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A PROOF THAT ESSERGY IS THE ONLY CONSISTENT MEASURE OF POTENTIAL WORK (FOR CHEMICAL SYSTEMS)

by

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June 1969

The study in this paper was supported by National Science Foundation Grant TGK-1344 in 1968 and by Air Force Office of Scientific Research Grant 69-1735 in 1969.

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ABSTRACT

An attempt is made to prove that all of the many seemingly-independent measures of potential work (such as availability, exergy, available work, Gibbs free energy, Gibbs chemical potential, Helmholtz free energy, and the other common available energy expressions -- e.g., kinetic energy, potential energy, and electrical energy) are necessarily all special cases of the one unique quantity, essergy (the word "essergy" being a contraction of the term "essence of energy").

The proof is attempted rigorously for chemical systems, from whence it is extended to apply more generally. If correct, the proof will be of consequence to the design of any engineering system in which potential work is a significant factor -- since it will show conclusively that by evaluating the one unique quantity, essergy, the designer may rest assured that all of the many seemingly-independent considerations of potential work will be automatically satisfied.

Another possible consequence of the proof might be a more general formulation of information -- based upon Brillouin's principle of the equivalence of thermodynamic information and potential work. It is thus hoped that the proof may eventually provide new insight into the foundations of science and information theory.

PREFACE

The proof presented in this thesis makes use of only macroscopic considerations which lie within the realm of classical thermodynamics. Thus the proof may if desired be viewed as being based solely upon classical thermodynamics -- in particular the classical treatment by J.W. Gibbs.

However, it should be mentioned that the proof was first made by using the information theory approach of Tribus[*] -- which is based upon contributions by Cox[**] and Jaynes[***]. The general method used in the proof was inspired by Cox's derivation of the functional form of probability.

This thesis was written in close association with Dean Myron Tribus, without whose guidance this work would not have been possible. A number of important changes in the proof were suggested by Prof. Paul T. Shannon and Prof. Graham B. Wallis, while several parts of it were considerably influenced by the writer's many consultations with Prof. Yehia M. El-Sayed and Mr. Jacques Pézier.

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[*] Tribus, Myron. Rational Descriptions, Decisions, and Designs. Pergamon Press Inc., New York (In print -- to be published in French, German, and Spanish as well as in English -- 1969).

[**] Cox, R.T. The Algebra of Probable Inference. Johns Hopkins Press, Baltimore, Md. (1961).

[***] Jaynes, E.T. Probability Theory in Science and Engineering. McGraw-Hill Book Co., New York (In print - 1969).

The study in this paper was supported by grants, for which the writer is most grateful, from the National Science Foundation and the Air Force Office of Scientific Research.

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PRINCIPAL SYMBOLS

C	Arbitrary Constant
$\mathcal{E}$	Essergy
E	Energy (total - reduces to internal energy for chemical systems)
$\mathcal{F}$	Potential Work Measure of the First Kind
$\mathcal{G}$	Potential Work Measure of the Second Kind
$\mathcal{H}$	Potential Work Measure of the Third Kind
H	Enthalpy: $H \equiv E + PV$
K	Arbitrary Constant
N	Quantity of Matter. In the manner of Gibbs, N may represent mass, mols, molecules, or any other extensive measure of matter which might be suitable for the given circumstances.
P	Absolute Pressure
Q	Heat
S	Entropy
T	Absolute Temperature
V	Volume
W	Work
μ_c	Gibbs potential (total - reduces to chemical potential for chemical systems)

SUBSCRIPTS:

c	Component
D	Displacement (see pages 66 and 102)
i	Species

PRINCIPAL SYMBOLS - Cont.

o	Condition of the system when it is in equilibrium with its environment

SIGNS:

$\equiv$	Equal to by definition (or "defined as")
Δ	Delta (a change or difference in a function)
$\dot{Y}$	Time derivative of a quantity Y
$\tilde{Y}$	Value of Y per unit of matter
$\bar{Y}$	Partial Value of Y (per unit of matter)
{ }	Set (see page 9)

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INTRODUCTION

In this paper, an attempt is made to prove that all of the many seemingly-independent measures of potential work (such as availability, exergy, available work, Gibbs free energy, Gibbs chemical potential, Helmholtz free energy and the other common available energy expressions -- e.g., kinetic energy, potential energy, and electrical energy) are necessarily all special cases of the one unique quantity, essergy[1] -- which by definition is a thermodynamic property whose extensive measure $\mathcal{E}$ is given for chemical systems by[2]

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[1] The name "essergy" is a contraction of the term "essence of energy", where the word "energy" is here taken in its common colloquial meaning as being that which drives physical processes. Thus in a non-technical sense, the term "essergy" represents the "essence (i.e., essential aspect) of that which drives physical processes."

[2] The symbols E, P, V, T, S, μ_c, and N_c denote energy, absolute pressure, volume, absolute temperature, entropy, Gibbs chemical potential of component "c", and quantity of component "c", respectively. The subscript "o" denotes the system when it is in equilibrium with its environment.

$$\mathcal{E} = E + P_o V - T_o S - \sum_c \mu_{co} N_c \qquad (1)$$

The proof is attempted rigorously for chemical systems, from whence it is extended to apply more generally. If correct, the proof will be of consequence to the design of any engineering system in which potential work is a significant factor -- since it will show conclusively that by evaluating the one unique quantity, essergy, the designer may rest assured that all of the many seemingly-independent considerations of potential work will be automatically satisfied.

In order to review some of the earlier measures of potential work, a very brief history of essergy will first be given.

A BRIEF HISTORY OF ESSERGY

Since the time of Carnot(1)(1824), the concept of potential work -- in the sense of the maximum work which can be produced by a system or process -- has been of concern to engineers dealing with power systems. This concept was inherent in the free energy and available energy functions of von Helmholtz and Gibbs(2)(1873). The concept was used by Darrieus(3)(1930) who defined "thermodynamic efficiency" as being the quotient of the actual work obtained divided by the potential work for materials in steady flow. These ideas were advanced by Keenan(4)(1932) who called Darrieus' efficiency the "effectiveness" -- in order that this efficiency not be confused with other efficiencies (such as the familiar Carnot efficiency, for example).

In 1941, Keenan(5) formulated the following measure Λ of the potential work of closed systems -- a measure which he called "availability":

$$\Lambda = E + P_oV - T_oS - (E_o + P_oV_o - T_oS_o) \qquad (2)$$

The subscript "o" denotes the closed system when it is in equilibrium with the surrounding medium, so that the quantities P_o, T_o, and $(E_o + P_oV_o - T_oS_o)$ are constants (it being noted that a closed system is by definition a system for which no material is allowed to cross the boundaries). Since Λ is thereby a function of the system properties E, V, and S, the availability Λ may be regarded as being a property of the system -- for any given surrounding medium. Keenan(5) pointed out that the property Λ had been described earlier in geometrical terms by Gibbs(2)(1873) who referred to it as being the available energy of the system and medium[3]. Keenan refers to the property Λ as being "the maximum work which can be delivered to things other than the system and medium by the two unaided by any changes (except cyclic changes) in any external things".

The availability Λ is a measure of the potential work of systems. In regard to the potential work of processes, Keenan(5) pointed out that the steady flow availability developed earlier by Darrieus(3) and Keenan(4) is given simply by $\Lambda + (P - P_o)V$ (where Λ is given by equation 2

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[3] Some of Gibbs' earlier formulations(2)(1873) were concerned with equilibrium surfaces as defined by the coordinates E, V, and S for a closed system. He called the surface of stable equilibrium the "surface of dissipated energy." In one case, he considered the closed system to be immersed in a medium of constant temperature and pressure, and pointed out that the available energy of the system and medium is equal to the vertical height of the state point in the E-V-S space above a plane which is tangent to the "surface of dissipated energy" at the point $P = P_m$, $T = T_m$ (where P_m and T_m represent the pressure and temperature of the medium respectively).

with V representing the volume of material which flows in some definite increment of time). For more general situations, Keenan(6)(1951) wrote a balance equation for the term $E + P_oV - T_oS$ which appears in equation (2). He pointed out that the use of the familiar Gibbs free energy function may be regarded as being a special case of this availability formulation. Further contributions to the availability concept were made by Rant(7)(1956) and Gaggioli(8)(1962). Rant introduced the term "exergy" -- a term which has been used considerably in Europe in virtually the same sense as the steady flow availability. (9,10)

In 1958, Tribus suggested to the writer that the potential work of processes should be given by a balance of availability rather than by a balance equation for the term $E + P_oV - T_oS$, since $E + P_oV - T_oS$ is not a general measure of the potential work of open systems. The writer attempted to write such a balance equation(11), and found that the required generalization could be carried out by replacing the term $(E_o + P_oV_o - T_oS_o)$ in availability by the term $\sum_c \mu_{co}N_c$. The result was the following measure $\mathcal{a}$ of the potential work of systems -- this measure at first having been called "available energy"(12)(1962):

$$\mathcal{a} = E + P_oV - T_oS - \sum_c \mu_{co}N_c \qquad (3)$$

The right side of equation (3) is identical to the right side of equation (1) above. As with the availability Λ, the quantities P_o, T_o and $\{\mu_{co}\}$ are constant for any given environment, so that the function $\mathcal{A}$ may likewise be regarded as a property of the system (for any given environment).

Gibbs(13)(1878) wrote a special formulation of the property $\mathcal{A}$ -- i.e., he formulated it for the special case of a system immersed in an existing medium with constant properties T_o, P_o. and $\{\mu_{co}\}$ (see Gibbs(13)equations 53, 56, 68, 82, and 133, for example). Gibbs used his special formulation mainly as a criterion of stability of the medium, and he didn't propose either a name or a symbol for it (although he used such symbols as Φ, W, and σ for particular cases -- Gibbs equations 164, 552, and 659, for example). The property $\mathcal{A}$ as given by equation (3) is considerably more general than Gibbs' special formulation in that it does not require an existing medium.

In 1963, Tribus suggested to the writer that Rant's term "exergy" would be a more appropriate name for the property $\mathcal{A}$ than "available energy". The term "exergy" seemed more appropriate, since the property $\mathcal{A}$ need not be viewed as a kind of energy at all (as such terms as "available energy" and "availability" would imply) but instead may be viewed as a measure of the departure of a system from equilibrium. Consequently the writer adopted the symbol "$\mathcal{E}$" for this property and called it "exergy"(14). However, as it became apparent that the term "exergy" is used by most workers to represent a quantity considerably more limited in scope than the property $\mathcal{A}$, the writer in Reference (15) changed the name to "essergy" (i.e., essence of energy). In view of these changes, the symbol "$\mathcal{A}$" was replaced by the symbol "$\mathcal{E}$" while the term "available energy" was replaced by the word "essergy" -- it being noted that equations (1) and (3) thus become identical. A summary of the above discussion is presented in Table I.

As indicated in Table I, the formulation given in Reference 12 (1962) is a rather general form of essergy. This formulation enables one to make potential-work balances upon systems under rather general circumstances, whereas balances of the previous forms of potential work (availability, free-energy, Gibb's special formulation of the property $\mathcal{A}$, etc.) could be made only under more limited circumstances.

It may be of interest to some readers to verify at this point that essergy is indeed a measure of potential work. First observe that for the transmission of work W through a shaft, differentiation of equation (1) for a given environment yields $d\mathcal{E} = dE$; since dV, dS, and $\{dN_c\}$ are all zero when the only effect is reversible shaft

TABLE I

CONNECTIONS AMONG ESSERGY, AVAILABILITY, EXERGY, AND FREE ENERGY

NAME	FUNCTION	COMMENTS
ESSERGY	$E + P_oV - T_oS - \sum_c \mu_{co}N_c$	This function was formulated for the special case of an existing medium in 1878 (by Gibbs) and in general in 1962 (Ref. 12). Its name was changed from "available energy" to "exergy" in 1963, and from "exergy" to "essergy" (i.e., "essence of energy") in 1968.
AVAILABILITY	$E + P_oV - T_oS - (E_o + P_oV_o - T_oS_o)$	Formulated by Keenan in 1941, this function is shown on page 32 to be a special case of the essergy function.
EXERGY	$E + PV - T_oS - (E_o + P_oV_o - T_oS_o)$	Introduced by Darrieus (1930) and Keenan (1932), this function (which Keenan has called the "availability in steady flow") was given the name "exergy" by Rant in 1956. As shown on page 39, this function is a special case of essergy.
FREE ENERGY	HELMHOLTZ: $E - TS$ GIBBS: $E + PV - TS$	The functions E-TS and E+PV-TS were introduced by von Helmholtz and Gibbs (1873). These two functions are Legendre transforms of energy which were shown by Gibbs to yield useful alternate criteria of equilibrium. As measures of the potential work of systems, these two functions are shown on page 44 to represent special cases of the essergy function.

work[4]. And since for this case $dE = -dW$, it follows that $d\mathcal{E} = -dW$. Thus when the only effect is the reversible transmission of work through a shaft, the essergy $\mathcal{E}$ will always decrease by precisely the amount of work done.

For heat transfer Q on the other hand, differentiation of equation (1) for a given environment yields $d\mathcal{E} = dE - T_o dS$, since dV and $\{dN_c\}$ are zero when the only effect is heat transfer. Noting that $dE = dQ$ while $dS = dQ/T$ for reversible heat transfer at temperature T, we have

$$d\mathcal{E} = \frac{T-T_o}{T} dQ \qquad (4)$$

The ratio $\frac{T-T_o}{T}$ will be recognized as the Carnot efficiency, which is conventionally looked upon as being the fraction of the heat dQ which is available as work. Thus the essergy formulation is seen to contain the Carnot principle within its framework.

In order to assess the effects of irreversibilities, one need only differentiate equation (1) for the case when the system is not interacting with its given environment

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[4] The symbol { } denotes a set; thus $\{dN_c\}$ denotes the set of differentials of the n components -- that is, $\{dN_c\} \equiv dN_1, dN_2, --- dN_n$. Since components are by definition always conserved, each N_c is constant in a closed system, so that $dN_c = 0$. A discussion of components (which are always conserved) vs. species (which usually are not) is given in Note 1 of Appendix A. It will also be noted that for a given environment, the quantities P_o, T_o. and $\{\mu_{co}\}$ are all constant.

(so that E, V, and $\{N_c\}$ are constant) to obtain,

$$d\mathcal{E} = -T_o dS^c \tag{5}$$

where the superscript "c" denotes that dS for this case represents entropy which is "created" -- it being noted from the Second Law that dS^c is always greater to or equal to zero for reproducible phenomena. And thus the well known equivalence between the creation of entropy and the loss of potential work is seen to be embraced by the essergy formulation.

A number of applications of essergy have appeared in the literature in addition to those cited above. Reference (16) made use of the writer's original outline of essergy as given in Reference (11). The general sea-water-conversion considerations of Silver(17,18) were done independently, and remained unknown to the writer until after Reference (12) had gone to publication. References (19) and (20) made use of the formulation of Reference (12). In Reference (21), the formulation of Reference (14) was applied to a number of proposed sea-water conversion processes (freezing; electrodialysis; distillation via vapor compression, multi-stage flash, and multi-effect; etc.). Reference (22) introduced non-linearities into the design formulation, while in Reference (23), detailed considerations of the values of different kinds of potential work (thermal, mechanical, chemical, etc.) were presented. References (24), (25), and (26) made use of the essergy concept in the optimization of systems where interdependencies between the subsystems cannot be neglected. Reference (27) introduces uncertainty considerations into the design procedure. Reference (41) serves to summarize the status of exergy in Europe as of 1961, and Reference (42) includes economic considerations while in Reference (43), (44), and (45), efficiencies and limits of applicability of exergy are considered.

In making this brief history, the writer has attempted to present a unified treatment of the development of essergy in which the similarities, rather than the differences, among the various previous measures of potential work have been emphasized. If, on the contrary, one examines some of the differences (as is done below in the discussion of the results of this paper), then one finds a situation in which (in the absence of reference to these results) many seemingly independent measures of potential work appear to coexist. This situation has served to keep the fundamental nature of essergy somewhat obscured. It is hoped that the proof given in the paper will help to remove this obscurity. Let us now proceed with the proof.

POTENTIAL WORK

The first step of the proof is to list those requirements needed to define potential work. As indicated above, the potential work of a system is the potential of that system to produce work -- where the work produced by a system or process is understood to be work which can always be completely converted (via theoretically reversible mechanical contrivances -- e.g., cranks, gears, etc.) into mechanical shaft work. Thus a system can have no potential work when it is in stable equilibrium with its environment. Or in more general terms, the potential work of a system must admit of a measure which exhibits no finite change whenever the system varies between any two different states, neither of which has any finite departure from equilibrium with the environment.

Also, the potential work of a system must be a thermodynamic property (of the system and its environment) which admits of an extensive measure, since work is a thermodynamic type of transmission of energy[5] -- and energy is an extensive quantity[6]. And finally, for any given environ-

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[5] Work is an energy transmission which is thermodynamic in its nature in that this transmission by definition involves no transmissions of either entropy or matter (it being understood that in relativistic considerations, the word "matter"implies material which has rest mass).

[6] An extensive quantity is one whose value for any group of systems taken together is equal to the sum of its values for the individual systems.

ment[7], the potential work of a system must admit of a measure which always increases when work is transmitted through a shaft into the system while the entropy of the system is constant (in the absence of any other interactions between system and environment). These requirements may be summarized as follows:

> The potential work of a system must be a thermodynamic property (of the system and its environment) which admits of the following three kinds of measures:
>
> 1. A measure which, for any given environment, always increases when work is transmitted through a shaft into the system while the entropy of the system is constant (in the absence of any other interactions between system and environment).
> 2. An extensive measure.
> 3. A measure which exhibits no finite change whenever the system varies between any two different

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[7] An environment will be said to be "given" whenever the system is considered to have a unique condition of equilibrium with the environment -- as discussed in Appendix 1. It should also be mentioned that a measure is by definition a single valued function -- as pointed out in the proof of Theorem 3 below. One may thereby wish to consider that what is being defined here is the expected value of the potential work, if fluctuation phenomena are considered.

states, neither of which has any finite departure from equilibrium with the environment.

These three requirements are listed here in the order that they are used in the proof. That there is at least one function which satisfies these requirements is immediately apparent from the fact that essergy satisfies them -- as discussed below. The sufficiency of these three requirements for the purpose of defining potential work (for chemical systems) is demonstrated by the proof itself -- which shows that they are satisfied by only one thermodynamic property, viz. essergy. Their necessity with respect to the proof is discussed in Appendix 2.

Requirements 1, 2, and 3 serve to define the potential work of systems. However, the unqualified term "potential work" by definition denotes the potential work of systems and/or processes. The potential work of any process must by definition admit of a measure which is equal to the net decrease in potential work which the process alone _necessarily_ causes in the systems involved. In this regard, it will be noted that any increase in the potential work of a system which results from the receipt of potential work _delivered_ by the process is not caused _necessarily_ by the process -- since this potential work may be delivered to any arbitrary system. Examples of the potential work of processes are given on pages 36-39.

POTENTIAL WORK MEASURES OF THE FIRST KIND

Let the symbol $\mathcal{F}$ denote any potential work measure of the first kind -- as described in Requirement No. 1 above. The following theorem may now be proven:

THEOREM 1: For any non-locking system[8] in any given environment, all measures $\mathcal{F}$ must remain constant if the entropy of the system remains constant while the system is not interacting with the environment.

PROOF: Suppose that while the system is not interacting with its given environment, a particular measure $\mathcal{F}$ were to undergo a finite change $\Delta\mathcal{F}$, without any change occurring in the entropy of the system. Since any isentropic, adiabatic process may be reversed in a non-locking system[8], there is nothing to prevent the process under consideration from moving in the reverse direction -- so that one could always obtain a change in the algebraic sign of $\Delta\mathcal{F}$ under these conditions (it being noted that for a given environment, it is always possible to consider a situation where all independent properties of the environment are constant

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[8] A non-locking system is by definition any thermodynamic system which has no locking constraints. In such a system by definition, any isentropic, adiabatic process may always be moved in the reverse direction -- as discussed in Appendix 4.

Before proceeding to the derivation of some theorems, it should be emphasized that equation (1) is only the definition of the extensive measure $\mathcal{E}$ of essergy for a chemical system. However, as pointed out in Appendix E, equation (1) also applies to certain generalized chemical systems (which may include such effects as electricity, magnetism, gravity, surface tension, stress, and nuclear considerations). The general definition of essergy is somewhat involved and is given in Appendix E.

It is shown in Appendix 3 that the essergy of chemical systems satisfies Requirements 1, 2, and 3. In other words, it is known prior to making the proof that essergy is a consistent measure of potential work (for chemical systems). What is not known (prior to the proof) is whether or not there might be other independent thermodynamic properties which equally well satisfy these three requirements.

