

9.3: The First Law of Thermodynamics: There Is No Free Lunch

Key Concept Video The First Law of Thermodynamics

Thermodynamics is the general study of energy and its interconversions. The laws of thermodynamics are among the most fundamental in all of science, governing virtually every process that involves change. The **first law of thermodynamics** is the law of energy conservation, which we state as follows:

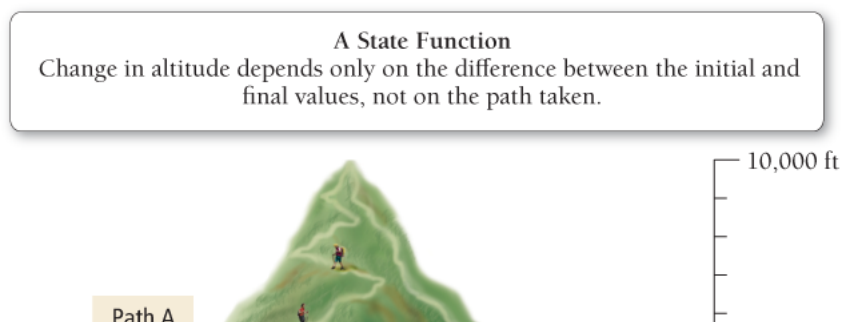
The total energy of the universe is constant.

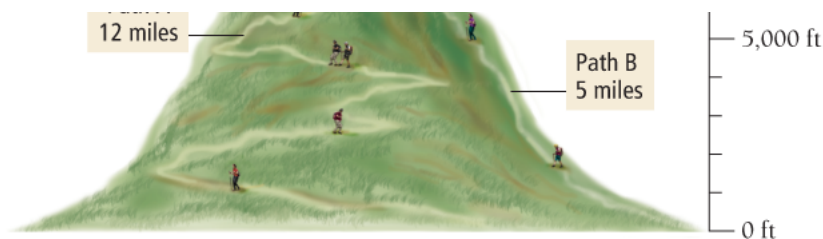
Einstein showed that it is mass–energy that is conserved; one can be converted into the other. This equivalence becomes important in nuclear reactions, discussed in [Chapter 20](#). In ordinary chemical reactions, however, the interconversion of mass and energy is not a significant factor, and we can regard mass and energy as independently conserved.

In other words, because energy is neither created nor destroyed, and because the universe does not exchange energy with anything else, its energy content does not change. The first law has many implications: the most important one is that, with energy, we cannot get something for nothing. The best you can do with energy is break even—there is no free lunch. According to the first law, a device that would continually produce energy with no energy input, sometimes known as a *perpetual motion machine*, cannot exist. Occasionally, the media report or speculate on the discovery of a machine that can produce energy without the need for energy input. For example, you may have heard claims about an electric car that recharges itself while driving, or a new motor that can create additional usable electricity as well as the electricity to power itself. Although some hybrid (electric and gasoline-powered) vehicles can capture energy from braking and use that energy to recharge their batteries, they cannot run indefinitely without additional fuel. As for a motor that powers an external load as well as itself—no such thing exists. Our society has a continual need for energy, and as our present energy resources dwindle, new energy sources will be required. Those sources, whatever they may be, will follow the first law of thermodynamics—energy must be conserved.

The **internal energy (E)** of a system is the sum of the kinetic and potential energies of all of the particles that compose the system. Internal energy is a **state function**, which means that its value depends only on the state of the system, not on how the system arrived at that state. The state of a chemical system is specified by parameters such as temperature, pressure, concentration, and physical state (solid, liquid, or gas). Consider the mountain-climbing analogy depicted in [Figure 9.5](#). The elevation at any point during a mountain climb is analogous to a state function. For example, when we reach 10,000 ft, our elevation is 10,000 ft, no matter how we got there. The distance we traveled to get there, by contrast, is not a state function; we could have climbed the mountain by any number of routes, each requiring us to cover a different distance.

Figure 9.5 Altitude as a State Function





Because state functions depend only on the state of the system, the value of a *change* in a state function is always the difference between its final and initial values. If we start climbing a mountain at an elevation of 3000 ft and reach the summit at 10,000 ft, then our elevation change is 7000 ft (10,000 ft – 3000 ft), regardless of which path we took.

Like an altitude change, we determine an internal energy change (ΔE) by the difference in internal energy between the final and initial states:

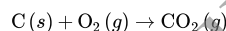
$$\Delta E = E_{\text{final}} - E_{\text{initial}}$$

In a chemical system, the reactants constitute the initial state and the products constitute the final state. So ΔE is the difference in internal energy between the products and the reactants:

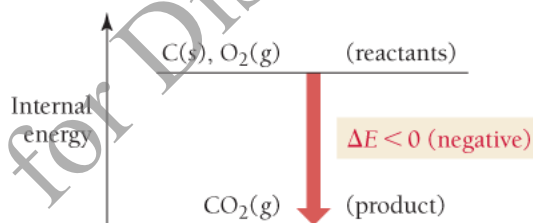
[9.1]

$$\Delta E = E_{\text{products}} - E_{\text{reactants}}$$

For example, consider the reaction between carbon and oxygen to form carbon dioxide:

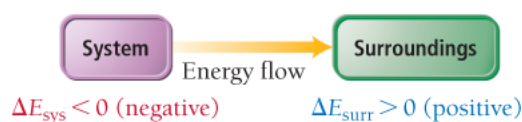


Just as we can portray the changes that occur when climbing a mountain with an *altitude* diagram, which depicts the *altitude* before and after the climb (see Figure 9.5), we can portray the energy changes that occur during a reaction with an *energy* diagram, which compares the *internal energy* of the reactants and the products:



The vertical axis of the diagram is *internal energy*, which increases as we move up on the diagram. For this reaction, the reactants are *higher* on the diagram than the products because they have higher internal energy. As the reaction occurs, the reactants become products, which have lower internal energy. Therefore, the reaction gives off energy, and ΔE (that is, $E_{\text{products}} - E_{\text{reactants}}$) is *negative*.

Where does the energy lost by the reactants (as they transform to products) go? If we define the thermodynamic *system* as the reactants and products of the reaction, then energy flows *out of the system* and *into the surroundings*:

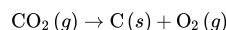


According to the first law, energy must be conserved. Therefore, the amount of energy lost by the system must exactly equal the amount gained by the surroundings:

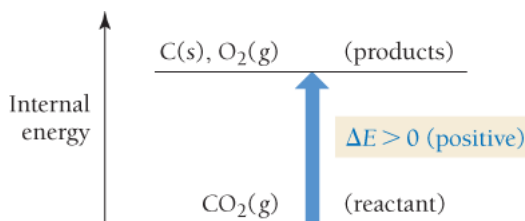
[9.2]

$$\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$$

Now, suppose the reaction is reversed:



The energy-level diagram is nearly identical, with one important difference: $\text{CO}_2(g)$ is now the reactant, and $\text{C}(s)$ and $\text{O}_2(g)$ are the products. Instead of decreasing in energy as the reaction occurs, the system increases in energy:



In this reversed reaction ΔE is *positive* and energy flows *into the system* and *out of the surroundings*:



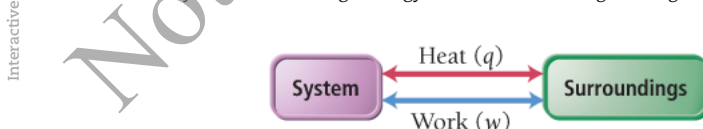
Summarizing Energy Flow:

- If the reactants have a higher internal energy than the products, ΔE_{sys} is negative and energy flows out of the system into the surroundings.
- If the reactants have a lower internal energy than the products, ΔE_{sys} is positive and energy flows into the system from the surroundings.

We can think of the internal energy of the system in the same way we think about the balance in a checking account. Energy flowing *out of* the system is like a withdrawal and therefore carries a negative sign. Energy flowing *into* the system is like a deposit and carries a positive sign.

Conceptual Connection 9.1 System and Surroundings

As we saw earlier, a system can exchange energy with its surroundings through *heat* and *work*:



According to the first law of thermodynamics, the change in the internal energy of the system (ΔE) is the sum of the heat transferred (q) and the work done (w):

[9.3]

$$\Delta E = q + w$$

In the above equation, and from this point forward, we follow the standard convention that ΔE (with no subscript) refers to the internal energy change of the *system*. As Table 9.1 illustrates, energy entering the system through heat or work carries a positive sign, and energy leaving the system through heat or work carries a negative sign. Again, recall the checking account analogy. The system is like the checking account—withdrawals are negative and deposits are positive.

Table 9.1 Sign Conventions for q , w , and ΔE

q (heat)	+ system <i>gains</i> thermal energy	– system <i>loses</i> thermal energy
w (work)	+ work done <i>on</i> the system	– work done <i>by</i> the system
ΔE (change in internal energy)	+ energy flows <i>into</i> the system	– energy flows <i>out</i> of the system

Conceptual Connection 9.2 Heat and Work

Example 9.1 Internal Energy, Heat, and Work

The firing of a potato cannon provides a good example of the heat and work associated with a chemical reaction. In the potato cannon, a potato is stuffed into a long cylinder that is capped on one end and open at the other. Some kind of fuel is introduced under the potato at the capped end—usually through a small hole—and ignited. The potato shoots out of the cannon, sometimes flying hundreds of feet, and the cannon emits heat to the surroundings. If the burning of the fuel performs 855 J of work on the potato and produces 1422 J of heat, what is ΔE for the burning of the fuel? (Note: A potato cannon can be dangerous and should not be constructed without proper training and experience.)

SOLUTION To solve the problem, substitute the values of q and w into the equation for ΔE . Because work is done by the system on the surroundings, w is negative. Similarly, because heat is released by the system to the surroundings, q is also negative.

$$\begin{aligned}\Delta E &= q + w \\ &= -1422 \text{ J} - 855 \text{ J} \\ &= -2277 \text{ J}\end{aligned}$$

FOR PRACTICE 9.1 A cylinder and piston assembly (defined as the system) is warmed by an external flame. The contents of the cylinder expand, doing work on the surroundings by pushing the piston outward against the external pressure. If the system absorbs 559 J of heat and does 488 J of work during the expansion, what is the value of ΔE ?

Not for Distribution

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