

THE TWO LOST-WORK STATEMENTS AND THE COMBINED FIRST- AND SECOND-LAW STATEMENT

NOEL DE NEVERS AND J. D. SEADER

*University of Utah
Salt Lake City, UT 84112*

ALL OF THE FUNDAMENTAL thermodynamic development for computing the reversible work of processes was apparently known and published by 1903. Therefore, this paper and similar papers discuss only the question of which of the many possible approaches for applying thermodynamic analysis to various kinds of processes is easiest to teach, easiest to understand, and most likely to be applied correctly by the average engineer.

WHY USE LOST WORK?

This paper is largely about the "lost work" approach, which has some advantages over other approaches. The first advantage of lost work is that it has a very high intuitive content. This was the reason it was first introduced. In many important cases, it is exactly equal to the work converted to friction heating.

The second advantage is that the sum of the lost work and the work actually performed is equal to the reversible work

$$dW_{\text{rev}} = dW + dLW \quad (1)$$

This reversible work has a character quite different from either the actual work or the lost work, which are both path functions whose value depends upon the path followed going from the initial to the final state. However, the reversible work, their sum, is a state function; its value depends only on the initial and final states of the system and the heat and matter flows across the system boundaries; it is independent of the path actually followed.

The third advantage of the lost work is that it can be used to make direct computations of the reversible work, the lost work, and the thermodynamic efficiency of any process.

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WHAT IS THE ALTERNATIVE?

If one does not wish to use the lost-work approach to the second-law analysis of chemical processes, the alternative is the availability-exergy-essergy approach. Another paper [5] attempts to show that, although the other approach has many advocates and is widely used, it is generally not as suitable for the analysis of chemical engineering processes as is the lost-work approach.

WHY ISN'T LOST WORK USED?

A principal purpose of this paper is to show that lost work has not been widely used because there exist in the literature two very different quantities that both go by the same name, "lost work." For reasons that will be clear later, we call these two definitions LW_m (for mechanical lost work) and LW_t (for thermodynamic lost work). The existence of these two different quantities has led to confusion and misapplication of the lost work with the result that the lost work has not been utilized as widely as it should have been.

Although the concept of "wasted work," "dissipated work," "useless work," or other such terms was present in the literature for many years and the correct theoretical basis for the application of the concept was shown by Gibbs in 1876 [7], as far as we know, the first to use the term "lost work" in the chemical engineering literature and in chemical engineering textbooks and handbooks was G. G. Brown [3]. As far as we can tell, he formulated it independently of others who may have had similar ideas before him. He then worked with Sliepcevich [2] and Martin [10] who extended and developed the idea. Several authors adopted



Noel deNevers has been a faculty member at the University of Utah since 1963. His principal technical interests are fluid mechanics, thermodynamics, and air pollution. He has also developed a course and edited a book of readings on Technology and Society. In this article he returns to one of his early loves, thermodynamics. He asserts that there is no "Energy Crisis," but there may be an "Entropy Crisis," although that may be hard for the public and the politicians to grasp. In addition to his technical work, he recently had three of his laws published in the 1982 Murphy's Laws compilation and won the coveted title "Poet Laureate of Jello" at the annual Jello Salad Festival in Salt Lake City. (L)

J. D. Seader has been a faculty member at the University of Utah since 1966. Prior to that, he was employed by Chevron Research and Rocketdyne. His principal technical interests are equilibrium-stage operations, process synthesis, process simulation, and synthetic fuels. He is a Director of the AIChE and was the Annual Institute Lecturer in 1983 for AIChE. He has prepared the section on distillation for the forthcoming sixth-edition of the **Chemical Engineers' Handbook** and is currently the Executive Officer of CACHE. (R)

lost work and used Brown's formulation in textbooks [1, 16, 17].

Meanwhile, Van Ness developed a different version of the lost work [14, 15]. His version appears in his thermodynamics textbook with Smith and in the 5th Edition of *Perry's Handbook*. On the other hand, Brown and Sliepceovich's version appears in the 3rd and 4th editions of *Perry's Handbook*. To our knowledge, no one has previously shown that between the 4th and 5th editions of *Perry's Handbook*, the fundamental thermodynamic orientation toward lost work changed. We believe that this change is significant and should be known and understood by chemical engineers.

