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LOST WORK: A MEASURE OF THERMODYNAMIC EFFICIENCY

NOEL DE NEVERS and J. D. SEADER
Department of Chemical Engineering, University of Utah, Salt Lake City, UT 84112, U.S.A.

Abstract—The introduction of "lost work" into the statement of the second law of thermodynamics allows us to combine it with the first law to obtain a statement of extreme breadth and generality. Because the combined first- and second-law statement defines reversible work, all other widely used statements of minimum or maximum work can be shown to be restricted cases of this combined statement.

With this combined statement, we can calculate thermodynamic efficiencies of all processes, including not only those conventionally treated—which are large work producers or consumers—but also those that do not have work production or consumption as their goals (as in absorption refrigerators or distillation columns). The results obtained this way, for example with turbines, are not the same as the conventional "isentropic efficiency" definition, but are more thermodynamically sound and much more practical for turbines whose outlet temperatures are far removed from the ambient temperature.

The combined first- and second-law statement leads naturally to the availability function and the batch availability function rather than to the availability. For practical process problems, where prime movers are not the most important concern, the availability function is a much more useful and practical quantity to utilize than the availability.

NOTATION

A	Helmholz free energy, J
b	availability function $= (h - T_0 s)$, J/kg or J/kgmole
G	Gibbs free energy, J
h	enthalpy, J/kg or J/kgmole
LW	lost work, J
m	mass or moles, kg or kgmole
P	pressure, kPa (which is dimensionally equivalent to J/m^3)
Q	heat, J
$Q_{0\text{-irr}}$	heat rejected to the surroundings at T_0 by an irreversible process, J
$Q_{0\text{-rev}}$	heat rejected to the surroundings at T_0 by a reversible process, J
S	entropy, J/°K
s	entropy, J/kg · °K or J/kgmole · °K
t	time, s
T	temperature, °K
T_0	temperature of infinite reservoir or surroundings, °K
u	internal energy, J/kg or J/kgmole
v	volume, m^3/kg or m^3/kgmole
W	work, J

Greek

η	efficiency

Subscripts

avg	average
C	cold
e	external
H	hot
i	portion of boundary across which heat flows
irr	irreversible
j	portion of a boundary across which mass flows
o	surroundings
rev	reversible
s	isentropic
sys	system

INTRODUCTION

The second law of thermodynamics is not new. It has been known in all of its important aspects since at least 1870. The objective of this paper and this conference is to seek out the most satisfactory ways of applying the second law to practical problems.

Although the public is slowly being educated to think about "the energy crisis", we technical people understand perfectly well that the real problem is "the entropy crisis". The energy of the earth is changing very little, if at all, and if solar radiation and outgoing heat flux are balanced, it is not changing at all. Energy is *conserved* (i.e. the first law is obeyed) in all of our most wasteful uses of fuels and electricity (e.g. refrigerated swimming pools in hot climates, the lights of Las Vegas, etc.). Our problem is that our low-cost sources of low-entropy materials from which we can extract useful work to drive our vehicles or to power our factories or to heat our homes have become inadequate for our current consumption. We will probably be well advised not to confuse the public by telling them about the "entropy crisis", but certainly all technical people must be aware of this.

The purpose of this conference is to evaluate various ways of applying the second law of thermodynamics to the calculation of thermodynamic efficiencies. There have been many proposals, of which the most commonly used method is "availability analysis".[1-3] In this paper, we extend the development of a less well-known approach involving "lost work". If all of these methods are used properly, they must all give the same answer since the second law is unambiguous. Thus, the criteria for selecting the best procedure to evaluate thermodynamic efficiency should be: (1) best ease of use, (2) best degree of correspondence with the viewpoint and background of intended users, and (3) greatest breadth of application. On these grounds, we believe that the lost work approach is superior to other approaches in common use.

THE SECOND LAW OF THERMODYNAMICS AS AN ENTROPY BALANCE WITH LOST WORK

Classical formulations of the second law of thermodynamics take the form of inequalities. The first form proposed was for closed systems

$$\Delta S_{sys} \geq \sum_i \frac{Q_i}{T_i}, \tag{1}$$

where Q_i refers to the heat transfer across a portion i of the boundary of the system and T_i is the corresponding temperature of that part of the boundary. Except for isothermal systems, T_i is not uniform, but has different values at different parts of the boundary. As will be shown later, the selection of the system, and therefore its boundary, is important and requires careful consideration. In general, so that all irreversibilities occur within the system, the boundary is placed such that values of T_i correspond to the various heat reservoir temperatures.

For open systems, we must include the possibility of material flowing across portions j of the system boundary. Thus

$$\Delta S_{sys} = \Delta(ms)_{sys} \geq \sum_i \frac{Q_i}{T_i} + \sum_j (ms)_j. \tag{2}$$

In both equations, the summations are algebraic so that a flow out of the system has a negative value of Q or m. Here, and in subsequent equations, the $\Delta(ms)_{sys}$ implies either that the system has uniform intensive properties or that the product of mass times the specific entropy (or other intensive property functions used later) is obtained by an integration over the entire mass contained within the system. In addition, the $\Sigma(ms)_j$ and $\Sigma(Q_i/T_i)$ terms imply either that the flows across the boundaries are uniform with respect to all variables or that the terms correspond to integrations over the boundaries of the system. The details of such integrations are given by Bird.[4]

A more useful equality form of Eq. (2) is obtained by adding a term for the irreversible entropy increase, to give

$$\Delta S_{sys} = \Delta(ms)_{sys} = \sum_i \frac{Q_i}{T_i} + \sum_j (ms)_j + \Delta S_{irr}. \tag{3}$$

Denbigh[5] stated that introducing such an irreversible entropy increase term to convert the second law from an inequality to an equality is largely due to de Donder. Although Denbigh

also utilized an equality form of the second law, he applied it to both the system and the surroundings. As shown later, the procedure adopted here leads to an equation that is more readily applied than the equation developed by Denbigh.

