THE THERMODYNAMIC FUNDAMENTALS OF EXERGY

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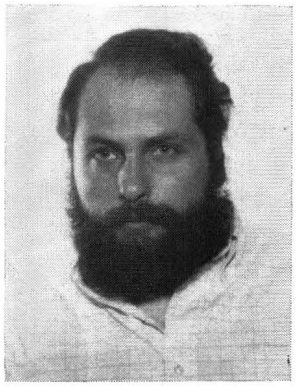

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AVAILABILITY IS A thermodynamic function whose difference between any two states of a system gives the limiting (reversible) value of work associated with a given change and environment conditions. Changes in availability, therefore, can be used to evaluate the thermodynamic performance of a process.

Exergy is shown to be an extension of the concept of availability when it becomes necessary to quantify a flowing stream's capacity to produce useful work, given stream and environment conditions. Exergy can therefore be thought of as a property of the stream (for a given environment), and can be used as a basis for assigning an economic value to it, based on its work producing capacity.

A stream's exergy is a function of the reference environment. Since this choice is completely arbitrary, except for the requirement that the environment be in equilibrium, computed values of exergy and exergetic efficiency can only be used for comparison (for a given reference state), not in an absolute sense. The equilibrium constraint, on the other hand, eliminates from consideration many realistic, non-equilibrium environments.

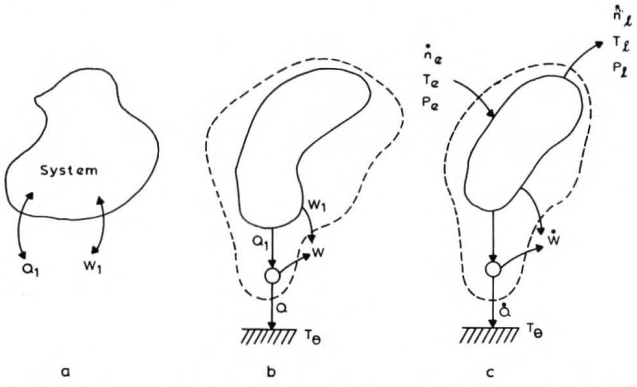

FIGURE 1. a) Closed system. b) Closed system showing boundaries needed for availability analysis. c) Open system showing boundaries needed for availability analysis.

Once these limitations are understood, however, exergy can be fruitfully used in process analysis and design, in cases where it is necessary to quantify the efficiency with which useful work is obtained from the process streams [1-9]. The thermodynamic fundamentals of exergy are developed below, emphasizing similarities and differences between exergy and availability.

AVAILABILITY

Availability is a thermodynamic function whose difference between any two given equilibrium states of a system is a measure of the maximum work obtainable from (or the minimum work required to effect) the given change. Since, as will be shown below, the concept of exergy follows quite naturally from the closely related thermodynamic function known as availability, the latter will be considered first.

Consider (Fig. 1.a) a closed, simple system i.e., a system whose boundaries are impermeable to mass flow, contains no internal adiabatic, impermeable, or rigid boundaries, and is not acted upon by force fields or inertial forces [10]. For the present analysis, the environment with which the system interacts can be imagined as consisting

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of a heat reservoir [11] at a temperature T_θ, and an isobaric work reservoir at a pressure P_θ. For any differential process, we can write (Fig. 1.a)

$$d\underline{U} = \delta Q_1 - \delta W_1 \tag{1}$$

where δQ_1 and δW_1 represent inexact differentials. Now consider Fig. 1.b, where any Carnot engine needed to transfer heat reversibly between the system and the environment has been added. The following relations apply

$$d\underline{S}_r = -\frac{\delta Q}{T_\theta} \tag{2}$$

$$d\underline{S}_s = \frac{\delta Q}{T_\theta} + \delta\underline{S}^* \tag{3}$$

$$d\underline{U} = \delta Q - \delta W \tag{4}$$

$$\delta\underline{S}^* \geq 0 \tag{5}$$

where δS^* is the entropy created as a result of the (irreversible) processes occurring within the boundaries shown in Fig. 1.a. Therefore

$$\delta W + T_\theta\, \delta\underline{S}^* = T_\theta\, d\underline{S} - d\underline{U} \tag{6}$$

For finite changes

$$W + T_\theta\underline{S}^* = T_\theta\Delta\underline{S} - \Delta\underline{U} \tag{7}$$

