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THE SECOND LAW OF THERMODYNAMICS AND THE ACCUMULATION THEOREM

by

Austin R. Maule

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ABSTRACT

The Second Law of Thermodynamics and The Accumulation Theorem

by

Austin R. Maule

The University of Wisconsin-Milwaukee, 2020
Under the Supervision of Professor Kevin McLeod

Abstract

In Serrin's proof of the Accumulation Theorem, the presence of an ideal gas $\mathscr{G}$ is assumed. In 1979 at the University of Naples, Serrin (allegedly) proved that the ideal system $\mathscr{G}$ can be replaced by a more general ideal system and still have the Accumulation Theorem hold. In this paper, we attempt to reconstruct Serrin's proof and supply a proof for a more general theorem stated in a paper of Coleman, Owen and Serrin.

Thank You.

Professor Kevin McLeod for working with me this semester and introducing me to an incredibly deep and interesting topic.
Professors Jeb Willenbring and Lijing Sun for serving on my thesis defense committee.

Austin Maule

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Introduction

I.1 Motivation of the Problem

Beginning in the middle of the 20th century, there was a great effort by mathematical physicists to put Thermodynamics into an axiomatically sound, mathematically rigorous framework. Despite the age of the subject, the field of Thermodynamics has been notorious for lacking rigor in its proofs. Unlike other scientific disciplines, many of the scientific laws in Thermodynamics are stated without any standard or usual mathematical formalism. Consequently, adding precision and rigorous mathematical justification of Thermodynamic principles became of interest to mathematical physicist's in the 20th century.

According to [C1], when thermodynamical concepts and principles are employed in a physical setting, one can isolate an assumption, called the Second Law. The Second Law in some sense is equivalent to the assertion that the sum along a cyclic process of the ratio of the heat gained to the absolute temperature at which it is gained cannot be positive. Determining a precise but general rule for deciding what is meant by the "sum along a process of the ratio of the heat gained to the absolute temperature at which it is gained" remained an open question. In order to answer this question, James Serrin introduced The Accumulation Theorem, essentially providing an analytic formulation of the Second Law. In his first statements of the Accumulation Theorem, Serrin hypothesizes the existence of a distinguished ideal gas $\mathscr{G}$. This is not a very realistic physical assumption, but the existence of such a gas allows one to discuss the empirical temperature scale associated with $\mathscr{G}$. This in turn allows one to have an absolute temperature scale for a thermodynamical system.

While Serrin's Accumulation Theorem provides an analytic formulation for the Second Law, it does come with several limitations. The first limitation of his Theorem is that it relies on the existence of a distinguished ideal gas $\mathscr{G}$. The existence of such a system in nature is clearly very unlikely. The second limitation is that it places emphasis on a small class of thermodynamical systems (namely those that possess a distinguished ideal gas).

During a lecture at the University of Naples, Serrin provided a new proof of his Accumulation Theorem. In his revised proof, he showed that the Accumulation Theorem still holds if one assumes the existence of a more general ideal system in place of the distinguished ideal gas. Unfortunately, these lecture notes have been lost to history and it's unknown whether or not these notes were recorded elsewhere.

One of the primary goals of this paper will be demonstrating the proof of the Accumulation Theorem for cycles; however, we show that a more general ideal system can be used in place of the distinguished ideal gas $\mathscr{G}$, essentially recovering Serrin's arguments from his University of Naples notes.

It is worth noting that Serrin's results are re-stated and generalized without proof in Section 6 of [C1]; in this thesis, we will provide proofs of the claims of [C1].

Systems and States

II.1 Formal Structure of Thermodynamics

In this section, we introduce the formal structure of Thermodynamics and give several important definitions that will be used repeatedly throughout this paper. This material is taken from [C1] and [S1].

When introducing the formal structure of Thermodynamics it is convenient to start with the concept of hotness. Hotness is represented by a *thermal manifold* $\mathscr{H}$, that is to say an open topological line with one of its two natural orientations identified as the direction of increasing hotness. Here, the points of $\mathscr{H}$ represent *hotness levels* L open to material systems. The manifold $\mathscr{H}$ is a totally ordered set with the order relation ”>” corresponding to increasing levels of hotness. In particular, if L_1 and L_2 are any two different hotness levels in $\mathscr{H}$, then either $L_1 > L_2$ or $L_2 < L_1$ (but not both). Moreover, if $L_1 > L_2$ and $L_2 > L_3$ then $L_1 > L_3$, that is, the order is transitive. The relation $L_1 > L_2$ will be read as ”L_1 is hotter than L_2” or alternatively ”L_2 is colder than L_1”. We also write $L_1 \geq L_2$ to indicate that either $L_1 > L_2$ or $L_1 = L_2$.

A *(empirical) temperature scale* is a strictly increasing map from $\mathscr{H}$ into the reals $\mathbb{R}$. If ψ is a temperature scale then $\psi(L)$ is called the *temperature of* L in the scale ψ.

A *System* is a pair (Σ, Π) of sets (with Σ called the set of **states** σ and Π the set of **processes** P) together with a function $P \to \varrho_P$. The function $P \to \varrho_P$ assigns to each process P a function $\varrho_P : \mathscr{D}(P) \to \Sigma$. Here, $\mathscr{D}(P)$ is a non-empty subset of Σ and the function ϱ_P is called the **transformation induced** by P. It is in accord with the present use of the term "process" to think of a pair (P, σ), with $\sigma \in \mathscr{D}(P)$, as a "bound process"; the set of all such pairs is denoted by $\Pi \oplus \Sigma$, where "$\oplus$" is understood to be the cartesian product. We will refer to σ as the **initial state** and to $\varrho_P\sigma$ as the **final state** associated with the bound process (P, σ).

We are now ready to define a thermodynamical system with states.

Definition 1. *A* Thermodynamical System(with states) *is a triple* $\mathscr{L} = (\Sigma, \Pi, Q)$*, with* (Σ, Π) *a system in the sense defined above and* Q *a real valued function on* $(\Pi \oplus \Sigma) \times \mathscr{H}$ *(called the* ***accumulation function*** *for* $\mathscr{L}$*), such that, for each pair* $(P, \sigma) \in \Pi \oplus \Sigma$ *the following hold:*

(a). There is a pair of hotness levels $L^l < L^u$ *for which*

$$Q(P, \sigma; L) = \begin{cases} 0\ , & L < L^l \\ Q(P, \sigma; L^u)\ , & L \geq\ L^u\ . \end{cases} \tag{1}$$

(b). The function $L \to Q(P, \sigma; L)$ *from* $\mathscr{H}$ *into* $\mathbb{R}$ *is bounded and has at most a countable number of points of discontinuity.*

[C1] interpret the value $Q(P, \sigma; L)$ of the accumulation function Q to be the *net heat transferred to* $\mathscr{L}$ *at levels of hotness at or below* L *in the process* P *starting at the state* σ. Here, a positive transfer means a gain of heat by $\mathscr{L}$, while a negative transfer means a loss. Note that (a) shows that the net heat transferred at or below L must be zero if L is below L^l, and the net heat transferred at or below L must be the number $Q(P, \sigma) = Q(P, \sigma; L^u)$ whenever L is above L^u. For a given pair (P, σ), when L^u is as in part (a), Coleman, Owen and Serrin state that (P, σ) **operates at or below** L^u. The number $Q(P, \sigma)$ is the **overall net transfer of heat for** (P, σ).

If an empirical temperature scale ψ is used to identify hotness levels L with real numbers $\xi = \psi(L)$, then $Q(P, \sigma; \psi^{-1}(\xi))$ is the *net heat transferred to* $\mathscr{L}$ *at temperatures (relative* *to ψ) at or below ξ when the system undergoes the process P starting at σ.* Part (a) in the previous definition implies that, for each pair (P, σ) and temperature scale ψ, $Q(P, \sigma; \psi^{-1}(\xi))$ as a function of ξ is a bounded function with at most countably many discontinuities and so, in particular, is locally Riemann integrable.

II.2 Ideal Gases

Simple but important examples of thermodynamical systems are ideal gases. These can be thought of as gaseous bodies (of unit mass) which are restricted to spatially homogeneous conditions. An ideal gas $\mathscr{G}$ is an "ideal material" or "homogeneous fluid body" in the sense that each state is a pair (v, τ), with τ a value of an empirical temperature scale $\bar{\phi}$ and v the volume, and the gain of heat along a path in the state space $\Sigma_{\mathscr{G}}$ can be calculated by integrating a differential form,

$$q = c d\tau + f dv, \tag{2}$$

in which the **heat capacity** c and the **latent heat** f are continuous functions on $\Sigma_{\mathscr{G}}$.

