

# Thermodynamics Should Be Built on Energy—Not on Heat and Work

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“Thermodynamics is not difficult if you can just keep track of what it is you are talking about” is Henry Bent’s (1) recollection of a remark made by Professor Giauque. That nice-sounding comment stayed with me, but it never seemed to be particularly pertinent or helpful. Then after a General Chemistry class a student asked “But what is heat?” I recognized that in using this term I did not know what I was talking about. In this regard I, and other teachers and students of thermodynamics, join the illustrious founders of the subject, men like Carnot, Joule, Thomson, and Clausius, and their disciples who have written the classic thermodynamics textbooks on which we depend.

“Heat” and “work” should vanish from the thermodynamic scene. That conclusion has already been reached by Bent (1) and its value demonstrated in the lucid developments of his book, *The Second Law* (2). Other texts (3) emphasize energies and stay away from, or provide alternatives to, traditional thermodynamic treatments that involve heat and work. Another effort needs to be made to rid thermodynamics of these two illegitimate troublemakers.

## Heat and Work

Look through your thermodynamics textbooks or any chemistry books that deal with thermodynamics or thermochemistry. See what is said about heat and about work. You will find many vague and strange statements. Heat “flows”, or “heat is a form of energy”, or “heat is energy in transit”, or it is “energy at a boundary”, or it is “the process”, or “the mechanism” by which energy is transferred. Work is “being done” or is “being transformed into heat”. The trouble is not with the writers—they feel compelled to use “heat” and “work”. But these quantities, or whatever they are, do not provide a proper base on which to build thermodynamics. They do not let us begin by knowing what it is we are talking about.

We were warned of the difficulties of these words at the birth of modern chemical thermodynamics. In *Thermodynamics* (4), Lewis and Randall wrote

There are two terms, heat and work, that have played an important part in the development of thermodynamics, but their use often brought an element of vagueness into a science capable of the greatest precision. It is not, however, convenient to avoid altogether the use of these terms . . . .

The problems that heat and work bring with them continue as thermodynamics is developed. They require arbitrary choices of signs and lower case “q” and “w” symbols that distinguish them from all thermodynamic properties. We are then led into a quite unnecessary treatment of “inexact differentials” and the introduction of strange symbols—curly d, capital d, d with a crossbar—for the differential.

The establishment of the entropy function from  $\oint \bar{d}q_{\text{rev}}/T$

suggests the extent to which we must leave easily appreciated quantities to proceed into thermodynamics—and it shows the cleverness of thermodynamicists. The differential,  $\bar{d}q$ , is “inexact” and we compensate for this by introducing the “integrating factor”,  $1/T$ . Then we add the circle to the integral sign even though it is the system that undergoes a cyclic process while the differential refers most directly to the thermal surroundings. Such procedures suggest the awkwardness that  $q$  and  $w$  impose on the development of thermodynamics.

Heat and work seem to float between the system we deal with and its surroundings. They are not properties of the system we are dealing with, or of any other system. As chemistry, or thermodynamics, is being developed we try to get our students to appreciate properties, such as mass and density. Then we rather casually mix  $q$  and  $w$  with actual properties like energy and heat capacity.

Our attachment to “work” stems from its use in introductory physics courses as “force times distance”. The term “work” can be recognized as just a crutch that paves the way for the later introduction of potential energy. Once potential energy is introduced, and the derivative of the potential energy is identified with force, “force times distance” can be treated as a change in potential energy. In all later mechanics problems, “work” is discarded and potential and kinetic energies are used. Unfortunately, “work” is passed along to thermodynamics.

Our attachment to “heat” stems from the caloric theory of the 18th and early 19th centuries. That theory held that heat was a manifestation of a material called “caloric”. This material flowed in or out of objects when the temperature changed. Studies such as those of Mayer, Thompson, and Joule showed that caloric could be created or destroyed and, therefore, that heat was not one of the substances of the material world. The “caloric period” had come to an end. By continuing to use “heat” we remain in a “modified caloric period”. It is time to give up this awkward remnant of the past and to discontinue building thermodynamics on heat and work.

