

Introduction to Thermodynamics



A steam engine uses heat transfer to do work. (credit: Gerald Friedrich, Pixabay)

Heat transfer is energy in transit, and it can be used to do work. It can also be converted to any other form of energy. A car engine, for example, burns fuel for heat transfer into a gas. Work is done by the gas as it exerts a force through a distance, converting its energy into a variety of other forms—into the car's kinetic or gravitational potential energy; into electrical energy to run the spark plugs, radio, and lights; and back into stored energy in the car's battery. But most of the heat transfer produced from burning fuel in the engine does not do work on the gas. Rather, the energy is released into the environment, implying that the engine is quite inefficient.

It is often said that modern gasoline engines cannot be made to be significantly more efficient. We hear the same about heat transfer to electrical energy in large power stations, whether they are coal, oil, natural gas, or nuclear powered. Why is that the case? Is the inefficiency caused by design problems that could be solved with better engineering and superior materials? Is it part of some money-making conspiracy by those who sell energy? Actually, the truth is more interesting, and reveals much about the nature of heat transfer.

Basic physical laws govern how heat transfer for doing work takes place and place insurmountable limits onto its efficiency. This chapter will explore these laws as well as many applications and concepts associated with them. These topics are part of *thermodynamics*—the study of heat transfer and its relationship to doing work.



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The First Law of Thermodynamics

- Define the first law of thermodynamics.
- Describe how conservation of energy relates to the first law of thermodynamics.
- Identify instances of the first law of thermodynamics working in everyday situations, including biological metabolism.
- Calculate changes in the internal energy of a system, after accounting for heat transfer and work done.

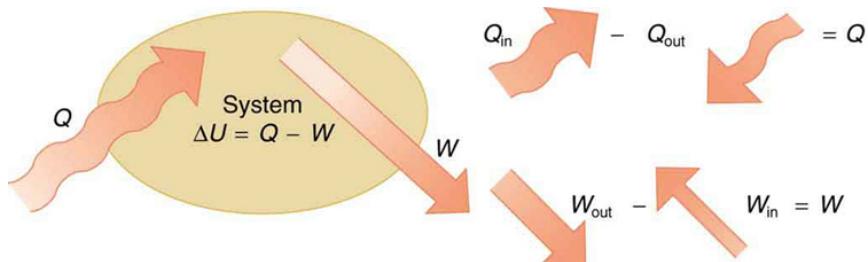


This boiling tea kettle represents energy in motion. The water in the kettle is turning to water vapor because heat is being transferred from the stove to the kettle. As the entire system gets hotter, work is done—from the evaporation of the water to the whistling of the kettle. (credit: Gina Hamilton)

If we are interested in how heat transfer is converted into doing work, then the conservation of energy principle is important. The first law of thermodynamics applies the conservation of energy principle to systems where heat transfer and doing work are the methods of transferring energy into and out of the system. The **first law of thermodynamics** states that the change in internal energy of a system equals the net heat transfer **into** the system minus the net work done **by** the system. In equation form, the first law of thermodynamics is

$$\Delta U = Q - W$$

Here ΔU is the *change in internal energy* UU of the system. QQ is the **net heat transferred into the system**—that is, QQ is the sum of all heat transfer into and out of the system. WW is the **net work done by the system**—that is, WW is the sum of all work done on or by the system. We use the following sign conventions: if QQ is positive, then there is a net heat transfer into the system; if WW is positive, then there is net work done by the system. So positive QQ adds energy to the system and positive WW takes energy from the system. Thus, $\Delta U = Q - W$. Note also that if more heat transfer into the system occurs than work done, the difference is stored as internal energy. Heat engines are a good example of this—heat transfer into them takes place so that they can do work. (See [Figure 2].) We will now examine QQ , WW , and ΔU further.



The first law of thermodynamics is the conservation-of-energy principle stated for a system where heat and work are the methods of transferring energy for a system in thermal equilibrium. (Q) represents the net heat transfer—it is the sum of all heat transfers into and out of the system. (Q) is positive for net heat transfer into the system. (W) is the total work done on and by the system. (W) is positive when more work is done by the system than on it. The change in the internal energy of the system, (ΔU), is related to heat and work by the first law of thermodynamics, ($\Delta U = Q - W$).

Making Connections: Law of Thermodynamics and Law of Conservation of Energy

The first law of thermodynamics is actually the law of conservation of energy stated in a form most useful in thermodynamics. The first law gives the relationship between heat transfer, work done, and the change in internal energy of a system.

Heat Q and Work W

Heat transfer (QQ) and doing work (WW) are the two everyday means of bringing energy into or taking energy out of a system. The processes are quite different. Heat transfer, a less organized process, is driven by temperature differences. Work, a quite organized process, involves a macroscopic force exerted through a distance. Nevertheless, heat and work can produce identical results. For example, both can cause a temperature increase. Heat transfer into a system, such as when the Sun warms the air in a bicycle tire, can increase its temperature, and so can work done on the system, as when the bicyclist pumps air into the tire. Once the temperature increase has occurred, it is impossible to tell whether it was caused by heat transfer or by doing work. This uncertainty is an important point. Heat transfer and work are both energy in transit—neither is stored as such in a system. However, both can change the internal energy UU of a system. Internal energy is a form of energy completely different from either heat or work.

Internal Energy U

We can think about the internal energy of a system in two different but consistent ways. The first is the atomic and molecular view, which examines the system on the atomic and molecular scale. The **internal energy** UU of a system is the sum of the kinetic and potential energies of its atoms and molecules. Recall that kinetic plus potential energy is called mechanical energy. Thus, internal energy is the sum of atomic and molecular mechanical energy. Because it is impossible to keep track of all individual atoms and molecules, we must deal with averages and distributions. A second way to view the internal energy of a system is in terms of its macroscopic characteristics, which are very similar to atomic and molecular average values.

Macroscopically, we define the change in internal energy ΔU to be that given by the first law of thermodynamics:

$$\Delta U = Q - W.$$

$$\Delta U = Q - W.$$

Many detailed experiments have verified that $\Delta U = Q - W$, where ΔU is the change in total kinetic and potential energy of all atoms and molecules in a system. It has also been determined experimentally that the internal energy UU of a system depends only on the state of the system and **not how it reached that state.** More specifically, UU is found to be a function of a few macroscopic quantities (pressure, volume, and temperature, for example), independent of past history such as whether there has been heat transfer or work done. This independence means that if we know the state of a system, we can calculate changes in its internal energy UU from a few macroscopic variables.

Making Connections: Macroscopic and Microscopic

In thermodynamics, we often use the macroscopic picture when making calculations of how a system behaves, while the atomic and molecular picture gives underlying explanations in terms of averages and distributions. We shall see this again in later sections of this chapter. For example, in the topic of entropy, calculations will be made using the atomic and molecular view.

To get a better idea of how to think about the internal energy of a system, let us examine a system going from State 1 to State 2. The system has internal energy U_1 in State 1, and it has internal energy U_2 in State 2, no matter how it got to either state. So the change in internal energy $\Delta U = U_2 - U_1$ is independent of what caused the change. In other words, ΔU is *independent of path*. By path, we mean the method of getting from the starting point to the ending point. Why is this independence important? Note that $\Delta U = Q - W$. Both QQ and WW depend on path, but ΔU does not. This path independence means that internal energy UU is easier to consider than either heat transfer or work done.

Calculating Change in Internal Energy: The Same Change in U U

is Produced by Two Different Processes

(a) Suppose there is heat transfer of 40.00 J to a system, while the system does 10.00 J of work. Later, there is heat transfer of 25.00 J out of the system while 4.00 J of work is done on the system. What is the net change in internal energy of the system?

(b) What is the change in internal energy of a system when a total of 150.00 J of heat transfer occurs out of (from) the system and 159.00 J of work is done on the system? (See [Figure 3]).

Strategy

In part (a), we must first find the net heat transfer and net work done from the given information. Then the first law of thermodynamics ($\Delta U = Q - W$) can be used to find the change in internal energy. In part (b), the net heat transfer and work done are given, so the equation can be used directly.

Solution for (a)

The net heat transfer is the heat transfer into the system minus the heat transfer out of the system, or

$$Q = 40.00\text{J} - 25.00\text{J} = 15.00\text{J}.$$

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Similarly, the total work is the work done by the system minus the work done on the system, or

$$W = 10.00\text{J} - 4.00\text{J} = 6.00\text{J}.$$

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Thus the change in internal energy is given by the first law of thermodynamics:

$$\Delta U = Q - W = 15.00\text{J} - 6.00\text{J} = 9.00\text{J}.$$

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We can also find the change in internal energy for each of the two steps. First, consider 40.00 J of heat transfer in and 10.00 J of work out, or

$$\Delta U_1 = Q_1 - W_1 = 40.00\text{J} - 10.00\text{J} = 30.00\text{J}.$$

$$\Delta U_1 = Q_1 - W_1 = 40.00\text{J} - 10.00\text{J} = 30.00\text{J}.$$

Now consider 25.00 J of heat transfer out and 4.00 J of work in, or

$$\Delta U_2 = Q_2 - W_2 = -25.00\text{J} - (-4.00\text{J}) = -21.00\text{J}.$$

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The total change is the sum of these two steps, or

$$\Delta U = \Delta U_1 + \Delta U_2 = 30.00\text{J} + (-21.00\text{J}) = 9.00\text{J}.$$

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Discussion on (a)

No matter whether you look at the overall process or break it into steps, the change in internal energy is the same.

