# RELEVANCE OF THE DEAD STATE TO ECOLOGICAL AND ECONOMIC ANALYSES

Richard A. Gaggioli

Department of Mechanical Engineering
Marquette University
Milwaukee, WI 53201-1881 USA
Richard.Gaggioli@mu.edu

## ABSTRACT

Traditionally, an exergy analysis has from the outset inherently *assumed* a 'reference state' and exergies of subsystems have been evaluated relative thereto. Moreover, the evaluations *assume* a limited class of processes (for example, thermal, mechanical and chemical) for bringing the subsystems to equilibrium with the 'reference'. These habitual practices have limitations, especially important in applications to ecology and thermoeconomics. The limitations, which may be misleading, can by and large be avoided by referring back to the more fundamental concept underlying exergy, namely Gibbs' *available energy of a body*, and the consequent *dead state* of the body. At any instant, given any *body* – any overall system – the overall dead state and the dead states of all subsystems and their materials is unique. The dead state may change with time, while the overall available energy decreases. At every instant the exergy of each subsystem can be defined and represents its contribution to the overall available energy. The preceding paragraph began with ". . . *given* any overall system . . . the overall dead state . . . is unique." That statement is subject to several, related stipulations:

- The classs of processes within each subsystem must be specified (i.e. *assumed*).
- The modes of interaction between subsystems must be specified.
- The constraints upon subsystems must be specified.

That is, defining the dead state of an overall system (making it 'given') requires not only identification of its parts, but also how they will be allowed to interact and what constraints are imposed upon the parts and the interactions.

The purpose of this presentation is

- to provide guidance for the selection of the dead state for exergy analysis, and to elucidate
    - the relevance of *assumptions* made at the outset of the analysis, and
    - their implications upon conclusions drawn from the analysis.

Every exergy and thermoeconomic analysis that has been (or will be) done makes assumptions, implicitly if not explicitly, that can make the conclusions misleading. It is of critical importance for the reader of any exergy analysis to realize the significance of the inherent assumptions upon the conclusions, especially when the analysis has implications upon ecology and sustainability.

## INTRODUCTION

This paper has two principal parts: Fundamentals, and Practical Applications.

**Fundamentals**. Following Gibbs [1,2] the 'available energy of a body' is defined for any 'body' – i.e., for any overall system, no matter how *complex* the system's structure. The structure generally includes several subsystems or processes *and* how they interact. While a subsystem *may* be an 'environment', an environment is not necessary. Given the structure, the 'dead state' of the system follows directly from this general definition of available energy. Moreover, the dead state of the overall system dictates the dead state of each subsystem. The overall dead state and hence the dead states of the subsystems can change with time.

In practice, the overall dead state and hence the subsystem dead states depend upon underlying *choices*. Above all, the practitioner must delineate the makeup of the overall system. That is, given the purpose of the analysis, choose the parts of the 'universe' to be included in the overall system (as subsystems). Moreover, it is essential to choose 'constraints' placed upon (i) spontaneous processes allowed within each subsystem, (ii) modes of interaction[1] between subsystems, (iii) modes whereby products are delivered from the overall system (to its 'market').

It is apparent that the available energy of a body – of an overall system – is a consequence of disequilibrium within the body. Conversely, were a body subjected to specified 'constraints' it would be at equilibrium if the available energy were zero. So, when a body is subjected to particular constraints, available energy can be used to define equilibrium, relative to those constraints.

**Applications**. Exergy is an additive property. The exergy of a subsystem represents its contribution to the available energy of the overall system. Exergy is definable whether or not any subsystem is an 'environment.'

Yet, in many if not most engineering applications of 'exergy analysis' to a conversion plant – for efficiency analysis and/or costing – an important subsystem is a local environment with which it interacts.[i] The dead state of each plant subsystem and its contents depends upon the assumed constraints applied to it and to the environment. The delineation ('choice') of constraints can have a significant effect upon the conclusions drawn from the analysis.

Among the factors that are relevant to the delineation of constraints (and hence to the outcome of an analysis) are:

- The projected time-period for which the analysis will be relevant

[1] Interaction is synonymous with 'exchange of additive property.'

- The scope of the environment
  - Its breadth
  - The accessibility of materials therein
  - The stability of the materials
  - Relevance of variations with time
- The scope of technology – i.e., its 'state of the art' for the projected time period
- The scope of science – i.e., its 'state of development' for the period

These delineations (relevant to engineering applications) are all the more important when exergy and 'dead state' considerations are applied to ecology and sustainability.

**Closure**. The fundamentals will be presented and illustrated in the context of simple examples. Nevertheless, these examples will be used to draw broad, general principles relevant to complex practical applications.

## GIBBS AVAILABLE ENERGY

In [1] Gibbs defines the *available energy*, for two cases.