Turning now from the history of the two concepts, let us contrast them by means of discussion and Table 1.

THE TWO LOST-WORK CONCEPTS

We begin by defining two auxiliary quantities,

$$\text{Work converted to heat (or to internal energy)} = \text{WCTH} \quad (2)$$

$$\text{Work to restore system} = \text{WTRS} \quad (3)$$

The first of these (WCTH) is the amount of shaft work, falling weight work, or its equivalent ($\int PdV$ work, electrical work, decrease in kinetic or potential energy, and decrease in magnetic or chemical or diffusional potential to do work) that is converted to heat or to internal energy. This is equivalent to mechanical, frictional rubbing as in a brake.

The second of these (WTRS) is the amount of work that must be supplied to restore a system to its original conditions after some process of change has occurred in the system. The restoration process exchanges heat only with the infinite surroundings at T_0 .

The quantities WCTH and WTRS are not *in general* the same; they are the same *if and only if* the system considered is uniformly isothermal at the temperature, T_0 , of the infinite surroundings.

The earliest published reference to the lost work that we have found is in Brown et al [3]

In any process the increase in internal energy due

to heat effects $\int_1^2 TdS$ is equal to the sum of the heat

absorbed from the surroundings and all other energy dissipated into heat effects within the system due to irreversibilities such as overcoming friction occurring in the process,

$$\int_1^2 TdS = q + (lw) \quad (58)$$

where lw = "lost work," energy that could have done

TABLE 1
Comparison of the Two Lost-Work Definitions

	LW _m Mechanical Lost Work	LW _t Thermodynamic Lost Work
Definition	LW _m = WCTH	LW _t = WTRS - W
Definition in terms of dS _{irr}	dLW _m = TdS _{irr}	dLW _t = T ₀ dS _{irr}
Unambiguously defined for non-isothermal systems?	NO	YES
Computable for an iso- thermal system without reference to surround- ings temperature?	YES	NO
Leads to a reversible work statement that is an unambiguous state function for all cases including non- isothermal cases?	NO	YES

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work but was dissipated in irreversibilities within the
 flowing material.

Although Brown directed it at irreversibilities in
 flowing streams, the concept of lost work given
 above can, in principle, be applied to any type of
 process.

This idea was expanded and placed in more
 general form by Brown and Sliepcevich [2]

Lost Work. Because, as commonly used, $\int TdS$ does
 not differentiate between heat and loss of potential
 energy, another expression (lw) is used to designate all
 potential work dissipated in overcoming resistances or
 in irreversibilities or "lost work." It represents the
 energy that might have been evident as work if it had
 not been so dissipated. Accordingly

$$\int TdS = q + (lw) \quad (1)$$

The lost work defined in these two equations is
 equivalent to

$$LW = WCTH \quad (4)$$

We may also utilize the formulation of the
 second law shown by Denbigh [6] (attributed by
 him to de Donder), in which a term is introduced
 for the irreversible entropy production. In it, for a
 closed system, we would have

$$dS = dQ/T + dS_{irr} \quad (5)$$

Comparing Eq. (5) with the definition of lw given
 in the two preceding quotes, we find that Brown's
 definition of lost work is equivalent to

$$d(LW) = TdS_{irr} \quad (6)$$

In Table 1, we have called this definition of the lost
 work LW_m ; i.e., mechanical lost work. Eqs. (4)
 and (6) are shown as the first two entries of Table
 1 under LW_m .

The other definition of lost work (which we
 call LW_t , thermodynamic lost work, and shown
 as a column with that heading in Table 1) was
 also apparently first defined by Brown and
 Sliepcevich [2]. In that article, they followed their
 basic definition of the lost work quoted above with
 two subcases. In an isothermal subcase, they write
 their entropy balance with a quantity $(lw)_T$. In
 the other subcase, for systems that exchange heat

only with the surroundings at T_o , they write their
 entropy balance with a quantity $(lw)_o$. They do
 not in any way remark in that article (or any other
 subsequent publication we have found) that $(lw)_o$
 is not the same quantity as $(lw)_T$. However, if we
 follow their examples, we find that $(lw)_T$ is the lost
 work in their basic defining equation while, sub-
 stituting their $(lw)_o$ into Eq. (5), we see that

$$d(lw)_o = T_o dS_{irr} \quad (7)$$

or

$$(lw)_o = \frac{T_o}{T} (lw)_T \quad (8)$$

(In the terms used in this paper, $LW_t = (T_o/T)LW_m$.)

