International Journal of Thermodynamics (IJoT)
ISSN 1301-9724 / e-ISSN 2146-1511
www.ijoticat.com

Vol. 15 (No. 4), pp. 191-199, 2012
doi: 10.5541/ijot.423

The Dead State

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Abstract

The purpose of this paper is to provide guidance for the selection of the dead state for exergy analysis, guidance that is especially important in applications to energy-conversion and materials processing plant engineering, and to ecology. First, the general definition of the dead state is provided, based on the concept of 'the available energy of a body' as originally presented by Gibbs. Gibbs 'body' can be any overall system, no matter how complex and a crucial point is that there is no need to include or have a 'reference environment.' On this groundwork, criteria underlying the selection of the appropriate dead state for a variety of practical engineering systems are referred to; while these cases are not exhaustive, they provide examples of the rationale for selection of an appropriate dead state for any case. Finally, the implications and relevance of the dead state on applications of exergy considerations to the issues of ecology and sustainability are discussed.

Keywords: *Dead State; exergy; reference environment; available energy; resource assessment.*

1. Introduction

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

Fundamentals. Following Gibbs (1873) 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').

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.'

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
- 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 (convincingly, it is hoped) broad, general principles relevant to complex practical applications.

1. Gibbs Available Energy

In his 1873 article "A Method of Geometrical Reperesenation of the Thermodynamic Properties of Substances by Means of Surfaces," 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). 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] The availa-

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

[2] The existence of entropy is taken for granted here. See Appendix I for an elaboration.

ble energy $A(t)$ of the ‘body’ at t, a characteristic of the ‘body’ alone, is the maximum amount of energy from the ‘body’ only – from the *subject* – 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.

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. Let us say that at an instant t each subsystem, by itself, is at equilibrium with a uniform temperature and pressure within. But, supposing $[p_1 - p_2] > 0$ and $[T_1 - T_2] > 0$, the *overall* system is not at equilibrium and has available energy. That is, energy could be delivered from the overall system by exchange of volume and/or entropy; the net amount of energy delivered would equal $\int p_1\, dV_1 + \int p_2\, dV_2 - \int T_1\, dS_{\tau 1} - \int T_2\, dS_{\tau 2} = \int [p_1 - p_2]dV_1 + \int [T_1 - T_2][dS_{\tau 2} - dS_{\pi}]$.[3] This net output of energy would be a maximum, equal to the available energy A, when the entropy production dS_{π} is zero throughout the delivery, and the overall system has reached an equilibrium state, with $[p_1 - p_2] = 0$ and $[T_1 - T_2] = 0$. The remaining energy content of the overall system would be the minimum value reachable from the initial state with its volume $V(t)$ and entropy $S(t)$.

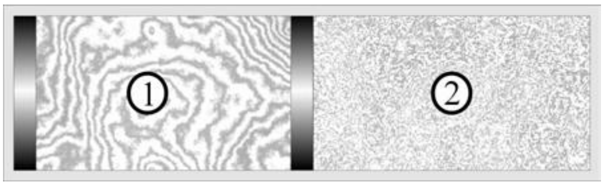

Figure 1. Example of an overall system or ‘subject’

At *any* particular state of *any* overall system, with its particular entropy S and volume V, there is a minimum possible energy, E_{min}. That is, there is a function $E_{min}(S, V)$. Thus, at any state of the system, the Gibbs available energy is given by $A = E - E_{min}(S, V)$. When the energy of the body equals $E_{min}(S, V)$, the body is at an equilibrium state at (S, V), and there is no available energy. On Figure 2, from Gibbs, 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 of that state. Figure 3 (from Gaggioli et al, 1999a) 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.[4]

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.

Gibbs called $E_{min}(S, V)$ “the surface of dissipated energy”. If an overall system, like that in Figure 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.

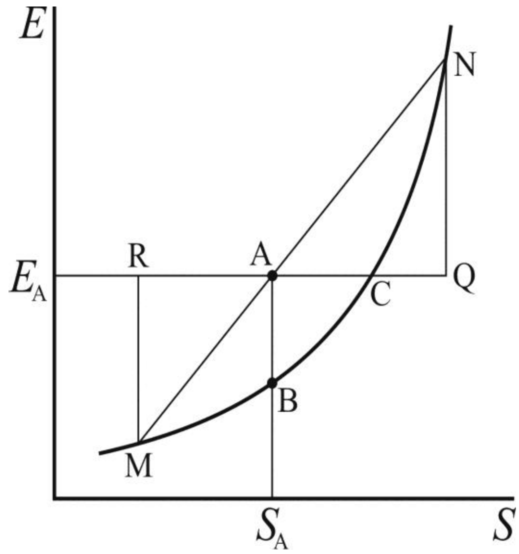

Figure 2. Depiction of E_{min} vs. S at fixed V, of available energy, and of available entropy