One may now proceed to derive some theorems.

POTENTIAL WORK MEASURES OF THE FIRST KIND

Let the symbol $\mathcal{F}$ denote any potential work measure of the first kind -- as described in Requirement No. 1 above. The following theorem may now be proven:

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---

[8] A non-locking system is by definition any thermodynamic system which has no locking constraints. In such a system by definition, any isentropic, adiabatic process may always be moved in the reverse direction -- as discussed in Appendix 4.

while the system is not interacting with it -- so that $\mathcal{F}$ for such a situation would depend upon independent properties of the system only).

After completing this process, let the absence-of-interaction restriction be relaxed by permitting a finite amount of work to be transmitted through a shaft into the system while its entropy is constant (without any other interaction occurring between the system and its given environment). The measure $\mathcal{F}$ must by definition increase in this case. Denoting this second change by $\underline{\Delta\mathcal{F}}$, let this second process be restricted in a manner such that $|\underline{\Delta\mathcal{F}}| < |\Delta\mathcal{F}|$, where $\Delta\mathcal{F}$ still denotes the change in $\mathcal{F}$ due to the first process. Since one could always obtain a change in the algebraic sign of $\Delta\mathcal{F}$ for the first process, one could thereby always obtain a change in the algebraic sign of $\Delta\mathcal{F} + \underline{\Delta\mathcal{F}}$ for the combination of these two processes.

But this is a violation of the definition of $\mathcal{F}$, since the combination of these two processes constitutes a process where a finite amount of work is transmitted through a shaft into the system while its entropy is constant -- without any other interaction occurring between the system and its given environment -- and for such a process, Requirement No. 1 dictates that $\Delta\mathcal{F} + \underline{\Delta\mathcal{F}}$ must always be positive. The only way to prevent such a violation is to set $\Delta\mathcal{F}$ for the first process equal to zero. Hence $\mathcal{F}$ must remain constant if the entropy of the system remains constant while the system is not interacting with the environment. Theorem 1 is thereby proven.

Theorem 1 may be used to derive the following theorem which serves to indicate the functional form of the measures $\mathcal{F}$:

THEOREM 2: For any chemical system in any given environment, each measure $\mathcal{F}$ is completely determined by a function of the form $\mathcal{F}(E, V, S, \{N_c\})$.

PROOF: It is convenient to include in the set of a chemical system's independent properties its energy E, volume V, entropy S, and components $\{N_c\}$ -- it being noted that S will be independent of E, V, and $\{N_c\}$ for such non-equilibrium states as the heterogeneous non-equilibrium states considered by Gibbs(13) (such states being made up of homogeneous parts which are at equilibrium within themselves but not at equilibrium with each other). With these quantities included as independent variables, there can be no independent properties of the system other than E, V, S, and $\{N_c\}$ which must remain constant in a chemical system whose entropy is constant while the system is not interacting with its environment (this proposition is verified in Appendix A). But from Theorem 1, $\mathcal{F}$ must also remain constant for any given environment while S is constant during such a period[9]. Since for a given environment all independent variables of the system and its environment other than E, V, S, and $\{N_c\}$ are thus allowed to vary[10] while $\mathcal{F}$ is constant, $\mathcal{F}$ cannot for a given environment depend upon any of these other variables. Hence for any chemical system in any given environment, each measure $\mathcal{F}$ is completely determined by a function of the form $\mathcal{F}(E, V, S, \{N_c\})$.

Theorem 2 enables us to determine for chemical systems the functional form of potential work measures of the second kind.

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[9] In regards to Theorem 1, it may be noted that any chemical system is a non-locking system by definition (as indicated in Appendix A).

[10] In view of the definition of a given environment, all independent properties of the given environment may in general be allowed to vary while the system is not interacting with it (as discussed in Appendix 1).

POTENTIAL WORK MEASURES OF THE SECOND KIND

Let the symbol $\mathcal{G}$ denote any potential work measure of the second kind -- i.e., any extensive measure as set forth in Requirement No. 2 above. The following theorem may now be proven:

THEOREM 3: Each extensive measure $\mathcal{G}$ is completely determined by a function of the form $\mathcal{G}(E, V, S, \{N_c\})$ for any chemical system in any given environment.

PROOF: Let $\mathcal{B}$ represent any particular thermodynamic property which qualifies as being the potential work of systems (i.e., any thermodynamic property which satisfies Requirements 1, 2, and 3). Any measure $\mathcal{D}$ of the property $\mathcal{B}$ must by definition be a one-to-one mapping[11] onto $\mathcal{B}$. Thus in particular, any measure $\mathcal{F}$ of the first kind which $\mathcal{B}$ admits of (in accordance with Requirement 1) must be a one-to-one mapping onto $\mathcal{B}$. This means that any measure $\mathcal{D}$ of the property $\mathcal{B}$ must be a one-to-one mapping onto $\mathcal{F}$, since both $\mathcal{F}$ and $\mathcal{D}$ are one-to-one mappings onto $\mathcal{B}$ (in general, y is always a one-to-one mapping onto z if both y and z are one-to-one mappings onto x).(28) Thus each extensive measure $\mathcal{G}$

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[11] Following the definition used in Reference (28), a variable y is said to be a one-to-one mapping onto x if y = y(x) and x = x(y) -- it being recalled that in modern terminology, any function y = y(x) is understood to be single-valued unless otherwise specified.(28,29)

of the property $\mathcal{B}$ must be a one-to-one mapping onto $\mathcal{F}$. Combining $\mathcal{A} = f(\mathcal{F})$ with Theorem 2, it follows that $\mathcal{A} = \mathcal{A}(E, V, S, \{N_c\})$.

Theorem 3 leads to the following theorem:

THEOREM 4: For any chemical system in any given environment, each extensive measure $\mathcal{A}$ is completely determined by a function of the form $\mathcal{A} = K_E E + K_V V + K_S S + \sum_c K_{Nc} N_c + C$ where K_E, K_V, K_S $\{K_{Nc}\}$, and C are constants, C being necessarily zero for any unconstrained chemical system.

PROOF: From Theorem 3, $\mathcal{A} = \mathcal{A}(E, V, S, \{N_c\})$. But $\mathcal{A}$, E, V, S, and $\{N_c\}$ are all extensive quantities. Therefore, for any chemical system in any given environment, $\mathcal{A}$ must have the form $\mathcal{A} = K_E E + K_V V + K_S S + \sum_c K_{Nc} N_c + C$, where K_E, K_V, K_S, $\{K_{Nc}\}$ and C are constants (a detailed demonstration of this proposition is given in Appendix B where it is shown that C is necessarily zero for any unconstrained chemical system). Hence the theorem.

The constant K_E may be shown to be a unit conversion constant, so that the following statement may be proven:

THEOREM 5: For any chemical system in any given environment, $\mathcal{A}$ is determined by $\mathcal{A} = KE + K_V V + K_S S +$

$\sum_c K_{Nc} N_c$ + C where K is an arbitrary unit conversion constant.

PROOF: As shown in Appendix C, the constant K_E must have a fixed, non-zero value independent of the given environment. Thus K_E may be regarded as an arbitrary unit conversion constant, so that $\mathcal{U} = KE + K_V V + K_S S + \sum_c K_{Nc} N_c + C$ (the subscript "E" being dropped from the unit conversion constant K_E).

In order to determine the identity of the constants K_V, K_S, and $\{K_{Nc}\}$, reference to potential work measures of the third kind will be needed.

POTENTIAL WORK MEASURES OF THE THIRD KIND

Reference to potential work measures of the third kind will serve to identify the constants K_V, K_S, and $\{K_{Nc}\}$ of Theorem 5, from whence the following theorem will result:

THEOREM 6: The only extensive measure $\mathcal{A}$ of the potential work of any chemical system is $\mathcal{A} = K(E + P_oV - T_oS - \sum_c \mu_{co}N_c) + C$, where K is an arbitrary unit conversion constant while P_o, T_o and μ_{co} denote the properties P, T, and μ_c of the system at the condition "o" when the system is in equilibrium with its environment -- the constant C being an arbitrary scale constant which is necessarily zero for any unconstrained chemical system.

PROOF: Let the symbol $\mathcal{H}$ denote any potential work measure of the third kind -- as described in Requirement No. 3 above. This requirement dictates that $\mathcal{H}$ must not change by any finite amount whenever a chemical system varies between any two states which have no finite departure from equilibrium with a given environment. In other words, for all such variations, $\Delta\mathcal{H}$ must be zero to within all non-finite deviations such as non-finite second and higher order infinitesimals. This implies that $d\mathcal{H}$ must be zero for all infinitesimal variations of this kind, since $d\mathcal{H}/\Delta\mathcal{H}$ approaches unity as $\Delta\mathcal{H}$ approaches zero. And since $\mathcal{H}$ is a one-to-one mapping onto $\mathcal{U}$ (for the same reason that $\mathcal{U}$ had to be a one-to-one mapping onto $\mathcal{T}$ in the proof of Theorem 3) it follows that $d\mathcal{U}$ is also zero for all such variations. Thus in view of the expression for $\mathcal{U}$ in Theorem 5, we have for all variations of this kind (for any given environment),

$$d\mathcal{U} = KdE + K_V dV + K_S dS + \sum_c K_{Nc} dN_c = 0 \quad (6)$$

Now for all such variations, the Gibbs expression (13, 30, 31, 32, 33, 39) $dE = TdS - PdV + \sum_c \mu_c dN_c$ holds (to within non-finite second order infinitesimals) -- in view of the definition of a chemical system (Appendix A), and in compliance with the stipulation that for such variations the system has no finite departure from equilibrium. Letting the subscript "o" denote the condition of the system when it is in equilibrium with its environment, the Gibbs expression for the system in this condition is,

$$dE = T_o dS - P_o dV + \sum_c \mu_{co} dN_c \qquad (7)$$

Equation (6) may be put into the form of equation (7) by dividing by the unit conversion constant K and transposing terms:

$$dE = -\frac{1}{K}(K_S dS + K_V dV + \sum_c K_{Nc} dN_c) \qquad (8)$$

Since the differentials dS, dV, and $\{dN_c\}$ may be assigned arbitrarily, a comparison of equations (7) and (8) yields,

$$-\frac{K_S}{K} = T_o \qquad (9)$$

$$\frac{K_V}{K} = P_o \qquad (10)$$

$$-\frac{K_{Nc}}{K} = \mu_{co} \qquad c = 1,2 \text{ --- } n \qquad (11)$$

Substitution of $K_S = -KT_o$, $K_V = KP_o$, and $K_{Nc} = -K\mu_{co}$ into the expression (from Theorem 5) $\mathcal{A} = KE + K_V V + K_S S + \sum_c K_{Nc} N_c + C$ yields,

$$\mathcal{A} = K(E + P_o V - T_o S - \sum_c \mu_{co} N_c) + C \qquad (12)$$

It is shown in Appendix D that the constant C must have a fixed value independent of the given environment. C is therefore an arbitrary scale constant, which (as shown in Theorem 4) is necessarily zero for any unconstrained chemical system. Since both K and C are independent of the given environment, while the values of P_o, T_o, and $\{\mu_{co}\}$ serve to represent any given environment, equation (12) applies whether or not the effect of the environment is held fixed -- it being noted that P_o, T_o, and μ_{co} are constants for any given environment, while they will be variables if the effect of the environment is varied. It follows that the only extensive measure $\mathcal{E}$ of the potential work of any chemical system is $\mathcal{E} = K(E + P_oV - T_oS - \sum_c \mu_{co}N_c)+C$ where K is a unit conversion constant as shown in Theorem 5, and C is an arbitrary scale constant which is necessarily zero for any unconstrained chemical system. Theorem 6 is thereby proven.

Theorem 6 serves to demonstrate that the environment's influence upon the potential work of any chemical system is totally reflected by the system's intensive properties T, P, and $\{\mu_c\}$ at the condition "o" when the system is at equilibrium with the environment. We may now proceed to considerations of the uniqueness of essergy.

THE UNIQUENESS OF ESSERGY

Theorem 6 enables us to demonstrate the uniqueness of essergy as a measure of potential work for chemical systems. We begin with the following theorem:

THEOREM 7: The only consistent extensive measure of the potential work of any chemical system is the essergy function $\mathcal{E}$.

PROOF: Since the constant K which appears in Theorem 6 may be regarded as a unit conversion constant, it will be recognized that KE represents energy. Letting E' denote energy in different units, we have, $E' = KE$. The terms PV, TS, and $\{\mu_c N_c\}$ must all have units of energy so that we likewise have $P' = KP$, $S' = KS$, and $\{\mu_c' = K\mu_c\}$, since V, T, and $\{N_c\}$ are not normally expressed in units related to energy (if S were to be dimensionless, then we would write $T' = KT$ instead of $S'=KS$). Letting it be understood that the symbols E, P, S, and $\{u_c\}$ used in equation (1) correspond to E', P', S', and $\{\mu_c'\}$ (or T in equation (1) corresponds to T' in case S is dimensionless), we may drop the primes -- from whence Theorem 6 states that $E + P_o V - T_o S - \sum_c \mu_{co} N_c + C$ is the only extensive measure of the potential work of a chemical system.

> Or in other words, the only extensive measure of the potential work of a chemical system is the essergy function $\mathcal{E}$ as defined in equation (E-1) of Appendix E -- it being recalled that C is necessarily zero for any unconstrained chemical system. This means that in actuality there are no other consistent extensive measures of the potential work of a chemical system -- i.e., any apparent "other" extensive measure must be a special case of $\mathcal{E}$, and any appearance of its being something other than $\mathcal{E}$ must be due to superfluities or inconsistencies (or both). One thereby concludes that the essergy function $\mathcal{E}$ is the only consistent extensive measure of the potential work of any chemical system.

As indicated in the first footnote on page 95, one may have a set of constrained chemical systems which is not itself a chemical system as defined in Appendix A. For such sets of chemical systems, the following theorem applies:

THEOREM 8: The only consistent extensive measure of the potential work of chemical systems is the essergy function $\mathcal{E}$.

PROOF: The extensive measure $\mathcal{G}$ of the potential work of any set of chemical systems is by definition given by $\mathcal{G} = \sum_r \mathcal{G}_r$, where $\mathcal{G}_r$ denotes the extensive measure $\mathcal{G}$ for the r'th chemical system. Thus in view of

Theorem 7, $\mathcal{A}$ is given by $\sum_r(E_r+P_{or}V_r-T_{or}S_r-\sum_c\mu_{cor}N_{cr}+C_r)$, which is identical to the essergy $\mathcal{E}$ for such a set as defined by equation (E-2) of Appendix E. Hence the theorem.

The following theorem serves to complete the demonstration of the consistency and uniqueness of essergy as a measure of the potential work of chemical systems:

THEOREM 9: Essergy is the only consistent measure of the potential work of chemical systems.

PROOF: Any consistent measure $\mathcal{D}$ of the potential work of chemical systems must be a one-to-one mapping onto the essergy function $\mathcal{E}$, for otherwise $\mathcal{D}$ would not consistently measure the same thermodynamic property which $\mathcal{E}$ measures -- and in that case, in view of Requirement 2 and Theorem 8, $\mathcal{D}$ would not be a consistent measure of the potential work of chemical systems. After the manner of the quantity temperature (it being recalled that any one-to-one mapping onto the absolute temperature is itself an example of temperature -- on some particular scale of temperature),(31,32,33,39) all such one-to-one mappings onto $\mathcal{E}$ are specific examples of the quantity, essergy, by definition (Appendix E). It follows that any consistent measure $\mathcal{D}$ of the potential work of chemical systems must be a specific example of the quantity, essergy. Or in other words, essergy is the only consistent measure of the potential work of chemical systems.[12]

In order to complete the proof given in this paper, the potential work of processes will now be considered:

THEOREM 10: Essergy is the only consistent measure of potential work (for chemical systems).

PROOF: As defined on page 14, the potential work of any process must admit of a measure which is equal to the net decrease in potential work which the process alone necessarily causes in the systems involved. Thus any consistent measure of the potential work of any process must (in view of Theorem 8) be a one-to-one mapping onto the net decrease $-\Delta\mathcal{E}$ in the essergy which the process alone necessarily causes in the chemical systems involved. Since any such one-to-one mapping onto an essergy change $\Delta\mathcal{E}$ (or $-\Delta\mathcal{E}$) is itself a specific example of the quantity, essergy[13], it follows

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[12] The meaning of the phrase "essergy is the only consistent measure" is intended to be synonymous with the phrase "any consistent measure must be a specific example of essergy".

[13] After the manner of the quantity, energy (it being noted that any energy change ΔE (or $-\Delta E$) is itself a specific example of energy -- e.g., an energy increase ΔE constitutes energy which is transferred into the system), any essergy change $\Delta\mathcal{E}$ (or $-\Delta\mathcal{E}$) is itself a specific example

that for chemical systems, any consistent measure of the potential work of any process must be a specific example of essergy. Or in other words, essergy is the only consistent measure of potential work for processes in chemical systems[12]. And since (as indicated on page 14) the unqualified term "potential work" denotes the potential work of systems and/or processes, it follows (in view of Theorem 9) that essergy is the only consistent measure of potential work (for chemical systems).

Theorems 2 through 10 may be extended to apply to generalized chemical systems -- thereby including effects of electricity, magnetism, gravity, surface tension, stress, and nuclear considerations. Before doing this however, it may be of interest to discuss how for chemical systems essergy includes previous measures of potential work as special cases.

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of essergy by definition (Appendix E). And after the manner of the quantity, temperature (it being recalled that any one-to-one mapping onto an absolute temperature change ΔT is itself a specific example of temperature -- on some particular scale of temperature)(31,32,33,39) any one-to-one mapping onto the essergy $\Delta\mathcal{E}$ is itself a specific example of essergy by definition (Appendix E). It should be pointed out here that changes such as ΔT and $\Delta\mathcal{E}$ are considered to start from a particular state, so that any one-to-one mappings onto ΔT and $\Delta\mathcal{E}$ coincide with the corresponding one-to-one mappings onto T and $\mathcal{E}$ respectively.

A DISCUSSION OF SOME SPECIAL CASES OF ESSERGY

Theorem 10 dictates that for chemical systems, all previous measures of potential work must be special cases of essergy -- for otherwise they would in view of this theorem have to be inconsistent. Let us first consider the availability defined by equation (2):

1. AVAILABILITY:

The availability defined by equation (2) applies to closed systems. Since each N_c is constant for a closed system, we have $N_c = N_{co}$ from whence $\sum_c \mu_{co} N_c = \sum_c \mu_{co} N_{co} =$ $E_o + P_o V_o - T_c S_o$ in view of the Gibbs expression $E = PV - TS + \sum_c \mu_c N_c$. Substitution of this result into equation (1) yields

$$\mathcal{E} = E + P_o V - T_o S - (E_o + P_o V_o - T_o S_o) \quad (13)$$

A comparison of equations (2) and (13) shows that availability is a special case of essergy. As for the medium which is mentioned in the definition of availability, one may for any <u>given</u> environment always arbitrarily introduce a medium of fixed P, T, and $\{\mu_c\}$ into essergy considerations -- such mediums being discussed in detail in Reference 12. That such a medium is actually superfluous is apparent from the fact that no mention of a medium appears in the definition of potential work (page 13). With respect to a stable medium of positive absolute temperature, the essergy $\mathcal{E}$ of an unconstrained system will (as shown in detail in Reference 12) always be the minumum shaft work required to create the system from the medium -- or alternately, the maximum work which the system can produce via interaction with the medium. In this regard, it will be recalled from page 12 that the work produced by a system or process is understood to be work which can always be completely converted into mechanical shaft work. The distinction between work produced by a system vs. work done by a system will be discussed in the following section.

Let us first, however, make use of the arbitrary scale constant C which may be added to the essergy of a closed system (equation E-1 of Appendix E). For a closed system in a given environment, $\sum_c \mu_{co} N_c$ is constant, so that C may arbitrarily be set equal to $\sum_c \mu_{co} N_c$ in equation (E-1) to yield Keenan's(5) availability function $E + P_oV - T_oS$:

$$\mathcal{E} = E + P_oV - T_oS \qquad (14)$$

Thus the availability function $E + P_oV - T_oS$ is seen to be a special case of the essergy $\mathcal{E}$ of a closed system. As pointed out by Keenan(5), the availability $E + P_oV - T_oS - (E_o + P_oV_o - T_oS_o)$ is equal to the amount by which the availability function $E + P_oV - T_oS$ exceeds its value $(E + P_oV - T_oS)_o \equiv$

$E_o + P_oV_o - T_oS_o$ at the condition "o" when the system is at equilibrium with its environment.