The defining property of an ideal gas $\mathscr{G}$ is the form of the **pressure**, p, given by

$$p = \frac{R\tau}{v}. \tag{3}$$

In Serrin's original formulation of the Accumulation Theorem (to be stated later) he assumes the existence of an ideal gas $\mathscr{G}$. The physical existence of such an object in nature is very unlikely. It then becomes natural to question whether this ideal gas $\mathscr{G}$ can be replaced by a more general ideal system and still have the accumulation theorem hold.

The First Law of Thermodynamics

Although the goal of this paper is to prove results about the Second Law, we will briefly discuss the First Law in this section.

We say a process P is *cyclic* if the initial and final state of the system is the same. We define a *thermodynamical universe* to be a set $\mathscr{U}$ of thermodynamical systems $\mathscr{L}$.

Every thermodynamical system $\mathscr{L}$ comes endowed with a set $\mathscr{P}(\mathscr{L})$ of processes, typically denoted by P, R, S, etc., which the system may undergo, together with a subset $\mathscr{P}_c(\mathscr{L})$ of cyclic processes of the system. To every process $P \in \mathscr{P}(\mathscr{L})$ there correspond real numbers $\bar{W}(P)$ and $\bar{Q}(P)$, called the **total work** done by the process P and the **total heat** used by the process P. Formally, we can write

$$\bar{W} : \mathscr{P}(\mathscr{L}) \to \mathbb{R} \tag{4}$$

$$\bar{Q} : \mathscr{P}(\mathscr{L}) \to \mathbb{R} \tag{5}$$

We adopt the standard sign convention that $\bar{W}(P) > 0$ if work is done by the system on the exterior environment and $\bar{W}(P) < 0$ if the exterior environment deos work on the system. Similarly $\bar{Q}(P) > 0$ if heat is supplied to the system, while $\bar{Q}(P) < 0$ means that the system has supplied heat to the environment.

A particularly valuable idea that is used throughout the study of thermodynamics is that of a product of thermodynamical systems. To make this idea precise, we record the following definition:

Definition 2. *Let $\mathscr{L}_1$ and $\mathscr{L}_2$ be a pair of thermodynamical systems. The* ***product system****, $\mathscr{L}_1 \oplus \mathscr{L}_2$, is characterized by its processes and their work and heat functions, which are required to satisfy the following conditions:*

1. $\mathscr{P}(\mathscr{L}_1 \oplus \mathscr{L}_2) = \mathscr{P}(\mathscr{L}_1) \times \mathscr{P}(\mathscr{L}_2)$
2. $\mathscr{P}_c(\mathscr{L}_1 \oplus \mathscr{L}_2) = \mathscr{P}_c(\mathscr{L}_1) \times \mathscr{P}(\mathscr{L}_2)$
3. $\bar{W}(P_1 \oplus P_2) > 0$ *provided that* $\bar{W}(P_1) + \bar{W}(P_2) > 0$
4. $\bar{Q}(P_1 \oplus P_2) < 0$ *provided that* $\bar{Q}(P_1) + \bar{Q}(P_2) < 0$
5. $Q(P_1 \oplus P_2, \bullet) \geq 0$ *provided that* $Q(P_1, \bullet) + Q(P_2, \bullet) \geq 0$.

Note that the function Q in 5 refers to the accumulation function associated with the given process. Here, $\bullet$ represents the argument for the accumulation function (namely a particular hotness level $L \in \mathscr{H}$). In this context, $P_1 \oplus P_2$ denotes the union process (in $\mathscr{P}(\mathscr{L}_1 \oplus \mathscr{L}_2)$) corresponding to the pair of processes $P_1 \in \mathscr{P}(\mathscr{L}_1)$ and $P_2 \in \mathscr{P}(\mathscr{L}_2)$. Additionally, × is used to denote the Cartesian product.

It is natural to question whether the concept of a product system should be meaningful for all conceivable pairs of thermodynamical systems. To avoid confusion, we shall restrict the formation of product systems only to special and distinguished pairs of systems, called *thermodynamically compatible systems* (or simply *compatible* systems). Thus, if $\mathscr{L}_1$ and $\mathscr{L}_2$ are a pair of compatible systems, then the product system $\mathscr{L}_1 \oplus \mathscr{L}_2$ is itself assumed to be a meaningful thermodynamical system satisfying the laws of thermodynamics.

If $\mathscr{U}$ is a thermodynamical universe, we shall say that $\mathscr{U}$ is compatible with a thermodynamical system $\mathscr{K}$ if and only if $\mathscr{K} \in \mathscr{U}$ and each system $\mathscr{L}$ in $\mathscr{U}$ is compatible with $\mathscr{K}$.

Definition 3. *We will say that a process P of a thermodynamic system $\mathscr{L}$ is* ***weakly reversible*** *if there exists at least one associated process $P^{'}$ of $\mathscr{L}$ such that:*

1. $\bar{W}(P^{'}) = -\bar{W}(P)$
2. $\bar{Q}(P^{'}) = -\bar{Q}(P)$
3. $Q(P^{'}, \bullet) = -Q(P, \bullet)$
4. $P^{'} \in \mathscr{P}_c(\mathscr{L})$ *provided that* $P \in \mathscr{P}_c(\mathscr{L})$.

The process $P^{'}$ will be called a *weak reversal* of P. Observe that there is no requirement that $P^{'}$ be unique for a given reversible process P or that it should follow some "path" reverse to the "path" of P. In general, this will certainly not be the case.

At last, with the previous definitions in place, we are able to discuss the first law of thermodynamics.

The First Law of Thermodynamics is intimately connected to the principle of conservation of energy. In fact, the first law is often taken to be a statement of interconvertibility of work and heat, such as:

For any cyclic process of any thermodynamical system, the total work done by the system is equal to the heat supplied to the system. In our notation, we can express this as:

$$\bar{W}(P) = \bar{Q}(P) \ for \ any \ P \in \mathscr{P}_c(\mathscr{L}). \tag{6}$$

When one is studying thermodynamics, one often sees the equation $\bar{W}(P) = \mathscr{J}\bar{Q}(P)$ instead of the equation written above. The constant $\mathscr{J}$ is called **Joule's Constant** and $\mathscr{J} = 1$ means that we are measuring heat in mechanical units. It was discovered by Silhavy [Si1] that the equation $\bar{W}(P) = \bar{Q}(P)$ can actually be deduced from weaker assumptions. This brings us to the Weak First Law for Cycles.

Weak First Law for Cycles: If $\bar{W}(P) > 0$ for a cyclic process P of a thermodynamical system $\mathscr{L}$, then $\bar{Q}(P) > 0$.

In this form, the first law simply says that a cyclic process cannot do work without the supply of some heat. It's perfectly reasonable to believe that a supply of heat is not only necessary but sufficient for a cyclic process to do work. This leads us to consider what is called the Strong First Law for Cycles.

Strong First Law for Cycles: $\bar{W}(P) > 0$ for a cyclic process P of a thermodynamical system $\mathscr{L}$ if and only if $\bar{Q}(P) > 0$.

Definition 4. *A thermodynamical system $\mathscr{R}$ is called a* ***reversible heat engine*** *if there exists at least one weakly reversible cyclic process R of $\mathscr{R}$, such that $\bar{W}(R) \neq 0$.*

Theorem 5 (The Energy Inequality)**.** *Let $\mathscr{U}$ be a thermodynamical universe which is compatible with a reversible heat engine. If the weak first law holds in $\mathscr{U}$, then there exists a unique universal constant $\mathscr{J} > 0$ such that for every cyclic process P of every thermodynamical system $\mathscr{L} \in \mathscr{U}$, we have $\bar{W}(P) \leq \mathscr{J}\bar{Q}(P)$.*

Proof. Let $\mathscr{R}$ be a reversible heat engine which is compatible with $\mathscr{U}$, and let R be a weakly reversible cyclic process of $\mathscr{R}$ with $\bar{W}(R) \neq 0$, and weak reversal R'. By interchanging the roles of R and R', if necessary, we can assume $\bar{W}(R) > 0$. By the weak first law for cycles, $\bar{Q}(R) > 0$, and so we may define the positive quantity

$$\mathscr{J} = \frac{\overline{W}(R)}{\overline{Q}(R)}. \tag{7}$$

Let P be a cyclic process of an arbitrary system $\mathscr{L} \in \mathscr{U}$, and suppose for contradiction that

$$\bar{W}(P) > \mathscr{J}\bar{Q}(P). \tag{8}$$

Let $P^{(m)}$ denote the cycle R repeated m times, and $R^{(n)}$ the cycle R repeated n times. For $n < 0$, define $R^{(n)} = (R')^{(-n)}$; *i.e.* the cycle R' repeated $-n > 0$ times. By the axioms for union systems

$$\bar{W}(P^{(m)} \oplus R^{(n)}) = m\bar{W}(P) + n\bar{W}(R) \tag{9}$$

and

$$\bar{Q}(P^{(m)} \oplus R^{(n)}) = m\bar{Q}(P) + n\bar{Q}(R), \tag{10}$$

at least when $n > 0$, and the definition of the weak reversal R' implies that these equations remain true for $n < 0$. The weak first law applied to $P^{(m)} \oplus R^{(n)}$ therefore implies that

$$m\bar{Q}(P) + n\bar{Q}(R) > 0 \text{ whenever } m\bar{W}(P) + n\bar{W}(R) > 0. \tag{11}$$

Now consider the vectors A, B in $\mathbb{R}^2$ given by $A = (\bar{W}(P), \bar{W}(R))$, $B = (\mathscr{J}\bar{Q}(P), \mathscr{J}\bar{Q}(R))$. Their second components are equal and positive, and their first components satisfy $\bar{W}(P) > \mathscr{J}\bar{Q}(P)$. Drawing a figure shows easily that there is a vector $C = (m, n)$ with $m, n \in \mathbb{Z}$, $m > 0$, $n \neq 0$, such that $A \cdot C > 0$ and $B \cdot C < 0$, contradicting (11).