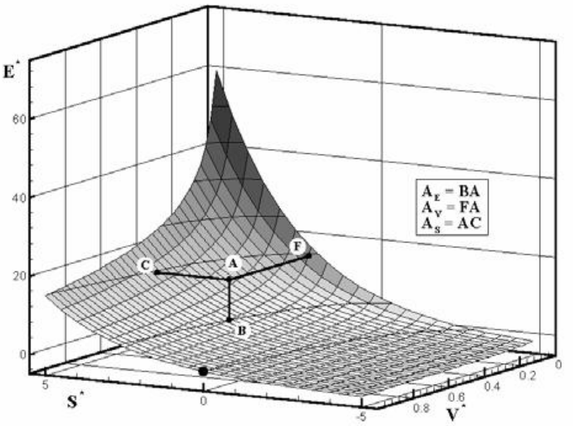

Figure 3. Depiction of $E_{min}(S,V)$, of available energy, of available vacuum and capacity for entropy.

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’

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[3] Here, the equal sign depends upon volume and entropy balances for the case of no net transfers of volume or entropy to or from the overall system.

[4] States with the same E could differ as a result, simply, from disparities in the pressure and temperature differences between the subsystems. Furthermore, many states with the same E will differ because of gradients within a subsystem, and so on.

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.

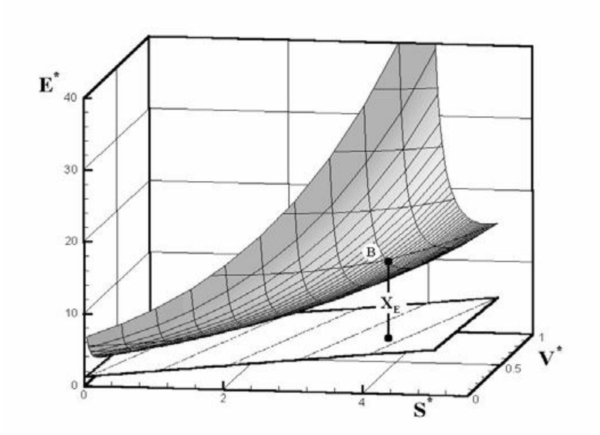

Figure 4. Depiction of the available energy of a body-and-medium (exergy of a body).

(b) *Case* 2, 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. 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. Figure 4 (from Gaggioli et al, 1999a) shows two surfaces, the curved surface 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. (As explained below, the available energy can be attributed to the body, and called the 'exergy' of the body. In this case the exergy of the medium is zero.)

At the dead state of the overall 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," 1875, 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*.[5]

2. 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 $A(E, S, V, V_1) = E - E_{min}(S, V, V_1) < A(E, S, V) = E - E_{min}(S, V)$.[6]

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 article 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.

See Gaggioli and Paulus (1999b) 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

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[5] 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, 1965). In the case at hand, components are constituents of the 'medium' from which the constituents of the 'body' could be composed.

[6] 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 $E_{min}(S, V)$.

available energy. The author (Gaggioli, 1999) 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 author's derivation 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:

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

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

When one of the subsystems is a 'medium', large and at equilibrium (or constrained equilibrium) – with pressure p_0, temperature T_0 and chemical potentials μ_{i0} – it has zero exergy. 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. In practice, the choices made to determine the overall dead state are affected (even when one subsystem is an 'environment').

(The author's 1999 derivation of exergy is a simplification of one with Wepfer (1980), where there is an error in line 2 of Eq. (14); the subscripts shown as B should be A.)

3. 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.)

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. That is, the p_f, T_f, and μ_{if} need to be determined for each subsystem. (When a material flows between subsystems, it of course has the same dead state in each.)

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.

2nd step: (*b*) the practical, technological constraints on the interactions between subsystems need to be specified.

These principles – (*a*) and (*b*) – are illustrated with several cases, by Wepfer and Gaggioli (1980). That article includes a section on "The selection of reference datums [dead states] for subsystem [exergy]." Rather than duplicate that section, here only one of those cases will be presented, in order to illustrate the application of principles.

One case that illustrates the relevance of constraints is the situation where a 'working fluid' is confined, within some of the subsystems. An example is the H_2O confined in the 'cycle' of a power plant. Another is the refrigerant confined in a vapor-compression refrigeration system. In these circumstances the total volume and mass of the working fluid are fixed, constrained. As long as a refrigeration system is intact (working, practically), the refrigerant cannot equilibrate its pressure (or composition) with that of the surrounding environment. Its equilibration would be constrained, so that only thermal equilibration could occur. The appropriate dead state for the refrigerant is that which it would reach upon system shut-down; typically that would be a state at environmental temperature and at the refrigerant's saturation pressure at that temperature.

