

the first law means “you can’t win.” He paraphrased the second law as “you can’t break even, except on a very cold day.” Unless you are at zero kelvin, you cannot convert 100% of thermal energy into work. We start by discussing spontaneous processes and explain why some processes require work to occur even if energy would have been conserved.

4.1 | Reversible and Irreversible Processes

Learning Objectives

By the end of this section, you will be able to:

- Define reversible and irreversible processes
- State the second law of thermodynamics via an irreversible process

Consider an ideal gas that is held in half of a thermally insulated container by a wall in the middle of the container. The other half of the container is under vacuum with no molecules inside. Now, if we remove the wall in the middle quickly, the gas expands and fills up the entire container immediately, as shown in **Figure 4.2**.

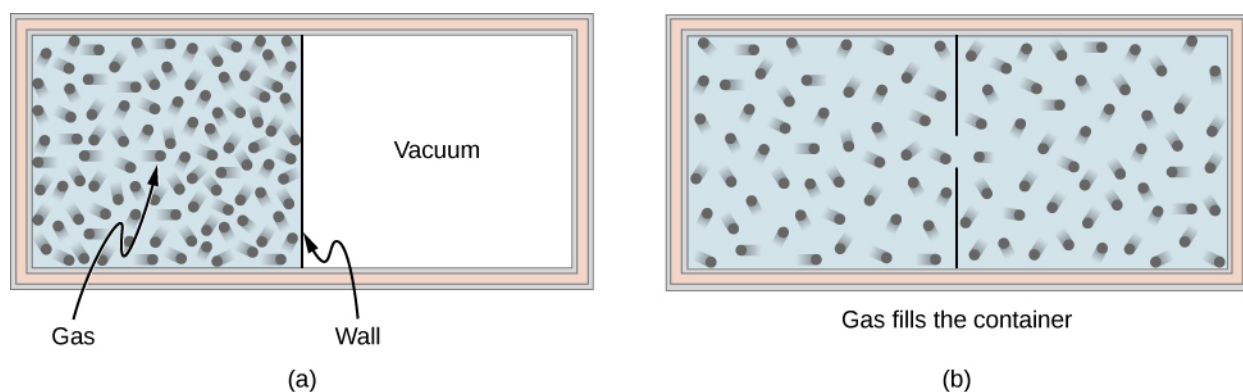


Figure 4.2 A gas expanding from half of a container to the entire container (a) before and (b) after the wall in the middle is removed.

Because half of the container is under vacuum before the gas expands there, we do not expect any work to be done by the system—that is, $W = 0$ —because no force from the vacuum is exerted on the gas during the expansion. If the container is thermally insulated from the rest of the environment, we do not expect any heat transfer to the system either, so $Q = 0$. Then the first law of thermodynamics leads to the change of the internal energy of the system,

$$\Delta E_{\text{int}} = Q - W = 0.$$

For an ideal gas, if the internal energy doesn’t change, then the temperature stays the same. Thus, the equation of state of the ideal gas gives us the final pressure of the gas, $p = nRT/V = p_0/2$, where p_0 is the pressure of the gas before the expansion. The volume is doubled and the pressure is halved, but nothing else seems to have changed during the expansion.

All of this discussion is based on what we have learned so far and makes sense. Here is what puzzles us: Can all the molecules go backward to the original half of the container in some future time? Our intuition tells us that this is going to be very unlikely, even though nothing we have learned so far prevents such an event from happening, regardless of how small the probability is. What we are really asking is whether the expansion into the vacuum half of the container is *reversible*.

A **reversible process** is a process in which the system and environment can be restored to exactly the same initial states that they were in before the process occurred, if we go backward along the path of the process. The necessary condition for a reversible process is therefore the quasi-static requirement. Note that it is quite easy to restore a system to its original state; the hard part is to have its environment restored to its original state at the same time. For example, in the example of an ideal gas expanding into vacuum to twice its original volume, we can easily push it back with a piston and restore its temperature and pressure by removing some heat from the gas. The problem is that we cannot do it without changing something in its surroundings, such as dumping some heat there.

A reversible process is truly an ideal process that rarely happens. We can make certain processes close to reversible and therefore use the consequences of the corresponding reversible processes as a starting point or reference. In reality, almost

all processes are irreversible, and some properties of the environment are altered when the properties of the system are restored. The expansion of an ideal gas, as we have just outlined, is irreversible because the process is not even quasi-static, that is, not in an equilibrium state at any moment of the expansion.

From the microscopic point of view, a particle described by Newton's second law can go backward if we flip the direction of time. But this is not the case, in practical terms, in a macroscopic system with more than 10^{23} particles or molecules, where numerous collisions between these molecules tend to erase any trace of memory of the initial trajectory of each of the particles. For example, we can actually estimate the chance for all the particles in the expanded gas to go back to the original half of the container, but the current age of the universe is still not long enough for it to happen even once.

