



The University of Rochester

DEPARTMENT OF CHEMICAL ENGINEERING

ROCHESTER, NEW YORK 14627

TELEPHONE (716) 275-4041

June 30, 1978

Professor James Serrin
School of Mathematics
127 Vincent Hall
206 Church Street, S.E.
University of Minnesota
Minneapolis, MN 55455

Dear Jim:

As I mentioned in our phone conversation after the Venice meeting, I did quite a bit of thinking about thermodynamics constructed along the lines you sketched in our lunch conversation with David Owen. I found everything you said extremely attractive; but, on the other hand, I could not escape the feeling that existence of a temperature scale suitable for the Clausius inequality could (and should) be obtained without presupposing materials with special constitutive properties. At the time I believe I said that results you obtained were reminiscent of results provided by Kuhn-Tucker type theorems. On returning to Rochester, I realized that what I probably had in mind were topological vector space theorems to the effect that certain pairs of disjoint convex sets can be separated by hyperplanes. After convincing myself that these could probably be made to work, I enlisted the considerable help of Rick Lavine, a friend in the math department.

Rick and I worked together on and off for a period of about ten days, and I think we have some very pretty results. I have compiled some of these, tentative though they are, in some hand-written notes. I am sending these to you in the hope that we can discuss them in Muncie. Because Rick left for Cape Cod before I wrote the notes, I haven't had the benefit of his comments. Although he would probably endorse the general thrust of the notes, he might have done at least some things in a different (and no doubt better) way. Should you visit Rochester, perhaps the three of us could get together.

I will probably call you during the second week in July to get advice on my phase rule talk.

Sincerely,

Marty

Martin Feinberg
Associate Professor

MF:dp

Preliminary Notes on the Second Law of Thermodynamics

(Motivated by conversations with James Serrin)

M. Feinberg & R. Levine

University of Rochester

July 2, 1978

1. Primitives

Empirical temperature scale: E is an open (possibly unbounded) interval of the real line called an empirical temperature scale.

Heatings: Let M denote the vector space of finite Borel measures on E with compact support; and, for later use, let M^+ denote the convex cone in M consisting of the non-negative measures.

With each process that a material body might undergo we identify a heating $\mu \in M$ with the following interpretation: If $J \subseteq E$ is an open interval, $\mu(J)$ is the net amount of heat received (by the body during the process) at empirical temperatures contained in J .

Remark: That we choose to work with the finite Borel measures with compact support reflects the view that every process we are likely to encounter in nature will operate within a bounded range of empirical temperatures and will involve at most a finite receipt of heat by the body and/or a finite emission of heat from it.

Cyclic Heatings: We distinguish a set Cyc Htg $\subset M$ called the cyclic hearings. Elements of Cyc Htg are given the following interpretation: $\mu \in \text{Cyc Htg}$ if and only if there exists a body which can undergo a cyclic process with heating μ . We presume the set Cyc Htg to have these properties:

Cyc Htg 1. $0 \in \text{Cyc Htg}$ (where 0 denotes the zero measure)

Cyc Htg 2. $\mu_1, \mu_2 \in \text{Cyc Htg} \Rightarrow \mu_1 + \mu_2 \in \text{Cyc Htg}$

Cyc Htg 3. $\mu \in \text{Cyc Htg}$ and $\alpha \in \mathbb{R}^+$ (pos. real nos.) $\Rightarrow \alpha\mu \in \text{Cyc Htg}$

Remark: Cyc Htg 1 reflects the view that a "null process", in which an equilibrated body remains in some fixed state for a time period with ^{no} heat being supplied or extracted, is cyclic.

Cyc Htg 2 is motivated by the idea that if a body can undergo a cyclic process with heating μ_1 , and a separate body can undergo a cyclic process with heating μ_2 , then the two processes acting on the two bodies constitute a cyclic process with heating $\mu_1 + \mu_2$.

Cyc Htg 3 reflects the view that if there exists a body which can undergo a cyclic process with heating μ , then for any $\alpha \in \mathbb{R}^+$ there exists a body (perhaps a "scaled" copy of the first) which can undergo a cyclic process with heating $\alpha\mu$.

