Int.J. Applied Thermodynamics,
Vol.1 (No.1-4), pp.1-8, 1998

ISSN 1301-9724

Available Energy and Exergy

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Abstract

An "available energy" is defined for every state of any system. The definition is independent of (a) the concept of work, (b) any reference environment, and (c) the make-up of the system (e.g., "macro" or "micro). On the basis of this available energy, given any composite system, the contribution of each subsystem to the available energy -- that is, the exergy content of a subsystem -- is defined, as well as the instantaneous "dead state" of the composite and each subsystem.

Some pedagogical, scientific and engineering implications are discussed.

Key words: available energy, thermostatic state, equilibrium, exergy, dead state.

1. Basic Concepts

A *system* is distinguished at any instant by its *contents.* Associated with each content is an *additive property*. For any composite system consisting of two or more systems, the amount of any additive property is equal to the sum of the values for the systems comprising the composite.

For each system, a *balance* equation can be written for changes in the amount of any additive property in the system. The balance equation represents any change in an additive property in terms of the causes of the change, namely *transports* and *productions*. Thus, given any additive property of a system, symbolized by N(t),

$$dN = dN_t + dN_p \qquad (1)$$

For any additive property represented by N(t), the *net* transport into the system from some reference time-zero up to time t is $N_t(t)$; this function reflects exchanges of content with other systems. An *interaction* between two systems occurs whenever there is any exchange between them. An exchange between two systems has an equal and opposite immediate effect on the additive properties of the two, and it has no effect on the additive properties of the composite of the two. When there are exchanges with more than one other system, the function $N_t(t)$ can be expressed as a sum with each term representing an exchange with one of the others. A system is *isolated* when there are no interactions with other systems (or, in practice, when any interactions with other systems have negligible effect upon the phenomenon being modeled).

The *net* production within the system up to time *t* is given by the function $N_p(t)$, which reflects any change of N(t) which is not a result of transports. Hence for any composite system the value of $N_p(t)$ equals the sum of the values associated with the systems making up the composite. Any phenomenon which changes an additive property independently from a transfer thereof is said to occur spontaneously. An additive property is said to be *conserved* when there is no production, positive or negative, thereof. Obviously, the conserved additive properties of an isolated system are constant in value.

Among the additive properties employed to model a phenomenon, some are *primitive*, namely those representing contents whose existence is simply accepted, postulated. Examples of additive properties which are commonly taken as primitive are "number of electrons" and "number of H atoms", and "number of H_2 molecules" or "number of H^+ ions", and momentum.

Herein, energy *and* entropy are taken as primitive, as for example by Obert (1949) and Callen (1960). However unlike Callen, who postulates the existence of entropy only for "equilibrium" states, here it is postulated that every state has a value of entropy (as in the case of energy). This *postulate* is in accord with the *conclusion*, that every state has an associated entropy, deduced by Gyftopoulos and Baretta (1991) on the basis of alternative postulates.

Among the dependent variables associated with a system at an instant *t*, those which make no reference to earlier times are called *properties.* Included, of course, are those variables called additive properties above. The transport functions represent "historical logs" -- amounts transported from the beginning of the phenomenon being modeled up to the instant *t* -- and hence are not properties. The same is true for the production functions.

The *state* of the system at an instant t is determined by the values of its properties. The state of any composite system is determined by the states -- the values of the properties -- exhibited by its subsystems.

2. First Law

Herein, the first law is taken to postulate (1) the existence of the additive property, energy, with a finite value at every state of a system, (2) conservation of energy, and (3) that *whenever systems interact there is a transfer of energy between them, and every energy transfer is associated with the transfer of another additive property.*

That is, for every independent dN_{ti} there corresponds a dE_{ti}, and hence a coefficient, to be called C_i, relating the two and defined by:

$$dE_{ti} = C_i \cdot dN_{ti} \qquad (2)$$

3. Thermostatic States

Consider any set of additive properties associated with a system, excluding its energy. For example, consider the set consisting of the entropy, the volume and the *component* amount of *a*, $\{S, V, N_a\}$ -- component as defined by Hatsopoulos and Keenan (1965). Given any state of the system, with its values of (S, V, N_a), many other states of the system may have those same values. Each of the states with these values of the constraints has its own value of the energy *E*. Among all of these values of the energy, there can be only one minimum value, and many of the states may have that minimum value.