An **irreversible process** is what we encounter in reality almost all the time. The system and its environment cannot be restored to their original states at the same time. Because this is what happens in nature, it is also called a natural process. The sign of an irreversible process comes from the finite gradient between the states occurring in the actual process. For example, when heat flows from one object to another, there is a finite temperature difference (gradient) between the two objects. More importantly, at any given moment of the process, the system most likely is not at equilibrium or in a well-defined state. This phenomenon is called **irreversibility**.

Let us see another example of irreversibility in thermal processes. Consider two objects in thermal contact: one at temperature T_1 and the other at temperature $T_2 > T_1$, as shown in **Figure 4.3**.

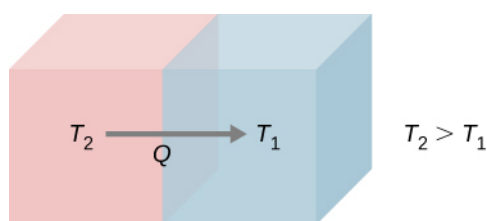


Figure 4.3 Spontaneous heat flow from an object at higher temperature T_2 to another at lower temperature T_1 .

We know from common personal experience that heat flows from a hotter object to a colder one. For example, when we hold a few pieces of ice in our hands, we feel cold because heat has left our hands into the ice. The opposite is true when we hold one end of a metal rod while keeping the other end over a fire. Based on all of the experiments that have been done on spontaneous heat transfer, the following statement summarizes the governing principle:

Second Law of Thermodynamics (Clausius statement)

Heat never flows spontaneously from a colder object to a hotter object.

This statement turns out to be one of several different ways of stating the second law of thermodynamics. The form of this statement is credited to German physicist Rudolf Clausius (1822–1888) and is referred to as the **Clausius statement of the second law of thermodynamics**. The word “spontaneously” here means no other effort has been made by a third party, or one that is neither the hotter nor colder object. We will introduce some other major statements of the second law and show that they imply each other. In fact, all the different statements of the second law of thermodynamics can be shown to be equivalent, and all lead to the irreversibility of spontaneous heat flow between macroscopic objects of a very large number of molecules or particles.

Both isothermal and adiabatic processes sketched on a pV graph (discussed in **The First Law of Thermodynamics**) are reversible in principle because the system is always at an equilibrium state at any point of the processes and can go forward or backward along the given curves. Other idealized processes can be represented by pV curves; **Table 4.1** summarizes the most common reversible processes.

Process	Constant Quantity and Resulting Fact
Isobaric	Constant pressure $W = p\Delta V$
Isochoric	Constant volume $W = 0$

Table 4.1 Summary of Simple Thermodynamic Processes

Process	Constant Quantity and Resulting Fact
Isothermal	Constant temperature $\Delta T = 0$
Adiabatic	No heat transfer $Q = 0$

Table 4.1 Summary of Simple Thermodynamic Processes

4.2 | Heat Engines

Learning Objectives

By the end of this section, you will be able to:

- Describe the function and components of a heat engine
- Explain the efficiency of an engine
- Calculate the efficiency of an engine for a given cycle of an ideal gas

A **heat engine** is a device used to extract heat from a source and then convert it into mechanical work that is used for all sorts of applications. For example, a steam engine on an old-style train can produce the work needed for driving the train. Several questions emerge from the construction and application of heat engines. For example, what is the maximum percentage of the heat extracted that can be used to do work? This turns out to be a question that can only be answered through the second law of thermodynamics.

The second law of thermodynamics can be formally stated in several ways. One statement presented so far is about the direction of spontaneous heat flow, known as the Clausius statement. A couple of other statements are based on heat engines. *Whenever we consider heat engines and associated devices such as refrigerators and heat pumps, we do not use the normal sign convention for heat and work.* For convenience, we assume that the symbols Q_h , Q_c , and W represent only the amounts of heat transferred and work delivered, regardless what the givers or receivers are. Whether heat is entering or leaving a system and work is done to or by a system are indicated by proper signs in front of the symbols and by the directions of arrows in diagrams.

It turns out that we need more than one heat source/sink to construct a heat engine. We will come back to this point later in the chapter, when we compare different statements of the second law of thermodynamics. For the moment, we assume that a heat engine is constructed between a heat source (high-temperature reservoir or hot reservoir) and a heat sink (low-temperature reservoir or cold reservoir), represented schematically in **Figure 4.4**. The engine absorbs heat Q_h from a heat source (**hot reservoir**) of Kelvin temperature T_h , uses some of that energy to produce useful work W , and then discards the remaining energy as heat Q_c into a heat sink (**cold reservoir**) of Kelvin temperature T_c . Power plants and internal combustion engines are examples of heat engines. Power plants use steam produced at high temperature to drive electric generators, while exhausting heat to the atmosphere or a nearby body of water in the role of the heat sink. In an internal combustion engine, a hot gas-air mixture is used to push a piston, and heat is exhausted to the nearby atmosphere in a similar manner.