**(a) Case 1**, the more general case, is for that of a 'body' – *any* closed system which, *overall*, may have parts (subsystems). Shown in Figure 1 is a very simple example of an overall system. In this special case the overall system, the *subject*, consists of two subsystems, *1* and *2*. The subsystems are separated by an impermeable movable piston. At any instant $t$ the system has values of energy, entropy and of volume. Using different symbols than Gibbs, here they are denoted by $E(t)$, $S(t)$, $V(t)$.[2]

- Subject to the 'constraints' that (a) energy transfers from the overall system are restricted to transfers via volume or entropy exchange, but (b) that there be no *net* transfers of volume or entropy, then
- The available energy $A(t)$ of the overall system at $t$, a characteristic of this system only, is the maximum amount of energy attainable from this system. That is,
  - attainable from the *subject*, and deliverable to any other system – to any *object*,
  - with no *net* transfer of either entropy or volume to external systems.
  - During the hypothetical delivery, entropy and volume can be exchanged between the subject's parts.
  - Furthermore, except for the object, external devices may be employed to deliver the energy from the subject to the object, while transferring entropy and/or volume between subsystems of the subject.
  - Moreover, in order to assure that no external devices makes a net contribution to the energy delivered from subject to object, their net change of energy must be zero.

Reference [3] presents some elaboration on processes for delivering the available energy, $A(t)$. It is shown that

- The energy delivered is a maximum, $A(t)$, when there is no entropy generation within the subject.
- $A(t) = E(t) – E_{min}(S,V)$ when $S = S(t)$ and $V = V(t)$
  - The function $E_{min}(S,V)$ represents the energy at 'thermostatic equilibrium', when $\{S,V\}$ are the constrained variables.
    - It represents what Gibbs called 'the surface of dissipated energy'.
    - The 'thermostatic property relations' follow from it.

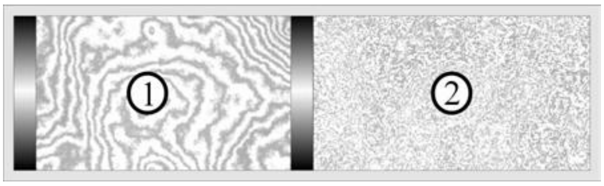


Figure 1. Example of an overall system or 'subject'

On Figure 2, from Gibbs [1], the curve through MBCN represents a hypothetical $E_{min}(S, V)$, at a fixed $V$. The location A represents an arbitrary nonequilibrium state of the system, and the distance AB is the available energy $A$ of that state. Figure 3 (from Gaggioli et al, [5]) shows a complete $E_{min}(S, V)$ surface and the points A and B. It is notable that Point A with its unique vales of $E$, $S$ and $V$ – does not represent a unique state of the overall system. For example, consider Figure 1 again; at any fixed ($S$, $V$) there are many conceivable states of the 'subject' with the same energy $E$.[3]

**The Dead State**. When the overall system is at Point B, it is at a 'dead state' – a state of zero available energy. Whenever the overall system is at a condition vertically above B, Point B is the corresponding dead state.

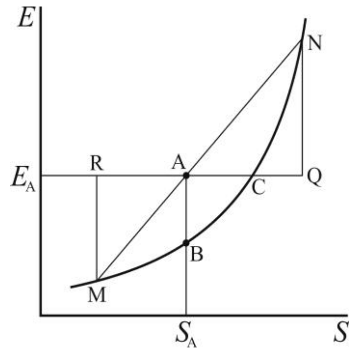


Figure 2. Depiction of $E_{min}$ vs. S at fixed V, of available energy (AB), and capacity for entropy (AC).

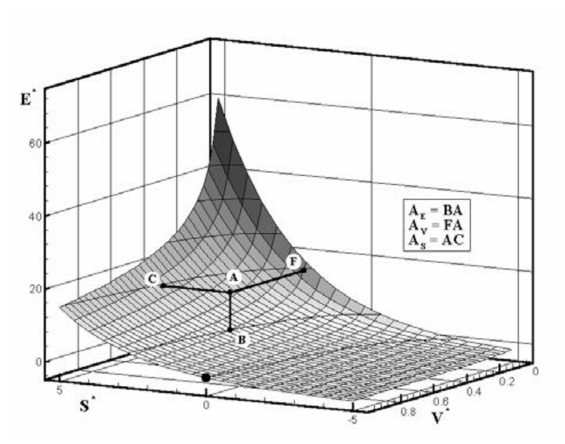


Figure 3. Depiction of $E_{min}(S,V)$, of available energy (AB), of 'available vacuum' (AF), and 'capacity for entropy' (AC).

[2] The existence of entropy is taken for granted here. See Appendix I of Reference [3] for an elaboration, as well as [4].

[3] States with the same $E$ could differ as a result, for example, from disparities in the pressure and temperature differences between the subsystems. (Notably, Gibbs also defined 'capacity for entropy' and 'available vacuum' as alternative measures of disequilibrium.)