Since we are interested in useful work, we must subtract from W the portion that constitutes expansion work against the surrounding pressure. For reversible operation, therefore, the maximum useful work that can be obtained from a closed system in going from a specified initial to a specified final state, while interacting with surroundings at P_θ and T_θ, is

$$W_{max,net} = T_\theta(\underline{S}_f - \underline{S}_i) - (\underline{U}_f - \underline{U}_i) - P_\theta(\underline{V}_f - \underline{V}_i) \tag{8}$$

Eq. (8), as written, is not restricted to cases where $\underline{V}_f > \underline{V}_i$. If a partially evacuated container fitted with a frictionless piston and filled with an ideal gas is compressed reversibly and isothermally by the surroundings up to P_θ, the work obtained is now $P_\theta(\underline{V}_i - \underline{V}_f)$ minus the compression work done by the environment on the container, $T_\theta(\underline{S}_i - \underline{S}_f)$.

The right hand side of Eq. (8) is only a function of the end states, T_θ and P_θ; the following state function is normally called availability

$$-\underline{B} = T_\theta\underline{S} - \underline{U} - P_\theta\underline{V} \tag{9}$$

so that finally

$$W_{max,net} = -\Delta\underline{B} \tag{10}$$

If we now consider an open system, under steady

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state conditions, the First Law now yields, (Fig. 1.c)

$$0 = \dot{Q} - \dot{W} + \sum_e H_e\dot{n}_e - \sum_\ell H_\ell\dot{n}_\ell \tag{11}$$

where summations are over all entering and leaving streams, respectively, and $\dot{n}_e$ may differ from $\dot{n}_\ell$ if chemical reactions occur. The corresponding entropy balance, with T_θ denoting the heat reservoir's temperature, reads

$$0 = \frac{\dot{Q}}{T_\theta} + \dot{\underline{S}}^* + \sum_e S_e\dot{n}_e - \sum_\ell S_\ell\dot{n}_\ell \tag{12}$$

substituting for $\dot{Q}$

$$\dot{W} = \sum_e (H_e - T_\theta S_e)\dot{n}_e - \sum_\ell (H_\ell - T_\theta S_\ell)\dot{n}_\ell - T_\theta\dot{\underline{S}}^* \tag{13}$$

For reversible operation

$$\dot{W}_{max} = \sum_e (H_e - T_\theta S_e)\dot{n}_e - \sum_\ell (H_\ell - T_\theta S_\ell)\dot{n}_\ell \tag{14}$$

As before (see Eq. 8), the maximum (reversible) work obtainable is a function only of the end states and the environment's conditions. Accordingly, we can define an availability for flow systems [3]

$$B' = H - T_\theta S \tag{15}$$

$$W_{max} = \sum_e B'_e\dot{n}_e - \sum_\ell B'_\ell\dot{n}_\ell \tag{16}$$

Given an environment which is the sole net heat source (or sink) with which the system under consideration interacts, and which is characterized by T_θ and P_θ (closed systems) or T_θ (open systems), differences in availability, therefore, represent limiting values for the maximum (minimum) work that can be obtained from (that is required to achieve) any given change.

EXERGY

If we define efficiency as $\dot{W}/\dot{W}_{max}$, it follows from the preceding discussion that, for open systems under steady state conditions and with given end states, the thermodynamic performance (efficiency) of a process can be analyzed by means of the function known as availability.

Even though availability is a property of the

stream (given T_θ), only changes in availability are of interest, since B′ is only defined up to an arbitrary constant. Exergy is a function introduced to overcome this limitation; this is done by selecting an equilibrium environment as the reference state. Then, the availability change arising from the complete equilibration of any given stream with the environment is defined as the stream's exergy.

Specifically, for a flowing process stream of components $1, \ldots, j, \ldots, n$ at arbitrary conditions T, P, y_j, exergy is defined as the maximum work (per mole of stream) that can be obtained upon its equilibration with the environment, the latter being characterized by T_θ, P_θ and $\hat{\mu}_{j\theta}$, when heat interactions take place with a single source-sink at T_θ. Here, $\hat{\mu}_{j\theta}$ denotes the chemical potential of component j in the environment.

$$\text{Exergy} = \psi = H_e(T_e,P_e,y_{je}) - T_\theta S_e(T_e,P_e,y_{je}) - \sum_{j=1}^{n} y_{je}\hat{\mu}_{j\theta}(T_\theta,P_\theta,y_{j\theta}) \qquad (17)$$

$$\dot{W}_{max} = \left(\sum_{j=1}^{n} \dot{n}_j\right)\left(H_e - T_\theta S_e - \sum_{j=1}^{n} y_{je}\hat{\mu}_{j\theta}\right) \qquad (18)$$

Eq. (18) can be obtained either by direct calculation of the various heat and work interactions resulting from the reversible equilibration process, or by setting outlet conditions equal to environment conditions in Eq. (16).