To prove that $\mathscr{J}$ is unique, suppose that $\mathscr{J}'$ is another constant satisfying $\bar{W}(P) \leq \mathscr{J}'\bar{Q}(P)$ for all cyclic processes P of systems $\mathscr{L}$ in $\mathscr{U}$. Choose for P the special cyclic processes R and R' of $\mathscr{R}$. Then, in particular,

$$\bar{W}(R) \leq \mathscr{J}'\bar{Q}(R) \text{ and } \bar{W}(R') \leq \mathscr{J}'\bar{Q}(R'). \tag{12}$$

On the other hand, by properties of R and R', we have

$$\frac{\bar{W}(R)}{\bar{Q}(R)} = \frac{\bar{W}(R')}{\bar{Q}(R')} = \mathscr{J}, \tag{13}$$

where $\bar{Q}(R) > 0$ and $\bar{Q}(R') < 0$. Thus the two inequalities (12) imply both $\mathscr{J} \leq \mathscr{J}'$ and $\mathscr{J}' \leq \mathscr{J}$.

□

Note that it can be shown that the energy inequality implies the weak first law for cycles, and so these two principles are equivalent, given the existence of a reversible heat engine. If the strong first law is assumed, then we have the following result:

Corollary 6 (Interconvertibility of Work and Heat)**.** *Let* $\mathscr{U}$ *be a thermodynamical universe which is compatible with a reversible heat engine. If the strong first law holds in* $\mathscr{U}$*, then there exists a unique universal constant* $\mathscr{J} > 0$ *such that for every cyclic process* P *of every thermodynamical system* $\mathscr{L} \in \mathscr{U}$*, we have* $\bar{W}(P) = \mathscr{J}\bar{Q}(P)$*.*

A very important observation here is that we do not need to assume the strong first law to deduce interconvertibility of work and heat in many cases. To show this, suppose that the weak first law holds, and P is a weakly reversible cyclic process with weak reversal $P^{'}$. By the energy inequality, we have

$$\bar{W}(P) \leq \mathscr{J}\bar{Q}(P) \tag{14}$$

and

$$\bar{W}(P^{'}) \leq \mathscr{J}\bar{Q}(P^{'}). \tag{15}$$

Since

$$\bar{W}(P^{'}) = -\bar{W}(P) \tag{16}$$

and

$$\bar{Q}(P^{'}) = -\bar{Q}(P), \tag{17}$$

it follows that

$$\bar{W}(P) = \mathscr{J}\bar{Q}(P). \tag{18}$$

For many simple systems (common examples are that of ideal gases and van der Waal fluids) every process is (weakly) reversible. As a result, interconvertibility of work and heat follows for all processes of such systems.

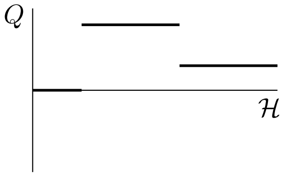
Second Law for Systems with Cycles

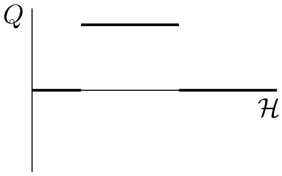
IV.1 Statement of Second Law for Systems with Cycles

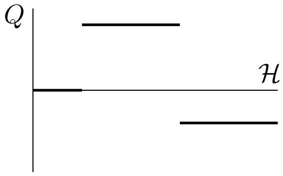
In this section we record versions of the Second Law for cycles as stated in [S2] and [C1]. **Second Law (Serrin)**-*The condition* $Q(P,\sigma;L) \geq 0$ *can occur for a cyclic process* P *of a thermodynamical system* $\mathscr{L}$ *only in the exceptional case when* $Q(P,\sigma;L) \equiv 0$.

Definition 7. *An* ***absorptive cycle*** *is a cycle in which we have* $Q(P,\sigma;L) \geq 0$ *for every* $L \in \mathscr{H}$.

It is obvious that Serrin's formulation of the Second Law is a strong statement regarding the accumulation function for a cyclic process. In particular, Serrin's formulation prohibits the first two of the accumulation function graphs from occuring:







Notice that the third graph is prohibited from occuring for cyclic processes with $\bar{W}(P) \geq 0$, by the Weak First Law and The Energy Inequality.

Serrin's formulation of the Second Law is derived from the physical idea that if heat should be so strongly added to a thermodynamical system that the accumulation function is non-negative at every hotness level, and positive at least at some hotness levels, then the system must necessarily move away from its initial condition. There is an interesting duality that exists between the First and Second Law of Thermodynamics. Namely, when $\bar{W}(P) > 0$ for a cyclic process P the First Law requires a positive value for $\bar{Q}(P)$ while the Second Law implies a negative value for $Q(P, \sigma; L)$ at some hotness level.

The Second Law is an intrinsic statement about the relation between heat and hotness in cyclic processes. Exactly in the case of the First Law, the Second Law also has an equivalent analytical formulation that is incredibly useful. This formulation of the Second Law is called **The Accumulation Theorem**.

Theorem 8 (Serrin's Accumulation Theorem)**.** *Let $\mathscr{U}$ be a thermodynamical universe which is thermodynamically compatible with a perfect gas $\mathscr{G}$. Then there exists an (absolute) temperature scale $\tilde{T}$ on the hotness manifold $\mathscr{H}$, with $\tilde{T}(\mathscr{H}) \equiv \mathbb{R}^+$, such that for every cyclic process P of every thermodynamic system $\mathscr{L}$ in $\mathscr{U}$ we have*

$$\int_0^\infty \frac{Q(P, L)}{T^2}\, dT \;\leq\; 0, \tag{19}$$

where $L = \tilde{L}(T)$ is the hotness level associated with the temperature T in the scale $\tilde{T}$. Any temperature scale $\tilde{T}$ with the above property either agrees with the perfect gas scale of $\mathscr{G}$ or is a positive constant multiple of this scale.

Here, $Q(P, L)$ denotes the limiting value of the accumulation function. The importance of The Accumulation Theorem is that it accomplishes two major goals: it establishes the concept of absolute temperature without ambiguity, and it characterizes the allowable behavior of the accumulation function of any cyclic process.

It is true that the accumulation inequality(inequality located above) implies the Second Law, for if $Q(P, \sigma; L) \geq 0$ in a cyclic process P then the accumulation integral above will of necessity be positive unless $Q(P, \sigma; L) \equiv 0$.

[C1] provides a more relaxed formulation of the Second Law, namely:

Second Law (Coleman, Owen, Serrin)- *If $Q(P, \sigma; L) \geq 0$ for all $L \in \mathscr{H}$ for some cyclic process P, then $Q(P, \sigma) = 0$.*

One key difference between the two formulations is that [C1] allows the 2nd accumulation function graph to occur, whereas Serrin's formulation prohibits this graph from occuring. Serrin's stronger notion of the Second Law rules out the possibility of an accumulation function with two jumps, say at $L_1 < L_2$ with the jump at L_2 being equal and opposite to the jump of L_1, so that $Q(P, \sigma) = 0$ even though $Q(P, \sigma; L)$ is not identically 0. This subtlety between the formulations allows for a different type of behavior of $Q(P, \sigma; L)$ (case **b)** in the first major Theorem of the next section).

IV.2 Carnot Systems and Carnot Cycles

In this section we discuss carnot cycles and give neccessary background that will be used in our proof of Theorem 14. Before we move into key definitions, we first must discuss the mathematical structure of "ideal" systems.