A state which has the minimum value is said to be *thermostatic*, when subject to the *constraints* (i.e., for this example, when subject to specified values of $\{S, V, N_a\}$).

Figure 1 may be helpful for illustrating the concepts being developed here. The overall *system* consists of two subsystems, 1 and 2, composed of gas *a*, of total fixed amount N_a. At the instant at hand the total entropy is S(t) and total volume is V(t). Traditionally we call any least-energy state which is consistent with S(t) and V(t), *the* equilibrium state of the system at that S and V. Here such a state is called a thermostatic state. This alternative terminology is chosen in order to emphasize that "thermostatic state" is *defined* in a manner which is different from the usual definition for "equilibrium state." Here it is not implied that, at a thermostatic state "nothing moves" or "nothing is happening" or "if the system were isolated, then nothing would happen."

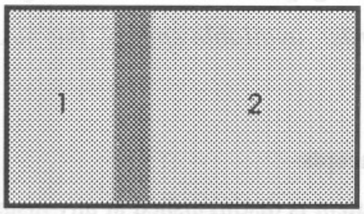

Figure 1

It follows that for thermostatic states there exists a function relating the value of the energy to the constraints. For the case at hand,

$$E_\theta = E_\theta(S, V, N_a) \qquad (3)$$

At *any* state with the values (S, V, N_a) for the constraints, E_θ will be called the *thermostatic* energy of that state, which may of course be less than the actual energy. The function which relates the thermostatic energy to the values of the constraints will be called the *fundamental* thermostatic property relation.

The thermostatic energy, being a function of other properties, is a property of every state.

Any variable which is a function of the constraints alone will be called a thermostatic property. Thus, in addition to E_θ, every derivative of the fundamental property relation is a thermostatic property. For examples, given the function $E_\theta(S, V, N_a)$ then $T_\theta \equiv \partial E_\theta(S, V, N_a)/\partial S$ and $p_\theta \equiv -\partial E_\theta(S,V,N_a)/\partial V$ are thermostatic properties, called the *thermostatic* temperature and pressure respectively. At *any* state, there are associated values of all the thermostatic properties. These *associated* values are in general not identical to *actual* values, just as the thermostatic energy is not identical to the actual energy (except at a thermostatic state).

4. Available Energy

Given any set of constraints, such as {S, V, N_a,}, the corresponding *available energy* at *any* state, is equal to the actual energy minus the thermostatic energy.

$$A(t) \equiv E(t) - E_\theta(t) \qquad (4)$$

For example, with the constraints {S,V,N_a},

$$A(t) = E(t) - E_\theta[S(t), V(t), N_a(t)\,] \qquad (5)$$

Clearly, since $E_\theta(S(t), V(t), N_a(t))$ is the minimum value of energy consistent with the constraints {S(t), V(t), N_a(t)}, the available energy cannot be negative. And it is positive at all but thermostatic states, where the actual energy equals the thermostatic energy.

The value of E_θ and hence the available energy corresponding to one set of constraints will in general differ from that corresponding to another set of constraints.

The available energy of a system which consists of two or more subsystems is not an additive property. That is, if each subsystem is subject to the same constraining properties as the overall subsystem, the sum of the subsystem available energies is generally not equal to the available energy of the overall system. In fact the available energy of every subsystem could be zero -- that is, each could be, alone, at a thermostatic state -- while the available energy of the overall system were positive.

For example, in *Figure 1*, each of the two samples of gas could, alone, be "at equilibrium," while they were not "in equilibrium with each other." Or better, subject to *its* entropy and volume {S_1,V_1} subsystem 1 could be at a thermostatic state, and so could 2 relative to {S_2,V_2}. Whereas, at the same instant, the overall system could be at a state which is not thermostatic relative to the overall {S,V}.