The second definition of lost work ($(lw)_o =$
 LW_t) was arrived at independently by Van Ness.
 He informs us that his development was totally
 independent of that of Brown, Sliepcevich, and
 Martin. In 1956, Van Ness published his first paper
 on the topic, in which he defined the lost work as
 minus the value in Eq. (7). (The choice of whether
 to make the lost work positive or negative is
 arbitrary; Brown makes it positive, Van Ness
 originally made it negative, then switched and
 made it positive [12]. We use the positive value
 here.)

In his 1956 article [14], Van Ness arrived at
 his definition by considering the reversible work
 necessary to restore a system to its original con-
 dition after some change has occurred in the
 system, allowing heat exchange with the sur-
 roundings only at T_o and subtracting the work
 done by the system during that change. The proofs
 are shown there that

$$LW_t = WTRS - W \quad (9)$$

Thus, we show in Table 1 this property of LW_t .

At this point, the application of the two defini-
 tions to a simple example may make their differ-
 ence clear. Consider a system consisting of an
 isobaric, adiabatic container filled with a vapor-
 liquid mixture of helium at its normal boiling
 point of 4°K. Work added to the system by means
 of a friction brake, as shown in Fig. 1, is converted
 to internal energy of the helium. The irreversible
 entropy increase of the system is equal to the work
 input ($WCTH$) divided by the system tempera-
 ture, T_{sys} , where the conversion takes place. But
 is the *work input* the same as the *lost work*? Accord-
 ing to the definition proposed by Brown (Eq. 4),
 it is the same; work input converted to friction
 heat equals lost work.

Suppose we decide that the lost work is not simply the work input converted to internal energy but also the amount of reversible work that would be required to restore the system to its original state, as apparently first suggested by Van Ness [14]. To restore the system, suppose we use a refrigerator of some ideal type to extract heat from the system in an amount equal to the increase in internal energy and reject heat to the surroundings (assumed to be infinite) at temperature T_o . By straightforward application of the theory of Carnot refrigerators, we have

$$WTRS = LW_m \left(\frac{T_o - T_{sys}}{T_{sys}} \right) \quad (10)$$

Unlimited amounts of heat may be rejected to or absorbed from the infinite surroundings at T_o . Normally, the surroundings temperature can be taken as that of the nearest body of water (for example, a river, lake, or ocean) or the water temperature that can be easily reached in atmospheric cooling towers or atmospheric air. Assuming that T_o is 25°C (298°K), from Eq. (10), the reversible work to restore the helium system is $(298 - 4) / 4$ or 73.5 times the work input converted to internal energy.

For the system in Fig. 1, Brown defined the

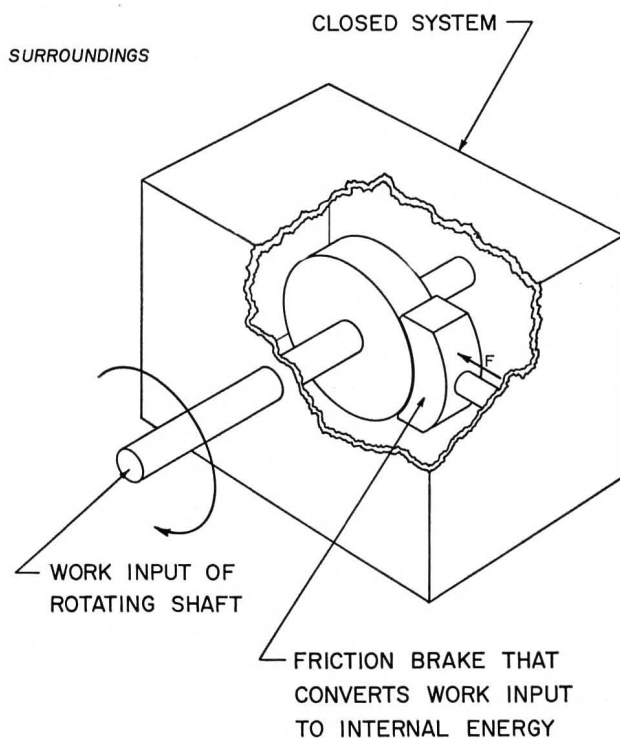


FIGURE 1. Friction brake to convert work to internal energy.