2. AVAILABLE WORK

Gibbs at one point states in effect that any supply of work may be transformed into any other via mechanical and thermodynamic devices, supposed theoretically perfect[14]. It will be convenient to refer to the general condition under which this statement holds as being the "Gibbs condition". In Figures 1 and 2, a situation is illustrated for which the Gibbs condition need not apply. The point is that the work $P_o\Delta V$ which system A does upon system B cannot be harnessed through a shaft if the temperature T and pressure P are <u>everywhere</u> constant at T_o and P_o respectively. Or in other words, for this case we have a supply of work which cannot be transformed into any other so that the Gibbs condition need not apply.

This situation is analyzed in greater detail on pages 49 and 70, where it is shown that whenever the Gibbs

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[14] Gibbs' complete statement (Ref. 13, third sentence of first page) is, "For by mechanical and thermodynamic contrivances, supposed theoretically perfect, any supply of work and heat may be transformed into any other which does not differ from it either in the amount of work and heat taken together or in the value of the integral $\int \frac{dQ}{T}$." If one considers supplies of work only, then this statement says in effect that by mechanical and thermodynamic devices, supposed theoretically perfect, any supply of work may be transformed into any other.

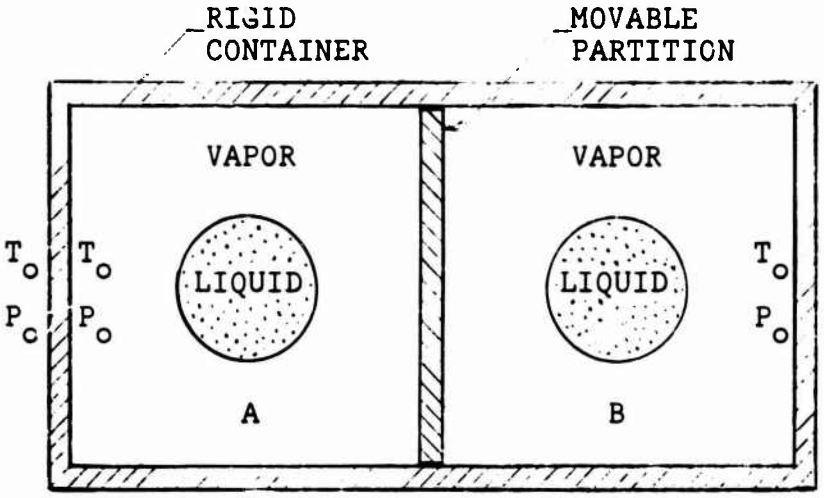

FIGURE 1: A SITUATION FOR WHICH THE GIBBS CONDITION NEED NOT APPLY. Systems A and B are chemical systems which contain liquid and vapor of a given substance oriented in a manner consistent with the absence of gravity. The temperature T and pressure P of systems A and B and the surroundings are stipulated to be everywhere fixed at T_o and P_o. Even though T and P are everywhere fixed, heat may flow from B to A and evaporate some of the liquid in A while an equal mass of vapor condenses in B -- resulting in the movement of the partition shown in Fig. 2 while T and P remain everywhere constant.

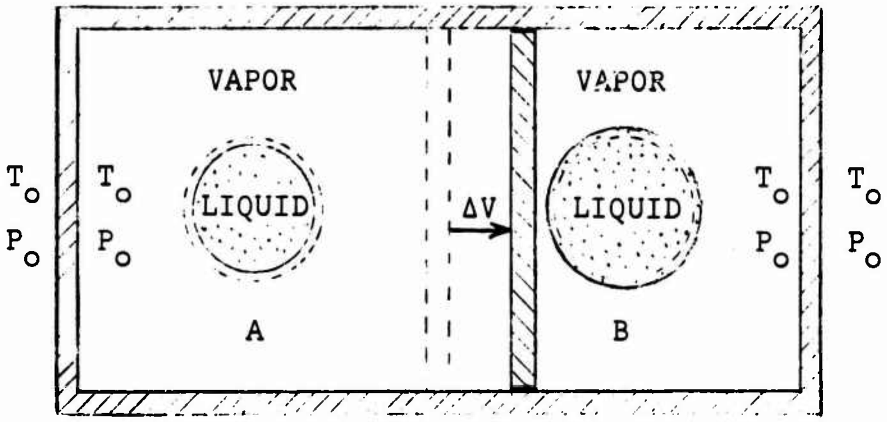

FIGURE 2. THE SYSTEM OF FIG. 1 WITH THE PARTITION MOVED WHILE T AND P REMAIN EVERYWHERE CONSTANT. The amount of work done by system A upon system B due to the movement of this partition through a volume ΔV is equal to $P_o \Delta V$. With T and P stipulated to be everywhere constant at T_o and P_o at all times, there will be no way to harness this work through a shaft, so that for this case, the Gibbs' condition need not apply.

condition is applied, the equilibrium pressure P_o must be set equal to zero, in which case the work produced by a system will coincide with the work done by a system. Applying the Gibbs condition to equation (14), we set $P_o = 0$ to obtain

$$\mathcal{E} = E - T_o S \qquad (15)$$

Hatsopoulous and Keenan have called the function $\mathcal{E} = E - T_o S + C$ the "available work" (the arbitrary constant C being added in view of the arbitrariness of the scale constant C in equation (E-1). They have used this function as the basis for deriving entropy without direct a priori reference to heat. In view of equation (15) and the arbitrariness of the constant C, we see that the available work $E - T_o S + C$ is a special case of the essergy $\mathcal{E}$.

3. EXERGY

The potential work for flows of matter and energy constitute examples of the potential work of processes. For instance, the Carnot expression $(1 - T_o/T)dQ$ is an example of the potential work of a process -- it being observed that $(1 - T_o/T)dQ$ represents a necessary decrease of potential work in the system from which dQ flows, if we consider the process dQ alone. Hence in view of Theorem 10, the quantity $(1 - T_o/T)dQ$ is a special example of essergy -- as is illustrated by the derivation of equation (4). In other words, $(1 - T_o/T)dQ$ is the amount of essergy which flows into a system as a result of a flow of heat dQ at temperature T. Similarly, as illustrated on page 9, the mechanical shaft work $-dW$ is the amount of essergy which flows into a system as a result of this increment of shaft work. For the case of material flowing across a stationary boundary, the essergy which flows may be found by differentiating equation (1) for a given environment to obtain

$$d\mathcal{E} = dE - T_o dS - \sum_c \mu_{co} dN_c \qquad (16)$$

it being noted that $dV = 0$ when the only effect upon a system is the flow of material across a stationary boundary. The term "flow" is meant to exclude all diffusion effects, so that for the homogeneous <u>flow</u> of matter, one has $dE = \tilde{H}dN$ and $dS = \tilde{S}dN$ via the definition of flow -- where N is the quantity of matter which flows, $N \equiv \sum_c N_c$, while H is the enthalpy $H \equiv E + PV$ (it being noted that $\tilde{H}$ denotes the enthalpy H per unit of material, while $\tilde{S}$ denotes the entropy S per unit of material). Defining the quantity[15]

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[15] The notion of a "quantity fraction" is in keeping with the notation of Gibbs(13), who expressed his general relationships in terms of units of matter which could be arbitrarily interpreted as mass units, mols, molecules, or any other material unit which might be suitable for the given circumstances.

fraction x_c by $dN_c = x_c dN$, one may substitute the flow relationships $dE = \tilde{H}dN$ and $dS = \tilde{S}dN$ into equation (16) to obtain the following expression for the essergy $d\mathcal{E}$ which flows with the homogeneous flow of matter across a stationary boundary:

$$d\mathcal{E} = (\tilde{H} - T_o\tilde{S} - \sum_c \mu_{co}x_c)dN \tag{17}$$

For the flow of an amount N of material, the essergy $\mathcal{E}^f \equiv \int_0^{\mathcal{E}^f} d\mathcal{E}$ is given by,

$$\mathcal{E}^f = \int_0^N (\tilde{H} - T_o\tilde{S} - \sum_c \mu_{co}x_c)dN' \tag{18}$$

For steady flow, the values $\tilde{H}$, $\tilde{S}$, and $\{x_c\}$ are constant so that equation (18) reduces to

$$\mathcal{E}^{fs} = H - T_oS - \sum_c \mu_{co}N_c \tag{19}$$

where $\mathcal{E}^{fs}$ denotes the value of $\mathcal{E}^f$ which results for steady flow. In summary, the essergy $\mathcal{E}^{fs}$ represents the amount of essergy which flows across a stationary boundary as a result of the steady homogeneous flow of N units of matter.

In view of the identity $H = E + PV$, a comparison of equation (1) and (19) yields Keenan's relationship(5)

$$\mathcal{E}^{fs} = \mathcal{E} + (P - P_o)V \tag{20}$$

where V represents the volume of material which crosses the boundary during the steady homogeneous flow. Keenan derived this relationship for the case where $N_c = N_{co}$ in equation (19) so that $\sum_c \mu_{co} N_c = \sum_c \mu_{co} N_{co} = H_o - T_o S_o$ in view of the Gibbs expression $H = TS + \sum_c \mu_c N_c$. Substitution of this result into equation (19) yields

$$\mathcal{E}^{fs} = H - T_o S - (H_o - T_o S_o) \qquad (21)$$

Keenan(5) called this example of the essergy $\mathcal{E}^{fs}$ the "availability in steady flow", while Rant(7) has called it "exergy" -- a term which has gained considerable usage(9,10). A comparison of equations (13) and (21) yields the Keenan relationship, equation (20), in the manner first given by Keenan.

In view of the identity $H = E + PV$, the essergy $\mathcal{E}^{fs}$ in equation (21) is seen to be identical to the function exergy as given in Table 1 on page 8. Thus exergy is seen to be a special case of essergy. However, the name "exergy" has been applied to other special cases of essergy as well. For example, the essergy $(1 - T_o/T)dQ$ derived in equation (4) has been called by this name(10). In order to describe more comprehensively the scope of the terms "availability" and "exergy", it will be convenient to derive an essergy balance. One may begin by integrating equation (4) to obtain

$$\mathcal{E}^q = \int_0^Q \frac{T - T_o}{T} dQ' \qquad (21')$$

where $\mathcal{E}^q \equiv \int_0^{\mathcal{E}^q} d\mathcal{E}$ with respect to equation (4). For the case of the steady flow of heat Q at constant temperature T, equation (21′) reduces to

$$\mathcal{E}^q = \frac{T - T_o}{T} Q \tag{22}$$

When the only effect upon a system is an amount of work dW, differentiation of equation (1) for a given environment yields, $d\mathcal{E} = dE + P_o dV$, since S and $\{N_c\}$ are constant when the only effect is reversible work dW. Noting that dE = -dW for this case, we have

$$d\mathcal{E} = P_o dV - dW \tag{23}$$

Integration of equation (23) yields the essergy $\mathcal{E}^w \equiv \int_0^{\mathcal{E}^w} d\mathcal{E}$ which results from the transmission of an amount of work W:

$$\mathcal{E}^w = P_o \Delta V - W \tag{24}$$

And finally, integration of equation (5) for a given environment yields

$$\mathcal{E}^d = T_o S^c \qquad S^c \geq 0 \tag{25}$$

where $\mathcal{E}^d$ and S^c denote $-\int_0^{\mathcal{E}^d} d\mathcal{E}$ and $\int_0^{S^c} dS$ respectively -- for equation (5).

On the basis of equations (1), (18), (21′), (24), and (25), one may set up an essergy balance as follows:

$$d\mathcal{E} = \sum_b d\mathcal{E}_b^f + \sum_b d\mathcal{E}_b^q + d\mathcal{E}^w - d\mathcal{E}^d \tag{26}$$

Here the subscript "b" denotes each particular homogeneous region b which is located on the boundary of the system. Thus for example, $\sum_b d\mathcal{E}_b^q$ denotes the sum of the essergy flows $d\mathcal{E}^q$ for each homogeneous region b of the boundary, while $\sum_b d\mathcal{E}_b^f$ denotes the sum of the essergy flows $d\mathcal{E}^f$ for each homogeneous stream b. As in any expression for a total differential such as $d\mathcal{E}$, the independent differentials in equation (26) such as $d\mathcal{E}_b^f$ and $d\mathcal{E}_b^q$ may be evaluated by setting all the other independent differentials arbitrarily equal to zero. In view of equations (4), (5), (17), and (23), one thereby obtains

$$d\mathcal{E}_b^f = (\tilde{H} - T_o\tilde{S} - \sum_c \mu_{co}x_c)_b dN_b \qquad (27)$$

$$d\mathcal{E}_b^q = \frac{T_b - T_o}{T_b} dQ_b \qquad (28)$$

$$d\mathcal{E}^w = P_o dV - dW \qquad (29)$$

$$d\mathcal{E}^d = T_o dS^c \qquad dS^c \geq 0 \qquad (30)$$

It is convenient to summarize this result in time derivative form via introducing the notation $\dot{Y} = dY/dt$ where Y is an arbitrary property and t denotes time. Introducing this notation into equation (26) through (30), one obtains the following essergy balance which applies to any open chemical system in any given environment in the absence of non-flow mass transport such as diffusion (a more general essergy balance being given on page 70):

$$\dot{\mathcal{E}} = \sum_b \dot{\mathcal{E}}_b^f + \sum_b \dot{\mathcal{E}}_b^q + \dot{\mathcal{E}}^w - \dot{\mathcal{E}}^d \qquad (31)$$

where $$\dot{\mathcal{E}}_b^f = (\tilde{H} - T_o\tilde{S} - \sum_c \mu_{co} x_c)\dot{N}_b \qquad (31a)$$

$$\dot{\mathcal{E}}_b^q = \frac{T_b - T_o}{T_b}\dot{Q}_b \qquad (31b)$$

$$\dot{\mathcal{E}}^w = P_o\dot{V} - \dot{W} \qquad (31c)$$

$$\dot{\mathcal{E}}^d = T_o\dot{S}^c \qquad \dot{S}_c \geq 0 \qquad (31d)$$

and where from equation (1),

$$\dot{\mathcal{E}} = \dot{E} + P_o\dot{V} - T_o\dot{S} - \sum_c \mu_{co}\dot{N}_c \qquad (31e)$$

In words, equation (31) says that the net essergy $(\sum_b \dot{\mathcal{E}}_b^f + \sum_b \dot{\mathcal{E}}_b^q + \dot{\mathcal{E}}^w)$ being transferred into a system is either stored $(\dot{\mathcal{E}})$ or else dissipated $(\dot{\mathcal{E}}^d)$ -- it being noted that the net essergy input is by definition the excess of essergy entering the system over essergy leaving the system.

For steady state systems, $\dot{\mathcal{E}}$ and $\dot{V}$ are zero, from whence equation (31) reduces to

$$\sum_b \dot{\mathcal{E}}_b^f + \sum_b \dot{\mathcal{E}}_b^q + \dot{\mathcal{E}}^w - \dot{\mathcal{E}}^d = 0 \qquad (32)$$

where $\dot{\mathcal{E}}_b^f$, $\dot{\mathcal{E}}_b^q$, and $\dot{\mathcal{E}}^d$ are given by equations (31a), (31b), and (31d) respectively, while equation (31c) reduces to

$$\dot{\mathcal{E}}^w = -\dot{W} \qquad (32a)$$

Equation (32) corresponds to the balances of availability and exergy given by Keenan$^{(5)}$ and Bosnjakovic$^{(10)}$ -- it being noted that they have written $\mathcal{E}^f$ in the limited form, equation (21), rather than the more general form, equation (19). Keenan$^{(6)}$ also formulated a special case of equation (26) which corresponds to the special condition $\mu_{co} = 0$ for all c in equations (1) and (27) -- this special condition having to be introduced since for an unconstrained system, the measure $E + P_o V - T_o S$ would otherwise violate Requirement 3 on page 13. Keenan wrote his balance expressions in the form of inequalities (i.e., he never introduced the quantity $\mathcal{E}^d = T_o S^c$).

Since the availability and exergy balances are special cases of the more general essergy balance, it is seen -- in view of equations(13) and (21) -- that both availability and exergy are completely embraced as special cases of essergy.

4. FREE ENERGY

The Helmholtz free energy E - TS is known to be a measure of potential work for isothermal processes$^{(13,31,32)}$. For such a process, the only equilibrium value T_o of the temperature which can be reached is the constant temperature T -- or in other words $T = T_o$. Considering a closed system and stipulating that the Gibbs condition applies (from whence $P_o = 0$) so that the essergy $\mathcal{E}$ is given (to within an arbitrary constant) by equation (15), we find by substituting $T_o = T$ into equation (15),

$$\mathcal{E} = E - TS \tag{33}$$

The Gibbs free energy E + PV - TS is known to be a measure of potential work for isothermal, isobaric processes(13, 31, 32). For such a process, T_o and P_o can have only the values of the constant temperature T and constant pressure P respectively. Substituting $T_o = T$ and $P_o = P$ into the closed-system essergy expression, equation (14), one obtains

$$\mathcal{E} = E + PV - TS \tag{34}$$

In view of equations (33) and (34), the Helmholtz and Gibbs free energies are seen to be special cases of the essergy function $\mathcal{E}$. As Legendre transforms of energy(40), these two functions of course each have a separate meaning, and it is only when they are viewed as measures of potential work that they are special cases of essergy. Similarly, the chemical potential μ_c is a special case of essergy when μ_c is regarded as being a measure of potential work, since in view of the Gibbs expression $E = TS - PV + \sum_c \mu_c N_c$, equation (34) may be written

$$\mathcal{E} = \sum_c \mu_c N_c \tag{35}$$

The Gibbs free energy also may be regarded as being a special case of the steady flow essergy $\mathcal{E}^{fs}$ for an isothermal process ($T_o = T$) with respect to the special condition $\mu_{co} = 0$ for all c, in which case equation (19) reduces to

$$\mathcal{E}^{fs} = H - TS \tag{36}$$

or in view of the Gibbs expression $H = TS + \sum_c \mu_c N_c$,

$$\mathcal{E}^{fs} = \sum_c \mu_c N_c \tag{37}$$

The other more common available-energy expressions -- such as kinetic energy, gravitational energy, electrical energy, etc. -- involve non-chemical effects, so that they will be considered after generalizing the proof of Theorem 10. It may, however, first be of interest to investigate the role played by the equilibrium pressure P_o.

SPATIAL ESSERGY

Before discussing spatial essergy, let us after Gibbs$^{(13)}$ set the constant C in equation (E-1) equal to zero. The Gibbs convention is desirable because C is necessarily zero for unconstrained systems -- and inconsistencies would occur if one set $C \neq 0$ for a system which was only temporarily constrained, and for which the constraint (or constraints) were to be removed later. Thus having used nonzero values of C in the preceding section to illustrate the generality of which the essergy function $\mathcal{E}$ is capable, we will from this point on always refer to the essergy $\mathcal{E}$ as though it were defined completely by equation (1) (for chemical systems).

With this convention understood, the essergy $\mathcal{E}$ has some characteristics which may be of interest. First we note from equation (1) that $\mathcal{E}$ must be zero when the system is at the equilibrium condition "o" in view of the Gibbs expression $E = TS - PV + \sum_c \mu_c N_c$. Next it should be pointed out that for stable equilibrium of a system with the environment, $\mathcal{E}$ is always greater than or equal to zero (for $T_o \geq 0$). This was first pointed out by Gibbs$^{(13)}$ who showed that for unstable equilibrium with the environment, $\mathcal{E}$ may be negative as well as positive. Demonstrations that $\mathcal{E} \geq 0$ for stable equilibrium with the environment (for $T_o > 0$) are also given in References (12) and (14). Another way of illustrating $\mathcal{E} \geq 0$ is to substitute the Gibbs expression $dE = TdS - PdV + \sum_c \mu_c dN_c$ into the differential (for a given environment) of equation (1), $d\mathcal{E} = dE + P_o dV - T_o dS - \sum_c \mu_{co} dN_c$ to obtain for any equilibrium chemical system,

$$d\mathcal{E} = (T-T_o)dS - (P-P_o)dV + \sum_c(\mu_c-\mu_{co})dN_c \qquad (38)$$

Integration of equation (38) yields for any chemical system at equilibrium,

$$\mathcal{E} = \int_o^s (T-T_o)dS + \int_s^o (P-P_o)dV + \sum_c \int_o^s (\mu_c-\mu_{co})dN_c \qquad (39)$$

where the limits of integration are the state "o" when the system is in equilibrium with its environment and the given equilibrium state "s". For $T_o \geq 0$, each of these integrals must when evaluated in succession[16] be positive, in view of the well known relationships(13,31,32,33) $\left(\frac{\partial T}{\partial S}\right)_{V,\{N_c\}} \geq 0$,

---

[16] The term "evaluated in succession" means that each integral is evaluated while the contribution to each of the other integrals is held fixed -- the integrals not yet evaluated being held at the value "zero" by staying on the "o" line (for example if for a closed system one were to evaluate $\int_o^s(T-T_o)dS$ first, then one would integrate $\int_{S_o,P_o}^{S,P_o}(T-T_o)dS'$ while the not-yet-evaluated integral $\int_s^o(P-P_o)dV$ remains at zero since $P = P_o$).

