

FIRST AID to Ailing Thermodynamics

H. T. Bates

Professor of Chemical Engineering
Kansas State University, Manhattan, Kansas

Engineering educators stand accused by those investigating the drop in engineering enrollment, of practices that tend to discourage students (2). It appears that there may be just basis for the accusation, particularly apropos of some of the literature with which students are forced to contend.

There is a literary form called the objective correlative. It was used extensively by T. S. Eliot. It has been likened to beefsteak that a burglar carries to divert the watchdog while he robs the safe (3). Mr. Eliot's poetry abounds in this sort of thing; the casual reader gets something—the beefsteak—but it takes real digging to find the underlying idea—the contents of the safe. Eliot must have felt a little sorry for his readers, because he later published footnotes to trace some of his ideas. His good friend, Ezra Pound, on the contrary, felt that it wasn't sporting to put in any footnotes at all.

Even some of the scientific disciplines are producing technical literature that resembles the objective correlative in the confusion it offers the reader. (Nicholas Vanserg's pieces "Mathmanship" and "How to Write Geologese" are entertaining commentaries on publications in two fields (6, 7).) Engineering has not been a major offender in this respect, although examples of misleading prose and illogical terminology can be found in our literature (1, 5). An important instance occurs in the subject of thermodynamics. It is the purpose of this article to propose reforms in the subject; to rearrange the concepts into forms that are more logical under modern conditions; to alter some definitions and conventions in the interest of clarity; and to propose a unifying treatment that can be presented immediately to beginning scholars.

If this objective is to be successful, a certain amount of re-education of faculty

members and research workers will be necessary in advance of its introduction to students in the classroom. It should be emphasized at the outset that these proposals represent some changes in point of view, but they are in every respect algebraically compatible with the more traditional treatment. These changes, evolved from experience with the difficulties that learners have with the subject, were acceptable to those students who were honestly trying to get the picture.