We say a thermodynamical system $\mathscr{L} = (\Sigma, \Pi, Q)$ is *ideal* if it has the following type: The set Σ is an open connected set in $\mathbb{R}^k$ with the associated Euclidean topology; for the states $\sigma \in \Sigma$ we write $\sigma = x = (x_1, ..., x_k)$. The collection Π of processes of $\mathscr{L}$ is the set of all piecewise continuous functions,

$$P_t : [0, t) \to \mathbb{R}^k, t > 0, \tag{20}$$

for which there is at least one element σ_0 of Σ such that

$$\bar{\sigma}(s) \equiv \sigma_0 + \int_0^s P_t(u) du \in \Sigma, for\ all\ s \in [0, t]. \tag{21}$$

For each $P_t \in \Pi$, $\mathscr{D}(P_t)$ is the set of all states for which the line above holds. As in the case of an ideal gas, the function $s \to \bar{\sigma}(s)$, $s \in [0, t]$, determines a parameterized path $\Gamma(P_t, \sigma)$ in Σ.

For an ideal system the function Q (accumulation function) is determined by a differential form,

$$q = Y_i dx_i \tag{22}$$

with the function $\sigma \to Y(\sigma) = (Y_1(\sigma), ..., Y_k(\sigma))$ continuous on Σ. We assume that such a form is given, and for each $P_t \in \Pi$ and $\sigma \in \mathscr{D}(P_t)$, we put

$$Q(P_t, \sigma; L) = \int\limits_{S(P_t,\sigma;L)} Y((\bar{\sigma}(s))) \cdot P_t(s)\ ds \tag{23}$$

where

$$S(P_t, \sigma; L) = \{s \in [0, t] \mid L^{'}(\bar{\sigma}(s)) < L\}. \tag{24}$$

In this construction it is understood that the state space Σ is equipped not only with the differential form q, but also with a continuous function $L^{'} : \Sigma \to \mathscr{H}$ defined by

$$\sigma \to L^{'}(\sigma) \in \mathscr{H} \tag{25}$$

that associates a level of hotness $L = L^{'}(\sigma)$ with each point σ of Σ. Here any component (in this sense we mean maximal connected subset) of a level set of $L^{'}$ is an isothermal surface. In particular, if the dimension of our state space is 2, then these components are called isotherms.

A particularly useful class of ideal thermodynamical systems are called Carnot systems. These systems are general enough to describe the behavior of many materials and yet have enough special structure to allow a large family of Carnot cycles.

Definition 9. *We will say a thermodynamical system $\mathscr{C}$ is a* ***Carnot system*** *if it has the following properties:*

1. *The state space Σ of $\mathscr{C}$ has dimension $k = 2$.*

2. *The differential form q is non-degenerate, that is, $Y(\sigma) \neq 0$ for all states σ.*

3. *Each isotherm in Σ is a C^1 curve.*

4. Along each adiabat in Σ the associated hotness level L' is a strictly monotone function of distance along the curve.

Here, an adiabat is a trajectory of the differential form $q = Y_i dx_i$, so that no heat is transferred as the process traverses an adiabat. The physical meaning of 2 is that the adiabatic trajectories of the system have no singularities, whereas 3 tells us that isothermal reversible processes exist. The physical meaning of 4 is that adiabatic reversible processes of the system must produce either a cooling or a heating of the system. If 4 were satisfied for no ideal system, then reversible adiabatic heating and cooling would be excluded from physical occurrence. Thus, the existence of Carnot systems is a very reasonable assumption. An ideal gas is an example of a Carnot system in which the isotherms are horizontal straight lines and the adiabats are curves sloping downward to the right.

For a general Carnot system, a **Carnot cycle** is, exactly as in the case of an ideal gas, a path $\Gamma(P_t, \sigma)$ composed of two adiabatic parts joined by two isothermal parts. The accumulation function of a Carnot cycle (P_t, σ) can be characterized as a step function with exactly 2 jumps, say at $L_1 < L_2$. In any Carnot cycle, the magnitude of the jump at L_2 must be greater than or equal that at L_1.

Before recording a few observations about Carnot cycles, we first introduce the notion of a "subcycle" of a Carnot cycle.

Definition 10. *A* ***subcycle*** *of a Carnot cycle is a Carnot cycle which operates within the hotness interval defined by the isotherms of the original cycle, and whose adiabatic portions lie on the same adiabats as those of the original cycle.*

We will always assume that the orientation at which subcycles are traversed is the same as the original Carnot cycle. Then, we have the following lemmas:

Lemma 11. *For a given Carnot system $\mathscr{C}$ with state space Σ, there exists a unique adiabatic curve through any point $\sigma_0 \in \Sigma$.*

Proof. Along any adiabat, the net heat added to the system is 0. Thus, the heat form q is 0. So we have the equation

$$q = Y_1 dx_1 + Y_2 dx_2 = 0 \tag{26}$$

It is important to note here that Y_1 and Y_2 cannot both be equal to zero at σ_0 (this is impossible for a Carnot system). So, assume wlog that $Y_1 \neq 0$ at σ_0; then, by continuity, $Y_1 \neq 0$ in some neighborhood of σ_0. We will work in this neighborhood from now on. Thus, rearranging the above equation yields:

$$\frac{dx_1}{dx_2} = -\frac{Y_2}{Y_1}. \tag{27}$$

Note that the RHS of the equation above is continuous since it is the ratio of two continuous functions. Hence, the existence of an adiabat through σ_0 follows from the theory of differential equations. Next, we show uniqueness.

If there are two distinct adiabats through some point σ_0, we can construct a closed path γ in Σ consisting of portions of these adiabats and a single isothermal segment. The accumulation function of any cycle C corresponding to γ is a step function with a single jump, but a step function with a single jump is prohibited by [C1] formulation of the second law, as either C or a reversal of C will contradict the second law. □

Lemma 12. *Given* $\sigma_0 \in \Sigma$, $\exists$ *a Carnot cycle* C *with an operating hotness interval* $[L_1, L_2]$ *with* $L_1 < L^{'}(\sigma_0) < L_2$.

Proof. Let $\sigma_0 \in \Sigma$. Consider two points $\sigma_1, \sigma_2 \in \Sigma$ that lie on the isotherm $L^{'}(\sigma_0)$, where σ_1, σ_2 are sufficiently close to σ_0. By the previous lemma, there exists unique adiabats through σ_1, σ_2. We can construct a closed path in the state space by joining these adiabats via two isotherms, say at hotness levels L_1 and L_2, with $L_1 < L^{'}(\sigma_0) < L_2$. Hence, we have a carnot cycle that operates in the hotness interval $[L_1, L_2]$. □

Lemma 13. *1. Let (P, σ) be a Carnot cycle operating between hotness levels $L_1 < L_2$. Let Q_1 and Q_2 be the heat supplied to the system at hotness levels L_1 and L_2 respectively. Then*

$$Q_1 Q_2 < 0 \text{ and } \mid Q_2 \mid \geq \mid Q_1 \mid \tag{28}$$

2. Let (P_1, σ_1) and (P_2, σ_2) be Carnot cycles operating between hotness levels $L_1 < L_2$. Then

$$\frac{Q_1}{Q_1'} = \frac{Q_2}{Q_2'} \tag{29}$$

3. If a Carnot cycle C has $Q = 0$, then any subcycle of C also has $Q = 0$.

Proof. 1. For a given Carnot cycle, the associated accumulation function is a step function with two jumps. Namely, a jump of Q_1 at hotness level L_1, and a jump of Q_2 at hotness level $L_2 > L_1$. If both jumps are positive, then the associated accumulation function would be non-negative with $Q > 0$ (here, Q is the limiting value of the accumulation function as $L \to \infty$). This clearly violates the second law. On the other hand, if both jumps are negative then reversing the cycle multiplies the accumulation function by -1. Thus, the reversed cycle has two positive jumps and again we reach a contradiction. Hence, the two jumps must have opposite sign and it follows that $Q_1 Q_2 < 0$.

If the first jump were positive and the second jump negative but with smaller magnitude, the associated accumulation function is still non-negative with $Q > 0$. Again, a contradiction of the second law. If the second jump has magnitude equal to the first, then $Q = 0$. This is in accordance with the C-O-S formulation of the second law. Hence, we have that $\mid Q_2 \mid \geq \mid Q_1 \mid$.

2.

Let γ^1 and γ^2 be the paths corresponding to (P_1, σ_1) and (P_2, σ_2) respectively, and consider a path γ^3 consisting of γ^1 traversed m times and γ^2 traversed n times, with a smooth joining path, making γ^3 as a whole closed. Here, $m, n \in \mathbb{Z}$ and we interpret negative values in the obvious way.