$(\frac{\partial P}{\partial V})_{S,\{N_c\}} \leq 0$, and $(\frac{\partial \mu_c}{\partial N_c})_{S,V,\{N_c^-\}} \geq 0$ (where $\{N_c^-\}$ indicates that all $\{N_c\}$ except the one in the denominator are held constant). Since each of the terms in equation (39) may always be positive for any given equilibrium state s (for stable equilibrium with the environment and $T_o \geq 0$), it follows that $\mathcal{E} \geq 0$.

It is interesting to observe that in view of equation (39), the essergy $\mathcal{E}$ may be evaluated by finding the area between the curve and the "o" line on such conventional graphs as T-S and P-V diagrams. It may also be of interest to observe that the following specific form of equation (39) may be obtained by substituting the Gibbs expression $E = TS - PV + \sum_c \mu_c N_c$ into equation (1):

$$\mathcal{E} = (T - T_o)S - (P - P_o)V + \sum_c (\mu_c - \mu_{co})N_c \qquad (40)$$

In order to investigate the phenomenon of spatial essergy, we first note that the essergy $\mathcal{E}_v$ of a volume V of empty space is

$$\mathcal{E}_v = P_o V \qquad (41)$$

since E, S, and $\{N_c\}$ are all zero for a vacuum (since for chemical systems, vacuums can have no energy) -- from whence equation (1) reduces to $\mathcal{E} = P_o V$. In this regard, we note that $P_o V$ is the work required to push back a medium of pressure P_o to form the empty space V. The essergy $\mathcal{E}$ of the medium remains at the value, zero, as it is pushed back since a medium of constant temperature $T = T_o$, pressure $P = P_o$, and potentials $\mu_c = \mu_{co}$ always has no finite potential work (as has been shown rigorously in Ref. 14).

The nature of the spatial essergy $\mathcal{E}_v$ may be illustrated with reference to Fig. 3. Here, as the volume V_A of system A increases by an amount ΔV, the essergy P_oV_A of system A increases by $P_o\Delta V$ while the essergy P_oV_B of system B decreases by this same amount because the volume V_B of system B decreases by the same volume increment ΔV. Neither system A nor system B has any energy (since for chemical systems, vacuums can have no energy), and neither of systems A and B do any work upon each other -- and yet it is clear that potential work is transferred from B to A.

The effect of spatial essergy may be studied further by analyzing the situation depicted in Figures 1 and 2. Here, we find that the amount of work $W = P_o\Delta V$ is precisely equal to the required increase in the spatial essergy $\mathcal{E}_v$ (i.e., $\Delta\mathcal{E}_v = P_o\Delta V$), from whence the essergy transferred between systems A and B is zero (as may be verified by equation 24). It follows from equation (24) that the work W will be transformable into shaft work if and only if $P_o = 0$. In other words, the Gibbs condition applies if and only if the spatial essergy P_oV is zero. The general implications of this result are discussed on page 70.

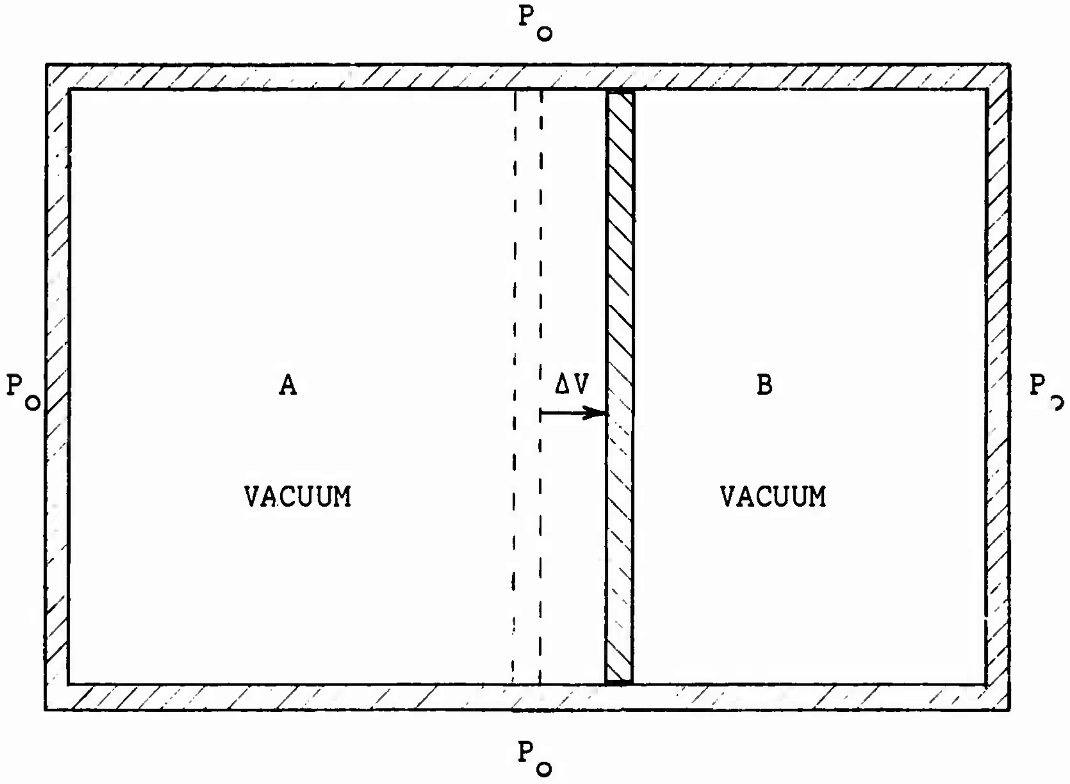

FIGURE 3: A VACUUM IMMERSED IN A MEDIUM OF PRESSURE $P = P_o$, THE TWO PARTS A AND B BEING SEPARATED BY A MOVABLE PARTITION. As the partition moves to the right, system A does no work upon system B -- and yet this movement causes the essergy of system A to increase by an amount $P_o\Delta V$ at the expense of an equal essergy decrease of system B.

ON GENERALIZING THE PROOF

As a means for generalizing the proof of Theorem 10, it will be convenient to introduce the following generalization of the Gibbs expression $dE = TdS - PdV + \sum_c \mu_c dN_c$ after the manner of Tribus$^{(30,31)}$ and Hatsopoulos and Keenan$^{(33,46)}$:

$$dE = TdS + \sum_k F_k dX_k + \sum_c \mu_c dN_c \qquad (42)$$

Here the energy E is understood to be the total energy -- including kinetic energy, gravitational energy, electrical energy, etc. The parameters X_k represent variables by which the energy may be varied while the entropy S and components $\{N_c\}$ remain fixed. Examples of X_k include the scalar components of the position of a system in a field of force (gravitational, electrical, etc.), the scalar components of the strength of a field of force (electrical, magnetic, etc.), the area of a surface film, the length of a stressed body, the angular displacement of a body under shearing stress, etc. The parameters F_k are defined by

$$F_k \equiv \left(\frac{\partial E}{\partial X_k}\right)_{S,\{N_c\},\{X_{\bar{k}}\}} \qquad (43)$$

where $\{X_{\bar{k}}\}$ denotes the constancy of all X_k except the one in the denominator. The total potentials μ_c are defined by,

$$\mu_c \equiv \left(\frac{\partial E}{\partial N_c}\right)_{S,\ \{X_k\},\{N_{\bar{c}}\}} \qquad (44)$$

while the absolute temperature T is defined by

$$T \equiv \left(\frac{\partial E}{\partial S}\right)_{\{X_k\},\{N_c\}} \tag{45}$$

It is convenient to include the volume V as being one of the variables $\{X_k\}$ in equation (42). Let us thereby separate V out of the set $\{X_k\}$ by writing $\{X_k\} = V,\{X_I\}$, where X_I represents any independent X_k except the volume V. Using this notation, a generalized chemical system will now be defined as follows:

> A generalized chemical system is by definition any thermodynamic system which has the following four characteristics:
>
> a. When the system is at equilibrium with its environment, its equilibrium state is uniquely determined by that state's energy E, volume V, components $\{N_c\}$ and work variables $\{X_I\}$ -- whence, for constant $\{X_I\}$, the expression $dE = TdS - PdV + \sum_c \mu_c dN_c$ is stipulated to apply (at equilibrium with the environment)[17].
>
> b. All properties of the system are differentiable functions of any set of independent

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[17] The generalized pressure P is defined by

$$P \equiv -\left(\frac{\partial E}{\partial V}\right)_{S,\{N_c\},\{X_I\}}$$

variables whose values uniquely describe the state of the system.

c. The system has no locking constraints (Appendix 4) -- it thus being stipulated that while the system is not interacting with its environment, any given state can be reached from any other state which has the same values of E, V, S, $\{N_C\}$, and $\{X_I\}$.

d. Any two systems with the same values of E, V, S, $\{N_C\}$ and $\{X_I\}$ are always free to assume identical states.

Comparing this definition with the definition of an ordinary chemical system in Appendix A, one will see (in view of the footnote on page 77) that with the $\{X_I\}$ held constant, Characteristics a, b, c, and d are identical for these two definitions. It follows that with the exception of the considerations of Appendix D (as mentioned in the footnote on page 77), the proof of Theorems 1 through 10 remains completely unchanged -- under the stipulation that the variables $\{X_I\}$ are all held constant. The considerations of Appendix D may be taken into account in a manner such as the following:

First we note from Appendix B that since the constant C in equation (B-8) is zero for an unconstrained chemical system, it is also zero for any generalized chemical system with E, V, S, and $\{N_c\}$ unconstrained (but with $\{X_I\}$ held constant) -- so that equation (12) reduces to

$$\mathcal{A} = K(E + P_oV - T_oS - \sum_c \mu_{co}N_c) \qquad (46)$$

As pointed out in the paragraph preceding equation (6), $d\mathcal{A}$ is zero for all infinitesimal variations of the type considered in Requirement 3. Differentiation of equation (46) with $\{X_I\}$ constant and $d\mathcal{A} = 0$ yields

$$dE = T_odS - P_odV + \sum_c \mu_{co}dN_c + SdT_o - VdP_o + \sum_c N_cd\mu_{co} \qquad (47)$$

Equation (47) implies that when a generalized chemical system is at equilibrium with its environment, the following expression holds (for constant $\{X_I\}$):

$$dE = TdS - PdV + \sum_c \mu_c dN_c + SdT - VdP + \sum_c N_c d\mu_c \qquad (48)$$

Equation (48) may be rewritten in the form

$$dE = d(TS - PV + \sum_c \mu_c N_c) \qquad (49)$$

Integration of equation (49) yields

$$E = TS - PV + \sum_c \mu_c N_c + B \qquad (50)$$

where B is the arbitrary integration constant (i.e., constant for fixed $\{X_I\}$). For systems with $\{X_I\}$ fixed but with E, V, S, and $\{N_c\}$ unconstrained, the constant B may be determined to be zero by noting that the energy E must be zero for a state of zero volume, entropy and matter (i.e., for a state where V, S, and $\{N_c\}$ are all zero). Hence for any system unconstrained in this manner, equation (50) reduces to

$$E = TS - PV + \sum_c \mu_c N_c \tag{51}$$

Since equation (51) would result regardless of the choice of the fixed values of $\{X_I\}$, it follows that this relationship remains valid when the work variables X_I are allowed to vary. Consequently, equation (51) applies to any generalized chemical system (at equilibrium with its environment) for which none of the variables E, V, S, or $\{N_c\}$ are constrained. It follows via differentiation of equation (51) that equation (48) applies to any generalized chemical system (at equilibrium with the environment) with the variables $\{X_I\}$ allowed to vary -- it being noted that for constrained systems (such as closed systems, constant volume systems, etc.), certain terms in equation (48) (such as $\mu_c dN_c$, PdV, etc.) may be zero. And finally, it follows that equation (47) also applies to any generalized chemical system (at equilibrium with its environment) with $\{X_I\}$ allowed to vary -- whence dC must be zero in equation D-2 of Appendix D. Thus the considerations of

Appendix D are satisfied, so that the proof of Theorems 1 through 10 remains valid when the proof is extended to generalized chemical systems -- with $\{X_I\}$ held constant as the system comes to equilibrium with its environment (since as mentioned in the footnote on page 77, the considerations of Appendix D are the only part of the proof affected by using the more general version of Characteristic "a" which appears on page 52).

In order to complete the extension of the proof to generalized chemical systems, we must determine the effect (upon P_o, T_o, $\{\mu_{co}\}$ and K) of varying the quantities $\{X_I\}$ as the system comes to equilibrium with its environment. First it may be observed (from Characteristic "a" of the definition of a generalized chemical system) that while equation (48) has been shown to be true for any generalized chemical system with $\{X_I\}$ allowed to vary, it is necessarily valid only for the condition when the system is in equilibrium with its environment. For this condition, equation (42) may be rewritten in the following form:

$$dE = TdS - PdV + \sum_I F_I dX_I + \sum_c \mu_c dN_c \qquad (52)$$

Combining equations (48) and (52), one obtains the following general form of the Gibbs-Duhem equation:

$$VdP + \sum_I F_I dX_I = SdT + \sum_c N_c d\mu_c \qquad (53)$$

Since equation (53) contains one less independent variable than does equation (52), it follows that one may vary the volume V in equation (52) while holding each of the variables P, T, $\{\mu_c\}$, and $\{X_I\}$ constant. Since E, S, and $\{N_c\}$ will for this process be dependent variables, one may integrate equation (52) along the resulting path to obtain equation (51) (in the exact manner that Gibbs(13) integrates $dE = TdS - PdV + \sum_c \mu_c dN_c$ to obtain $E = TS - PV + \sum_c \mu_c N_c$). Since for such a process the system stays at a constant intensive state, it follows that the work variables $\{X_I\}$ must all be intensive.

The intensive nature of the work variables X_I may be illustrated by considering the flow of material across a stationary control boundary such as that shown in Figure 4. Here, matter flows from system A into system B across the stationary control boundary C. If it is stipulated that this flow is the only interaction which either of the systems has with its own surroundings, then all of the work variables $\{X_k\}$ must be held constant in compliance with the fact that no work is done upon either of these systems.[18] Now suppose the systems were to be moving with a constant transverse velocity, such that the control boundary C remains stationary relative to the flow as shown in Figure

---

[18] In the absence of work, the variables $\{X_k\}$ are required to be constant in order to comply with the definition of the total potential μ_c (equation 44), which corresponds to an increase in energy (per unit increase of component c) with the work variables $\{X_k\}$ all held constant.

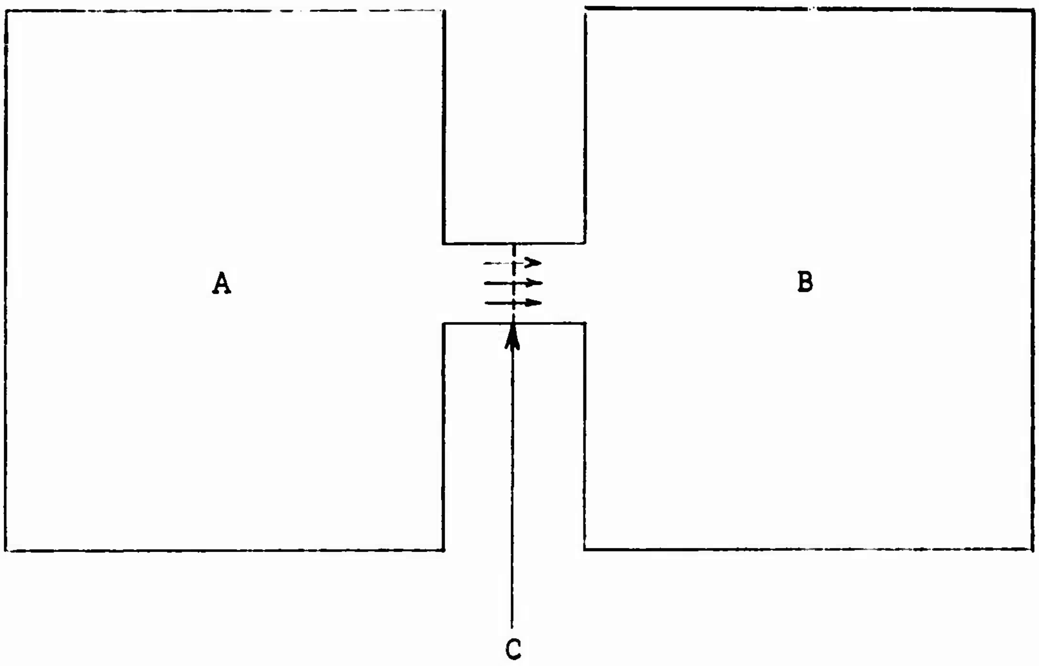

FIGURE 4: FLOW OF MATTER ACROSS A STATIONARY CONTROL BOUNDARY. Matter flows from A to B across the stationary control boundary C, it being stipulated that this flow is the only interaction which either of the systems has with its own surroundings.

5 -- it again being stipulated that this flow is the only interaction affecting either of these systems. If the extensive quantity, scalar momentum (i.e., a scalar component of momentum), were to be chosen as a work variable for kinetic energy, then the velocities of systems A and B would have to vary as shown in Figure 6. This follows since the required constancy[18] of the momentum of system A would force that system to increase in velocity in order to offset its loss of mass and thus maintain the required constancy of its momentum. Since this situation violates our stipulation that the flow of matter is the only interaction affecting either of systems A and B, it is seen that the extensive quantity, momentum, is not a suitable work variable for open systems. On the other hand, the intensive quantity, scalar velocity (i.e., a scalar component of velocity) is a suitable work variable, since the constancy of the velocities of A and B reflect the absence of work without upsetting the flow picture.

Similar difficulties have been found to arise with respect to open systems when other extensive quantities have been tried out as tentative work variables X_I. However, a complete study of these would carry us far beyond the scope of this thesis, and must be left to some future paper. Here it will only be pointed out that such work variables as the scalar components of position in a force

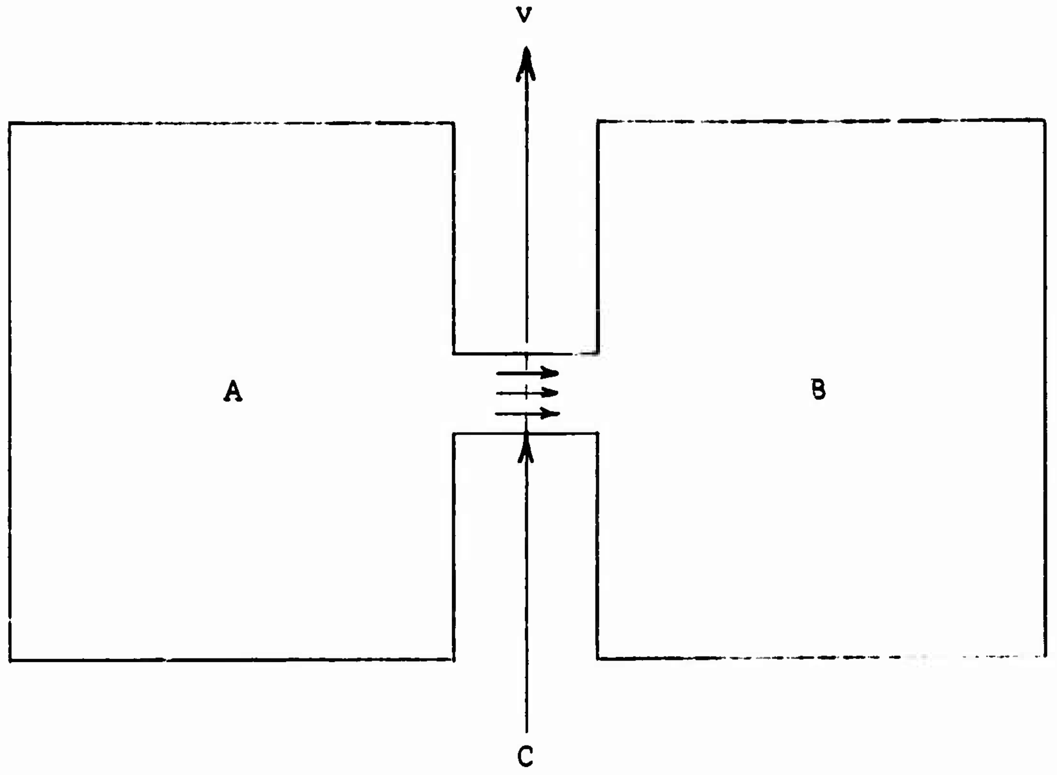

FIGURE 5: THE SYSTEM OF FIGURE 4 MOVING WITH A CONSTANT TRANSVERSE VELOCITY v. The control boundary C remains stationary relative to the flow of matter -- it again being stipulated that this flow is the only interaction which either of the systems has with its own surroundings.