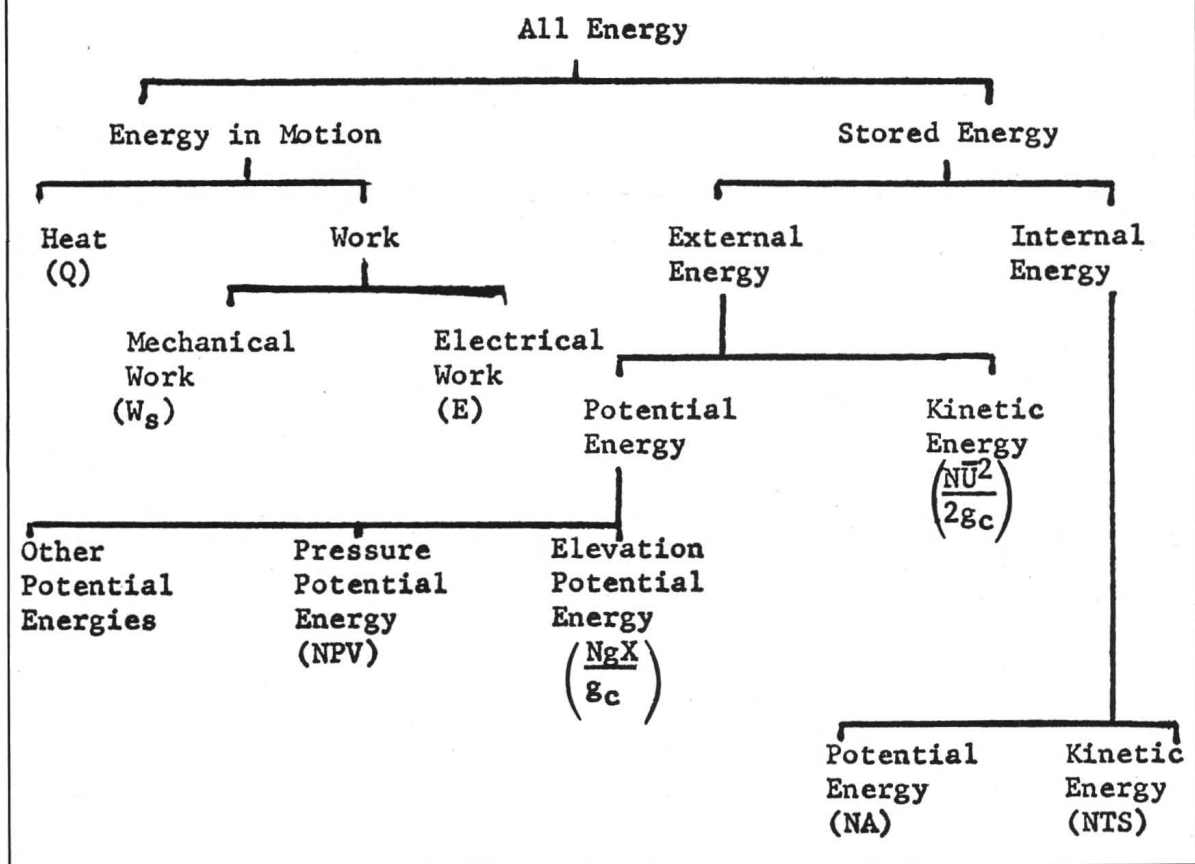
Improving the Terminology

A little investigation will reveal a number of examples of confusing nomenclature in thermodynamics. It is almost as if the terminology had not been brought up to date for 40 years. Surely it is time for a reappraisal in the educational methods that are needed today.

We may start with the word thermodynamics itself, which means literally "heat in motion," although other kinds of energy transformation are just as important to the subject as heat. A better term would be *energetics*. It is really redundant to say *thermodynamics* because any proper definition of *heat* must include the idea that it is energy in motion. *Heat*, *work*, and *electricity* are all — by definition — manifestations of energy in motion. Unlike *stored energy*, they are not associated with any particular mass of material. They may flow across the boundaries of a system and they may flow through the interior. They are not point functions. The quantity of energy transferred across the boundaries of a system as heat, work, or electricity depends upon the path as well as upon the initial and final values of state conditions such as *temperature*, *pressure*, *volume*, and *voltage*.

The terms *thermostatics*, *stored heat*, *heat content*, *heat capacity*, *stored work*, and *stored electricity* are misnomers. They conflict with the definitions; they confuse students. We must stop using them if we are to have a truly logical body of knowledge. The idea of dividing all energy first

TABLE 1
THE DICHOTOMY OF ENERGY



into two classes of *energy in motion* and *stored energy* is basic to the understanding of the subject, but we should not allow the idea to be undermined by the use of unprecise and contradictory terms.

Stored energy should be represented by a number of names corresponding to all the commonly recognized classifications. It is worth noting that the classification is complex. The early workers appear to have been afraid that some little understood kind of energy might be left out. As a result they organized a *dichotomy of energy*. This is outlined in Table I. Notice that the subdivisions are always made by dividing into two classes—those that do and those that do not meet some criterion. Thus *stored energy* is divided into *external energy* and *internal energy*. At the next level both of these are divided into *kinetic energy* and

potential energy. Now there are clearly several kinds of potential energies on the external side and two of these are shown—but one must remember that in certain special kinds of problems *magnetic potential energy*, *surface potential energy*, or other kinds must be included.

All stored energy terms are associated with a mass of material. They are point functions; differences in their values associated with a change of state of the system are determined solely by the initial and final conditions and are independent of the path.

Certain common energy terms have been left out of Table I deliberately: *non-flow work*, *internal energy*, *enthalpy*, and *Gibbs free energy*. Some of these have their uses, but none of them should be taught to students at first. The reason for this is

that each of these terms represents an arbitrary combination of simpler terms, as can be seen from the following equations

$$dW = dW_s + d(PV) \quad (1)$$

$$dU = dA + d(TS) \quad (2)$$

$$dH = dU + d(PV) \quad (3)$$

$$dF = dH - d(TS) \quad (4)$$

where A = Helmholtz free energy, F = Gibbs free energy, H = enthalpy, P = absolute pressure, S = entropy, T = absolute temperature. U = internal energy, V = volume, W = non-flow work, and W_s = shaft work.