Our continuing attachment to the caloric theory is illustrated by a procedure that is still used in introductory chemistry texts. One finds, for example,



The modifications of the original caloric theory that we seem to have accepted, and our ties to the caloric theory, are expressed by Zemansky (5):

Although we know that heat is not a substance whose total amount remains constant, nevertheless we ascribe the changes that take place . . . to the transfer of something from the body at the

higher temperature to the one at the lower, and this something we call heat. We therefore adopt as a *calorimetric* definition of heat that which is transferred between a system and its surroundings by virtue of a temperature difference.

The structure of thermodynamics can, of course, be built on heat and work. You can even retain some of the features of caloric. But, unless you specifically want to present the historical struggles that led to our present understanding you need not do so. If the comfortable terms of heat and work are given up there is a chance that, at all levels, more teachers will know what it is they are talking about, and more students will appreciate chemical thermodynamics.

### Energy

In contrast to heat and work, energy is a well defined property. It has its origin in the ideas of the potential and kinetic energy of simple mechanical systems. Experiments such as Joule's "mechanical equivalent of heat" let us extend the concept, and definition, to include thermal energy. Then, with the conservation of energy idea, changes in the energy of a chemical system of any complexity can be dealt with.

The use of energy, instead of heat and work, helps us move away from the traditional system-centered point of view. With that view, heat flows into or out of the system, and work is done on or by the system. A focus on the system has survived in spite of the recognition that, as Davidson (6) says, "it is important, however, that one defines heat and work in terms of changes occurring in the surroundings, not the system." When we deal with energy we more easily give equal billing to the *system* and to its *thermal surroundings* and *mechanical surroundings*. For most situations that we deal with in chemistry these three components comprise the *universe* of the system, as suggested in Figure 1.

With this attitude we can think of changes in the energy of the thermal surroundings,  $\Delta U(\text{therm})$  instead of heat. The energy of the thermal surroundings depends on their temperature. The thermal surroundings can be made as definite as you like. They can be a bucket of water or a block of material. The energy of this water or material can change, if these are imagined to be large, without an appreciable change in their temperature.

You can also think of changes in the energy of the mechanical surroundings,  $\Delta U(\text{mech})$ , instead of work. Again you can imagine the mechanical surroundings as some specific mechanical device, such as a weight-and-pulley system. The energy of the mechanical system can increase or decrease as the weight is raised or lowered.

With a focus on the system and its surroundings we can treat measurables, or properties, of the three components of the thermodynamic universe of the system. This modest

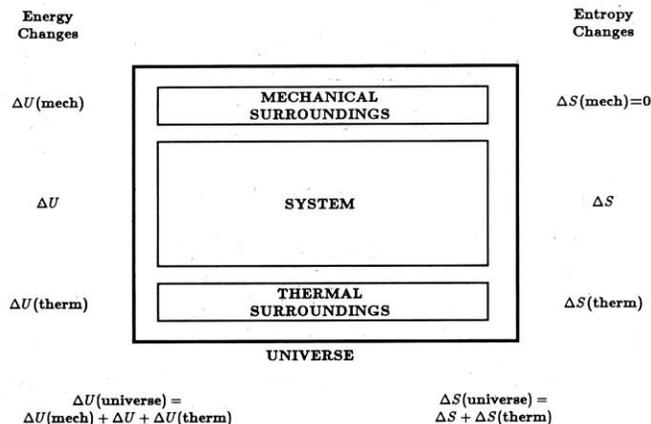


Figure 1. The components of the universe of a system and their energies and entropies.

change in point of view makes many parts of the development of thermodynamics easier to teach and to learn. This is illustrated by the route that can be taken to the first-law energy property and the second-law entropy property.