The available energy of a system can be reduced (a) by lowering the energy toward the thermostatic value with no *net* change of the constraints, or (b) by raising the thermostatic energy toward the current value by changing the value of one or more constraints, or (c) by any combination thereof. Any such reduction of the available energy can result in (a) an equal increase in the available energy of another system, (b) a lesser increase, or (c) no increase in the available energy of any other system.

For example, consider the (very) special case where Subsystems *1* and *2* are each, alone, at a thermostatic state, both have the same pressure and the same amounts of each component, but the temperature of *2* is greater than that of *1*. The overall system has positive available energy. We could envision lowering the available energy without net change of any *overall* constraint in several manners: *(a)* The available energy could be obtained from the overall system by removing energy from *2* with entropy and adding energy to *1* with equal amounts of entropy, until the temperatures were equal -- while allowing their pressures to remain equal (but not constant); *(b)* the available energy could be obtained by isentropically compressing *1* and expanding *2* until the temperatures are equal and then -- keeping their temperatures equal (but not constant) -- compressing *2* and expanding *1* until the pressures are equal. In the former case all of the available energy is obtained via the exchange of entropy between the subsystems, and in the latter via the exchange of volume. The *net* energy obtained is the same in both cases, equal to the energy of the initial state of the overall system minus the energy of the thermostatic state corresponding to the initial (S, V). The amount is shown by the shaded area in *Figure* 2a, corresponding to the first scheme, and by the shaded area in *Figure* 2b, corresponding to the second. Although it is *not* recommended, one could say that in Scheme *a* the available energy is obtained as a "useful heat output" and in Scheme *b* it is obtained as a "useful work output." It is true that the "useful heat output" could be converted to the "the useful work output." It is equally true that the "useful work output" could be converted to the "the useful heat output." Therefore, neither is better than the other.

Although only one is *necessary*, the available energy *could be* obtained by any combination of "useful heat" transfers and "useful work" transfers.

Even though available energy is not additive, given (a) any breakdown of an overall system into subsystems, and (b) a set of constraints imposed upon the *overall* system, it is possible to attribute a portion of *its* available energy to each of the subsystems composing it. That portion of the overall available energy attributed to

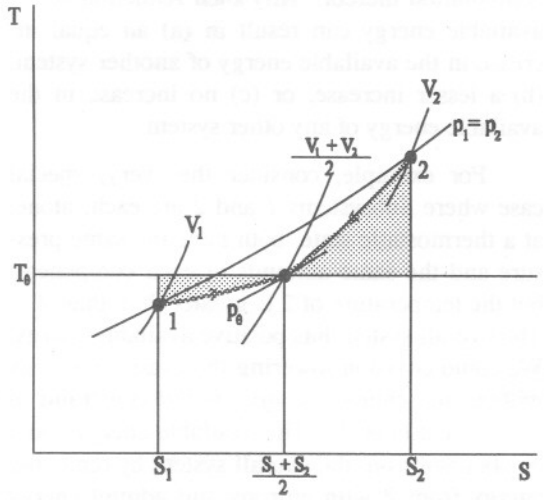

Figure 2(a)

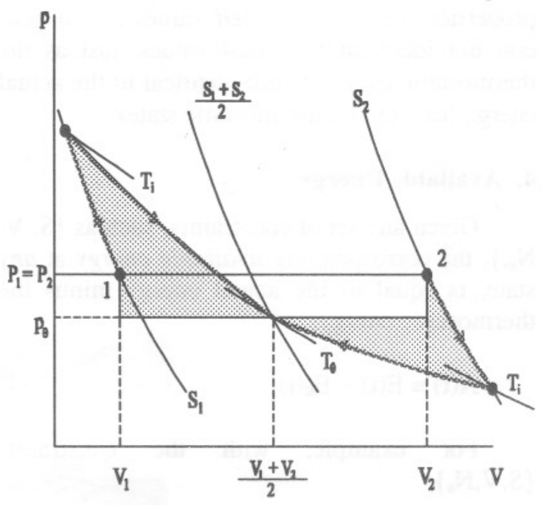

Figure 2(b)

a sub-system is called the *exergy* of the subsystem, to be developed presently. First, though, it is necessary to determine conditions which must be satisfied at a thermostatic state of a system which is a composite of several subsystems.