A Canon for the First Law

The first law of thermodynamics is an energy balance. Unfortunately, the literature is full of different statements of this law. There seems to be no clearly recognized, generally agreed upon, form that could always be used as a starting point. Students need such a statement which they can use to avoid the possibility of leaving out some energy terms that are important to their problem. If they were to be given a universal formulation or *canon* to begin every problem, and it were clearly stated that subsequent manipulations apply only to a particular situation, it would be easier to break the habit of formula snatching which many of them attempt to practice.

In view of the fact that the first division employed in the dichotomy of energy, Table I, is that between energy in motion and stored energy, it is suggested that an equality be used to relate the two kinds of quantities in a system. As a matter of fact, some textbooks do this by putting heat, work, and electricity on the left side and all stored energy terms on the right side. On the stored energy side it is recommended that one term be provided for each kind of energy, all combination terms being avoided. It is also recommended that the standard form of the energy balance be written with differentials, since deltas and integral signs raise questions about datum levels, the initial and final states, or constants of integration—all matters having to do with a particular problem. Beginning engineering students should be able to perform the necessary integrations.

With these recommendations in mind a *canonical statement of the first law* can be formulated as follows:

$$dQ - dW_s - dE = dA + d(TS) + d(PV) + d\left(\frac{NgX}{g_c}\right) + d\left(\frac{N\bar{U}^2}{2g_c}\right) \quad (5)$$

where E = electricity, g = acceleration of gravity, g_c = gravitational conversion factor, N = mass, Q = heat, \bar{U} = velocity, and X = absolute elevation.

What Is Work?

The so-called work terms in the energy balance do not always satisfy the criterion of representing energy in motion. Lectures intended to establish the principle that heat, work, and electricity are always energy in motion are weakened by the algebra in many textbooks. That which is usually called non-flow work (W) in a batch process is one such instance. This can be shown by algebraic manipulation to be:

$$W = W_s + \Delta(PV) \quad (6)$$

The *shaft work* (W_s) clearly satisfies the definition of work; i.e., it is energy in motion. It requires a machine with a rotating shaft or a moving piston rod. The so-called *flow work* or *flowing energy* term, $\Delta(PV)$, is a different matter. It represents stored energy, for it is a point function. For this reason the terms flow work and flow energy also should be avoided.

An excellent exercise to give students early in their course work involves them in a pressure-volume graph. They are asked to choose points on the graph representing arbitrary initial and final states and to draw two arbitrary paths between these points with a French curve. They are then asked to evaluate graphically for each path the quantity

$$\int_1^2 PdV + \int_1^2 VdP$$

and to compare the two values with the value of the function $P_2V_2 - P_1V_1$. Since all of the expressions give the same result, the students can see readily that $\Delta(PV)$ is a point function and that the individual integrals are *not* point functions, for they do depend upon the path.

Another approach is to write $\Delta(PV)$ as $N \Delta(P/\rho)$. The mass N is the capacity factor and P/ρ is the intensity factor of the energy term. The later is readily recognizable as the pressure head in Bernoulli's equation. Therefore, $\Delta(PV)$ is really *pressure potential energy*. For example: putting work into a compressor that delivers compressed air to a pressure tank at the corner service station is analogous to putting work into a pump that supplies water to an elevated tank at the water works. Both the air in the pressure tank and the water in the elevated tank possess stored potential energy. In order to differentiate them $Ng \Delta X/g_c$ should be called *elevation potential energy* and $\Delta(PV)$ should be called *pressure potential energy*.

Thus W turns out to be a mixture of work and stored energy, and it should no longer be referred to as work. Some books try to make W look like pure work by attempting to show that $\Delta(PV)$ is work. The explanation usually goes something like this: "The gas that goes into the process enclosure is pushed in by the gas that follows it, and the gas that leaves the enclosure pushes back the atmospheric air." This is very confusing to students because they cannot visualize other gas or air as being the same as the face of a piston. They also find it hard to follow an imaginary boundary that shifts as the gas passes through it. The educational advantage of the new point of view should be clear, for it does not require such explanation.

The Trouble With Enthalpy

Kammerling Onnes (4) invented the term *enthalpy* as a substitute for such terms as *stored heat* and *heat content*. Although it was a worthwhile advance, it still gives trouble. Some students tend to equate enthalpy with heat without regard to the effects of other terms in the energy balance. Of course enthalpy is a hybrid concept consisting of part internal energy and part external pressure potential energy. Such a mixture is quite illogical though convenient in many practical problems. A logical alternative would be to discard enthalpy and return to internal energy. Unfortunately, this is not likely to come to pass; for the literature is full of tables and graphs of enthalpy, and there are comparatively few

data in the form of internal energy.