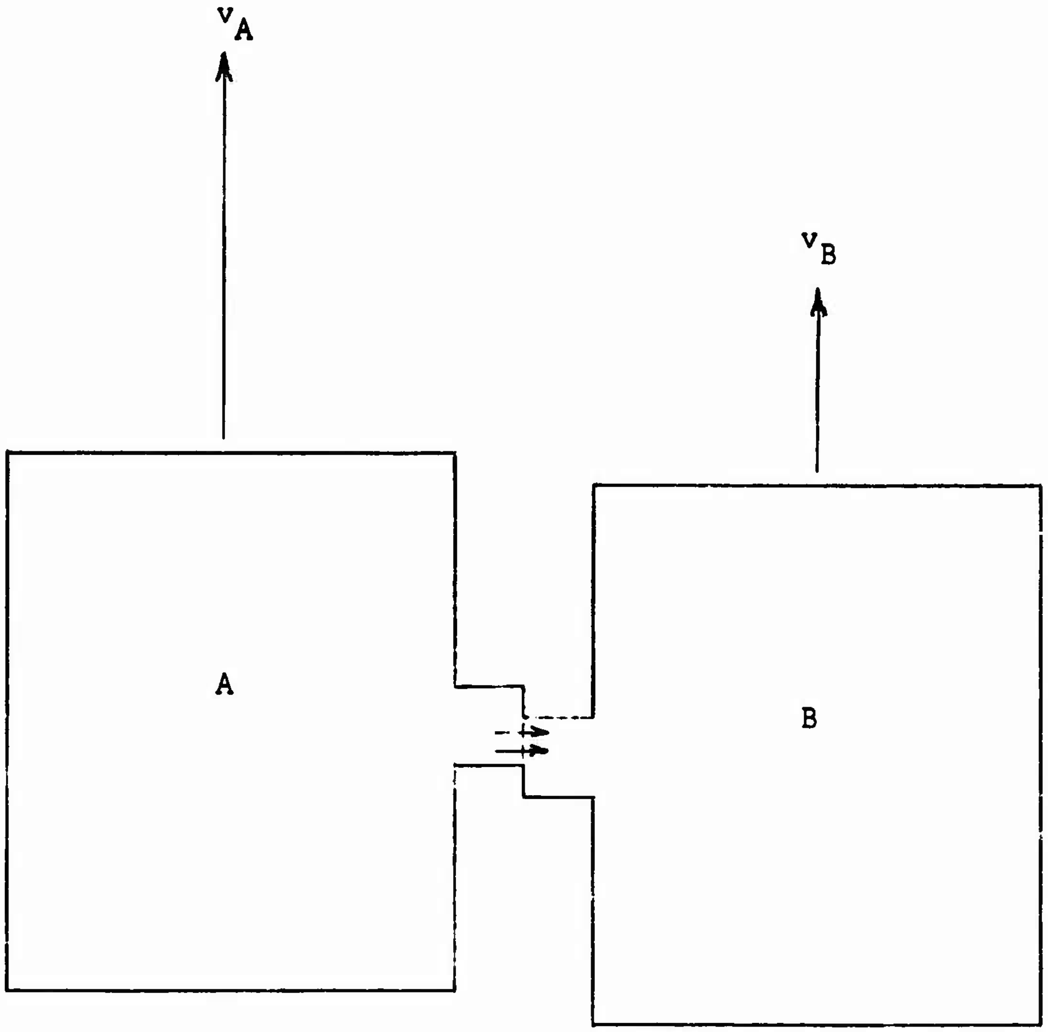

FIGURE 6: THE SYSTEM OF FIGURE 5 WITH MOMENTUM AS A WORK VARIABLE. With the momentums of A and B required to be fixed, the velocity of A must increase in order to offset A's loss of mass, while the velocity of B must decrease in order to offset B's gain in mass.

field and the scalar components of the field strength are intensive quantities which cause no difficulty with open systems. It should also be mentioned with regards to stress and surface tension that such extensive work variables as length, width, and area are not independent of the volume V of the <u>same</u> system (and thus they may appear as <u>independent</u> X_k if and only if the volume V is eliminated via the dependency) -- so that certain affects of stress and surface tension might perhaps sometimes be included in the generalized pressure P as defined in footnote 17 on page 52.

Having determined via equations (52) and (53) that the work variables $\{X_I\}$ are all intensive, we may now use these equations to determine the effect of varying the $\{X_I\}$. Since as shown above, Theorems 1 through 10 are valid for fixed $\{X_I\}$, we have from Theorem 6 for any given values of $\{X_I\}$:

$$\mathcal{A} = K(E + P_o V - T_o S - \sum_c \mu_{co} N_c) + C \qquad (54)$$

where K is an arbitrary unit conversion constant while C is an arbitrary scale constant which must be zero for any system where E, V, S, and $\{N_c\}$ are unconstrained. The effect of varying the X_I may be assessed by considering two systems A and B, each of which are at equilibrium with an intermediate system C, as shown in Figure 7. Now let energy pass from A to B while all variables $\{X_k\}$ and components $\{N_c\}$ remain constant for all three systems, and S

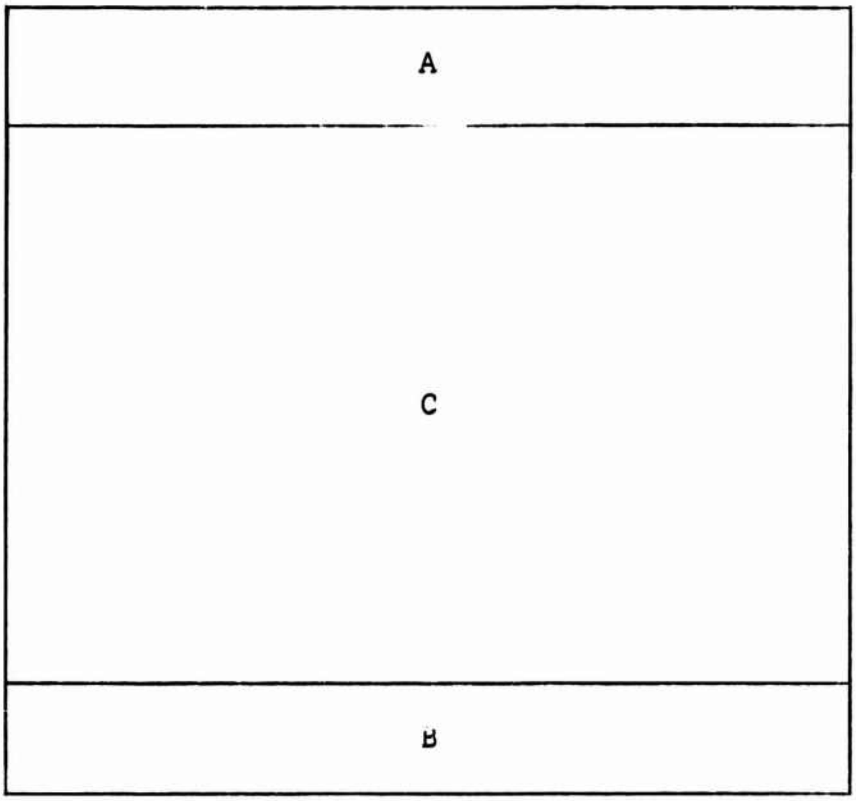

FIGURE 7: TWO GENERALIZED CHEMICAL SYSTEMS AT EQUILIBRIUM WITH AN INTERMEDIATE GENERALIZED CHEMICAL SYSTEM. Systems A and B are both stipulated to be at equilibrium with the intermediate system C. Energy and matter may pass between A and B without affecting the state of C, while volume cannot.

and E remain constant for system C. Since all three systems are at equilibrium with each other and they are not interacting with any other systems, the total entropy must be a maximum, from whence

$$dS_A + dS_B = 0 \tag{55}$$

since S is constant for system C. Applying equation (52) to each of systems A and B for this process, one obtains

$$dE_A = T_A dS_A \tag{56}$$

$$dE_B = T_B dS_B \tag{57}$$

Substitution of (56) and (57) into (55) yields

$$\frac{dE_A}{T_A} + \frac{dE_B}{T_B} = 0 \tag{58}$$

And since $dE_B = -dE_A$,

$$\left(\frac{1}{T_A} - \frac{1}{T_B}\right)dE_A = 0 \tag{59}$$

dE_A is arbitrary, so that $\left(\frac{1}{T_A} - \frac{1}{T_B}\right)$ is zero, from whence

$$T_A = T_B \tag{60}$$

Since matter may also pass between A and B without affecting the state of C, one finds in a similar fashion, for each component c,

$$\mu_{cA} = \mu_{cB} \qquad c = 1,2,3 \ldots\ldots. n \tag{61}$$

As has been pointed out by Keenan and Hatsopoulos(46), equation (61) is in agreement with Gibbs(13) equation (234) -- it being noted that the total potential μ_c defined by equation (44) is (in non-relativistic considerations(46)) equal to the sum of the Gibbs chemical potential plus an energy term -- since Gibbs defined his chemical potentials with respect to the internal energy rather than the total energy.

Volume, however, may not be transferred between A and B without affecting the state of C, (it being stipulated that A, B, and C are not interacting with the surroundings) since the position of at least some part of C will change -- whence C will interact with any force field which applies (such as gravity). Thus one cannot write $P_A = P_B$. Instead, substitution of the equilibrium conditions $dT = 0$ and $d\mu_c = 0$ (which result from equations (60) and (61)) into equation (53) yields the following equilibrium condition:

$$VdP + \sum_I F_I dX_I = 0 \qquad (62)$$

Equation (62) shows that the pressure P must vary with $\{X_I\}$ -- in agreement with Pascal's law[19].

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[19] This agreement with Pascal's law may be manifested by holding all X_I constant except the height z in a gravitational field, whence equation (62) reduces to $VdP = -mgdz$, it being noted from equation (43) that $F_I = mg$, where $m \equiv$ mass and $g \equiv$ acceleration of gravity. It may also be of interest (especially with respect to systems

In view of equations (60), (61) and (62), it is seen that at equilibrium the constants T_o and $\{\mu_{co}\}$ do not vary with respect to position, whereas the pressure P_o does vary in accordance with equation (62) -- it being noted that each X_I may vary with respect to position. If a system moves upon coming to equilibrium, it may come to a different value of P_o than that which appears in equation (54). The value of P_o which appears in (54) corresponds to the pressure P_D of the region of space occupied by the system when that region has come to equilibrium with the environment -- at which time the system need no longer occupy that region. Thus to account for variations in the X_I, the pressure P_o in equation (54) must be replaced by the pressure P_D, so that equation (54) becomes for the general case,

$$\mathcal{A} = K(E + P_D V - T_o S - \sum_c \mu_{co} N_c) + C \qquad (63)$$

The constant C is zero for any unconstrained system (since as shown by equation (46), C is zero for any given $\{X_I\}$ when the variables E, V, S, and $\{N_c\}$ are not constrained). And since the considerations of Appendix D are satisfied

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of very large vertical extent) to observe that the generalized pressure P (defined in Footnote 17) is related to the generalized pressures P_r or the parts r of the system by $P = \sum_r P_r V_r / V$ where $V = \sum_r V_r$. In this regard it will be noted that with T and $\{\mu_c\}$ held constant, any variation of V which is accompanied by a change in P will also be accompanied by a change in $\{X_I\}$ via equation (62) -- so that such a variation is not an independent variation of the volume V.

with $\{X_I\}$ allowed to vary (as shown above in the paragraph following equation (51)), the constant C for constrained systems is independent of $\{X_I\}$ -- so that C is completely independent of the given environment, whence C is an arbitrary scale constant whose value must be zero for unconstrained systems. And finally, the constant K is also independent of $\{X_I\}$ (since one of the systems of Appendix C -- say system B -- could always have $\{X_I\}$ fixed, and the selection of differing values of $\{X_I\}$ for the other system would not alter equations C-4, C-5, C-6, and C-7), so that K continues to be a unit conversion constant with $\{X_I\}$ allowed to vary. It follows from these considerations that with equation (63) replacing equation (12), Theorem 6 applies to any generalized chemical system whether or not $\{X_I\}$ may vary.

A comparison of equation (63) and equation (E-3) of Appendix E shows that Theorem 7 applies in general to generalized chemical systems. The proof of Theorem 8 follows in view of equation (E-4) of Appendix 4, while the proofs of Theorems 9 and 10 remain completely unchanged. It is thereby to be concluded that essergy is the only consistent measure of potential work for generalized chemical systems.

Still further generalizations of the proof may be made, but they are beyond the scope of this thesis. Such generalizations would include considerations of locking systems (page 16) and a covariant relativistic formulation. In this regard, it should be mentioned that certain relativistic considerations are automatically satisfied by a generalized chemical system -- in view of the conclusions of Hatsopoulos and Keenan(46). It should also be pointed out that chemical reaction considerations are completely included in the essergy of generalized chemical systems as well as chemical systems -- in view of the treatment given in Note 2 of Appendix A.

ON THE GIBBS CONDITION

As discussed above at the beginning of the section on spatial essergy, we will always assume that C = 0 in equations (E-1), (E-2), (E-3), and (E-4), unless otherwise specified. We thereby write

$$\mathcal{E} = E + P_D V - T_o S - \sum_c \mu_{co} N_c \qquad (64)$$

Noting from equation (62) that $VdP_D = -\sum_I F_{Io} dX_I$, differentiation of equation (64) for any given environment yields (noting that P_D is variable)

$$d\mathcal{E} = dE + P_D dV - T_o dS - \sum_c \mu_{co} dN_c - \sum_I F_{Io} dX_I \qquad (65)$$

If the only effect upon a system is a work effect dW, then $dE = -dW$ while $dS = 0$ and $\{dN_c = 0\}$ so that equation (65) reduces to the following expression for $d\mathcal{E}^W$ (where $d\mathcal{E}^W \equiv d\mathcal{E}$ for this case):

$$d\mathcal{E}^W = P_D dV - \sum_I F_{Io} dX_I - dW \qquad (66)$$

or per unit of time,

$$\dot{\mathcal{E}}^W = P_D \dot{V} - \sum_I F_{Io} \dot{X}_I - \dot{W} \qquad (67)$$

Thus for generalized chemical systems, equation (31c) on page 42 must be generalized to the form given by equation (67). A general form of the open system essergy balance, equation (31) must include the non-flow transport of matter $\dot{\mathcal{E}}^n$ -- so that a more general essergy balance is,

$$\dot{\mathcal{E}} = \sum_b \dot{\mathcal{E}}^n_b + \sum_b \dot{\mathcal{E}}^f_b + \sum_b \dot{\mathcal{E}}^q_b + \dot{\mathcal{E}}^w - \dot{\mathcal{E}}^d \qquad (68)$$

where $\dot{\mathcal{E}}^w$ is given by equation (67), while $\dot{\mathcal{E}}^f_b$, $\dot{\mathcal{E}}^q_b$, and $\dot{\mathcal{E}}^d$ are given by equations (31a), (31b), and (31d) respectively -- it being noted that the enthalpy $\tilde{H}$ in equation (31a) includes all the energy, such as kinetic and potential energy. The non-flow transport terms $\dot{\mathcal{E}}^n_b$ are found from equation (65) in the manner of the derivation of equation (31a).

In view of equation (66), the Gibbs condition (pages 34 and 49) will not be satisfied unless $P_D \equiv 0$, for one may always hold all X_I constant, so that $d\mathcal{E}^w = P_D dV - dW$, from whence the work dW is not completely transformable into shaft work if $P_D \not\equiv 0$. On the other hand, if $P_D \equiv 0$, then $dP_D = 0$ so that from equation (62), $\sum_I F_{Io} dX_I = 0$, from whence equation (66) reduces to $d\mathcal{E}^w = -dW$. It follows that the Gibbs condition applies if and only if the displacement pressure P_D is identically zero.

It is thus seen that applying the Gibbs condition coincides identically with considering the spatial essergy $P_D V$ to be zero. This corresponds to the conventional view of looking upon matter as occupying empty space, from whence an unconstrained system would always be free to expand and approach zero pressure.

ON AVAILABLE ENERGY

For the sake of simplicity, let us neglect the effect of buoyancy by setting $P_D = P_o$ in equation (64) so that equation (64) reduces to

$$\mathcal{E} = E + P_oV - T_oS - \sum_c \mu_{co}N_c \tag{69}$$

The maximum work which may be obtained from a closed system of constant volume corresponds to the work done in a reversible process, so that $\{N_c\}$, V, and S are all constant for this case. Thus $V = V_o$, $S = S_o$, and $\{N_c = N_{co}\}$ so that equation (69) reduces to

$$\mathcal{E} = E + P_oV_o - T_oS_o - \sum_c \mu_{co}N_{co} \tag{70}$$

And in view of equation (51),

$$\mathcal{E} = E - E_o \tag{71}$$

The energy difference $E - E_o$ includes such available energies as kinetic energy, gravitational potential energy, electrical energy, magnetic energy, etc. It also of course includes available chemical energy, and it may include nuclear energy as well. It thereby follows from equation (71) that such forms of available energy as kinetic energy, gravitational energy, electrical energy, nuclear energy, etc., are all special cases of the essergy function $\mathcal{E}$.

RESULTS

By looking at some of the differences between the various previous measures of potential work, one finds a situation in which (without reference to the results of this paper) many seemingly independent measures of potential work appear to coexist. For example, some of these measures (such as availability and exergy) require a medium of fixed T_o and P_o (such as the atmosphere) while others (such as free energy, kinetic energy, potential energy, etc.) may be evaluated without making any reference whatsoever to such a medium. Again, some measures (such as available work and Helmholtz free energy) represent the potential of a system for doing work, while other measures (such as availability and Gibbs free energy) represent the potential for doing only that part of the work (which Keenan(5) has called the "useful" work) which does not include the work done in pushing back the surrounding medium.

The main result of the proof given in this paper is to show that for a large class of thermodynamic systems, all of these seemingly diverse measures of potential work are special cases of the one unique quantity, essergy. While the proof itself is (if correct) sufficient to guarantee this result, illustrations have been provided on pages 32-45 and 71 which show that the following measures are all special cases of essergy: Availability, exergy, available work, Gibbs free energy, Gibbs chemical potential, Helmholtz free energy, and also such available energies as kinetic energy, gravitational energy, electrical energy, nuclear energy, etc. The proof has been done carefully only for chemical systems, but it has nevertheless been shown to apply to generalized chemical systems, where such effects as kinetic energy, gravity, electricity, magnetism, surface tension, stress, and nuclear considerations are taken into account.

The proof also indicates that Brillouin's negentropy(38) function is not a completely general measure of potential work. This follows since as is shown in References (12) and (14), the negentropy $S_o - S$ (where S_o is a value of the arbitrary constant in negentropy which is set equal to the maximum entropy of the system when it is isolated) corresponds to the function $\mathcal{E}/T_o$ (where $\mathcal{E}$ is the essergy function of equation (1)). That the function $\mathcal{E}/T_o$ is not a completely general measure of potential work may be illustrated by considering two systems A and B with different values of T_o as is done in Appendix C. Substituting $\mathcal{A} = \mathcal{E}/T_o$ into equations (C-1) through (C-4), equation (C-5) becomes,

$$d\mathcal{A}_{AB} = (\frac{1}{T_{oB}} - \frac{1}{T_{oA}})dE_B \qquad (72)$$

Since neither dE_B nor $(\frac{1}{T_{oB}} - \frac{1}{T_{oA}})$ is necessarily zero, it follows that $d\mathcal{U}_{AB}$ is not necessarily zero for the process considered, so that Theorem 1 is violated -- whence Requirement 1 on page 13 is not in general satisfied. It thus appears that negentropy is not as general a measure of potential work as essergy is. If Brillouin's principle of the equivalence of potential work and thermodynamic information is nevertheless retained, this result would imply that essergy is a more general measure of thermodynamic information than is negentropy.

Another result which may be of interest is that in view of Theorem 2, potential work necessarily depends upon conserved quantities only, since only conserved quantities (or functions of such quantities) need remain constant while a chemical system is not interacting with its environment. Also, the result that the work variables $\{X_I\}$ in equation (52) are necessarily intensive for a generalized chemical system may be of some importance.