Gibbs called $E_{min}(S, V)$ "the surface of dissipated energy". If an overall system like that in Fig. 1 were allowed to reach equilibrium without delivering energy (say by letting entropy flow through the piston and letting it oscillate, uncontrolled), entropy would be produced. The system would end up at Point C, another dead state.

*Additional Measures of Potential Influence.* The available energy represents the system's intrinsic potential to influence any other system. Gibbs defined other equivalent measures of disequilibrium and potential to influence. The distance AC on either figure represents the system's 'capacity for entropy' – at least that amount of entropy could be extracted from any system (at $T > 0$), no matter how cold. The distance AF on Figure 3 is Gibbs 'available vacuum' which is the volume increase imposable upon any system no matter how low its pressure.

These three characteristics (represented by AB, AC and AF) are measures of a system's disequilibrium and potential to influence *any* object; they are attributes of the system alone. Gibbs also described the potential influence upon specific objects. For example consider a large object, at any temperature *T* represented by the slope of the straight line MAN on Figure 2. The distance QA on the figure is the amount of entropy that could be extracted from the object; starting at A the system would end up at N. The distance AR is the amount of entropy that could be imposed upon the object.

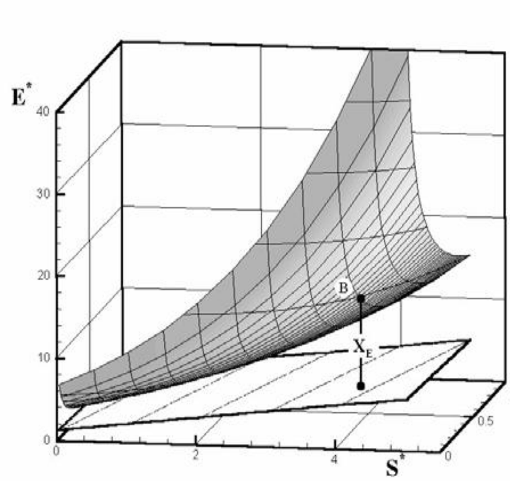


Figure 4. Depiction of the available energy of a body-and-medium (exergy of a body).

**(b) Case 2**. This is the *special case* presented by Gibbs, for a circumstance where one part of the *overall* system is a 'medium' – a large subsystem which has a constant temperature and a constant pressure and, by itself, is at equilibrium. In Gibbs' terminology the *overall* system consists of a 'body' (*any* body) and the 'medium' (made up of the same components as the body). In both cases, 1 and 2, his development is for circumstances where the *overall* system – the *subject* – reaches equilibrium without *net* transports of entropy or volume between the *overall* system and *its* surroundings. In Case 2, net transports between the body and the medium (subsystems) are allowed; the body and medium together represent the *subject.* Its available energy – energy transmittable to any *object* – is what we call, today, the exergy of the 'body'. Figure 4 (from Gaggioli et al, [5]) shows two surfaces, the curved surface of Figure 2 for the 'body' *alone*, and a planar surface. The plane is tangent to the curved surface at the location where the body and the medium have the same temperature and pressure – namely the constant *T* and *p* of the medium. If the body is at internal equilibrium at B (of Figures 3 and 4), the vertical distance from B to the planar surface represents the available energy of the composite subject of body and medium together. If the body is at A, the available energy from the composite subject equals that vertical distance plus AB.

At the dead state of the overall, subject system (body and medium) the body will be at the location where its *T* and *p* are equal to that of the medium – where the body's surface is tangent to that of the medium.

*Gibbs Available Energy with Variable Composition.* Subsequently, in "On the Equilibrium of Heterogeneous Substances," [2], Gibbs presented – implicitly – the available energy of a body and medium for the case of open systems, where exchanges with a 'medium' include not only entropy and volume but also chemical *components*.[4]

## GENERALIZED AVAILABLE ENERGY

In the foregoing review of Gibbs 1873 development of available energy, leading to $A = E - E_{min}(S, V)$, the entropy and volume were 'constrained'. That is, the hypothetical process that delivers available energy is carried out with limitations: no *net* transport of volume or entropy to or from the surroundings of the overall system. Such limitations will, herein, be called *constraints*. This word will be used not only for limitations upon *transports* but also for restrictions on *spontaneous changes* (such as changes of composition by chemical reactions).

**Constraints.** To illustrate the concept of constraints, consider Figure 1 again. Suppose the piston to be fixed in place (or replaced by an immovable wall). This additional constraint upon the overall system could be represented by the symbol $V_1$ (for the volume of *1*). When $V_1$ is constrained, interchanges of volume between the two subsystems would be precluded, and full advantage of pressure difference between the two could not be taken. In general the available energy from the composite of *1* and *2* would be less. Because, the minimum energy reachable would in general be greater than that reachable if the constraint on $V_1$ were removed: $E_{min}(S, V, V_1) > E_{min}(S, V)$, and so $A(E, S, V, V_1) = E - E_{min}(S, V, V_1) < A(E, S, V) = E - E_{min}(S, V)$.[5]

This example illustrates that the imposition of additional constraints changes the amount of available energy, and it changes the dead state. While adding constraints may *seem* to be 'strictly theoretical' and even questionable, later in this paper it will be illustrated that it has important consequences in practice. There are relevant effects on delivery of available energy, on subsystem dead states, on calculated exergy values, and on costing.

