The "Global" Formulation of Thermodynamics and the First Law: 50 Years On

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Ⓢ *Supporting Information*

ABSTRACT: Nearly 50 years ago, Henry Bent published his groundbreaking article in this *Journal* introducing the "global" formulation of thermodynamics. In the following years, the global formulation was elaborated by Bent and by one of the present authors. The global formulation of the first law focuses on conservation of energy and the recognition that all energy changes involve state functions. This presentation, different from the standard, "local" formulation, has led to a deeper understanding of the foundations of thermodynamics. In this article, for the first time, a complete account of the global formulation of the first law is presented. In particular, the various possible energy changes in all subsystems that make up an experiment, including the atmosphere, are summarized. By focusing on changes in state functions, all results apply *as readily to irreversible processes as to reversible processes*. The original global formulation excluded work and heat, which are, in general, path dependent and can be difficult to measure experimentally. However, a particular protocol for defining work and heat relies only on changes in state functions in the surroundings, and this approach allows the reconciliation of work and heat with the philosophy of the global formulation.

$$\Delta E_{\text{tot}} = \sum_l \Delta E_{\text{pot},l} + \sum_m \Delta H_m + \sum_n \Delta U_n = 0$$

Global Formulation of the First Law

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Nearly 50 years ago, Henry Bent published a revolutionary article in this *Journal*[1] entitled "The Second Law of Thermodynamics: Introduction for Beginners at Any Level". This article contained the first presentation of the "global" formulation of thermodynamics. Bent followed the article with a book[2] and several papers.[3−5] Our conviction that first-year college students understand this formulation better than the standard, "local" formulation led one of us to write several papers[6−8] and an introductory textbook[9] on the global formulation. A well-known textbook on physical chemistry[10] uses the global approach to present thermodynamics. Taking a more advanced point of view, we have continued to explore differences between the global and local formulations of thermodynamics[11−15] as they relate to the first law.

The usual, *local* formulation of the first law is stated

$$\Delta E = w + q \tag{1}$$

Here, the overall energy change, ΔE, of the system is related to the work, w, and heat, q, which are energy *flows* through the interface between system and surroundings. Thus, for a system confined below a movable piston, w is given by

$$w = -\int P dV \tag{2}$$

where P is the instantaneous pressure exerted by the system on the piston and dV is the infinitesimal change in volume of the system. The integral must be evaluated over the detailed motion of the piston. Similarly, q is defined as the net thermal energy that flows into the system from the surroundings. Further discussion

of the local formulation and these "sys-based" definitions of w and q is given elsewhere.[13]

The global formulation[1−9] was particularly innovative, because it developed the first law without mention of work and heat. Rather, it identified the first law with conservation of energy. The original presentation involves a reactive system, σ, where a chemical reaction could take place, in mechanical contact with a weight, denoted wt, and in thermal contact with a thermal reservoir, denoted θ. A global version of the first law is

$$\Delta E_{\text{tot}} = \Delta E_\sigma + \Delta E_{\text{wt}} + \Delta E_\theta = 0 \tag{3}$$

where ΔE_i ($i = \sigma$, wt, or θ) is the change in the energy of subsystem i, and ΔE_{tot} is the total energy change. Expressions for ΔE_{wt} and ΔE_θ are

$$\Delta E_{\text{wt}} = mg\Delta h \tag{4}$$

$$\Delta E_\theta = m_\theta c_\theta \Delta T_\theta \tag{5}$$

Here, m is the weight's mass, g is the acceleration of gravity, Δh is the change in height of the weight, and m_θ, c_θ, and ΔT_θ are the mass, specific heat capacity, and temperature change of the thermal reservoir, respectively. Equation 3 can be readily expanded to

include additional thermal, mechanical, and electrical energy changes. Equation 3 can be rewritten as

$$\Delta E_\sigma = -\Delta E_{\text{wt}} - \Delta E_\theta \tag{6}$$

Because ΔE_{wt} and ΔE_θ are changes in state functions and easily measured, the first law allows the determination of ΔE_σ for any process, reactive or nonreactive, reversible or irreversible. Equation 3 incorporates two important principles, conservation of energy and the state function property of all energies.