CONCLUSIONS

The proof given in this paper demonstrates that for a large class of thermodynamic systems, the many seemingly independent measures of potential work (such as availability, exergy, available work, Gibbs free energy, Gibbs chemical potential, Helmholtz free energy, and such available energies as kinetic energy, gravitational energy, electrical energy, nuclear energy, etc.) are necessarily all special cases of the one unique quantity, essergy. While the proof has been carried out carefully only for chemical systems, it nevertheless has been shown to apply to generalized chemical systems (where such effects as kinetic energy, gravitational energy, electricity, magnetism, surface tension, stress, and nuclear considerations are taken into account).

Thus by evaluating the one unique quantity, essergy, a designer may be assured that all of the many seemingly independent considerations of potential work will automatically be satisfied. The proof is therefore of consequence to the design of any system in which potential work is a significant factor. The results of this paper should thereby be of importance to the continued development of that branch of engineering design known as thermoeconomics(12, 20,23,26).

The proof also indicates that negentropy is not as general a measure of potential work as essergy is. If

Brillouin's principle of the equivalence of potential work and thermodynamic information is nevertheless retained, this result would imply that essergy is a more general measure of thermodynamic information than is negentropy -- an implication which might lead to a broader formulation of information in general. It is thus hoped that the proof may eventually provide new insight into the foundations of science and information theory.

APPENDIX A

CONCERNING CHEMICAL SYSTEMS

A chemical system is by definition any thermodynamic system which has the following four characteristics:

a. The equilibrium state of the system is uniquely determined by that state's energy E, volume V, and components $\{N_c\}$ -- from whence the Gibbs expressions $dE = TdS - PdV + \sum_c \mu_c dN_c$ and $VdP = Sdt + \sum_c N_c d\mu_c$ are stipulated to apply*.

b. All properties of the system are differentiable functions of any set of independent variables whose values uniquely describe the state of the system.

c. The system has no locking constraints (Appendix 4) -- it thus being stipulated that while the system is not interacting with its environment, any given state can be reached from any other which has the same values of E, V, S, and $\{N_c\}$.

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* Except for the considerations of Appendix D, the proof of Theorems 2 through 10 may be carried out via the following more general version of Characteristic "a".

a. When the system is at equilibrium with its environment, its equilibrium state is uniquely determined by that state's energy E, volume V, and components $\{N_c\}$ -- from whence the expression $dE = TdS - PdV + \sum_c \mu_c dN_c$ is stipulated to apply (at equilibrium with the environment).

d. Any two systems with the same values of E, V, S, and $\{N_c\}$ are always free to assume identical states.

Characteristic "a" serves to exclude most non-chemical effects from states of equilibrium. For example, the addition of another state variable (in addition to the energy, volume, and components -- say for example one includes as a variable the position of the system in a gravitational field) would introduce a non-chemical effect (e.g., gravity) which Characteristic "a" serves to rule out for equilibrium states. Characteristic "b" rules out any discontinuities which might be associated with certain non-chemical effects, while Characteristic "c" rules out any locking effects which might be considered to be of a non-chemical nature. Characteristic "d" rules out any non-chemical effects which might be associated with constraints which prevent certain states from being attainable.

In view of Characteristics "a" and "c" it follows that when E, V, S, and $\{N_c\}$ are chosen as independent variables, there can be no additional independent properties which must remain constant in a chemical system whose entropy is constant while the system is not interacting with its environment (it being noted that E, V, and $\{N_c\}$

must be constant during such a period)*. For if an additional independent property were to be held constant, then there would be states having different values for this property which could not be reached while S is constant and the system is not interacting with its environment -- in violation of Characteristic "c". Examples of such properties which must in this case be allowed to vary whenever they are independent (as they are in heterogeneous chemical systems) include the energy, volume, ahd components of the various parts of the system**.

It will also be noted that the Gibbs expression

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* The amount of each component N_c is constant during the absence of any interactions between system and environment, since as indicated in Note 1 of this appendix, components by definition are always conserved.

** It may be of interest to observe the contrast between the non-interaction of a system with its environment and Gibbsian isolation. Gibbs(13) employed a kind of quasi-isolation which he called "isolation from external influences" in which the system's only allowable external communication is to deliver (but not to receive) the equivalent of shaft work. Thus in any physical process during Gibbsian isolation in which the energy is not at its minimum value, the energy E is allowed to decrease (but never to increase -- Gibbs,(13) top of page 59) while the volume V and components $\{N_c\}$ must remain constant. These allowed physical variations during Gibbsian isolation must not be confused with Gibbs' "possible variations" in which decreases in the entropy of an isolated system are allowed (Gibbs(13) equation 1) via heat transfer (Gibbs(13) page 56). The meaning of Gibbs' possible variations has been explained by Hatsopoulos and Keenan(33).

$$dE = TdS - PdV + \sum_c \mu_c dN_c \qquad \text{(A-1)}$$

has been written in terms of components "c" rather than the more familiar species "i" -- as discussed in Note 1 of this appendix.

Finally, a brief discussion of the meaning of shaft work for chemical systems is in order, since chemical systems by definition need not have the directional stress which is inherent in the functioning of any kind of shaft. The shaft system must thereby in general be an accessory system which is understood to undergo no change in state (other than changes in neutral properties -- such as translation or rotation of the shaft). Consider for example a chemical system consisting of two homogeneous parts which are at different pressure, due to being separated by a rigid, impermeable wall. By allowing and harnessing translation of the wall via mechanical contrivances such as shafts and cranks, one may obtain shaft work without a change in the volume of the system -- the volume decrease of the low pressure part offsetting the volume increase of the high pressure part. It is in this type of context that the notion of shaft work for chemical systems may in general be understood.

NOTE 1, APPENDIX A

ON COMPONENTS VERSUS SPECIES

The Gibbs equation is usually expressed in terms of chemical species rather than components*, the more usual form of equation (A-1) being,(13,30,31,32,33,39)

$$dE = TdS - PdV + \sum_i \mu_i dN_i \qquad \text{(A-2)}$$

where μ_i is the Gibbs chemical potential of species i and N_i is the amount of species i. In general, the amounts N_i of the species i are not all independent variables; instead some of the N_i are determined via chemical reactions (and other stoichiometric relationships -- such as restrictions which require the number of positive and negative ions to comply with electrical neutrality). For example, in an equilibrium mixture of hydrogen, oxygen, and water at a particular elevated temperature and pressure, the amount of water is dependent upon the amounts of hydrogen and oxygen via the dissociation reaction $2H_2O \rightleftarrows 2\ H_2 + O_2$.

Thus the use of equation (A-2) requires the formulation of chemical reactions. With equation (A-1) on the other hand, the amounts N_c of the components c are independent;

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* Gibbs referred to components as "ultimate" components (Gibbs,(13) page 79) while he used the unqualified word "component" in the sense that some components may be formed from combinations of other components (Gibbs(13), pages 68-69). In the language of chemical engineers, Gibbs' "component" is called a "species".(34)

hence one may use equation (A-1) without having to formulate chemical reactions. At equilibrium, equations (A-1) and (A-2) are necessarily connected by the following fundamental relationship which is demonstrated in Note 2 of this appendix:

$$\sum_i \mu_i dN_i = \sum_c \mu_c dN_c \qquad \text{(A-3)}$$

In the example of the preceding paragraph, there need be only two components -- e.g. atomic hydrogen and oxygen -- which must appear in equation (A-1), whereas with equation (A-2) a representative accounting of $\{N_i\}$ must include not only H_2, O_2, and H_2O, but ions such as H^+, OH^-, and $O^=$ and also the complicated crystalline hydrols which appear in the liquid phase. In using equation (A-1), one accounts for the components in exactly the same manner as atoms are conventionally accounted for when making elementary balances of H and O in reactions such as $2H_2 + O_2 \rightleftarrows 2H_2O$ and $H^+ + OH^- \rightleftarrows H_2O$. The reader who wishes to have a clearer picture of the logic underlying equation (A-1) will find it useful to study the derivation given in Note 2 of this appendix.

It should be pointed out that an essential feature of a component is that it is always conserved. A species, on the other hand, is conserved only when it does not take part in any significant chemical or nuclear reactions. If there are no recognized chemical or nuclear reactions of significance in a system, then the species are components by definition. For example, in an idealized two-species mixture of conserved O_2 and conserved N_2, the substances O_2 and N_2 are components.

Note 2 of this appendix also gives a derivation of the following two relationships, the first of which holds at equilibrium, while the second is true in general:

$$\sum_i \mu_i N_i = \sum_c \mu_c N_c \qquad \text{(A-4)}$$

$$\sum_i \mu_{io} N_i = \sum_c \mu_{co} N_c \qquad \text{(A-5)}$$

Equation (A-4) enables one to write,

$$E = TS - PV + \sum_c \mu_c N_c \qquad \text{(A-6)}$$

which is a useful expression if one wishes to avoid consideration of the cumbersome chemical reactions which must be treated when working with the more conventional integrated from of equation (A-2),

$$E = TS - PV + \sum_i \mu_i N_i \qquad \text{(A-7)}$$

Equation (A-5) enables one to write the essergy function $\mathcal{E}$ in the following alternate form:

$$\mathcal{E} = E + P_o V - T_o S - \sum_i \mu_{io} N_i \qquad \text{(A-8)}$$

Equation (A-8) is useful when one wishes to calculate the essergy of chemical reactions, whereas equation (1), page 2, is to be preferred when one is not particularly concerned with reaction essergy.

NOTE 2, APPENDIX A

DEMONSTRATION OF THE RELATIONSHIPS $\sum_i \mu_i dN_i = \sum_c \mu_c dN_c$, $\sum_i \mu_i N_i = \sum_c \mu_c N_c$, and $\sum_i \mu_{io} N_i = \sum_c \mu_{co} N_c$

The set {i} of species i may be divided into two sets, viz. the set {c} of components c plus the set {e} of those species e which may be regarded as being formed from the components c:

$$\{i\} = \{c\} + \{e\} \qquad \text{(A-9)}$$

The set {e} includes each species of ion as well as each species of molecule other than those molecules or atoms which are accounted for by the set {c}. In view of equation (A-9), the term $\sum_i \mu_i dN_i$ may be separated as follows:

$$\sum_i \mu_i dN_i = \sum_c \mu_c dN_c^f + \sum_e \mu_e dN_e \qquad \text{(A-10)}$$

The superscript "f" denotes that N_c^f includes only that portion of N_c which appears as free components -- it being noted that the remainder $N_c - N_c^f$ of the components c is tied up in other molecules and ions.

Each species e is formed from the components c in accordance with the chemical reaction,

$$e \rightleftarrows \sum_c \nu_c^e c \qquad \text{(A-11)}$$

where ν_c^e represents the stoichiometric coefficient ν of component c with respect to species e. From equation (A-11), the chemical potential μ_e at equilibrium is given via the familiar relationship of reaction equilibria (see, for example, Gibbs$^{(13)}$ equation 33 or Tribus$^{(31)}$ equation 14.65, or any other comprehensive text):$^{(32,33,39)}$

$$\mu_e = \sum_c \nu_c^e \mu_c \qquad \text{(A-12)}$$

Substitution of (A-12) into (A-10) yields,

$$\sum_i \mu_i dN_i = \sum_c \mu_c dN_c^f + \sum_e \sum_c \mu_c \nu_c^e dN_e \qquad \text{(A-13)}$$

The stoichiometric coefficients ν_c^e are by definition given by,

$$\nu_c^e = \frac{N_c^e}{N_e} \qquad \text{(A-14)}$$

where the superscript "e" denotes that N_c^e includes only that portion of N_c which is tied up in species e. Differentiation of (A-14) gives,

$$dN_c^e = \nu_c^e dN_e \qquad \text{(A-15)}$$

Substitution of (A-15) into (A-13) yields,

$$\sum_i \mu_i dN_i = \sum_c \mu_c dN_c^f + \sum_e \sum_c \mu_c dN_c^e \qquad \text{(A-16)}$$

Interchanging the order of summation and collecting terms, we have

$$\sum_i \mu_i dN_i = \sum_c \mu_c (dN_c^f + \sum_e dN_c^e) \qquad \text{(A-17)}$$

But $N_c^f + \sum_e N_c^e$ is simply the total amount N_c of component c:

$$N_c = N_c^f + \sum_e N_c^e \tag{A-18}$$

Or in differential form,

$$dN_c = dN_c^f + \sum_e dN_c^e \tag{A-19}$$

Substitution of (A-19) into (A-17) yields the final result:

$$\sum_i \mu_i dN_i = \sum_c \mu_c dN_c \tag{A-20}$$

The identity of the term $\sum_i \mu_i N_i$ may be found in a similar manner -- it being observed from equation (A-9) that we may write,

$$\sum_i \mu_i N_i = \sum_c \mu_c N_c^f + \sum_e \mu_e N_e \tag{A-21}$$

Substitution of (A-12) and (A-14) into (A-21) gives,

$$\sum_i \mu_i N_i = \sum_c \mu_c (N_c^f + \sum_e N_c^e) \tag{A-22}$$

while substitution of equation (A-18) into (A-22) yields the expected result:

$$\sum_i \mu_i N_i = \sum_c \mu_c N_c \tag{A-23}$$

The identity of the term $\sum_i \mu_{io} N_i$ is found in virtually the same manner: From equation (A-9) we may write,

$$\sum_i \mu_{io} N_i = \sum_c \mu_{co} N_c^f + \sum_e \mu_{eo} N_e \tag{A-24}$$

Since μ_{eo} and μ_{co} represent the potentials μ_e and μ_c at a particular equilibrium condition, equation (A-12) always applies:

$$\mu_{eo} = \sum_c \nu_c^e \mu_{co} \tag{A-25}$$

Substitution of equations (A-14), (A-18), and (A-25) into equation (A-24) yields the final result,

$$\sum_i \mu_{io} N_i = \sum_c \mu_{co} N_c \tag{A-26}$$

APPENDIX B

CONCERNING THE EXTENSIVE MEASURE $\mathcal{U}$

In Theorem 4 it is stated that for any chemical system in any given environment, $\mathcal{U}$ must have the form

$$\mathcal{U} = K_E E + K_V V + K_S S + \sum_c K_{Nc} N_c + C$$

where K_E, K_V, K_S, $\{K_{Nc}\}$, and C are constants, C being necessarily zero for any unconstrained chemical system. This proposition will be demonstrated here in detail.

In view of Theorem 3, each extensive measure $\mathcal{U}$ for any chemical system in any given environment is given by,

$$\mathcal{U} = \mathcal{U}(E, V, S, \{N_c\}) \tag{B-1}$$

Let the subscripts A and B denote systems A and B respectively while AB denotes systems A and B taken together. Since the quantities $\mathcal{U}$, E, V, S, and $\{N_c\}$ are all extensive, we may write*,

$$\mathcal{U}_{AB} = \mathcal{U}_A + \mathcal{U}_B \tag{B-2}$$

$$E_{AB} = E_A + E_B \tag{B-2a}$$

---

* It will be observed that systems A and B are assumed to be independent of each other. For small systems, it may be required that system B be separated in space from system A, since because of intermolecular forces, adjacent small systems may exhibit significant interdependence. In regard to the resulting system AB, it will be observed that we define a thermodynamic system to be a well-defined region of space which may consist of nonconnected (but nevertheless well-defined) parts.

$$V_{AB} = V_A + V_B \tag{B-2b}$$

$$S_{AB} = S_A + S_B \tag{B-2c}$$

$$N_{cAB} = N_{cA} + N_{cB} \quad c = 1,2,3 \ldots\ldots n \tag{B-2d}$$

where $\mathcal{G}_{AB} \equiv \mathcal{G}_{AB}(E_{AB}, V_{AB}, S_{AB}, \{N_{cAB}\})$, $\mathcal{G}_A \equiv \mathcal{G}_A(E_A, V_A, S_A, \{N_{cA}\})$, and $\mathcal{G}_B \equiv \mathcal{G}_B(E_B, V_B, S_B, \{N_{cB}\})$.

In view of the definition of a chemical system (Appendix A), $\mathcal{G}(E, V, S, \{N_c\})$ is a differentiable function. Differentiation of equation (B-2) with respect to E_A with E_B, V_A, V_B, S_A, S_B, $\{N_{cA}\}$ and $\{N_{cB}\}$ all held constant yields*,

$$\frac{\partial \mathcal{G}_{AB}}{\partial E_{AB}} = \frac{\partial \mathcal{G}_A}{\partial E_A} \tag{B-3a}$$

Similarly, differentiation w.r.t. E_B yields,

$$\frac{\partial \mathcal{G}_{AB}}{\partial E_{AB}} = \frac{\partial \mathcal{G}_B}{\partial E_B} \tag{B-3b}$$

The right sides of equations (B-3a) and (B-3b) are equal, since the left sides are identical: $\dfrac{\partial \mathcal{G}_A}{\partial E_A} = \dfrac{\partial \mathcal{G}_B}{\partial E_B}$ (B-4)

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* It follows from the chain rule for the functions $\mathcal{G}_{AB} = \mathcal{G}(X_{AB}, Y_{AB})$ and $X_{AB} = X_A + X_B$ that

$$\frac{\partial \mathcal{G}_{AB}}{\partial X_A} = \frac{\partial \mathcal{G}_{AB}}{\partial X_{AB}}, \text{ since } \frac{\partial \mathcal{G}_{AB}}{\partial X_A} = \frac{\partial \mathcal{G}_{AB}\,\partial X_{AB}}{\partial X_{AB}\,\partial X_A} + \frac{\partial \mathcal{G}_{AB}\,\partial Y_{AB}}{\partial Y_{AB}\,\partial X_A} \text{ while}$$

$$\frac{\partial X_{AB}}{\partial X_A} = 1 \text{ and } \frac{\partial Y_{AB}}{\partial X_A} = 0.$$

The left side of equation (B-4) is a property of system A only, while the right side is a property of system B only. These two properties will be independently variable in violation of the equality unless they are both constant. Equating the right side of equation (B-4) to a constant K_E, the left side must equal this same constant:

$$\frac{\partial \mathscr{S}_A}{\partial E_A} = K_E \tag{B-5}$$

or omitting the subscript "A" for convenience:

$$\frac{\partial \mathscr{S}}{\partial E} = K_E \tag{B-6}$$

In exactly the same manner, the derivatives $\partial \mathscr{S}/\partial V$, $\partial \mathscr{S}/\partial S$, and $\partial \mathscr{S}/\partial N_c$ are found to be equal to arbitrary constants K_V, K_S, and K_{Nc} respectively:

$$\frac{\partial \mathscr{S}}{\partial V} = K_V \tag{B-6a}$$

$$\frac{\partial \mathscr{S}}{\partial S} = K_S \tag{B-6b}$$

$$\frac{\partial \mathscr{S}}{\partial N_c} = K_{Nc} \qquad c = 1,2,3 \;.......n \tag{B-6c}$$

In view of equations (B-6), (B-6a), (B-6b), and (B-6c), the total differential of equation (B-1), $d\mathscr{S} = \frac{\partial \mathscr{S}}{\partial E}\, dE + \frac{\partial \mathscr{S}}{\partial V}\, dV + \frac{\partial \mathscr{S}}{\partial S}\, dS + \sum_c \frac{\partial \mathscr{S}}{\partial N_c}\, dN_c$, is given by

$$d\mathscr{S} = K_E dE + K_V dV + K_S dS + \sum_c K_{Nc} dN_c \tag{B-7}$$

Integration of equation (B-7) yields,

$$\mathcal{A} = K_E E + K_V V + K_S S + \sum_c K_{Nc} N_c + C \qquad \text{(B-8)}$$

where C is the arbitrary constant of integration.

For constrained chemical systems (such as closed systems, constant volume systems, etc.), certain terms in equation (B-7) (such as $K_{Nc} dN_c$, $K_V dV$, etc.) may be zero -- whence the corresponding terms in equation (B-8) will be constant and may be absorbed into the constant of integration if desired.