Moreover, it is important to recognize that available energy is *defined*:

- For an overall system, consisting of specific relevant subsystems (and one *may be* a large 'medium'),
- Subject to constraints, which may restrict
  - how subsystems can interact, and
  - spontaneous changes within a subsystem, and
  - modes of interaction between the subject system and external devices.

---

[4] The word 'component' is to be understood as distinct from 'constituent'. Constituents are species actually present; components are species from which the constituents could be composed (e.g., see Hatsopoulos and Keenan [11]). In the case at hand, components are constituents of the 'medium' from which the constituents of the 'body' could be composed.

[5] In theory, the > and the < shown should be ≥ and ≤ because there are special, though rare circumstances when, upon taking advantage of temperature difference between *1* and *2*, upon reducing that difference to zero, the pressure difference would also happen to become zero. The $E_{min}(S, V, V_1)$ surface would be tangent to $E_{min}(S, V)$. Otherwise $E_{min}(S, V, V_1)$ will be above $E_{min}(S, V)$.

See Gaggioli and Paulus [5] for further elaboration on generalization of Gibbs available energy, including the relevance of constraints to equilibrium.

**Exergy.** Available energy is not an additive property, which is readily illustrated by considering Figure 1. Suppose that Subsystem 1, alone is at equilibrium; likewise for Subsystem 2. Then each, alone, has zero available energy. Whereas, when the two are not in equilibrium with each other, the composite of the two (the overall system) has available energy.[6]

For *any* overall system the author [7] has derived 'subsystem exergy' such that (i) exergy is additive, (ii) the sum of the subsystem exergies is equal to the available energy of the overall system, (iii) hence each subsystem's exergy can be viewed as its contribution to the overall available energy, and (iv) because it is additive, an 'exergy balance' can be written for any subsystem, so that 'exergy analysis' can be carried out.

Unlike the usual, 'textbook' derivations for exergy equations, which depend upon having a 'reference environment', the derivation in [7] is for any overall system. No reference environment is required. In the derivation, the dead state of the overall system becomes relevant, in lieu of a reference environment. The dead state of each subsystem is dictated by the dead state of the overall system. Incidentally, these dead states can change with time, when $E_{min}$ increases because of dissipations.

For the case when subsystems are free to exchange entropy $S$, volume $V$, and chemical components $N_i$, the expression for exergy *content* of a subsystem is:

$$X = E + p_f V - T_f S - \Sigma \mu_{if} N_i \qquad (1)$$

The subscript *f* denotes the pressure, temperature and component chemical potential at the dead state. The expressions for exergy *transports* and *destruction* follow directly from this expression for *content*.

When one of the subsystems is a 'medium', large and at equilibrium (or constrained equilibrium), it has zero exergy. And the medium dictates the dead state of all the subsystems.

In the foregoing expression for exergy, the *f*'s become the usual 0's. However, as argued later, there are many practical instances where it is erroneous (if not presumptuous) to assume an *equilibrium* environment (or a finite, non-equilibrium environment with a quasi-stable equilibrium 'dead state').

Understanding (a) the meaning of 'dead state' in general (including in the absence of an 'environment'), and (b) the relevance of constraints upon the dead state is important. Otherwise, in practice, the choices made to determine the overall dead state can be questionable if not erroneous (even when one subsystem is an 'environment').

(The author's 1999 derivation of exergy [7] is a simplification of one made by Wepfer [6], where there is an error in line 2 of Eq. (14); the subscripts shown as B should be A.)

## PRACTICAL EXAMPLES

### Subsystem Dead States for Engineering Exergy Analysis of Conversion Systems and Plants.

What is meant here by *Engineering* Exergy Analysis is this: analysis of an existing, operating plant (or system), or analysis of a plant that is being designed. The intent is that all of the subsystems should consist of technologies that are currently available. (Comments relevant to R&D and resource assessment are presented later in this paper.)

Before a plant (or system) is analyzed it is important to ascertain (or make reasonable assumptions) regarding the dead state of the materials in every subsystem.

Given a plant and its surroundings, (*a*) the *first step* in determining appropriate subsystem dead states is to *establish* the *relevant* "composite system" (overall system, consisting of subsystems). That is, what parts of the 'universe' have *significant effect* on the performance of the plant or system.

- *Relevant*: considering the purpose of the analysis.
- *Significant effect*: having an effect that influences the outcome of the analysis within the desired *significant* figures.

