ENERGY CONVERSION SYSTEMS
and
EXERGY

Nomenclature

A	Availability
Cp	Constant pressure specific heat
Cv	Constant volume specific heat
E	Total thermodynamic energy
EX	Exergy
ex	Specific exergy
$\overline{ex}$	Molal specific
G	Gibbs free energy
g	Specific free energy, gravitational acceleration constant
$\bar{g}$	Molal specific free energy
g_c	Gravitation constant
H	Enthalpy
h	Specific enthalpy
$\bar{h}$	Molal specific enthalpy
I	Irreversibility
i	Specific irreversibility
J	Mechanical equivalent of heat, 778.26 ft-lb per btu
KE	Kinetic energy
LHV	Lower heating value of a fuel
M	Molecular weight
m	Mass

N	Number of moles
P	Pressure (lower case designates partial pressure)
PE	potential energy
Q	Heat transfer
q	Specific heat transfer
R	Gas constant, energy grade function
S	Entropy
s	Specific entropy
$\bar{s}$	Molal specific entropy
T	Temperature
t	Time
U	Internal energy
u	Specific internal energy
$\bar{u}$	Molal specific internal energy
u'	utilization factor
V	Velocity
$\forall$	Volume
v	Specific volume
$\bar{v}$	Molal specific volume
W	Work
w	Specific work
Z	Elevation above datum plane

Greek Symbols:

ϵ	Effectiveness
η	Efficiency Chemical
μ	Potential

Subscripts:

j	Relating to the jTH specie in a mixture
o	Relating to the dead state
rev	Denotes a reversible process
e	Exit
i	Inlet
1.	Initial state
2.	Final state
surr	Denotes surroundings
max	Maximum
min	Minimum
ave	Average
cv	Control volume
HE	Heat engine
tot	Total

Overscripts:

. (dot)	Over a variable, denotes rate quantity.

c_{ex}: specific exergetic cost, J/J
c_w: monetary cost of work, $/J
e: specific exergy of stream, J/kg
E: total exergy flow, W
ee: specific extended exergy, J/kg
h: specific total enthalpy, J/kg
I: exergy input flow, W
K_{Cap}: monetary equivalent of exergy, $/MJ
K_{Lab}: exergetic equivalent of Labour, MJ/(work/hour)
m: mass flow rate, kg/s
n: number of individuals
O: exergy flow output, W
PF: plant factor [(equivalent operating hours per year)/8760]
R: Capital Recovery Factor (Sect. 7)
R: Gas constant, kJ/(kg K)
s: specific entropy, J/(kg °K)
T: Temperature, °K
w: specific work, J
β: compression ratio
ε: exergetic conversion efficiency
η: energetic conversion efficiency
μ: chemical potential, J/kg
ζ: environmental penalty factor

EXERGY ANALYSIS OF ENERGY CONVERSION SYSTEMS

The idea of available energy dates back to the last century, when it was first understood by the French engineer Sadi Carnot for the specialized case of heat engines. In the next decades the concept of “available work” was further developed theoretically, especially by Herman Helmholtz and J. Willard Gibbs. It has been applied to many kinds of processes, for different purposes, under several different names–availability, available work, essergy, physical information – but only recently has a standard definition been formulated and the name *exergy* definitely adopted (Rant 1956; Gyftopoulos *et al.* 1974; Wall 1977; Szargut *et al.* 1988). However, for the purposes of this study, it is sufficient to present only the essential features of the theory. An adequate definition of exergy is the following: “Exergy is the amount of work obtainable when some matter is brought to a state of thermodynamic equilibrium with the common components of the natural surroundings by means of reversible processes, involving interaction only with the above–mentioned components of nature” (Szargut *et al.* 1988). In short, exergy is an extensive nonconservative variable, which synthesizes in a concise and useful expression both the first and second law of thermodynamics. It is definable and computable (in principle) for any substance, or system, with respect to the real environment in which the system is located and/or operates. In principle, four different types of exergy B can be identified. These are denoted, respectively, as kinetic, potential, physical and chemical exergy, viz. The exergy method of energy systems analysis uses a combined statement of the first and second laws of

thermodynamics to evaluate the performance of energy conversion processes. Exergy is a thermodynamic property that represents the maximum useful work theoretically available from a fuel, fluid or mass as a result of nonequilibrium with a specified reference system, usually the surroundings. As such, it provides a relative measure of energy resource quality, regardless of form.

Exergy equations for closed systems and steady flow open systems are derived in this paper using the control volume approach. A historical background tracing the development of exergy analysis is presented. Also included are discussions regarding the selection of a suitable reference system for exergy calculations, and on defining efficiency parameters for performance evaluation. A discussion of no technical factors that must also be considered in conjunction with exergy analysis and energy system design is also provided.

Introduction

Modern industrial society generally uses high quality energy resources to provide either high quality or low quality energy output, depending on the end use requirement. 8igh quality energy resources are those that have a high potential for conversion to useful work. Petroleum, natural gas and fissionable materials are examples of high quality energy resources. Conversely, low quality energy has relatively little potential for conversion to useful work.

Intuitively, something of value is lost when high quality energy is degraded into low quality energy in a process. Traditional methods of energy accounting, which are based on the first law of thermodynamics, cannot quantify this loss in conversion effectiveness. Analyses incorporating the second law of thermodynamics, however, provide a quantitative measure of the effectiveness of a process in utilizing the thermodynamic potential of a resource or energy supply.

Using the second law of thermodynamics in conjunction with the first law offers three basic methods of analysis:

1. Analyses based on entropy production.
2. Analyses based on the method of lost work.
3. Analyses based on exergy and irreversibility.

All three of these have been broadly categorized as •second law analysis" in contemporary literature. Actually, only the first of these is strictly based on the second law (performance measured by entropy production). The second two methods rely upon combined statements of the first and second laws, with the equations solved simultaneously rather than separately. Although each varies in approach, all three methods will ultimately lead to the same result. That is, they will provide a quantitative measure of energy degradation in conversion processes.

Although the benefits are generally understood, practical use of the second law in industry has been slow to emerge. One reason cited for its lack of acceptance is the disagreement in defining methodology and terminology (1). A survey of literature on the subject revealed that there is indeed considerable debate regarding convention. Other reasons cited include the lack of specific data regarding the benefits of using the second law in energy systems analysis, and the complexity of the concept and the difficulty in defining entropy (2). Until the "energy crisis" of the early 1970's, there had been little incentive to develop the concepts of exergy and irreversibility into practical analysis tools. Over the past decade, however, there has been renewed interest in exergy analysis.

Exergy is a composite thermodynamic property that defines the maximum theoretical useful work that could be produced by a fuel, fluid or mass as a result of nonequilibrium with respect to a specified reference condition. Physically it represents a departure from equilibrium, whether it be chemical, thermal or mechanical. Thus work and heat can also be expressed in terms of exergy. Exergy balances, analogous to energy balances, can be written for systems or processes and used to define efficiency parameters that include second law constraints.

The benefits of exergy are not limited to energy systems design. It is also very useful for demonstrating the significance of entropy production in energy conversion processes. It is an excellent vehicle for providing insight into the interrelationship between the first and second laws. For this reason, it should be given more attention in undergraduate courses in thermodynamics.

Background

The concepts of exergy and irreversibility are certainly not new to the science of thermodynamics but was not widely spread at that time. A review of literature reveals that the value of using combined statements of the first and second laws in thermodynamic analysis has been discovered and rediscovered by numerous scientists and engineers over the past 100 years. Many trace the origin of this concept to M. Gouy in 1889, and others to J.W. Gibbs in 18S7.

Nineteenth century scientists credited with participating in the development of exergy analysis include P.G. Tait, 1886, J.C. Maxwell, 1871, and Lord Kelvin in 1879 (3). The fundamentals of exergy were established by Carnot in 1824, and Clausius in 1865. Both of these men presented the basic concepts that led to the mathematical statements for defining the irreversible production of entropy. Gibbs and Helmholtz are credited with being the first to introduce practical applications of combined first and second law analysis (4). The phenomenon is directly responsible for the loss in the potential of energy to produce useful work. Exergy concepts were further developed by J. Keenan in 1941. He devoted a significant portion of his thermodynamics text to availability analysis, with application to thermal and mechanical systems (5). Up to this time most of the documented work was for the purpose of illustrating concepts rather than to demonstrate the usefulness of the methodology.

Recent work using exergy has been done primarily in the Soviet Union and the eastern European nations, with the greatest application in the design of cryogenic systems. This particular field has had the most influence in renewing interest in exergy analysis, and in developing exergy analysis into a practical design tool. There is Considerable confusion appears to exist with respect to the definition of the efficiency (ε) of an energy system or energy process versus the definition of its coefficient of performance (COP). Thus, the purpose of this paper is to show the distinction and the relationship between these two important concepts. The low coefficient of performance (COP) and relatively large amounts of work required to produce ultra-low temperatures provides an excellent means to demonstrate the benefits of second law analysis in process design (6). The definition of thermodynamic efficiency for cryogenic systems be based on the second law as opposed to the standard COP.

There are papers on cryogenic and power system design and performance based on exergy calculations. Brodyanskii used exergy methods to evaluate the performance of a Linde air liquefaction process, and compared the results with analyses based solely on the first law. The study showed consistently lower component efficiencies than obtained by using simple energy balances. The exergy analysis also revealed where improvements could be made to improve the overall efficiency of the system. These improvements would not have been discovered by first law analysis without considering entropy production (8).

Interest in exergy analysis diminished in the late 1960's and early 1970's in the United States. The oil embargo of 1974, however, brought a renewed interest in energy resource conservation and efficient utilization. During this time C.A. Berg published several papers advocating availability analysis for evaluating the efficiency of energy conversion processes, and for matching processes to specific tasks. His papers provide several examples of processes that consume large quantities of exergy, but appear to be very efficient when only the first law is considered. He also provides examples of processes that were improved after being redesigned using exergy methods of analysis (10).

M. Ross and R. Williams analyzed the residential, commercial, industrial and transportation sectors of the U.S. Energy economy using exergy or availability analysis. Their work produced some interesting results when first law and exergy efficiencies for various processes in each sector were compared. Their studies showed that many processes appear to be efficient on the basis of simple energy balances, but have very low exergy efficiencies. This discrepancy demonstrates a poor match between process and task. Their analyses also showed that zero energy growth is technically feasible through 1990 by implementing conservation measures based on entropy considerations (11).