In analyzing any particular process, therefore, availability balances can be made around the various process blocks (unit operations) to determine thermodynamic efficiencies. Exergy, on the other hand, is useful if, in addition to the thermodynamic efficiency of a given unit operation, we are interested in analyzing how the overall process utilizes the capacity to produce useful work of all its streams.

An availability balance around a turbine, for example, will yield a value for its isoentropic efficiency. The exhaust stream exergy, however, is not taken into account in such an analysis. If the exhaust stream is neither recycled nor used downstream, for example, it should have as low an exergy as possible. For energy recovery schemes, on the other hand, a compromise must be reached between exhaust exergy and power output.

It should be emphasized, however, that since the choice of the reference environment is arbitrary, except for the requirement that it must be in chemical equilibrium, comparisons are only meaningful for a particular ground state.

EXERGY BALANCES

In defining exergy, the requirement that the environment be in chemical equilibrium has been introduced at the outset, since exergy has been defined as a maximum work. It should be clear that only in the limit where equilibration with the environment occurs reversibly is the resulting work maximum and path-independent. If irreversibilities are allowed in the hypothetical equilibration process, then the work becomes path-dependent and exergy loses its meaning; it is no longer meaningful to quantify a stream's capacity for producing work, since we no longer have a "measuring rod" (the maximum work). In this section, the above considerations will be translated into thermodynamic relationships and the concept of an exergy balance will be developed.

Consider (Fig. 2) a steady process. Whenever heat interactions result in a finite change in process temperature, an infinite series of differential Carnot engines, rather than a single engine, must be used. Since there may be any number of such infinite series, with $\dot{Q}_1$ referring to the system (see Eq. (1) for sign convention)

$$\dot{W}_{Carnot} = -\sum \int \eta\, \delta\dot{Q}_1 \qquad (19)$$

where the summation has as many terms as process temperature changes, and η is the Carnot efficiency, $1 - T_\theta/T$. Therefore

$$\dot{W} = \sum \dot{W}_1 - \sum \int \eta\, \delta\dot{Q}_1 \qquad (20)$$

where the first summation contains as many terms as there are adiabatic work interactions

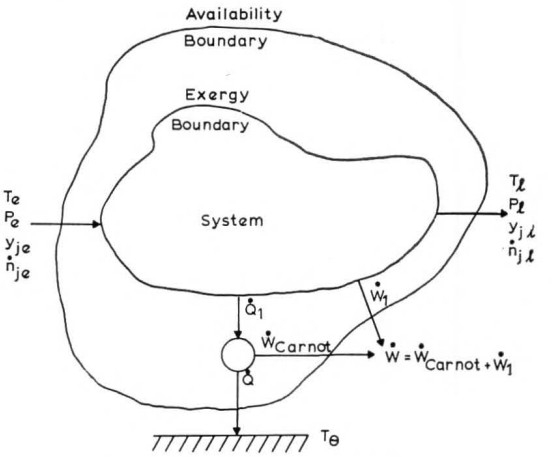

FIGURE 2. Open system. Availability and exergy boundaries are shown.

across the exergy boundary (Fig. 2).

Eq. (13) can now be rewritten in terms of heat and work interactions taking place across the exergy boundary (the actual system's boundary)

$$\sum \dot{W}_l - \sum \int \eta\, \delta\dot{Q}_l = \sum_e (H_e - T_\theta S_e)\dot{n}_e - \sum_\ell (H_\ell - T_\theta S_\ell)\dot{n}_\ell - T_\theta \dot{\underline{S}}^* \quad (21)$$

To obtain an exergy balance, consider the quantity

$$\underline{X} = \sum_e \left(\sum_{j=1}^{n} y_{je}\hat{\mu}_{j\theta}\right)\dot{n}_e - \sum_\ell \left(\sum_{j=1}^{n} y_{j\ell}\hat{\mu}_{j\theta}\right)\dot{n}_\ell \quad (22)$$

Rearranging

$$\underline{X} = \sum_{j=1}^{n} \dot{n}_{je}\hat{\mu}_{j\theta} - \sum_{j=1}^{n} \dot{n}_{j\ell}\hat{\mu}_{j\theta} = \sum_{j=1}^{n} (\dot{n}_{je} - \dot{n}_{j\ell})\hat{\mu}_{j\theta} \quad (23)$$