Any discussion of thermodynamic or second-law efficiency must be concerned with ΔS_{irr}. If it is zero, the process is reversible and is as efficient as is theoretically possible. The larger ΔS_{irr}, all other things being equal, the less efficient the process. This form of the second law also allows us to formulate this neat verbal statement of it: ΔS_{irr} is positive in the real world, zero in the theoretical reversible world, and negative in some impossible worlds.

The main idea of this paper is to show that, if we define a new quantity called "the lost work" as

$$LW = T_0 \Delta S_{irr}, \tag{4}$$

and introduce it into Eq. (3), we will have a very powerful and convenient method of assessing the thermodynamic efficiency of processes. In this equation, T_0 is the temperature of the infinite surroundings, normally taken as the temperature of the nearest large body of ambient water like a river, lake, or ocean. Because they are assumed to be infinite in size, infinite surroundings are an ultimate heat source or sink that is always available and does not need to be restored or replenished.

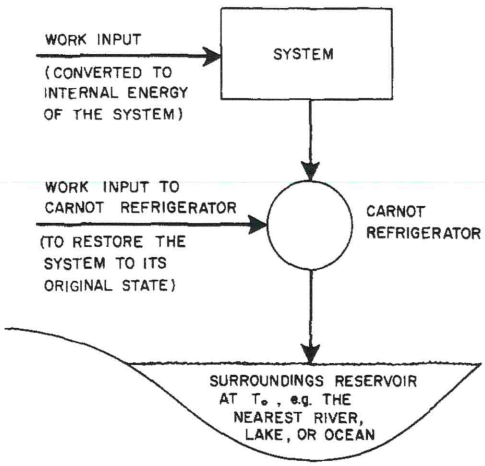
Although one could work totally with ΔS_{irr}, or perhaps mentally substitute $T_0 \Delta S_{irr}$ whenever LW appears, we believe that formulations in terms of LW are simpler, easier to use, and more intuitively satisfying than any other formulation of the second law now in common usage. Indeed, as we show later, lost work is exactly what the term implies—work that is irreversibly lost.

Table 1 lists the most common ways in which irreversible entropy increases (ΔS_{irr}) occur. Conceptually, all of these are equivalent to the conversion of work to heat. Hence, at least as early as 1950,[6] the idea of "lost work" had been used as a measure of irreversibility or of the degradation of energy from more useful to less useful forms. As we discussed in an earlier paper,[7] there are two definitions of lost work in common usage. The first one indicates that lost work is simply the amount of work that is irreversibly converted to heat. The other, which we consider the superior definition, indicates that lost work is not only the amount of work that is irreversibly converted to heat, but also includes the additional work that must be transferred to the system to offset the consequences of this degradation.

This idea is illustrated in Fig. 1. Here, we see an irreversible process occurring in a system that may be open or closed, where the irreversible work input is lost. In addition, a Carnot refrigerator offsets this irreversible work conversion by removing the incremental heat and rejecting it to the surroundings at T_0 so as to restore the system to its original state. Lost work, as we believe it should be defined, is the sum of these two works. One may also show that lost work is equivalent to the incremental heat that must be rejected to the infinite surroundings at T_0 due to irreversibilities (see Appendix 1). Since thermal energy in the heat reservoir at T_0 cannot be put to any practical use, this is energy that has been degraded to its ultimate uselessness.

Table 1. Common modes of thermodynamic irreversibility.

1. Heat transfer through finite temperature driving force
2. Mass transfer through finite concentration driving force
3. Conversion of other energy to heat or internal energy by friction
4. Chemical reaction occurring at non-equilibrium conditions
5. Electrical current flow through a finite resistance
6. Loss of magnetic field without energy recovery



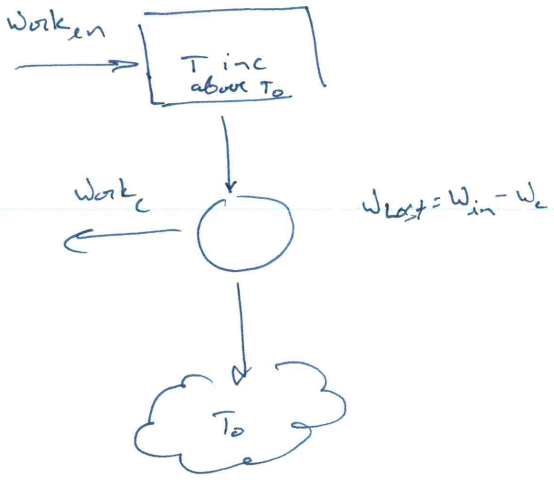


Fig. 1. Schematic diagram of two work inputs that make up lost work.

THE ADVANTAGES OF THE LOST WORK CONCEPT

(1) The lost work concept allows us to formulate the second law in an equality form rather than in an inequality form

$$\Delta S_{sys} = \Delta(ms)_{sys} = \sum_i \frac{Q_i}{T_i} + \sum_j (ms)_j + \frac{LW}{T_0}. \tag{5}$$

This is merely a restatement of Eq. (3), in which the ΔS_{irr} term is replaced by Eq. (4). However, this substitution replaces a term of low intuitive content with two others. One is an external variable that changes little from location to location, and the other is directly related to external variables and is the term of practical significance. Lost work is the equivalent of the incremental extra electric power that must be purchased to offset irreversibilities, but there is no such simple intuitive interpretation of ΔS_{irr}.