Solution for (b)

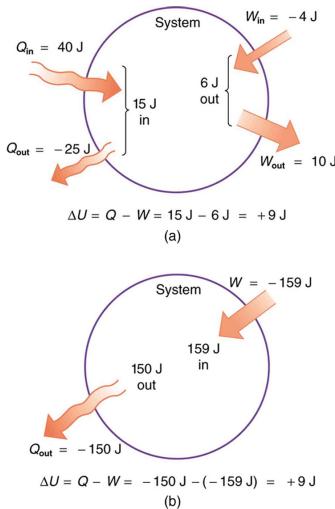
Here the net heat transfer and total work are given directly to be $Q = -150.00\text{J}$, $Q = -150.00\text{J}$ and $W = -159.00\text{J}$, $W = -159.00\text{J}$, so that

$$\Delta U = Q - W = -150.00\text{J} - (-159.00\text{J}) = 9.00\text{J}.$$

$$\Delta U = Q - W = -150.00\text{J} - (-159.00\text{J}) = 9.00\text{J}.$$

Discussion on (b)

A very different process in part (b) produces the same 9.00-J change in internal energy as in part (a). Note that the change in the system in both parts is related to ΔU and not to the individual Q s or W s involved. The system ends up in the **same** state in both (a) and (b). Parts (a) and (b) present two different paths for the system to follow between the same starting and ending points, and the change in internal energy for each is the same—it is independent of path.



Two different processes produce the same change in a system. (a) A total of 15.00 J of heat transfer occurs into the system, while work takes out a total of 6.00 J. The change in internal energy is $\Delta U = Q - W = 9.00 \text{ J}$.

(b) Heat transfer removes 150.00 J from the system while work puts 159.00 J into it, producing an increase of 9.00 J in internal energy. If the system starts out in the same state in (a) and (b), it will end up in the same final state in either case

Human Metabolism and the First Law of Thermodynamics

—its final state is related to internal energy, not how that energy was acquired.

Human metabolism is the conversion of food into heat transfer, work, and stored fat. Metabolism is an interesting example of the first law of thermodynamics in action. We now take another look at these topics via the first law of thermodynamics. Considering the body as the system of interest, we can use the first law to examine heat transfer, doing work, and internal energy in activities ranging from sleep to heavy exercise. What are some of the major characteristics of heat transfer, doing work, and energy in the body? For one, body temperature is normally kept constant by heat transfer to the surroundings. This means Q is negative. Another fact is that the body usually does work on the outside world. This means W is positive. In such situations, then, the body loses internal energy, since $\Delta U = Q - W$.

Now consider the effects of eating. Eating increases the internal energy of the body by adding chemical potential energy (this is an unromantic view of a good steak). The body **metabolizes** all the food we consume. Basically, metabolism is an oxidation process in which the chemical potential energy of food is released. This implies that food input is in the form of work. Food energy is reported in a special unit, known as the Calorie. This energy is measured by burning food in a calorimeter, which is how the units are determined.

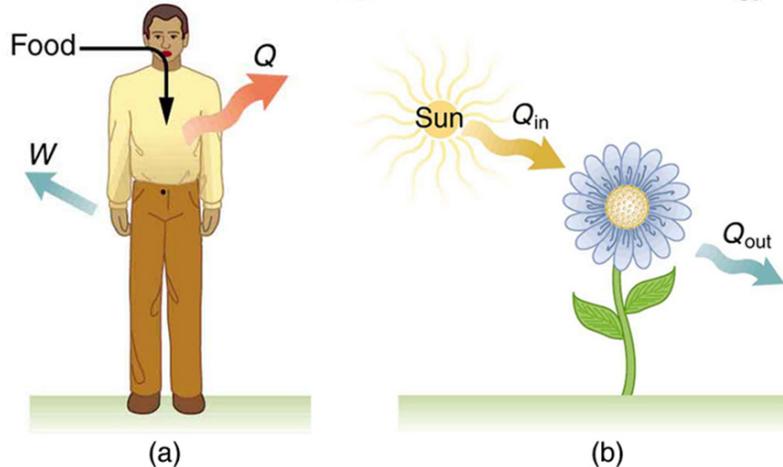
In chemistry and biochemistry, one calorie (spelled with a *lowercase c*) is defined as the energy (or heat transfer) required to raise the temperature of one gram of pure water by one degree Celsius. Nutritionists and weight-watchers tend to use the *dietary* calorie, which is frequently called a Calorie (spelled with a *capital C*). One food Calorie is the energy needed to raise the temperature of one *kilogram* of water by one degree Celsius. This means that one dietary Calorie is equal to one kilocalorie for the chemist, and one must be careful to avoid confusion between the two.

Again, consider the internal energy the body has lost. There are three places this internal energy can go—to heat transfer, to doing work, and to stored fat (a tiny fraction also goes to cell repair and growth). Heat transfer and doing work take internal energy out of the body, and food puts it back. If you eat just the right amount of food, then your average internal energy remains constant. Whatever you lose to heat transfer and doing work is replaced by food, so that, in the long run, $\Delta U = 0$. If you overeat repeatedly, then $\Delta U / \Delta U$ is always positive, and your body stores this extra internal energy as fat. The reverse is true if you eat too little. If $\Delta U / \Delta U$ is negative for a few days, then the body metabolizes its own fat to maintain body temperature and do work that takes energy from the body. This process is how dieting produces weight loss.

Life is not always this simple, as any dieter knows. The body stores fat or metabolizes it only if energy intake changes for a period of several days. Once you have been on a major diet, the next one is less successful because your body alters the way it responds to low energy intake. Your basal metabolic rate (BMR) is the rate at which food is converted into heat transfer and work done while the body is at complete rest. The body adjusts its basal metabolic rate to partially compensate for over-eating or under-eating. The body will decrease the metabolic rate rather than eliminate its own fat to replace lost food intake. You will chill more easily and feel less energetic as a result of the lower metabolic rate, and you will not lose weight as fast as before. Exercise helps to lose weight, because it produces both heat transfer from your body and work, and raises your metabolic rate even when you are at rest. Weight loss is also aided by the quite low efficiency of the body in converting internal energy to work, so that the loss of internal energy resulting from doing work is much greater than the work done. It should be noted, however, that living systems are not in thermalequilibrium.

The body provides us with an excellent indication that many thermodynamic processes are **irreversible**. An irreversible process can go in one direction but not the reverse, under a given set of conditions. For example, although body fat can be converted to do work and produce heat transfer, work done on the body and heat transfer into it cannot be converted to body fat. Otherwise, we could skip lunch by sunning ourselves or by walking downstairs. Another example of an irreversible thermodynamic process is photosynthesis. This process is the intake of one form of energy—light—by plants and its conversion to chemical potential energy. Both applications of the first law of thermodynamics are illustrated in [Figure 4]. One great advantage of conservation laws such as the first law of thermodynamics is that they accurately describe the beginning and ending points of complex processes, such as metabolism and photosynthesis, without regard to the complications in between. [Table 1] presents a summary of terms relevant to the first law of thermodynamics.

$$\Delta U = -Q - W + \text{food energy} \quad \Delta U = \text{stored food energy}$$



(a) The first law of thermodynamics applied to metabolism. Heat transferred out of the body ((Q)) and work done by the body ((W)) remove internal energy, while food intake replaces it. (Food intake may be considered as work done on the body.) (b) Plants convert part of the radiant heat transfer in sunlight to stored chemical energy, a process called

Summary of Terms for the First Law of Thermodynamics, $\Delta U = Q - W$
 $\Delta U = Q - W$

Term	Definition
U U	Internal energy—the sum of the kinetic and potential energies of a system's atoms and molecules. Can be divided into many subcategories, such as thermal and chemical energy. Depends only on the state of a system (such as its P , V , and T), not on how the energy entered the system. Change in internal energy is path independent.
Q Q	Heat—energy transferred because of a temperature difference. Characterized by random molecular motion. Highly dependent on path. Q entering a system is positive.
W W	Work—energy transferred by a force moving through a distance. An organized, orderly process. Path dependent. W done by a system (either against an external force or to increase the volume of the system) is positive.

Section Summary

- The first law of thermodynamics is given as $\Delta U = Q - W$, where ΔU is the change in internal energy of a system, Q is the net heat transfer (the sum of all heat transfer into and out of the system), and W is the net work done (the sum of all work done on or by the system).
- Both Q and W are energy in transit; only ΔU represents an independent quantity capable of being stored.
- The internal energy U of a system depends only on the state of the system and not how it reached that state.
- Metabolism of living organisms, and photosynthesis of plants, are specialized types of heat transfer, doing work, and internal energy of system

Conceptual Questions

Describe the photo of the tea kettle at the beginning of this section in terms of heat transfer, work done, and internal energy. How is heat being transferred? What is the work done and what is doing it? How does the kettle maintain its internal energy?

The first law of thermodynamics and the conservation of energy, as discussed in [Conservation of Energy](#), are clearly related. How do they differ in the types of energy considered?

Heat transfer Q and work done W are always energy in transit, whereas internal energy U is energy stored in a system. Give an example of each type of energy, and state specifically how it is either in transit or resides in a system.

How do heat transfer and internal energy differ? In particular, which can be stored as such in a system and which cannot?

If you run down some stairs and stop, what happens to your kinetic energy and your initial gravitational potential energy?

Give an explanation of how food energy (calories) can be viewed as molecular potential energy (consistent with the atomic and molecular definition of internal energy).

Identify the type of energy transferred to your body in each of the following as either internal energy, heat transfer, or doing work: (a) basking in sunlight; (b) eating food; (c) riding an elevator to a higher floor.

