ON THE MATHEMATICAL FOUNDATION
OF CLASSICAL THERMODYNAMICS

by

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1. Introduction

Since Carathéodory's pioneer work on the foundation of thermodynamics, many authors (e.g. [3,4,7]) have written on this subject from a similar viewpoint. However, in most of these expositions, there lacks a clear separation between the mathematical theory and the physical consideration. As a consequence, many mathematically technical points are either overlooked or ignored. It is the purpose of this paper to construct a mathematical modelwhich rectifies these shortcomings and at the same time brings out clearly all the mathematical hypotheses that are required in order to draw the desired conclusions. In this regard, the present investigation is influenced by the work of Aren [1] and Carter [6]. Also, instead of following a traditional approach in proving the existence of entropy and absolute temperature, we give a somewhat different and refined proof, in §4, for simple thermodynamic systems. Roughly speaking, simple thermodynamic systems are those systems whose states are specified by two thermodynamic variables, e.g. pressure and volume. The development in this section can be easily generalized to include more complicated systems.

In $^\wedge 2$, we first introduce the notion of a quasi-thermodynamic system. By imposing additional conditions on it, we arrive at the concept of a thermodynamic system. A basic property for the thermodynamic system, namely, its " heat form" has local integrating factors, is summarized in Theorem 2.5. Since we restrict our attention later to simple systems, we describe a proof only for

such simple cases.

Although multi-temperature systems have been discussed
recently by several authors, we elect to follow the traditional
line in considering only single temperature systems. The characteri-
zation of such systems is given in §3.

In the last section, we discuss the principle of increase
of entropy during an irreversible adiabatic process for those
simple systems whose constant entropy submanifolds are connected.
We first identify the irreversible adiabatic processes with a
certain subset of the set of ordered pairs of states. By generalizing
the Carathéodory's principle, we are able to show that, for an
irreversible adiabatic process, the entropy of the final state
is strictly greater than that of the initial state.

Throughout this paper, the notations and terminologies
borrowed from differential geometry follow closely with those
used in [2,lo]. By a differentiable manifold, we mean a separable,
Hausdorff topological space together with a family of compatible
coordinate systems defined on it. For a precise definition and
many other basic facts in differential geometry which are used in our
discussion, we again refer readers to [2,10].

2.   Thermodynamic Systems

A quasi-thermodynamic system (S,Ae,w)   consists of a
C^2-differentiable manifold S   of dimension $n \geq 2$ together with
a differential 1-form w of class 1 on S   and a real-valued
C^2-function Δe defined on the product manifold SXS such that
for all s_1, s_2 and $s_3 \in S$,

(2.1) $Ae(s_1,s_2) + \Delta e(s_2, s_3) = \Delta e(s_1, s_3)$.

The members of S are called the states, and the real-valued
functions defined on S are called state functions. We will
interpret $\Delta(s_1, s_2)$ as the energy which must be added or taken
away from the system in going from state s_1 to s_2. It follows
from equation 2.1 that we have, for all $s_1, s_2 \in S$, $Ae(s_1, s_1) = 0$
and $\Delta e(s_1, s_2) = -As(s_2, s_1)$. The 1-form w is called the work
form of the system.

2.2 Theorem. For each quasi-thermodynamic system (S,Δe,w),
there exists a state function e, unique up to an additive constant,
such that

$$\Delta e(s_1, s_2) = e(s_2) - e(s_1)$$

for all $s_1, s_2 \in S$. Moreover, e is a C^2-function.

Proof: Choose any $s_0 \in S$ and define $e: S \to R^1$ by

$$e(s) = \Delta e(s_0, s).$$

Clearly, e is a C^2-function. Since $\Delta e(s_1, s_2) = -Ae(s_2, s_1)$,
we have

$$\Delta e(s_1, s_2) = \Delta e(s_1, s_0) + \Delta e(s_0, s_2)$$

$$= e(s_9) - e(s_n)$$

for all $s_1, s_0 \in S$.

Now suppose e^1 is another such function. Then $\Delta e(s_0, s) = e'(s) - e'(s_0) = e(s)$. Hence, $e'(s) - e(s) = e'(s_0)$ for all $s \in S$.

We shall call e an <u>internal energy function</u> of the system. The 1-form q defined on S by the equation

(2.3) $$q = de + w$$

is called the <u>heat form</u> of the system. Equation 2.3 is the statement of the first law of thermodynamics.

