

7.10: The First Law of Thermodynamics

A **state function** must return to its original value if a system is taken through a series of changes and finally returned to its original state. We say that the change in a state function must be zero if the system is taken through a cyclic process, or somewhat more picturesquely, if the system traverses a cyclic path. While we can measure the heat and work that a system exchanges with its surroundings, neither the heat nor the work is necessarily zero when the system traverses a cycle. Heat and work are not state functions. Nevertheless, adding heat to a system increases its energy. Likewise, doing work on a system increases its energy. If the system surrenders heat to the surroundings or does work on the surroundings, the energy of the system is decreased. In any change that a closed system undergoes, the total energy change is $E = q + w$, where q and w can be either positive or negative. For very small changes, we write

$$dE = dq + dw.$$

Anything we do to increase the energy of a closed system can be classified as either adding heat to the system or doing work on the system.

Heat, work, and energy are all extensive variables. They are additive. If a system acquires an increment of heat q_1 from one source and an increment q_2 from another source, the total heat acquired by the system is $q_1 + q_2$. If work, w_1 , of one kind, and work, w_2 , of a second kind are done on the system, the total work is $w_1 + w_2$.

In keeping with the thermodynamic perspective that we can partition the universe into system and surroundings, we assume that any energy lost by the system is taken up by the surroundings, and *vice versa*. By definition, we have $q = -\hat{q}$, $w = -\hat{w}$, and $E = -\hat{E}$; for any process, $E_{universe} = E + \hat{E}$. This is the **principle of conservation of energy**, which is usually stated:

For any change in any system, the energy of the universe remains constant.

So, conservation of energy is built into our energy accounting scheme. It is a consequence of the thermodynamic perspective and our rules for keeping track of exchanges of heat and work between system and surroundings. Conservation of energy is an “accounting convention,” but it is not arbitrary. That is, we are not free to choose another convention for this “energy accounting.” Ample experimental evidence supports our assumption that energy conservation is a fundamental property of nature.

In summary, we postulate that for any change whatsoever that a closed system may undergo, we can identify energy inputs either as heat or as one or more forms of work such that

$$E = q + w$$

and, if a system undergoes a series of changes that ultimately return it to its original state, the energy change for the entire series of changes will be zero. There are two components to this postulate. The first component is an operational definition of energy. An important aspect of this definition is that the principle of conservation of energy is embedded in it. The second is an assertion that energy is a state function. Our operational definition of energy is open-ended. An essential element of the postulate is that we can always identify work inputs that make the energy, whose changes we compute as $q + w$, a state function. The facts that energy is conserved and that energy is a state function are related properties of a single aspect (energy) of nature. The relationship between these facts is a characteristic property of physical reality; it is not a matter of logic in the sense that one fact implies the other.

All of these ideas are essential components of the concept of energy. We roll them all together and assert them as a postulate that we call the first law of thermodynamics. We introduce the first law in Chapter 6. We repeat it here.

The first law of thermodynamics

In a process in which a closed system accepts increments of heat, dq , and work, dw , from its surroundings, the change in the energy of the system, dE , is $dE = dq + dw$. Energy is a state function. For any process, $dE_{universe} = 0$.

This statement of the first law does not deal explicitly with the mechanical energy of the system as a whole or with the energy effects of a transport of matter across the boundary of an open system. Because dw can include work that changes the position or motion of a system relative to an external reference frame, increments of mechanical energy can be included in dE . In chemical applications, we seldom need to consider the mechanical energy of the system as a whole; we can assume that the system has no kinetic or potential energy associated with the movement or location of its mass. When this is case, the total incremental energy change, dE , is the same thing as the incremental change in the internal energy of the system. When we need to distinguish the

internal energy of a system from its total energy, we write U for the **internal energy** and E for the **total energy**. Letting incremental changes in the kinetic and potential energy of the whole system be $d\tau$ and $d\upsilon$, respectively, we have

$$dU = dq + dw$$

and

$$dE = dU + d\tau + d\upsilon.$$

For processes of interest in chemical systems, we normally have $d\tau = d\upsilon = 0$. Then the total energy and the internal energy are the same thing: $dE = dU$.