Important note: Cyc Htg 3 reflects a strong supposition about natural processes. It is included here for the sake of simplicity. In fact, Cyc Htg 3 can be dispensed with for our purposes, provided that the Weak Second Law of the next section is given a more technical (but equally plausible) statement.

2. The Weak Second Law and the Clausius Inequality

An expedient philosophy: For certain technical reasons it will be convenient, at least in this preliminary study, to work not with the entire empirical temperature scale E but rather with an arbitrarily large closed (and therefore compact) interval $K \subset E$. Although this state of affairs is hardly desirable, it is not altogether unreasonable. For if one accepts the fact that the range of empirical temperatures we have ever experienced (or perhaps will ever experience) is bounded, then any statement of "law" concerning processes must necessarily be based upon experience with processes which involved empirical temperatures within those bounds. Statements concerning other processes represent extrapolations which might, in fact, be false.

With this in mind, we let $K \subset E$ represent a closed interval in E , however large. (For the purposes of the mathematics, K can be any compact subset of E , not necessarily a closed interval) M_K is the linear subspace of M consisting of all measures of M which have support in K . $M_K^+ := M_K \cap M^+$, and $(\text{Cyc Htg})_K := M_K \cap (\text{Cyc Htg})$. Both M_K^+ and $(\text{Cyc Htg})_K$ are convex cones which contain 0 (the zero measure). Note that $(\text{Cyc Htg})_K$ is comprised of those cyclic heatings corresponding to processes on bodies in which heat is received by the body or emitted from it only at ^{empirical} temperatures within K .

We give M_K its weak* topology: Let $C(K, \mathbb{R})$ denote the set of real valued continuous functions on K . For

each $\varphi \in C(K, \mathbb{R})$, let $\Gamma_\varphi : M_K \rightarrow \mathbb{R}$ be the linear functional defined by

$$\Gamma_\varphi(\mu) = \int_K \varphi d\mu.$$

The weak* topology on M_K is the weakest topology that renders Γ_φ continuous for every $\varphi \in C(K, \mathbb{R})$. Henceforth, all topological operations in M_K (in particular the taking of closures) will be with respect to the weak* topology. Note that M_K , given its weak* topology, is a Hausdorff locally convex topological vector space.

The Weak Second Law: $\text{Cl}(\text{Cyc Htg})_K \cap M_K^+ = \{0\}$ (zero measure), where Cl denotes closure.

In rough terms the "Weak Second Law" says the following: No cyclic heating can be a positive measure; in a cyclical process (involving some body) in which heat is absorbed by the body in some Borel set of empirical temperatures it must be the case that heat is emitted by the body on some other Borel set of empirical temperatures. Moreover, no positive measure is arbitrarily close to the cyclic heatings in the sense that each positive measure is contained in a weak* neighborhood disjoint from the cyclic heatings.

The following theorem asserts the equivalence of the Weak Second Law and the Clausius inequality:

Theorem A: The following statements are equivalent:

(i) Weak Second Law: $\text{Cl}(\text{CycHtg})_K \cap M_K^+ = \{0\}$

(ii) Clausius Inequality: There exists a continuous function $T_K: K \rightarrow \mathbb{R}^+$ such that

$$\int_K \frac{1}{T_K} d\mu \leq 0, \quad \forall \mu \in (\text{CycHtg})_K$$

Idea of Proof:

(i) \Rightarrow (ii) The proof invokes the following "Separation Theorem", which is readily available in the topological vector space literature. (See, for example, Choquet's Lectures on Analysis, Vol. II, p. 31.)

Separation Thm. Let V be a Hausdorff locally convex topological vector space, and let $A, B \subset V$ be disjoint closed convex subsets of V with A compact. Then there exists a continuous linear functional $f: V \rightarrow \mathbb{R}$ and a number γ such that $f(x) > \gamma$ for all $x \in A$ and $f(x) < \gamma$ for all $x \in B$.