Let I be a closed and bounded interval of the reals. A function $f: I \to S$ is called a $\underline{C^1\text{-curve}}$ if it is the restriction of a C^1-function defined on some open interval containing I, and if $df(t) \neq 0$ for all $t \in I$. A <u>piecewise differentiable</u> <u>curve</u> is a continuous function $f: I \to S$ together with a subdivision of I on whose closed subintervals f is a C^1-curve. By a <u>process</u> (or quasi-static process) we mean a peicewise differentiable curve in S. The restriction of a process $f: I \to S$ to any closed subinterval of I is called a <u>subprocess</u> of " f. The amount of <u>work</u> done by the system in traversing a process $f: [a,b] \to S$ is given by $\int w = \int^b_a f^*w$. The amount of heat added to the system in going along f is equal to

$$\int q = e(s_2) - e(s_1) + \int w$$

where $s_i = \$(a)$ is the initial state and $s_2 = \pounds(b)$ the final

state. A process $\pounds$ is said to be an <u>adiabatic process</u> if $\oint_C q = 0$

for every subprocess $\pounds$ of $\pounds$. A state s_1 is <u>adiabatically</u>

<u>connected</u> to s_2 if there exists an adiabatic process $\pounds:[a,b] - S$

such that $\pounds(a) = s^\wedge$ and $\pounds(b) = s_2$.

~~2.4 Definition~~   A ~~thermodynamic system~~ is a quasi-thermo-

dynamic system which satisfies the following additional conditions:

(2.4.a) The heat form q of the system is nowhere zero.

(2.4.b) In every neighborhood of a given state s , there

exist states which are not adiabatically connected to s .

The second condition is a mathematical statement of the

second law of thermodynamics, commonly known as the Carathéodory's

principle. As a consequence of (2.4.a) and (2.4.b), we have the

following result:

2.5 <u>Theorem</u>   Let (S,As,w) be a thermodynamic system.

For each state $s \in S$, there exist an open neighborhood U of

s and two real-valued functions A,σ defined on U such that

A is a positive C^1 -function, a is a C^2 -function, and Ada

is equal to the restriction of q to U .

In the usual axiomatic treatment of thermodynamics [3,4,5,11]

the above theorem provides a basic tool in establishing the existence

of entropy and absolute temperature. However, for our later

discussion, a restricted version of this theorem to the cases

where S has dimension two is sufficient. In this case, the

proof does not depend on condition (2.4.b), and we argue as follows: Given any state $s \in S$, let (V, φ) be a coordinate system about s. Then the heat form q can be written locally as

$$q = (\frac{\partial}{\partial x_1}(e) + w_1) dx_1 + (\frac{\partial}{\partial x_2}(e) + w_2) dx_2 "$$

Let us denote $\frac{\partial}{\partial x_1}(e) + w_1$, $\frac{\partial}{\partial x_2}(e) + w_2$ by a_1 and a_2, respectively, and let y be an O-form on V. The 1-form yq is exact iff y satisfies the following partial differential equation:

(2.6) $$a_2 \frac{\partial}{\partial x_2}(y) - a_1 \frac{\partial}{\partial x_1}(y) = (\frac{\partial}{\partial x_2}(a_1) - \frac{\partial}{\partial x_1}(a_2)) y.$$

Since a_1, a_2 are C^1-functions and not simultaneously equal to zero, the local existence of solutions for equation 2.6 is guaranteed by the theorem on p. 59 [9]. Moreover, we may assume that $y > 0$. Thus, there exists a C^2-function or such that $da = yq$ or $q = A da$ at some neighborhood $U \subset V$ of s.

We will call A an integrating factor, cr an integrator, and (A, a) an integrating pair of the heat form q about s.

3. Single Temperature Systems

Let U denote the class of all thermodynamic systems. A family of single temperature thermodynamic systems is a subclass U of 3" which satisfies the four conditions listed below.

(3.1.a) For each member (S,^e,w) of U, S is simply connected and dw(s) ^ 0 for all s e S.

(3.1.b) Given any two members S_i ,S_2 of U, there exists a certain distinguished subset S,*S_0 of S.XS_0 such that

x. £   x. £

(i) for each s. e S,, there exists an s_2 e S_2 such that ($s_{1J}s_2$) e S_1*S_2,

(ii) if (s_1,s_2) € $Si*S_2$} tlien (s^s^) e S_2*S_1* and

(iii) if (SpSj) e S^^*^ and (s_2,s_3) e S_2*S_3, then (s_1,s_3) € S^Sy

If (s^,s_2) e S,*S_2, we say that s^ and s_2 have the same temperature. Now suppose s e S. By (i), there exists an s^ e S such that (s,s,^) e S*S. Hence, by (ii), (s^,s) e S*S. It then follows from (iii) that (s^s) e S*S. Thus, the above condition defines an equivalence relation on each S of \i, and the equivalence classes of S are called isothermals. A temperature function J^ of S is a state function which is constant on each isothermal, and is a different constant on different isothermals. A temperature scale is a collection ® of temperature functions, one for each S e U, such that if e l,e∠ e © are the temperature functions for the systems S+ and S_9, respectively, then 9_1(s_1) = 9_2(s_2) iff ($s_{;L}$,s_2) e S_1*S_2. We point out here that it follows from 3.1.b and the fact that each S e 3"

is separable that one can always construct a temperature scale for

U. However, such a temperature scale does not, in general, possess

the desired smoothness. For this reason, we impose the next

condition on U.