The progress of understanding would be aided, however, if the terms *heat capacity* and *latent heat* were abandoned. These terms provide a misleading connection between heat and enthalpy that should be discouraged. Students will get along with much less trouble with the terms *enthalpy capacity* instead of "heat capacity at constant pressure," *internal energy capacity* instead of "heat capacity at constant volume," *latent enthalpy* instead of "latent heat at constant pressure," and *latent internal energy* instead of "latent heat at constant volume." At first these new names seem cumbersome to old timers, but this is not the case with beginning learners.

Extending the First Law of Energetics

In Table I and Equation 5 internal energy is divided into internal potential energy and internal kinetic energy. This is done arbitrarily, calling TS the *internal kinetic energy* and A (the Helmholtz free energy) the *internal potential energy*. In view of the statistical difficulties of dealing with the interactions of all of the molecules and sub-atomic particles this may seem to be questionable. However, in view of the relationship of Equation 2, the fact that there are only two subdivisions under internal energy (no unknown form of energy thus being overlooked), and the convention of a form of the first law that includes no combination terms, it is logical to make such a division.

Handling Irreversible Processes

For a reversible process,

$$dQ_{\text{reversible}} = Tds \quad (7)$$

$$dW_{\text{reversible}} = -VdP \quad (8)$$

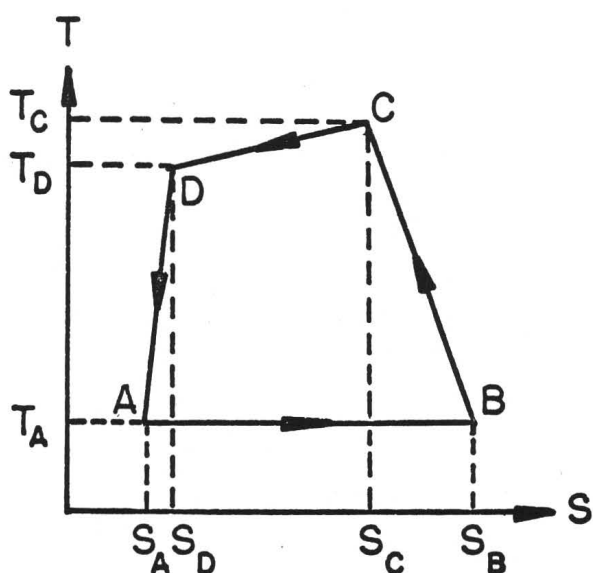
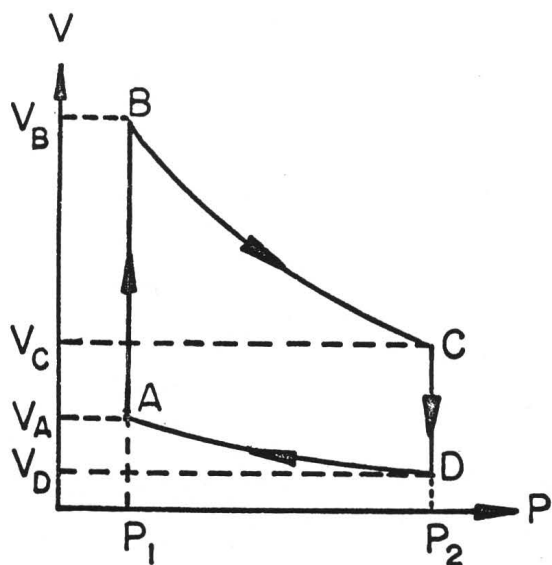
The canonical statement of the energy balance for such a process results from the substitution of Equations 7 and 8 into Equation 5 (with electricity assumed to be zero):

$$TdS + VdP = dA + (TdS + SdT) + (VdP + PdV) + \frac{Ng}{g_c} dX + \frac{N}{g_c} d\left(\frac{\bar{U}^2}{2}\right) \quad (9)$$