(2) We can multiply Eq. (5) by T_0, subtract it from the general energy balance, and then rearrange to produce the combined statement form

$$(\Sigma W_e + LW) = \Sigma[m(h - T_0 s)]_j + \sum_i \left(1 - \frac{T_0}{T_i}\right) Q_i - \Delta[m(u - T_0 s)]_{sys}. \tag{6}$$

Here we have followed the thermodynamic sign convention that heat flowing into the system is positive, and work flowing out of the system is positive.

We can further simplify this result by introducing a combination of thermodynamic variables, often defined on a unit mass or mole basis as the "availability function", or

$$b = h - T_0 s = u + Pv - T_0 s. \tag{7}$$

This function and symbol—but not name—were apparently introduced into engineering by Keenan,[8] although it had been proposed earlier by others in different forms.[9] Haywood calls it the "steady-flow availability" function, while Faires and Simmang[10] refer to it as the "availability" or "Darrieus" function. However, since "availability function" seems to be its most common name, it will be used here. It is unfortunate that the word "availability" appears in its name, however, since it leads to confusion with what many authors,[2,10,11] in writing of a steady-state, steady-flow process, have called the "availability" or $(h - T_0 s) - (h_0 - T_0 s_0)$ in the absence of potential and kinetic energy effects

Substituting Eq. (7) into Eq. (6), we obtain

$$(\Sigma W_e + LW) = \sum_j (mb)_j + \sum_i \left(1 - \frac{T_0}{T_i}\right) Q_i - \Delta[m(b - Pv)]_{sys}. \tag{8}$$

The term on the far right contains the combination $(b - Pv)$, which is logically called a "batch" or "nonflow" availability function. Haywood[9] suggests that it should have the symbol a, but, to our knowledge, no symbol or name has been widely adopted for it.

We can easily divide Eq. (8) by the time change Δt to obtain the equivalent form in terms of power, mass flow rates, heat flow rates, and time rate of change of the system.

(3) We can see that, in this combined statement, the two work terms of actual external work and lost work appear together. Their sum is equal to the reversible work of a process that has the same material flows in and out and the same heat exchange at all temperatures other than T_0 so that

$$W_{rev} = \Sigma W_e + LW. \tag{9}$$

This is an extremely broad and powerful result. It means that, for any real process where we can define the state of the system before and after any system change, the mass flows or mass flow rates into and out of the system, and the heat flow rates and temperatures at which heat flows into and out of the system, we can directly and unambiguously compute the work flows for a reversible process. From the difference between that work flow and the actual work flow, we can compute the lost work.

(4) With this lost work definition, we can easily compute thermodynamic efficiencies for processes that involve exchange of work with the surroundings and for those that do not. For processes that exchange work with the surroundings, and whose purpose is either to produce work or to consume work, the definitions are simply

$$\eta_{\text{work producing}} = \frac{\Sigma W_e}{W_{e_{rev}}} = 1 - \frac{LW}{W_{e_{rev}}}, \tag{10}$$

$$\eta_{\text{work consuming}} = \frac{W_{e_{rev}}}{\Sigma W_e} = 1 + \frac{LW}{\Sigma W_e}. \tag{11}$$

(5) We can see that efficiency definitions given in Eqs. (10) and (11) are not the same as the ones commonly shown in many engineering thermodynamics textbooks. For example, Eq. (10) does not lead to the conventional definition of the "isentropic efficiency" of a turbine, but to a much more powerful definition. The conventional definition, according to Van Wylen and Sonntag,[11] is

$$\eta_{\text{turbine mechanical}} = \frac{W_e}{W_s} = \frac{h_1 - h_2}{h_1 - h_{2_s}}, \tag{12}$$

which is a mechanical efficiency definition. The initial state and the final pressure of the real and reversible (isentropic) processes are chosen to be the same. This fixes the outlet temperature and entropy of the isentropic process. The outlet temperature of the real turbine process can be arbitrarily estimated or determined experimentally. We may see this from Fig. 2, where a conventional Mollier diagram representation of the process path of an adiabatic steam turbine with negligible kinetic energy changes is shown. The initial state is 1; the final actual state is 2; and the reversible path leads from 1 to 2_s. In contrast, the definition which follows from Eq. (9) is a thermodynamic definition, where the inlet and outlet states are the same for both the real and the reversible turbines.

If we apply Eq. (10) to the same system, we see that

$$\eta_{\text{turbine thermodynamic}} = \frac{W_e}{W_{e_{rev}}} = \frac{h_1 - h_2}{b_1 - b_2} = \frac{h_1 - h_2}{h_1 - h_2 - T_0(s_1 - s_2)}. \tag{13}$$

To see the relation between the thermodynamic turbine efficiency and the more common mechanical turbine efficiency, we define

$$T_{\text{avg}} = \frac{h_2 - h_{2_s}}{s_2 - s_{2_s}}, \tag{14}$$

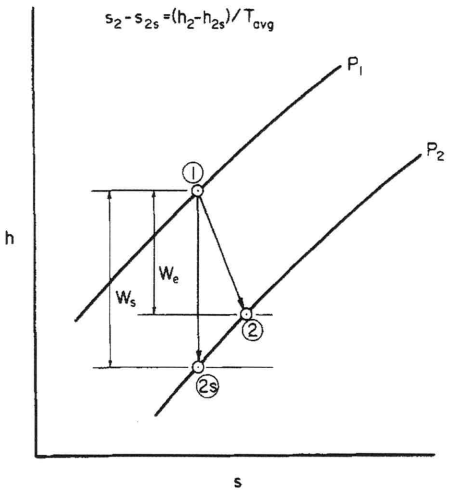


Fig. 2. Schematic representation of adiabatic and actual turbine work.

and note that $s_{2_s} = s_1$. Then, solving Eq. (14) for h_{2_s}, and substituting in Eq. (12), we find

$$\eta_{\text{turbine mechanical}} = \frac{h_1 - h_2}{h_1 - h_2 - T_{\text{avg}}(s_1 - s_2)}. \tag{15}$$

This shows that, if $T_{\text{avg}} = T_0$, the two efficiency definitions are the same.