Problems & Exercises

What is the change in internal energy of a car if you put 12.0 gal of gasoline into its tank? The energy content of gasoline is $1.3 \times 10^8 \text{ J/gal}$. All other factors, such as the car's temperature, are constant.

How much heat transfer occurs from a system, if its internal energy decreased by 150 J while it was doing 30.0 J of work?

A system does $1.80 \times 10^8 \text{ J}$ of work while $7.50 \times 10^8 \text{ J}$ of heat transfer occurs to the environment. What is the change in internal energy of the system assuming no other changes (such as in temperature or by the addition of fuel)?

What is the change in internal energy of a system which does 4.50×10^5 J of work while 3.00×10^6 J of heat transfer occurs into the system, and 8.00×10^6 J of heat transfer occurs to the environment?

Suppose a woman does 500 J of work and 9500 J of heat transfer occurs into the environment in the process. (a) What is the decrease in her internal energy, assuming no change in temperature or consumption of food? (That is, there is no other energy transfer.) (b) What is her efficiency?

(a) How much food energy will a man metabolize in the process of doing 35.0 kJ of work with an efficiency of 5.00%? (b) How much heat transfer occurs to the environment to keep his temperature constant? Explicitly show how you follow the steps in the Problem-Solving Strategy for thermodynamics found in [Problem-Solving Strategies for Thermodynamics](#).

(a) What is the average metabolic rate in watts of a man who metabolizes 10 500 kJ of food energy in one day? (b) What is the maximum amount of work in joules he can do without breaking down fat, assuming a maximum efficiency of 20.0%? (c) Compare his work output with the daily output of a 187-W (0.250-horsepower) motor.

(a) How long will the energy in a 1470-kJ (350-kcal) cup of yogurt last in a woman doing work at the rate of 150 W with an efficiency of 20.0% (such as in leisurely climbing stairs)? (b) Does the time found in part (a) imply that it is easy to consume more food energy than you can reasonably expect to work off with exercise?

(a) A woman climbing the Washington Monument metabolizes 6.00×10^2 kJ of food energy. If her efficiency is 18.0%, how much heat transfer occurs to the environment to keep her temperature constant? (b) Discuss the amount of heat transfer found in (a). Is it consistent with the fact that you quickly warm up when exercising?

Glossary

first law of thermodynamics

states that the change in internal energy of a system equals the net heat transfer **into** the system minus the net work done **by** the system

internal energy

the sum of the kinetic and potential energies of a system's atoms and molecules

human metabolism

conversion of food into heat transfer, work, and stored fat



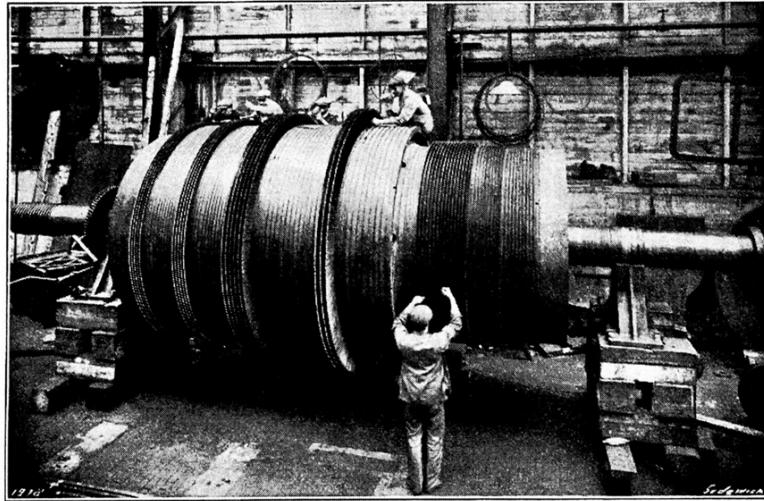
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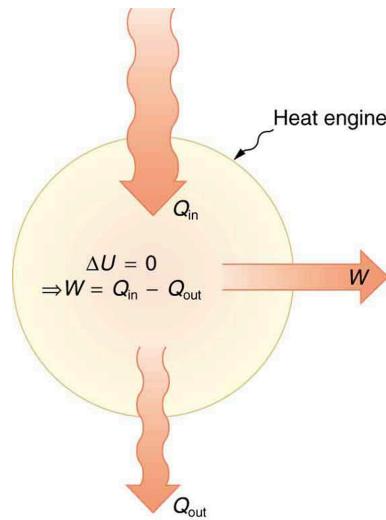
The First Law of Thermodynamics and Some Simple Processes

- Describe the processes of a simple heat engine.
- Explain the differences among the simple thermodynamic processes—isobaric, isochoric, isothermal, and adiabatic.
- Calculate total work done in a cyclical thermodynamic process.

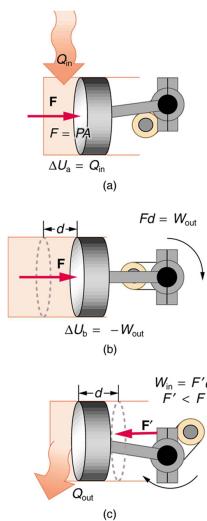


Beginning with the Industrial Revolution, humans have harnessed power through the use of the first law of thermodynamics, before we even understood it completely. This photo, of a steam engine at the Turbinia Works, dates from 1911, a mere 61 years after the first explicit statement of the first law of thermodynamics by Rudolph Clausius.

One of the most important things we can do with heat transfer is to convert it into work for our use. Such a device is called a **heat engine**. Car engines and steam turbines that generate electricity are examples of heat engines. [Figure 2] shows schematically how the first law of thermodynamics applies to the typical heat engine.



Schematic representation of a heat engine, governed, of course, by the first law of thermodynamics. It is impossible to devise a system where ($Q_{out}=0$), that is, in which no heat transfer occurs to the environment.



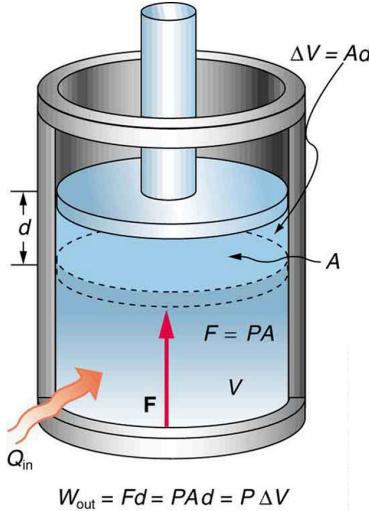
(a) Heat transfer to the gas in a cylinder increases the internal energy of the gas, creating higher pressure and temperature. (b) The force exerted on the movable cylinder does work as the gas expands. Gas pressure and temperature decrease when it expands, indicating that the gas's internal energy has been decreased by doing work. (c) Heat transfer to the surroundings so that its pressure decreases, and a force is exerted by the surroundings to push the piston back through some distance. Variations of this process are employed daily in hundreds of millions of heat engines. We will examine heat engines in detail in the next section. In this section, we consider some of the simpler underlying processes on which heat engines are based.

The illustrations above show one of the ways in which heat transfer does work. Fuel combustion produces heat transfer to a gas in a cylinder, increasing the pressure of the gas and thereby the force it exerts on a movable piston. The gas does work on the outside world, as this force moves the piston through some distance. Heat transfer to the gas cylinder results in work being done. To repeat this process, the piston needs to be returned to its starting point. Heat transfer now occurs from the gas to the surroundings so that its pressure decreases, and a force is exerted by the surroundings to push the piston back through some distance. Variations of this process are employed daily in hundreds of millions of heat engines. We will examine heat engines in detail in the next section. In this section, we consider some of the simpler underlying processes on which heat engines are based.

PV Diagrams and their Relationship to Work Done on or by a Gas

A process by which a gas does work on a piston at constant pressure is called an **isobaric process**. Since the pressure is constant, the force exerted is constant and the work done is given as

$$P\Delta V.$$



An isobaric expansion of a gas requires heat transfer to keep the pressure constant. Since pressure is constant, the work done is $(P \Delta V)$.

$$W = Fd$$

See the symbols as shown in [Figure 4]. Now $F = PA$, and so

$$W = PAd.$$

$$W = PAd.$$

Because the volume of a cylinder is its cross-sectional area AA times its length dd , we see that $Ad = \Delta V$, the change in volume; thus,

$$W = P\Delta V \text{ (isobaric process).}$$

$$W = P\Delta V \text{ (isobaric process).}$$

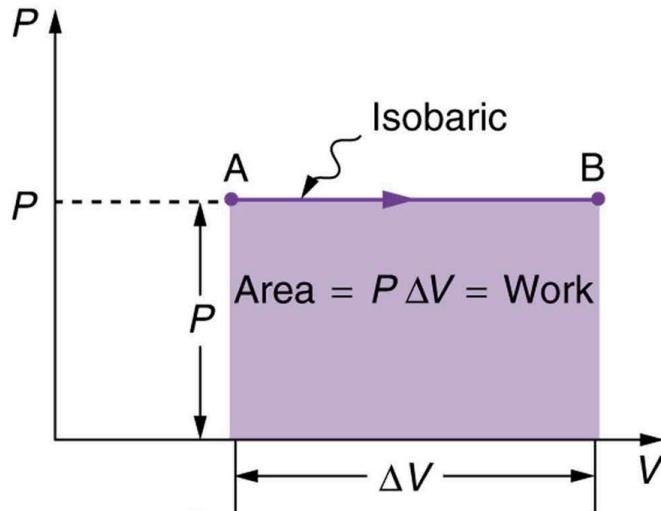
Note that if ΔV is positive, then WW is positive, meaning that work is done *by* the gas on the outside world.