For non-reacting components, $\dot{n}_{je} = \dot{n}_{jl}$; for reacting components, on the other hand, stoichiometric constraints apply, so that

$$\sum_{j=1}^{n} (\dot{n}_{je} - \dot{n}_{j\ell})\hat{\mu}_{j\theta} = (\dot{n}_{ke} - \dot{n}_{k\ell}) \sum_{j=1}^{n} \nu_j \hat{\mu}_{j\theta} \quad (24)$$

where $(\dot{n}_{ke} - \dot{n}_{kl})$ is the reaction rate (molar basis) of any arbitrary reacting component, and ν_j is the j^{th} component's stoichiometric coefficient.

The summation on the right hand side of Eq. (24) represents the sum of Gibbs energy changes resulting from all reactions actually taking place in the process under consideration, if they were to occur in the environment. However, as discussed above, the latter must be in equilibrium, hence these chemical potentials must necessarily satisfy

$$\sum_{j=1}^{n} \nu_j \hat{\mu}_{j\theta} = 0 \quad (25)$$

Eq. (25) is a direct consequence of the equilibrium constraint without which, as discussed above, exergy cannot be defined. Its significance can best be shown by means of an example: suppose we consider a process where the reaction

$$CO + \tfrac{1}{2}\, O_2 \rightarrow CO_2$$

takes place. Then, for an environment containing specified mole fractions of CO_2 and O_2, and no measurable amount of CO, the equilibrium constraint imposes a non-zero, trace mole fraction of CO. As will be shown in the next section, in calculating the exergy of a flowing stream, this quantity is explicitly or implicitly calculated.

Because of Eq. (25), we can now rewrite Eq. (21) as an exergy balance

$$\sum \dot{W}_l - \sum \int \eta\, \delta\dot{Q}_l = \sum_e \left(H_e - T_\theta S_e - \sum_{j=1}^{n} y_{je}\hat{\mu}_{j\theta}\right)\dot{n}_e - \sum_\ell \left(H_\ell - T_\theta S_\ell - \sum_{j=1}^{n} y_{j\ell}\hat{\mu}_{j\theta}\right)\dot{n}_\ell - T_\theta \dot{\underline{S}}^* \quad (26)$$

Taking into account the definition of exergy,

$$\sum \dot{W}_l - \sum \int \eta\, \delta\dot{Q}_l = \sum_e \psi_e \dot{n}_e - \sum_\ell \psi_\ell \dot{n}_\ell - T_\theta \dot{\underline{S}}^* \quad (27)$$

From Eq. (20), it follows that the left hand side of Eqs. (13) and (27) are identical. Consequently, so are the respective right hand sides. Thus, from a strictly thermodynamic viewpoint, no new information has been gained from the introduction of exergy. Moreover, in deriving Eq. (27), the condition of chemical equilibrium has been imposed upon the environment.

It is the above mentioned possibility of using exergy as a basis for the quantification of the work producing capacity of a stream that justifies its use, at the expense of introducing arbitrary restrictions on the environment's characteristics. Exergetic efficiency is defined as

$$\eta_{ex} = \frac{\text{rate of generalized exergy transport from control volume}}{\text{rate of generalized exergy transport into control volume}} \quad (28)$$

In computing exergy flows,

- exergy associated with any stream is given by

$$(H - T_\theta S - \sum_{j=1}^{n} y_j \hat{\mu}_{j\theta})$$

- heat interactions are converted into exergy flows by introducing a Carnot efficiency (thus, for example, if the process were isothermal and $T_e = T_l = T_\theta$, there would be no heat flux contribution to exergy even under non-adiabatic conditions).
- all work interactions are equal to corresponding exergy fluxes. Therefore,

$$\eta_{ex} = \frac{\sum_\ell (H_\ell - T_\theta S_\ell - \sum_{j=1}^{n} y_{j\ell}\hat{\mu}_{j\theta})\dot{n}_\ell + \sum \dot{W}_l - \sum \int \eta\, \delta\dot{Q}_l}{\sum_e (H_e - T_\theta S_e - \sum_{j=1}^{n} y_{je}\hat{\mu}_{j\theta})\dot{n}_e} = 1 - \frac{T_\theta \dot{\underline{S}}^*}{\sum_e (H_e - T_\theta S_e - \sum_{j=1}^{n} y_{je}\hat{\mu}_{j\theta})\dot{n}_e} \quad (29)$$

