3.1: Heat, Work, and the First Law

The box below gives two forms of the **first law of thermodynamics**.

> In a closed system:
> $$\mathrm{d}U = đq + đw \qquad \Delta U = q + w$$
> where U is the internal energy of the system, a state function;
> q is heat; and
> w is thermodynamic work.

The equation $\mathrm{d}U = đq + đw$ is the *differential* form of the first law, and $\Delta U = q + w$ is the *integrated* form.

The heat and work appearing in the first law are two different modes of energy transfer. They can be defined in a general way as follows.

- An infinitesimal quantity of energy transferred as heat at a surface element of the boundary is written $đq$, and a finite quantity is written q (Sec. 2.5). To obtain the total finite heat for a process from $q = \int đq$ (Eq. 2.5.3), we must integrate over the total boundary surface and the entire path of the process.

  An infinitesimal quantity of work is $đw$, and a finite quantity is $w = \int đw$. To obtain w for a process, we integrate all kinds of work over the entire path of the process.

  The first-law equation $\Delta U = q + w$ sets up a balance sheet for the energy of the system, measured in the local frame, by equating its change during a process to the net quantity of energy transferred by means of heat and work. Note that the equation applies only to a *closed* system. If the system is open, energy can also be brought across the boundary by the transport of matter.

  An important part of the first law is the idea that heat and work are *quantitative* energy transfers. That is, when a certain quantity of energy enters the system in the form of heat, the same quantity leaves the surroundings. When the surroundings perform work on the system, the increase in the energy of the system is equal in magnitude to the decrease in the energy of the surroundings. The principle of conservation of energy is obeyed: the total energy (the sum of the energies of the system and surroundings) remains constant over time.

  > Strictly speaking, it is the sum of the energies of the system, the surroundings, and any potential energy shared by both that is constant. The shared potential energy is usually negligible or essentially constant (Sec. G.5).

Heat transfer may occur by conduction, convection, or radiation. (Some thermodynamicists treat radiation as a separate contribution to ΔU, in addition to q and w.) We can reduce conduction with good thermal insulation at the boundary, we can eliminate conduction and convection with a vacuum gap, and we can minimize radiation with highly reflective surfaces at both sides of the vacuum gap. The only way to completely prevent heat during a process is to arrange conditions in the surroundings so there is no temperature gradient at any part of the boundary. Under these conditions the process is adiabatic, and any energy transfer in a closed system is then solely by means of work.

3.1.1 The concept of thermodynamic work

Appendix G gives a detailed analysis of energy and work based on the behavior of a collection of interacting particles moving according to the principles of classical mechanics. The analysis shows how we should evaluate mechanical thermodynamic work. Suppose the displacement responsible for the work comes from linear motion of a portion of the boundary in the $+x$ or $-x$ direction of the local frame. The differential and integrated forms of the work are then given by

$$đw = F_x^{\mathrm{sur}} \, \mathrm{d}x \qquad w = \int_{x_1}^{x_2} F_x^{\mathrm{sur}} \, \mathrm{d}x \qquad\qquad (3.1.1)$$

(These equations are Eq. G.6.11 with a change of notation.) Here F_x^{sur} is the component in the $+x$ direction of the force exerted by the surroundings on the system at the moving portion of the boundary, and $\mathrm{d}x$ is the infinitesimal displacement of the boundary in the local frame. If the displacement is in the same direction as the force, $đw$ is positive; if the displacement is in the opposite direction, $đw$ is negative.

The kind of force represented by F_x^{sur} is a short-range contact force. Appendix G shows that the force exerted by a conservative time-independent external field, such as a gravitational force, should not be included as part of F_x^{sur}. This is because the work done by this kind of force causes changes of potential and kinetic energies that are equal and opposite in sign, with no net effect on the internal energy (see Sec. 3.6).

Newton's third law of action and reaction says that a force exerted by the surroundings on the system is opposed by a force of equal magnitude exerted in the opposite direction by the system on the surroundings. Thus the expressions in Eq. 3.1.1 can be replaced by

$$\text{đ}w = -F_x^{\text{sys}}\,\text{d}x \qquad w = -\int_{x_1}^{x_2} F_x^{\text{sys}}\,\text{d}x \tag{3.1.2}$$

where F_x^{sys} is the component in the $+x$ direction of the contact force exerted by the *system* on the surroundings at the moving portion of the boundary.

An alternative to using the expressions in Eqs. 3.1.1 or 3.1.2 for evaluating w is to imagine that the only effect of the work on the system's surroundings is a change in the elevation of a weight in the surroundings. The weight must be one that is linked mechanically to the source of the force F_x^{sur}. Then, provided the local frame is a stationary lab frame, the work is equal in magnitude and opposite in sign to the change in the weight's potential energy: $w = -mg\Delta h$ where m is the weight's mass, g is the acceleration of free fall, and h is the weight's elevation in the lab frame. This interpretation of work can be helpful for seeing whether work occurs and for deciding on its sign, but of course cannot be used to determine its *value* if the actual surroundings include no such weight.