In recent work, the basic presentation of the first law in eqs 3−6 has been extended considerably.[11−15] In this article, a complete global formulation of the first law is presented. This formulation is first presented in a general, axiomatic way, and then a systematic description of possible experimental measurements of energy changes in the subsystems that make up the experiment is presented. The global formulation is extended in a natural way to include the concepts of work and heat. The "hidden" role of the atmosphere in thermodynamic events is emphasized. An example of an irreversible process where the analysis using the global formulation is more logical and more general than that of the local formulation is described and additional examples of processes that allow experimental confirmation of the first law follow. The pedagogical value of the global formulation is discussed, and finally, a summary is given.

■ THE FIRST LAW AND THE GLOBAL FORMULATION OF THERMODYNAMICS

A generalization of the global formulation[1−9] begins with definitions of certain terms. A thermodynamic event involves a number of *subsystems* or *parts*[11] numbered $k = 1, 2, ...$, that interact via energy exchanges during the event. Examples of different subsystems would be 1 mol of a gas (σ), a cylinder holding the gas (θ_1), a thermally isolated piston above the gas that moves up and down in the cylinder (wt), and a calorimeter in thermal contact with the cylinder (θ_2). The symbols relate to the designations in eq 3 after allowing for two thermal reservoirs. All subsystems are treated on an equal footing, and any one of them could, in principle, be denoted the "system". The totality of parts that interact is referred to as the *universe* of the event.

The concept of *thermodynamic state*[16,17] is assumed to be familiar to the reader. Once the state of a subsystem k is specified, all properties of the subsystem, known as *state functions*, such as pressure P_k, temperature T_k, volume V_k, and internal energy U_k, are fixed. In this article, a chemical *process* is identified by specifying the initial (i) and final states (f) of the reactive system, typically the part denoted $k = 1$. The *path* followed by the system is then identified by specifying the initial and final states of all other parts k ($k \neq 1$). Finally, the word *event* encompasses the totality of process and path.

The global formulation of the first law involves two statements. The first (statement IA) is that for any event the total energy E_{tot} of the universe is constant. The second (statement IB) is that the energy E_k of every subsystem k is a state function. The total energy can be written formally as the sum of the energies of each part:

$$E_{\text{tot}} = \sum_k E_k = \text{constant}$$

but absolute values of E_k are not measurable. An experimental investigation of statement IA requires the determination of the energy change ΔE_k in every part, and the result is (see eq 3):

$$\Delta E_{\text{tot}} = \sum_k \Delta E_k = 0 \tag{7}$$

For statement IB, consider a series of experiments for which one subsystem (say, $k = 1$) always undergoes the same process from state i to state f. By contrast, each of the other subsystems undergoes a variety of changes of state with different values of ΔE_k for $k \neq 1$. Then, eq 7 can be rewritten

$$\Delta E_1 = E_1(\text{f}) - E_1(\text{i}) = -\sum_{k \neq 1} \Delta E_k \tag{8}$$

Because energy is a state function, ΔE_1 must be constant, regardless of path. Statement IB requires that equations equivalent to eq 8 hold for every part k, not just $k = 1$. Statements IA and IB are not equivalent, and the first law must include both statements. Statements IA and IB are discussed further in the Supporting Information.

■ MEASURING ENERGY CHANGES IN A THERMODYNAMIC EVENT

Originally, the global formulation[1−9] was presented without a *systematic* description of how to measure energy changes ΔE_k under varying conditions. Here such measurements are described. Initially, subsystems are excluded where irreversible chemical reactions occur, because one cannot directly determine ΔE_k within them. Once the results in this section are available, however, irreversible chemical reactions can be analyzed by determining ΔE_k in every subsystem other than the reactive one. This temporary exclusion of irreversible chemical reactions does not apply to other types of energy *transfers*, which, in general, are irreversible, as, for example, in energy flow between thermal reservoirs at different temperatures.

The total energy of any part k can be decomposed[11,18−20] as

$$E_k = E_{\text{kin},k} + E_{\text{pot},k} + U_k \tag{9}$$

where $E_{\text{kin},k}$ and $E_{\text{pot},k}$ are the macroscopic kinetic and potential energies of the part, regarded as a single body, and U_k is the microscopically diverse internal energy. It is assumed that all parts are at rest at the beginning and end of an event, although certain parts, such as a piston, are allowed to move during the event. In this case, ΔE_k reduces to

$$\Delta E_k = \Delta E_{\text{pot},k} + \Delta U_k \tag{10}$$

because $\Delta E_{\text{kin},k} = 0$. The common case for which $\Delta E_{\text{pot},k} \neq 0$ is a piston that has been raised or lowered. Changes in other types of potential energy, such as electrical energy, may also contribute.[9,21] Otherwise, $\Delta E_{\text{pot},k} = 0$.