When explicit attention is paid to the thermal and mechanical surroundings we can see that the energy and entropy properties are developed through common steps.

- (1) We describe, or specify, the property of the surroundings that we will deal with.
- (2) We see if our experiences with natural phenomena let us make a statement about the properties of the surroundings when we deal with processes that return the system to its original state. That is, we try to understand the quantity we are dealing with without, at first, involving the system. In setting up the energy and entropy functions we find that we can make "conservation" statements about the surroundings of the system.
- (3) On the basis of (1) and (2) we extend the conservation statement to changes that do not return the system to its original state. In so doing we ascribe the extent to which the net changes in the surroundings are not zero to contributions from the system.

### Energy and the First Law

In developing the idea of the energy of a system we begin with the concept of the energy of the thermal and mechanical surroundings, or "reservoirs". Then we find, from studies of real world phenomena, that, in processes that return the system to its original state, the sum of the energy changes in these surroundings is zero. We can write

$$\Delta U(\text{universe}) = 0 \quad \text{or} \quad \Delta U(\text{mech}) + \Delta U(\text{therm}) = 0$$

[system cycled]

To extend this conservation principle to processes in which the system is not returned to its original state, we must ascribe a change in energy to the system. If  $\Delta U$  represents this system change we write

$$\Delta U(\text{universe}) = 0 \quad \text{or} \quad \Delta U(\text{mech}) + \Delta U + \Delta U(\text{therm}) = 0$$

and

$$\Delta U = -\Delta U(\text{mech}) - \Delta U(\text{therm})$$

We now can say "On the basis of the idea that energy is conserved, we can measure an energy change that can be ascribed to the system." That is, we can deal with energy as a property of the system.

### Entropy and the Second Law

A similar strategy leads to the entropy property. We consider the thermal surroundings and the quantity  $\Delta U(\text{therm})/T$ . We call this the *entropy* change of the thermal surroundings, and we use the symbol  $\Delta S(\text{therm})$ . Then, in studies of specific processes, like the Carnot cycle, we find that for *reversible* processes that return the system to its original state the entropy change of the surroundings of the system is zero. That is,

$$\Delta S(\text{universe}) = 0$$

or

$$\Delta S(\text{therm}) = \Delta U(\text{therm})/T = 0 \quad \text{[reversible, system cycled]}$$

This conservation statement can be extended by first setting, for all processes,  $\Delta S(\text{mech}) = 0$ . Then the conservation of entropy for reversible processes can be described by ascribing an entropy change,  $\Delta S$ , to the system so that

$$\Delta S(\text{universe}) = 0$$

or

$$[\Delta S(\text{mech}) = 0] + \Delta S + \Delta S(\text{therm}) = 0 \quad \text{[reversible]}$$

and

$$\Delta S = -\Delta S(\text{therm}) \quad \text{[reversible]}$$

Now we say "On the basis of the idea that changes in the entropy of the universe of a system for any reversible process is zero, the entropy change of the system can be measured." The entropy, therefore, qualifies as a property of the system.

Some of the standard developments of thermodynamics look different when we give up  $q$  and  $w$ . These developments follow the same lines, but are based on more concrete ideas when we deal with  $\Delta U(\text{therm})$  and  $\Delta U(\text{mech})$ . Here are some illustrations.

### Example: Enthalpy and $P\Delta V$ Energy

The energy-related enthalpy property lets us deal conveniently with constant-pressure processes. No great change enters when enthalpy is developed from energy instead of heat and work, but the bases of the manipulations are more obvious.

The mechanical surroundings diagram can be elaborated, as suggested in Figure 2. The energy change in these surroundings as a result of expansions or compressions of the system, energy changes that we label  $\Delta U_1(\text{mech})$ , is distinguished from energy changes in the mechanical surroundings produced in other ways, energies which we call  $\Delta U_2(\text{mech})$ . A good student-type mnemonic is that these two mechanical energies are that of "the first kind" and that of "the second kind".