Let $(M_K^+)^1 := \{\mu \in M_K^+ : \mu(K) = 1\}$. It is readily seen that $(M_K^+)^1$ is convex; what is less clear is that $(M_K^+)^1$ is weak* compact (proof omitted). Since $(\text{CycHtg})_K$ is convex, $\text{Cl}(\text{CycHtg})_K$ is closed and convex (proof omitted).

From (i) it follows that $(M_K^+)^{\perp} \cap \text{Cl}(\text{Cyc Htg})_K$ is empty. Thus, the Separation Thm. ensures that there exists a continuous linear functional $f: M_K \rightarrow \mathbb{R}$ and $\delta \in \mathbb{R}$ such that

$$f(\mu) > \delta, \quad \forall \mu \in (M_K^+)^{\perp} \quad (a)$$

and

$$f(\mu) < \delta, \quad \forall \mu \in \text{Cl}(\text{Cyc Htg})_K \quad (b)$$

Since $0 \in \text{Cl}(\text{Cyc Htg})_K$, (b) implies that $\delta > 0$. Moreover, it follows from (b) that

$$f(\mu) \leq 0, \quad \forall \mu \in \text{Cl}(\text{Cyc Htg})_K. \quad (b')$$

For, if for some $\mu \in \text{Cl}(\text{Cyc Htg})_K$ $f(\mu)$ were positive, then for appropriately large $\alpha \in \mathbb{R}^+$ $f(\alpha\mu) > \delta$ — thereby violating (b) since $\alpha\mu \in \text{Cl}(\text{Cyc Htg})_K$.

It is well known that the only continuous linear functionals on M_K (given the weak* topology) are of the type $\int \varphi(\cdot) d\mu$ mentioned earlier, where $\varphi \in C(K, \mathbb{R})$. Thus f has a representation

$$f(\mu) \equiv \int \frac{1}{T_K} d\mu,$$

where $\frac{1}{T_K}: K \rightarrow \mathbb{R}^+$ is continuous*. (That $\frac{1}{T_K}$ can take only positive values follows from (a) and the fact that, for each $x \in K$,

$$f(\delta_x) = \int \frac{1}{T_K} d\delta_x = \frac{1}{T_K}(x),$$

* \mathbb{R}^+ denotes the strictly positive real nos.

where $\delta_x \in (M_K^+)^1$ is the Dirac measure at x . From these observations and (b) it follows that there exists a continuous function $T_K: K \rightarrow \mathbb{R}^+$ such that

$$\int_K \frac{1}{T_K} d\mu \leq 0, \forall \mu \in \text{Cyc Htg}.$$

This completes the proof of (i) \Rightarrow (ii).

(ii) \Rightarrow (i) With M_K given the weak* topology, the ^{linear} functional $\mu \in M_K \xrightarrow{f} \int_K \frac{1}{T_K} d\mu$ is continuous. Thus $f^{-1}(\mathbb{R}^+)$ is open, contains $M_K^+ \setminus 0$, and contains no element of $(\text{Cyc Htg})_K$. Therefore, the complement (in M_K) of $f^{-1}(\mathbb{R}^+)$ is closed, contains $(\text{Cyc Htg})_K$ (and hence its closure) and no element of M_K^+ other than 0. Consequently,

$$\text{cl}((\text{Cyc Htg})_K) \cap M_K^+ = 0.$$

This completes the proof of Theorem A. \square

3. Uniqueness of $T_K(\cdot)$ and the (Inexorable) Role of Carnot Elements

If a function $T_K: K \rightarrow \mathbb{R}^+$ is continuous and satisfies the Clausius inequality stated in (ii) of Theorem A, then any positive constant multiple of $T_K(\cdot)$ will also have these qualities. It is natural to ask whether there can exist another continuous function $\hat{T}_K: K \rightarrow \mathbb{R}^+$ which also satisfies the Clausius inequality but which is not a positive constant multiple of $T_K(\cdot)$. It is clear that, in vaguely suggestive terms, the answer resides in the "richness" of the set $(\text{Cyc Htg})_K$: the more varied the nature of elements in $(\text{Cyc Htg})_K$, the less varied will be the nature of continuous functions which satisfy the requirement the Clausius inequality demands. It is reasonably well known that if $(\text{Cyc Htg})_K$ is suitably well endowed with what we shall call Carnot elements, then uniqueness of $T_K(\cdot)$ (up to a positive constant multiple) is ensured. The argument is more or less routine.