(3.1.c) There exists a temperature scale $\copyright_o$ for $\backslash j$,

with the property that each temperature function $6 \ 6\circledR_o$ is a

C^2-function. Furthermore, if (A,σ) is an integrating pair as

described in Theorem 2.5, and if $6 \ e \ \copyright_o$ is the corresponding

temperature function for the system, then $d9(s)Ad0(s) \ \hat{} \ 0$ for

all $s \ e \ dom(a) \bullet$

If the dimension of $^sT_\perp * ^s2 \ 6 \ \hat{} \ ^{are} \ m \ an<\hat{} \ ^n>$ respectively,

then it follows from condition (3.1.c) that $^s i_\perp * ^s o_2 \ \hat{}^{s \ a} \ m+n-1$

dimensional C^2-submanifold of $S_\perp x S_2$. We will show next that

$S^\perp * S_2$ can be made naturally into a quasi-thermodynamic system.

To this end, let $Ai^\perp,, A<5_2 \ ^{be} \ the$ functions induced on

$(S_1 x S_2) x (S_1 x S_2)$ by $£\&\hat{}$ and $£e_2$, respectively, and let $\#^-,,w_2$

be the 1-forms induced on $^sT^\perp x^s 2$ by $w..^\perp$ and w_2, respectively.

We denote the restriction of $Ae^\hat{}_\sim + ££_2 \ ^{to} \ (S_1 * S_2) x (S_1 * S_2)$

by $^\hat{}e$, and the restriction of $w_n + w^*_o.$ to $S,*S\_$ by w .

Then $(S,*S_0,Ae ,w$) is clearly a quasi-thermodynamic system,

and is called the composite system of $S,$ and S_2.

$(3ol.d)$ For each pair $^sT>s_2 \ \in \ 1J,$ the composite system

$S-,*S_?$ is a thermodynamic system.

To save writing, we will denote a single temperature system

by $(S,£e,w,9)$ where 0 is the corresponding temperature function
for S in $\copyright_o$.

3.2 Theorem Let $\circledR_o$ be a temperature scale for li as described in (3.1.c). Then all the members of $\circledR_Q$ have the same range and the range is an open interval in R^1.

Proof: Let $6,, 9_o$ be members of $\circledcirc$ which correspond to the systems S_i and S_2, respectively. For each $s_{'i} \in S_i$, by (3.1.b) and (3.1.c), there exists an $s_2 \in S_2$ such that $e^{\wedge}s^{\wedge}) = 6_2(s_2)$. Hence, range($9_i$) c range($6_?$). Similarly, one can show the other inclusion. Thus, all the members in 0_o have the same range.

Since 9_i is continuous and $S._i$ is connected, the range of 9_i is clearly connected. To show that it is open, we observe that at each state $s \in S_{i}$, $d9_i(s) \wedge 0$ according to (3.1.c). This implies that $9._i$ cannot achieve maximum or minimum. Hence, range(9_i) is an open interval in R^1.

4. The Existence of Entropy and Absolute Temperature for Simple Systems

A simple system is defined to be a single temperature system $(S, \pounds e, w, Q)$ where S has dimension two. Henceforth, we will restrict our discussion to simple systems, and will establish, in this section, the existence of global entropy function and absolute temperature for such systems.