Practically speaking, this is what happens when steam turbines exhaust into condensers, for which the common definition was first devised. However, if these temperatures are not the same, then the efficiencies are not the same. If $T_{\text{avg}} > T_0$, then the thermodynamic efficiency is greater than the mechanical efficiency; but if $T_{\text{avg}} < T_0$, the thermodynamic efficiency is less than the mechanical efficiency. Both of these cases occur in practice. In a gas-turbine combined-cycle power plant, T_{avg} of the gas turbine is much greater than T_0. The kinetic energy of the fluid that is converted to internal energy increases the internal energy of the outlet stream relative to the outlet temperature of a reversible turbine. Some of this internal energy is captured by the waste-heat boiler/steam-turbine combination, which follows the gas turbine, and is converted to work, so that the real loss due to turbine inefficiency is not the mechanical lost work (on which the conventional turbine efficiency is based) but the thermodynamic lost work (on which the thermodynamic turbine efficiency is based). At the other extreme, expansion engines in Kaptiza-type helium liquefiers[12] have a T_{avg} much less than T_0. The loss due to engine irreversibility is much greater than the mechanical lost work which is normally thrown away. It is the loss of refrigeration found by an analysis using the thermodynamic lost work that leads to the thermodynamic engine efficiency.

Similarly, the straightforward application of Eq. (11) to a mechanical refrigerator leads to an efficiency definition that is the ratio of the coefficient of performance[11] of the actual refrigerator to the coefficient of performance of a reversible refrigerator operating between the same two thermal reservoirs. This is the true thermodynamic efficiency.

(6) Perhaps most important, we can use Eq. (8) to formulate efficiency definitions of processes that have no significant work exchange with the surroundings. We begin searching for such a definition with Eq. (8) and observe that, if work production or work consumption are not the goals of the process, then the terms on the right side of the equation represent the possible accomplishments of the process plus the inputs necessary to accomplish them. If we make a general definition of efficiency as (desired result/inputs necessary to accomplish that result) we see from Eq. (8) that we would define the efficiency of such a non-work-producing or consuming process as

$$\eta_{\text{non-work process}} = \frac{\text{desired term from right side of Eq. (8)}}{\text{all other terms from right side of Eq. (8)}}. \tag{16}$$

The denominator of Eq. (16) can also be written as the lost work minus the desired term from Eq. (8) so that an alternative formulation of Eq. (16) is

$$\eta_{\text{non-work process}} = \frac{-[\text{desired term from Eq. (8)}]}{-LW-[\text{desired term from Eq. (8)}]}. \tag{17}$$

The minus sign appears in this definition because the two terms will have opposite algebraic signs due to thermodynamic sign conventions. We can see this by considering a reversible, zero-work process in which the sum of the terms on the right side of Eq. (8) is zero so that the efficiency according to Eq. (16) would be unity. Although Eqs. (16) and (17) appear abstract, we will see that they are easily applied and have many practical applications.

Consider an absorption refrigeration process of negligible work exchange, where the system is the closed set of vessels containing the refrigerant and the main task is the removal of heat from the stream being cooled at the boundary of, but outside of, the system. Equation (8), for a cyclic steady-state process involving a reboiler, an evaporator, a condenser, and no external work is

$$LW = Q_H\left(1-\frac{T_0}{T_H}\right)+Q_C\left(1-\frac{T_0}{T_C}\right), \tag{18}$$

where the term for the condenser does not appear because $T_i = T_0$. Since the main task is the removal of heat from the steam being cooled, we can apply Eq. (16), finding

$$\eta = \frac{-Q_C\left(1-\frac{T_0}{T_C}\right)}{Q_H\left(1-\frac{T_0}{T_H}\right)} = -\frac{Q_C}{Q_H}\left(\frac{T_C}{T_H}\right)\left(\frac{T_C-T_0}{T_H-T_0}\right). \tag{19}$$

For a reversible device, the numerator and denominator of Eq. (19) are equal so that the efficiency would be 1.0. For real absorption refrigerators, it is much less than unity.

Two such absorption refrigerators are described in detail by Hougen *et al.*[13] and Norris.[14] For a home absorption refrigerator, as discussed by Dodge,[15] there is zero work input or output, while for commercial units the work input (to a circulating liquid pump) is small. If we ignore the work input to this pump, we can apply Eq. (19) to calculate the thermodynamic efficiencies of these two examples. For the one from Hougen *et al.*, we must take some of the temperatures as those internal to the process because the external temperatures are not given. By doing so, we have T_H = 148.9°C (steam), T_C = − 1.1°C (boiling temperature of the ammonia that cools the external load), T_0 = 37.8°C (estimated average temperature of the cooling water). Substituting these values and the heat flows from our example into Eq. (19), we then find that the thermodynamic efficiency is 0.255, which means that this device removes 25.5% as much heat from the cooling load as would a totally reversible device accepting heating and cooling inputs at the same temperature levels. By similar calculations (taking stream temperatures as averages of input and output), one can show that the lithium bromide system described by Norris is 22.5% efficient.