If thermodynamic efficiency is evaluated using availability rather than exergy, then, from Eq. (13) we obtain

$$\eta = \frac{\dot{W} + \sum_{\ell} (H_\ell - T_\theta S_\ell)\dot{n}_\ell}{\sum_{e} (H_e - T_\theta S_e)\dot{n}_e} = 1 - \frac{T_\theta \dot{S}^*}{\sum_{e} (H_e - T_\theta S_e)\dot{n}_e} \quad (30)$$

which has a different numerical value than η_{ex}. As stated before, availability balances provide a complete description of the efficiency of the process under study. Exergy is introduced when, in addition, streams are ranked according to their potential for work production.

In Eq. (29) it must be noted that, if some work interaction terms are negative, or any heat interaction terms are positive, they should be included in the denominator with a positive sign according to the definition in Eq. (28). Eq. (29), as written, is only valid for positive work and negative heat interactions. (See Eq. (1) for sign convention.)

CALCULATION OF THE EXERGY OF A FLOWING STREAM

Eq. (17) can be rewritten as follows,

$$\psi = H(T,P,y) - T_\theta S(T,P,y) - H(T_\theta,P_\theta,y) + T_\theta S(T_\theta,P_\theta,y) + \sum_{j=1}^{n} y_j\left[\bar{H}_j(T_\theta,P_\theta,y) - T_\theta \bar{S}_j(T_\theta,P_\theta,y) - \hat{\mu}_{j\theta}\right] \quad (31)$$

This can be expressed as

$$\psi = \int_{T_\theta}^{T} C_p(P)\left(1 - \frac{T_\theta}{T}\right)dT + \int_{P_\theta}^{P} R/P\left(\frac{\partial Z(T_\theta)}{\partial 1/T}\right)_p dP + T_\theta \int_{P_\theta}^{P} \frac{R}{P}\left[Z(T_\theta) + T_\theta\left(\frac{\partial Z(T_\theta)}{\partial T}\right)_p\right] dP + \sum_{j=1}^{n} y_j\left[\hat{\mu}_j(T_\theta,P_\theta,y_j) - \hat{\mu}_{j\theta}(T_\theta,P_\theta,y_{j\theta})\right] \quad (32)$$

If we consider the case of an ideal gas stream,

$$\psi = \int_{T_\theta}^{T} C_p\left(1 - \frac{T_\theta}{T}\right)dT + RT_\theta \ln \frac{P}{P_\theta} + \sum_{j=1}^{n} y_j(\hat{\mu}_j - \hat{\mu}_{j\theta}) \quad (33)$$

In the exergy literature, the three terms on the right hand side are called,

- **"thermal availability"**
- **"pressure availability"**
- **"chemical availability"**

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P-V-T data are needed in order to evaluate the pressure availability for streams which cannot be treated as ideal gases.

The last contribution to Eq. (33) is the work that can be obtained when a stream component already at T_θ and P_θ is reversibly equilibrated with the environment.

As an example, suppose a stream contains CO, while the reference environment contains quantities of O_2 and CO_2. Then, for an equilibrium environment containing CO_2 and O_2

$$\hat{\mu}_{\theta CO} + \tfrac{1}{2}\hat{\mu}_{\theta O_2} - \hat{\mu}_{\theta CO_2} = 0 \quad (34)$$

Assuming ideal gas behavior, and for P_θ = 1 bar

$$\hat{\mu}_{\theta i} = \mu_i^\circ(T_\theta) + RT_\theta \ln y_{\theta i} \quad (35)$$

which, when substituted into Eq. (34), yields

$$RT_\theta \ln y_{\theta CO} = \Delta G^\circ(T_\theta) - RT_\theta[\ln y_{\theta CO_2} - \tfrac{1}{2}\ln y_{\theta O_2}] \quad (36)$$

so that, finally,

$$\hat{\mu}_{CO}(T_\theta,P_\theta,y_{CO}) - \hat{\mu}_{\theta CO}(T_\theta,P_\theta,y_{\theta CO}) = RT_\theta \ln \frac{y_{CO}}{y_{\theta CO}} \quad (37)$$

with $RT_\theta \ln y_{\theta CO}$ calculated from Eq. (36).