5. Sufficient Conditions for Thermostatic States

The overall available energy at any state is equal to the actual energy minus the energy at the corresponding thermostatic state. That is, in accord with the preceding equation, A(t) = E(t) minus the energy at the thermostatic state which has the same values of the constraints as the actual state. For simplicity, suppose that the system consists of only two subsystems. Then,

$$E(t) = E_1(t) + E_2(t) \qquad (6)$$

and

$$E_\theta[S(t), V(t), N_a(t)] =$$

$$E_\theta[S_1(t)+S_2(t), V_1(t)+V_2(t), N_{a1}(t)+N_{a2}(t)] \qquad (7)$$

where the function $E_\theta(S, V, N_a)$ is for the overall system.

If, relative to the same set of constraint properties, a subsystem has available energy then so must the overall system have at least as much. Hence, when the overall system is at a thermostatic state, each of its subsystems *must be* at a thermostatic state of its own. So,

$$E_\theta[S(t), V(t), N_a(t)] = E_{1\theta}[S_{\theta1}(t), V_{\theta1}(t), N_{a\theta1}(t)]$$

$$+ E_{2\theta}[S_{\theta2}(t), V_{\theta2}(t), N_{a\theta2}(t)] \qquad (8)$$

Here, the functions $E_{1\theta}(S, V, N_a)$ and $E_{2\theta}(S, V, N_a)$ are those of Subsystem 1 and Subsystem 2, specifically. On the other hand, for example $S_{\theta1}(t)$ denotes the value of the entropy of Subsystem 1 when the overall system is at its thermostatic state with overall entropy equal to S(t). (Notice that the subscript on $S_{\theta1}$ is in the reverse order of the subscript on the function $E_{1\theta}$.)

What are the implications of the last two equations? What necessarily follows from them? Of course, at the thermostatic state of the overall system, the following relations must be satisfied:

$$E_{\theta1}(t) + E_{\theta2}(t) = E_\theta(t) \qquad (9)$$

$$S_{\theta1}(t) + S_{\theta2}(t) = S(t) \qquad (10)$$

$$V_{\theta1}(t) + V_{\theta2}(t) = V(t) \qquad (11)$$

Similar relations hold for $N_a(t)$, but to simplify the deductions suppose that all of the actual states under consideration have fixed values of $N_{a\theta1}$ and $N_{a\theta2}$.

Then, with Equations (9) through (11), at the specified S(t) and V(t),

$$dE_\theta = [\partial E_{1\theta}/\partial S](S_{\theta1}, V_{\theta1})dS_{\theta1}$$

$$+ [\partial E_{1\theta}/\partial V](S_{\theta1},, V_{\theta1})dV_{\theta1}$$

$$+ [\partial E_{2\theta}/\partial S](S_{\theta2}, V_{\theta2})[-dS_{\theta1}]$$

$$+ [\partial E_{2\theta}/\partial V](S_{\theta2}, V_{\theta2})[-dV_{\theta1}] \qquad (12)$$

Since the overall S and V are fixed, $dE_\theta = 0$. Then Equation (12) requires

$$[\partial E_{1\theta}/\partial S](S_{\theta 1}, V_{\theta 1}) = [\partial E_{2\theta}/\partial S](S_{\theta 2}, V_{\theta 2})$$

or

$$T_{1\theta}(S_{\theta 1}, V_{\theta 1}) = T_{2\theta}(S_{\theta 2}, V_{\theta 2}) \qquad (13)$$

$$[\partial E_{1\theta}/\partial V](S_{\theta 1}, V_{\theta 1}) = [\partial E_{2\theta}/\partial V](S_{\theta 2}, V_{\theta 2})$$

or

$$p_{1\theta}(S_{\theta 1}, V_{\theta 1}) = p_{2\theta}(S_{\theta 2}, V_{\theta 2}) \qquad (14)$$

These two *apparently* trivial equations along with Equations (10) and (11) *suffice* to determine values of $S_{\theta 1}$, $V_{\theta 1}$, $S_{\theta 2}$ and $V_{\theta 2}$ which satisfy the requirements for the overall system to be at its thermostatic state.