The *2nd step*: (*b*) the practical, technological constraints on (i) the interactions between subsystems and on (ii) the spontaneous processes within each subsystem need to be specified.

These principles – (*a*) and (*b*) – are illustrated with several cases, by Wepfer and Gaggioli [6]. That article includes a section on "The selection of reference datums [dead states] for subsystem [exergy]." Rather than duplicate that section, see [6] and also [3].

### Relevance to Analyses for R&D and for Resource and Sustainability Assessment.

This section will be devoted to the importance of the constraint concept, and to the significance of choosing a relevant dead state.

***Significance of Constraints***. Again, consider a simple example, referred to earlier. Suppose that the system in Figure 1 is at a condition like A in Figure 2, and consider a *real* process that is striving to deliver the available energy represented by AB. Invariably there would be entropy production, due to 'mechanical friction' and to heat transfer through temperature differences. As a result the system would end up at a condition to the right of B on the curve, toward C; the more the entropy production the closer to C (but never above C, which is the condition reached if the system is allowed, uncontrolled, to equilibrate internally, so no energy is delivered). Let us suppose that, with more or less well-controlled, but real equilibration the final condition reached was at α, on Figure 5 (For convenience of the artwork the ordinate (for *E*) is not linear; α appears closer to C than if it were linear; i.e. the energy delivered ($E_A$ - $E_\alpha$) is supposed to be significantly greater than the dissipation of available energy ($E_\alpha$ - $E_B$).). Moreover suppose that the entropy production was predominantly caused by mechanical, viscous friction.

Now, consider the following alternative scheme, starting at A, for delivering available energy: If the piston were fixed in place (constraining $V_1$), and available energy was delivered with very little entropy production due to heat transfer, that delivery process would end up at a place like β, below and slightly to the right of A. Next, deliver more available energy by letting $V_1$ change by a modest amount (to $V_1$'), with some but less viscous friction (because of the controlling of $V_1$'s change). By repeating, once more, this procedure of fixing and then changing $V_1$, the path to equilibrium would be like that from A to γ on Figure 5.

[6] Figure 4 illustrates another example: B represents an equilibrium state of the 'body' and all points on the planar surface are equilibrium states of the 'medium'; $X_B$ represents the available energy of the overall system – the exergy attributed to the 'body'.

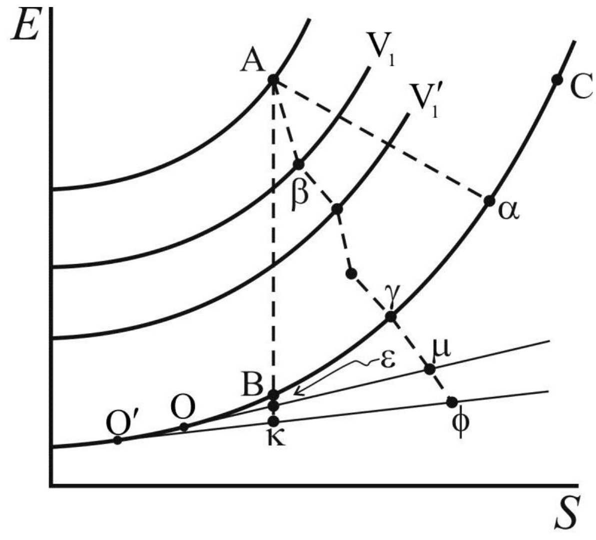


Figure 5. Some processes for delivering available energy.

More available energy, namely $E_A$ - $E_\gamma$, would be delivered (less dissipated) than from the path A to α. (By increasing the number of steps the delivery could be increased all the moreso.) This is a simplistic example of how adding constraints, and controlling them, can improve the delivery of available energy. The obvious conclusion to be drawn therefrom: improving the control of available energy transfer processes – by *adding* constraints – can improve the efficiency. However, a more important conclusion can be drawn from this simple example, namely that *discovering* new constraints can improve the efficiency.

The objective of *adding* constraints is control; that is accomplished by reducing states that otherwise would proceed more spontaneously, toward successive constrained-equilibrium states.

*Adding* effective constraints will generally depend upon advances in *technology*.

*Discovering* 'new' constraints will often depend on *scientific advancement* as well. Such constraints 'produce' 'new' constrained-equilibrium states (or better, *find* them, on a hypersurface with *E*, *S*, . . . and new constraints as variables). It can be surmised that constraints that could even 'increase' the available energy do exist. That is, by allowing states which (at the current status of science) are *believed* to be at equilibrium but are at metastable equilibrium – such that the metastability can be overcome by manipulation of the newly discovered constraints. Moreover, if the new constraints can be controlled well, the delivery of the additional available energy can be improved.

From the vantage point of one hundred years ago, that 'new' available energy could be what we call nuclear today.

Hopefully, and not surprisingly, several of the papers in these proceedings will lead to discovery of new constraints and means for their manipulation.