However, we prove something far deeper: If a continuous function $T_K: K \rightarrow \mathbb{R}^+$ which satisfies the Clausius inequality is unique up to a positive constant multiple, then $(\text{Cyc Htg})_K$ must be well endowed with Carnot elements.

Thus, the situation might be described roughly as follows: The existence of $T_K(\cdot)$ is implied by (and implies) the Weak Second Law, and nothing need be said about the nature of the set $(\text{Cyc Htg})_K$ apart from (at most) those of its crude features specified in § 1. However, any argument regarding the uniqueness of $T_K(\cdot)$ (up to a positive constant multiple) must necessarily invoke postulates at least equivalent to an assertion that $(\text{Cyc Htg})_K$ is suitably rich in Carnot elements.

Definition: A Carnot element for $(\text{Cyc Htg})_K$ is a member of M_K of the form $a\delta_x - a'\delta_{x'}$ (where $a, a' \in \mathbb{R}^+$, $x, x' \in K$, and δ_x and $\delta_{x'}$ are Dirac measures at x and x') such that both $a\delta_x - a'\delta_{x'}$ and $a'\delta_{x'} - a\delta_x$ are elements of $\text{Cl}(\text{Cyc Htg})_K$. A Carnot element $a\delta_x - a'\delta_{x'}$ for $(\text{Cyc Htg})_K$ is said to operate at empirical temperatures x and x' .

Remark: Carnot elements for $(\text{Cyc Htg})_K$ might be characterized in words roughly as those elements of M_K which represent absorption or emission of heat at no more than two empirical temperatures and which, along with their negatives, are approximated by elements of $(\text{Cyc Htg})_K$ in the weak* topology. Note that the definition requires no notion of reversible paths in some space of states.

Remark: Nothing said thus far about the structure of the set $(\text{Cyc Htg})_K$ requires that, for a specified pair of empirical temperatures $x, x' \in K$, there exist a Carnot element for $(\text{Cyc Htg})_K$ operating at x and x' . That is, for $x, x' \in K$, it may be the case that every measure of the form $a\delta_x - a'\delta_{x'}$ (where $a, a' \in \mathbb{R}^+$) is contained in a weak* neighborhood disjoint from $(\text{Cyc Htg})_K$. The following theorem asserts that $T_K(\cdot)$ is unique (up to a positive constant multiple) if and only if for every pair $x, x' \in K$ there exists a Carnot element for $(\text{Cyc Htg})_K$ operating at empirical temperatures x and x' .

Theorem B: The following statements are equivalent:

i. (Uniqueness of $T_K(\cdot)$) If $T_K: K \rightarrow \mathbb{R}^+$ and $\hat{T}_K: K \rightarrow \mathbb{R}^+$ are continuous and are such that

$$\int_K \frac{1}{T_K} d\mu \leq 0, \quad \forall \mu \in (\text{Cyc Htg})_K \quad (a)$$

$$\int_K \frac{1}{\hat{T}_K} d\mu \leq 0, \quad \forall \mu \in (\text{Cyc Htg})_K, \quad (b)$$

then there exists $\gamma \in \mathbb{R}^+$ such that $\hat{T}_K(x) = \gamma T_K(x), \forall x \in K$.

ii. (Abundance of Carnot elements) For every pair of empirical temperatures $x, x' \in K$, there exists a Carnot element for $(\text{Cyc Htg})_K$ operating at x and x' .

The proof that (i) \Rightarrow (ii) will be based upon the following

Proposition: Statement (i) of Theorem B is true only if $\int_K \frac{1}{T_K} d\mu = 0$

implies that $\mu \in \mathcal{C}(\text{Cyc Htg})_K$.