It is interesting to note, for example, that *if* the constraints imposed upon the system of *Figure* 1 were $\{S, V_1, V_2\}$ then the equality of thermostatic pressure of subsystem 1 and subsystem 2, as indicated by Equation (14), would not be necessary. There are practical instances when such constraints are appropriate (e.g., refrigeration systems, Wepfer and Gaggioli, 1980).

When *any* such values of $S_{\theta 1}$, $V_{\theta 1}$, $S_{\theta 2}$ and $V_{\theta 2}$ -- i.e., values satisfying Equations (10), (11), (13) and (14) -- and corresponding values for $N_{a\theta 1}$, and $N_{a\theta 2}$ are substituted into the right-hand side of Equation (8) and the result, along with Equation (6), is substituted into Equation (5) the following expression for the overall available energy is obtained:

$$A(t) = E_1(t) - E_{1\theta}[S_{\theta 1}(t), V_{\theta 1}(t), N_{a\theta 1}(t)] + E_2(t) - E_{2\theta}[(S_{\theta 2}(t), V_{\theta 2}(t), N_{a\theta 2}(t)] \qquad (15)$$

Then, the available energy of the overall system *could* be represented as a sum over subsystems in the following manner:

$$A(t) = Y(t) = \Sigma_i Y_i(t) \qquad (16)$$

where $Y_i(t)$ is defined by

$$Y_i(t) \equiv E_i(t) - E_{i\theta}[S_{\theta i}(t), V_{\theta i}(t), N_{a\theta i}(t)] \qquad (17)$$

provided that $S_{\theta i}(t)$, $V_{\theta i}(t)$ satisfy Equations (10), (11), (13) and (14) and $N_{a\theta i}(t)$ satisfies the counterpart to those equations. However, the function Y_j would not be a satisfactory representation of subsystem j's contribution to the available energy, because Y_j can be negative. No subsystem can take away from a system's available energy; removing a subsystem from a composite system could not cause its available energy to increase. So, to represent any subsystem's *contribution* to the overall available energy -- a contribution which must be at least zero -- what is needed is a function which is non-negative. Of course, when the subsystem values are added up, the sum must yield the overall available energy.

6. Exergy

When the fundamental thermostatic property relations are homogeneous functions of degree one (i.e., for *simple* systems in the terminology of Gyftopoulos and Beretta, 1991),

$$E_{j\theta}(S_j, V_j, N_{aj}) = T_{j\theta}(S_j, V_j, N_{aj})S_j - p_{j\theta}(S_j, V_j, N_{aj})V_j + \mu_{aj\theta}(S_j, V_j, N_{aj})N_{aj} \qquad (18)$$

From the additivity of energy and of the constraining additive properties, it is straightforward to prove that the subsystem values of $T_{j\theta}(S_j, V_j, N_{aj})$ -- which are equal according to Equation (13) -- are also equal to the overall system value, $T_\theta(S, V, N_a)$. And likewise for $p_{j\theta}$ and $\mu_{aj\theta}$. That is,

$$T_\theta(S_\theta, V_\theta) = T_{1\theta}(S_{\theta 1}, V_{\theta 1}) = T_{2\theta}(S_{\theta 2}, V_{\theta 2}) \qquad (19)$$

$$p_\theta(S_\theta, V_\theta) = p_{1\theta}(S_{\theta 1}, V_{\theta 1}) = p_{2\theta}(S_{\theta 2}, V_{\theta 2}) \qquad (20)$$

$$\mu_{a\theta}(S_{\theta 1}, V_{\theta 1}) = \mu_{a1\theta}(S_{\theta 1}, V_{\theta 1}) = \mu_{a2\theta}(S_{\theta 2}, V_{\theta 2}) \qquad (21)$$

Therefore,

$$\begin{aligned} E_\theta[S(t), V(t), N_a(t)] &= \textstyle\sum_j E_{j\theta}[S_{\theta j}(t), V_{\theta j}(t), N_{a\theta j}(t)] \\ &= \textstyle\sum_j [T_\theta(S,V,N_a)S_{\theta j} \\ &\quad - p_\theta(S,V,N_a)V_{\theta j} \\ &\quad + \mu_{a\theta}(S,V,N_a)N_{a\theta j}] \end{aligned} \qquad (22)$$