Let $(S_1, Ae_1, vr^\wedge, Qj)$, $(S_2, \pounds e_2, w_2, 62^\wedge$ be two simple systems, and let $(S, *S\sim, Ae\ jW)$ be the corresponding composite system. For any two given states $s_1 \in S_1$ and $s_2 \in S_2$, let (A_1, cr_1) be an integrating pair of the heat form q_1 about s_1 and let $(A_2, CT2^\wedge$ be a similar pair for q_2 about s_2. It follows from (3.1.c) that there exist neighborhoods V_1 of s_1 and V_2 of s_2 such that the function $o^\wedge xe, \pounds\ V. - . R$ defined by $cr.X6_1(s) = (a_1(s), Q_1(s))$ forms a coordinate system about s_1 and the function $a_2 xe_2 : V_2 \to R^2$ defined by $a_2 x6_2(s) = (a_2(s), 0_2(s))$ forms a coordinate system about s_2. We call such coordinate systems $a_1 jXS_1$, $CT_2 X8_2$, the "preferred" coordinate systems. We denote $cr_1[V_1]$, $6_1[V_1]$, $CT_2[V_2]$ and $6_2[V_2]$ by M_1, N_1, M_2 and N_2, respectively. Also, we adopt the following notational convention: If p is a differential form on S_1 or S_2, then by $\%$ we mean the form induced on $S_1 x S_2$ by p. In this notation, the function $(D: V_1 x V_2 - . R^4$ given by $<_0(s_1, s_2) = (\tilde{a_1}(s_1, s_2), \tilde{e'}_1(s_1, s_2), \tilde{CT_2}(s_1^\wedge s_2^\wedge ^\wedge 2^\wedge s_1 jS 2^\wedge$ is a coordinate system about $(s_1, s_2) \in S_1 x S_2$ Moreover, the range of w is $M_1 x N_1 x M_2 x N_0$. The set $V = (V_1 x V_0) \cap (S_1 * S_2)$

is a nonempty open set in S-j^^ iff N^K^ ^ j6. In this casd

the restriction of <p to V induces a coordinate system

i|): V -» R^3 of Sj^*^ given by ^(s^s^ = (cr~^s^s^, cf_2^(s.^s_2) ,,

$(s_1,s_2)) where § = ej1_v = ^v * The range of ^ is M_1 \times M_2 \times

(N_1 HNU). From our construction of the composite system, the heat

form q of S.*S_O is simply equal to the restriction of q =

$\tilde{q}_x + \tilde{q}_2$ to S_1*S_2. Thus, for all (s^s^ e V, we have

$$q_c(s_1,s_2) = \tilde{\lambda}_1(s_1,s_2)d\tilde{\sigma}_1(s_1,s_2) + \tilde{\lambda}_2(s_1,s_2)d\tilde{\sigma}_2(s_1,s_2).$$

The induced form $(ib^{-1})^* q_c$ on ly[xNUx (N_1 PN_2') is given by

$$(\backslash \tilde{b}^{1})^* q_c(\tilde{a}_1,\hat{a}f_2>'^{5'}) = {}^{1}(1^{1"}(\tilde{\sigma}_1,\tilde{\sigma}_2,\tilde{\theta})d^_1 +$$

$$^{"\wedge}_2 {}^{-i}{}_1 {}^{/\sim}, \tilde{\theta})d\tilde{\sigma}_2.$$

Note that it follows from the definition of $\tilde{A}_1,^$ and JJ that

we have

(4.1) $^i{}^\circ 0^{1}_\sim (\widetilde{ap0}f_2^{5\wedge} = {}^A{}_1{}^\circ(c^r{}_1{}^x6i)\sim^{1}(\tilde{a}_1,'\check{e}),$

and

$(^4\text{«}^2)$ $^_2{o?i)}^{-1}(\tilde{a}_{1J}c\hat{f}_{23}'\check{e}) = A_2o(a_2xe_2)\sim^{1}(^{\wedge\wedge}\tilde{e}i),$

for all $C\check{a}_1,\tilde{a}_2,'\check{Q})$ e M_1xM_2x(N_inN_2) .

   4.3 Lemma Let (S.^_J6e_1,w_{1J}) e_1) , (S_2, £&_2>vr_2, e_2) be two

simple systems, and let (A^C_N_1) be an integrating pair of q_1

about s^^ € S^ and let (A_2,a_2) be an integrating pair of q_2

about s_2 e S_2. Suppose (V^c^xe^ is a " preferred" coordinate

system about s_1 and (V_2, cr_2xe_2) is a " preferred" coordinate

system about s_2 such that ^[V^ n 6_2tV_2] ^ jb. Then the

ratio $\dfrac{H_{-'}{}^{\wedge}l*^6{}^{\wedge}\quad(gI^{\wedge}V^{\wedge}}{A_2o(a_2xe_2)^{-1}((T_2,e)}$ defined on $a^{\wedge}]x*_2[V_2]x$

$(GntV_{\perp},]ne_2[V_2])$, is independent of 9.

Proof Let us denote $A_1o((T_{-I}x6^1)^{-1}$ by $A^{\wedge}*$ and $^{\wedge}{}_2-(CT_2X6_2)^{-1}$

by A_2*. Suppose the ratio $\dfrac{A_{\perp}(a_{-|},6)}{A_2(a_2,9)}$ is not independent of 9.