The accumulation function of the corresponding process (P_3, σ_3) is

$$Q(P_3, \sigma_3; L) = mQ(P_1, \sigma_1; L) + nQ(P_2, \sigma_2; L). \tag{30}$$

Now, suppose the equality hypothesized fails. Then the vectors $(Q_1, Q_1^{'})$ and $(Q_2, Q_2^{'})$ in $\mathbb{R}^2$ are non-collinear. Thus, there exists integers m and n such that

$$mQ_1 + nQ_1^{'} > 0 \textit{ and } mQ_2 + nQ_2^{'} > 0. \tag{31}$$

But this shows that $Q(P_3, \sigma_3; L) = mQ(P_1, \sigma_1; L) + nQ(P_2, \sigma_2; L) \geq 0$, which contradicts the second law since the net heat transferred for the system is not identically zero.

3.

We will prove the simpler case of when two subcycles are produced. The general case follows by induction. Consider a Carnot cycle C which operates in some hotness interval and contains the isotherm $L^{'} = L_0$ in its interior. Let C_1 and C_2 denote the subcycles produced.

Then, by 1. we have the following:

- $Q_1 Q_2 < 0$ and $\mid Q_2 \mid \geq \mid Q_1 \mid$
- $Q_1^{(1)} Q_2^{(1)} < 0$ and $\mid Q_2^{(1)} \mid \geq \mid Q_1^{(1)} \mid$
- $Q_1^{(2)} Q_2^{(2)} < 0$ and $\mid Q_2^{(2)} \mid \geq \mid Q_1^{(2)} \mid$

for the cycles C, C_1, and C_2 respectively. It is clear from the notation that Q_1 and Q_2 denote the heat added or lost along the isotherms in the Carnot cycle C. Here, the superscript notation is intended to indicate the heat added or lost along the isotherms in the associated Carnot subcycles.

Now, suppose that $\mid Q_1 \mid = \mid Q_2 \mid$. Then

$$\mid Q_1 \mid = \mid Q_1^{(1)} \mid \leq \mid Q_2^{(1)} \mid = \mid Q_1^{(2)} \mid \leq \mid Q_2^{(2)} \mid = \mid Q_2 \mid . \tag{32}$$

However, since $| Q_1 | = | Q_2 |$ our chain of inequality's become equality. Hence,

$$| Q_1 | = | Q_1^{(1)} | = | Q_1^{(2)} | = | Q_2^{(1)} | = | Q_2^{(2)} | = | Q_2 | \tag{33}$$

and the result is established.

□

IV.3 The Accumulation Integral for Carnot Systems

With the preceding facts about Carnot cycles established, we are now ready to prove Theorem 6.1 from section 6 in [C1].

Theorem 14. *If $\mathscr{C}$ is a Carnot system obeying the Second Law and L_0 is a hotness level satisfying $L^{'}(\sigma_0) = L_0$ for some σ_0 in the state space of $\mathscr{C}$, then there is an open interval V of the hotness manifold which contains L_0 and is such that either:*

(a). There is a unique (up to a positive constant multiple) locally absolute empirical temperature scale $L \to \Theta(L)$, with domain V, such that

$$\int_0^\infty \frac{Q(P, \sigma; \Theta^{-1}(\theta))}{\theta^2} d\theta = 0 \tag{34}$$

for every Carnot cycle (P, σ) of $\mathscr{C}$ which operates in the range of V, or:

(b). $Q(P, \sigma) = 0$ for every Carnot cycle (P, σ) of $\mathscr{C}$ operating in the range of V.

Proof. Suppose that the hypothesis of the Theorem holds and let $\mathscr{F}$ denote the collection of Carnot cycles (P, σ) in which (P, σ) has operating hotness levels L_1 and L_2 with $L_1 < L_0 < L_2$. From lemma 12 in the previous section, $\mathscr{F}$ is non-empty. Since $\mathscr{F}$ is non-empty, there are two cases to consider:

1. $\exists (P, \sigma) \in \mathscr{F}$ with $Q(P, \sigma) = 0$.

2. $\nexists (P, \sigma) \in \mathscr{F}$ with $Q(P, \sigma) = 0$.

Suppose that case 1 holds. That is suppose $(P, \sigma) \in \mathscr{F}$ with $Q(P, \sigma) = 0$. Then, by lemma 13 part 3, we know that any subcycle constructed with the same adiabats as (P, σ) will have $Q = 0$. Now notice that the restriction that subcycles follow the same adiabats as the original cycle can (actually) be removed. By lemma 13 part 2, for any two Carnot cycles operating in the same hotness interval, the ratio of the heat gained or lost along the respective isotherms for both cycles is the same. Thus, if any Carnot cycle has a net heat gain of zero, then any other Carnot cycle operating with the same hotness interval will also have a net heat gain of zero. In particular, any other Carnot cycle operating with the same hotness interval as (P, σ) must have $Q = 0$. Thus, the interior of the hotness interval for (P, σ) is a neighbourhood V of L_0 in which every Carnot cycle has $Q = 0$, showing that part **b** of the Theorem holds.

Now suppose that case 2 holds. That is suppose there is no $(P, \sigma) \in \mathscr{F}$ with $Q(P, \sigma) = 0$. Then $\mid Q_2 \mid > \mid Q_1 \mid$ for every cycle. Define

$$\Theta(L) = \int_{\gamma_L} \mid Y_1 \frac{dx_1}{ds} + Y_2 \frac{dx_2}{ds} \mid ds \tag{35}$$

where $L \in [L_1, L_2]$ and γ_L denotes the isotherm corresponding to L. We claim that Θ is continuous, positive, and strictly increasing. This will show that Θ can be used as a local empirical temperature scale.

Proof. It is obvious from the definition that Θ is positive and continuous.
Let $L_3, L_4 \in [L_1, L_2]$, with $L_3 < L_4$. Note that if we choose the cycle small enough, we can arrange that $Y_1 \frac{dx_1}{ds} + Y_2 \frac{dx_2}{ds}$ has one sign on all of γ. Now, if we choose the direction of our cycle appropriately, the heat transfers in the cycle are given by $Q_3 = \Theta(L_3)$ and $Q_4 = -\Theta(L_4)$. Then, by lemma 13 part 1, we have that $\Theta(L_3) < \Theta(L_4)$, so that Θ is strictly increasing. □

Hence, Θ can be used as a temperature scale on the hotness interval for which our family of Carnot cycles operates.

Lemma 15. *Let C' be any Carnot cycle of $\mathscr{C}$ whose operating hotness levels are $L_3 < L_4$ in $[L_1, L_2]$. Then*

$$\frac{Q_3'}{\Theta(L_3)} \;=\; -\frac{Q_4'}{\Theta(L_4)}. \tag{36}$$

Proof. This follows immediately from lemma 13 part 2. □

Note that $Q(P, \sigma; \Theta^{-1}(\theta))$ is a step function function with two jumps, say at L_1 and L_2. Here, we will denote $\Theta^{-1}(\theta) = L$. Then we have that

$$Q(P, \sigma; L) = \begin{cases} 0\ , & L < L_1 \\ Q_1\ , & L_1 \leq L < L_2 \\ Q_1 + Q_2\ , & L \geq\ L_2\ . \end{cases}$$

Thus, we have

$$\int_0^\infty \frac{Q(P, \sigma; \Theta^{-1}(\theta))}{\theta^2} d\theta \;=\; \int_0^{L_1} \frac{0}{\theta^2} d\theta \;+\; \int_{L_1}^{L_2} \frac{Q_1}{\theta^2} d\theta \;+ \int_{L_2}^{\infty} \frac{Q_1 + Q_2}{\theta^2} d\theta. \tag{37}$$

Performing this computation, we arrive at:

$$\int_0^\infty \frac{Q(P, \sigma; \Theta^{-1}(\theta))}{\theta^2} d\theta \;=\; \frac{Q_1}{L_1} \;+\; \frac{Q_2}{L_2} \;=\; 0. \tag{38}$$

The last equality follows from a direct application of the previous Lemma. Lastly, we show uniqueness of the temperature scale Θ.

Let Θ be as described before and let $\tilde{\Theta}$ be another temperature scale operating on the same hotness interval as Θ. Let $U = (L_1, L_2)$ and let (P, σ) be a Carnot cycle of the corresponding thermodynamical system $\mathscr{C}$, with operating hotness levels $L_1 < L$, where $L \in \overline{U}$.