***Significance of the Dead State***. Consider the 'body' of Figure 1 again, but this time in conjunction with a medium like that depicted by the flat surface in Figure 4. Then, on Figure 5 the slope of BC at point 0 is the temperature at the dead state of the body and medium together.[7] The point ε lies on the tangent line, directly below point A. If the object is at A, the energy attainable from the composite by bringing it to thermal equilibrium is equal to the distance $E_A$ - $E_\varepsilon$ on Figure 5.[8] If the object is at B (with no available energy of its own), the energy attainable is $E_B$ - $E_\varepsilon$

When the energy is being delivered from the composite with real processes, the overall delivery would be typified by $E_A$ - $E_\mu$. Then, the entropy production *within* the object, when starting at A, is represented by the *horizontal* distance between A and γ. Further entropy production, as a result of thermal interactions with the medium, is the horizontal distance between γ and μ.

Finally, suppose there exists an alternative medium at say a much lower temperature, represented by the tangent line through 0' on Figure 5. Now the overall energy available from the composite is [$E_A$ - $E_\kappa$]; the delivery via real processes is represented by [$E_A$ - $E_\phi$]. Clearly, these are greater than [$E_A$ - $E_\varepsilon$] and [$E_A$ - $E_\mu$], respectively.

Again, consider the nonlinearity of the *E* scale, and for example consider what the differences would be if the slope of the straight line through 0 were 273K and that through 0' were 27.3K or 2.73K. Moreover, significantly, if the body started at internal equilibrium, at B, consider how large the ratio [$E_B$ - $E_\kappa$]/[$E_B$ - $E_\varepsilon$] would be.

***Intermediate Conclusions.*** In general terms,

- Controlling better with constraints that are available with current technology can improve the delivery of available energy (to desired products).
- Moreover, if additional, 'new' controlling constraints can be found, it is quite conceivable that delivery can be improved.
  - An obvious, simple *example* is control of chemical composition. In the examples presented above, chemical composition of Subsystems *1* and *2 could have* been changing, and there would have been associated entropy production during delivery. Inasmuch as only entropy and volume *exchanges* were allowed between *1* and *2* (and with the mediums), then:
    - If the compositions of *1* and *2* (when the object was at B) differed, there could be additional available energy deliverable, *if* exchange of chemicals between them were allowed, and controlled, while bringing the two subsystems to chemical equilibrium.
    - Moreover, if *1* and *2* were each, alone, at chemical equilibrium but not at chemical equilibrium with an accessible medium, there would be additional available energy.
    - Additionally, if the piston at the far left end in Figure 2 were controllable (in essence, making both $V_1$ and $V_2$ constraints that could be manipulated) spontaneous change of composition within **1** and **2** could be controlled, reducing (and in theory[9] eliminating) associated entropy production.
  - This simple *example*, chemical, is only an example. The important point is that it would be significant if 'new' constraints can be found, to unlock heretofore unavail-

[7] That is, at any location on the curve through BC, its slope is the temperature of the object when at that state. At location 0 the temperature is $T_0$, which is the temperature of body and medium at the overall dead state.

[8] $E_A$ - $E_\varepsilon$ is the available energy of the composite if $V_{body}$ is constrained to be equal to $V_B$ (= $V_A$).

[9] A theoretical scheme whereby chemical conversion of a fuel could be accomplished without entropy generation was proposed by Keenan [8] p. 269. The method is also presented in Obert [9] Article 3-19.

able energy. (Relatedly, there may exist available energy that is more or less 'hidden', within the context of today's science – like nuclear disequilibrium was hidden 100 years ago).

- If a medium is accessible with a lower temperature and/or with a lower pressure, and/or lower chemical potentials (or lower potentials associated with any new controlling constraint), the delivery can be increased.

## CLOSURE

Traditionally, the development of exergy has assumed the existence of a 'surrounding environment'. Necessarily then, in practice exergies are evaluated relative to a reference environment, which must be selected by the evaluator. Several alternative 'standard' reference environments have been proposed by various authors, and commonly the evaluator will choose one of them. In any case, the 'dead state' of zero exergy is dictated by the selected 'standard' environment. That is, by equilibrium with that environment. And it is commonly held that, in theory at least, the dead state should be the same for all of the contents of, and the flow streams between, the subsystems of the facility being analyzed.

These habitual practices have shortcomings. By and large the shortcomings can be circumvented by referring back to the more fundamental concept underlying exergy, namely available energy.