The procedure of evaluating w from the change of an external weight's potential energy requires that this change be the only mechanical effect of the process on the surroundings, a condition that in practice is met only approximately. For example, Joule's paddle-wheel experiment using two weights linked to the system by strings and pulleys, described latter in Sec. 3.7.2, required corrections for (1) the kinetic energy gained by the weights as they sank, (2) friction in the pulley bearings, and (3) elasticity of the strings (see Prob. 3.10).

In the first-law relation $\Delta U = q + w$, the quantities ΔU, q, and w are all measured in an arbitrary *local* frame. We can write an analogous relation for measurements in a stationary *lab* frame:

$$\Delta E_{\text{sys}} = q_{\text{lab}} + w_{\text{lab}} \tag{3.1.3}$$

Suppose the chosen local frame is not a lab frame, and we find it more convenient to measure the heat q_{lab} and the work w_{lab} in a lab frame than to measure q and w in the local frame. What corrections are needed to find q and w in this case?

If the Cartesian axes of the local frame do not rotate relative to the lab frame, then the heat is the same in both frames: $q = q_{\text{lab}}$ (Sec. G.7).

The expressions for $\text{đ}w_{\text{lab}}$ and w_{lab} are the same as those for $\text{đ}w$ and w in Eqs. 3.1.1 and 3.1.2, with $\text{d}x$ interpreted as the displacement in the *lab* frame. There is an especially simple relation between w and w_{lab} when the local frame is a center-of-mass frame—one whose origin moves with the system's center of mass and whose axes do not rotate relative to the lab frame (Eq. G.8.12):

$$w = w_{\text{lab}} - \tfrac{1}{2}m\Delta\left(v_{\text{cm}}^2\right) - mg\Delta z_{\text{cm}} \tag{3.1.4}$$

In this equation m is the mass of the system, v_{cm} is the velocity of its center of mass in the lab frame, g is the acceleration of free fall, and z_{cm} is the height of the center of mass above an arbitrary zero of elevation in the lab frame. In typical thermodynamic processes the quantities v_{cm} and z_{cm} change to only a negligible extent, if at all, so that usually to a good approximation w is equal to w_{lab}.

When the local frame is a center-of-mass frame, we can combine the relations $\Delta U = q + w$ and $q = q_{\text{lab}}$ with Eqs. 3.1.3 and 3.1.4 to obtain

$$\Delta E_{\text{sys}} = \Delta E_{\text{k}} + \Delta E_{\text{p}} + \Delta U \tag{3.1.5}$$

where $E_{\text{k}} = \tfrac{1}{2}mv_{\text{cm}}^2$ and $E_{\text{p}} = mgz_{\text{cm}}$ are the kinetic and potential energies of the system as a whole in the lab frame.

A more general relation for w can be written for any local frame that has no rotational motion and whose origin has negligible acceleration in the lab frame (Eq. G.7.3):

$$w = w_{\text{lab}} - mg\Delta z_{\text{loc}} \tag{3.1.6}$$

Here z_{loc} is the elevation in the lab frame of the origin of the local frame. Δz_{loc} is usually small or zero, so again w is approximately equal to w_{lab}. The only kinds of processes for which we may need to use Eq. 3.1.4 or 3.1.6 to calculate a non-

negligible difference between w and w_{lab} are those in which massive parts of the system undergo substantial changes in elevation in the lab frame.

Simple relations such as these between q and q_{lab}, and between w and w_{lab}, do not exist if the local frame has rotational motion relative to a lab frame.

Hereafter in this e-book, thermodynamic work w will be called simply *work*. For all practical purposes you can assume the local frames for most of the processes to be described are stationary lab frames. The discussion above shows that the values of heat and work measured in these frames are usually the same, or practically the same, as if they were measured in a local frame moving with the system's center of mass. A notable exception is the local frame needed to treat the thermodynamic properties of a liquid solution in a centrifuge cell. In this case the local frame is fixed in the spinning rotor of the centrifuge and has rotational motion. This special case will be discussed in Sec. 9.8.2.

3.1.2 Work coefficients and work coordinates

If a process has only one kind of work, it can be expressed in the form

$$\text{d}w = Y\,\text{d}X \qquad \text{or} \qquad w = \int_{X_1}^{X_2} Y\,\text{d}X \qquad\qquad (3.1.7)$$

where Y is a generalized force called a **work coefficient** and X is a generalized displacement called a **work coordinate**. The work coefficient and work coordinate are *conjugate* variables. They are not necessarily actual forces and displacements. For example, we shall see in Sec. 3.4.2 that reversible expansion work is given by $\text{d}w = -p\,\text{d}V$; in this case, the work coefficient is $-p$ and the work coordinate is V.