If one assumed that the dead state pressure should equal atmospheric pressure, erroneous subsystem efficiencies (and costs) will result. If the reader needs to be convinced that the correct dead state pressure should be the one recommended here, it is suggested that two exergy analyses be carried out: one with the recommended p_f and one with p_0 equal to atmospheric. Then draw exergy flow diagrams for the two cases and compare – noting that all of the exergy enters as supply to the compressor, which then delivers exergy to the other subsystems. (By the way, if one argued that atmospheric pressure is correct, then to be consistent the chemical exergy of the refrigerant should also be taken into account.)

Another, even more interesting, 'refrigerant example' would be for the case of a dual-purpose vapor compression system; one which delivered cooling to a load at temperature less than ambient and heating at temperature higher than ambient (and with no interaction with the ambient). See Paulus and Gaggioli (2000) for rationale for proper specification of T_f and, hence, p_f.

Other circumstances discussed by Wepfer and Gaggioli (1980), with different procedures for determining the dead states, include:

- Multiple, stable surrounding media
- Circumstances when variations in the environment, with time, are significant
- Metastable and Unstable Ambient Environments; e.g.
  - inherently unstable (such as weather changes; Gaggioli et al., 1978, and Wepfer et al., 1979)
  - unstable because of the impact of effluents from the plant

One point that can be made regarding the choice of an environment for analyzing a plant is this: *Alternative* choices may be appropriate, depending upon the purpose of the analysis. For example, suppose one analysis is being made for the purpose of improving efficiency or economy of a plant (which has state of the art equipment, and apparatus required in order to satisfy regulations and codes). Then an appropriate environment would be that immediately surrounding the plant. On the other hand, if a second analysis is to include assessment of environmental impact, then the selected environment will need to include chemical components for neutralizing the emissions, to stable non-toxic conditions. Such components might exist only remotely from the plant. (If costing were part of the analysis, the exergy in the emissions would have a negative unit cost – so that the cost of bringing the neutralizing components would be charged to the plant.)

For further elaboration on selection of dead states, see the 1980 article for details and examples.

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 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 is 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_α) is significantly greater than the dissipation of available energy (E_α - E_B).). Moreover suppose that the entropy production is predominantly caused by mechanical, viscous friction.

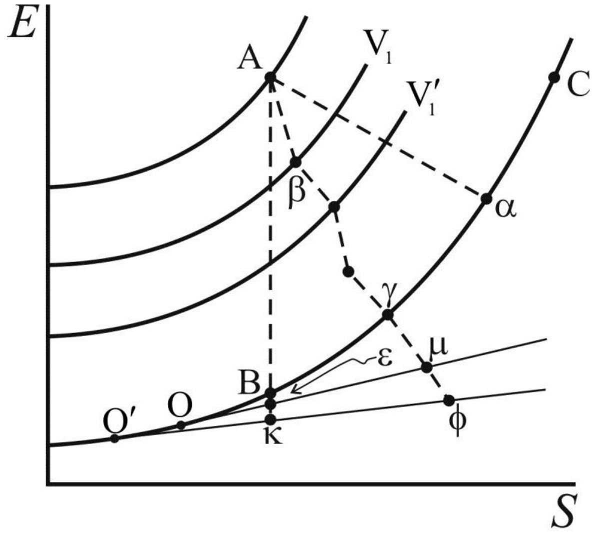

Figure 5. Some processes for delivering available energy.

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 were 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. More available energy, namely E_A - E_γ, 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 general conclusion to be drawn therefrom (which may appear obvious) is that improving the control of available energy transfer processes – by *adding*, **or** by *discovering* 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.

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_ε on Figure 5.[8] If the object is at B (with no available energy of its own), the energy attainable is E_B - E_ε

When the energy is being delivered from the composite with real processes, the overall delivery would be typified by E_A - E_μ. 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

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[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_ε is the available energy of the composite if V_{body} is constrained to be equal to V_B (= V_A).

line through 0’ on Figure 5. Now the overall energy available from the composite is [E_A - E_κ]; the delivery via real processes is represented by [E_A - E_ϕ]. Clearly, these are greater than [E_A - E_ε] and [E_A - E_μ], 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_κ]/[E_B - E_ε] 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.[9]
    - 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[10] 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 unavailable 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.

4. 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, and commonly the evaluator will choose one of them. In any case, the ‘dead state’ of zero exergy is dictated by the selected reference 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 shown 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, as referred to earlier, at its 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.)[11]

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 authors. 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 natu-

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[9] Earlier it was stated, for conceptual simplicity, that Subsystems *1* and *2* were identical. That assumption was unnecessary for the discussions that ensued, as long as *1* and *2* were constrained from exchanging chemicals.