G.M. Reistad published a similar article in 1975 that also identified large differences between first law and exergy efficiencies for various processes in each sector of the energy economy. Using exergy concepts, his results showed that for every unit of exergy consumed at end use, greater than three units are wasted in conversion processes. However, for every unit of energy utilized, only one unit is lost. Here again is another example of the discrepancy between first law energy balances and exergy analysis. His paper also advocated using exergy analysis to match processes with tasks in order to improve resource utilization (12).

Since the early 1970's, tremendous progress has been made to reduce resource consumption by improving the efficiency of energy conversion processes. Not all of these improvements required using exergy analysis; often economic constraints or advancements in materials technology forced better engineering design. The automobile is an excellent example of this. Presently resources appear to be abundant, and aside from economics, there is little incentive for resource conservation efforts being stepped up. Even still, exergy analysis is becoming a frequent topic at many of the major engineering society meetings (ASME, AIChE, etc.). The papers delivered indicate that there is interest in using exergy methods in energy system design, and that the second law is being considered more frequently in design.

Introduction to Exergy

As stated previously, exergy is the maximum theoretical useful work that could be obtained from a fuel, a fluid or a mass as a result of nonequilibrium with respect to a specified reference condition. The term exergy was originally introduced by Z. Rant in 1956 (13). Since then, it has been generally accepted throughout Europe. Other terms found in literature for this property include availability, available work, work capacity, essergy, and available energy. M. Tribus suggests that Rant's term is more appropriate than available energy, since exergy is more a measure of equilibrium departure than a measure of energy quantity (14). Exergy is a composite thermodynamic property. That is, its value is dependent upon the state of the surroundings as well as the state of the substance for which the exergy is being determined. An important characteristic is that it is only dependent upon the end states of a process and the reference environment, making it a path independent function. Its value is dependent on the mass within the system, and thus is an extensive thermodynamic property.

The general equations for the exergy of a pure substance can be derived by considering a control volume that exchanges heat, work, and mass with its surroundings. The following assumptions will be made:

1. The control volume remains constant with respect to the coordinate frame: i.e., it does not move relative to the coordinate frame.
2. The state of mass within the control volume can vary with time; however, at any instant the state is uniform.
3. The state of mass crossing each of the areas of flow on the control volume is constant with time, although the flowrate can be time varying.

Since the control volume is being established for the convenience of defining a property of the working fluid, one additional assumption is made:

4. The control volume boundaries are rigid so that no work is lost to unrestrained expansion against the surroundings.

In other words, the control volume will convert the thermodynamic potential of the fluid into useful work. Such a system is illustrated in Figure 1.

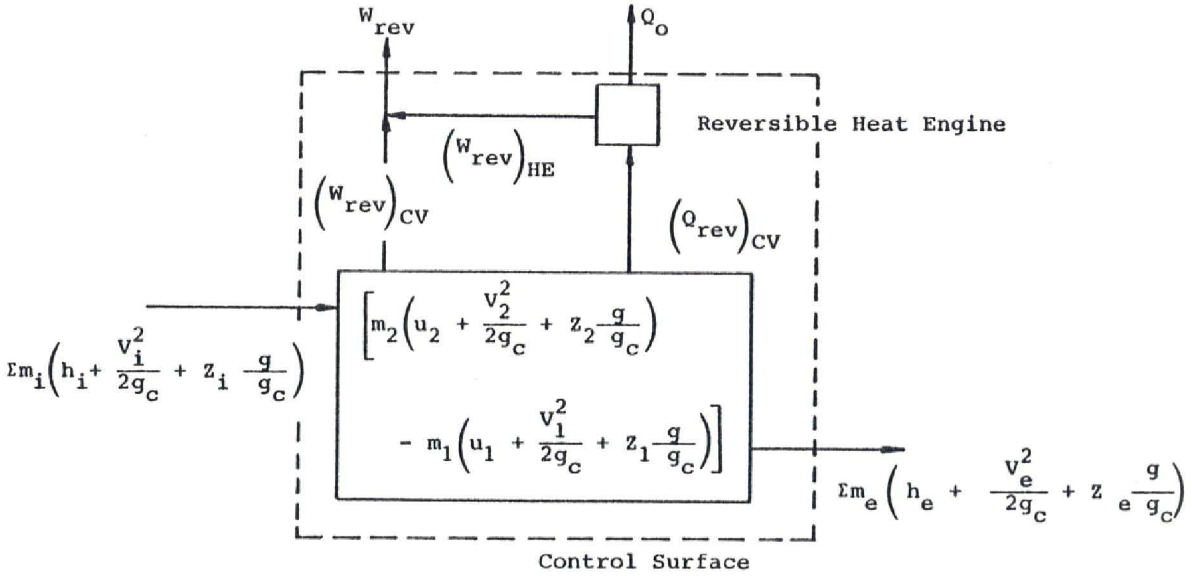


Figure 1

Steady Flow Control Volume

In order for the heat transfer between the environment and the control volume to occur reversibly, the process must be accomplished through a reversible heat engine. The sum of the reversible work crossing the control surface and the work produced by the heat engine will be the total theoretical work obtainable from the system:

$$W_{rev} = \left(W_{rev}\right)_{cv} + \left(W_{rev}\right)_{HE} \tag{3-1}$$

The first law of thermodynamics for the control volume can be written:

(3-2)

$$\begin{aligned}\left(Q_{rev}\right)_{cv} + \Sigma m_i\left(h_i + \frac{V_i^2}{2g_c} + z_i\frac{g}{g_c}\right) &= \left(W_{rev}\right)_{cv} \\ &+ \Sigma m_e\left(h_e + \frac{V_e^2}{2g_c} + z_e\frac{g}{g_c}\right) + \left[m_2\left(u_2 + \frac{V_2^2}{2g_c} + z_2\frac{g}{g_c}\right)\right. \\ &\left.- m_1\left(u_1 + \frac{V_1^2}{2g_c} + z_1\frac{g}{g_c}\right)\right]\end{aligned}$$

Where all quantities are taken with respect to the control volume, with the usual sign convention on the quantities:

Q in is positive W in is negative
Q out is negative W out is positive

The first law for the heat engine can be written:

$$(3\text{-}3) \qquad \left(Q_{rev}\right)_{cv} + Q_o = \left(W_{rev}\right)_{HE}$$

Where all quantities are taken with respect to the heat engine. The second law for the reversible control volume is

$$(3\text{-}4) \qquad m_2 s_2 - m_1 s_1 + \Sigma m_e s_e - \Sigma m_i s_i = \int_{cv} \frac{Q_{rev\ cv}}{A} \cdot \frac{1}{T}\, dA_{cv}$$

And is taken with respect to the control volume. However, since the heat engine is also reversible,

$$\int \frac{Q_{rev\ cv}}{A_{cv}} \frac{1}{T}\, dA_{cv} = \frac{Q_o}{T_o}$$

And equation (3-4) becomes:

$$(3\text{-}5) \qquad m_2 s_2 - m_1 s_1 + \Sigma m_e s_e - \Sigma m_i s_i = \frac{Q_o}{T_o}$$

Using equations (3-1) and (3-2), the reversible work becomes:

$$(3\text{-}6) \qquad W_{rev} = \left(Q_{rev}\right)_{cv} + \Sigma m_i \left(h_i + \ldots\right) - \Sigma m_e \left(h_e + \ldots\right) - \left[m_2 \left(u_2 + \ldots\right) - m_1 \left(u_1 + \ldots\right)\right] + \left(W_{rev}\right)_{HE}$$

Where the ... represents the kinetic and potential energy terms defined in equation (3-2).

Adding equat$(Q_{rev})_{cv}$3-3) to equation $(Q_{rev})_{cv}$(remembering that in (3-3) is of opposite sign to in (3-6) because of the selected references) results in

$$W_{rev} = \Sigma m_i\left(h_i + \ldots\right) - \Sigma m_e\left(h_e + \ldots\right) - \left[m_2\left(u_2 + \ldots\right) - m_1\left(u_1 + \ldots\right)\right] + T_o\left[m_2 s_2 - m_1 s_1 + \Sigma m_e s_e - \Sigma m_i s_i\right] \tag{3-7}$$

Equation (3-7) can be rearranged to give:

$$W_{rev} = \Sigma m_i\left(h_i - T_o s_i + \ldots\right) - \Sigma m_e\left(h_e - T_o s_e + \ldots\right) - \left[m_2\left(u_2 - T_o s_2 + \ldots\right) - m_1\left(u_1 - T_o s_1 + \ldots\right)\right] \tag{3-8}$$

Equation (3-8) can be used to develop expressions for the exergy of a pure substance in open or closed systems.

Exergy in Steady Flow

For the steady flow process,

$$m_1\left(u_1 - T_o s_1 + \ldots\right) - m_2\left(u_2 - T_o s_2 + \ldots\right) = 0 \tag{3-9}$$

And the reversible work becomes:

$$W_{rev} = \Sigma m_i\left(h_i - T_o s_i + \ldots\right) - \Sigma m_e\left(h_e - T_o s_e + \ldots\right) \tag{3-11}$$

The theoretical maximum useful work that could be obtained from this process would result if the exit stream left the control volume in stable equilibrium with the surrounding environment. This implies that the working fluid must leave the control volume at the same temperature and pressure of the surroundings, have minimum kinetic and potential energies, and be in chemical equilibrium with all constituents of the local environment. Thus the end state implies that the working fluid has lost all of its potential to produce useful work.