Since the right hand side of Eq. (36) does not contain $y_{\theta CO}$, it might be thought that the same result can be attained without the equilibrium constraint, just by specifying $y_{\theta CO_2}$ and $y_{\theta O_2}$, and setting the environmental content of CO to 0. However, in this alternate approach, Eq. (36) is arrived at by considering a series of reversible steps, one of which inevitably involves chemical reaction which, for maximum work, can only take place in an equilibrium environment (van't Hoff box). Thus, it is the inclusion of the equilibrium reaction vessel rather than the neglect of the equilibrium constraint that characterizes this approach. In the present paper, on the other hand, the van't Hoff box is indistinguishable from (and belongs to) the environment. It is important to understand, however, that equilibrium must always be assumed when calculating maximum work.

CONCLUSIONS

Availability contains all the thermodynamic information necessary for a Second Law analysis of efficiency. Exergy introduces no new thermodynamic information, but is useful in ranking process streams according to their potential for producing useful work. Hence, it is used to treat problems that require both economic and thermodynamic analysis [1, 2, 6, 7].

The following limitations, however, should be borne in mind:

1) An environment which is in stable thermodynamic equilibrium eliminates from consideration many realistic choices of environments whose components are not in equilibrium, but are prevented to react by kinetic barriers.

2) Although thermodynamic consistency is required in the selection of an equilibrium environment, such a choice, once consistency is satisfied, is completely arbitrary, and, moreover, the results are sensitive to the stable components selected.

3) The present analysis is limited to cases where the system under consideration exchanges heat with a single reservoir. □

REFERENCES

1. Evans, R. B. and M. Tribus, "Thermo-Economics of Saline Water Conversion," *Ind. & Eng. Chem.* (Proc. Des. & Dev.) *4* (2), 195-206, 1965.
2. Gaggioli, R. A. and P. J. Petit, "Use the Second Law, First," *Chemtech*, 7, 496-506, 1977.
3. Sussman, M. V., "Steady-Flow Availability and the Standard Chemical Availability," *Energy, 5*, 793-802, 1980.
4. DeNevers, N. and J. D. Seader, "Lost Work: A Measure of Thermodynamic Efficiency," *Energy, 5*, 757-769, 1980.
5. Szargut, J., "International Progress in Second Law Analysis," *Energy, 5*, 709-718, 1980.
6. El-Sayed, Y. M. and M. Tribus, "The Strategic Use of Thermoeconomic Analysis for Process Improvement," AIChE National Meeting; Detroit, MI, August 16-19, 1981.
7. Tsatsaronis, G., P. Schuster, and H. Rörtgen, "Exergy Analysis of the Nuclear Coal Hydrogasification Process," AIChE National Meeting; Detroit, MI, August 16-19, 1981.
8. Evans, R. B., Ph.D. Thesis, Dartmouth College, Hanover, NH, 1969.
9. Moran, M., *Availability Analysis: A Guide to Efficient Energy Use;* Prentice-Hall, Englewood Cliffs, N.J., 1982.
10. Modell, M. and R. C. Reid, *Thermodynamics and its Applications*, 1st Ed., Chapter 2, Prentice-Hall, 1974.
11. Denbigh, K., *The Principles of Chemical Equilibrium*, 4th Ed., Chapter 1, Cambridge University Press, 1981.

NOMENCLATURE

B	availability (J)
B'	open system flow availability (J/mole)
C_p	molar heat capacity (J/mole·K)
H	stream molar enthalpy (J/mole)
$\dot{n}$	molar flow rate (mole/s)
p	partial pressure (N/m^2)
P	pressure (N/m^2)
Q	heat interaction (J)
$\dot{Q}$	rate of heat interaction (W)
R	gas constant (8.3144 J/mole·K)
S	stream molar entropy (J/mole·K)
S	entropy (J/K)
S^*	created entropy (J/K)
$\dot{S}^*$	rate of entropy creation (W/K)
T	temperature (K)
U	energy (J)
V	volume (m^3)
W	work interaction (J)
$\dot{W}$	rate of work interaction (W)
X	defined in text
y	mole fraction
Z	compressibility factor
η	Carnot efficiency
η_{ex}	exergetic efficiency
ν	stoichiometric coefficient
ψ	exergy (J/mole)
μ°	molar free energy of formation at T_θ and P_θ (J/mole)
$\hat{\mu}$	component chemical potential in mixture (J/mole)

Subscripts

1	refers to boundary shown in Fig. 1.a or exergy boundary
e	entering stream
f	final state
i	initial state
j	jth component
l	leaving stream
r	heat reservoir
s	system
θ	environment conditions (T_θ, P_θ, $y_{j\theta}$)
$-$	extensive property

Superscripts

$-$	partial molar property
0	standard conditions