Combining previous lemma's and letting $\Theta^{-1}(\theta) = L$, we have that:

$$0 = \int_0^\infty \frac{Q(P, \sigma; \Theta^{-1}(\theta))}{\theta^2} d\theta = \int_0^\infty \frac{Q(P, \sigma; L)}{\theta^2} d\theta = \frac{Q_1}{\Theta(L_1)} + \frac{Q}{\Theta(L)}. \tag{39}$$

Similarly, we have

$$0 = \frac{Q_1}{\tilde{\Theta}(L_1)} + \frac{Q}{\tilde{\Theta}(L)}. \tag{40}$$

Then, eliminating Q/Q_1, we have

$$\tilde{\Theta}(L) = \frac{\tilde{\Theta}(L_1)}{\Theta(L_1)} \Theta(L). \tag{41}$$

It follows that $\tilde{\Theta}(L) = \alpha\Theta(L)$ in U, where $\alpha = \tilde{\Theta}(L_1)/\Theta(L_1)$ (a positive constant). Hence, Θ and $\tilde{\Theta}$ differ at most by a positive constant and it follows that the temperature scale Θ is unique on U. Then, case 2 leads to part a) of Theorem 14, and the proof of the Theorem is complete. $\square$

Note that part b) of the previous Theorem can be ruled out by supposing the **Thermometric Axiom**: to each hotness level L_0 in $\mathscr{H}$ there corresponds a system $\mathscr{C}$ in the family whose state space Σ contains a point σ_0 with $L^{'}(\sigma_0) = L_0$. Under this assumption, case b) is precluded, and, therefore, a) must hold.

We are now able to construct an absolute temperature scale ϑ by stitching together local empirical temperature scales on different hotness intervals. We are able to cover $\mathscr{H}$ with a locally finite collection of closed hotness intervals $\{\overline{U}_n\}_{n=1}^{\infty}$, where the open intervals U_n correspond to the local empirical temperature scales Θ_n described previously, and such that

(i) The open intervals U_n overlap;

(ii) For each U_n there are a corresponding $\mathscr{C}_n$ and Θ_n;

(iii) $\Theta_n : U_n \to \mathbb{R}^+$.

We can now multiply each Θ_n by a positive constant α_n, if required, to obtain a continuous function $\vartheta : \mathscr{H} \to \mathbb{R}$, such that $\vartheta|_{U_n} = \Theta_n$.

IV.4 Proof of the Accumulation Theorem for Cycles

In this section, we give a proof of the Accumulation Theorem for Cycles with a more generalized ideal system. We in fact show that the ideal gas $\mathscr{G}$ in Serrin's original formulation of the Accumulation Theorem can be replaced by a more general ideal system, namely that of a Carnot System described earlier in the paper. We believe this is likely to be the result Serrin obtained in 1979.

We restate the Accumulation Theorem with the appropiate modifications:

Theorem 16 (The Accumulation Theorem)**.** *Let $\mathscr{U}$ be a thermodynamical universe which contains a special family of Carnot systems that satisfy the Thermometric Axiom. Then there exists an (absolute) temperature scale $\tilde{T}$ on the hotness manifold $\mathscr{H}$, with $\tilde{T}(\mathscr{H}) \equiv \mathbb{R}^+$, such that for every cyclic process P of every thermodynamic system $\mathscr{L}$ in $\mathscr{U}$ we have*

$$\int_0^\infty \frac{Q(P,L)}{T^2}\, dT \;\leq\; 0, \tag{42}$$

where $L = \tilde{L}(T)$ is the hotness level associated with the temperature T in the scale $\tilde{T}$. Any temperature scale $\tilde{T}$ with the above property either agrees with the ideal scale of $\mathscr{C}$ or is a positive constant multiple of this scale.

Part 1: Uniqueness. Suppose that ϑ, as constructed above, satisfies the Accumulation Theorem, and let $\overline{\vartheta}$ be another absolute temperature scale which satisfies the Accumulation Theorem. Following the same argument used in showing that Θ was unique, it follows that the absolute temperature scale ϑ is unique.

Part 2: Existence

Lemma 17. *Let* $\phi : \vartheta(\mathscr{H}) \to \mathbb{R}$ *be a right-continuous step function, such that*

(i) $\phi(\vartheta) \equiv 0$ *for* $\vartheta < \vartheta_l$*, for some* $\vartheta_l > 0$*;*

(ii) $\phi(\vartheta) \equiv Q$ *(constant) for* $\vartheta \geq \vartheta_u$*, for some* $\vartheta_u > \vartheta_l$*;*

(iii) $\displaystyle\int_0^\infty \frac{\phi(\vartheta)}{\vartheta^2}\, d\vartheta = 0$.

Then there exists a finite collection $\{\mathscr{C}_n\}_{n=1}^N$ *of Carnot systems, and a finite collection* $\{(P_m, \sigma_m)\}_{m=1}^M$ *of Carnot cycles, not necessarily distinct, such that*

$$\sum_{m=1}^{M} Q(P_m, \sigma_m; \vartheta) = \phi(\vartheta)$$

Proof. Consider the closed interval $[L_l, L_u]$ of $\mathscr{H}$, where $L_l = \vartheta^{-1}(\vartheta_l)$ and $L_u = \vartheta^{-1}(\vartheta_u)$. Let $\{a_i\}$ be the (finite) set of discontinuities of ϕ, and let $\{b_j\}$ be the (finite) set of endpoints of the intervals $\{U_n\}$ which lie in $[L_l, L_u]$. Let $\vartheta_1, \vartheta_2, \ldots, \vartheta_K$ denote the points of $\{a_i\} \cup \{b_j\}$, listed in increasing order. Each Carnot cycle (P_m, σ_m) will have operating temperatures ϑ_k and ϑ_{k+1} for some k, which is possible, since each interval $[\vartheta_k, \vartheta_{k+1}]$ is contained in one of the hotness intervals $\overline{U}_n$ corresponding to a single thermodynamical system.

We start by choosing a Carnot cycle (P_1, σ_1), with operating temperatures ϑ_1 and ϑ_2, such that

$$Q_{1,(P_1,\sigma_1)} = \phi(\vartheta_1), \quad Q_{2,(P_1,\sigma_1)} = -\frac{\vartheta_1}{\vartheta_2}\phi(\vartheta_2)$$

Additionally, we have from Theorem 14 that

$$\int_0^\infty \frac{Q(P_1, \sigma_1; \vartheta^{-1}(\theta))}{\theta^2} d\theta = 0. \tag{43}$$

Note that $Q(P_1, \sigma_1; \vartheta^{-1}(\theta)) = \phi(\vartheta) for\ \vartheta < \vartheta_2$.

Now, we choose the cycle (P_2, σ_2) with operating temperatures ϑ_2 and ϑ_3, so that

$$Q_{1,(P_2,\sigma_2)} = \phi(\vartheta_2) + \frac{\vartheta_1}{\vartheta_2}\phi(\vartheta_2),$$

and $Q_{2,(P_2,\sigma_2)}$ equal to the value determined by lemma 15. Then we have

$$\int_0^\infty \frac{Q(P_2, \sigma_2; \vartheta^{-1}(\theta))}{\theta^2} d\theta = 0 \tag{44}$$

and $Q(P_1, \sigma_1; \vartheta^{-1}(\theta)) + Q(P_2, \sigma_2; \vartheta^{-1}(\theta)) = \phi(\vartheta)$ for $\vartheta < \vartheta_3$. We proceed inductively in this manner until, after $k - 1$ steps, we reach the last partition point ϑ_k. At this point we have

$$\int_0^\infty \frac{\sum_{m=1}^{k-1} Q(P_m, \sigma_m; \vartheta)}{\vartheta^2} d\vartheta = 0$$

and

$$\sum_{m=1}^{k-1} Q(P_m, \sigma_m; \vartheta) = \phi(\vartheta) \text{ for } \vartheta < \vartheta_k.$$

Now put

$$\psi(\vartheta) = \sum_{m=1}^{k-1} Q(P_m, \sigma_m; \vartheta) - \phi(\vartheta)$$

for all $\vartheta > 0$. Clearly, $\psi(\vartheta) \equiv 0$ for $\vartheta < \vartheta_k$, and $\psi(\vartheta)$ is constant for $\vartheta \geq \vartheta_k$. But

$$\int_0^\infty \frac{\psi(\vartheta)}{\vartheta^2} d\vartheta = 0,$$

so $\psi(\vartheta) \equiv 0$, and the lemma is proved.