Consider the steady flow control volume in Figure 2. The reversible work per unit mass flow is:

(3-12)

$$W_{rev} = \left[h_i - T_o s_i + \frac{V_i^2}{2g_c} + z_i \frac{g}{g_c}\right] - \left[h_e - T_o s_e + \frac{V_e^2}{2g_c} + z_e \frac{g}{g_c}\right]$$

This work will approach its theoretical maximum when the mass leaving the control volume is in stable equilibrium with the surroundings. Although the continuity equation constrains the exit velocity from being zero, it is assumed to be so small that it is negligible in relation to the other terms. The remaining end-state properties must be evaluated at the state of the local environment. Hence,

$$h_e = h_o \quad s_e = s_o \quad z_e = z_o \quad V_e \rightarrow 0$$

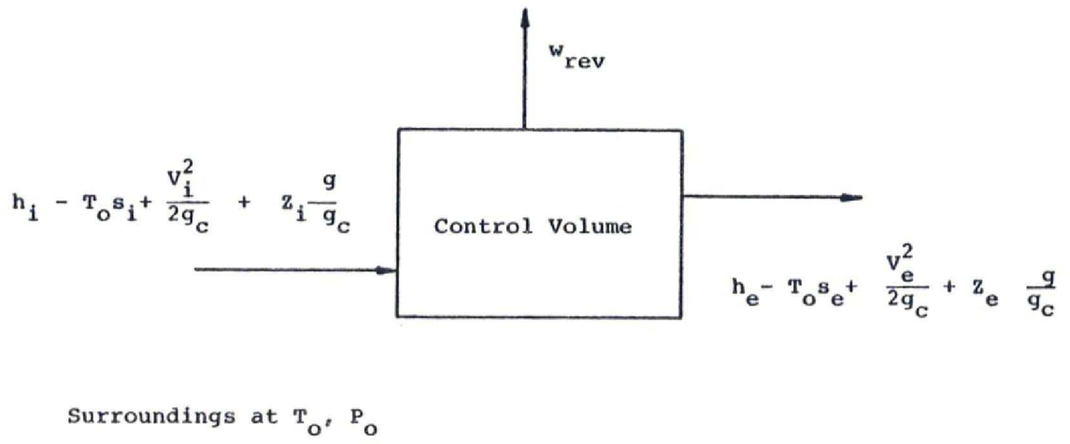


Figure 2

System Exergy Flow

This theoretical maximum work is defined as the exergy of the inlet flow stream.

Thus the exergy (Ex) at any point in a flow stream can be calculated by:

(3-13)

$$\begin{aligned} Ex &= \left[H - T_o S + \frac{V}{2g_c} + Z\frac{g}{g_c}\right] - \left[H_o - T_o S_o + Z_o \frac{g}{g_c}\right] \\ &= Ex(T) - Ex_o \end{aligned}$$

The expression Ex (T) is called the **exergy function** of the stream at temperature T. EXo represents the exergy function of the system in the dead state.

Exergy in a Closed System

The energy balance is the basic method of process investigation. It makes the energy analysis possible, points at the needs to improve the process, is the key to optimization and is also the basis to developing the exergy balance. Analysis of the energy balance results would disclose the efficiency of energy utilization in particular parts of the process and allow comparing the efficiency and the process parameters with the currently achievable values in the most modern installations. They will establish also the priority of the processes requiring consideration, either because of their excessive energy consumption or because of their particularly low efficiency.

Energy analysis is a basic and traditional approach to estimating various energy conversion processes. The analysis is using the concept of energy and its conservation. The forms of energy can be expressed as enthalpy, internal energy, chemical energy, work, heat, electricity, etc.

However, the energy approach has some deficiencies. The energy analysis is not able to recognize different quality of energy, (e.g., 1 MW of heat equals 1 MW of electricity). Accordingly, the energy analysis does not recognize the heat quality, which however depends on the heat source temperature, e.g., a 100 kJ of heat at 1000 C is dramatically more valuable than the 100 kJ of heat at the 50 C level.

The energy analysis is blind for the process direction, and, e.g., will not indicate any error considering a 100 kJ of heat at 5 C conducted through a partition to an environment at 100 C.

For these reasons the modern approach to the process analysis uses the exergy analysis, which provides a more realistic view of the process. The exergy analysis is the modern thermodynamic method used as an advanced tool for engineering process evaluation [1], [2], [3]. Whereas the energy analysis is based on the First Law of Thermodynamics, the exergy analysis is based on both the First and the Second Laws of Thermodynamics. Both analyses utilize also the material balance for the considered system. Analysis and optimization of any physical or chemical process, using the energy and exergy concepts, can provide the two different views of the considered process.

The exergy concept was introduced to overcome limitations of the energy analysis. The exergy expresses the practical value of any substance (or any field matter, e.g., a heat radiation), and is defined as a maximum ability of this substance to perform work relative to human environment.

In the background of the exergy concept it is assumed that all the common human environment components, available for free in the unlimited amounts, are practically worthless and their exergy is zero. However, any matter at parameters (e.g., pressure, temperature, composition) being not in equilibrium with the environment, has a certain practical value, which can be measured as its potential to work and is expressed as the exergy.

This nature of the exergy concept relating to the environment suggests a potential of successful involving exergy into some quantitative consideration of economy and ecology problems.

The exergy of a substance is the function of its temperature, pressure and composition, as well as of the temperature, pressure and chemical form of this substance when in physical and chemical equilibrium with human environment. Exergy can be also the function of the substance location and velocity. Therefore, the exergy can consist of the following components:

physical exergy resulting from the temperature and pressure of the substance measured with respect to the temperature and pressure of the environment. The physical exergy is used for analysis of physical processes, in which the kind of the considered substance is unchanged;

chemical exergy resulting from the difference in the substance composition with respect to the common components of this substance in the environment. The chemical exergy is used for analysis of chemical processes, in which unchanged are the chemical elements. The chemical exergy corresponds to the substance calorific value; **kinetic exergy** of the substance, which results from its velocity relative to the environment; **potential exergy** of the substance resulting from the substance location above the ground level. Most often, in the practical engineering considerations, only the **thermal exergy**, which is the sum of the physical and chemical exergy, is taken into account. The chemical exergy is important particularly for fuels. The physical exergy is possessed by any substance, whose temperature and/or pressure deviate from the environmental conditions. Exergy was introduced as the function of any matter which could be either a substance, which has a rest mass larger than zero, or a field matter, for which the rest mass is zero; e.g. the matter of radiation field (photon gas), a field of surface tension, magnetic field, acoustic field or gravitational field. Exergy analysis was already applied to many different processes, however, still some processes were not analyzed based on the exergy. Concluding, an energy analysis of the conversion process of energy, which conserves itself totally regardless of its quality, serves rather well for design calculations, whereas the exergy analysis, which takes into consideration the quality of energy and does not conserve itself, serves mostly for practical estimation and analysis of the process.

The exergy associated with a state in a closed system is derived similarly; however, unlike the steady flow process, the boundaries of the closed system are unrestrained and are capable of performing work against the surroundings. Consider the system shown in Figure 3, which undergoes a reversible change from state 1 to state

2. If the volume is allowed to expand reversibly and the work done on the surroundings cannot be considered as useful, then

$$W_{rev\ useful} = \left(W_{rev}\right)_{max} - \left(W_{rev}\right)_{surr} \qquad (3\text{-}14)$$

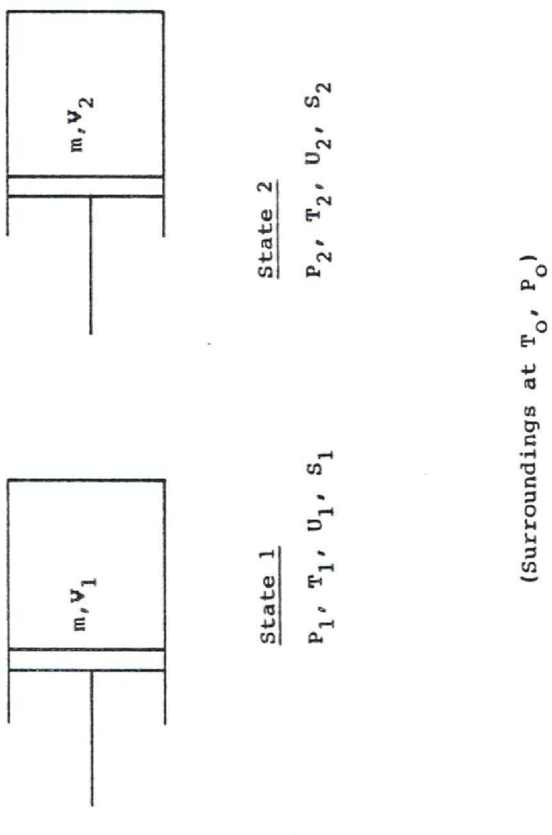


Figure 3

Closed System Control Volumes

$$= \left(W_{rev}\right)_{max} - P_o\,(\Delta \mathbb{V})$$

The maximum useful work between two states in a closed system with unrestrained expansion is found by dropping the flow terms from equation 3-8 and subtracting the work against the surroundings. Thus

$$(3\text{-}15)\quad \left(W_{rev}\right)_{useful} = U_1 - T_0S_1 + \frac{V_1}{2g_c} + Z_1\frac{g}{g_c} - \left[u_2 - T_0S_2 + \frac{V_2^{\;2}}{2g_c} + Z_2\frac{g}{g_c}\right] - \left(W_{rev}\right)_{surr}$$

$$\text{where } \left(W_{rev}\right)_{surr} = P_o(\mathbb{V}_2 - \mathbb{V}_1) = -P_0(\mathbb{V}_1 - \mathbb{V}_2)\ .$$

Equation 3-15 can then be written:

$$(3\text{-}16)\quad \left(W_{rev}\right)_{useful} = U_1 - U_2 - T_0\,(S_1 - S_2) + P_o\,(\mathbb{V}_1 - \mathbb{V}_2) + \frac{1}{2g_c}\,(V_1^{\;2} - V_2^{\;2}) + (Z_1 - Z_2)\frac{g}{g_c}$$

If the process were to occur such that the state 2 was in temperature and pressure equilibrium with the surroundings, then the maximum useful work obtained from state 1 would be:

$$(3\text{-}17)\quad \left(W_{rev}\right)_{useful\ max} = U_1 - U_0 - T_0\,(S_1 - S_0) + P_0\,(V_1 - V_0) + \frac{V^2_1}{2g_c} + (Z - Z_0)\frac{g}{g_c}$$

This also represents the exergy of the system at state 1. The maximum useful work between state 1 and state 2 is given by:

$$(3\text{-}18) \quad \left(W_{rev}\right)_{useful} = Ex_1 - Ex_2$$

A general expression for the exergy of a closed system at any state can be written in terms of the total energy, E, of the system. Let

$$E = U + PE + KE + \cdots$$

Where E is the sum of all energy forms characteristic of the system. Then the exergy of a closed system can be written:

$$(3\text{-}19) \quad Ex = E - E_o - T_o(S - S_o) + P_o(V - V_o)$$

Processes with Mass Transfer

The only requirement for the reference state thus far has been temperature and pressure equilibrium with the surroundings. For processes that involve the diffusion of chemical species to the surroundings, an additional constraint must be placed on the reference state. That is, the reference state for the diffused species must also be in chemical equilibrium with the surroundings. When mass transfer to the surroundings occurs, additional work could be obtained if the mass transfer occurred through a reversible process that brought the diffused species to the chemical potential of the surroundings. This concept is illustrated in Figure 4.