In order to find C = 0 for unconstrained chemical systems, we must first show that the functional operators $\mathcal{A}_A(\ )$, $\mathcal{A}_B(\ )$, and $\mathcal{A}_{AB}(\ )$ in equation (B-2) are identical to each other for such systems. To see that this is true, we first note that with the absence of any constraints upon the variables E, V, S, and $\{N_c\}$for each of systems A, B, and AB (other than reasonable upper bounds upon the possible values of E, V, S, and $\{N_c\}$), these systems will all be chemical systems with the same range of accessible values for E, V, S, and $\{N_c\}$, and hence the same range of accessible thermodynamic states*. Therefore, with such an absence of constraints, $\mathcal{A}$ must be determined by the same functional operator for each of these systems. Thus the operators $\mathcal{A}_A(\ )$, $\mathcal{A}_B(\ )$, and $\mathcal{A}_{AB}(\ )$ are identical for

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* Any two chemical systems with the same values for E, V, S, and $\{N_c\}$ are always free by definition (Appendix A) to assume identical states.

unconstrained systems -- whence substitution of equation (B-8) into equation (B-2) for this case yields C = 2C so that C = 0. Thus for any unconstrained chemical system, equation (B-8) reduces to

$$\mathcal{G} = K_E E + K_V V + K_S S + \sum_c K_{Nc} N_c \qquad \text{(B-9)}$$

For constrained systems, the constant C remains arbitrary -- it being noted that C_A, C_B, and C_{AB} will not be equal. Substitution of equation (B-8) into equation (B-2) for this case yields $C_{AB} = C_A + C_B$ as the required relationship among these constants.

APPENDIX C

CONCERNING THE CONSTANT K_E

On page 22, it was stated that the constant K_E must have a fixed, non-zero value independent of the given environment. In order to verify this proposition, consider any two chemical systems A and B, each of which have different given environments A' and B' respectively. Considering any particular extensive measure $\mathscr{U}$, it follows from the expression $\mathscr{U} = K_E E + K_V V + K_S S + \sum_c K_{Nc} N_c + C$ of Theorem 4 that $\mathscr{U}$ is given for each of systems A and B by

$$\mathscr{U}_A = K_{EA} E_A + K_{VA} V_A + K_{SA} S_A + \sum_c K_{NcA} N_{cA} + C_A \tag{C-1}$$

$$\mathscr{U}_B = K_{EB} E_B + K_{VB} V_B + K_{SB} S_B + \sum_c K_{NcB} N_{cB} + C_B \tag{C-2}$$

Since by definition A' and B' are different given environments, it follows that the constants K_{VA} and K_{VB} may not be equal in general. Similarly, K_{SA} may not equal K_{SB} and K_{NcA} may not equal K_{NcB}. However, the constants K_{EA} and K_{EB} may be shown to be always equal, as will now be demonstrated:

Considering systems A and B together as a single system*, the extensive measure $\mathscr{U}$ for the total system AB is by

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* As mentioned in the footnote on page 89, a thermodynamic system may consist of parts which are not directly connected together.

definition given by $\mathcal{A}_{AB} = \mathcal{A}_A + \mathcal{A}_B$, so that from equations (C-1) and (C-2),

$$\mathcal{A}_{AB} = (K_{EA}E_A+K_{VA}V_A+K_{SA}S_A+\sum_c K_{NcA}N_{cA}+C_A)+(K_{EB}E_B+K_{VB}V_B+K_{SB}S_B+\sum_c K_{NcB}N_{cB}+C_B) \qquad \text{(C-3)}$$

We observe in passing that equation (C-3) does not correspond directly to the expression $\mathcal{A} = K_E E+K_V V+K_S S+\sum_c K_{Nc}N_c+C$ of Theorem 4, because system AB is not a chemical system.*

Let us now consider the case where shaft work is transmitted from system A to system B with no other interactions occurring between systems A and B and their surroundings -- it being further stipulated that both S_A and S_B are constant)**. Differentiation of equation (C-3) for this

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* System AB is not a chemical system (even though both systems A and B are chemical systems) because the fact that A and B have different given environments means that A cannot come to equilibrium with B in the same sense that the parts of a chemical system can come to equilibrium with each other. In other words, equilibrium states of AB are not determined simply by their energy E_{AB}, volume V_{AB}, and composition $\{N_{cAB}\}$ (as would have to be the case if AB were a chemical system as defined in Appendix A), but instead the individual values, E_A, E_B, V_A, V_B, $\{N_{cA}\}$, and $\{N_{cB}\}$ must be specified.

**Shaft work is the only interaction which can be allowed between chemical systems A and B, since any other interactions would require locking constraints of the second kind (Appendix 4) which chemical systems by definition (Appendix A) cannot have.

case yields*

$$d\mathscr{G}_{AB} = K_{EA}dE_A + K_{EB}dE_B \tag{C-4}$$

And since $dE_A = -dE_B$ for this case,

$$d\mathscr{G}_{AB} = (K_{EB} - K_{EA})dE_B \tag{C-5}$$

It will now be observed that this case complies with the conditions of Theorem 1, since for this case the entropy of system AB remains constant while system AB is not interacting with its given environment**. From theorem 1, all measures $\mathscr{F}_{AB}$ must be constant for this case***, from whence $\mathscr{G}_{AB}$ must be constant -- since $\mathscr{G}$ must be a one-to-one mapping onto $\mathscr{F}$, as pointed out in the proof of Theorem 3. Hence $d\mathscr{G}_{AB} = 0$ for this case so that equation (C-5) reduces to,

$$(K_{EB} - K_{EA})dE_B = 0 \tag{C-6}$$

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* It should be emphasized that the constancy of K_{EA}, K_{EB}, K_{VA}, K_{VB}, K_{SA}, K_{SB}, $\{K_{NcA}\}$ and $\{K_{NcB}\}$ depends upon systems A and B each having *given* environments. In some cases this condition could require shaft work to be returned later from B to A.

** System AB has a given environment, since systems A and B each have given environments (it being recalled from page 13 that a system is said to have a given environment if the system is considered to have a unique condition of equilibrium with its environment).

*** In regards to Theorem 1, it is noted that system AB is a non-locking system since both A and B are chemical systems (which are non-locking by definition -- as indicated in Appendix A).

Since dE_B is arbitrary, equation (C-6) requires $(K_{EB} - K_{EA})=0$ so that,

$$K_{EB} = K_{EA} \tag{C-7}$$

Thus the constants K_{EA} and K_{EB} which appear in equations (C-1) and (C-2) are equal, as was stated above. And since systems A and B represent any two chemical systems in <u>any</u> two given environments A' and B', it follows that K_E must have a fixed value independent of the given environment.

The constant K_E cannot be zero, because a zero value of K_E would allow $\mathcal{S}$ to remain constant during the process described in Requirement 1 (since for such a process, V, S, and $\{N_c\}$ are constant so that equation (B-7) of Appendix B reduces to $d\mathcal{S} = K_E dE$). But $\mathcal{S}$ cannot be allowed to remain constant during such a process, since $\mathcal{S}$ must be a one-to-one mapping onto $\mathcal{F}$ (as pointed out in the proof of Theorem 3) and $\mathcal{F}$ must by definition increase. Thus K_E cannot be zero, so that from the conclusion of the preceding paragraph, K_E must have a fixed, non-zero value independent of the given environment -- as was to be shown.

APPENDIX D

CONCERNING THE INTEGRATION CONSTANT C

It was stated after equation (12) that the integration constant C must have a fixed value independent of the given environment. In order to verify this, one may first differentiate equation (12) for the general case (where the effect of the environment may vary so that P_o, T_o, and $\{\mu_{co}\}$ are not constant) to obtain*

$$d\mathcal{A} = K(dE+P_o dV-T_o dS-\sum_c \mu_{co} dN_c+VdP_o-SdT_o-\sum_c N_c d\mu_{co})+dC \quad \text{(D-1)}$$

As pointed out in the paragraph preceding equation (6), $d\mathcal{A}$ is zero for all infinitesimal variations of the type considered in Requirement 3, so that for all such variations equation (D-1) reduces to

$$dC = -K(dE+P_o dV-T_o dS-\sum_c \mu_{co} dN_c+VdP_o-SdT_o-\sum_c N_c d\mu_{co}) \quad \text{(D-2)}$$

Also, for all such variations, the Gibbs equation $dE = TdS - PdV + \sum_c \mu_c dN_c$ and the Gibbs-Duhem equation $VdP = SdT + \sum_c N_c d\mu_c$ apply, so that the right side of equation (D-2) is zero (since the equations $dE = T_o dS-P_o dV+\sum_c \mu_{co} dN_c$ and $VdP_o = SdT_o+\sum_c N_c d\mu_{co}$ are satisfied to within non-finite

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* For a closed system, each dN_c is zero throughout the equations of this appendix. For constrained systems more generally, every dN_c need not be zero. For example, one may consider a constrained system of constant volume in which all of the N_c are allowed to vary.

second order infinitesimals for variations between states which have no finite departure from equilibrium with the environment). Hence dC is zero, from whence C must have a fixed value independent of the given environment -- as was to be shown.

APPENDIX E

ON THE GENERAL DEFINITION OF ESSERGY

Essergy is by definition a quantity which is believed to have a broader interpretation than is encompassed by thermodynamics -- in the same manner that entropy has the broader interpretation from information theory given by C. Shannon(37). Thus all of the writer's formulations of essergy(12,14) were actually derived from information theory(30,31) -- as implemented by Brillouin's(38) principle of the equivalence of thermodynamic information and potential work. For the purpose of the proof given in this paper, however, essergy will be defined with respect to only macroscopic thermodynamics.

Equation (1) on page 2 is the definition of the extensive measure $\mathcal{E}$ of essergy for any chemical system. However, for constrained systems, an arbitrary scale constant C may be added to this equation -- this constant having to be set equal to zero for any unconstrained system -- so that a more general expression for the extensive measure $\mathcal{E}$ of the essergy of any chemical system is

$$\mathcal{E} = E + P_oV - T_oS - \sum_c \mu_{cc} N_c + C \qquad \text{(E-1)}$$

where C = 0 for any unconstrained system. The compliance of the right side of equation (E-1) with Requirements 1, 2, and 3 is discussed in Appendix 3. We will, after Gibbs(13), nearly always set the arbitrary constant C equal to zero (as was done in equations 1 and 3 and in Table 1 on page 8) since a non-zero value of C tends to obscure the fact that a system has no potential work when it is in stable equilibrium with its environment.

As indicated in the first footnote on page 95, one may have a set of constrained chemical systems which is not itself a chemical system as defined in Appendix A. For such a set, the extensive measure $\mathcal{E}$ of essergy is by definition found by summing equation (E-1) over all such chemical systems -- where each chemical system r has the intensive properties P_{or}, T_{or}, and $\{\mu_{cor}\}$ when the set of chemical systems is at equilibrium with its environment:

$$\mathcal{E} = \sum_r (E_r + P_{or}V_r - T_{or}S_r - \sum_c \mu_{cor}N_{cr} + C_r) \qquad \text{(E-2)}$$

It should be pointed out that the quantity essergy is defined such that any essergy change $\Delta\mathcal{E}$ (or $-\Delta\mathcal{E}$) is itself a specific example of essergy (after the manner of the quantity, energy -- it being noted that any energy change ΔE (or $-\Delta E$) is itself a specific example of energy -- e.g., an energy increase ΔE constitutes energy which is transferred into the system). And after the manner of the quantity, temperature (recalling that any one-to-one mapping onto the absolute temperature T or ΔT is itself a specific example of temperature* -- on some particular scale of temperature),(31,32,33,39) the quantity essergy is defined such that any one-to-one mapping onto the essergy $\mathcal{E}$ or $\Delta\mathcal{E}$ is itself a specific example of essergy.

For generalized chemical systems (which by definition include such effects as electricity, magnetism, gravity, surface tension, stress, and nuclear considerations) equation (E-1) still suffices to define the essergy $\mathcal{E}$, except that P_o is replaced by P_D (where P_D denotes the pressure of the region of space occupied by the system when that region has come to equilibrium with the environment -- at which time the system need no longer occupy that region):

$$\mathcal{E} = E + P_D V - T_o S - \sum_c \mu_{co} N_c + C \qquad \text{(E-3)}$$

where C = 0 for any unconstrained system. P_D is not necessarily constant with respect to location; for example, the pressure of the water in Figures 1-1, 1-2, 1-3 will increase with depth as a result of the effect of gravity. If this pressure variation is negligible over the range of locations considered, then P_D may be taken to equal P_o. Also, $P_D = P_o$ whenever the system continues to occupy the same region as it comes to equilibrium with its environment. It is thus seen that equations (1), (E-1), and

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* It should be pointed out here that changes such as ΔT and $\Delta\mathcal{E}$ are considered to start from a particular state, so that any one-to-one mappings onto ΔT and $\Delta\mathcal{E}$ coincide with the corresponding one-to-one mappings onto T and $\mathcal{E}$ respectively.

(E-2) apply to certain generalized chemical systems (viz. those systems for which $P_D = P_o$) -- it being noted that for a set of constrained generalized chemical systems, the defining equation (E-2) becomes,

$$\mathcal{E} = \sum_r (E_r + P_{Dr} V_r - T_{or} S_r - \sum_c \mu_{cor} N_{cr} + C_r) \qquad \text{(E-4)}$$

APPENDIX 1*

ON THE CONCEPT OF DEPARTURE FROM EQUILIBRIUM

The potential work of a system may intuitively be regarded as being a result of the system's departure from equilibrium -- i.e., its departure from the condition when it is in equilibrium with its environment. The concept of departure from equilibrium may be illustrated in the manner of Figures 1-1, 1-2, and 1-3. Figures 1-1 and 1-2 represent the beginning and end respectively of the process which results when the ice melts sufficiently to fall from the wire. During this process, the ice gives up that portion of its potential work which is due to its gravitational potential energy. Figures 1-2 and 1-3 represent the beginning and end respectively of the process in which the ice melts and the resulting water warms up to room temperature.

Both of these processes have one thing in common: In each process the ice proceeds towards a condition of stable equilibrium with its environment -- the final equilibrium condition being shown in Figure 1-3. Either of these processes may in principle be harnessed to yield mechanical power; the first process by means of strictly mechanical contrivances (pulleys, levers, gears, etc.) for transmitting the potential work of the falling ice,

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* This appendix is not necessary for the proof given in this paper, and is only included here as supplementary material.

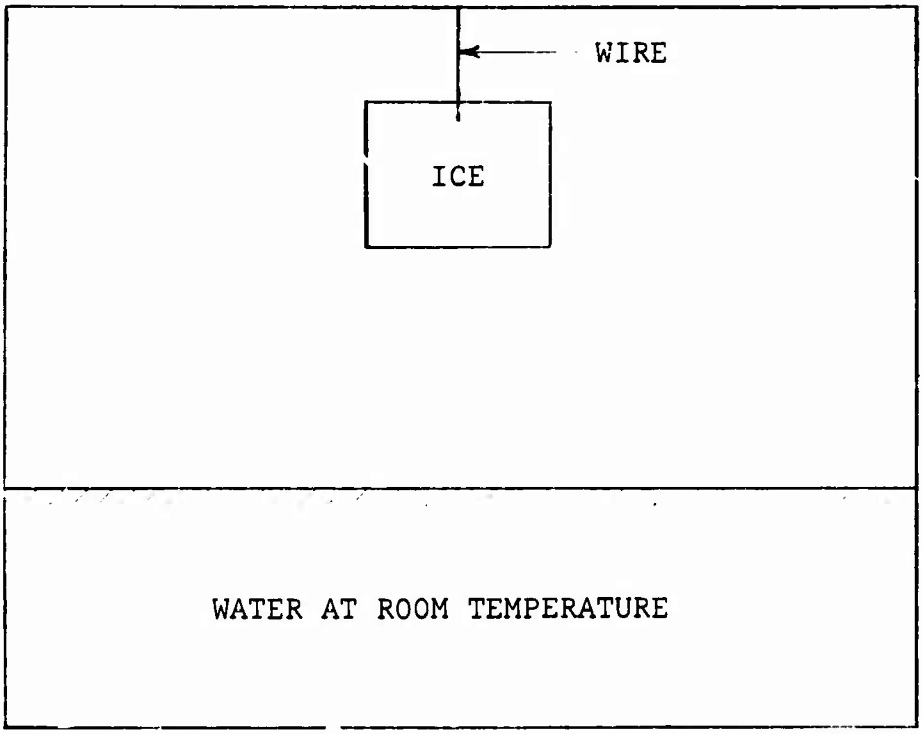

FIGURE 1-1: A BLOCK OF ICE SUSPENDED FROM A WIRE TO WHICH IT HAS BEEN FROZEN ABOVE A BODY OF WATER. When the ice melts sufficiently to drop from the wire, it will release that portion of its potential work which is due to its gravitational potential energy.

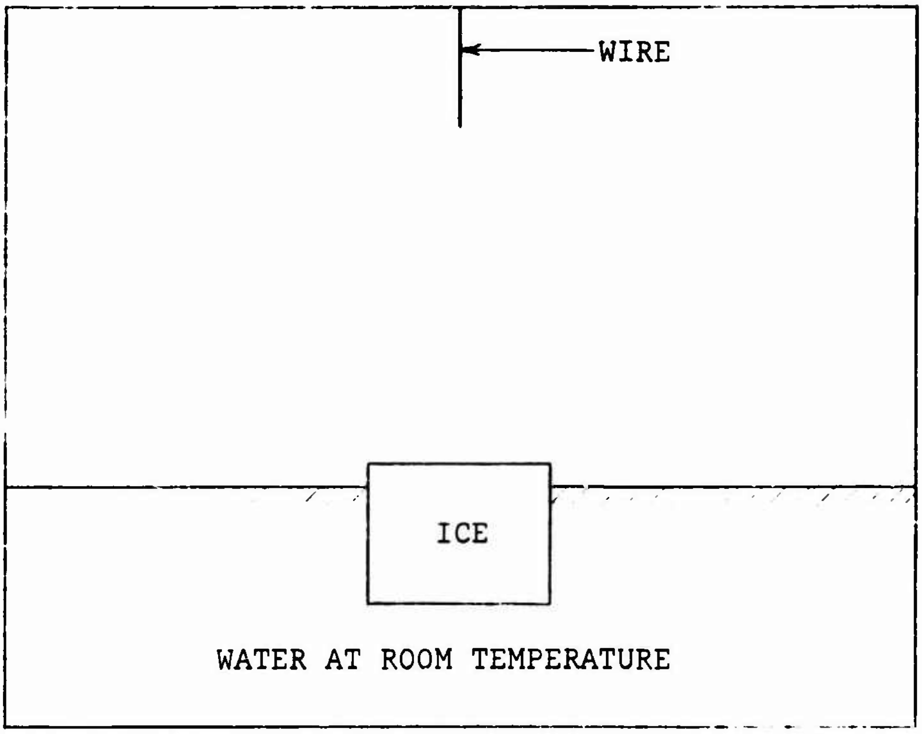

FIGURE 1-2: THE BLOCK OF ICE OF FIGURE NO. 1-1 AFTER IT HAS MELTED SUFFICIENTLY TO DROP FROM THE WIRE. The ice still departs from its final equilibrium condition, which is shown in Figure 1-3 below.

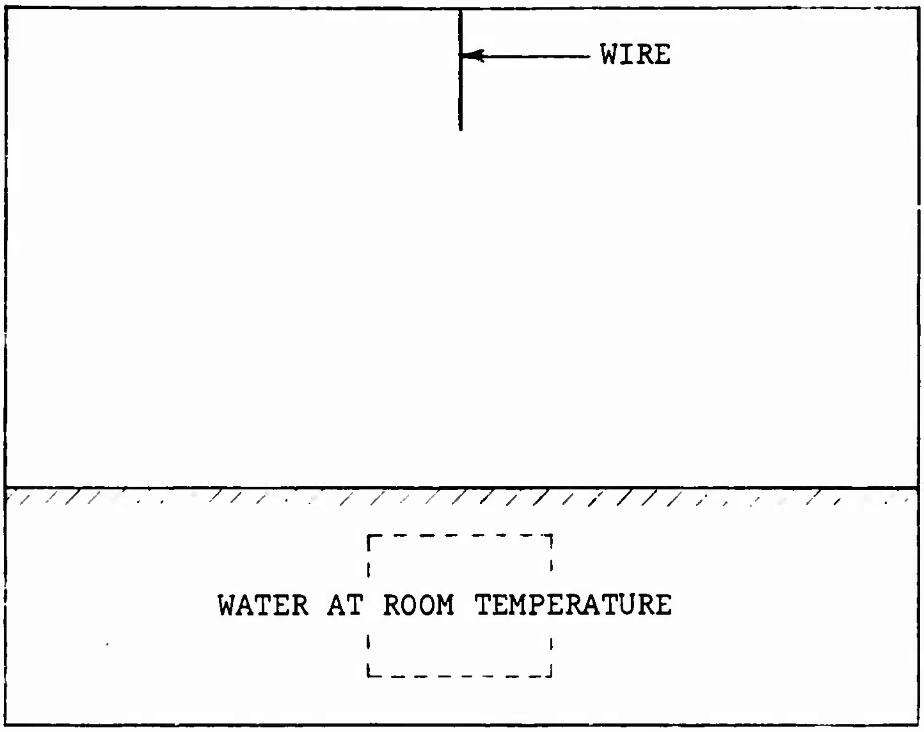

FIGURE 1-3: THE STABLE EQUILIBRIUM STATE OF THE SYSTEM SHOWN IN FIGURES 1-1 and 1-2 ABOVE. The dashed lines indicate an amount of water equal to that resulting from the melting of the ice.

the second process by means of heat engines. However, once the ice system has come to equilibrium with its environment (as shown in Fig. 1-3), then there is no further opportunity to harness mechanical power.