(Note that the pressure involved in this work that we've called PP is the pressure of the gas *inside* the tank. If we call the pressure outside the tank P_{ext} , an expanding gas would be working *against* the external pressure; the work done would therefore be $W = -P_{\text{ext}}\Delta V$. Many texts use this definition of work, and not the definition based on internal pressure, as the basis of the First Law of Thermodynamics. This definition reverses the sign conventions for work, and results in a statement of the first law that becomes $\Delta U = Q + W$.)

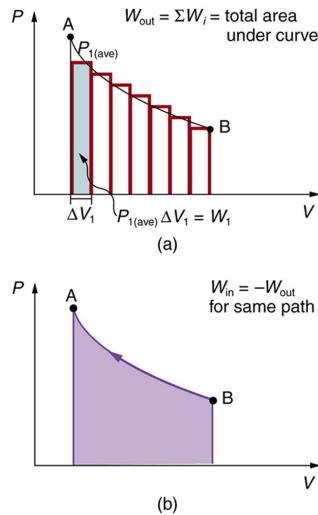
It is not surprising that $W = P\Delta V = P\Delta V$, since we have already noted in our treatment of fluids that pressure is a type of potential energy per unit volume and that pressure in fact has units of energy divided by volume. We also noted in our discussion of the ideal gas law that PV has units of energy. In this case, some of the energy associated with pressure becomes work.

[Figure 5] shows a graph of pressure versus volume (that is, a $\$PV$

diagram) for an isobaric process. You can see in the figure that the work done is the area under the graph. This property of diagram) for an isobaric process. You can see in the figure that the work done is the area under the graph. This property of $\$PV$ diagrams is very useful and broadly applicable :*the work done on or by a system going from one state to another equal the area under the curve on a $\$PV$ diagram*. diagram is very useful and broadly applicable: *the work done on or by a system going from one state to another equal the area under the curve on a $\$PV$ diagram*.



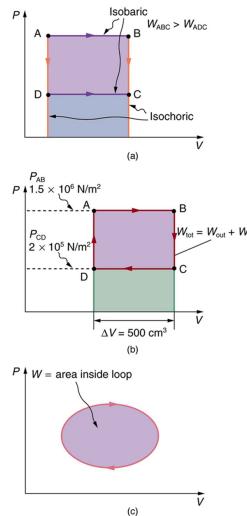
A graph of pressure versus volume for a constant-pressure, or isobaric, process, such as the one shown in [Figure 4] (#Figure4). The area under the curve equals the work done by the gas, since $W = P\Delta V = P\Delta V$.



(a) A PV diagram in which pressure varies as well as volume. The work done for each interval is its average pressure times the change in volume, or the area under the curve over that interval. Thus the total area under the curve equals the total work done. (b) Work must be done on the system to follow the reverse path. This is interpreted as a negative area

We can see where this leads by considering [Figure 6](a), which shows a more general process in which both pressure and volume change. The area under the curve is closely approximated by dividing it into strips, each having an average constant pressure $P_{i(\text{ave})}$. The work done is $W_i = P_{i(\text{ave})} \Delta V_i = P_{i(\text{ave})} \Delta V_i$ for each strip, and the total work done is the sum of the W_i . Thus the total work done is the total area under the curve. If the path is reversed, as in [Figure 6](b), then work is done on the system. The area under the curve in that case is negative, because $\Delta V \Delta V$ is negative.

PV diagrams clearly illustrate that *the work done depends on the path taken and not just the endpoints*. This path dependence is seen in [Figure 7](a), where more work is done in going from A to C by the path via point B than by the path via point D. The vertical paths, where volume is constant, are called **isochoric** processes. Since volume is constant, $\Delta V = 0$, and no work is done in an isochoric process. Now, if the system follows the cyclical path ABCDA, as in [Figure 7](b), then the total work done is the area inside the loop. The negative area below path CD subtracts, leaving only the area inside the rectangle. In fact, the work done in any cyclical process (one that returns to its starting point) is the area inside the loop it forms on a PV diagram, as [Figure 7](c) illustrates for a general cyclical process. Note that the loop must be traversed in the clockwise direction for work to be positive—that is, for there to be a net work output.



(a) The work done in going from A to C depends on path. The work is greater for the path ABC than for the path ADC, because the former is at higher pressure. In both cases, the work done is the area under the path. This area is greater for path ABC. (b) The total work done in the cyclical process ABCDA is the area inside the loop, since the negative area below CD subtracts out, leaving just the area inside the rectangle. (The values given for the pressures and the change in volume are intended for use in the example below.) (c) The area inside any closed loop is the work done in the cyclical process. If the loop is traversed in a clockwise direction, WW is positive—it is work done on the outside environment. If the loop is traveled in a counter-clockwise direction, WW is negative—it is work that is done to the system.

Total Work Done in a Cyclical Process Equals the Area Inside the Closed Loop on a *PV* Diagram

Calculate the total work done in the cyclical process ABCDA shown in [Figure 5](b) by the following two methods to verify that work equals the area inside the closed loop on the PV diagram. (Take the data in the figure to be precise to three significant figures.) (a) Calculate the work done along each segment of the path and add these values to get the total work. (b) Calculate the area inside the rectangle ABCDA.

Strategy

To find the work along any path on a PV diagram, you use the fact that work is pressure times change in volume, or $W = P\Delta V = P\Delta V$. So in part (a), this value is calculated for each leg of the path around the closed loop.

Solution for (a)

The work along path AB is

$$\begin{aligned} W_{AB} &= P_{AB}\Delta V_{AB} = (1.50 \times 10^6 \text{ N/m}^2)(5.00 \times 10^{-4} \text{ m}^3) = 750 \text{ J.} \\ W_{AB} &= P_{AB}\Delta V_{AB} \\ &= (1.50 \times 10^6 \text{ N/m}^2)(5.00 \times 10^{-4} \text{ m}^3) = 750 \text{ J.} \end{aligned}$$

Since the path BC is isochoric, $\Delta V_{BC} = 0$, and so $W_{BC} = 0$. The work along path CD is negative, since $\Delta V_{CD} \Delta V_{CD}$ is negative (the volume decreases). The work is

$$\begin{aligned} W_{CD} &= P_{CD}\Delta V_{CD} = (2.00 \times 10^5 \text{ N/m}^2)(-5.00 \times 10^{-4} \text{ m}^3) = -100 \text{ J.} \\ W_{CD} &= P_{CD}\Delta V_{CD} \\ &= (2.00 \times 10^5 \text{ N/m}^2)(-5.00 \times 10^{-4} \text{ m}^3) = -100 \text{ J.} \end{aligned}$$

Again, since the path DA is isochoric, $\Delta V_{DA} = 0$, and so $W_{DA} = 0$. Now the total work is

$$\begin{aligned} W &= W_{AB} + W_{BC} + W_{CD} + W_{DA} = 750 \text{ J} + 0 + (-100 \text{ J}) + 0 = 650 \text{ J.} \\ W &= W_{AB} + W_{BC} + W_{CD} + W_{DA} \\ &= 750 \text{ J} + 0 + (-100 \text{ J}) + 0 = 650 \text{ J.} \end{aligned}$$

Solution for (b)

The area inside the rectangle is its height times its width, or

$$\begin{aligned} \text{area} &= (P_{AB} - P_{CD})\Delta V = [(1.50 \times 10^6 \text{ N/m}^2) - (2.00 \times 10^5 \text{ N/m}^2)](5.00 \times 10^{-4} \text{ m}^3) = 650 \text{ J.} \\ \text{area} &= (P_{AB} - P_{CD})\Delta V \\ &= [(1.50 \times 10^6 \text{ N/m}^2) - (2.00 \times 10^5 \text{ N/m}^2)](5.00 \times 10^{-4} \text{ m}^3) = 650 \text{ J.} \end{aligned}$$

Thus,

$$\begin{aligned} \text{area} &= 650 \text{ J} = W. \\ \text{area} &= 650 \text{ J} = W. \end{aligned}$$

Discussion

The result, as anticipated, is that the area inside the closed loop equals the work done. The area is often easier to calculate than is the work done along each path. It is also convenient to visualize the area inside different curves on PV diagrams in order to see which processes might produce the most work. Recall that work can be done to the system, or by the system, depending on the sign of W . A positive W is work that is done by the system on the outside environment; a negative W represents work done by the environment on the system.

[Figure 8](a) shows two other important processes on a PV diagram. For comparison, both are shown starting from the same point A. The upper curve ending at point B is an **isothermal** process—that is, one in which temperature is kept constant. If the gas behaves like an ideal gas, as is often the case, and if no phase change occurs, then $PV = nRT$. Since T is constant, PV is a constant for an isothermal process. We ordinarily expect the temperature of a gas to decrease as it expands, and so we correctly suspect that heat transfer must occur from the surroundings to the gas to keep the temperature constant during an isothermal expansion. To show this more rigorously for the special case of a monatomic ideal gas, we note that the average kinetic energy of an atom in such a gas is given by

$$12m\overline{v^2} = 32k_B T.$$

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}k_B T.$$

The kinetic energy of the atoms in a monatomic ideal gas is its only form of internal energy, and so its total internal energy U is

$$U = N12m\overline{v^2} = 32Nk_B T, \text{ (monatomic ideal gas),}$$

$$U = N\frac{1}{2}m\overline{v^2} = \frac{3}{2}Nk_B T, \text{ (monatomic ideal gas),}$$

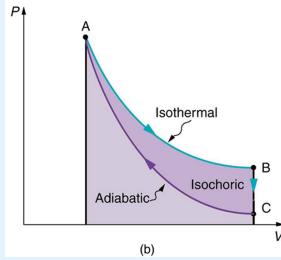
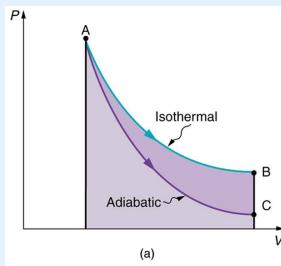
where N is the number of atoms in the gas. This relationship means that the internal energy of an ideal monatomic gas is constant during an isothermal process—that is, $\Delta U = 0$. If the internal energy does not change, then the net heat transfer into the gas must equal the net work done by the gas. That is, because $\Delta U = Q - W = 0$ here, $Q = W$. We must have just enough heat transfer to replace the work done. An isothermal process is inherently slow, because heat transfer occurs continuously to keep the gas temperature constant at all times and must be allowed to spread through the gas so that there are no hot or cold regions.