A process may have more than one kind of work, each with its own work coefficient and conjugate work coordinate. In this case the work can be expressed as a sum over the different kinds labeled by the index i:

$$\text{d}w = \sum_i Y_i\,\text{d}X_i \qquad \text{or} \qquad w = \sum_i \int_{X_{i,1}}^{X_{i,2}} Y_i\,\text{d}X_i \qquad\qquad (3.1.8)$$

3.1.3 Heat and work as path functions

Consider the apparatus shown in Fig. 3.1. The *system* consists of the water together with the immersed parts: stirring paddles attached to a shaft (a paddle wheel) and an electrical resistor attached to wires. In equilibrium states of this system, the temperature and pressure are uniform and the paddle wheel is stationary. The system is open to the atmosphere, so the pressure is constrained to be constant. We may describe the equilibrium states of this system by a single independent variable, the temperature T. (The angular position of the shaft is irrelevant to the state and is not a state function for equilibrium states of this system.)

Here are three experiments with different processes. Each process has the same initial state defined by $T_1 = 300.0\,\text{K}$, and each has the same final state.

- Although the paths in the three experiments are entirely different, the overall change of state is the same. In fact, a person who observes only the initial and final states and has no knowledge of the intermediate states or the changes in the surroundings will be ignorant of the path. Did the paddle wheel turn? Did an electric current pass through the resistor? How much energy was transferred by work and how much by heat? The observer cannot tell from the change of state, because heat and work are not state functions. The change of state depends on the *sum* of heat and work. This sum is the change in the state function U, as expressed by the integrated form of the first law, $\Delta U = q + w$.

  It follows from this discussion that neither heat nor work are quantities possessed by the system. A system at a given instant does not *have* or *contain* a particular quantity of heat or a particular quantity of work. Instead, heat and work depend on the path of a process occurring over a period of time. They are *path* functions.

3.1.4 Heat and heating

In everyday speech the noun *heat* is often used somewhat differently. Here are three statements with similar meanings that could be misleading:

"Heat is transferred from a laboratory hot plate to a beaker of water."

"Heat flows from a warmer body to a cooler body."

"To remove heat from a hot body, place it in cold water."

Statements such as these may give the false impression that heat is like a substance that retains its identity as it moves from one body to another. Actually heat, like work, does not exist as an entity once a process is completed. Nevertheless, the wording of statements such as these is embedded in our everyday language, and no harm is done if we interpret them correctly. This e-book, for conciseness, often refers to "heat transfer" and "heat flow," instead of using the technically more correct phrase "energy transfer by means of heat."

Another common problem is failure to distinguish between thermodynamic "heat" and the process of "heating." To *heat* a system is to cause its temperature to increase. A *heated* system is one that has become warmer. This process of *heating* does not necessarily involve thermodynamic heat; it can also be carried out with work as illustrated by experiments 1 and 2 of the preceding section.

The notion of heat as an indestructible substance was the essence of the caloric theory. This theory was finally disproved by the cannon-boring experiments of Benjamin Thompson (Count Rumford) in the late eighteenth century, and in a more quantitative way by the measurement of the mechanical equivalent of heat by James Joule in the 1840s (see Sec. 3.7.2).

3.1.5 Heat capacity

The **heat capacity** of a closed system is defined as the ratio of an infinitesimal quantity of heat transferred across the boundary under specified conditions and the resulting infinitesimal temperature change:

$$\text{heat capacity} \overset{\text{def}}{=} \frac{đq}{dT} \qquad\qquad (3.1.9)$$
$$(\text{closed system})$$

Since q is a path function, the value of the heat capacity depends on the specified conditions, usually either constant volume or constant pressure. C_V is the *heat capacity at constant volume* and C_p is the *heat capacity at constant pressure*. These are extensive state functions that will be discussed more fully in Sec. 5.6.

3.1.6 Thermal energy

It is sometimes useful to use the concept of **thermal energy**. It can be defined as the kinetic energy of random translational motions of atoms and molecules relative to the local frame, plus the vibrational and rotational energies of molecules. The thermal energy of a body or phase depends on its temperature, and increases when the temperature increases. The thermal energy of a system is a contribution to the internal energy.

It is important to understand that a change of the system's thermal energy during a process is not necessarily the same as energy transferred across the system boundary as heat. The two quantities are equal only if the system is closed and there is no work, volume change, phase change, or chemical reaction. This is illustrated by the three experiments described in Sec. 3.1.3: the thermal energy change is the same in each experiment, but only in experiment 3 is the work negligible and the thermal energy change equal to the heat.