lost work as the work input to the system, which is equal to LW_m . From a practical engineering viewpoint, we believe that this definition is incorrect. If the work input is converted to internal energy of helium, thus causing some of it to vaporize isobarically at its normal boiling point, then somewhere else in the world some helium liquefier is doing the work to remove that same amount of heat to supply us with liquid helium. That helium liquefier may be part of our plant or that of our

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liquid helium supplier; but, either way, we must pay for the work it does. Thus, in practical terms, the real loss is not only the work converted to internal energy but also the reversible work required to offset this irreversible conversion. Therefore, we assert that the practical definition of the lost work is that definition apparently first used by Brown and Sliepcevich [2], which they called $(lw)_o$, but which they apparently never subsequently used and which was later independently introduced by Van Ness [14] and which we term the "thermodynamic lost work" (LW_t), where, in general

$$LW_t = WTRS - W \quad (11)$$

In the particular case of the friction brake in helium,

$$LW_t = WTRS + LW_m \quad (12)$$

because LW_m is simply the negative of the thermodynamic work *produced* by the system. Combining Eqs. (10) and (12) to eliminate the $WTRS$, we obtain

$$LW_t = LW_m \frac{T_o}{T_{sys}} \quad (13)$$

Why is LW_t not equal to $WTRS$? If there is no exchange of work between the system and its surroundings during the irreversible process, then the W in Eq. (11) is zero, and $LW_t = WTRS$. But for cases in which the external work during the irreversible process is not zero, the W term is significant. We may see this by considering a general, irreversible process in a closed system that proceeds from State 1 to State 2. The work to restore the system to State 1, exchanging heat only with the surroundings at T_o , is independent of the ir-

Continued on page 146.

our teaching style. Professor Kyle has given us yet another option in that tradition. □

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LOST-WORK STATEMENTS

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reversible path that brought the system from State 1 to State 2. But if that path produced useful work, we could have stored it and used it to partly offset the work of restoration; if it produced no useful work, then all of the work of restoration must be supplied externally. Hence the thermodynamic lost work, as apparently first stated by Van Ness [14] is the work to restore the system minus the external work produced.

We can now proceed to complete Table 1, which shows the differences in properties of the two definitions of lost work. The first question is whether they are unambiguously defined for non-isothermal systems. From the definitions in terms of dS_{irr} , it is easy to see that LW_t is unambiguously defined for a non-isothermal system because the system temperature does not appear in its definition (only the infinite surroundings temperature does). The system temperature is implicitly present in the dS_{irr} term, but that is unambiguous. On the other hand, LW_m has a T in its definition in terms of dS_{irr} . If that T is constant, both in space and in time, then the definition is unambiguous. But if it is not, then there is no unambiguous definition of LW_m . For example, we could consider the irreversible flow of heat through a solid conductor from a reservoir at T_h to one at T_c . Here

$$dS_{irr} = dS = dQ \left(\frac{1}{T_c} - \frac{1}{T_h} \right) \quad (14)$$

so

$$dLW_t = T_o dS_{irr} = dQ \left(\frac{T_o}{T_c} - \frac{T_o}{T_h} \right) \quad (15)$$

and

$$dLW_m = T dS_{irr} = dQ \left(\frac{T}{T_c} - \frac{T}{T_h} \right) \quad (16)$$

LW_t is perfectly unambiguous, but LW_m is only defined if we can define a proper value for T . We could set it equal to T_c , in which case LW_m is equal to the work that would have been produced by a Carnot engine withdrawing dQ of heat from the high-temperature reservoir and operating between T_h and T_c . Or we could set it equal to T_h , in which case LW_m would be equal to the amount of work that a Carnot engine would produce by withdrawing $(T_h/T_c)dQ$ of heat from the high-temperature reservoir and rejecting dQ of heat to the low-temperature reservoir. One could persuasively argue for either of these values or perhaps for some intermediate one. The point is that there is no obvious or unambiguous definition of LW_m for this case. Van Wylen and Sliepcevich have tried to deal with this problem. Van Wylen [16] says

In summary, the lost-work concept assumes that there is a reservoir available at the temperature T required for the given situation. The concept of irreversibility assumes heat transfer with the surroundings only at temperature T_o .