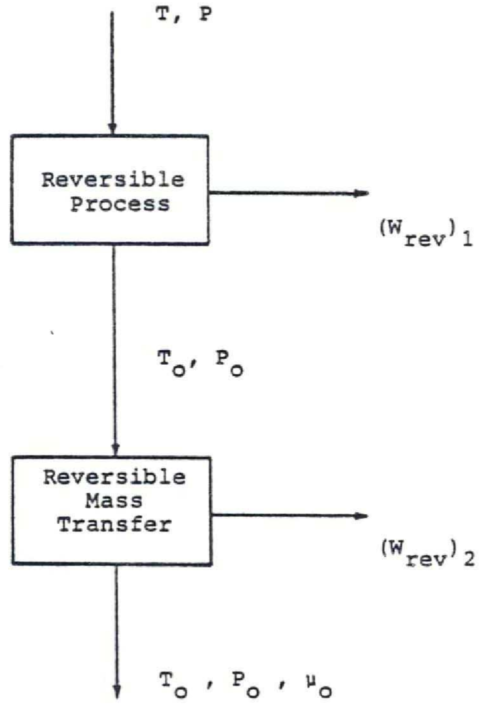
The exergy of the diffused species could be calculated by assuming that the chemical equilibrium of the mixture with the surroundings is achieved by two reversible processes. The first process takes the species to temperature and pressure equilibrium with the local environment. The maximum reversible work produced for steady state, steady flow will be denoted (W_{rev}), and is given by:

$$\text{(3-20)} \quad (W_{rev})_1 = H - H_o - T_o(S - S_o)$$
$$= H - T_oS - G_o$$

Where the Gibbs free energy is used to denote the reference state.

The maximum useful work obtainable from the second process results from the diffused species reaching chemical equilibrium with the surroundings. This will be denoted $(W_{rev})_2$ and is given by:

$$\text{(3-21)} \quad (W_{rev})_2 = G_o - \Sigma N_i \mu_{io}$$



$$(W_{rev})_{tot} = (W_{rev})_1 + (W_{rev})_2$$

Figure 4

Exergy Available Through Mass Transfer

$(W_{rev})_2$ and is given by:

where μ_{io} = chemical potential of the i^{th} specie in the reference environment.

$= \bar{g}(p_{io}, T_o)$

And p_{io} denotes the partial pressure of the i^{th} specie in the reference environment.

The maximum useful work available from these processes is the exergy of the diffused species. Thus:

$$(3\text{-}22) \qquad (W_{rev})_{tot} = (W_{rev})_1 + (W_{rev})_2 = Ex$$

Summing equations 3-20 and 3-21 produces:

$$(3\text{-}23) \qquad Ex = H - T_o S - \sum_i N_i \mu_{io}$$

For the diffusion of chemical species from a closed system to the surroundings, equation 3-23 is written as:

$$(3\text{-}24) \qquad Ex = U - T_o S + P_o V - \sum_i N_i \mu_{io}$$

Equation 3-24 could be used to calculate the exergy of combustion products leaving a furnace or engine and diffusing into the local environment. It is required, however, to establish the chemical potentials of the diffused species in the reference state. This will be the subject of the following section.

Exergy Components

The total exergy of a substance can be expressed in terms of exergy components as follows:

$$Ex = Ex_{phy} + Ex_{kin} + Ex_{pot} + Ex_{chem} + \dots \qquad (3\text{-}25)$$

where Ex_{phy} = physical exergy

Ex_{kin} = kinetic exergy (kinetic energy)

Ex_{pot} = potential exergy

Ex_{chem} = chemical exergy

Physical exergy is the work obtainable by taking the substance through a reversible process from its initial state to a state determined by the temperature and pressure of the local environment. It is generally given by the following equations:

$$Ex_{phy} = H - T_o S - G_o \quad \text{(flow system)} \qquad (3\text{-}26)$$

$$Ex_{phy} = U - T_o S + P_o V - G_o \quad \text{(closed system)} \qquad (3\text{-}27)$$

Kinetic exergy is equal to the kinetic energy when the velocity is calculated relative to the earth.

Potential exergy is equal to the potential energy when it is evaluated with respect to the local elevation of the process under consideration.

Chemical exergy is the work that can be obtained by taking a substance that has intensive properties T_o and

P_o to chemical equilibrium with components in the surroundings or reference state. Note that equation 3-25 permits other forms of energy to be considered in defining the total exergy. A summary of exergy components is provided in Table 1.

A summary of the equations for calculating exergies is provided in Table 2. Also given in this table are the various terms encountered in the technical literature for exergy and exergy components.

Table 1

Exergy Contribution of Various Energy Forms

Exergy Contribution	Expression
(1) Physical Exergy	
(a) Open system (flow)	(a) $Ex_{phy} = (H - T_oS) - G_o$
(b) Closed system	(b) $Ex_{phy} = (U - T_oS + P_oV) - G_o$
(2) Kinetic Exergy	$Ex_{kin} = \frac{v^2}{2g_c}$
(3) Potential Exergy	$Ex_{pot} = (Z - Z_o) \frac{g}{g_c}$
(4) Chemical Exergy	$Ex_{ch} = G_o - \Sigma N_i \mu_{io}$

Table 2

Summary of Exergy Equations and Terminology

Equation	Conditions	Terminology
(1) $E + P_oV - T_oS$	General expression (Closed system)	Exergy function Availability
(2) $(E-E_o)+P_o\ (V-V_o)$ $+(S-S_o)\ T_o$	Pure Substance (Closed system)	Exergy Availability Available energy Essergy
$E+P_oV-T_oS-G_o$	Pure substance	
$E+P_oV-T_oS-\ \ N_i\mu_{io}$	Mixtures	
$(T-T_o)S+\ \ N_i\ (\mu-\mu_{io})$	Systems with negligible KE and PE	
(3) $(U-U_o)+P_o(V-V_o)$ $-T_o(S-S_o)$	Closed systems	Physical exergy Availability Available energy
$(H-H_o)-T_o(S-S_o)$	Open systems, negligible kinetic and potential energy	

Table 2 (Continued)

Equation	Conditions	Terminology
(4) $V^2/2g_c$		Kinetic exergy (Component of egn 3-2)
(5) $(Z-Z_o)\ \frac{g}{g_c}$		Potential exergy (Component of egn 3-2)
(6) $N_i\ (\mu_i - \mu_{io})$	Diffusion processes where species interact with the surroundings.	Chemical exergy
(7) $I = (\Delta S_{sys} + \Delta S_{surr})To$ $= To(\Delta S_{tot})$		Irreversibility Lost work Dissipation Exergy subsidy Anergy
(8) $(1-\frac{To}{T})\ Q(T)$	Heat transfer from source at T	Thermal exergy
(9) $W_{rev} = Ex_1 - Ex_2$	Maximum reversible work produced (or required) between two states.	Available work Available energy Maximum reversible work.

Chapter 4

Reference States

The reference datum selected for exergy calculations must be given careful consideration, usually on a case by-case basis when analyzing different systems or processes. Exergy must be related to a reference condition at which the system working matter has no further capacity to produce useful work. As such, the reference datum for absolute values of exergy cannot be arbitrary, and has more stringent requirements than the reference conditions selected for enthalpy or internal energy. This state at which the working matter has no further capacity to produce work is called the dead state (15).
In the models used for exergy calculations, the dead state is usually regarded as a reservoir that is in mechanical, chemical and thermal equilibrium. The reservoir is not capable of producing work~ however, its intensive properties (T_0, P_0, μ_0) determine the potentially useful work that can be obtained from a substance. Thus the dead state will be characterized by the intensive properties of the reference reservoir.

Thermodynamic theory does not explicitly dictate a generalized reference state for all situations. In many cases, particularly for open systems that exchange mass with the surroundings, the reference state must be selected based on the chemical species involved in the process. In other cases, it is often selected on the basis of intuition and convenience. Fortunately, certain conventions have been widely accepted for defining the appropriate reference datum, and these will be summarized in the paragraphs that follow.

When analyzing closed cyclic processes (power or refrigeration cycles), it is usually sufficient to apply physical exergy only, and neglect kinetic, potential and chemical exergy in the analysis. Since it is only changes in exergy between points in a cycle that is of interest, only the reference temperature must be specified. The pressure, composition and chemical potentials of the dead state are not necessary.

There are some situations, however, that require complete definition of the reference system (T_0, P_0, μ_0). Absolute values of exergy with respect to a dead state are required when analyzing open processes; i.e., those that interact with their surroundings by mass transfer. In such cases, there is an external exergy loss when a substance that is not in complete equilibrium with the receiving environment is released from a system. Fortunately, the contribution of external exergy losses is usually small, and can often be neglected.

For cases where a thermodynamic system is surrounded by a stable ambient environment of infinite extent, then the reference temperature, pressure and chemical potentials (T_0, P_0, μ_0) are taken as those of the local surroundings. If the local environment is undisturbed by other processes or systems, then the reference values can be assumed constant. A reference datum based on the above assumption is called an environmental reference (16).

The use of this kind of reference datum offers several advantages. It is the most practical since the local environment is the ultimate heat sink for most energy conversion processes, thus making it a logical choice. Any system (having no restraint) will undergo changes until its potentials (T, P, μ) are in balance with the surroundings. In most cases, use of the temperature and pressure of the surroundings for the reference condition will produce positive values of exergy, as the case should be.

The rejection of mass into the local environment does result in some loss of exergy as a result of mixing with the surroundings. In most cases this is negligible compared with the total exergy consumed in the process, and recovery of mixing losses is generally not practical anyway. In many cases, the exergy loss involving the chemical potential of the mass rejected to the surroundings is also negligible. For these processes, the environmental reference state is well suited for open systems involving chemical reactions. Clearly it is the choice for noncreative closed systems or steady flow systems that do not exchange mass with the surroundings.