For the reversible case the like terms on both sides of the equation may be cancelled. *But wait! All actual processes are irrevers-*

Table II

An irreversible ideal-gas compressor



$P_1 = 14.7 \text{ psia}$
 $P_2 = 85.0 \text{ psia}$
 $V_A = 0.0255 \text{ ft}^3$
 $V_B = 0.850 \text{ ft}^3$
 $V_C = 0.2245 \text{ ft}^3$
 $V_D = 0.00675 \text{ ft}^3$
 $C_p = 7.00 \text{ Btu}/(\text{Lb mole} \cdot ^\circ\text{R})$
 $C_v = 5.01 \text{ Btu}/(\text{Lb mole} \cdot ^\circ\text{R})$
 $K = 1.400$
 $n = 1.318$

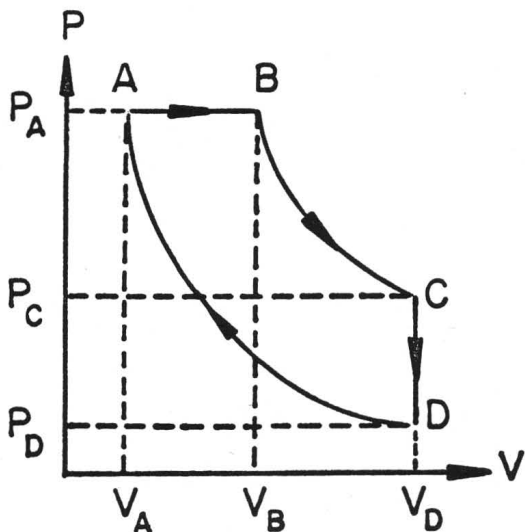
$T_A = T_B = 530. \text{ }^\circ\text{R}$
 $T_C = 808. \text{ }^\circ\text{R}$
 $T_D = 700. \text{ }^\circ\text{R}$
 $S_A = + 0.040 \times 10^{-3} \text{ Btu}/^\circ\text{R}$
 $S_B = + 3.91 \times 10^{-3}$
 $S_C = + 2.377 \times 10^{-3}$
 $S_D = + 0.157 \times 10^{-3}$
 $N_A = N_D = 0.000,0764 \text{ Lb mole}$
 $N_B = N_C = 0.00220 \text{ Lb mole}$

Energies in Btu

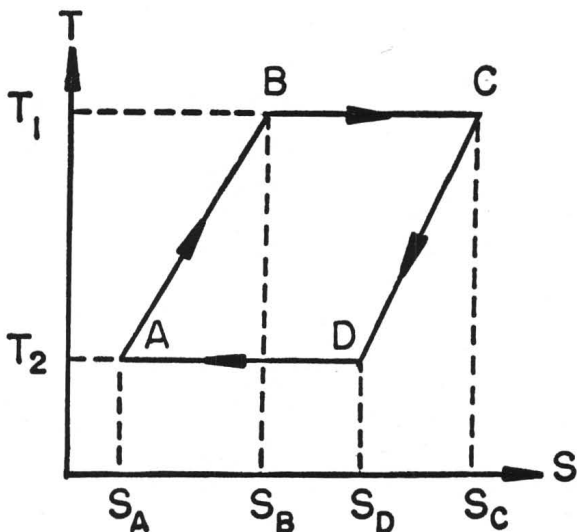
Function	AB	BC	CD	DA	A B C D
Q	0.00	- 0.76	- 1.67	+ 0.11	- 2.32
W_s	0.00	- 5.05	0.00	+ 0.15	- 4.90
W	+ 2.24	- 3.82	- 3.43	+ 0.11	- 4.90
$\Delta(PV)$	+ 2.24	+ 1.23	- 3.43	- 0.04	0.00
ΔU	0.00	+ 3.05	- 0.47	0.00	+ 2.58
ΔH	+ 2.24	+ 4.28	- 3.90	- 0.04	+ 2.58
$T \Delta S$	+ 1.86	- 0.76	- 1.67	- 0.09	- 0.66
$\Delta(TS)$	+ 0.004	0.00	- 0.004	0.00	0.00
ΔA	- 0.004	+ 3.05	- 0.466	0.00	+ 2.58
ΔF	+ 2.236	+ 4.28	- 3.896	- 0.04	+ 2.58
$\Delta S \times 10^3$	+ 3.510	- 1.155	- 2.22	- 0.117	0.00