Here he is clearly referring only to LW_m and does not mention the existence of the other definition (LW_t). Van Wylen uses another quantity which he calls "irreversibility" which is identical to what we call LW_t .

Sliepcevich [11] says

It is apparent that the evaluation of the terms $\delta(Q_i/T_i)$ and $(\delta l_w/T)$ in Eq. (4-155) [a general entropy balance] will pose certain difficulties either if the temperature of the system is not uniform throughout or if the temperature, even though uniform throughout, changes during the process.

and also

Note that the latter [Eq. 4-193, a steady flow entropy balance using LW_m] cannot be solved explicitly for $(dQ)_i$ or $(dLW)_i$ unless the temperature of the system T is constant and uniform throughout, in which case, $T_i = T = T_i = T_o$. For this very special case, Eq. 4-193 yields....

These three statements must surely have convinced any practitioner that the lost work definition to which they apply, (LW_m), is of very little, if any, practical utility.

The next line on Table 1 asks whether the two values of LW are computable without reference to the surroundings temperature. LW_m obviously is because in its definition, nothing related to T_o appears. One unit of mechanical work converted to internal energy has the same value of LW_m whether it is at the temperature of the sun or that of liquid helium. On the other hand, LW_t cannot be

computed independently of the surroundings temperature. If the surroundings temperature is, for example, 20°C, then the conversion to frictional heat of one unit of mechanical work has a value of LW_t less than one unit for system temperatures greater than 20°C and more than one unit for system temperatures lower than 20°C.

To close this section, consider a non-thermodynamic analogy that may clarify the distinction between the two kinds of lost work. If one drops a bottle of wine on his kitchen floor and the bottle breaks, then he has certainly lost the wine. The LW_m is analogous to the assertion that what is lost is the wine. The LW_t is analogous to the assertion that not only is the wine lost, but also someone must clean the kitchen floor.

REVERSIBLE WORK OR COMBINED-LAW STATEMENTS

To consider the next line in Table 1, we must introduce the idea of the reversible work, or the combined first- and second-law statement. We believe that the simplest way to show such a statement is to begin with open-system, unsteady-state energy and entropy balances,

$$d(mu)_{\text{sys}} = \sum_j h_j dm_j + \sum_i dQ_i - dW \quad (17)$$

$$d(ms)_{\text{sys}} = \sum_j s_j dm_j + \sum_i \frac{dQ_i}{T_i} + \frac{dLW_t}{T_o} \quad (18)$$

Then we multiply Eq. (18) by T_o and subtract it from Eq. (17), finding (after rearrangement)

$$dW + dLW_t = \sum_j (h - T_o s)_j dm_j + \sum_i \left(1 - \frac{T_o}{T_i}\right) dQ_i - d[m(u - T_o s)]_{\text{sys}} \quad (19)$$

or, in terms of the availability function ($b = h - T_o s$),

$$dW + dLW_t = \sum_j b_j dm_j + \sum_i \left(1 - \frac{T_o}{T_i}\right) dQ_i - d[m(b - Pv)]_{\text{sys}} \quad (20)$$

The sum of the two terms on the left of the equal sign is the reversible work

$$dW_{\text{rev}} = dW + dLW_t \quad (21)$$

for a process occurring in the system and having the same initial and final states of the system, the same flows of matter in and out, and the same exchanges of heat at all temperatures except T_o .

This equation has the remarkable property of showing that the sum of two path functions (dW and dLW_t) form a state function.