Also shown in [Figure 8](a) is a curve AC for an **adiabatic** process, defined to be one in which there is no heat transfer—that is, $Q = 0$. Processes that are nearly adiabatic can be achieved either by using very effective insulation or by performing the process so fast that there is little time for heat transfer. Temperature must decrease during an adiabatic expansion process, since work is done at the expense of internal energy:

$$U = 32Nk_B T.$$

$$U = \frac{3}{2}Nk_B T.$$

(You might have noted that a gas released into atmospheric pressure from a pressurized cylinder is substantially colder than the gas in the cylinder.) In fact, because $Q = 0$, $\Delta U = -W$, $Q = 0$, $\Delta U = -W$ for an adiabatic process. Lower temperature results in lower pressure along the way, so that curve AC is lower than curve AB, and less work is done. If the path ABCA could be followed by cooling the gas from B to C at constant volume (isochorically), [Figure 6](b), there would be a net work output.



(a) The upper curve is an isothermal process $\Delta T = 0$, whereas the lower curve is an adiabatic process ($Q = 0$). Both start from the same point A, but the isothermal process does more work than the adiabatic because heat transfer into the gas takes place to keep its temperature constant. This keeps the pressure higher all along the isothermal path than along the adiabatic path, producing more work. The adiabatic path thus ends up with a lower pressure and temperature at point C, even though the final volume is the same as for the isothermal process. (b) The cycle ABCA produces a net work output.

Reversible Processes

Both isothermal and adiabatic processes such as shown in [Figure 8] are reversible in principle. A **reversible process** is one in which both the system and its environment can return to exactly the states they were in by following the reverse path. The reverse isothermal and adiabatic paths are BA and CA, respectively. Real macroscopic processes are never exactly reversible. In the previous examples, our system is a gas (like that in [Figure 4]), and its environment is the piston, cylinder, and the rest of the universe. If there are any energy-dissipating mechanisms, such as friction or turbulence, then heat transfer to the environment occurs for either direction of the piston. So, for example, if the path BA is followed and there is friction, then the gas will be returned to its original state but the environment will not—it will have been heated in both directions. Reversibility requires the direction of heat transfer to reverse for the reverse path. Since dissipative mechanisms cannot be completely eliminated, real processes cannot be reversible.

There must be reasons that real macroscopic processes cannot be reversible. We can imagine them going in reverse. For example, heat transfer occurs spontaneously from hot to cold and never spontaneously the reverse. Yet it would not violate the first law of thermodynamics for this to happen. In fact, all spontaneous processes, such as bubbles bursting, never go in reverse. There is a second thermodynamic law that forbids them from going in reverse. When we study this law, we will learn something

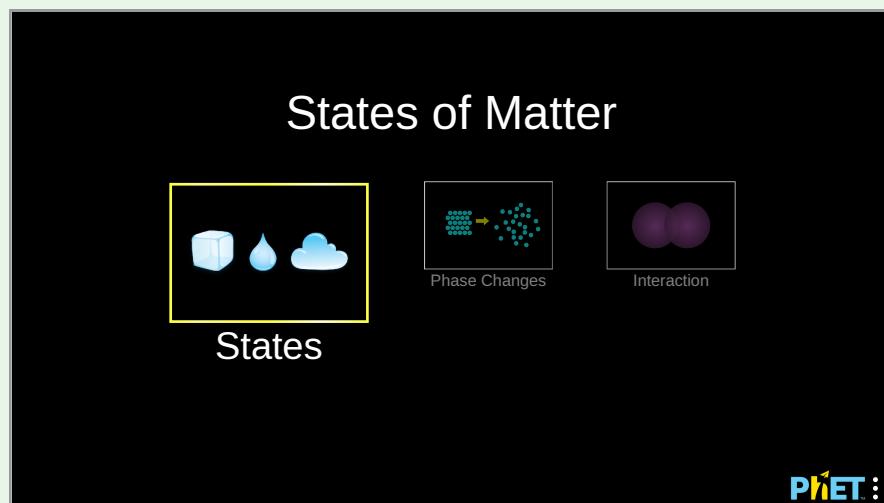
about nature and also find that such a law limits the efficiency of heat engines. We will find that heat engines with the greatest possible theoretical efficiency would have to use reversible processes, and even they cannot convert all heat transfer into doing work. [Table 1] summarizes the simpler thermodynamic processes and their definitions.

Summary of Simple Thermodynamic Processes

Summary of Simple Thermodynamic Processes	
Isobaric	Constant pressure $W=P\Delta V$ $W = P\Delta V$
Isochoric	Constant volume $W=0$ $W = 0$
Isothermal	Constant temperature $Q=W$ $Q = W$
Adiabatic	No heat transfer $Q=0$ $Q = 0$

PhET Explorations: States of Matter

Watch different types of molecules form a solid, liquid, or gas. Add or remove heat and watch the phase change. Change the temperature or volume of a container and see a pressure-temperature diagram respond in real time. Relate the interaction potential to the forces between molecules.



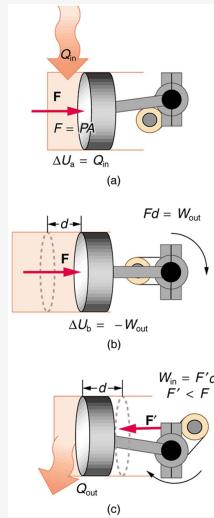
Section Summary

- One of the important implications of the first law of thermodynamics is that machines can be harnessed to do work that humans previously did by hand or by external energy supplies such as running water or the heat of the Sun. A machine that uses heat transfer to do work is known as a heat engine.
- There are several simple processes, used by heat engines, that flow from the first law of thermodynamics. Among them are the isobaric, isochoric, isothermal and adiabatic processes.
- These processes differ from one another based on how they affect pressure, volume, temperature, and heat transfer.
- If the work done is performed on the outside environment, work (WW) will be a positive value. If the work done is done to the heat engine system, work (WW) will be a negative value.
- Some thermodynamic processes, including isothermal and adiabatic processes, are reversible in theory; that is, both the thermodynamic system and the environment can be returned to their initial states. However, because of loss of energy owing to the second law of thermodynamics, complete reversibility does not work in practice.

Conceptual Questions

A great deal of effort, time, and money has been spent in the quest for the so-called perpetual-motion machine, which is defined as a hypothetical machine that operates or produces useful work indefinitely and/or a hypothetical machine that produces more work or energy than it consumes. Explain, in terms of heat engines and the first law of thermodynamics, why or why not such a machine is likely to be constructed.

One method of converting heat transfer into doing work is for heat transfer into a gas to take place, which expands, doing work on a piston, as shown in the figure below. (a) Is the heat transfer converted directly to work in an isobaric process, or does it go through another form first? Explain your answer. (b) What about in an isothermal process? (c) What about in an adiabatic process (where heat transfer occurred prior to the adiabatic process)?

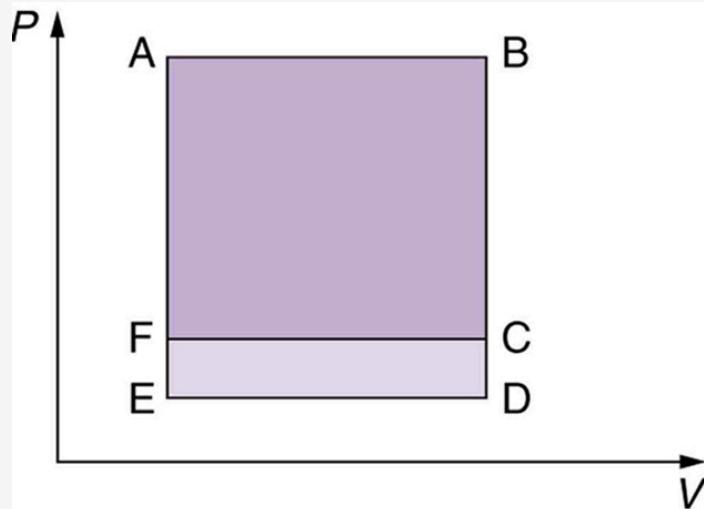


Would the previous question make any sense for an isochoric process? Explain your answer.

We ordinarily say that $\Delta U = 0$ for an isothermal process. Does this assume no phase change takes place? Explain your answer.

The temperature of a rapidly expanding gas decreases. Explain why in terms of the first law of thermodynamics. (Hint: Consider whether the gas does work and whether heat transfer occurs rapidly into the gas through conduction.)

Which cyclical process represented by the two closed loops, ABCFA and ABDEA, on the PV diagram in the figure below produces the greatest *net* work? Is that process also the one with the smallest work input required to return it to point A? Explain your responses.