To complete the proof of the Accumulation Theorem, suppose (for a contradiction) that there is some cyclic process (P, σ) for which

$$A \equiv \int_0^\infty \frac{Q(P, \sigma; \vartheta^{-1}(\theta))}{\theta^2} d\theta = \int_0^\infty \frac{Q(P, \sigma; L)}{\theta^2} d\theta > 0.$$

Suppose that the operating limits of (P, σ) are $\vartheta_l < \vartheta_u$. Given $\epsilon > 0$, we can find a step function f, such that $f(\vartheta) \geq -\ Q(P, \sigma; \vartheta)$ for $\vartheta \in [\vartheta_l, \vartheta_u]$, and such that

$$\int_{\vartheta_l}^{\vartheta_u} \mid f(\vartheta) + \ Q(P, \sigma; \vartheta) \mid \, d\vartheta < \epsilon. \tag{45}$$

Extend f to all of $\mathbb{R}$ in the natural way: $f(\vartheta) \equiv 0$ for $\vartheta < \vartheta_l$, $f(\vartheta) \equiv -\ Q(P, \sigma; \vartheta) \equiv -Q(P, \sigma)$ for $\vartheta \geq \vartheta_u$. Then

$$\int_0^\infty \frac{f(\vartheta)}{\vartheta^2} \, d\vartheta = -\int_0^\infty \frac{Q(P, \sigma; \vartheta)}{\vartheta^2} \, d\vartheta + \int_{\vartheta_l}^{\vartheta_u} \frac{f(\vartheta) + \ Q(P, \sigma; \vartheta)}{\vartheta^2} \, d\vartheta \leq -A + \frac{\epsilon}{\vartheta_l^2}. \tag{46}$$

Now choose ϵ so small that

$$\int_0^\infty \frac{f(\vartheta)}{\vartheta^2} \, d\vartheta < 0. \tag{47}$$

Put

$$B = -\vartheta_l \int_0^\infty \frac{f(\vartheta)}{\vartheta^2} \, d\vartheta > 0, \tag{48}$$

and

$$\phi(\vartheta) = \begin{cases} f(\vartheta), & \vartheta < \vartheta_l \\ f(\vartheta) + B, & \vartheta \geq \vartheta_l. \end{cases} \tag{49}$$

Now ϕ satisfies the conditions of the Lemma recently proved above, and so we can find Carnot cycles $\{(P_m, \sigma_m)\}_{m=1}^M$ described in that lemma so that the union process

$$(P^{'}, \sigma^{'}) = (P_1, \sigma_1) \oplus \cdots \oplus (P_M, \sigma_M) \tag{50}$$

satisfies

$$Q(P^{'}, \sigma^{'}; \vartheta) = \phi(\vartheta). \tag{51}$$

But then the process

$$(\tilde{P}, \tilde{\sigma}) = (P, \sigma) \oplus (P_1, \sigma_1) \oplus \cdots \oplus (P_M, \sigma_M) \tag{52}$$

satisfies the following:

$$\begin{aligned}
Q(\tilde{P}, \tilde{\sigma}; \vartheta) &= Q(P, \sigma; \vartheta) + \phi(\vartheta) \qquad (53)\\
&= Q(P, \sigma; \vartheta) + \begin{cases} f(\vartheta), & \vartheta < \vartheta_l \\ f(\vartheta) + B, & \vartheta \geq \vartheta_l \end{cases} \qquad (54)\\
&\geq Q(P, \sigma; \vartheta) + \begin{cases} 0, & \theta < \vartheta_l \\ -Q(P, \sigma; \vartheta) + B, & \vartheta \geq \vartheta_l \end{cases} \qquad (55)\\
&\geq 0, \qquad (56)
\end{aligned}$$

and so we have

$$Q(\tilde{P}, \tilde{\sigma}) = Q(P, \sigma) + (-Q(P, \sigma) + B) = B > 0. \tag{57}$$

This contradicts the Second Law, and thus completes the proof of the Accumulation Theorem.

□

□

Second Law for Systems with Approximate Cycles

There are many physical systems with very few exact cycles (such as materials with memory). For these systems, the First and Second laws for cycles give very little information, so [C1] developed a theory for systems with approximate cycles. Approximate Cycles, as discussed in [C1], is a generalization of the notion of a cycle. Prior to this point, cycles have been defined to be processes in which the initial and final states are the same. In an approximate cycle, the final state is not equal to the initial state. However, the final state is "close to" the initial state.

The theory for systems with approximate cycles follows the same formulation as that discussed in chapter 2 section 1. Namely:

A *System* is now a pair (Σ, Π) of sets (with Σ called the set of **states** σ and Π the set of **processes** P) together with a topology on Σ and a function $P \to \varrho_P$. The function $P \to \varrho_P$ assigns to each process P a function $\varrho_P : \mathscr{D}(P) \to \Sigma$, where $\mathscr{D}(P)$ is a non-empty subset of Σ.

With the notion of a topology in place, we are now ready to state the Second Law as it applies to approximate cycles:

Second Law for thermodynamical systems- Let $\mathscr{L} = (\Sigma, \Pi, Q)$ be a thermodynamical system. For each state σ in Σ, for each $\epsilon > 0$, and for each hotness level $\bar{L}$ in $\mathscr{H}$, there is a neighborhood $\mathscr{A} = \mathscr{A}(\sigma, \epsilon, \bar{L})$ of σ such that

$$0 \le Q(P, \sigma) < \epsilon \tag{58}$$

for every process P for which (P, σ) is absorptive, operates at or below $\bar{L}$, and has its final state $\varrho_P \sigma$ in $\mathscr{A}$.

With Theorem 14 in hand, it is possible to obtain a generalization of the Accumulation Theorem as it applies to approximate cycles. Consider a thermodynamical universe $\mathscr{U}$ which contains a special family of Carnot systems for which

$$\mathscr{L} \in \mathscr{U} \implies \mathscr{L} \oplus \mathscr{C} \in \mathscr{U} \tag{59}$$

for any system $\mathscr{C}$ in the family. Note that this ideal system $\mathscr{C}$ is the same ideal system discussed last chapter. Suppose further that the *Thermometric Axiom* holds. We are now ready to state and prove Theorem 6.2 from [C1], a generalization of the Accumulation Theorem to that of approximate cycles:

Theorem 18 (Generalized Accumulation Theorem)**.** *Let $\mathscr{U}$ be a universe of thermodynamical systems with states which satisfy the Second Law. Assume that $\mathscr{U}$ contains a special family of Carnot systems such that the following hold:*

1. $\mathscr{L} \in \mathscr{U} \implies \mathscr{L} \oplus \mathscr{C} \in \mathscr{U}$
2. *the thermometric axiom*
3. *for each neighborhood V of each level L in $\mathscr{H}$, there is a cycle (P, σ) of a Carnot system $\mathscr{C}$ in $\mathscr{U}$ with L^l and L^u in V and $Q(P, \sigma) > 0$.*

Then there is an empirical temperature scale Φ such that, for every system $\mathscr{L} = (\Sigma, \Pi, Q)$ in $\mathscr{U}$, for every state σ in Σ, for every hotness level $\bar{L}$ in $\mathscr{H}$, and for every $\epsilon > 0$, there is *a neighborhood $\mathscr{O} = \mathscr{O}(\sigma, \epsilon, \bar{L})$ of σ for which*

$$\int_0^\infty \frac{Q(P, \sigma; \Phi^{-1}(\theta))}{\theta^2} d\theta < \epsilon \tag{60}$$

whenever the pair (P, σ) operates at or below $\bar{L}$ and has its final state in $\mathscr{O}$. Moreover, any other scale $\overline{\Phi}$ with this property must be a constant positive multiple of Φ.

Proof. [C1] Suppose first that the accumulation integral (located above) holds, and let $\bar{L}$ in $\mathscr{H}$, $\mathscr{L} = (\Sigma, \Pi, Q)$ in $\mathscr{U}$, σ in Σ and $\epsilon > 0$ be given. Then there is is a neighborhood $\mathscr{O} = \mathscr{O}(\sigma, \epsilon, \bar{L})$ of σ such that, if (P, σ) operates at or below $\bar{L}$ and $\varrho_P \sigma$ is in $\mathscr{O}$, then

$$\int_{\Phi(L^l)}^{\Phi(\bar{L})} \frac{Q(P, \sigma; \Phi^{-1}(\theta))}{\theta^2} d\theta \; + \; \frac{Q(P, \sigma)}{\Phi(\bar{L})} \; < \; \epsilon. \tag{61}$$

If, in addition, (P, σ) is absorptive, then this inequality implies

$$0 \; \leq \; Q(P, \sigma) \; < \; \epsilon \Phi(\bar{L}). \tag{62}$$

Replacement of ϵ with $\frac{\epsilon}{\Phi(\bar{L})}$ (and hence $\mathscr{O}(\sigma, \epsilon, \bar{L})$ with $\mathscr{O}(\sigma, \frac{\epsilon}{\Phi(\bar{L})}, \bar{L})$) here yields the assertion that whenever (P, σ) is absorptive, operates at or below $\bar{L}$, and has its final state $\varrho_P \sigma$ in $\mathscr{A} \equiv \mathscr{O}(\sigma, \frac{\epsilon}{\Phi(\bar{L})}, \bar{L})$, there holds

$$0 \; \leq \; Q(P, \sigma) \; < \; \frac{\epsilon}{\Phi(\bar{L})} \Phi(\bar{L}) \; = \; \epsilon, \tag{63}$$

and hence $\mathscr{L}$ obeys the Second Law.