For those systems involving significant losses of chemical exergy, it must be remembered that the reference system must be capable of assimilating all substances of interest by production and/or consumption of the reference components (17}.

The assimilation process (i.e., allowing the rejected mass to reach equilibrium with the surroundings) should produce positive values of exergy to be consistent with the definition of the dead state.

Differences in temperature and concentration in the natural environment require modifying this reference system with each process considered according to its geographical location. Exergies calculated for a system in Siberia will differ significantly when calculated for the same system in the Sahara desert. The problem of a general condition of equilibrium has not been established for the environmental reference state. Until resolved, it will remain a serious deficiency for this reference datum.

Because of the disturbances of chemical equilibrium in the natural environment, J. Szargut recommends that the use of an environmental references state be discontinued when evaluating chemical exergy (IS). He proposes that an artificial reference system containing a reference substance of fixed concentration for each element be used instead. The reference substances are selected as the most devaluated compounds of the elements found in nature. The reference potentials are thus fixed, and all other substances have their chemical potentials in the reference state derived from the equilibrium condition applying to the reaction of formation for these reference substances.

M. Sussman recommends a reference state identical to that on which the tables of Standard Enthalpies of Combustion are based (19). The reference substances include selected products of combustion in their normal state of aggregation: $H_2O(l)$, $CO_2(g)$, $SO_2(g)$, etc., plus $N_2(g)$ and $O_2(g)$

each pure and at standard temperature and pressure (298.15°C and 1 atm). Sussman's reference system is similar to that of Szarqut; however, the latter is in not related to reference substances occurring in the natural environment.
J. Ahrendts recommends a reference system defined by the equilibrium of the atmosphere, the oceans, and a layer of the earth's surface 1 meter thick (20). The principles of chemical equilibrium are applied to establish exergies for any substance that is composed of elements found in the reference system. The procedure for calculating the reference exergies is complicated, and requires careful interpretation and judgment.

In summary, selection of the reference system will depend on the following:

1. The system under consideration.
2. The substances within the system.
3. Whether or not mass exchange between the system and surroundings occurs.
4. The properties of the local environment.

There are, however, some general criteria for establishing a suitable reference system, including:

1. The reference system must be in stable thermodynamic equilibrium.
2. The reference system should produce positive values of exergy for chemically active substances.

Further, the reference system should not be so complex that it deteriorates the intuitive appeal of exergy analysis.

Chapter 5

Steady Flow Exergy Equation

Unlike energy, exergy is not conserved in a real process. This destruction of exergy is the result of entropy production caused by irreversible processes within the system, including but not restricted to:

1. Friction
2. Mixing
3. Unrestrained expansion
4. Heat transfer through a finite temperature difference.

The destruction of exergy in a system (open or closed) results in the loss of potentially useful work, and is measured by irreversibility. Irreversibility $(T_o \Delta S_{tot})$ is also a composite property, having the same units as exergy. Other terms for irreversibility encountered in literature include **dissipation**, **exergy subsidy**, and **energy**.

Since irreversibility is also a composite property it is possible to write a general equation to account for the destruction of exergy as a result of work transfer, heat transfer and fluid flow. It will be seen that the steady flow exergy equation is analogous to the familiar first law energy balance, and has the following general form:

Exergy into system + Exergy **into** system
by heat transfer by fluid flow

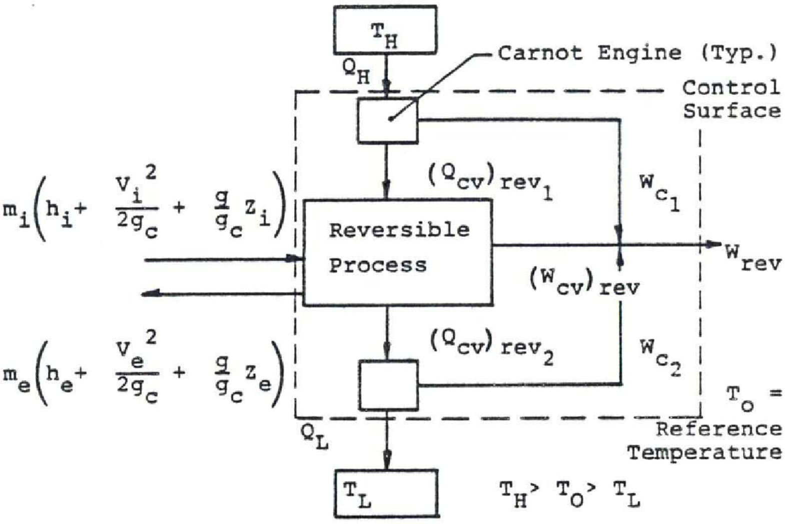
= Exergy out of system + Exergy **out** of system by work transfer by fluid flow

+ Exergy loss
(Irreversibility)

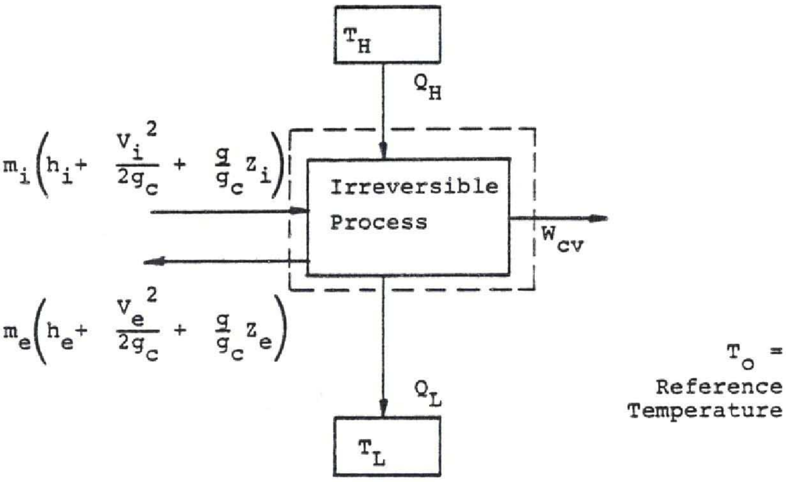
The steady flow exergy equation can be derived by considering a reversible process as illustrated in Figure 5. Carnot heat engines are used to provide reversible heat transfer from a high temperature reservoir and to a low temperature sink. A control surface (dashed line) is taken around the reversible process and the heat engines.

It should also be noted that $T_H > T_O > T_L$, making the derivation applicable to a heat engine, or by reversing the arrows, to a heat pump. The following sign convention will be used whenever numerical quantities are entered into the equation:

1- Heat **into** the system, +
2. Heat **out** of the system, -
3. Work **out** of the system, +
4. Work **into** the system, -



(A) Reversible SFSS Process



(B) Irreversible SFSS Process

Figure 5

Reversible and Irreversible Control Volumes

Neglecting the potential and kinetic energies of the inlet and exit flow streams, the first law for the control volume (with respect to the control volume) is:

$$(5\text{-}1) \qquad Q_H + Q_L + \Sigma m_i h_i = \Sigma m_e h_e + W_{rev}$$

The second law for the control volume, again with respect to the control volume, is:

$$(5\text{-}2) \qquad \Sigma m_e s_e - \Sigma m_i s_i = \frac{Q_H}{T_H} + \frac{Q_L}{T_L}$$

Where the equality holds for a reversible process. Multiplying equation 5-2 through by the dead state temperature, T_o, gives:

$$(5\text{-}3) \qquad \Sigma m_e T_o s_e - \Sigma m_i T_o s_i = \frac{Q_H}{T_H} T_o + \frac{Q_L}{T_L} T_o$$

Adding equations (5-1) and (5-3) produces:

$$(5\text{-}4) \qquad Q_H + Q_L + \Sigma m_e T_o s_e - \Sigma m_i T_o s_i + \Sigma m_i h_i = \Sigma m_e h_e + W_{rev} + \frac{Q_H}{T_H} T_o + \frac{Q_L}{T_L} T_o$$

Equation (5-4) can be arranged to give:

$$(5\text{-}5)\quad Q_H\left(1-\frac{T_o}{T_H}\right)+Q_L\left(1-\frac{T_o}{T_L}\right)+\Sigma\, m_i(h_i-T_os_i) = \Sigma m_e\,(h_e-T_os_e)+W_{rev}$$

The irreversibility of the real process can be calculated by:

$$(5\text{-}6)\qquad I_{cv} = W_{rev} - W_{cv}$$

Where W_{cv} is the actual work produced by the corresponding irreversible process (Figure 5). Note that the sign convention selected makes this equation valid for either a heat engine or a heat pump: that is, the calculated irreversibility will always be a positive quantity.

Equation 5–5 can now be written:

$$(5\text{-}7)\qquad Q_H\left(1-\frac{T_o}{T_H}\right)+Q_L\left(1-\frac{T_o}{T_L}\right)+\Sigma m_i(h_i-T_os_i) = \Sigma m_e(h_e-T_os_e)+W_{cv}+I_{cv}$$

The first two terms in equation 5–7 represent the exergy into the system as a result of heat transfer. In general,

$$(5\text{-}8)\qquad Ex_Q = Q_i\left(1-\frac{T_o}{T_i}\right)$$

where Ex_Q is the exergy of heat transfer.

If the dead state exergy of the flow streams is subtracted from each side of equation 5-7, then the flow terms in 5-7 become $\Sigma m_i ex_i$. and $\Sigma m_e ex_e$, where

$$\Sigma m_i ex_i = \Sigma m_i (h_i - T_o s_i) - (\Sigma m_i\ h_o - T_o s_o)$$

$$\Sigma m_e ex_e = \Sigma m_e\ (h_e - T_o s_e) - \Sigma m_e\ (h_o - T_o s_o)$$

The exergy of work transfer can be calculated by:

$$(5\text{-}9) \qquad Ex_w = W_{cv} - P_o \Delta \mathbb{V}_{cv}$$

Where $P_o \Delta \mathbb{V}$ represents the unrecoverable work of unrestrained expansion (recall that exergy is defined in terms of useful work). As a result of the derivation, W_{cv} represents the total work of the control volume; i.e., useful work plus work against the surroundings.