[10] A theoretical scheme whereby chemical conversion of a fuel could be accomplished without entropy generation was proposed by Keenan (1941), p. 269. The method is also presented in Obert (1973) Article 3-19.

[11] 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. (Wepfer et al., 1979).

rally 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.
- What is the overall system? (Same question!) 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).
    - Again, the reader of assessments should realize that there is an implicit science and technology being assumed. (Future developments likely will introduce 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 disequilibrium 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!).[12]

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.

ACKNOWLEDGEMENTS

I would like to acknowledge the following 'schools of thermo' that I have learned from: Goodenough-Obert, Hirschfelder-Curtiss-Bird, Tribus-Evans-El-Sayed, 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 (Gaggioli, 1999). Finally, I appreciate and thank all of the students, colleagues, and contemporaries that I have learned with.

APPENDIX I. Entropy

The concept of entropy has been taken for granted in this presentation. The author (2010) prefers to take the existence of entropy axiomatically, rather than derive it in manners such as the common $dS = dQ_{rev}/T$ or methods similar to the $dS = C\, d[E\text{-}\Omega]$ of Hatsopoulos and Keenan (1965), where Ω is the 'available work'. To the extent of the author's awareness, Obert (1949) was the first to postulate the existence of entropy, and then Callen (1960); these authors defined entropy only for equilibrium states.

Using the likes of $dS = C\, d[E\text{-}\Omega]$, Hatsopoulos and Gyftopoulos (1976) proved the existence of entropy for non-equilibrium states, too (or, see Gyftopoulos and Beretta, 1991). In a somewhat analogous procedure, start-

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[12] 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. Appendix II outlines, I believe, reasons for optimism.

ing with available energy, Goodenough (1920) defines entropy for states of irreversible processes.

If, then, it is *accepted* that entropy exists for non-equilibrium states then there can be no logical objection to *postulating* that it exists for these states as well as equilibrium states, as long as it can subsequently be proved that $dS = C \bullet d[E\text{-}\Omega]$ is then a result. Whether to 'begin' with $dS = C \bullet d[E\text{-}\Omega]$ or with the postulation of entropy's existence is then a matter of preference. The author contends that postulation is preferable, because then all of useful thermodynamic relations can be derived in a much more streamlined manner (Gaggioli, 2010). Many concepts that students struggle with or are 'superfluous' are eliminated. For examples, the concepts of reservoir or, even, reversibility are not needed. Unlike available work or adiabatic availability, available energy is deliverable by any mode – mechanical, with Force or Torque (momentum currents); electrical, with charge current; . . . ; thermal, with entropy current – and by the way, available energy (and exergy) delivered with any one current is as good as that delivered with any other). With the postulation of entropy, maintaining strict logic doesn't require ponderous definitions of work and/or heat.[13] As a matter of experience, students find the concept of entropy and, in turn, all of thermodynamics easier to comprehend (and hence to apply) when entropy is postulated. Developing and then putting 'heat' – a transport not an additive property – ahead of entropy is in the author's opinion, putting the cart ahead of the horse, and very difficult to 'operate'.[14]

APPENDIX II. Regarding the Future

Predicting it requires *assumptions*:

- The Subject (overall system) – its 'extent'
  - The Subsystems; i.e., Resources
- 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 resulting from exploration.

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

- 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!
- Let the resourcefulness of the young – of today and the future (near and distant) – find them: Discover, develop, . . . with exploration: physical, mental.

Optimism, versus stultifying pessimism.

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[13] It is a matter of convenience and 'standard practice' that the assignment of units to energy is via mechanical work. Keenan and Shapiro (1947) proposed a thermal method for stating the 1st Law and assigning units to energy. That possibility supports, implicitly, the rationality of postulating the existence of entropy.

[14] It should have been mentioned that, following Shannon and Jaynes, Tribus (1961) postulates *an* entropy (call it η here) to be a certain probability-measure of uncertainty, namely $\eta = -k\Sigma[p_i \ln(p_i)]$ where p_i is the probability of the *i*th quantum state of the material. With that postulate certain 'general' and useful relationships of Statistical Thermostatics (the 'Boltzmann distribution' and the associated 'partition function') follow straightforwardly. To relate *that* entropy to the entropy of thermodynamics, a resulting equation for 'reversible' processes, $d\langle e\rangle = [1/\beta]d\eta - p\, dv$ is compared to $de = T\, ds - p\, dv$. Assuming that η and s are the same thing, and that the probable energy $\langle e\rangle$ is what *e is*, then it is rational to conclude that $\beta = 1/T$. The deduction is applicable only for equilibrium states. More commonly, treatises on statistical mechanics (e.g., Andrews, 1975) take the converse approach, deducing $S = -k\Sigma[p_i \ln(p_i)]$ after assuming that $de_{\text{rev}} = d\langle e\rangle$.

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