Proof of Proposition: Let $f: M_K \rightarrow \mathbb{R}$ be the continuous linear functional defined by

$$f(\mu) \equiv \int_K \frac{1}{T_K} d\mu$$

It follows easily from (a) and the continuity of f that

$$f(\mu) \leq 0, \quad \forall \mu \in \text{Cl}(\text{CycHtg})_K \quad (c)$$

Moreover, it is clear that

$$f(\mu) > 0, \quad \forall \mu \in (M_K^+)^{\perp} (= \{\mu \in M_K^+ : \mu(K) = 1\}). \quad (d)$$

We note, as in the proof of Thm. A, that $\text{Cl}(\text{CycHtg})_K$ is a closed convex cone and that $(M_K^+)^{\perp}$ is convex and compact.

Now suppose there exists $\mu^0 \in M_K$ such that $\mu^0 \notin \text{Cl}(\text{CycHtg})_K$ and $f(\mu^0) = 0$. Under such a circumstance, we shall prove the existence of a continuous $\hat{T}_K: K \rightarrow \mathbb{R}^+$ which satisfies (b) but which is not a positive constant multiple of $T_K(\cdot)$.

Let $A \subset M_K$ be the convex set defined as follows:

$$A := \{\mu \in M_K : \mu = \lambda \mu^0 + (1-\lambda)\mu', \text{ where } \mu' \in (M_K^+)^{\perp} \text{ and } 0 \leq \lambda \leq 1\}.$$

A is compact since the continuous function $P: (M_K^+)^{\perp} \times [0,1] \rightarrow A$ defined by

$$P(\mu', \lambda) \equiv \lambda \mu^0 + (1-\lambda)\mu'$$

maps its compact domain onto A . It follows easily from (d), from the

definition of A , and from the fact that $f(\mu^0) = 0$ that

$$f(\mu) > 0, \quad \forall \mu \in A - \mu^0 \quad (e)$$

Thus, (c), (e), and the supposition that $\mu^0 \notin \mathcal{C}(\text{Cyc Htg})_K$ imply that

$$A \cap \mathcal{C}(\text{Cyc Htg})_K = \emptyset.$$

The Separation Theorem of § 2 and arguments similar to those employed in the proof of Thm A ensure the existence of a continuous linear functional $\hat{f}: M_K \rightarrow \mathbb{R}$ such that

$$\hat{f}(\mu) \leq 0, \quad \forall \mu \in \mathcal{C}(\text{Cyc Htg})_K \quad (f)$$

and

$$\hat{f}(\mu) > 0, \quad \forall \mu \in A \quad (g)$$

Moreover, as in the proof of Thm A, \hat{f} has a representation

$$\hat{f}(\mu) \equiv \int_K \frac{1}{T_K} d\mu, \quad (h)$$

where $\hat{T}_K: K \rightarrow \mathbb{R}^+$ is continuous. The function $\hat{T}_K(\cdot)$ cannot be a positive constant multiple of $T_K(\cdot)$ since by supposition

$$\int_K \frac{1}{T_K} d\mu^0 = 0,$$

whereas (g), (h), and the fact that $\mu^0 \in A$ imply

$$\int_K \frac{1}{T_K} d\mu^0 > 0.$$

Thus, $\mu^0 \notin \text{Cl}(\text{Cyc Htg})_K$ such that $\int_K \frac{1}{T_K} d\mu^0 = 0$ ensures the existence of a continuous function $\hat{T}_K: K \rightarrow \mathbb{R}^+$ which is not a positive constant multiple of T_K and which satisfies (b). \square

Before proving Thm. B, we record two corollaries of the proposition (proofs omitted). The first of these asserts that uniqueness of $T_K(\cdot)$ requires that $\text{Cl}(\text{Cyc Htg})_K$ is either a hyperplane or a half space.

Corollary 1: If statement (i) of Thm. B is true, then either

$$\text{Cl}(\text{Cyc Htg})_K = \left\{ \mu \in M_K : \int_K \frac{1}{T_K} d\mu = 0 \right\}$$

or

$$\text{Cl}(\text{Cyc Htg})_K = \left\{ \mu \in M_K : \int_K \frac{1}{T_K} d\mu \leq 0 \right\}.$$

The following corollary asserts that if $T_K(\cdot)$ is unique and if $\mu \in M_K$ is such that $\int_K \frac{1}{T_K} d\mu = 0$, then μ is "approximately a revers. ble cyclic heating" in the sense that both μ and $-\mu$ are weak* approximated by elements of $(\text{Cyc Htg})_K$.