Then with $\sum_j V_{\theta j} = V(t)$ and $\sum_j S_{\theta j} = S(t)$ and $\sum_j N_{a\theta j} = N_a(t)$, Equation (22) yields

$$\begin{aligned} E_\theta[S(t), V(t), N_a(t)] &= \textstyle\sum_j [T_\theta(S,V,N_a)S_j - p_\theta(S,V,N_a)V_j \\ &\quad + \mu_{a\theta}(S,V,N_a)N_{a,}] \end{aligned} \qquad (23)$$

Thus, with Equations (5), (6) and (7),

$$\begin{aligned} A(t) = \textstyle\sum_j [&E_j - T_\theta(S,V,N_a)S_j \\ &+ p_\theta(S,V,N_a)V_j - \mu_{a\theta}(S,V,N_a)N_a] \end{aligned} \qquad (24)$$

Hence, with the *exergy* defined for any subsystem j by

$$X_j \equiv E_j - T_\theta(S, V, N_a)S_j + p_\theta(S, V, N_a)V_j - \mu_{a\theta}(S, V, N_a)N_{aj} \quad (25)$$

it follows that

$$A(t) = X(t) \equiv \Sigma_j X_j(t) \quad (26)$$

Thus, the exergy is additive, and the total value equals the overall available energy.

It remains to be proven that the exergy is non-negative. Consider a subsystem state such that S_j differs from $S_{j\theta}$ and/or V_j differs from $V_{j\theta}$. Furthermore suppose that the subsystem is at a state which is thermostatic, relative to the constraints {S,V} and, for convenience, that N_{aj} is fixed so, for subsystem j, $dE = T\,dS - p\,dV$ and

$$dX = T\,dS - p\,dV - T_\theta\,dS + p_\theta\,dV \quad (27)$$

Initially, consider the special case when $T < T_\theta$ at the given state. First, take the subsystem isothermally from the state at (T_θ, p_θ) to a state 1 which has volume equal to that at the given state, then cool at constant volume to reach the given state. Thus, with Equation (27) applied to the first step,

$$\begin{aligned} X_1 &= X_1 - X_\theta \\ &= T_\theta[S_1 - S_\theta] - p_m[V_1 - V_\theta] \\ &\quad - T_\theta[S_1 - S_\theta] + p_\theta[V_1 - V_\theta] \\ &= [p_\theta - p_m][V - V_\theta] \end{aligned}$$

where p_m is the mean value of the integrand. And, applied to the second step,

$$X - X_1 = T_m[S - S_1] - T_\theta[S - S_1]$$

The quantity $X - X_1 = T_m[S - S_1] - T_\theta[S - S_1]$ is positive because for the cooling process $[S - S_1]$ is negative and $T_m < T_\theta$. Furthermore, the quantity $X_1 = [p_\theta - p_m][V_1 - V_\theta]$ is non-negative because either

(a) $[V - V_\theta] > 0$ in which case $p_m < p_\theta$ because of the expansion, or

(b) $[V - V_\theta] < 0$ in which case $p_m > p_\theta$ because of the compression, or

(c) $[V - V_\theta] = 0$. Therefore,

$$X = X_1 + X - X_1 > 0.$$

When $T > T_\theta$ the conclusions are the same, because heating is required to go from state 1 to the given state, so that $[S - S_1] > 0$ and $T_m > T_\theta$.

The foregoing proof is for the case when the given state is thermostatic, and it depends upon the relations $[\partial p_\theta/\partial V]_S > 0$ and $[\partial T_\theta/\partial S]_V > 0$ (e.g., Gyftopoulos and Beretta 1991). If the given state is not thermostatic, then the energy is greater than the thermostatic value and the exergy is all the more positive.

Transfer and production relations.