With this subdivision of the energy of the mechanical surroundings, the first law is written as

$$\Delta U_1(\text{mech}) + \Delta U_2(\text{mech}) + \Delta U + \Delta U(\text{therm}) = 0$$

If the mechanical surroundings exert a constant force during the process, a change in the volume of the system,  $\Delta V$ , will produce a force-times-distance potential energy change, equal to  $P\Delta V$ , in the mechanical surroundings of Figure 2. We then have

$$P\Delta V + \Delta U_2(\text{mech}) + \Delta U + \Delta U(\text{therm}) = 0$$

Rearrangement that puts the system variables together gives

$$\Delta U + P\Delta V = -\Delta U(\text{therm}) - \Delta U_2(\text{mech})$$

Now recall that the system property known as enthalpy, symbol  $H$ , is defined by  $H = U + PV$ . For a constant pressure process,  $\Delta H = \Delta U + P\Delta V$ . Then we have

$$\Delta H = -\Delta U(\text{therm}) - \Delta U_2(\text{mech})$$

If  $\Delta U_2(\text{mech})$  is zero, as it is in ordinary chemical processes

$$\Delta H = -\Delta U(\text{therm})$$

Changes in the enthalpy, a property of the system, is given by changes in the energy of the thermal surroundings—for constant pressure process with only  $P\Delta V$  energy is acquired by the mechanical surroundings. Notice that  $H$  is defined so that  $\Delta H$  includes the energy change of the system together with the energy change of that part of the mechanical surroundings that we have called  $\Delta U_1(\text{mech})$ .

### Reversible and Irreversible Expansions

How do we treat processes that, with the  $q$  and  $w$  procedure, require us to use inexact differentials and to be concerned with the "path" of the process?

Consider the isothermal expansion of one mole of an ideal gas, in which no energy other than  $P\Delta V$ -type energy is exchanged between the system and the mechanical surroundings, that is, processes for which  $\Delta U_2(\text{mech})$  is zero.

If the process is a reversible expansion we calculate  $\Delta U_1(\text{mech})$  as

$$\Delta U_1(\text{mech}) = \int P dV = RT \int_{V_i}^{V_f} dV/V = RT \ln(V_f/V_i)$$

Since the temperature is constant and an ideal gas is being dealt with,  $\Delta U = 0$ . The first law then requires that  $\Delta U(\text{therm}) = -\Delta U_1(\text{mech}) = -RT \ln(V_f/V_i) = RT \ln(V_i/V_f)$ . The entropy change of the thermal surroundings is  $\Delta U(\text{therm})/T = R \ln(V_i/V_f)$  and the second law requires  $\Delta S = -\Delta S(\text{therm}) = -R \ln(V_i/V_f) = R \ln(V_f/V_i)$ .

If the expansion is free, no action against a force occurs in the mechanical surroundings and no energy change occurs in these or in the thermal surroundings. Then  $\Delta U(\text{therm}) = 0$  and  $\Delta S(\text{therm}) = 0$ . With  $\Delta S = R \ln(V_f/V_i)$ , which applies no matter how the expansion occurs, we have  $\Delta S(\text{universe}) = \Delta S + \Delta S(\text{therm})$  equal to the positive quantity  $R \ln(V_f/V_i)$ .