Table III

A reversible diesel engine cycle



$V_A = 2.46$ liters
 $V_B = 4.10$ liters
 $V_D = 24.6$ liters
 $P_A = 10.0$ atmos
 $P_C = 1.670$ atmos
 $P_D = 1.000$ atmos



$T_1 = 500.^\circ\text{K}$
 $T_2 = 300.^\circ\text{K}$
 $S_A = -4.11$ cal./ $^\circ\text{K}$
 $S_B = -0.53$ cal./ $^\circ\text{K}$
 $S_C = +3.03$ cal./ $^\circ\text{K}$
 $S_D = +0.46$ cal./ $^\circ\text{K}$

Energies in Calories

Function	AB	BC	CD	DA	ABCD
Q	+1,400.	+1,780.	-1,001.	-1,375.	+ 804.
W_s	0.	+1,780.	+ 399.	-1,375.	+ 804.
W	+ 399.	+1,780.	0.	-1,375.	+ 804.
$\Delta(PV)$	+ 399.	0.	- 399.	0.	0.
ΔU	+1,003.	0.	-1,003	0.	0.
ΔH	+1,400.	0.	-1,400.	0.	0.
$T \Delta S$	+1,400	+1,780.	-1,001.	-1,375.	+ 804.
ΔF	0.	-1,780.	- 399.	+1,375.	- 804.
ΔS	+ 3.58	+ 3.56	- 2.57	- 4.57	0.

ible. The right side of the equation represents *stored energy*; all of the functions on the right side are point functions. The left side of the equation represents *energy in motion*, namely heat and work. If the work goes into the enclosure and heat comes out, irreversibilities and friction increase both heat and work beyond the limiting case. Now either the Tds or the VdP term on the left side will have to be integrated (graphically or formally) over the actual path. It is not necessary to integrate both terms, for the energy balance can be solved for the second term on the left side. The right side can be evaluated with the aid of the second law.

Many textbooks seem to place too much emphasis on reversible cases. In engineering the greatest emphasis should be on the irreversible. A useful technique in teaching students is to represent cycles, reversible or irreversible, on both P - V and T - S plots. The various steps of the cycle and the complete cycle should be investigated completely. All of the terms and their components should be calculated, and all of the numbers should be tested in the light of the first and second laws and the various defining equations to locate errors and reinforce understanding. A few such exercises are the equivalent of a much larger number of discrete one-step, one-question, one-answer problems. Tables II and III illustrate this technique. Students to whom algebraic equations are somewhat unreal achieve quicker understanding when they are required to substitute numbers, and the inevitable mistakes that crop up are illuminated immediately.

What Sign Should the Work Term Have?

The usual convention is that heat flowing into the system is positive and work flowing out of the system is also positive. This appears so illogical that teachers should keep their eyes open for a clue showing which of these signs can be changed the more reasonably. Evidence appears very quickly. Inasmuch as work input, like heat inflow, is associated with an increase in the value of such thermodynamic properties of the system as enthalpy and free energy, its sign should be positive for consistency with the general convention. If it were, both heat and work would be positive for flow into

the system and negative for flow out of the system—a much more satisfactory situation.

Conclusion

Thermodynamics (energetics, that is) is ailing—or, speaking more precisely, its pedagogy is. The illness is neither organic nor incurable, but it is debilitating and it should be checked. This critique has suggested some therapeutic measures. Will they be effective? Can they help students understand one of the foundation subjects of their engineering education? The experience of one instructor is affirmative, but in the end each must try them himself to find out.

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NOMENCLATURE

A = Helmholtz free energy
 E = Electricity
 F = Gibbs free energy
 g = Acceleration of gravity
 g_c = Gravitational conversion factor
 H = Enthalpy
 N = Mass
 P = Absolute pressure
 Q = Heat
 S = Entropy
 T = Absolute temperature
 U = Internal energy
 \bar{U} = Velocity
 V = Volume
 W = Non-flow work
 W_s = Shaft work
 X = Absolute elevation
 ρ = Density