In order to prove the converse statement, i.e., to show that the Second Law implies the accumulation integral, we wish to show the contrapositive assertion: if the accumulation integral fails to hold somewhere in $\mathscr{U}$, then so does the Second Law. Thus, suppose that the accumulation integral is false. That is, suppose there is a system $\mathscr{L}_0 = (\Sigma_0, \Pi_0, Q_0)$, a hotness level L_0, a state σ_0 in Σ_0, and a positive number ϵ_0 such that, for each neighborhood $\mathscr{O}$ of σ_0, there is a corresponding process $P = P(\mathscr{O})$ for which

$$\varrho_P \sigma_0 \in \mathscr{O} \text{ and } (P, \sigma_0) \text{ operates at or below } L_0, \tag{64}$$

and

$$\int_0^\infty \frac{Q_0(P, \sigma_0; \Phi^{-1}(\theta))}{\theta^2} d\theta \ \geq \ \epsilon_0. \tag{65}$$

For the pair (P, σ_0), let $L^u = L_0$; furthermore, let $\theta^{'} = \Phi(L^l)$ and $\theta^{''} = \Phi(L_0)$, and let $\tau_0 \in \Sigma_{\mathscr{C}}$ be any fixed state for $\mathscr{C}$ of the form $(x_0, \theta^{''})$. By definition, the function

$$f : \mathbb{R}^+ \to \mathbb{R}, \tag{66}$$

defined by

$$f(\theta) \ = \ -Q_0(P, \sigma_0; \Phi^{-1}(\theta)), \tag{67}$$

is bounded, has only countably many points of discontinuity, and satisfies:

$$f(\theta) = \begin{cases} 0, & 0 < \theta < \theta^{'} \\ -Q_0(P, \sigma_0), & \theta^{''} \leq \theta. \end{cases} \tag{68}$$

The fact that f is Riemann integrable implies that there is a right-continuous step function $q : [\theta^{'}, \theta^{''}) \to \mathbb{R}$ such that

$$f(\theta) \leq q(\theta) \ for \ \theta^{'} \leq \theta < \theta^{''} \tag{69}$$

and

$$\int_{\theta'}^{\theta''} q(\theta)\,\mathrm{d}\theta \;\le\; \int_{\theta'}^{\theta''} f(\theta)\,\mathrm{d}\theta \;+\; \frac{\epsilon_0}{2}{\theta'}^2. \tag{70}$$

As $\mathscr{C}$ is the ideal system for $\mathscr{U}$, and τ_0 is the state for $\mathscr{C}$ selected earlier, there is a cycle (P_t, τ_0) for (a finite collection of Carnot systems) such that Lemma 17 holds. Note that τ_0 depends only on L_0, whereas P_t depends upon $\mathscr{O},\ \epsilon_0,\ \sigma_0$ and L_0.

Now consider the union system $\mathscr{L}_0 \oplus \mathscr{C} = (\Sigma_0 \times \Sigma_{\mathscr{C}}, \Pi_0 \times \Pi_{\mathscr{C}}, Q_0 + Q_{\mathscr{C}})$.
By the assumed properties of $\mathscr{U}$, $\mathscr{L}_0 \oplus \mathscr{C}$ is in $\mathscr{U}$ and (σ_0, τ_0) is in $\Sigma_0 \times \Sigma_{\mathscr{C}}$, i.e., (σ_0, τ_0) is a state of $\mathscr{L}_0 \oplus \mathscr{C}$. For each neighborhood $\mathscr{A}$ of (σ_0, τ_0) (with respect to the product topology on $\Sigma_0 \times \Sigma_{\mathscr{C}}$), there are neighborhoods $\mathscr{O}$ and $\mathscr{O}_{\mathscr{C}}$ of σ_0 and τ_0, respectively, such that

$$\mathscr{O} \times \mathscr{O}_{\mathscr{C}} \subset \mathscr{A}. \tag{71}$$

Now, it follows that the pair $((P, P_t), (\sigma_0, \tau_0))$, with $P = P(\mathscr{O})$, operates at or below L_0 and has its final state $(\varrho_P \sigma_0, \varrho_{P_t} \tau_0)$ in $\mathscr{A}$. By previous facts and Lemma 17 we see that for $L < L_0$

$$Q((P, P_t), (\sigma_0, \tau_0); L) \;=\; Q_0(P, \sigma_0; L) \;+\; Q_{\mathscr{C}}(P_t, \tau_0; L) \;\ge\; 0. \tag{72}$$

Moreover, by Lemma 17, the definition of $f(\theta)$, and some algebra,

$$\begin{aligned} Q_0(P, \sigma_0) + Q_{\mathscr{C}}(P_t, \tau_0) &= Q(P, \sigma_0; L_0) + Q_{\mathscr{C}}(P_t, \tau_0; L_0) \\ &= Q_0(P, \sigma_0; L_0) + \theta'' \int_{\theta'}^{\theta''} Q_0(P, \sigma_0; \Phi^{-1}(\theta))\theta^{-2}\,\mathrm{d}\theta \\ &+ Q_{\mathscr{C}}(P_t, \tau_0; L_0) + \theta'' \int_{\theta'}^{\theta''} Q_{\mathscr{C}}(P_t, \tau_0; \Phi^{-1}(\theta))\theta^{-2}\,\mathrm{d}\theta \\ &- \theta'' \int_{\theta'}^{\theta''} (q(\theta) - f(\theta))\theta^{-2}\,\mathrm{d}\theta. \end{aligned} \tag{73}$$

The sum of the first two terms after the second sign of equality is

$$\theta'' \int_0^{\infty} Q_0(P, \sigma_0; \Phi^{-1}(\theta))\theta^{-2}\,\mathrm{d}\theta; \tag{74}$$

the sum of the next two terms is zero because of Theorem 14; and, in view of the properties of the step function q, we have

$$\int_{\theta'}^{\theta''} (q(\theta) - f(\theta))\theta^{-2}\,\mathrm{d}\theta \;\leq\; \frac{\epsilon_0}{2}. \tag{75}$$

Therefore, we have that

$$Q_0(P, \sigma_0) + Q_{\mathscr{C}}(P_t, \tau_0) \;\geq\; \theta'' \int_0^\infty Q_0(P, \sigma_0; \Phi^{-1}(\theta))\theta^{-2}\,\mathrm{d}\theta \;-\; \frac{1}{2}\theta''\epsilon_0 \tag{76}$$

and hence

$$Q((P, P_t), (\sigma_0, \tau_0)) \;\geq\; \epsilon_0\theta'' \;-\; \frac{1}{2}\epsilon_0\theta'' \;=\; \frac{1}{2}\epsilon_0\Phi(L_0) \;>\; 0. \tag{77}$$

This and the fact that $Q((P, P_t), (\sigma_0, \tau_0); L) \geq 0$ shows that the pair $((P, P_t), (\sigma_0, \tau_0))$ is absorptive. It has already been stated that this pair operates at or below L_0 and has its final state in $\mathscr{A}$. Moreover, by the line above, its overall net transfer of heat is no less than $\frac{1}{2}\epsilon_0\Phi(L_0)$.

To summarize, for each neighborhood $\mathscr{A}$ of (σ_0, τ_0), the pair $((P, P_t), (\sigma_0, \tau_0))$ operates at or below the fixed level L_0, is absorptive, has a positive net transfer of heat, and has its final state in $\mathscr{A}$. Consequently, the Second Law fails to hold for $\mathscr{L}_0 \oplus \mathscr{C}$ when $\bar{L} = L_0$, $\epsilon = \frac{1}{2}\epsilon_0\Phi(L_0)$ and $\sigma = (\sigma_0, \tau_0)$, and the proof is complete. $\square$

Summary and Conclusion

Serrin's Accumulation Theorem is of great importance as it provides an analytical formulation of the Second Law. It accomplishes two major goals: it establishes the concept of absolute temperature without ambiguity, and it also characerizes the allowable behavior of the accumulation function of any cyclic process. We showed in this paper that it is possible to prove the Accumulation Theorem for cycles by using a more generalized ideal system (namely Carnot systems). Moreover, we showed that The Accumulation Theorem holds for more general cycles, known as approximate cycles. However, there is more to be done. In a footnote, [C1] claim that the proof of The Accumulation Theorem can be made to go through with an even more general class of systems (in place of Carnot Systems).

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