Now consider an expansion in which the pressure is suddenly decreased from some initial value to a value  $P$  that is maintained throughout the expansion. You can think of the expansion being against a constant force, that exerted by a particular weight in Figure 2, for example. As the expansion occurs, this weight is raised and the energy of the mechanical surroundings increases. The force-times-distance potential energy increase in the mechanical surroundings is equal to  $P\Delta V$ . With this specific attention to the mechanical surroundings we are easily led to think about the mechanical energy change, which equals  $P\Delta V$ , in terms of the force that acts in the mechanical surroundings during the expansion process. With  $\Delta U_1(\text{mech}) = P\Delta V$  and  $\Delta U = 0$  we have  $\Delta U(\text{therm}) = -P\Delta V$ . The entropy change of the thermal surroundings is  $-P\Delta V/T$ . That of the system is, still,  $R \ln(V_f/V_i)$ . The entropy of the universe is positive to the extent that  $R \ln(V_f/V_i)$  is greater than  $P\Delta V/T$ . (If the pressure throughout the expansion is equal to that reached at the end of the process, we can write  $P_f = RT/V_f$ . Then, with  $\Delta V = V_f - V_i$ , the expression for  $\Delta S(\text{therm})$  becomes  $R(V_f - V_i)/V_f$ . This can be conveniently compared to  $R \ln(V_f/V_i)$  for the reversible expansion.)

These expansion processes illustrate that, when we deal explicitly with the mechanical and thermal surroundings, we deal with whatever process occurs. We are not tempted to group together a variety of processes just because the change in the state of the system is the same for these processes. This simple change in attitude eliminates all dealings with paths and inexact differentials—and it sacrifices nothing of value.

### Example: Free Energy and Spontaneity

As we move farther away from explicit dealings with "heat" and "work" the approach using the energies of the thermal and mechanical surroundings merges with the traditional one. But the two approaches are recognizably different at the introduction of the free-energy property, and the

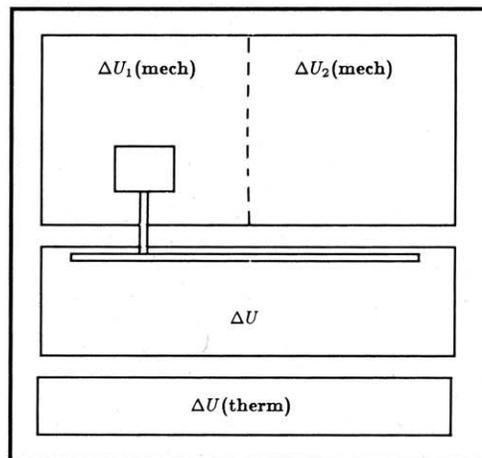


Figure 2. Energy changes when the energy due to volume occupancy is recognized as a separate part of the energy of the mechanical surroundings.

use of this property in the treatment of spontaneity and "available work".

Suppose we are dealing with a process that occurs at constant temperature and pressure. The tendency of the reaction to proceed spontaneously can be seen by calculating  $\Delta S(\text{universe})$  as

$$\Delta S(\text{universe}) = \Delta S + \Delta S(\text{therm})$$

We can use the defining equation  $\Delta S(\text{therm}) = \Delta U(\text{therm})/T$ , with  $\Delta U(\text{therm}) = -\Delta H$ , to develop this equation to

$$\begin{aligned} \Delta S(\text{universe}) &= \Delta S + (-\Delta H/T) \\ &= \Delta S - \Delta H/T \end{aligned}$$

The extent to which  $\Delta S(\text{universe})$  is positive is a measure of the extent to which the process can proceed spontaneously.

We can deal with energy terms by multiplying through by  $T$  to obtain

$$T\Delta S(\text{universe}) = T\Delta S - \Delta H$$

and

$$-T\Delta S(\text{universe}) = \Delta H - T\Delta S$$

Now we recognize the free energy property,  $G$ , defined as  $G = H - TS$ . Changes in  $G$ , for constant temperature processes are given by  $\Delta G = \Delta H - T\Delta S$ . We see that

$$-T\Delta S(\text{universe}) = \Delta G$$

or

$$T\Delta S(\text{universe}) = -\Delta G$$

Since the extent to which  $T\Delta S(\text{universe})$  is positive is a measure of spontaneity, the extent to which  $\Delta G$  is negative is a measure of the spontaneity of the process. From this idea,  $G$  becomes a "chemical potential".