Here we use the term "state function" in a

somewhat broader sense than it appears in many thermodynamics texts. There it refers to a property of a fixed mass of matter, like entropy, showing that the changes of this property depend only on the initial and final states of the system, and do not depend on the path taken to get from the initial to the final state. Here we expand that idea to include the possibility that there is heat exchange with the system at temperatures other than T_o and that there may be flows of matter across the system boundaries.

The value of dW_{rev} can be computed unambiguously for any system using only the terms on the righthand side of Eq. (19) or (20); i.e., the data on the initial and final states of the system and the flows of heat and matter across its boundaries. (It is not necessary to know the value of dQ at T_o or of dW .) If we also have data on dW or on dQ at T_o , it allows an equally unambiguous computation of dLW_t .

Is the same type of formulation possible for LW_m ? Apparently not. If we substitute from Eq. (13), we find

$$dW + \frac{T_o}{T_{\text{sys}}} dLW_m = \sum_j b_j dm_j + \sum_i \left(1 - \frac{T_o}{T_i}\right) dQ_i - d[m(b - Pv)]_{\text{sys}} \quad (22)$$

but unless the system is isothermal, both over time and space, there seems no way to evaluate or attach meaning to the lefthand side of Eq. (22). Thus, in Table 1 we indicate that LW_t leads to an unambiguous combined statement but that LW_m does not.

It is also interesting to ask who introduced Eq. (20) or its equivalents into engineering. The fundamental ideas go back as far as Gibbs [7]. The idea of maximum reversible work, exchanging heat only with the surroundings at T_o , goes back at least as far as Gouy [8] and Stodola [13]. Kestin [9] refers to the basic result as the "Gouy-Stodola Theorem."

Brown and Sliepcevich [2] show an equation similar in form to Eq. (20) (using what they called $(lw)_o$), including terms for kinetic and potential energy but without the terms for a change in the system nor for heat flows at temperatures other than T_o . Martin [10] devotes a considerable fraction of his thermodynamics slides to developing equations of the same form and content as Eq. (20). Denbigh [6] thoroughly works out a batch equivalent of Eq. (20) and indicates how one would find the open-system equivalent. Smith and Van Ness [12] also show forms that are equivalent

to Eq. (20). Certainly others could be cited.

THE UTILITY OF LOST WORK AND THE COMBINED STATEMENT

As shown elsewhere [4, 5], the lost-work approach to second-law analysis of processes is generally simpler than the competing approaches. Its assumptions and limitations are clearly stated and can be removed when needed (e.g., one easily can include terms for kinetic energy, etc.). The combined statement is one of extreme power and generality, which should occupy a central place in any treatment of thermodynamic efficiency.

CONCLUSIONS

The adoption and use of the lost-work concept has been strongly hindered by the existence, in the chemical engineering literature, of two very different quantities that both bear the name "lost work."

The "thermodynamic lost work" is much more useful and practical than the "mechanical lost work." Using the thermodynamic lost work, one can formulate a combined statement of the first and second laws, which shows that, although the actual work and the lost work are path functions, their sum, the reversible work, is a state function. This allows the direct computation of the reversible work of irreversible processes. □

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NOTATION

b	availability function per unit mass ($h - T_0s$), J/kg
h	enthalpy per unit mass, J/kg
lw	lost work (used in Brown and Sliepcevich papers), J
(lw) _T	lost work of an isothermal process (used in Brown and Sliepcevich papers), J
(lw) _o	lost work of a process that exchanges heat only with the surroundings at T _o (used in Brown and Sliepcevich papers), J
LW	lost work, J
LW _m	mechanical lost work, J
LW _t	thermodynamic lost work, J
m	mass, kg
P	pressure, pa
Q	heat, J
q	heat (used in Brown and Sliepcevich papers), J
S	entropy, J/°K
s	entropy per unit mass, J/kg°K
S _{irr}	irreversible entropy production, J/°K
T	temperature, °K
T _o	temperature of the infinite surroundings, °K
T _{sys}	system temperature, °K
T _c , T _h	temperatures of hot and cold reservoirs, °K
v	volume per unit mass, m ³ /kg
V	volume, m ³
W	work, J
W _{rev}	reversible work, J
WCTH	work irreversibly converted to heat or internal energy, J
WTRS	work required to restore a system, exchanging heat only with the infinite surroundings at T _o , J