Changes of the exergy of any system or subsystem can be expressed in terms of productions and transports, hence exergy balances can be written. With Equation (25),

$$\begin{aligned} dX &\equiv dE - T_\theta(S,V,N_a)dS + p_\theta(S,V,N_a)dV \\ &\quad - \mu_{a\theta}(S,V,N_a)dN_a \\ &\quad - S\,dT_\theta + V\,dp_\theta - N_a\,d\mu_{a\theta} \end{aligned}$$

With the Gibbs-Duhem relation for simple states, it then follows that

$$\begin{aligned} dX &\equiv dE - T_\theta(S,V,N_a)dS + p_\theta(S,V,N_a)dV \\ &\quad - \mu_{a\theta}(S,V,N_a)dN_a \end{aligned}$$

In turn, insofar as energy, volume and the amount of *components* are conserved,

$$\begin{aligned} dX &\equiv dE_t - T_\theta(S,V,N_a)dS_t - T_\theta(S,V,N_a)dS_p \\ &\quad + p_\theta(S,V,N_a)dV_t - \mu_{a\theta}(S,V,N_a)dN_{at} \quad (28) \end{aligned}$$

Hence, the change in exergy can be written

$$dX \equiv dX_t + dX_p \quad \text{or} \quad dX \equiv dX_t - dX_d \quad (29)$$

and the usual Gouy-Stodola relation is a result:

$$-dX_p = dX_d = T_\theta(S, V, N_a)\,dS_p \quad (30)$$

If in lieu of components (from which the system has been composed), the symbol $\tilde{N}_i$ represented constrained constituents (species present within the system at the instant t), then the counterpart to Equation (28) would yield

$$\begin{aligned} dX_p &= T_\theta(S, V, \tilde{N}_1, \tilde{N}_2, ...)\,dS_p \\ &\quad - \sum_i \mu_{i\theta}(S, V, \tilde{N}_1, \tilde{N}_2, ...)\,d\tilde{N}_{ip} \end{aligned} \quad (31)$$

Suppose, for example, at the thermostatic state of the system the affinity of a reaction were positive, because of the absence of a reactant.

Then at a state which is not thermostatic, the last term could contribute to dX_p.

From Equations (28) and (29),

$$dX_t = dE_t - T_\theta(S,V,N_a)dS_t + p_\theta(S,V,N_a)dV_t - \mu_{a\theta}(S,V,N_a)dN_{at} \quad (32)$$

Then, with Equation (2), $d\mathbf{E}_t = \sum \mathbf{C}_i \cdot d\mathbf{N}_{ti}$ wherein $d\mathbf{N}_{ti}$ represents a transport of any additive property. Hence, from Equation (32),

$$d\mathbf{X}_{tV} = d\mathbf{E}_{tV} + p_\theta\, d\mathbf{V}_t = -[\mathbf{P} - p_\theta\, \delta]\cdot d\mathbf{V}_t \quad (33a)$$

$$d\mathbf{X}_{tS} = d\mathbf{E}_{tS} - T_\theta\, d\mathbf{S}_t = [\mathbf{T} - T_\theta\, \delta]\cdot d\mathbf{S}_t = d\mathbf{Q} - T_\theta d\mathbf{S}_t \quad (33b)$$

$$d\mathbf{X}_{ta} = d\mathbf{E}_{ta} - \mu_{a\theta}\, d\mathbf{N}_{at} = [\mu_a - \mu_{a\theta}\, \delta]\cdot d\mathbf{N}_{at} \quad (33c)$$

More generally, whatever the constraints $\{N_i\}$ might be,

$$d\mathbf{X}_{ti} = d\mathbf{E}_{ti} - \mathbf{C}_{i\theta}\cdot d\mathbf{N}_{it} = [\mathbf{C}_i - \mathbf{C}_{i\theta}]\cdot d\mathbf{N}_{it} \quad (33)$$

To develop a convenient transfer relation for bulk flow, let the expression for exergy given by Equation (25) be re-presented in the following manner: $X = E - [T_\theta(S,V,N_a)s + p_\theta(S,V,N_a)v - \mu_{a\theta}(S,V,N_a)n_a]m$. Then,

$$d\mathbf{X}_{tm} = d\mathbf{E}_{tm} - [T_\theta(S,V,N_a)\, s + p_\theta(S,V,N_a)\, v - \mu_{a\theta}(S,V,N_a)n_a]\, d\mathbf{m}_t \quad (33d)$$

7. Conclusions

Available energy has been defined for every state of any system. The definition is independent of (a) the concept of work, (b) any reference environment, and (c) the make-up of the system.