#### Example: Free Energy and Available Mechanical Energy

Now consider a process, such as those occurring in an electrochemical cell, from which we can draw mechanical energy. The first-law accounting gives

$$\Delta U_1(\text{mech}) + \Delta U_2(\text{mech}) + \Delta U + \Delta U(\text{therm}) = 0$$

Setting  $\Delta U_1(\text{mech}) = P\Delta V$ , and rearranging gives

$$\Delta U + P\Delta V = -\Delta U(\text{therm}) - \Delta U_2(\text{mech})$$

or, with the enthalpy function

$$\Delta H = -\Delta U(\text{therm}) - \Delta U_2(\text{mech})$$

or

$$-\Delta H = \Delta U(\text{therm}) + \Delta U_2(\text{mech})$$

The total energy acquired by the thermal surroundings and by the "second kind" of the mechanical surroundings is equal to  $-\Delta H$ . How much of this energy can be delivered to the mechanical surroundings, that is, how much can show up in  $\Delta U_2(\text{mech})$ ?

The second law provides the answer by telling us how much  $\Delta U(\text{therm})$  must be for the process to occur spontaneously. To see this we return to the idea that  $\Delta S(\text{universe}) \geq 0$  or  $[\Delta S(\text{therm}) + \Delta S] \geq 0$  or  $[\Delta U(\text{therm})/T + \Delta S] \geq 0$  or,

finally,  $\Delta U(\text{therm}) \geq -T\Delta S$ . The value of the entropy change,  $\Delta S$ , in the system determines the value of  $\Delta U(\text{therm})$  if the process is to proceed spontaneously.

Similar considerations can be made using the free energy property. The maximum value of  $\Delta U_2(\text{mech})$  is obtained when  $\Delta S(\text{universe})$ , which is equal to  $\Delta U(\text{therm})/T + \Delta S$ , is just positive or in the limit equal to zero. This limit gives  $\Delta U(\text{therm}) = -T\Delta S$ . We can use this result in  $-\Delta H = \Delta U(\text{therm}) + \Delta U_2(\text{mech})$ , or  $\Delta U_2(\text{mech}) = -\Delta H - \Delta U(\text{therm})$  to obtain

$$[\Delta U_2(\text{mech})]_{\text{max}} = -\Delta H - T\Delta S$$

This expression can be compared with the constant-temperature expression  $\Delta G = \Delta H - T\Delta S$  or, more conveniently, with

$$-\Delta G = -\Delta H + T\Delta S$$

In this way you see that a calculated value of  $\Delta G$  shows the maximum energy, over and above any expansion-type energy, that can be delivered to the mechanical surroundings.

#### Conclusions

There is no thermodynamic role for the slippery terms "heat" and "work". We should deal with energies and, in thermodynamics, with the energies of the system and its thermal and mechanical surroundings. Then all first-law energy calculations can be done with a good accounting system. A corresponding attention to the entropies of the components of the universe of the system brings similar, and additional, gains.

A niche can, however, be found for the action terms "heating" and "doing work". They can be used to indicate that the process by which the energy of the system changes is accompanied by a change in the energy of the thermal or the mechanical surroundings. The molecular-level, or statistical, description of heating a system or doing work on a system has been described, as by Davidson (6), and recently in *this Journal* by Waite (7).

If we build thermodynamics on energies instead of heat and work,

- (1) we can know what we are talking about.
- (2) our thoughts can be focussed on the three components of the universe of the system as thermodynamic quantities are developed and used.
- (3) we avoid all dealings with inexact differentials and clever but unnecessary maneuvers such as that which recognizes  $1/T$  as being an integrating factor for  $\bar{d}q_{\text{rev}}$ .
- (4) we make it apparent that energy and entropy are "measurables" or properties, like mass, density, or viscosity. They are not just mathematical expressions, as is suggested by "state function".
- (5) all the thermodynamic derivations that we are accustomed to can be carried out in terms of energies rather than heat and work. But if the results need to be expressed in the vernacular, these words can be added after the energy-based analysis has been made.

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