The two cyclical processes shown on this PV diagram start with and return the system to the conditions at point A, but they follow different paths and produce different amounts of work.

A real process may be nearly adiabatic if it occurs over a very short time. How does the short time span help the process to be adiabatic?

It is unlikely that a process can be isothermal unless it is a very slow process. Explain why. Is the same true for isobaric and isochoric processes? Explain your answer.

Problem Exercises

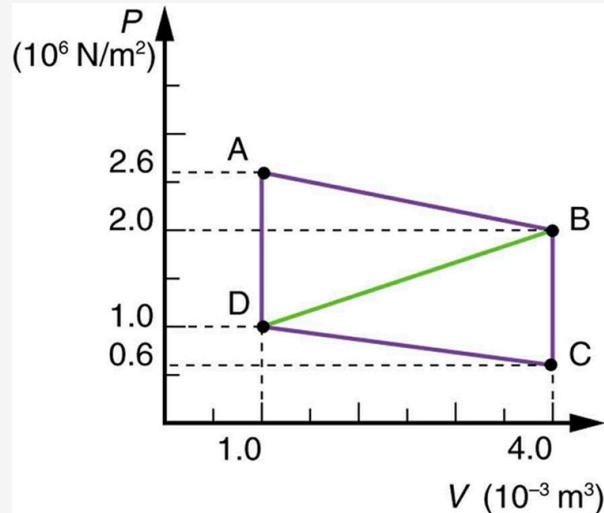
A car tire contains 0.0380 m^3 of air at a pressure of $2.20 \times 10^5\text{ N/m}^2$ (about 32 psi). How much more internal energy does this gas have than the same volume has at zero gauge pressure (which is equivalent to normal atmospheric pressure)?

A helium-filled toy balloon has a gauge pressure of 0.200 atm and a volume of 10.0 L. How much greater is the internal energy of the helium in the balloon than it would be at zero gauge pressure?

Steam to drive an old-fashioned steam locomotive is supplied at a constant gauge pressure of $1.75 \times 10^6 \text{ N/m}^2$ (about 250 psi) to a piston with a 0.200-m radius. (a) By calculating $P\Delta V P\Delta V$, find the work done by the steam when the piston moves 0.800 m. Note that this is the net work output, since gauge pressure is used. (b) Now find the amount of work by calculating the force exerted times the distance traveled. Is the answer the same as in part (a)?

A hand-driven tire pump has a piston with a 2.50-cm diameter and a maximum stroke of 30.0 cm. (a) How much work do you do in one stroke if the average gauge pressure is $2.40 \times 10^5 \text{ N/m}^2$ (about 35 psi)? (b) What average force do you exert on the piston, neglecting friction and gravitational force?

Calculate the net work output of a heat engine following path ABCDA in the figure below.



What is the net work output of a heat engine that follows path ABDA in the figure above, with a straight line from B to D? Why is the work output less than for path ABCDA? Explicitly show how you follow the steps in the [Problem-Solving Strategies for Thermodynamics](#).

Unreasonable Results

What is wrong with the claim that a cyclical heat engine does 4.00 kJ of work on an input of 24.0 kJ of heat transfer while 16.0 kJ of heat transfers to the environment?

(a) A cyclical heat engine, operating between temperatures of 450°C and 150°C produces 4.00 MJ of work on a heat transfer of 5.00 MJ into the engine. How much heat transfer occurs to the environment? (b) What is unreasonable about the engine? (c) Which premise is unreasonable?

Construct Your Own Problem

Consider a car's gasoline engine. Construct a problem in which you calculate the maximum efficiency this engine can have. Among the things to consider are the effective hot and cold reservoir temperatures. Compare your calculated efficiency with the actual efficiency of car engines.

Construct Your Own Problem

Consider a car trip into the mountains. Construct a problem in which you calculate the overall efficiency of the car for the trip as a ratio of kinetic and potential energy gained to fuel consumed. Compare this efficiency to the thermodynamic efficiency quoted for gasoline engines and discuss why the thermodynamic efficiency is so much greater. Among the factors to be considered are the gain in altitude and speed, the mass of the car, the distance traveled, and typical fuel economy.

Glossary

heat engine

a machine that uses heat transfer to do work

isobaric process

constant-pressure process in which a gas does work

isochoric process

a constant-volume process

isothermal process

a constant-temperature process

adiabatic process

a process in which no heat transfer takes place

reversible process

a process in which both the heat engine system and the external environment theoretically can be returned to their original states

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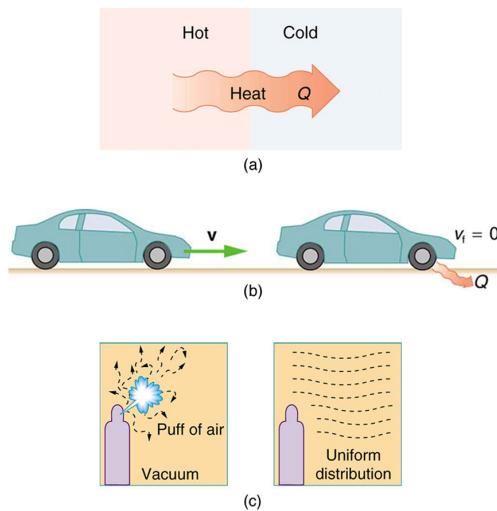
Introduction to the Second Law of Thermodynamics: Heat Engines and Their Efficiency

- State the expressions of the second law of thermodynamics.
- Calculate the efficiency and carbon dioxide emission of a coal-fired electricity plant, using second law characteristics.
- Describe and define the Otto cycle.



These ice floes melt during the Arctic summer. Some of them refreeze in the winter, but the second law of thermodynamics predicts that it would be extremely unlikely for the water molecules contained in these particular floes to reform the distinctive alligator-like shape they formed when the picture was taken in the summer of 2009. (credit: Patrick Kelley,

The second law of thermodynamics deals with the direction taken by **spontaneous processes**. Many processes occur spontaneously in one direction only—that is, they are irreversible, under a given set of conditions. Although irreversibility is seen in day-to-day life—a broken glass does not resume its original state, for instance—complete irreversibility is a statistical statement that cannot be seen during the lifetime of the universe. More precisely, an **irreversible process** is one that depends on path. If the process can go in only one direction, then the reverse path differs fundamentally and the process cannot be reversible. For example, as noted in the previous section, heat involves the transfer of energy from higher to lower temperature. A cold object in contact with a hot one never gets colder, transferring heat to the hot object and making it hotter. Furthermore, mechanical energy, such as kinetic energy, can be completely converted to thermal energy by friction, but the reverse is impossible. A hot stationary object never spontaneously cools off and starts moving. Yet another example is the expansion of a puff of gas introduced into one corner of a vacuum chamber. The gas expands to fill the chamber, but it never regroups in the corner. The random motion of the gas molecules could take them all back to the corner, but this is never observed to happen. (See [\[Figure 2\]](#).)



Examples of one-way processes in nature. (a) Heat transfer occurs spontaneously from hot to cold and not from cold to hot. (b) The brakes of this car convert its kinetic energy to heat transfer to the environment. The reverse process is impossible. (c) The burst of gas let into this vacuum chamber quickly expands to uniformly fill every part of the chamber.

The fact that certain processes never occur suggests that there is a law forbidding them to occur. The first law of thermodynamics would allow them to occur—none of those processes violate conservation of energy. The law that forbids these processes is called the second law of thermodynamics. We shall see that the second law can be stated in many ways that may seem different, but which in fact are equivalent. Like all natural laws, the second law of thermodynamics gives insights into nature, and its several statements imply that it is broadly applicable, fundamentally affecting many apparently disparate processes.

The already familiar direction of heat transfer from hot to cold is the basis of our first version of the **second law of thermodynamics**.

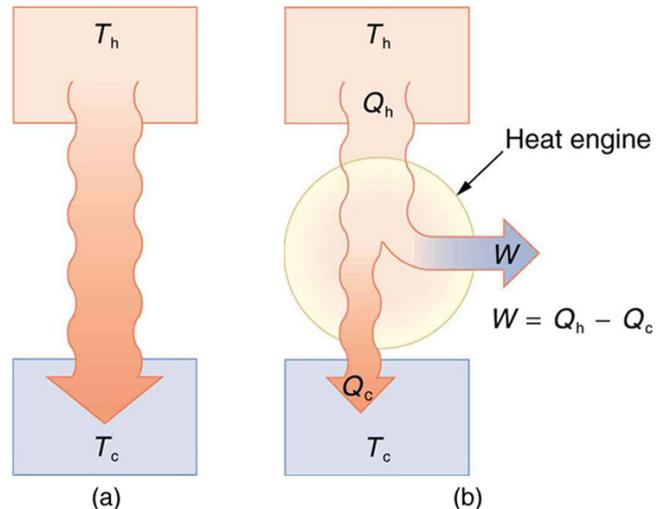
The Second Law of Thermodynamics (first expression)

Heat transfer occurs spontaneously from higher- to lower-temperature bodies but never spontaneously in the reverse direction.

Another way of stating this: It is impossible for any process to have as its sole result heat transfer from a cooler to a hotter object.

Heat Engines

Now let us consider a device that uses heat transfer to do work. As noted in the previous section, such a device is called a heat engine, and one is shown schematically in [Figure 3](b). Gasoline and diesel engines, jet engines, and steam turbines are all heat engines that do work by using part of the heat transfer from some source. Heat transfer from the hot object (or hot reservoir) is denoted as $Q_h Q_h$, while heat transfer into the cold object (or cold reservoir) is $Q_c Q_c$, and the work done by the engine is WW . The temperatures of the hot and cold reservoirs are $T_h T_h$ and $T_c T_c$, respectively.