When irreversible chemical reactions and electrical energy changes are excluded, there are only two changes in internal energy U_k to be considered: thermal and mechanical.[1−7,22,23] To calculate thermal energy changes, one measures ΔT_k and uses the constant-volume $C_{V,k}$ or constant-pressure $C_{P,k}$ heat capacities of part k (see eq 5). For mechanical events, if part k undergoes a constant-pressure process that involves a volume change, ΔV_k, the change in U_k is given by $-P_k\Delta V_k$.[11] That is, the part must expend energy to expand against the opposing pressure.

Part k is assumed to undergo either a constant volume or constant pressure change. In the former case, $V_k(\text{i}) = V_k(\text{f})$ and, in the latter, $P_k(\text{i}) = P_k(\text{f})$. (Because state functions are involved, there is no need for P_k to remain constant during the

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event. Many authors presume otherwise.) For the *constant-volume* case, ΔE_k is[11]

$$\Delta E_{V,k} = \Delta E_{\text{pot},k} + \Delta U_{V,k}$$

$$= \Delta E_{\text{pot},k} + \int_{T_i}^{T_f} C_{V,k}\, dT \tag{11}$$

and for the *constant-pressure* case, ΔE_k is:[11]

$$\Delta E_{P,k} = \Delta E_{\text{pot},k} + \Delta U_{P,k}$$

$$= \Delta E_{\text{pot},k} + \int_{T_i}^{T_f} C_{P,k}\, dT - P_k \Delta V_k \tag{12}$$

where

$$\Delta H_{P,k} = \int_{T_i}^{T_f} C_{P,k}\, dT$$

Equations 11 and 12 confirm that E and U are state functions, because the right-hand sides are fixed once the initial and final states are specified. It is irrelevant whether the change took place reversibly or irreversibly.

Many constant-pressure events are carried out in mechanical contact with the atmosphere, and the potential energy of the atmosphere will, in general, change. (The assumption is made that the *thermal* interaction between the experiment and the atmosphere is insignificant.) If subsystem k, in mechanical contact with the atmosphere (P_k = 1 atm), undergoes a volume change $\Delta V_k > 0$, it raises the atmosphere in the earth's gravitational field and causes a change in the potential energy of the atmosphere equal to $\Delta E_{\text{atm},k}$ = (1 atm)ΔV_k.[14,15] This energy change is equal in magnitude but opposite in sign to the last term in eq 12. The sum of energy changes in the system and atmosphere are

$$\Delta E_k + \Delta E_{\text{atm},k} = \left(\Delta E_{\text{pot},k} + \int_{T_i}^{T_f} C_{P,k}\, dT \right.$$

$$- (1\text{ atm})\Delta V_k) + (1\text{ atm})\Delta V_k = \Delta E_{\text{pot},k}$$

$$+ \int_{T_i}^{T_f} C_{P,k}\, dT = \Delta E_{\text{pot},k} + \Delta H_k \tag{13}$$

This result removes the necessity of actually calculating the $P_k \Delta V_k$ energy change in, for example, a calorimeter, because it and the energy change of the atmosphere are "tucked" into the enthalpy change.[14] *Equation 13 holds for any subsystem, including the system, in mechanical contact with the atmosphere.*

This section has presented expressions for ΔE_k, ΔU_k, and ΔH_k for constant-volume and constant-pressure changes. Interestingly enough, those cases are the only two for which general expressions exist without invoking the second law of thermodynamics.[11] The most general expression for conservation of energy (cf. eq 7) can be written

$$\Delta E_{\text{tot}} = \sum_l \Delta E_{\text{pot},l} + \sum_m \Delta H_m + \sum_n \Delta U_n = 0 \tag{14}$$

where the first sum is over all subsystems, the second sum is over all subsystems in mechanical contact with the atmosphere, and the third sum is over all subsystems not in mechanical contact with the atmosphere. All sums explicitly exclude the atmosphere.