Then there exists a point $(CT°,CT_2,9°) \in a^{\wedge}V^{\wedge} X a_2[V_2]x(Q_{\pm}[V_{\pm}]n9_2[V_2])$

such that

$$\frac{\partial}{\partial\theta}\frac{\lambda_1^*(\sigma_1^0,\theta^0)}{\lambda_2^*(\sigma_2^0,\theta^0)} \neq 0.$$

Let $M_1XM_2XNCCT_1[V_1]xc_2[V_2]x(9_1tV_1]n9_2[V_2])$ be a compact

neighborhood of $((a_1^?,a_2^{0*},99°))$ •• FFor each 9 e N, consider the

following differential systems:

(i) $\qquad \dfrac{d\sigma_1}{dt} = \dfrac{1}{W^* fil}$

$\qquad\qquad CT_1=CT_1^0 \, atfc= \quad 0$

(ii) $\qquad \dfrac{da_2}{dt} = \dfrac{\pm}{\sim\sim* A_2(Cfn j 9)}$

$\qquad\qquad v_2 \sim CT_2 \mathrel{--} t - 0$

From the existence theorem in the theory of ordinary differential

equations, we know that there exists a $T > 0$, independent of

9, such that (i) and (ii) have unique solutions in $M_{\perp}x[0,T]$

and $IV^{\wedge}xtOjT]$, respectively. The solutions of (i) and (ii) can

be written as

(iii) $Ej\_(t,e) = c_1^0 + J \int_o^t \dfrac{1}{\tilde{\lambda}_1^*(\Sigma_1(t',\theta),\theta)} dt'$

and

(iv) $So(t,e) = a? + \int_o^t \dfrac{-1}{\lambda_2^*(\Sigma_2(t',\theta),\theta)} dt'$

For each T, 0 < T < T, we calculate the determinant of
the Jacobian of the transformation $cr_1 = \underline{y}^\wedge(t,e)$, $a_2 = !_{\underline{\gg}}(t,e)$
at (T,9°), Clearly, $\hat{\ } f_1(^9\circ) = (-1)^{i+1} \dfrac{I}{A_i(CT_{i>6})} + o(l)$
for i = 1,2. Also, from (iii) and (iv), one can show that

$$\frac{\partial}{\partial\theta} \wedge\{^9\circ) = \frac{\tau}{[A_i^*(c_i;e^\theta)]^2} \; 96 \; \wedge(a?,\rho^\circ) + O(T)$$

for $\dot{I}$ = 1,2.   Thus,

$$\det\begin{pmatrix} \dfrac{\partial\Sigma_1}{\partial\theta} & \dfrac{\partial\Sigma_2}{\partial\theta} \\[2ex] \dfrac{\partial\Sigma_1}{\partial t} & \dfrac{\partial\Sigma_2}{\partial t} \end{pmatrix} = \frac{\tau}{[A_1(CT_1,9)]^2} \; 99 \; \frac{\lambda_1(\sigma_1^0,\theta^0)}{A_\theta(CT_\theta J 6)} + o(\tau)$$

which is different from zero for sufficiently small T.   For such
a r, let $<j_1 = f_{-},(T,9^o)$ and $r_2 = TZyif\}\circledR^0)$- It follows from
the inverse function theorem that there exist a neighborhood
AxB of (T,0°) and a neighborhood CXD of (CT_1,a_2) such that
the transformation $a_, = J\}-,(t,Q)$; $<j_0 = v_o(t,8)$ maps AXB 1-1,
onto CxD.   Thus, every point $(a_1,,cr_2je)$ e CxDxN can be connected
to $\{o_1,,a2>\circledR$ ^ ^the following piecewise differentiable curve
in CxDxN: Let (T*,6*) be the inverse image of $(c_Njc_2^{2}Z)$.
Then

$$a(t) = \begin{cases} (\sigma_1^2, \sigma_2^2, (1+t)\theta^* - t\theta^O), & -1 \leq t \leq 0 \\ (\Sigma_1(\tau^* - t, \theta^*), \Sigma_2(\tau^* - t, e^*), e^*), & o \wedge t \wedge T^* \\ (\sigma_1^O, \sigma_2^O, (1+\tau^* - t)\theta^* + (t-_T^*)e^O), & \tau^* \leq t \pounds T^* + 1 \\ (\Sigma_1(t-\tau^*-1, \theta^O), \Sigma_2(t-\tau^*-1, \theta^O), \theta^O), & \tau^*+1 \leq t \leq \tau^* + \tau + 1 \end{cases}$$

which, in view of equations 4.1 and 4.2, satisfies that $(\$\sim^1)^* q_c(cs(t)) = 0$ for all $t \in [-1, T^*+T+1]$. This, of course, implies that every state in the neighborhood $j\pounds^{-1}[CxDxN]$ of $\psi \sim^1 [c\bar{r}\wedge c\bar{T}_2 J \ G^o]$ is **adiabatically** connected to $i/T^1(a-._1^1 > Q_-^1 >> 9^o)$ which contradicts 3.1.d.