For a continuous, steady-state process that exchanges heat with more than one reservoir but has negligible work exchange (for example, a distillation process), we can assume that the main task is to accomplish the separation, for which the reversible work is the increase in the availability function. From Eq. (16), the efficiency can be written as

$$\eta = \frac{\Sigma(bm)_j}{\sum_i\left(1-\frac{T_0}{T_i}\right)Q_i}. \tag{20}$$

This is similar to the widely used formula given by Robinson and Gilliland.[16] However, they obtained their formula by constructing the ratio of the *isothermal* work of separating the components to the Carnot equivalent work based on the assumption that the reboiler and condenser temperatures were the appropriate T_H and T_C for a Carnot engine. Equation (20) is more general because it does not have the restriction that all feeds and products enter and leave at

the same temperature, and it does not contain the assumption that the condenser temperature is the reservoir temperature as implied in the treatment of Robinson and Gilliland. Applications of Eq. (20) and the more general forms given by Eqs. (16) and (17) to a complex distillation problem and to a process involving a chemical reaction are given by de Nevers and Seader.[7]

THE ROLE OF THE COMBINED STATEMENT IN MINIMUM WORK CALCULATIONS

Figure 3 shows how various minimum work statements result from the combined statement of the first and second laws in Eq. (8). At the left of the figure, we restrict our attention to steady-flow or cyclical processes where the system itself does not change or only changes in a cyclical way. Branching again to the left, we see that if all heat transfer with the surroundings occurs only at T_0, then we have the reversible work equal to $\Sigma(bm)_j$. This relation is particularly useful for analysis of cryogenic systems, where the conditions of steady flow and heat exchange with the surroundings are only met at T_0. For that reason, this relation was known in cryogenics at least as early as 1937.[12]

At that time, however, the useful inference was not made that the reversible work so calculated is the sum of the actual work and the lost work. That inference was drawn by Van Ness.[17] However, he drew it only for systems that exchanged heat with the surroundings at T_0. As shown above in Eq. (8), it is a general property of the combined balance equation that no such restrictions apply. In the form proposed by Van Ness, the lost work concept is inapplicable to the processes shown in the central branch of Fig. 3; but in the form we propose, the lost work concept applies to these processes as well.

Continuing down the left-hand side of Fig. 3, we see that, if the system is isothermal at $T = T_0$, then we have the well-known statement that the work is equal to minus the Gibbs free energy change.

Returning now to the middle branch on the figure, we see that, for a steady-flow or cyclicial process with no mass flow, the reversible work is equal to the sum of the heat flows multiplied by $(1 - T_0/T_i)$, where T_i refers to the temperatures of the heat sources or sinks at temperatures

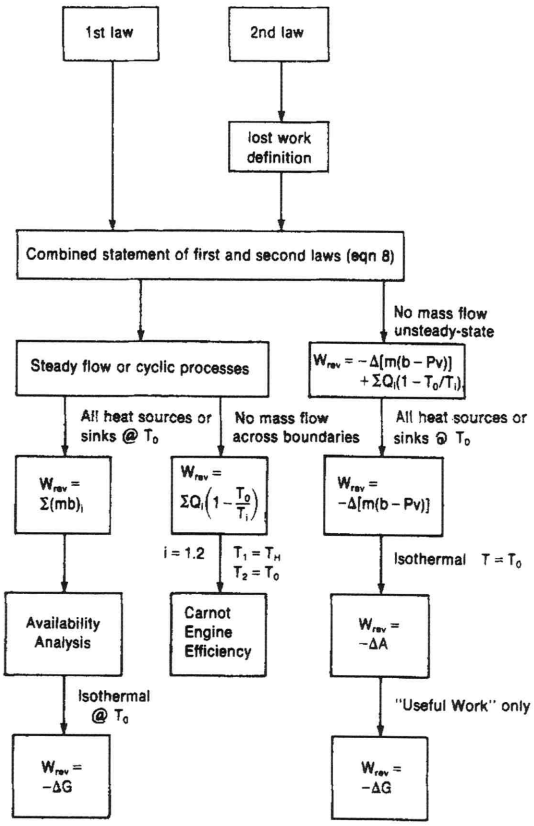


Fig. 3. Conceptual framework of reversible work statements.

other than T_0. If, in addition, there are only two such heat flows, and one of these occurs at $T_i = T_0$, then the combined statement reduces to the Carnot engine efficiency definition.

The existence of heat sources and sinks at temperatures other than T_0 requires some discussion. At some places on earth, two such infinite sources exist in close proximity where a warm tropical ocean covers a much colder deep ocean. There is significant interest in the commercial exploitation of these adjacent reservoirs at different temperatures, which is currently known as "Ocean Thermal Energy Conversion".[18, 19] The reservoirs in the ocean may be assumed infinite, as compared to any possible rate of extraction or rejection of energy by humans in the near future.

Similarly, the designer of one part of a large industrial complex normally looks upon cooling water, several pressure levels of steam, and possibly chilled water as such reservoirs. These are clearly not infinite, nor are they free. But such large complexes have utility departments that supply these heat sources and sinks to the individual parts of the plant. Thus, the common view of a plant designer or operator is that these utilities are also sources and sinks at T_i not equal to T_0 and that he can utilize and pay for these without assuming responsibility. In this sense, our approach matches the viewpoint of the designer or operator of such a part of a large facility. The designer or operator of the utility system of such a facility should also subject his operation to analysis of the type shown here in order to understand and improve its efficiency.

Branching now to the far right on Fig. 3, we see that, for a closed system, the reversible work is equal to the change in the batch availability function times system mass plus a term that is equivalent to a Carnot engine heat flow. If all heat exchange takes place at T_0, then this latter term is zero; and we have the statement that the reversible work is equal to the change in the batch availability function. Continuing down this branch, we see that, when the system is isothermal at $T = T_0$, we obtain the well-known result that the reversible work is equal to minus the change in the Helmholtz free energy. However, as is widely stated in textbooks, some of this reversible work is the generally useless work of driving back the atmosphere. On the other hand, if the system contracts, then the work actually produced may exceed the reversible work because the atmosphere acts upon the system. If we compute the useful work instead of the reversible work, we will find that this also, for a batch system, is equal to minus the Gibbs free energy change.