Using equations 5-8 and 5-9, equation 5-7 can be written

$$(5\text{-}10)$$
$$Ex_{Q_H} + Ex_{Q_L} + \Sigma m_i ex_i = \Sigma m_e ex_e + Ex_w + I_{cv} + P_o \Delta \mathbb{V}$$

Equation 5-10 can be generalized and written as a rate equation as follows:

$$(5\text{-}11) \qquad \Sigma \dot{E}x_Q + \Sigma \dot{m}_i ex_i = \Sigma \dot{E}x_W + \Sigma \dot{m}_e ex_e + \dot{I}_{cv} + P_o \Delta \dot{\mathbb{V}}$$

Where

$$(5\text{-}12) \qquad \Sigma \dot{E}x_Q = \sum_j \dot{Q}_j \left(1 - \frac{T_o}{T_j}\right)$$

$$(5\text{-}13) \qquad \Sigma \dot{E}x_W = \sum_k (\dot{W}_k - P_o \, \Delta \dot{\forall}_k)$$

Equation (S-11) is the general exergy equation for a steady flow control volume. Note that if there is no work against the surroundings, the term $P_o \Delta \forall = 0$.
It is of interest to note that equation 5-7 reveals that if $T_L = T_o$, then the exergy of heat transfer, Q_o, is zero. Thus heat transfer at the dead state temperature has zero potential to produce useful work.

Chapter 6
Efficiency Parameters

The most commonly used measure for energy conversion efficiency is the ratio of the energy transformed for a useful purpose to the energy input. This is based on the first law of thermodynamics, which states that energy is neither created nor destroyed, but can only be transformed from one form to another. First law efficiency simply accounts for the fraction of energy transformed that is used for a specific task.

The second law of thermodynamics goes one step further, and reveals the amount of energy that is theoretically usable if we are willing to invest enough time, money and other resources to make it useful. This theoretical usable energy was previously defined as the exergy input of a system or process.

Intuitively, something of value is lost when high quality energy is converted into low quality energy with no other end product. Even when energy is conserved according to the first law, there is always a loss of energy quality in any real process. For example, when electricity is passed through resistance coils to increase the temperature of a room only a few degrees, the first law indicates that this process has an efficiency of nearly 100% (neglecting heat losses from the walls). Electricity, however, is a high quality form of energy that can be converted almost entirely to useful work. In this case, it is used to provide low quality heat transfer and all of the exergy is lost. Thus the conversion potential of the electricity has been poorly utilized. A similar reasoning can be applied to the use of chemical energy in gas or oil fired furnaces.

Exergy efficiencies are evaluated on the basis of exergy losses in a system or device. A survey of literature reveals that there are two basic forms of this parameter. One form accounts for the actual degradation of exergy in relation to the exergy input of a process. The other uses the theoretical minimum exergy for a given process as the datum. In addition to these efficiencies, several other parameters have been proposed. One author uses a grade function to express the exergy content of an energy source. Another uses a utility function which relates the useful output of a process to the exergy consumed. These parameters will each be addressed, using the terminology selected by the various authors.

Hamel and Brown (21) use three but essentially different parameters for their analysis of energy systems. The first is a nondimensional thermodynamic variable that characterizes the fraction of energy within a system that is theoretically available to provide useful work. The energy **grade function** is defined as:

$$R = \frac{A}{E} \qquad (6\text{-}1)$$

Where A • availability (exergy) input to the system
E • energy input to the system.

Because it is determined by well defined thermodynamic properties, and because it is insensitive to mass, R gives an instant view to the match between a particular task and energy source in terms of exergy. Values of R calculated by Hamel and Brown for various energy sources are given in Table 3.

The second parameter from Hamel and Brown is called the **utility factor**. It applies to the demand element of the system at the point of consumption, and is defined by:

$$u' = \frac{A_s - A_d}{A_s} \quad (6-2)$$

Where A_s = availability (exergy) of the energy supply

A_d = availability of the energy discharge.

This parameter is analogous to the first law efficiency, but is based on exergy instead.

Table 3

Energy Grade Functions for Various Energy Sources

Primary Source	R
(1) Electricity	1.0
(2) Natural Gas	0.913
(3) Steam (212°F)	0.1385
(4) Hot Water (150°F)	0.00921
(5) Hot Air (150°F)	0.00596
(6) Air (65°F)	0.00072

Note: Ambient environment assumed to be at 85°F.

For individual components within a system, Hamel and Brown use a formulation similar to the utility factor, but which accounts for the intermediate status of a particular element with the system. They call this the **availability efficiency**, given by:

$$\epsilon = \frac{A_{out}}{A_{in}} \tag{6-3}$$

where A_{out} = availability output of component
A_{in} = availability input to component.

Neither u' nor ϵ explicitly show how much availability or exergy has been wasted in relation to the theoretical Maximum work that could have been produced. This can, however, be easily calculated from the data used to determine u' and E.

Reistad (22) defined a parameter similar to those given by Hamel and Brown. He calls this the second law effectiveness, calculated by:

$$\epsilon = \frac{\text{increase in availability of output}}{\text{decrease in availability required}} \tag{6-4}$$

In this case, £ is the thermodynamic quality of the output in relation to the thermodynamic quality of the input. Like u', it does not distinguish wasted availability that the second law exacts, even in an ideal system where all losses from mechanical imperfections have been eliminated.

These parameters can be useful design aids. They express how much exergy is given up in any conversion or any energy end use, irrespective of the theoretical minimum or maximum. Selected values of first law efficiency and second law effectiveness from Reistad's calculations for typical processes are summarized in Table 4, and show the disparity between parameters for space heating and cooling systems relative to other types of energy conversion.

Kreith and Kreider (23) use $^{n}2$ which they call **second law efficiency**. Unlike Hamel and Brown and

Table 4

Selected Values of First Law Efficiency
and Second Law Effectiveness

System	Efficiency	Effectiveness
Electric Generator	96-99	98
Electric Motor	85-95	90
Storage Battery	75-90	80
Steam Boiler	88-92	49
Diesel Engine	30-44	36
Home Furnace (Gas)[a]	60-85	13
Home Furnace (Oil)[a]	45-70	11
Coal Fired Steam Electric Generating Plant	33-42	36
Home Electric Heat Pump	2.0-4.5 (COP)	60(23)[b]
Home Electric Resistance Heater[a]	100(38)	17(6.5)
Home Gas Water Heater[c]	30-70	17
Electric Air Conditioner	2.0-4.5 (COP)	17(6.5)

[a] Required heating temperature = 590°R.

[b] Numbers in parentheses account for generation and transmission losses.

[c] Required heating temperature = 590°R.

Reistad, Kreith uses the theoretical minimum for his datum. Thus:

$$\eta_2 = \frac{A_{min}}{A} \qquad (6-5)$$

where A_{min} = minimum availability required to perform task

A = actual consumption of availability by the process

Kreith's formulation is consistent with that given by the American Institute of Physics:

$$\varepsilon = \frac{B_{min}}{B} \qquad (6-6)$$

where B_{min} = minimum availability required to perform task

B = actual availability consumed.

Ross and Williams (24) use this formulation for second law efficiency calculations. Their analyses give slightly lower values of effectiveness than Reistad's for the same processes. Results from Ross and Williams are given in Table 5.

Table 5

Second Law Efficiencies for Typical Processes

Activity	Efficiency
Furnace (space heating)	5.0%
Resistance space heating	2.5
Air conditioning	4.5
Water heating (gas)	3.0
Water heating (electric)	1.5
Electric power generation	33.0
Process steam production	34.0

An alternative formulation to equations 6-2 and 6-3 is the following:

$$\eta_{ex} = \frac{(\text{exergy into system}) - (\text{irreversibility})}{(\text{exergy into system})} \tag{6-7}$$

Equation 6-7 is useful for determining the overall efficiency of a system if each component is analyzed individually. This form is sometimes referred to as the exergy efficiency. The advantage of equations 6-5 and 6-6 is that they base efficiency on a theoretical minimum, which is a more restrictive datum than those used by the other formulations.

It will be noted from Reistad's calculations that for several processes, values of the first law efficiency and the second law effectiveness are nearly equal. The hydraulic turbine are two examples. The reason for this is that when the output of a process is electricity or shaft work, energy is almost entirely available for point of consumption usage. This high quality conversion is manifested by first and second law efficiencies being nearly equal. There are many processes where the effectiveness is significantly less than the thermal efficiency. Some of these are the fuel fired boiler, the gas furnace, the electric water heater, and electric cooking and clothes drying. Large losses in exergy occur because of the irreversibilities resulting from the combustion of fuels and the point of consumption losses. These processes typically use high quality forms of energy to produce low grade heat. The second law efficiency or effectiveness indicates a mismatch between resource and task.

A summary comparing the relative merits of first law efficiency and exergy efficiency is provided in Table 6.

Table 6

Comparison of Efficiency Parameters

Attribute	First Law	Second Law
1. Accounting for quantity of energy	1. Specific	1. Specific
2. Accounting for quality of energy conversion	2. Silent	2. Specific
3. Identification of true thermodynamic limit	3. Silent	3. Specific
4. Applicability to different types of systems	4. Misleading when useful energy out exceeds energy input (refrigeration)	4. No limit; always less than 1.0
5. Sensitivity to state of surroundings	5. Second order	5. First order
6. Comparative indicator	6. Similar equipment designs	6. Less restrictive
7. Utility to decision makers	7. Easy to understand	7. Unfamiliar
8. Accounting for cost trade-offs, environmental impacts, consumer preferences, etc.	8. Silent	8. Silent

Chapter 7

Illustrative Example

Exergy analysis provides a quantitative methodology for determining the true thermodynamics effectiveness of energy conversion processes. By expressing energy quantities in terms of exergy, a scale for comparing the relative quality of energy quantities can be established. This characteristic of exergy permits matching energy conversion processes to specific tasks on the basis of energy quality. If, for example, low grade thermal energy is the desired output of a process (e.g. space heating), then the energy input to the process should ideally be some form of low grade energy, such as waste heat. A simple example will serve to illustrate this concept.

Consider the following task: heating 30 gallons of water from 60°F to 140°F. Three methods for heating the water will be compared using exergy analysis:

1. Electrical resistance heating
2. Natural gas combustion
3. Solar heating.

It will be assumed that the local environment is at 77°F and 1 atm pressure, and this will be used for the reference state for the exergy calculations. To simplify the calculations, it will be assumed that the water heaters are adiabatic with respect to the local environment (except the solar water heater which receives the local solar flux). This constraint implies a 100% first law efficiency for the process regardless of heating method. Figure 6 illustrates the processes considered.