(a) Heat transfer occurs spontaneously from a hot object to a cold one, consistent with the second law of thermodynamics. (b) A heat engine, represented here by a circle, uses part of the heat transfer to do work. The hot and cold objects are called the hot and cold reservoirs. (Q_h) is the heat transfer out of the hot reservoir, (W) is the work output, and (Q_c) is the heat transfer into the cold reservoir.

Because the hot reservoir is heated externally, which is energy intensive, it is important that the work is done as efficiently as possible. In fact, we would like WW to equal $Q_h Q_h$, and for there to be no heat transfer to the environment ($Q_c = 0 Q_c = 0$). Unfortunately, this is impossible. The **second law of thermodynamics** also states, with regard to using heat transfer to do work (the second expression of the second law):

The Second Law of Thermodynamics (second expression)

It is impossible in any system for heat transfer from a reservoir to completely convert to work in a cyclical process in which the system returns to its initial state.

A **cyclical process** brings a system, such as the gas in a cylinder, back to its original state at the end of every cycle. Most heat engines, such as reciprocating piston engines and rotating turbines, use cyclical processes. The second law, just stated in its second form, clearly states that such engines cannot have perfect conversion of heat transfer into work done. Before going into the underlying reasons for the limits on converting heat transfer into work, we need to explore the relationships among W , $Q_h Q_h$, and $Q_c Q_c$, and to define the efficiency of a cyclical heat engine. As noted, a cyclical process brings the system back to its original condition at the end of every cycle. Such a system's internal energy U is the same at the beginning and end of every cycle—that is, $\Delta U = 0 \Delta U = 0$. The first law of thermodynamics states that

$$\Delta U = Q - W, \\ \Delta U = Q - W,$$

where QQ is the *net* heat transfer during the cycle ($Q = Q_h - Q_c Q = Q_h - Q_c$) and WW is the net work done by the system. Since $\Delta U = 0 \Delta U = 0$ for a complete cycle, we have

$$0 = Q - W, \\ 0 = Q - W,$$

so that

$$W = Q. \\ W = Q.$$

Thus, the net work done by the system equals the net heat transfer into the system, or

$$W = Q_h - Q_c \text{ (cyclical process)}, \\ W = Q_h - Q_c \text{ (cyclical process)},$$

just as shown schematically in [Figure 3](b). The problem is that in all processes, there is some heat transfer $Q_c Q_c$ to the environment—and usually a very significant amount at that.

In the conversion of energy to work, we are always faced with the problem of getting less out than we put in. We define *conversion efficiency* Eff to be the ratio of useful work output to the energy input (or, in other words, the ratio of what we get to what we spend). In that spirit, we define the efficiency of a heat engine to be its net work output divided by heat transfer to the engine divided by heat transfer to the engine $\{Q\}_{\{h\}}$; that is,

$$Eff = \frac{W}{Q_h} \\ Eff = \frac{W}{Q_h}$$

Since $W = Q_h - Q_c W = Q_h - Q_c$ in a cyclical process, we can also express this as

$$Eff = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h} \text{ (cyclical process)},$$

making it clear that an efficiency of 1, or 100%, is possible only if there is no heat transfer to the environment ($Q_c = 0 Q_c = 0$). Note that all QQ s are positive. The direction of heat transfer is indicated by a plus or minus sign. For example, $Q_c Q_c$ is out of the system and so is preceded by a minus sign.

Daily Work Done by a Coal-Fired Power Station, Its Efficiency and Carbon Dioxide Emissions

A coal-fired power station is a huge heat engine. It uses heat transfer from burning coal to do work to turn turbines, which are used to generate electricity. In a single day, a large coal power station has 2.50×10^{14} J to 2.50×10^{14} J of heat transfer from coal and 1.48×10^{14} J to 1.48×10^{14} J of heat transfer into the environment. (a) What is the work done by the power station? (b) What is the efficiency of the power station? (c) In the combustion process, the following chemical reaction occurs: $C + O_2 \rightarrow CO_2$ $C + O_2 \rightarrow CO_2$. This implies that every 12 kg of coal puts 12 kg + 16 kg + 16 kg = 44 kg of carbon dioxide into the atmosphere. Assuming that 1 kg of coal can provide 2.5×10^6 J to 2.5×10^6 J of heat transfer upon combustion, how much CO_2 is emitted per day by this power plant?

Strategy for (a)

We can use $W = Q_h - Q_c$ to find the work output WW , assuming a cyclical process is used in the power station. In this process, water is boiled under pressure to form high-temperature steam, which is used to run steam turbine-generators, and then condensed back to water to start the cycle again.

Solution for (a)

Work output is given by:

$$W = Q_h - Q_c$$

Substituting the given values:

$$\begin{aligned} W &= 2.50 \times 10^{14}J - 1.48 \times 10^{14}J = 1.02 \times 10^{14}J \\ W &= 2.50 \times 10^{14}J - 1.48 \times 10^{14}J \\ &= 1.02 \times 10^{14}J. \end{aligned}$$

Strategy for (b)

The efficiency can be calculated with $Eff = \frac{W}{Q_h}$ since Q_h is given and work WW was found in the first part of this example.

Solution for (b)

Efficiency is given by: $Eff = \frac{W}{Q_h}$. The work WW was just found to be 1.02×10^{14} J to 1.02×10^{14} J, and Q_h is given, so the efficiency is

$$\begin{aligned} Eff &= \frac{1.02 \times 10^{14}J}{2.50 \times 10^{14}J} = 0.408, \text{ or } 40.8\% \\ Eff &= \frac{1.02 \times 10^{14}J}{2.50 \times 10^{14}J} \\ &= 0.408, \text{ or } 40.8\% \end{aligned}$$

Strategy for (c)

The daily consumption of coal is calculated using the information that each day there is 2.50×10^{14} J to 2.50×10^{14} J of heat transfer from coal. In the combustion process, we have $C + O_2 \rightarrow CO_2$ $C + O_2 \rightarrow CO_2$. So every 12 kg of coal puts 12 kg + 16 kg + 16 kg = 44 kg of CO_2 into the atmosphere.

Solution for (c)

The daily coal consumption is

$$\begin{aligned} 2.50 \times 10^{14}J &2.50 \times 10^{14}J/kg = 1.0 \times 10^8 \text{kg} \\ \frac{2.50 \times 10^{14}J}{2.50 \times 10^6 \text{J/kg}} &= 1.0 \times 10^8 \text{kg}. \end{aligned}$$

Assuming that the coal is pure and that all the coal goes toward producing carbon dioxide, the carbon dioxide produced per day is

$$\begin{aligned} 1.0 \times 10^8 \text{kg coal} &\times 44 \text{kg } CO_2/12 \text{kg coal} = 3.7 \times 10^8 \text{kg } CO_2 \\ 1.0 \times 10^8 \text{kg coal} &\times \frac{44 \text{kg } CO_2}{12 \text{kg coal}} = 3.7 \times 10^8 \text{kg } CO_2. \end{aligned}$$

This is 370 000 metric tons of CO_2 produced every day.

Discussion

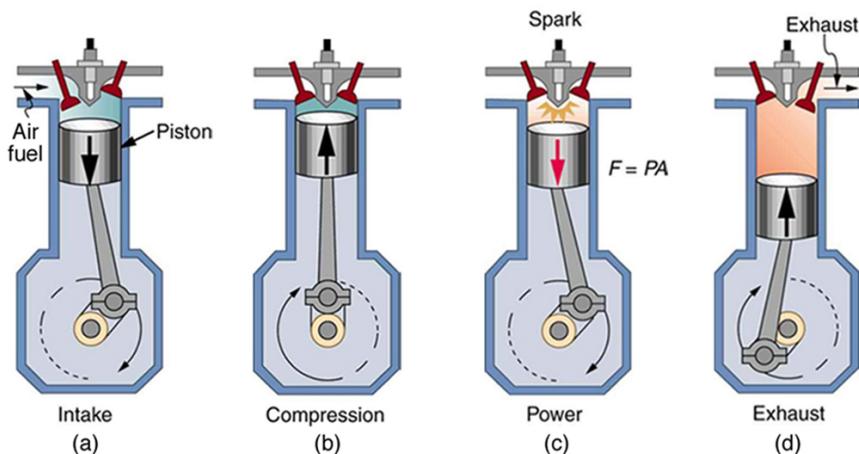
If all the work output is converted to electricity in a period of one day, the average power output is 1180 MW (this is left to you as an end-of-chapter problem). This value is about the size of a large-scale conventional power plant. The efficiency found is acceptably close to the value of 42% given for coal power stations. It means that fully 59.2% of the energy is heat transfer to the environment, which usually results in warming lakes, rivers, or the ocean near the power station, and is implicated in a warming planet generally. While the laws of thermodynamics limit the efficiency of such plants—including plants fired by nuclear fuel, oil, and natural gas—the heat transfer to the environment could be, and sometimes is, used for heating homes or for industrial processes. The generally low cost of energy has not made it economical to make better use of the waste heat transfer from most heat engines. Coal-fired power plants produce the greatest amount of CO_2 per unit energy output (compared to natural gas or oil), making coal the least efficient fossil fuel.

With the information given in [Example 1], we can find characteristics such as the efficiency of a heat engine without any knowledge of how the heat engine operates, but looking further into the mechanism of the engine will give us greater insight. [Figure 4] illustrates the operation of the common four-stroke gasoline engine. The four steps shown complete this heat engine's cycle, bringing the gasoline-air mixture back to its original condition.