    <u>4.4 Lemma</u>   Let (S,Ae,w,9) be a simple system and let (A, αr) be an integrating pair about $s \in S$. Suppose (V, ax6) is a "preferred" coordinate system about s. Then there exist a C^1-function $f > 0$ on αr[V] and a C^1-function $g > 0$ on 9[V] such that

$$\lambda \bullet (\sigma \times \theta)^{-1}(\sigma, \theta) = f(cr)g(6).$$

If (f',g') is any other such pair, then $g' = eg$ and $f' = \frac{1}{c}f$ for some positive constant c.

    <u>Proof</u>: Setting $S_1 = S_2 = S$ and $A_1 = A_2 = A$ in Lemma 4.3, we obtain

$$\frac{\lambda^*(\sigma_1, \theta)}{\lambda^*(\sigma_2, \theta)} = F(\sigma_1, \sigma_2) > o$$

for all $(a_1 < J_2, Q) \in a[V] x_{CT}[V] xe[V]$. Now fixing $a_2 = cr_2^O \in a[V]$, we have

$$A^*(o-, e) = F(\sigma, \sigma_2^O)\lambda(\sigma_2^o, Q) = f(<x)g(e).$$

Clearly, f and g are positive C^1-functions.

Suppose (f,g') is another pair of such functions. Then
we have f (*)g(e) = f ' (cx)g' (9) or _fff^) = f^f^1 for all
(a^Q) e a[V]x6[V]. Thus, there exists a constant C > 0 such
that g' = eg and f' = $\frac{1}{-}$f .

4.5 Lemma   Let A^Cc^xQ^" , A$_2$o(o$_2$x6$_2$)   be a pair of
functions as described in Lemma 4.3. Suppose A^o (cr^G-^) (a-^ 6^) = $_{(\theta_2)}$
f$_1$(a$_1$)g$_1$(e$_1$) on cr$_1$[V$_1$]xe^1[V^] and A$_2$o(a$_2$xe$_2$) (CT$_2$,6$_2$) = f$_2$ (cr$_2$)g$_2$
on cr$_o$[V$_o$] X6$_o$[V$_o$] . Then there exists a constant C > 0 such that
g$_1$(e) = cg$_2$(e) on e^v:^ ne$_2$[v$_2$i.
   Proof; By Lemma 4.3,

$$\^ - - - F \left(\frac{\backslash (a_{lt}Q)}{\sigma_2, \theta} \right) (\ll r _r a_2) = \frac{f_1(CT_1)g_1(e)}{f_2(a_2)g_2(e)}$$

for all (a$_v$a$_2$,Q) e a$_]$_[V$_1$] xa$_2$tv$_2$] x(e$_1$[v$_]$_] ne$_2$[V$_2$]) . Hence, the
result follows.

4.6 Theorem   Let 0 $_o$ be a temperature scale for li as
described in (3.1.c) and let J be the common range for all members
of ©$_o$. Then there eixsts a C^1 -function T defined on J such
that for each A«(ax9)$^{-1}$ as described in Lemma 4.4, we have

$$Ao(crxe)""^1 = T(6)F(or)$$

for some F. The function T is unique up to a multiplicative
constant and if T is fixed then F is uniquely determined.
Moreover, T<>8 is a temperature function.

   Proof; Let us index the set of all integrating factors
for the simple systems by A. For each i e A, let h$_i$ = log g$_i$
where g$_i$ is a factor of A$_i$ as in Lemma 4.4. By Lemma 4.5,

h$_i$-h$_3$ = constant on their common domain. Thus the 1-form β
defined on J by p(e) = dh^e)   where 9 e dom(h$_i$)   is exact,
i.e. p = dh where h is a real-valued c^1-function defined on
J. The function T = exp h clearly has all the properties as
stated in the theorem except possibly the fact that Toe is a
temperature function.