In [Section 7.8](#), we introduce characteristic variables, θ_k , to represent changes in the system that result from various forms of non-pressure–volume work done on the system. We let $\Phi_k = (\partial E / \partial \theta_k)$, so that we can represent the incremental energy change that results from the non-pressure–volume work of all kinds as

$$dw_{NPV} = \sum_{k=1}^{\omega} \Phi_k d\theta_k$$

When both pressure–volume and non-pressure–volume work occur, we have

$$\begin{aligned} dw &= dw_{PV} + dw_{NPV} \\ &= -PdV + \sum_{k=1}^{\omega} \Phi_k d\theta_k \end{aligned}$$

When a non-thermal process changes the energy of a closed, constant-volume system, we have $dE = dw_{NPV}$.

We state the first law for a closed system. Extending the first law to open systems is straightforward. The energy of a system depends on the substances that are present, their amounts, and their states. At any specified conditions, a given amount of a particular substance makes a fixed contribution to the energy of the system. If we transfer matter across the boundary of a system, we change the energy of the system. We can always alter the original system to include the matter that is to be transferred. The altered system is closed; and so, by the first law, its energy is the same after the transfer as it was before. In [Section 14-2](#) we develop an explicit mathematical function to model the contribution made to the energy of a system by a specified quantity of matter in a specified state. If matter crosses the boundary of a system, the energy models for the separate collections of substances pre-transfer must equate to that for the new system post-transfer.

Finally, we make a further simple but important observation: We imagine that we can always identify an energy increment that crosses a system boundary as work, dw , or heat, dq . However, the essence of the first law is that these increments lose their identities—so to speak—in the system. The effect of a work input, dw , doesn't necessarily appear as an increase in the mechanical energy of the system; a heat input, dq , doesn't necessarily appear as an increase in the thermal energy of the system.

To illustrate this point, let us consider a reversible process and an irreversible process, each of which increases the temperature of one gram of water by one degree K. The initial and final states of the system are the same for both processes. In the reversible process, we bring the water, whose temperature is T , into contact with a thermal reservoir at an incrementally higher temperature $T + dT$ and allow 4.184 J of heat to transfer to the system by convection¹. No work is done. We have

- $q = -\hat{q} = 4.184 \text{ J}$,
- $w = -\hat{w} = 0$, and
- $E = q = 4.184 \text{ J}$.

In this case, there is no inter-conversion of heat and work.

In the irreversible process, we stir one gram of water that is thermally isolated. The stirring generates heat in the system. We supply the energy to drive the stirrer from the surroundings, perhaps by allowing a spring to uncoil. When 4.184 J of work from the surroundings has been frictionally dissipated in the system, the state of the one-gram system is the same as it was at the end of the reversible process. In this irreversible process, all of the energy traverses the system boundary as work (non-thermal energy). No heat traverses the system boundary. We have

- $w = -\hat{w} = 4.184 \text{ J}$,
- $q = -\hat{q} = 0$, and

- $\Delta E = w = 4.184 \text{ J}$.

Uncoiling the spring generates bulk motion within the water. Within a short time, the energy of this bulk motion is completely dissipated as molecular-level kinetic energy, or heat.

Beginning in §18, we consider the reversible isothermal expansion of an ideal gas. This simple process provides a further illustration of the inter-conversion of heat and work within a system. For this process, we find that thermal energy, $q > 0$, crosses the system boundary and is converted entirely into work that appears in the surroundings, $\hat{w} = -w > 0$. The energy of the system is unchanged. The energy of an ideal gas depends only on temperature. In an isothermal expansion, the temperature is constant, so the transport of heat across the system boundary has no effect on the energy of the system.

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