As described above, *if* an overall system is *given*, then (at any moment) the overall dead state and the dead states of all subsystem and their materials is unique. No reference environment is necessary. If, as usual, one of the subsystems is a large surrounding medium, in a sense it is 'just one more subsystem'. Nevertheless, it may have a dominant (if not total) effect upon the dead state of the other subsystems. However, those subsystem dead states will not necessarily all be in *complete* equilibrium with the surrounding medium. Generally, subsystems will be in constrained equilibrium with the surroundings (For example, the dead state the refrigerant in a vapor-compression system will be in thermal equilibrium with the system's surroundings, but not in pressure or chemical equilibrium; [6,3])[10]

The preceding paragraph began with ". . . *if* an overall system is *given* . . . the overall dead state . . . is unique." That statement is subject to several, related stipulations:

- The modes of interaction between subsystems must be specified.
- The constraints on subsystems must be specified.

That is, defining an overall system (making it 'given') requires not only identification of its parts, but also how they will be allowed to interact and what constraints are imposed upon the parts and the interactions.

**Defining an Overall System.** It is imperative that whenever the results of an exergy analysis or exergy evaluation of resources is presented, it should be clear to the reader what the underlying "overall system" is – its make-up and the assumed interactions and constraints. Ideally, this requirement should be fulfilled by the author(s). If they have not been fulfilled explicitly, a careful reader will seek to determine what overall system has been *assumed*. If an answer cannot be found or assumed judiciously, the reader should question (if not be skeptical, or even dismiss) the conclusions that have been drawn.

***Engineering Systems***. In the case of exergy analyses of engineering systems, it is generally straightforward for the reader to ascertain the overall system, as long as a reference environment has been clearly stated. The reader will naturally assume that the subsystems shown on the flowsheet, are 'standard' – current technology. If some are not standard the authors hopefully will have made that known.

***Resource and Ecologic Assessment***. Many laudable applications of exergy to ecology and sustainability have been carried out. These studies refer to the future and often project into the future – and make predictions (often dire) about the future, and then make recommendations. Care needs to be exercised when considering some of the conclusions drawn (especially when the conclusions and recommendations are presented ardently).

It seems that there generally are assumptions that go unrecognized or are taken for granted by both authors and readers. So the following kinds of questions arise:

- What is the overall system? Generally, it is evident that the overall system has been limited to the earth (or earth-sun) and its resources. Is that a reasonable limitation when predicting the future?
  - Are there resources outside our 'sphere' that will become accessible? Literal 'energy resources'? Or subsystems that could be invoked?
    - E.g., in some remote places, the night sky is used as a source of exergy today. The background temperature of the universe is about 3K; could it be used as a 'medium'? Consider the two straight lines on Figure 5.
  - 'What's the point of all this'? Only that the reader of the assessments should realize that the *assumed* scope of the overall system has a very big effect on the results and conclusions.
- Again, 'What is the overall system?' For available energy and exergy to be meaningful, there must be a *complete* overall system; that is, besides the resources there must be means for harvesting and converting them that are assumed.
  - What technologies have been assumed for the harvesting and converting? Presumably today's technologies, with their 'control constraints'? (Or improved equipment but with the same constraints.)
  - If so, that dismisses prospective, relevant developments in science and technology.
    - Scientific advances can lead not only to new technologies but also to new resources (like fission and fusion have 'made' new resources).
- What *are* the 'controlling constraints'?
  - Is it implicit that the control variables are classical? Electrical, mechanical, chemical and perhaps nuclear? – such that the perceived resource conversion is subject to the laws of 'classical' science (e.g. today's chemical thermodynamics, with its assumed variables – its thermostatic properties).
  - Again, the reader of assessments should realize that there is an implicit science and technology being assumed. (Future developments likely will introduce

[10] Some might think that it doesn't matter what the dead state is, because when one calculates exergy differences between points in a cycle, the dead state values cancel. That thinking is flawed; it is important to know the correct, total values at every point. Otherwise significant mistakes can occur in evaluating subsystem efficiencies and especially unit costs [6].

unforeseen variables, which could be employed to control/constrain phenomena relevant to resource conversion.)

**Viewpoints.** All ‘energy resources’ (for *example* hydrocarbons) have uesefulness because there exists an associated disequi-librium with our environment. It is typical of resources (like the hydrocarbons) that the disequilibrium is ‘constrained’ such that there is a metastable equilibrium. Their usefulness depends upon ‘breaking’ – overcoming – the metastable equilibrium. The better the control of the ensuing equilibration, using constraints, the more efficient the use of the resource.

Particularly regarding resources, history is filled with dreadful forecasts which have arisen in the face of *challenging* circumstances. Invariably, the forecasts have been made under the (inherently pessimistic) assumption that the then-current science and technology was definitive.

However, humankind has not only overcome the *challenges* but in dealing with them has *advanced* – has discovered ‘new’ resources, unlocked them with new science and new technologies, improved the efficiency of usage, . . . and as a consequence has *improved* our subsistence.

One could say that the advances resulted, at least in part, as consequences of the challenges. So assessments of the type referred to above should be appreciated – as challenges and as opportunities, for improvement.