■ HEAT AND WORK IN RELATIONSHIP TO THE GLOBAL FORMULATION

Measurements of heat and work are easily described within the spirit of the global formulation using the "surr-based" definitions.[11] These are based upon the results for ΔE_k in the previous section. Part $k = 1$ is the reactive system. The energy change ΔE_k of each part of the surroundings (all $k \neq 1$) is decomposed as

$$\Delta E_k = \Delta E_k^W + \Delta E_k^Q \tag{15}$$

Here ΔE_k^W is the mechanical portion of ΔE_k that is potentially convertible into lifting or lowering a mass in the earth's gravitational field, and ΔE_k^Q is the remaining, thermal portion of ΔE_k. If part k undergoes a *constant-pressure* change with temperature change from $T_{i,k}$ to $T_{f,k}$, then (cf. eq 12)

$$\Delta E_k^W = \Delta E_{\text{pot},k} - P_k \Delta V_k \tag{16}$$

$$\Delta E_k^Q = \int_{T_{i,k}}^{T_{f,k}} C_{P,k}\, dT = \Delta H_k \tag{17}$$

Similar expressions can be written if part k undergoes a *constant-volume* change (cf. eq 11):

$$\Delta E_k^W = \Delta E_{\text{pot},k} \tag{18}$$

$$\Delta E_k^Q = \int_{T_{i,k}}^{T_{f,k}} C_{V,k}\, dT = \Delta U_k \tag{19}$$

The values of w and q are given by:[11]

$$w = -\sum_{k \neq 1} \Delta E_k^W \tag{20}$$

$$q = -\sum_{k \neq 1} \Delta E_k^Q \tag{21}$$

Both sums are taken over all parts of the surroundings including the atmosphere (see below). Some parts can undergo constant-volume changes and others constant-pressure changes, and *these changes need not be reversible.* Clearly, heat and work are defined, on an equal footing, by easily measured changes in state functions in the surroundings.

The simplest setup to measure work and heat consists of one subsystem that supplies only w and one subsystem that supplies only q. This simple case is usually envisioned with the local formulation in eq 1. Equations 20 and 21 generalize these contributions. Several subsystems may contribute to w, others to q, and yet others may contribute to both w and q. The local formulation of thermodynamics does not suggest this type of generalization nor accommodate it easily.

One common experimental arrangement is for the system ($k = 1$) and certain parts of the surroundings to be in mechanical contact with the atmosphere.[14,15] As demonstrated earlier, a volume change ΔV_k in part k changes the potential energy of the

atmosphere by $(1\text{ atm})\Delta V_k$. The total potential energy change in the atmosphere is

$$\Delta E^W(\text{atm}) = (1\text{ atm})\Delta V_1 + (1\text{ atm})\sum_{m\neq 1}\Delta V_m \qquad (22)$$

The first term reflects any change in volume of the system, and the index m sums over all parts of the *surroundings* in mechanical contact with the atmosphere. The result for ΔE^Q is

$$\Delta E^Q(\text{atm}) = 0 \qquad (23)$$

because no thermal interaction between the experiment and the atmosphere is assumed. When these results are combined with eqs 16, 17, 20, and 21, the general result is obtained (cf. eq 14)

$$w = -(1\text{ atm})\Delta V_1 - \sum_{l\neq 1}\Delta E_{\text{pot},l} \qquad (24)$$

$$q = -\sum_{m\neq 1}\Delta H_m - \sum_{n\neq 1}\Delta U_n \qquad (25)$$

The index l sums over all parts of the surroundings, and the index n sums over all parts of the surroundings not in mechanical contact with the atmosphere. All sums exclude the atmosphere. If the *system* is not in mechanical contact with the atmosphere, the first term in eq 24 is dropped.

In summary, w and q are computed from changes in state functions, so there is no difficulty treating irreversible processes. The quantities w and q can usually be determined[a] when irreversible chemical reactions take place in the system, because the only system change needed is $\Delta V(\text{system})$. By contrast, $\Delta U(\text{system})$ cannot be generally evaluated from measurable changes in state properties of the reactive system itself. These definitions of w and q represent an obvious extension of the global formulation. So extended, the global formulation presents an attractive alternative to the indirect "axiomatic" adiabatic-work formulation of the first law, in which heat is defined in terms of work for alternative paths.[12,24,25]

■ EXAMPLE: PROOF THAT ΔH(SYS) = q_P IN AN IRREVERSIBLE CONSTANT-PRESSURE PROCESS

An irreversible process that demonstrates the power of the global formulation is considered. *Throughout this section, it is assumed that no work other than $P\Delta V$ work is done.* The initial and final pressures P_1 and P_2 of the system are 1 atm, but the pressure P of the system during the process is typically variable and unknown. The goal is to prove that

$$\Delta H(\text{sys}) = \Delta U(\text{sys}) + (1\text{ atm})\Delta V(\text{sys})$$
$$= w + q + (1\text{ atm})\Delta V(\text{sys}) = q_P \qquad (26)$$

for any process. It is sufficient to prove

$$w = -(1\text{ atm})\Delta V(\text{sys}) \qquad (27)$$

This is first demonstrated for the global formulation, where eq 24 applies.