From Fig. 3 and this discussion, it should be clear that the many fragmented statements about minimum and maximum work that appear in all books on thermodynamics are readily obtained from Eq. (8) by simply applying the appropriate restrictions. Thus, we see that combining the first and second laws through the lost work definition produces an equation of extreme breadth and power capable of determining the true thermodynamic efficiency of any process we choose to analyze.

THE COMPARISON OF LOST WORK ANALYSIS AND AVAILABILITY ANALYSIS

The most widely used competitor to the type of analysis we present here is what is called "availability analysis", where one determines a value of the availability for each stream entering or leaving the process, computes changes in availability, and then compares these to work production. As shown in the preceding section, application of the combined first and second laws leads naturally to an equation in terms of the availability function, rather than to the availability. In this section, the two approaches are compared.

The significant difference between the availability function and the availability is that the former is based on an arbitrary datum for enthalpy and entropy, while the availability is based on datum states for the enthalpy and entropy in the "dead states". The reason for this difference is that the availability function normally appears only in the form of availability function changes. Thus, since only Δ of the availability function appears, the datum does not in any way influence the numerical values of Δ that are calculated. This allows one to use ordinary steam-table or thermodynamic-table values of the enthalpy and entropy. However, if chemical reactions occur, it is necessary that the data for the various reactants and products be chosen in a consistent way. There are many satisfactory ways to do this, the most common being to take enthalpy reference states as the elements in the ideal gas state at 0°K and zero pressure and the entropy reference states as the compounds at 0°K and unit pressure. Tables of properties and computer programs using this approach are widely available.[13,19,21]

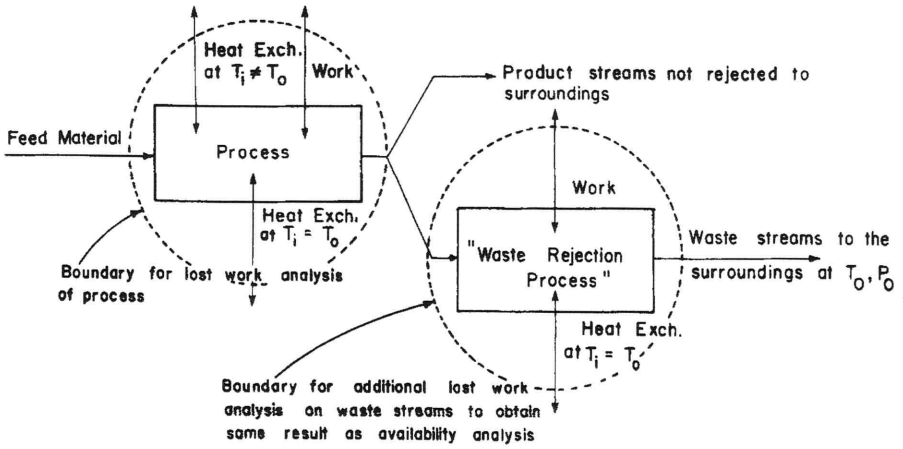


Fig. 4. Block diagram of 2-stage lost work analysis.

On the other hand, the availability is an absolute value attached to a mass of matter and is a function of the values of the enthalpy and entropy at surrounding temperatures and pressures. It can also be based on steam-table entropies and enthalpies, but each value is a difference between two readings. As with the availability function, it must use a consistent set of data if chemical changes occur.

What are the advantages of the availability approach? If the process under consideration has the objective to produce power with no saleable commodity other than power being produced (as is the case in all prime movers); then the streams leaving the process will be thrown away to the environment. The availability of these streams at the point they leave the process represents a potential to do work which is, in general, thrown away. This idea is further extended by introducing the concept of exergy, in which the availability is expanded not only to bring the exiting stream into temperature and pressure equilibrium with the surroundings, but also to bring it into chemical equilibrium through reversible diffusion. Although methods are readily available to bring the exit streams into pressure and temperature equilibrium and gain the calculated amount of reversible work, no such schemes are readily apparent, for example, for reducing the CO_2 concentration of a combustion exhaust gas from the typical 12 mole percent to the fraction of a mole percent that is the equilibrium concentration of the surroundings.

If, on the other hand, the objective of the process is to produce a valuable commodity, as is common in the process industries that supply us with food, fiber, building materials, chemicals, motor fuels, and the like, then the exit stream is not thrown away to the environment but rather is the desired object of the process. Assigning an availability to such a stream makes relatively little sense, since its value resides in its high availability. To consider that availability as being thrown away when the stream leaves the process, makes very little sense.

Figure 4 shows how the two views can be integrated. In it, we see a process that has feed streams and product streams and exchanges heat and work with the surroundings, including heat at temperatures other than T_0. Lost work looks only at this process and asks how much work is lost due to irreversibilities within the process boundaries. If some of the exit streams from the process are not at the "dead state" but are nonetheless rejected to the surroundings, then there will be additional lost work in the dilution and cooling that occur as these waste streams come to equilibrium with the surroundings. Figure 4 shows that one can perform a perfectly straightforward lost work analysis on the "Waste Rejection Process" of bringing these waste streams to the "dead state".

If we further add the restrictions that there is no heat exchange for either process at temperatures other than T_0 and that there are no product streams wasted to the surroundings, then the results of the lost work and the availability analysis become identical. This illustrates what was stated earlier—that availability analysis is a restricted subcase of the broader approach shown in Eq. (8).