   To shew that T»e is a temperature function, it suffices
to show that $\frac{d}{ay}$ T(e) ? 0 for all 9 e J. Since ((crx9)$^{-1}$)* q(a> 6) =
λ*(σ,θ)dσ = T(e)P(cr) d$_{CT}$ = [• $-$ eo(<JX9)"^{1}(CT,6)+W$_1$o (CTX9)"^{1}($_{CT}$,6)]dcr +
[$\frac{\partial}{\partial}$r eo(aX9)~^{1}((T$_J$9)+w.o(CTXe)~^{1}(CT,6)]de,   we have

(4.7)   T(e)F(o) = ^" eo(ax9)"^{1}(a,6) + w$_h$o (CTXQ) ~^{1}($_c$r$_J$ 9)

and

(4.8)   0 = ^r eo(ax9)~^{1}(a,9) + w$_{90}$(CTX9)"^{1}(CT,6) •

Differentiating equation 4.7 with respect to 9 and equation 4.8
with respect to a and subtracting the two, we obtain

$$F(\sigma)^\wedge \ T(9) \ = \ ^\wedge \ W_1\ll)(CTX9)"^1(CT,\ 9) \ - \ ^\wedge \ w_2 o(\sigma\times\theta)^{-1}(\sigma,\theta)$$

which, by 3.1.a, is different from zero. Thus, $\frac{d}{dr}$T(6) ^ 0 for
all 9 e J.

   The function To9 is called an <u>absolute temperature function</u>
of the system.

   <u>4.9 Theorem</u> For each simple system (S$_5$£e,w,9),   there
exists a global entropy function *r)* such that

$$q = Toe \ d\eta.$$

<u>Proof</u>   As shown in Theorem 4.6, locally, q(s) =

T(e(s))F(a(s))d$_a$(s) = T(e(s))daoa(s) where a($_{cr}$) = jF(cr)dcr.

If q($_s$) = T(e(s))da'o a'(s) is another such local representation

of q then d(ctocr - a'o a^1) = 0 on the overlap. Thus, we can

define a 1-form p on S by

$$p(s) = d(aoff)(s) \text{ if } s \text{ e dom(aocr)} \bullet$$

Clearly, p is closed. Since S is simply connected, p is

exact. Hence, there exists a C^2-function r\ defined on S such

that q = ToQ drj=

4.10 <u>Corollary</u>   For each closed quasi-static process £,

$$\int_F \frac{q}{T \bullet \theta} = 0$$

(A closed quasi-static process is a process £: [a,b] -• S. such

that A(a) = f(b)).

Finally, it is worth noting that all the propositions in

this section can be generalized to single termperature systems of

higher dimension. One starts, in this case, from Theorem 2.5, and

then uses this fact to prove Lemma 4.3 in a usual manner.

5.   Irreversible Processes and the Principle of Increase of Entropy.

The theory we have developed so far deals strictly with physical systems which are in " thermal equilibrium" . However, one would like to draw some conclusions from it in regard to irreversible processes such as free expansion of gases, etc. Although such processes do not fall into our definition of quasi-static processes, nevertheless, the initial and final state of such processes lies in the equilibrium states. Therefore, for an irreversible process where " no exchange of heat" takes place, one would like to conclude that the entropy of the final state is strictly greater than that of the initial state. To show this, we first restrict our attention to those simple systems which have the following property: Let r) be an entropy function of the simple system (S,£e,w,6). Then the constant entropy submanifolds {s e S: t](s) = constant} are connected. We denote a class of such simple systems by \r, and prove that

5.1 Lemma Let (S,^,w,e) e \s, and let 77 be an entropy function of S. Two states $^s v^s o$ ∈ s are a3iabatically connected iff T)^) = r?(s_2) .

Proof: Suppose $s_{1'}$, s_2 are connected by an adiabatic process f: [a,b] – S. Then T)U(t)) is constant for all a _£ t £ b. For if not, let t ^ ^ e [a,b] such that r?(f(t_1)) ^ t)U(t_2)) and t_1 < t_2. Let C_Q = min{T(6 (£ (t)) : t - ^ t ^ t ^ . We have

$$\Gamma^{t_2}{}_q = \int^{t_2} t^* q = \int^{t_2} T(e(Mt))d_{T?}(f(t))$$

$$\geq c_o \int_{t_1}^{t_2} d\eta(f(t)) = c_o[\eta(f(t_2)) - \eta(f(t_1))] \neq 0$$

which contradicts the fact that t is an adiabatic process.

Now suppose $r](s_1) = T?(S_2)$. Then s_1, s_2 is arcwise connected [2, Proposition 1.5.2]. Moreover, by a similar argument as to Proposition 1.5.1 [2], one can construct a piecewise differentiable curve connecting s_1, s_2 in the submanifold $\{s \in S: T7(s) = TJ(s,)\}$. Clearly, such a process is an adiabatic process.