Two possible experimental arrangements are considered. In the first, the system is *in mechanical contact with the atmosphere*. An example might be the mixing of an acidic solution with a basic solution in a container sitting open in a

calorimeter. In this case, the second term of eq 24 is zero, and eq 27 is satisfied. In the second, suppose the system, *not in mechanical contact with the atmosphere*, undergoes an exothermic chemical reaction inside a cylinder beneath a piston. The apparatus is in thermal contact with a calorimeter at 25 °C. The space above the piston is assumed to be a vacuum and the piston's volume is constant. The pressure exerted on the gas by the piston, 1 atm, can also be written m_Pg/A, where m_P is the mass of the piston, g the acceleration due to gravity, and A the surface area of the piston. Then, the first term in eq 24 is zero and w is given by (cf. eq 4)

$$-\Delta E_{\text{pot}}(\text{piston}) = -(m_Pg)\Delta h$$
$$= -(1\text{ atm }A)[\Delta V(\text{sys})/A]$$
$$= -(1\text{ atm})\Delta V(\text{sys}) \qquad (28)$$

in agreement with eq 27. In fact, for any experimental arrangement, the global formulation gives this result for w. Consequently, $q_P = \Delta H$ for any process where $P_1 = P_2$, even if the process is irreversible and P is not known during the process, as is true for many actual reactions. State functions are the key.

Now consider the same process using the local formulation of thermodynamics. Equation 2 gives the expression for w. If the process is reversible, $P = 1$ atm, the integral is straightforward, and eq 27 is satisfied. Similarly, if the process is irreversible but the system pressure P is constant at 1 atm throughout the process, eq 27 is satisfied. This describes the first example given above. In the more general case, such as the second example above, the work process is irreversible, P is not known, and w cannot be calculated. Consequently, eq 27 is not satisfied, and $q_P \neq \Delta H$. Authors who use the local formulation seldom acknowledge this problem. Instead, they restrict all discussions of q and w either to reversible processes or (less often) to processes where the system's pressure is constant throughout. In that case, $q_P = \Delta H$. The problem, then, is that $\Delta H(\text{sys}) = q_P$ is only true for these types of processes. Because most real processes involve changes where the pressure of the system is not even known, this result is not general. By contrast, in the global formulation, $q_P = \Delta H$ is seen *always* to be true.

■ EXPERIMENTAL EXAMPLES OF THE FIRST LAW IN THE GLOBAL FORMATION

As an example of the truth of the first law, consider an experiment involving five subsystems where all $\Delta E_{\text{pot},k}$ terms are zero. Suppose part #1 is 1 mol of $N_2(g)$ with known heat capacity $C_{V,1}$ held at constant volume by a glass bulb. The bulb itself is held at constant pressure (1 atm) by the atmosphere and has known heat capacity $C_{P,2}$. The remaining parts (#3, #4, and #5) are constant-pressure calorimeters initially operating at temperatures near $T_3 = 25$ °C, $T_4 = 30$ °C, and $T_5 = 35$ °C with known heat capacities $C_{P,3}$, $C_{P,4}$, and $C_{P,5}$. Then, eqs 11, 12, and 14 combine to give

$$\Delta E_{\text{tot}} = 0$$
$$= \int_{T_{i,1}}^{T_{f,1}} C_{V,1}\,dT + \sum_{k=2}^{5}\int_{T_{i,k}}^{T_{f,k}} C_{P,k}\,dT \qquad (29)$$