CONCLUSIONS

By using the lost work approach, we can: (1) formulate the second law as an equality rather

than as an inequality, (2) combine this with the first law, (3) use this to compute the reversible work of an irreversible process that has the same material flows in and out and the same heat exchange at all temperatures other than T_0, (4) easily compute thermodynamic efficiencies in terms of the lost work, (5) use these efficiencies to gain a deeper insight into processes such as combined cycle power-generation processes, and (6) use this type of thermodynamic efficiency analysis in processes whose purpose is not to produce work but rather to produce valuable materials.

The lost work concept is simple, and intellectually and intuitively satisfying. The calculations can be readily made with design and simulation computer programs with thermodynamic property subroutines that can estimate multicomponent enthalpy and entropy on a consistent basis. With such calculations, the designer can identify the principal sources of lost work and strive to minimize them.

All of the common computation methods and statements of thermodynamic minimum or maximum work arise naturally from the combined first and second law statement shown here, by simply applying restrictions to it. Thus, the combined statement may be seen as the general statement of minimum or maximum work.

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APPENDIX I

Relation between lost work and heat rejection to the surroundings

Although the lost work idea evolved from occurrences in the system and the amount of irreversible entropy production, it has another interpretation which is mentioned in the text but not demonstrated. To demonstrate it, we consider the general flow diagram shown in Fig. I-1.

Here, we see that all the terms appearing in Eq. (8) are represented except LW. The heat flow terms (Q_i) have been organized so that the heat flow to the surroundings at T_0 are one group and all heat flows at temperatures other than T_0 are another group. If the process represented is a reversible process, then LW will be zero and the actual work will be equal to the reversible work. In this case, the heat transfer to the surroundings may be called $Q_{0\text{-rev}}$.

Now if we consider an irreversible process that has the identical values of all material flows across system boundaries, all heat flows other than T_0, and $\Delta[m(b - Pv)]$, we see that the only flows that will change in Fig. I-1 are the external work and the heat flow to the surroundings at T_0. From Eq. (8), we can see that the sum of those terms is the same for the reversible and irreversible cases. Then, writing the first law twice (for the reversible and irreversible cases), and equating like terms, we find

$$W_{rev} + Q_{0\text{-rev}} = W_e + Q_{0\text{-irr}}, \tag{I-1}$$

where $Q_{0\text{-irr}}$ is the heat flow to the surroundings for the irreversible case. Rearranging Equation I-1, we obtain

$$W_{rev} - W_e = LW = Q_{0\text{-irr}} - Q_{0\text{-rev}}. \tag{I-2}$$

Thus, we see that for two processes with identical material flows across system boundaries, identical heat flows across system boundaries (except for heat exchange with the surroundings at T_0), and an identical change in the value of

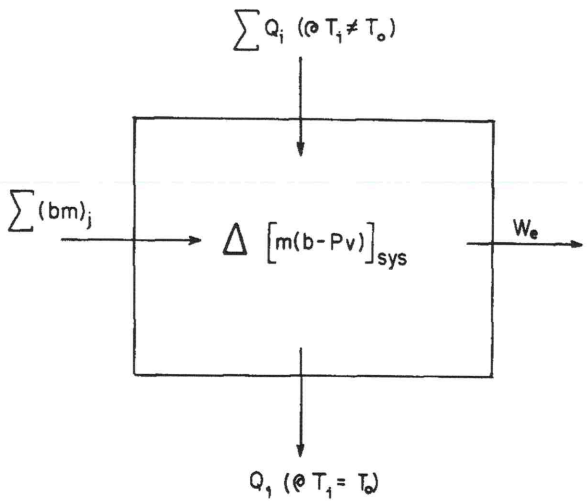

Fig. I-1. General process flow for a reversible or irreversible process.

$[m(b - Pv)]_{sys}$, the lost work is exactly the amount of incremental heat that must be rejected to the surroundings at T_0.† Since heat flow at any temperature other than T_0 can, in principle, be put to some use, while that at T_0 cannot be put to any use, we see that the thermodynamic lost work can be redefined. It becomes the increased amount of some other useful energy term that must be ultimately rejected as useless to the surroundings at T_0, as compared to what would be rejected by a reversible process with the identical material flows, identical heat flows at temperatures other than T_0, and identical change in the system described.

DISCUSSION

Richard Gaggioli, Marquette University, U.S.A. Isn't lost work, as you define it, simply synonymous with what others call "availability dissipation", "exergy consumption", etc?

Author's reply. If all are properly defined, then the answer is "yes". For any properly stated problem, the accurate application of any of these approaches will give the same answer. Thus, the choice of which to use should be based on convenience of use, or, for academics, on which approach is most easily learned by our students and which they are most likely to be able to apply correctly on the job.

Richard Gaggioli, Marquette University, U.S.A. If your approach can only evaluate exergy consumption, which can be obtained from the second law by analysis of the entropy production, then what is the function of your combined first and second law statement?

Author's reply. The relation between work and entropy changes arises from the combination of the first and second law. One cannot formulate any meaningful statements about work production or dissipation using the second law alone; no work term appears in it. The combined first and second statement is an explicit, rigorous way of computing the reversible work of any process. It appears to be the simplest way of doing that.

yet

Myron Tribus, Massachusetts Institute of Technology, U.S.A. In order to evaluate the overall process, isn't it necessary to analyze the essergy of not only the waste products but also of the primary products?

Author's reply. If the feed materials come directly from an equilibrium environment, and the products are directly released to an equilibrium environment, then the essergy or exergy approach you suggest makes sense. But, if the feed materials are not in equilibrium with the environment and the products are not discarded but used (as for example in a chemical plant), then the lost work approach presented in the paper which focuses on the irreversibilities/inefficiencies/lost work inside the system seems more appropriate.