Next we _identify_ the irreversible adiabatic processes for a simple system $(S, Ae, w, 9) \in \backslash s$ with a subset j of $S \times S$ which has the following properties:

5.2.a If $(s_1., , s_2) \in \&$, then s_1 is not adiabatically connected to $s_2 \ll$

5.2.b If $(3^82) fL 3$ and if $s_{\gg}$ is not adiabatically connected to $s_\sim$, then $(s^\wedge jS_1) \in 3$.

5.2.c If $(3^{\wedge\wedge}, 32)^\wedge(32, 32) \in 3$, then $(s-^\wedge s^\wedge \in 3$.

5.2.d For each state $s \in S$, the set $K_S = \{s_1 : (s, s.) \in 3$ or s is adiabatically connected to $s\}$ and its complement are connected.

The above four conditions together with Lemma 5.1 imply that

5.3 Lemma Let $s, , s_o$ and $s_\_ \in S$. If $s_o \in K$ and $s, \in K$, then $s_2 \in K$.

A state s_1 is said to be <u>adiabatically</u> <u>and</u> <u>irreversibly</u> connected to s_0 if $(s,,s_9)$ e «9. By generalizing the Caratheodory's principle 2.4.b to include the irreversible adiabatic processes as well, we have

<u>5.4 Lemma</u> Let $(S,£e,w,e)$ e V and let 77 be an entropy function of S. Then for each s e S, we have either $r>(s)$ £ $_T|(s_1)$ for all $s_\pm$ e K_g or 77(s) ^ TjCs^ for all s_L e K_g.

<u>Proof</u> For each s e S, by 5.2.d, i?t^K_sl $^{is\ an}$ interval in R^1. Suppose T?$(^s)$ belongs to the interior of this interval. Then there exists an open interval J such that ri(s) e J c 77[K] . Let $(V, T?X6)$ be a coordinate system about s. Then every state in the neighborhood U = (TJX9)~ ↑ (T)[V] HJ) XB[V]] of s can be connected to s as follows: Suppose s_1 € U. Then there exists a state s_9 e K such that T)(s,) = 77(s$_0$). By Lemma 5.1$_3$ s, e K . Hence, by Lemma 5.3, s, e K which contradicts the
X   Sn   X   S
generalized Caratheodory's principle. Since s e K , r/(s) must be an end point of the interval rj[K] .

<u>5.5 Lemma</u> Let $(S,£\&,w,0)$ e \s and let 77 £>e an entropy function of S. Suppose s e S is such that TJ(S) ^ ^(s$_1$) for all $s^\wedge$ e K_g. Then every state s_2 e S with $rj(s)$ $\leq_i$ rj(s$_2$) belongs to K_g. A similar result holds if the inequalities are reversed.

<u>Proof</u> Suppose there exists a state s_0 e S such that t?(s) £ T?($^s_0$) ^{and} $^s_0$ ^ K_s« In view of Lemmas 5.1 and 5.3, we must have $n(s') < v(s_Q)$ for all s' e K_g. But this would imply

that 71[~K] is not connected which contradicts 5.2.d.

    5.6 Lemma Let (S,£e,w, 6) e If and let 77 be an entropy function of S. Then either 77^) < rj(s_2) for all (s^Sj) € 3 or •n(s_1) > TJ(s_2) for all (s-^s^ e J.

    Proof: First we show that either T)(S) ^ I7(s') for all s e S and s' e K_g or r?(s) ^ T?(S') for all s e S and s^1 e K_g. Suppose not. Let $^s i^s o^6$ s such that T?(s,) <, TJ(S) for all s e K_S and T?(S_0) J>= 77(S) for all s e $K_{s_{\sim 2}}$. We consider the following three cases:

    Case 1 n(s,) < TJ(S_0). By Lemma 5.5, we have s_9 e K and s, e K . Thus j (spsj € j and (s^sj e j which^ by 5.2.c, implies that (s_1,s_1) e J. But this contradicts 5.2.a.

    Case 2 17(s_2-) < r)(s_1,). Let s e S be such that 77(s_2) < 77(s) < 77(s,). Then (s_2,s) and (s_1.,s) / J. By 5.2.b, we have (s,s_1) e j and (s,s_2) e j. This implies that 77(5) belongs to the interior of ^[K] which was shown impossible. _s

    Case 3 *Tjis-,)* - T?(s_2). This case again contradicts Lemma 5.4.

    Finally, the strict inequality follows from 5.2.a which completes the proof.

    By a proper choice of the sign of the absolute temperature, we obtain our principle result of this section.

    5.7 Theorem Let (S,£e,w, 6) e \\s. There exists an entropy function 77 of the system such that if (s_1,s_2) e $_rg$, then T)(s,) < *v(s_0)* .

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