No distinction between "heat" and "work" has been employed because any such distinction is, as shown, unnecessary. Furthermore, it is held to be erroneous to contend that "a work transfer of energy is better -- more valuable -- than a heat transfer thereof." To state that (everything else being equivalent) work can always be used as a substitute for heat is erroneous. For example, consider Equations (33a) and (33). Energy extracted from a system with an expansion "work transfer" cannot, totally, be substituted for any "heat transfer" dead-state pressure p_θ were zero. It it is conceivable to have $p_\theta = 0$, then it is conceivable to have $T_\theta = 0$ so that a "heat transfer" could then be substituted for any "work transfer." To imply to students that a work transfer of energy is fundamentally better than a heat transfer thereof is pedagogically unsound and confusing.

As amply illustrated by *Figure* 2, the available energy of a system can be extracted via work transfers or heat transfers or any combination of the two.

Dead State. No mention has been made of any reference environment for exergy nor, explicitly, to the concept of "dead state." The thermostatic state of *the* isolated system is conceptually sufficient, in lieu of "reference environment," and that thermostatic state *is* the "dead state." The appropriate dead state for engineering calculations is determined by (a) the engineering system of interest and the systems with which it interacts, and (b) the modes of (i) interaction between all of these systems, and (ii) spontaneous changes within each system, conceived for modeling the systems. These modes are the *constraints*, which the definitions of available energy of the isolated system and the subsystem exergies, as well as the sufficient conditions for the thermostatic (i.e., dead) state depend upon.

It is not the intent to criticize much important, excellent work which has been carried out to help determine the appropriate contents of the isolated system and appropriate thermostatic states -- *including* constraints needed to define them -- but to elucidate what is essential. This is not only of fundamental importance but also of practical. For example, the engineer's choice of the isolated system should not include subsystems which, if added, would increase the available energy but at greater marginal cost. Also, the choice of constraints should be adequate to maintain the integrity of the subsystem-equipment.

Closure. On the basis of the available energy defined herein, given any composite system, it has been shown (a) how to determine sufficient conditions to be satisfied at the instantaneous "dead state" of the composite and each subsystem, (b) how to define the contribution of each subsystem to the available energy -- that is, the exergy *content* of a subsystem so that exergy balances can be written, (c) how to determine exergy transfers in terms of transports of other additive properties, (d) how to determine the generalized Gouy-Stodola relation, which may have important consequences associated with productions other than entropy.

This last statement certainly reflects upon the Second Law of Thermodynamics, for which no explicit statement has been made in this article. One might state the second law as, "The available energy of the isolated system decreases as a consequence of all real processes, and is conserved only with hypothetical ideal processes." However, the author believes that this is only a corollary of a more fundamental statement, which would include "the equation of motion" referred to by Gyftopoulos and Beretta (1991), as "one of the most intriguing and challenging problems in physics."

Little reference has been made to the "state principle" in this paper, although its domain has been elucidated. An important aspect, which hopefully will be further developed in future articles, is the relevance of the work presented here to the selection of appropriate properties for the conventional modeling of "nonequilibrium processes,." (Gaggioli 1996).

Nomenclature

A	Available energy content
C	Transport coefficient
E	Energy content
N	Additive property
N_a	Content of component a
$\tilde{N}_i$	Content of constituent I
m	Mass
n_a	Specific amount of component a
p	Thermostatic pressure
S	Entropy content
s	Specific Entropy
T	Thermostatic temperature
t	Time instant
V	Volume content
v	Specific volume
X	Energy content
μ_a	Component potential of species a
$\tilde{\mu}_i$	Constituent potential of species I

Subscripts

a	Component a
i	Index
j	Subsystem j
m	Mean value
p	Production
t	Transport
1	Subsystem 1
2	Subsystem 2
θ	Thermostatic

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