The energy requires to increase the water temperature can be calculated by:

$$(7\text{-}1) \qquad Q = MC_p(T_f - T_i)$$

where Q = heat input, Btu

M = mass of water stored, lb_m

C_p = specific heat of water, Btu/lb_m-°F

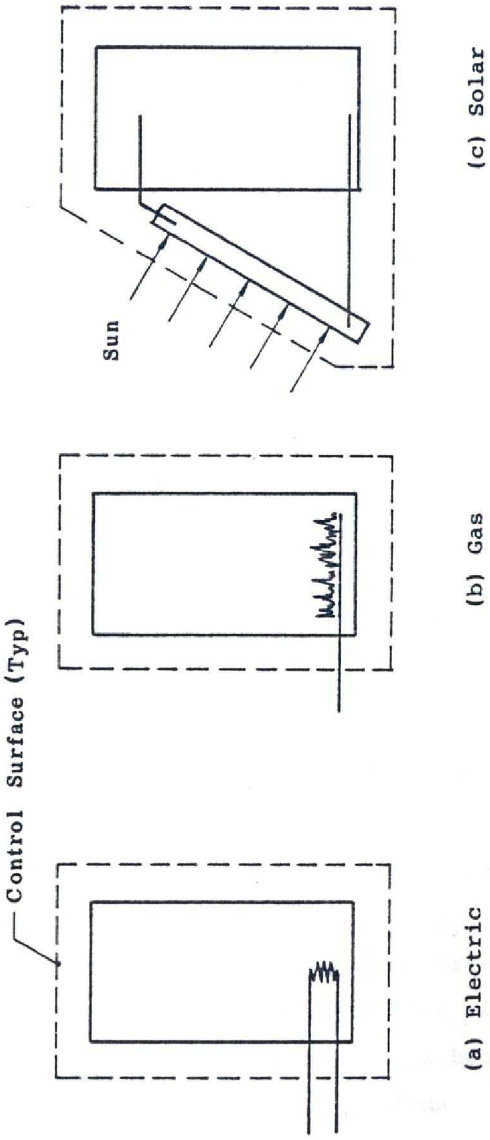
T_f, T_i = final and initial water temperatures, °F.

A constant specific heat is assumed over the temperature range considered. Thus the heat input required is:

$$Q = 30 \text{ gal} \times 62.4 \frac{\text{lb}}{\text{ft}^3} \times 0.133 \frac{\text{ft}^3}{\text{gal}} \times 0.988 \frac{\text{Btu}}{\text{lb-°F}} \times (140-60\text{°F})$$

$$= 19{,}878 \text{ Btu}$$

The increase in exergy of the water can also be calculated from the data provided. The exergy difference between two states in a closed system is given by:



(a) Electric

(b) Gas

(c) Solar

Figure 6

Three Water Heating Processes

$$(7\text{-}2) \qquad \Delta Ex = (U_2 - T_0S_2 + P_0V_2) - (U_1 - T_0S_1 + P_0V_1)$$
$$= (U_2 - T_0S_2) - (U_1 - T_0S_1)$$

Since $P_0V_1 = P_0V_2$. The properties of the water can be taken from the steam tables (25):

Temperature (°F)	State	u(Btu/lb)	S(Btu/lb°R)
60°F	Sat. liq.	28.08	0.05555
140°F	Sat. liq.	107.95	0.19851

The increase in specific exergy is:

$$\Delta ex = (107.95 - 28.08) - (77 + 459.67)(0.19851 - 0.05555)$$

$$= 3.148 \text{ Btu/lb}_m$$

The total exergy increase of the water is

$$\Delta Ex = M_w \ (\Delta ex)$$

$$= 30 \text{ gal} \times 62.4 \frac{\text{lb}}{\text{ft}^3} \times 0.133 \frac{\text{ft}^3}{\text{gal}} \ (3.148)$$

$$= 784 \text{ Btu}$$

Exergy efficiencies will be calculated for each case by determining the exergy value of the input energy supplies.

Electric Water Heater

Electricity is high quality energy that is entirely available for conversion to useful work, and as such, is considered a form of work. Since this work can be converted entirely into heat, the exergy and energy of the electricity supplied are equal. The assumption of 100% energy efficiency implies that the electrical energy input is equal to the internal change of the water.

Hence the exergy input is also equal to the change in sensible heat:

$$Ex_{in} = 19{,}878 \text{ Btu}$$

The energy efficiency for the electric water heater is:

$$\eta_{ex} = \frac{\Delta Ex}{\Delta Ex_{in}} = \frac{784}{19,878}\ 100 = 3.9\%$$

Gas Water Heater

It will be assumed that the gas water heater operates using methane (CH4). The exergy of the energy supply can be calculated by the following equation (26):

$$\frac{ex}{LHV} = 1.0334 + 0.0183\,\frac{H}{C} - 0.0694\,\frac{1}{C} \qquad (7\text{-}4)$$

where ex = specific chemical exergy of the gas, Btu/lb_m

LHV = lower heating value ($21,502\ Btu/lb_m$)

C = no. of carbon atoms per molecule

Equation (7–4) can be used to determine the chemical exergy of gaseous hydrocarbon fuels for a reference condition of $T_0 = 77°F,\ P_0 = 1$ atm it is an analytical correlation based on the known composition and the lower heating value of the gas. The correlation is based on the predicted chemical exergy determined analytically, not empirically. The difference between the exergy calculated by equation (7–4) and the exergy determined by

Rigorous analytical procedure is, on the average, ±0.15% (27).

Using equation (7-4), the specific chemical exergy of the methane is:

$$ex_{CH_4} = \left[1.0334 + (0.0183)\,\frac{4}{1} - (0.0694)\,\frac{1}{1}\right](21{,}502\ \text{Btu/lb})$$

$$= 22{,}302\ \text{Btu/lb}_m$$

The mass of methane required to heat the water can be calculated from the higher heating value (23,861 Btu/lb) and the energy requirement of the water heater:

$$M_{CH_4} = \frac{19{,}878\ \text{Btu}}{23{,}861\ \text{Btu/lb}_4} = 0.83\ \text{lb}_m\ CH_4$$

The total exergy input to the water heater is:

$$Ex_{in} = (0.83\ \text{lb})(22{,}302\ \text{Btu/lb}) = 18{,}597\ \text{Btu}$$

The exergy efficiency of the gas water heater is:

$$\eta_{ex} = \frac{784}{18{,}597} \times 100 = 4.2\%$$

Solar Water Heater

It will be assumed that a flat plate solar collector with a receiving area of 50 sq. ft. is used to heat the water. The total energy and exergy fluxes of solar radiation as a function of air mass and turbidity are provided by Edgerton. These data will be used to calculate the exergy efficiency of the solar heating process.

Assuming an air mass of 1.0 and turbidity factors a = 0.66 and ß = 0.17, the incident radiant flux on a surface normal to the sun is 0.79 kW/m². (28). Thus the energy received and collected by the hypothetical collector is:

$$\dot{E} = 0.79 \frac{\text{kW}}{\text{m}^2} \times 317.06 \frac{\text{Btu/hr-ft}^2}{\text{kW/m}^2} \times 50\text{ft}^2$$
$$= 12{,}524 \text{ Btu/hr}$$

The time required to heat the water from 60 to 140°F is:

$$\Delta t = \frac{MC_p\ (T_f - T_i)}{\dot{E}} = \frac{19{,}878 \text{ Btu}}{12{,}524 \text{ Btu/hr}}$$
$$= 1.59 \text{ hr.}$$

The exergy flux for the same atmospheric condition is 0.46 kW/m². (29). Thus the total exergy input to the solar collector is:

$$Ex_{in} = 0.46 \frac{\text{kW}}{\text{m}^2} \times 317.06 \frac{\text{Btu/hr-ft}^2}{\text{kW/m}^2} \times 1.59 \text{ hrs} \times 50\text{ft}^2$$
$$= 11{,}595 \text{ Btu}$$

This gives exergy efficiency:

$$\eta_{ex} = \frac{784}{11{,}595} \times 100\% = 6.8\%$$

A summary of the results is given below:

Process	**Exergy Efficiency**
Electric water heater	3.9%
Gas water heater	4.2%
Solar water heater	6.8%

The results show that although the energy efficiency is 100% (based on the assumptions), the exergy efficiencies are very low. Less than 10\ of the potentially useful work available from each energy source has been utilized. The example indicates that the conversion of electrical, chemical, and electromagnetic energy into heat energy is a highly irreversible process that destroys most of the potentially useful work.

The small differences in exergy efficiency among the three processes reveal that the quality of the three energy sources is similar. Some authors argue that solar energy is a low quality form of energy as compared to fossil fuels or electricity. The argument is based on the equilibrium temperature of the solar collector, and not on the exergy content of the incident solar flux.

This neglects the large irreversibility associated with converting electromagnetic energy into heat, and thus is not really correct. For example, assume that the flat plate solar collector considered previously operates with a mean plate temperature of 2S0°F. The energy of the heat delivered to the water from a source at 250°F can be calculated by equation (5-12):

$$\begin{aligned} Ex_Q &= 1 - \frac{(\ 77 + 460)}{(250 + 460)} \times (19{,}878) \\ &= 4{,}844 \text{ Btu.} \end{aligned}$$

Basing the exergy efficiency of the solar water heater on this gives:

$$\eta_{ex} = \frac{874}{4,844} \times 100 = 18.0\%$$

The exergy efficiency of the solar water heater appears to be several times that of the other two; however, the conversion of the electromagnetic energy supply to heat has been neglected. Whenever comparative efficiencies are being calculated, consistency should be maintained. If the solar collector efficiency is based on plate temperature, then the gas water heater efficiency should be based on the combustion flame temperature.

Chapter 8

Conclusions

The discrepancies that can result between energy and exergy efficiencies provide a basis for the concept of task matching. That is, when low grade energy is the output of a process, then low grade energy should be input to produce the desired effect.

