landsberg has kindly pointed out (private communication) that the proof of (10) assumes that  $S(0) = 0$ . However, an examination of the proof shows that the property  $S \geq 0$  suffices to establish (11).

<sup>16</sup>B. H. Lavenda and J. Dunning-Davies, "The essence of the second law is concavity", *Found. Phys. Lett.* **3**, 435-441 (1990); P. T. Landsberg and Tranah, Ref. 15; P. T. Landsberg and R. B. Mann "New types of thermodynamics from (1 + 1)-dimensional black holes, *Class. Quantum Grav.* **10**, 2373-2378 (1993).

<sup>17</sup>Lavenda and Dunning-Davies, "The essence of the second law is concavity", *Found. Phys. Lett.* **3**, 435-441 (1990). I have no disagreement with the technical content of the paper, only the conclusion expressed in its title.

<sup>18</sup>H. A. Buchdahl, Ref. 3, p. 42.

<sup>19</sup>J. B. Boyling, "Thermodynamics of non-differentiable systems", *Int. J. Th. Phys.* **9**, 379-392 (1974). J. L. B. Cooper, Ref. 12, pp. 172-193 (1967).

<sup>20</sup>F. O. König, Ref. 1, p. 171.

<sup>21</sup>J. Thomsen. "Thermodynamics of an irreversible quasi-static process", *Am. J. Phys.* **28**, 119-122 (1960).

<sup>22</sup>P. T. Landsberg "On suggested simplifications of Carathéodory's thermodynamics", *Physica Status Solid* **1**, 120-126 (1961).

<sup>23</sup>H. A. Buchdahl, Ref. 3.

<sup>24</sup>M. Zemansky and R. Dittman, Ref. 1.