Corollary 2: If statement (i) of Thm. B is true, and if $\mu \in M_K$ is such that $\int_K \frac{1}{T_K} d\mu = 0$, then μ and $-\mu$ are elements of $\text{Cl}(\text{Cyc Htg})_K$.

Remark: Once Thm B is proved, statement (ii) of Thm B can be used in the hypotheses of Cor. 1 & 2 in place of statement (i).

Proof of Theorem B

(i) \Rightarrow (ii) Let x and x' be elements of K , and let $\mu^0 = T_K(x) \delta_x - T_K(x') \delta_{x'}$.

Note that

$$\int_K \frac{1}{T_K} d\mu^0 = 0 \quad \text{and} \quad \int_K \frac{1}{T_K} d(-\mu^0) = 0.$$

Thus, (i) and the Proposition ensure that μ^0 and $-\mu^0$ are elements of $\mathcal{C}l(\text{CycHtg})_K$. Therefore, μ^0 is a Carnot element for $(\text{CycHtg})_K$.

(ii) \Rightarrow (i) Suppose there exist two continuous functions $T_K: K \rightarrow \mathbb{R}^+$ and $\hat{T}_K: K \rightarrow \mathbb{R}^+$ such that (a) & (b) of (i) are satisfied. For any pair $x, x' \in K$, let $a\delta_x - a'\delta_{x'}$ be a Carnot element for $(\text{CycHtg})_K$. Since both $a\delta_x - a'\delta_{x'}$ and $a'\delta_{x'} - a\delta_x$ lie in $\mathcal{C}l(\text{CycHtg})_K$, it follows from (a) & (b) that

$$\frac{a}{T(x)} - \frac{a'}{T(x')} = 0 \quad \text{and} \quad \frac{a}{\hat{T}(x)} - \frac{a'}{\hat{T}(x')} = 0$$

Thus,
$$\frac{T(x)}{T(x')} = \frac{\hat{T}(x)}{\hat{T}(x')}.$$

Since this equation holds for any pair $x, x' \in K$ it follows that for some fixed $x' \in K$

$$\hat{T}(x) = \left[\frac{\hat{T}(x')}{T(x')} \right] T(x), \quad \forall x \in K.$$

By taking $\sigma = \hat{T}(x')/T(x')$ we get the desired result. \square

4. Miscellaneous Comments

1. Without additional stipulations about $(\text{Cyc Htg})_K$, the Weak Second Law cannot guarantee that any of the possible functions $T_K: K \rightarrow \mathbb{R}^+$ supplied by Thm. A is injective (and order-preserving). By way of counterexample, suppose that $(\text{Cyc Htg})_K = \{ \mu \in M_K: \int_K d\mu \leq 0 \}$. Then T_K must be a positive constant function.

On the other hand, if $T_K: K \rightarrow \mathbb{R}^+$ is unique (up to a positive constant multiple) and if, for every Carnot element for $(\text{Cyc Htg})_K$ of the form $a\delta_x - a'\delta_{x'}$ with $x \neq x'$, it is the case that $a \neq a'$, then T_K is injective (and therefore monotonic). If, in addition, there exists for $(\text{Cyc Htg})_K$ ~~a single~~ even one Carnot element $a\delta_x - a'\delta_{x'}$ with $x > x'$ and $a > a'$, then T_K is monotonically increasing.

2. Even if the Weak Second Law is presumed to hold for every closed interval $K \subseteq E$, the existence of a continuous function $T: E \rightarrow \mathbb{R}^+$ such that $\int_E \frac{1}{T} d\mu \leq 0, \forall \mu \in \text{Cyc Htg}$ remains unproven. However, if $(M^+)^{\perp} = \{ \mu \in M^+: \mu(E) = 1 \}$ is contained in an open convex set disjoint from Cyc Htg (where M is given, for example, the weak* topology induced by the continuous real functions on E), then the existence of $T: E \rightarrow \mathbb{R}^+$ is assured.