Richard Gaggioli, Marquette University, U.S.A. In your opinion, when the availability function is simplified as $(h - T_0S)$, are the results obtained sufficiently accurate for engineering purposes? Does it matter what reference state is used?

Author's reply. This question implies that one obtains the availability function by simplifying some more complex function. That is not correct. One obtains it by combining the first and second laws applied to a general system. The same result can be obtained by starting with availability or exergy, but it is more simply obtained by the method shown in the paper.

The only simplification leading to the availability function is that of dropping terms in kinetic, potential, electrostatic, magnetic, and surface energies as discussed in our paper. In most cases of interest to process engineers, dropping them makes negligible errors. However if there are significant velocity changes, then these terms must be reinserted.

With this caveat, the only limitation on the accuracy of the method is the accuracy of the tables of thermodynamic data used. If the data tables have steam-table accuracy, then the calculated result will have steam-table accuracy.

One of the distinct advantages of this approach is that the choice of datum states is unimportant, because it does not influence the results. One can use tables such as the steam tables with no significant chance of error. For chemically reacting systems, however, a consistent set of tables must be used.

†For a cryogenic process, this net heat flow may be negative, and the lost work is then the decrease in the flow of heat into the system at T_0.

Richard Gaggioli, Marquette University, U.S.A. What is the advantage of your comparison of isentropic efficiency and second law efficiency of turbines to previous ones in the text books of Obert and Gaggioli (1963), Obert (1960), Obert (1948), and Keenan (1941)?

Author's reply. 1. It follows directly from the general definition of efficiency without the *ad hoc* definitions of isentropic outlet states. Thus, it allows the use of the same efficiency definition for turbines and compressors as is used for other devices.

2. It relies only on *actual* inlet and outlet states, rather than including *hypothetical* states not actually observed.

3. It gives much more realistic appraisals of the thermodynamic consequences of turbine or compressor inefficiencies for devices exhausting at temperatures far removed from T_0, as for example in Kapitza helium liquefiers or combined-cycle power plants.

As discussed in the paper, it also gives the identical result to those obtained by the definition mentioned in the question for the case where the exhaust stream is at T_0. This is the case of most practical interest in older style prime movers.

Ernest Geskin, Clarkson College of Technology, U.S.A. What difference exists between the notions of "exergy dissipation" and "lost work"?

Author's reply. If both are properly defined and applied, there is no difference. Thus, the choice between them should be based on ease and convenience of use (including ease of use and probability of correct application by average engineers instead of specialists).

Ernest Geskin, Clarkson College of Technology, U.S.A. How is "lost work" affected by the "rate of a process"?

Author's reply. It is a general observation that the rates of processes are roughly proportional to their degree of departure from equilibrium. For example, heat transfer is faster with a large temperature difference than with a small one. Thus, we would expect more lost work in a rapid process than with a slow one.

Adrian Bejan, University of Colorado, U.S.A. Reffering to the Guoy-Stodola theorem ($LW = T_0\Delta S_{irrev}$), shouldn't it be stressed that lost work (LW) is relative to T_0 whereas entropy generation (ΔS_{irrev}) is not?

Author's reply. It would be better to stress that the entropy generation (ΔS_{irrev}) doesn't have practical significance, while the lost work does. An entropy generation of one Btu/°R costs more where T_0 is high (e.g. at an air-cooled power plant in the Sahara) than where it is low (e.g. at a sea-water cooled power plant in Antarctica).

Francis Huang, San Jose State University, U.S.A. The concepts of exergy (available energy) and that of work are not mutually exclusive. Entropy production can be defined as a measure of lost work (unavailable energy). Do you have any comments on these remarks?

Authorfls reply. As discussed in the paper, there are basically two ways to approach the problem of evaluating irreversible (real) processes. One is to attach to each piece of matter a quantity that represents the amount of work that could be extracted from it by bringing it reversibly to equilibrium with some surroundings. That leads to the exergy/availability analysis formulation. The other approach is to focus attention on a traditional engineering thermodynamic system (open or closed, steady or unsteady state) and evaluate the energy and entropy *changes* which occur in it. This second approach leads to the lost work (or entropy production or irreversibility) concept shown in our paper. Both approaches have supporters and have classes of problems for which they excel. We have tried to show that, for a very broad class of problems including almost all chemical/petroleum/food and fiber processing processes, the lost work approach is simplest and easiest to apply correctly.

Richard Gaggioli, Maequette University, U.S.A. When you evaluate the hypothetical lost work in the dissipation of effluents, isn't that another way of evaluating the exergy of the effluents?

Author's reply. As shown in Dr. Vakil's discussion of Dr. Ahrendts' paper, there is considerable arbitrariness in defining exergy to include the possibility of extracting diffusional work from gas streams not at chemical equilibrium with the environment (e.g. different CO_2 content or water content) and not simultaneously including the possibility of nuclear rearrangements to the most stable states. Furthermore, as Dr. Ahrendts' paper shows, one can also logically penalize the efficiency of a process for not bringing about equilibrium for the reactions $N_2 + O_2 = 2NO$ and $NO + 1/2O_2 = NO_2$. All three of these represent potential work sources for which no technical means of accomplishments are now available. Most exergy analysts select one of them (CO_2 and water vapor equilibrium) and ignore the others.This appears arbitrary. There seems no logical basis for including one unrealizable work gain in an analysis and leaving out two others. By using the lost work approach on this problem, one is forced to make this decision explicitly instead of burying it in exergy tables. This seems to be a better way to decide what to include in this case, in which any choice is inherently arbitrary.