It should be pointed out there is a difference between the notion of a "condition" of equilibrium and a "state" of equilibrium. Consider for example the melted ice depicted by the dashed lines in Figure 1-3. Here the resulting water is quite free to move about -- it could even vaporize -- while the complete system of Figure 1-3 remains at stable equilibrium. Thus the ice system has no unique state of equilibrium. Nevertheless, it has a unique condition of equilibrium in that the entire region in which it may be located (that is, the entire system of Figure 1-3) has a unique state of equilibrium. In this manner, a system may in general be said to have a unique condition of equilibrium with its environment whenever the entire region in which it might be located has a unique state of equilibrium.

It may be of interest to note that the state of the environment need not be constant in order for a system to have a unique condition of equilibrium with its environment. For example, suppose that we consider a system which consists of only part of the suspended ice of Figure 1-1. This system will have a unique condition of equilibrium in accordance with the discussion of the preceding paragraph. However, since the remainder of the suspended ice will now belong to the system's environment, it is clear that the state of the environment must change considerably (it could even change quite rapidly) in order to reach the equilibrium condition of Figure 1-3.

It should also be pointed out that the notion of a *given* environment (that is an environment with which the system under consideration has a unique condition of equilibrium) is a device for considering the dependence of potential work upon the system alone. In other words, with a *given* environment, the net effect of the environment is constant so that the potential work is a property of the system alone under this condition. In general, potential work is of course a property of both the system and its environment. The net effect of the environment will in general vary -- either from external influences (such as for example an influx of solar energy which may increase the ambient temperature -- thus increasing the final equilibrium temperature of the system) or from internal influences (for example, the final equilibrium temperature may also increase as a result of a less efficient process within a system whose only external communication is the transmission of shaft work to its environment -- the lower efficiency resulting in less shaft work delivered so that more energy is retained to yield the higher final equilibrium temperature).

In regard to this latter example, it should be noted that any condition of equilibrium is always subject to the given constraints. For example, two systems separated by a rigid, impermeable wall may come to a state of stable equilibrium with each other (subject to this constraint) in which their pressures may differ. Throughout this thesis the terms, "stable equilibrium," "unstable equilibrium," and "constraint," are used in accordance with the definitions given by Gibbs(13).

Finally, it is of interest to note that while a system is not interacting with its environment, every independent property of its given environment may be allowed to vary (as mentioned in Footnote 10, page 19). Suppose for example that the ice cube in Figure 1-1 were not to interact with its environment for a period. During this period the independent properties of the ice cube's environment could be perturbed by external influences (i.e., influences external to the water-vapor system shown as the ice cube's environment in Fig. 1-1) in any manner whatsoever, and so long as the final equilibrium condition of the ice cube is stipulated to remain unchanged, the given environment by definition remains unchanged.

APPENDIX 2*

ON THE NECESSITY OF REQUIREMENTS 1, 2, AND 3 WITH RESPECT TO THE PROOF

Requirements 1, 2, and 3 on page 13 reflect necessary characteristics which must be exhibited by any measure of the potential work of systems. However, it is not immediately obvious that one of these requirements might not be superfluous with respect to the proof given in this paper. For example, one may ask if Requirements 1 and 2 alone might be sufficient for the proof. To see that this is not the case, we note that Requirements 1 and 2 are both satisified by the energy E (since E is extensive -- satisfying Requirement 2 -- and E always increases whenever the only effect is an input of work -- in satisfaction of Requirement 1). But as a proposed measure of the potential work of systems, the energy E is inconsistent**, since E does not in general satisfy Requirement 3. Thus Requirements 1 and 2 by themselves fail to rule out the inconsistent proposed measure E, so that Requirement 3 must not be omitted.

Similarly, Requirements 1 and 3 alone are not sufficient for the proof, since these two requirements by

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[*] This appendix is not essential to the proof given in this paper, and is only included here as supplementary material.

[**] In this appendix, any proposed measure (of the potential work of systems) will be referred to as being "inconsistent" if it is not in general a consistent measure of potential work.

themselves fail to rule out the inconsistent** proposed measure $V\mathcal{E}$ (where $V \equiv$ volume and $\mathcal{E} \equiv$ the essergy function).* Thus Requirement 2 must not be omitted.

And finally, Requirements 2 and 3 alone are not sufficient for the proof, since these two requirements by themselves fail to rule out the inconsistent proposed measured $\sum_{i=1}^{n} K_i \mathcal{E}_i$ (where $\mathcal{E}_i$ denotes the essergy $\mathcal{E}$ of the i'th part of the system -- the system being considered to consist of n parts where $n \geq 2$ -- while each K_i denotes a positive constant associated with the i'th part -- it being stipulated that each K_i has a different value)**. Hence Requirement 1 must not be omitted.

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* The proposed measure $V\mathcal{E}$ satisfies Requirement 1, since $\mathcal{E}$ satisfies this requirement in view of Appendix 3, while the volume V is constant when the only effect is work done through a shaft. $V\mathcal{E}$ satisfies Requirement 3, because for any open system, $d(V\mathcal{E})$ is zero for the variations considered in equation (6) -- since for any unconstrained system, both $\mathcal{E}$ and $d\mathcal{E}$ are zero for these variations (as indicated in Appendix 3 and Pg. 46). However, $V\mathcal{E}$ is inconsistent because it does not in general satisfy Requirement 2 (since $V\mathcal{E}$ is not always extensive -- it being noted that both V and $\mathcal{E}$ are always extensive).

** The proposed measure $\sum_{i=1}^{n} K_i \mathcal{E}_i$ satisfies Requirement 2, since $\sum_{i=1}^{n} K_i \mathcal{E}_i$ is extensive by definition. And $\sum_{i=1}^{n} K_i \mathcal{E}_i$ satisfies Requirement 3, since each $\mathcal{E}_i$ satisfies Requirement 3 (as demonstrated in Appendix 3) while each K_i is a positive constant. The proposed measure $\sum_{i=1}^{n} K_i \mathcal{E}_i$ is inconsistent, since $\sum_{i=1}^{n} K_i \mathcal{E}_i$ fails to comply in general with Theorem 1, from whence $\sum_{i=1}^{n} K_i \mathcal{E}_i$ fails in general to satisfy Requirement 1 (it being noted that $\sum_{i=1}^{n} K_i \mathcal{E}_i$ need not always be constant under the conditions of Theorem 1, while the essergy $\mathcal{E} \equiv \sum_{i=1}^{n} \mathcal{E}_i$ is always constant under these conditions.)

It has been shown that one may not allow either of Requirements 1, 2, or 3 to be omitted. However, the possibility remains that Requirements 1, 2, or 3 might be weakened in a consistent manner, and yet remain strong enough to support the proof.

Requirement 1 might tentatively be weakened via replacing it by Theorem 1 (with the restriction to non-locking systems omitted). However, this weaker requirement would fail to rule out the value zero for the unit conversion constant K (as is done at the end of Appendix C). In other words, the inconsistent proposed measure C (where C is the scale constant in equation 12) would satisfy this weaker requirement as well as satisfying Requirements 2 and 3. One might at first suppose that the stipulation that potential work must be a thermodynamic property might be sufficient to rule out the constant C. However, there is nothing in Theorem 1 plus Requirements 2 and 3 which rules out a potential-work property which might happen to be constant with respect to the properties of the special systems under consideration. Thus Theorem 1 is not a sufficient form of Requirement 1, so that this requirement may not be weakened in this manner.

However, Requirement 1 may be reworded in several alternate forms which would leave its content completely unchanged. For example, the content of Requirement 1 would remain exactly the same if the phrase "always increases" were to be replaced by the phrase "always decreases" -- since if potential work admits of measure $\mathcal{F}$ which always increases under certain conditions, then it must of course admit of a measure $-\mathcal{F}$ which always decreases under the same conditions. Another such alternate form of Requirement 1 results from replacing the phrase "always *increases* when work is transmitted through a shaft *into* the system" by the phrase "always *decreases* when work is transmitted through a shaft *from* the system." In this alternate form, it might be supposed that the phrase "while the entropy of the system is constant" could be excluded -- in view of the Second Law. However, without this phrase, this form of Requirement 1 would not be satisfied for environments of negative absolute temperature (33,35,36) -- so that this phrase would have to be retained, if one desires complete generality.

There would seem to be no way of weakening Requirement 2 without omitting it altogether -- and the omission of this requirement has already been ruled out above. Requirement 3 could be weakened to a differential form which would required only that $d\mathcal{H}$ be zero for the variations considered in equation (6). However, any definition involving differentials such as $d\mathcal{H}$ is unsatisfactory, since there is nothing in the mathematical definition of a differential which actually requires it to be small(39).

Requirement 3 might also tentatively be weakened by replacing it with two separate tentative requirements 3' and 3" -- where Tentative Requirement 3' is the admission of a positive measure, while Tentative Requirement 3" is the admission of a measure which is zero at the equilibrium condition "o". However, the tentative set of Requirement 1, 2, 3', and 3" fails to rule out the inconsistent proposed measure E', where E' is a relative energy defined by,

$$E' \equiv E - \sum_c \bar{E}_{co} N_c \qquad (2\text{-}1)$$

Here $\bar{E}_c$ denotes the partial energy per unit of component "c" (discussions of partial quantities are given in References 31, 32, and 33) and $\bar{E}_{co}$ represents the partial energy $\bar{E}_c$ of the system at the equilibrium condition "o" -- so that each $\bar{E}_{co}$ is a constant for any chemical system which has no more than one phase at the equilibrium condition "o". The relative energy E' satisfies Requirement 1, since the energy E satisfies this requirement (as pointed out in the first paragraph of this appendix) while $\sum_c \bar{E}_{co} N_c$ is constant for the process described in this requirement. E' satisfies Requirement 2 since E' is extensive -- it being observed that $E - \sum_c \bar{E}_{co} N_c$ corresponds to the extensive measure $KE + K_V V + K_S S + \sum_c K_{Nc} N_c$ of Theorem 5 when $K = 1$,

$K_V = 0$, $K_S = 0$, and $K_{Nc} = -\bar{E}_{co}$ for each component "c". The relative energy E' satisfies Tentative Requirement 3', since E' admits of the positive measure $e^{E'}$ (that is $e^{E'}$ is a one-to-one mapping onto E'). And finally, E' satisfies Tentative Requirement 3" since at the equilibrium condition "o", the expression $E - \sum_c \bar{E}_{co} N_c$ reduces to an expression $E_o - \sum_c \bar{E}_{co} N_{co}$ which is identically zero (due to the familiar identity $Y = \sum_c \bar{Y}_c N_c$ relating any extensive thermodynamic property Y to its corresponding partial values $\{\bar{Y}_c\}^{(31,32,33)}$. The inconsistency of the proposed measure E' is demonstrated in Note 1 of this appendix. Since the replacing of Requirement 3 with Tentative Requirements 3' and 3" permits the inconsistent proposed measure E', we see that Requirement 3 must not be weakened in this manner.

Tentative Requirements 3' and 3" may be combined into a single requirement under which potential work would admit of a measure which is always an extremum at the equilibrium condition "o". However, such a measure would be inconsistent since it would not in general be a one-to-one mapping onto the essergy $\mathcal{E}$ -- in view of the fact that $\mathcal{E}$ need not admit of a measure which is an extremum with respect to an unstable equilibrium condition "o" (as indicated on page 46).

It would thereby seem that the only additional possibilities for allowing either the weakening or omission of one of Requirements 1, 2, or 3 would be to introduce simultaneous changes in at least two of these requirements. However, any such changes (other than a mere rewording of the requirements) would appear to introduce conditions which are either superfluous or else inconsistent with the definition of potential work as set forth in these requirements. It would thus seem that neither the omission nor weakening of Requirements 1, 2, or 3 may be allowed -- so that these requirements appear to be necessary with respect to the proof given in this paper.

NOTE 1, APPENDIX 2

ON THE INCONSISTENCY OF E'

It may not be immediately obvious that E' is inconsistent. Suppose for example that one substitutes the identity $\bar{E}_c = T\bar{S}_c - P\bar{V}_c + \mu_c$ into equation (2-1) to obtain,

$$E' = E + P_o \sum_c \bar{V}_{co} N_c - T_o \sum_c \bar{S}_{co} N_c - \sum_c \mu_{co} N_c \qquad (2\text{-}2)$$

A comparison of equation (2-2) with equation (1) on page 2 shows that E' would be identical to $\mathcal{E}$ if V were to equal $\sum_c \bar{V}_{co} N_c$ and S were to equal $\sum_c \bar{S}_{co} N_c$.

However V is not in general equal to $\sum_c \bar{V}_{co} N_c$, since N_c and $\bar{V}_{co}$ refer to the system in two different states (i.e., N_c is the amount of component c for the given state of the system while $\bar{V}_{co}$ is the partial volume of the chemical system at the equilibrium condition "o". Similarly, S is not in general equal to $\sum_c \bar{S}_{co} N_c$. These non-equalities may be brought into sharper focus via differentiating equations (1) and (2-2) for a closed system (N_c = constant) to obtain,

$$d\mathcal{E} = dE + P_o dV - T_o dS \qquad (2\text{-}3)$$

$$dE' = dE \qquad (2\text{-}4)$$

For variations at condition "o", equation (2-3) yields $d\mathcal{E} = 0$ in compliance with Requirement 3 (since dE = TdS-PdV for a closed system) whereas equation (2-4) gives $dE' \neq 0$ in violation of Requirement 3. Hence E' is inconsistent (since E' does not in general satisfy Requirement 3).

APPENDIX 3*

ON THE CONSISTENCY OF ESSERGY AS A MEASURE OF THE POTENTIAL WORK OF CHEMICAL SYSTEMS

It was mentioned on page 15 that it is known prior to making the proof that essergy is a consistent measure of the potential work of chemical systems (or in other words, essergy for chemical systems satisfies Requirements 1, 2, and 3 on page 13). This proposition will be verified here:

In order to show that the essergy $\mathcal{E}$ of a chemical system is consistent with Requirement (1), one may first differentiate equation (E-1) for a given environment (for which P_o, T_o, and $\{\mu_{co}\}$ are constant) to obtain

$$d\mathcal{E} = dE + P_o dV - T_o dS - \sum_c \mu_{co} dN_c \tag{3-1}$$

For the process of Requirement 1, the quantities V, S, and $\{N_c\}$ are all constant (since any change in V or $\{N_c\}$ would represent an interaction in addition to the transmission or work through a shaft) so that equation (3-1) reduces to

$$d\mathcal{E} = dE \tag{3-2}$$

Since the energy E of a system always increases when the only effect is an input of work, it follows from equation

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* This appendix is not essential to the proof given in this paper, and is only included here as supplementary material.

(3-2) that $\mathcal{E}$ always increases for the process of Requirement 1 -- so that this requirement is satisfied.

Requirement 2 is satisfied, since the right side of equation (E-1) is extensive -- in view of the fact that it is a linear combination of the extensive quantities E, V, S, $\{N_c\}$, and C (it being noted that P_o, T_o and $\{\mu_{co}\}$ are all intensive).

In order to see that Requirement 3 is satisfied, we observe from equation (E-1) that an essergy change $\Delta\mathcal{E}$ is in general given by

$$\Delta\mathcal{E} = \Delta E + \Delta(P_oV) - \Delta(T_oS) - \sum_c \Delta(\mu_{co}N_c) \qquad (3\text{-}3)$$

-- it being noted that the environment is being allowed to vary so that P_o, T_o and $\{\mu_{co}\}$ are not necessarily constant. In view of the familiar integrated form $E = TS - PV + \sum_c \mu_c N_c$ of the Gibbs expression $dE = TdS - PdV + \sum_c \mu_c dN_c$, a change ΔE in the energy of any equilibrium chemical system (as defined in Appendix A) is given by,

$$\Delta E = \Delta(TS) - \Delta(PV) + \sum_c \Delta(\mu_c N_c) \qquad (3\text{-}4)$$

For any chemical system at equilibrium with its environment, one has $T = T_o$, $P = P_o$, and $\mu_c = \mu_{co}$ (where the subscript "o" by definition denotes the condition of the system when it is at equilibrium with its environment) so that one may write

$$\Delta E = \Delta(T_o S) - \Delta(P_o V) + \sum_c \Delta(\mu_{co} N_c) \qquad (3\text{-}5)$$

Substitution of equation (3-5) into equation (3-3) yields, for any change between two states, both of which are at equilibrium with the environment,

$$\Delta \mathcal{E} = 0 \qquad (3\text{-}6)$$

If the state of a system has no finite departure from equilibrium with the environment, then equation (3-4) is satisfied to within all non-finite deviations such as non-finite second and higher order infinitesimals. Thus for any change between such states, the essergy change $\Delta\mathcal{E}$ is equal to zero to within all non-finite deviations -- so that Requirement 3 is thereby seen to be satisfied.

APPENDIX 4*

ON LOCKING CONSTRAINTS

It is convenient to define the following two kinds of locking constraints:

1. Constraints which prevent an isentropic, adiabatic process from moving in the reverse direction.
2. Environmental constraints which allow some matter, energy, or volume to be transferred from a system, and then limit the amount transferred by means of some valve, locking device, or other type of barrier.**

The absence of the first kind of locking constraint allows any isentropic, adiabatic process to always be moved in the reverse direction. The chemical systems (and generalized chemical systems) considered in this paper are defined to be capable of undergoing isentropic, adiabatic processes as well as the other so-called quasistatic processes of thermodynamics, which by definition pass through states of equilibrium only.

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[*] It was first thought by the writer that this appendix was not actually necessary for the proof given in this paper. However, the absence in chemical systems of locking constraints of the second kind plays an important role in Appendix C.

[**] An environmental constraint is by definition a constraint which influences the system's state of equilibrium with its environment.

The absence of the second kind of locking constraint serves to guarantee that all parts of a chemical system will have the same intensive state of equilibrium with the environment.

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Unclassified
Security Classification

DOCUMENT CONTROL DATA - R & D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*
Dartmouth College
Thayer School of Engineering
Hanover, New Hampshire 03755

2a. REPORT SECURITY CLASSIFICATION

2b. GROUP

3. REPORT TITLE
A PROOF THAT ESSERGY IS THE ONLY CONSISTENT MEASURE OF POTENTIAL WORK (FOR CHEMICAL SYSTEMS)

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*
scientific; ; final

5. AUTHOR(S) *(First name, middle initial, last name)*
Robert B. Evans

6. REPORT DATE June 1969	7a. TOTAL NO. OF PAGES 129	7b. NO. OF REFS 46

8a. CONTRACT OR GRANT NO. AFOSR 69-1735	9a. ORIGINATOR'S REPORT NUMBER(S)
b. PROJECT NO. 9769-06	
c. 61445O1F	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d. 681304	AFOSR 69 1976 TR

10. DISTRIBUTION STATEMENT
1. This document has been approved for public release and sale; its distribution is unlimited.

11. SUPPLEMENTARY NOTES Tech Other	12. SPONSORING MILITARY ACTIVITY Air Force Office of Scientific Research Directorate of Information Sciences (SRI) Arlington, Va. 22209

13. ABSTRACT

An attempt is made to prove that all of the many seemingly independent measures of potential work, such as availability, exergy, available work, Gibbs free energy, Gibbs chemical potential, Helmholtz free energy, and other common energy expressions are necessarily all special cases of a unique quantity that is called essergy, a contraction of the term essence of energy. The proof is attempted rigorously for chemical systems, and then is extended. If correct, the proof will be of consequence to the design of any engineering system in which potential work is a significant factor, since it will show that by evaluating the one quantity, essergy, the designer will have taken account of the other seemingly independent considerations. A possible consequence of the proof may be a more general formulation for the concept of information based on Brillouin's principle of the equivalence of thermodynamic information and potential work. The proof indicates that negentropy is not as general a measure of potential work as is the quantity, essergy. This result could imply that essergy is a more general measure of thermodynamic information than negentropy, an implication that might lead to a broader formulation about information and, thus, new insight into the foundations of information theory.

DD FORM 1473

Unclassified

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Information theory						
Thermodynamics						
Chemical systems						
Potential work measures						
Engineering system design						
Energy						
Essergy						
Chemical processes						