Perhaps the most significant example of misused energy is in residential heating where electricity is used to provide low grade space heat with resistance coils. The first low efficiency for this process is on the order of 90-99% (neglecting generation and transmission losses). The exergy efficiency, however, is only about 2.5% (see Table 5). In reality, over 99% of the electrical potential energy is destroyed by irreversibility. A far more efficient scheme would be to use a heat pump powered by electricity. Such a device can transfer more Btu's of heat per Btu of electricity than can be dissipated by the heating coils operating at 100% energy efficiency.

Thus a purely technological or thermodynamic approach to energy conservation dictates that process optimization should be directed at minimizing the consumption of exergy, and not strictly minimizing the raw consumption of energy resources. In high temperature processes, gains in exergy performance can be achieved by improved heat transfer or better thermal control. In low temperature processes, low grade thermal energy should be used, as has been proposed by using cogeneration for district heating needs. Waste

heat recovery is another source of low grade thermal energy.
There are several factors, however, that make the purely technological approach to energy conservation and resource allocation impractical. There are sociological factors that drive the selection of energy conversion processes, including:

1. Environmental impact
2. Consumer preferences
3. Aesthetics.

Although it might be thermodynamically more efficient to use low Btu coal in some applications, the impact on the environment as a result of utilization and mining must certainly be considered. Consumer preference and aesthetics are also factors that cannot be determined by thermodynamic analysis. Conservation by modification of lifestyle is generally not an acceptable alternative to the public.

A subtle but important factor that is often neglected in thermodynamic analysis is that of time. From the entropy equation

$$d\dot{Q} \leq Td\dot{S}$$

it can be seen that the rate of energy transfer in a process is directly proportional to the rate of entropy production. In the case of the domestic water heater, the more rapidly the water is heated, the greater the irreversibility associated with the process and the lower the exergy efficiency. Higher heat transfer rates require a larger thermal potential, which is usually supplied by resources having higher energy content per pound (i.e., higher quality). In any real process, there is a finite time limit beyond which the process is undesirable. A thermodynamically reversible water heater would require an infinitesimal AT between the energy supply and the water which would require an infinite amount of time or area to heat the water. Consumer preference dictates a heat up rate on the order of hours for the device to be of practical use.

Finally, cost must be considered in any real energy conversion process. Entropy production, and hence irreversibility, are directly proportional to the rate of heat transfer. If it is desired to keep the same quantity of energy output but reduce the rate of energy supply, then the surface area for energy transfer must increase. This requires a greater expenditure in process equipment to accomplish a given task. Low heat transfer rates generally require large energy storage also. For example, solar heating, which operates at relatively low heat transfer rates, requires larger energy transfer surfaces and storage volumes than an equivalent gas fired system.

Thus it is important to understand that the thermodynamic maximum is not necessarily the ideal maximum for energy conversion processes in general. The energy minimum usually corresponds to a higher cost than the cost minimum. In many cases, irreversibility is intentionally permitted simply to reduce cost or to satisfy consumer preferences.

Energy system design requires careful optimization of several quantitative parameters, including time, cost and energy requirements. End-use matching must also be considered for determining resource allocation for satisfying energy requirements. Process design by exergy analysis, traded off against the other economic and social factors, offers the most effective method for system optimization. It also provides a sound technical basis for resource allocation and distribution.

References:

1. Joseph Kestin, "Availability, the Concept and Associated Terminology," Energy, S (1980), p. 679.
2. John Ahern, **the Exergy Method of Energy Systems Analysis** (New York: McGraw-Hill Book Company, 1980), pp. 38-9.
3. Kestin, p. 679.
4. Ahern, pp. 38-9.
5. Joseph Keenan, **Thermodynamics** (New York: McGraw-Hill Book Company, 1941), pp. 289-313.
6. Ahern, p. 39.
7. Ahern, p. 39.
8. Ahern, p. 40.
9. Ahern, p. 41.
10. Charles A. Berg, "A Technical Basis for Energy Conservation," **Mechanical Engineering**, 96 (1974), pp. 30-42.
11. Marc H. Ross and Robert H. Williams, "Energy Efficiency: Our Most Underrated Resource," **Bulletin of the Atomic Scientists**, 32 (1976), pp.30-8.
12. G. M. Reistad, "Available Energy Conversion and Utilization in the United States," **Journal of Engineering for Power**, 97 (1975), pp. 429-34.

13. Ahern, p. 41.
14. Ahern, p. 42.
15. Keenan, p. 20.
16. Joachim Ahrendts, "Reference States," **Energy: The International Journal**, 5 (1980), p. 670.
17. Ahrendts, p. 670.
18. Jan Szargut, "International Progress in Second Law Analysis, · **Energy: The International Journal**, 5 (1980), pp, 709-17.
19. Martin Sussman, •Steady Flow Availability and the Standard Chemical Potential, · **Energy: The International Journal**, 5 (1980), pp. 793-804.
20. Ahrendts, pp. 667-78.
21. Bernard B. Hamel and Harry L. Brown, ·Utilization Analysis of Energy Systems, Part 1, Fundamentals of Energy Utilization, · Drexel University, 1978, pp. 1196-1208.
22. Reistad, p. 430.
23. Frank Kreith and Jan F. Kreider, **Principles of Solar Engineering**, (New York: McGraw-Hill Book Company, 1978), p, 28.
24. Ross and Williams, p. 31.
25. Gordon J. Van Wylen and Richard E. Sonntag, **Fundamentals of Classical Thermodynamics**, (New York: John Wiley and Sons, Inc., 1976), pp. 127-8.
26. Luis Rodriguez, "Calculation of Available Energy Quantities," **Thermodynamics: Second Law Analysis**, ed. Richard A. Gaggioli (New York: American 50-51. Chemical Society, 1980), pp.
27. Rodriquez, p. 51.

28. Robert H. Edgerton, "Second Law and Radiation," **Energy: The International Journal**, 5 (1980), p, 70S.

29. Edgerton, p. 705.

30. Ahrendts, J.: *"Reference states."* Energy 5(5): 667-677, 1980

31. Altenpohl, Dieter: *Aluminum viewed from within*. Aluminium-Verlag, Dusseldorf, Germany,1982

32. Ayres, Robert U.: *"Eco-thermodynamics: Economics and the second law."* Ecological Economics 26: 189-209, 1998

33. Ayres, Robert U., Leslie W. Ayres, Paolo Frankl, Howard Lee, Nichole Wolfgang and Paul M. Weaver: *Materials-optimization in the production of major finished materials*, Center for the Management of Environmental Resources of INSEAD: January 25. Final Report:Contract BRE2-CT93-0894, Fontainebleau, France, 1995

34. Ayres, Robert U. and Leslie W. Ayres: *Industrial ecology: Closing the materials cycle*.Cheltenham, UK and Lyme MA, Edward Elgar. ISBN 1-85898-397-5, 1996

35. Ayres, Robert U. and Leslie W. Ayres: *Accounting for resources 1: Economy-wide applications of mass-balance principles to materials and waste*. Cheltenham, UK and Lyme MA, Edward Elgar. ISBN 1-85898-640-0, 1998

36. Ayres, Robert U. and Katalin Martinàs: “Waste potential entropy: The ultimate ecotoxic?” Économie Appliqué XLVIII(2): 95120, 1995

37. Ayres, Robert U., Katalin Martinàs and Leslie W. Ayres: “Exergy, waste accounting and life cycle analysis.” *Energy* 23(5): 355-363, 1998

38. Gaines, Linda L.: *Energy and material flows in the copper industry*. Argonne IL: Argonne National Laboratory, 1980

39. Gyftopoulos, E. P., L. J. Lazaridis and T. F. Widmer: *Potential fuel effectiveness in industry*. Cambridge MA, Ballinger Publishing Company, 1974

40. Hall, E. H., W. H. Hanna, L. D. Reed, J. Jr. Varga, D. N. Williams, K. E. Wilkes, B. E.

41. Johnson, W. J. Mueller, E. J. Bradbury and W. J. Frederick: *Evaluation of the theoretical potential for energy conservation in seven basic industries*. Columbus OH: Battelle Columbus Laboratories: July 11. Final Report: PB-244,772, 1975

42. Morris, D. R., F. R. Steward and P. Evans: "*Energy efficiency of a lead smelter.*" Energy 8(5): 337-349, 1983

43. PEDCo-Environmental: *Industrial process profiles for environmental use: Chapter 29; primary copper industry*. Cincinnati OH: PEDCo-Environmental: July.

NTIS:PB81-164915, EPA-600/2-80-170, 1980

44. PEDCo-Environmental: *Industrial process profiles for environmental use: Chapter 27; primary lead industry*. Cincinnati OH: PEDCo-Environmental: July. NTIS:PB81-110926,EPA-600/2-80-168, 1980
45. PEDCo-Environmental: *Industrial process profiles for environmental use: Chapter 28; primary zinc industry*. Cincinnati OH: PEDCo-Environmental: July. NTIS:PB80-225717,EPA-600/2-80-169, 1980

46. Rant, Z.: "Exergy, a new word for technical available work." *Forsch. Ing. Wis.* 22(1): 36-37,1956

47. Szargut, Jan, David R. Morris and Frank R. Steward: *Exergy analysis of thermal, chemical and metallurgical processes*. New York, Hemisphere Publishing Corporation. ISBN 0-89116-574-6, 1988

48. Tellus Institute: *CSG/Tellus packaging study: Inventory of material and energy use and air and water emissions from the production of packaging materials*. Boston MA: Tellus Institute: May. Technical Report:89-024/2, 1992

49. Thomas, R., Ed.: *Operating handbook of mineral processing*. New York, McGraw-Hill., 1977 TME - Institute for Applied Environmental Economics, 1995

50. TME: *Operational indicators for progress towards sustainability*. The Hague, The Netherlands:

Institute for Applied Environmental Economics, 1995 TME: Internal Report.

51. USBuMines-United States Bureau of Mines, *Minerals yearbook: 1991*. Washington DC,United States Government Printing Office. (USBuMines annual) United States Bureau of Mines, annual. *Minerals yearbook*. Washington DC, United States Government Printing Office, 1991

52. Wall, Goran: *Exergy: A useful concept within resource accounting*. Goteborg, Sweden: Institute of Theoretical Physics, Chalmers University of Technology and University of Goteborg: Research Report:77-42, 1977

53. Wall, Goran: "Exergy conversion in the Swedish society." *Energy* 11: 435-444, 1986