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Small temperature changes are regarded as measurable. If the N_2(gas) is the system, then eqs 11, 24, and 25 give

$$\Delta E_1 = \Delta U_1 = \int_{T_{i,1}}^{T_{f,1}} C_{V,1}\, dT$$

$$w = 0$$

$$q = -\sum_{k=2}^{5} \int_{T_{i,k}}^{T_{f,k}} C_{P,k}\, dT$$

Clearly, eq 1 is consistent with these results. A typical experiment might be that the bulb, initially in the 25 °C calorimeter, is placed in the 30 °C calorimeter for a time and then finishes in the 35 °C calorimeter. This sequence is denoted 25 °C → 30 °C → 35 °C. Each term in eq 29 can be measured, and the sum can be compared with the value zero as a demonstration of conservation of energy (statement IA). Other experiments could be carried out. One might be 25 °C → 30 °C → 35 °C → 25 °C. In no way do such experiments "prove" statement 1A, because conservation of energy has been invoked in measuring C_V, C_P, and pressure-volume energy changes, but the experiments do confirm statement 1A. These multistep examples of applications of the first law are easily analyzed with the global formulation.

As a second example, one can use the same experimental setup to demonstrate statement IB of the first law by considering a series of experiments where the gas is always initially at 25 °C and always finishes in the 35 °C calorimeter, but visits other calorimeters in between. The initial and final states of the system are fixed, and the constancy of the state function change ΔE_1 for a variety of paths supports statement IB.

The global formulation, with its emphasis on conservation of energy and the state function property of energy, is the natural formalism for interpreting experiments such as these. A recent article by Rosenberg[25] points out that Bent[1] took "conservation of energy as a postulate, rather than using Joule's experiment as evidence that U is a state function". Although true, the examples above show that the global formulation lends itself naturally to interpreting the Joule experiment.

It is instructive to apply these results to a chemical reaction carried out under different conditions. Consider the reaction

$$2\ \text{mol}\quad H_2(g) + 1\ \text{mol}\quad O_2(g) \rightarrow 2\ \text{mol}\quad H_2O(l)$$
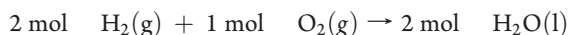
with each reactant and product at exactly 1 atm and 25 °C. For simplicity, the gases and gas mixture are assumed to behave as ideal gases and the liquid water has negligible volume. The experiments are carried out in three ways. For the first two experiments, the system is contained in a cylinder below a piston (both with negligible heat capacities, for simplicity) that exerts a pressure down on the system of exactly 1 atm. The cylinder sits in a calorimeter at exactly 25 °C with heat capacity $C_{P,cal}$, and the temperature change is measured. The piston is initially at a height $h = h_0$ above the base of the cylinder, and there is a vacuum above the piston. The details of the three experiments are

1. *Direct:* The reaction is ignited. Initially, the piston rises rapidly due to the pressure rise from the exothermicity of the reaction and, after oscillations, settles down on top of the negligible volume of products at $h = 0$.
2. *Heat Engine:* The process begins with an additional weight "wt" being placed on the piston, which raises the pressure acting on the reactants to exactly 11 atm and lowers the

Table 1. Energy Changes in Chemical Reactions

Energy	Energy Change[a] /kJ		
	Exp #1: Direct	Exp #2: Heat Engine	Exp #3: Fuel Cell
ΔE(piston)	−7.4	−7.4	−7.4
ΔE(wt)	-	74.4	-
ΔE(electrical)	-	-	474.2
ΔE(all weight equiv.)	−7.4	67.0	466.8
ΔH(calorimeter)	571.6	497.2	97.4
ΔU(system)	−564.2	−564.2	−564.2
w	7.4	−67.0	−466.8
q	−571.6	−497.2	−97.4

[a] See note b for further details.

piston to $h = h_0/11$. The system is temporarily isolated from the calorimeter, the gases are ignited, the piston plus weight is raised by the energy release, and the weight wt is caught and held at height $h = 2h_0$. The system is put back in thermal contact with the calorimeter, and the piston settles on top of the products.
3. *Fuel Cell:* The reaction is carried out in a fuel cell run near the reversible limit[9,26] at 1 atm and 25 °C. Some energy from the fuel cell raises a series of weights, and the process releases thermal energy to a calorimeter. A detailed description of such an experiment is given by Hladky.[27]

The various energy changes are summarized in Table 1.[b] Most of these values should be regarded as measurements, even though they are computed from thermodynamic functions.