There is a great amount of disequilibrium, particularly metastable equilibrium in our *universe*. Our future technology is not earthbound. Moreover, it can be hoped (and from a historical perspective, *expected*) that – spurred on by challenges – future science and technology will unlock not only remote resources but ‘hidden’ or currently ‘unreachable’ earthly resources as well. Some would say, “That’s overly optimistic.” “Careless.” “We should ‘play it safe!” The readers will have a variety of viewpoints (worth discussing!).[11]

In any case, let the readers of ‘assessment’ papers that refer to the future understand that there are implicit assumptions that are very important, and will prove to have been very significant – rightly or wrongly.

The Appendix outlines what I believe are reasons for optimism.

## ACKNOWLEDGEMENTS

I would like to acknowledge the following ‘schools of thermo’ that I have learned from: Goodenough-Obert, Hirschfelder-Curtiss-Bird, Tribus-Evans-ElSayed, Keenan-Hatsopoulos-Gyftopoulos-Beretta. Also, study of the early history of the 2nd Law, of available energy and of entropy – particularly the contributions of Thomson (Lord Kelvin), Rankine, Gibbs and Maxwell – has been enlightening [10]. Finally, I appreciate and thank all of the students, colleagues, and contemporaries that I have learned with.

## REFERENCES

[1] Gibbs, J.W., 1873, “A Method of Geometrical Reperesenation of the Thermodynamic Properties of Substances by Means of Surfaces,” in The Scientific Papers of J.W. Gibbs, vol. 1, Dover Publications, 1961.

[2] Gibbs, J.W., 1875, “On the Equilibrium of Heterogeneous Substances,” in The Scientific Papers of J.W. Gibbs, vol. 1, Dover Publications, 1961.

[3] Gaggioli, R.A., 2012, “The Dead State,” Int. J. of Thermodynamics, vol. 15 (No. 4), pp. 191-199.

[4] Gaggioli, R.A., 2010, “Teaching Elementary Thermodynamics and Energy Conversion: Opinions,” Energy, Vol. 35, pp. 1047–1056.

[5] Gaggioli, R.A., Richardson, D.H., Bowman, A.J., Paulus, D.M. Jr., 2002, “Available Energy: a. Gibbs Revisited, b. Gibbs Extended”, Trans. ASME, vol. 124, pp. 105-115).

[6] Wepfer, W.J. and Gaggioli, R.A., 1980, “Reference Datums for Available Energy [Exergy]”, Ch. 5, pp. 78-92, Thermodynamics: Second Law Analysis, American Chemical Society, Symposium Series Vol. 122.

[7] Gaggioli, R.A., 1999, “Available Energy and Exergy”, International Journal of Thermodynamics, Vol. 1, pp. 1-8.

[8] Keenan, J.H., 1941, Thermodynamics, Wiley.

[9] Obert, E.F., 1973, Internal Combustion Engines, Harper and Row.

[10] Gaggioli, R.A., 1999, “Reflections on the History of Exergy,” pp. 5-13, Proc. ECOS’99, M. Ishida, ed., Tokyo Institute of Technology, Japan.

[11] Hatsopoulos, G.N. and Keenan, J.H., 1965, Principles of General Thermodynamics, Wiley.

## Appendix. Regarding the future

*Predicting* it requires *assumptions*:

- The Subject (overall system) – its ‘extent’
  - The Subsystems; i.e., Resources from the universe.
- Exergy content of subsystems
  - Depends upon the available science.
- Constraints/Controls – depend upon:
  - Available Science
  - Available Technology

*Assessing* predictions requires knowing:

- The assumed subject – its ‘extent’
  - The Subsystems
- The assumed future Constraints/Controls
  - The assumed future available science

Future Prospects:

The subject – determined by exploration, prospecting, discovering, and ‘mining’ of *disequilibrium*:

- Unexplored land and sea, and depths of earth
- Space – e.g., asteroids
- Solar system, . . . Universe – e.g., night sky at 2.5 K
  Reducing $E_{min}$ – Recuperation of generated entropy
- New ‘elements’ (subjects) – exergetic; functional
  Unexpected discoveries of resources, resulting from exploration.

Constraints/controls – exploration, prospecting, discovering, ‘mining’ of *knowledge* about:

[11] There is an old saying, “Don’t let a crisis go by without taking advantage of the opportunity.” Pessimists miss the opportunity. It should not be assumed that to ‘play it safe’ is without ‘cost’. Entrepeneurs – including many scientists – are optimists.

- Science: Universe, megaverse, . . . Nanoverse, microverse, . . .
- Technology, from Science, for: Controlling constraints; Unlocking and controlling metastable constraints

Again, . . . and again, . . . because:

- There is a tremendous amount of disequilibrium ….
- There is a tremendous amount of unknown science, I believe – I am sure!
- The resourcefulness of the ‘young at heart’ – of today and the future (near and distant) – find them: Discover, develop, . . . with exploration: physical, mental.

Optimism, versus stultifying pessimism.