For the first experiment, the energy changes of the piston and calorimeter are measured, and eq 14 is used to obtain ΔE(system) = (ΔU)(system). Then, the rules in eqs 24 and 25 are used to obtain w and q. In spite of the considerable energy released, the work done *by the system* ($-w$) is negative. In the second experiment, the system does net work. The value for ΔE(piston) is the same. For the weight wt, its mass is 10 times that of the piston and its height change from h_0 to $2h_0$ is equal in magnitude but opposite in sign from the piston's change in height. The work done by the system is not the maximum possible value. Measurement of ΔH(calorimeter) allows q and ΔU(system) to be determined.

Once the second law is available, it is possible to obtain an expression for the maximum possible work that can be done in this process. Using a fuel cell running at the reversible limit, the values of ΔE are measured for all weights, including those raised by the electrical energy produced by the fuel cell, and ΔH(calorimeter). From these numbers, ΔU(system), q, and w can be calculated. For this experiment, 83% of the energy released by the reaction (ΔU) is converted into work done by the system. This work is the maximum possible value, and consequently, the rest of the exothermicity is released as thermal energy (heat).

We see that $\Delta U_{sys} = -564.2$ kJ in all three cases, consistent with statement IB. In addition, eqs 7 and 14 are satisfied for all three experiments. In all cases, $w = -\Delta E$(all weights) and $q = -\Delta H$(calorimeter). However, the values of w and q vary dramatically depending upon the path. Additional examples of processes that demonstrate the power of the global formulation are given in refs 11, 13 and 15.

■ DISCUSSION

Our teaching experience has shown that students have difficulty understanding thermodynamics when it is introduced using the local formulation. The concepts of work and heat are particularly difficult to master. The global formulation has proven to be much easier for students to comprehend when meeting thermodynamics for the first time. There are several reasons for this. First, the global formulation analyzes *irreversible* processes as easily as reversible ones, while the local formulation typically has difficulty with irreversible processes. This difficulty is exemplified by those textbook authors, working within the local formulation, who hold that work is only defined for reversible processes, and then do not account for real processes, which are irreversible. Second, the global formulation is expressed entirely in terms of changes in (easily understood) state functions, which are signaled by the Δ symbols. By contrast, the local formulation includes two (rather vague) path-dependent quantities, w and q, which are not, of course, denoted Δw and Δq. Because heat and work are energy transfer terms, which have directionality, their signs can also be confusing. Third, the global formulation is also relevant to the second law, where one of the key results, $\Delta S_{univ} \geq 0$ for any process, can only be understood in the context of the global formulation. Fourth, the global formulation is "symmetrical" in that all energy changes in eq 7 enter in the same way on an equal footing. By contrast, the local formulation is "asymmetrical" because eq 1 gives primacy to changes in the system's energy, as compensated by energy transfers into the system. Because of this asymmetry, how to introduce other energy trading terms from an additional thermal reservoir or another work partner is not obvious.

The global formulation of thermodynamics is pedagogically useful even in a course taught primarily based upon the local formulation. The philosophy of the global formulation helps deepen the students' understanding of the local formulation. This benefit is equivalent to the improved understanding of the first language gained by studying a second language. The two formulations of thermodynamics have much in common (with a few key differences), but it does take some time and effort for instructors to master the global formulation and see how to teach it. The payoff for instructors and students is a much deeper understanding of the science of thermodynamics with none of the "fuzziness" that can affect serious students exposed only to the local formulation.

■ SUMMARY

A complete account of the global formulation of the first law is presented. This includes a systematic description of measuring energy changes in subsystems including the atmosphere, a presentation of work and heat consistent with the formulation, and examples that demonstrate its power. The global formulation as described here will appeal to both students and teachers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

An elaboration of the two statements that make up the first law. This material is available via the Internet at http://pubs.acs.org.

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■ ADDITIONAL NOTES

[a] As shown in ref 11, work and heat can always be determined using surr-based definitions provided every subsystem in the surroundings undergoes either a constant-pressure or constant-volume or constant-temperature process.

[b] The energy changes in Table 1 including ΔU_{sys} and $\Delta G_{sys} = -474.3$ kJ were determined from the standard enthalpy of formation and the Gibbs energy of formation [28] of $H_2O(l)$. For all three examples, ΔH(calorimeter) was calculated from the other energy changes using eqs 12 and 14. The maximum work possible by the system, $-w_{max}$, was calculated as $-\Delta G_{sys} + \Delta(PV)$, and ΔE(piston) was computed as $\Delta(PV)$. Neglecting the volume of the products, $\Delta(PV) = RT\Delta n_{gas} = -7.44$ kJ.

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