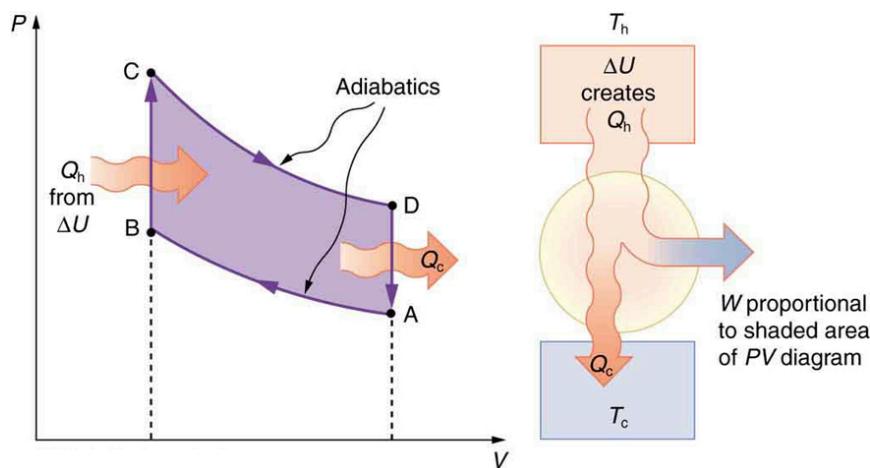
The **Otto cycle** shown in [Figure 5](a) is used in four-stroke internal combustion engines, although in fact the true Otto cycle paths do not correspond exactly to the strokes of the engine.

The adiabatic process AB corresponds to the nearly adiabatic compression stroke of the gasoline engine. In both cases, work is done on the system (the gas mixture in the cylinder), increasing its temperature and pressure. Along path BC of the Otto cycle, heat transfer $Q_{\text{h}}Q_{\text{h}}$ into the gas occurs at constant volume, causing a further increase in pressure and temperature. This process corresponds to burning fuel in an internal combustion engine, and takes place so rapidly that the volume is nearly constant. Path CD in the Otto cycle is an adiabatic expansion that does work on the outside world, just as the power stroke of an internal combustion engine does in its nearly adiabatic expansion. The work done by the system along path CD is greater than the work done on the system along path AB, because the pressure is greater, and so there is a net work output. Along path DA in the Otto cycle, heat transfer $Q_{\text{c}}Q_{\text{c}}$ from the gas at constant volume reduces its temperature and pressure, returning it to its original state. In an internal combustion engine, this process corresponds to the exhaust of hot gases and the intake of an air-gasoline mixture at a considerably lower temperature. In both cases, heat transfer into the environment occurs along this final path.

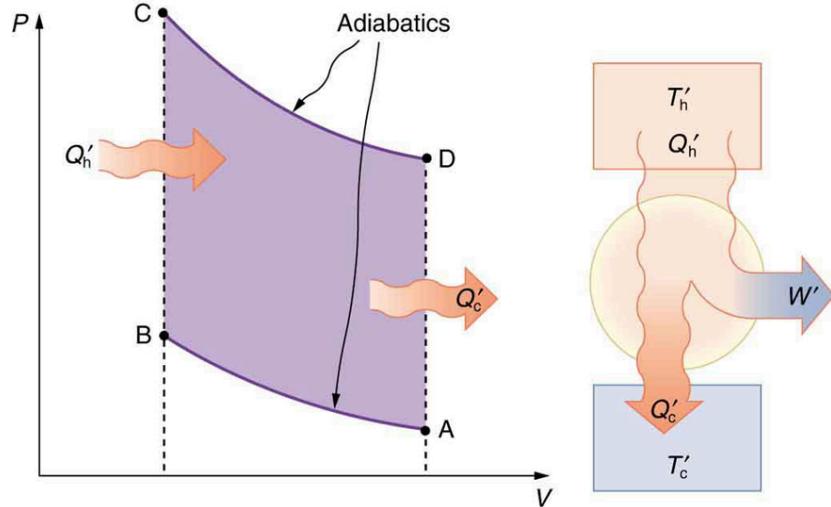
The net work done by a cyclical process is the area inside the closed path on a PV diagram, such as that inside path ABCDA in [Figure 5]. Note that in every imaginable cyclical process, it is absolutely necessary for heat transfer from the system to occur in order to get a net work output. In the Otto cycle, heat transfer occurs along path DA. If no heat transfer occurs, then the return path is the same, and the net work output is zero. The lower the temperature on the path AB, the less work has to be done to compress the gas. The area inside the closed path is then greater, and so the engine does more work and is thus more efficient. Similarly, the higher the temperature along path CD, the more work output there is. (See [Figure 6].) So efficiency is related to the temperatures of the hot and cold reservoirs. In the next section, we shall see what the absolute limit to the efficiency of a heat engine is, and how it is related to temperature.



In the four-stroke internal combustion gasoline engine, heat transfer into work takes place in the cyclical process shown here. The piston is connected to a rotating crankshaft, which both takes work out of and does work on the gas in the cylinder. (a) Air is mixed with fuel during the intake stroke. (b) During the compression stroke, the air-fuel mixture is rapidly compressed in a nearly adiabatic process, as the piston rises with the valves closed. Work is done on the gas. (c) The power stroke has two distinct parts. First, the air-fuel mixture is ignited, converting chemical potential energy into thermal energy almost instantaneously, which leads to a great increase in pressure. Then the piston descends, and the gas does work by exerting a force through a distance in a nearly adiabatic process. (d) The exhaust stroke expels the hot gas to prepare the engine for another cycle, starting again with the intake stroke.



(P-V) diagram for a simplified Otto cycle, analogous to that employed in an internal combustion engine. Point A corresponds to the start of the compression stroke of an internal combustion engine. Paths AB and CD are adiabatic and correspond to the compression and power strokes of an internal combustion engine, respectively. Paths BC and DA are isochoric and accomplish similar results to the ignition and exhaust-intake portions, respectively, of the internal combustion engine's cycle. Work is done on the gas along path AB, but more work is done by the gas along path CD, so



This Otto cycle produces a greater work output than the one in [Figure 5](#Figure5), because the starting temperature of path CD is higher and the starting temperature of path AB is lower. The area inside the loop is greater, corresponding to greater net work output.

Section Summary

- The two expressions of the second law of thermodynamics are: (i) Heat transfer occurs spontaneously from higher- to lower-temperature bodies but never spontaneously in the reverse direction; and (ii) It is impossible in any system for heat transfer from a reservoir to completely convert to work in a cyclical process in which the system returns to its initial state.
- Irreversible processes depend on path and do not return to their original state. Cyclical processes are processes that return to their original state at the end of every cycle.
- In a cyclical process, such as a heat engine, the net work done by the system equals the net heat transfer into the system, or $W = Q_h - Q_c$, where Q_h is the heat transfer from the hot object (hot reservoir), and Q_c is the heat transfer into the cold object (cold reservoir).
- Efficiency can be expressed as $\text{Eff} = W/Q_h$, the ratio of work output divided by the amount of energy input.
- The four-stroke gasoline engine is often explained in terms of the Otto cycle, which is a repeating sequence of processes that convert heat into work.

Conceptual Questions

Imagine you are driving a car up Pike's Peak in Colorado. To raise a car weighing 1000 kilograms a distance of 100 meters would require about a million joules. You could raise a car 12.5 kilometers with the energy in a gallon of gas. Driving up Pike's Peak (a mere 3000-meter climb) should consume a little less than a quart of gas. But other considerations have to be taken into account. Explain, in terms of efficiency, what factors may keep you from realizing your ideal energy use on this trip.

Is a temperature difference necessary to operate a heat engine? State why or why not.

Definitions of efficiency vary depending on how energy is being converted. Compare the definitions of efficiency for the human body and heat engines. How does the definition of efficiency in each relate to the type of energy being converted into doing work?

Why—other than the fact that the second law of thermodynamics says reversible engines are the most efficient—should heat engines employing reversible processes be more efficient than those employing irreversible processes? Consider that dissipative mechanisms are one cause of irreversibility.

Problem Exercises

A certain heat engine does 10.0 kJ of work and 8.50 kJ of heat transfer occurs to the environment in a cyclical process. (a) What was the heat transfer into this engine? (b) What was the engine's efficiency?

With 2.56×10^6 J of heat transfer into this engine, a given cyclical heat engine can do only 1.50×10^5 J of work. (a) What is the engine's efficiency? (b) How much heat transfer to the environment takes place?

(a) What is the work output of a cyclical heat engine having a 22.0% efficiency and 6.00×10^9 J of heat transfer into the engine? (b) How much heat transfer occurs to the environment?

- (a) What is the efficiency of a cyclical heat engine in which 75.0 kJ of heat transfer occurs to the environment for every 95.0 kJ of heat transfer into the engine?
 (b) How much work does it produce for 100 kJ of heat transfer into the engine?

The engine of a large ship does 2.00×10^8 J of work with an efficiency of 5.00%. (a) How much heat transfer occurs to the environment? (b) How many barrels of fuel are consumed, if each barrel produces 6.00×10^9 J of heat transfer when burned?

- (a) How much heat transfer occurs to the environment by an electrical power station that uses 1.25×10^{14} J of heat transfer into the engine with an efficiency of 42.0%? (b) What is the ratio of heat transfer to the environment to work output? (c) How much work is done?

Assume that the turbines at a coal-powered power plant were upgraded, resulting in an improvement in efficiency of 3.32%. Assume that prior to the upgrade the power station had an efficiency of 36% and that the heat transfer into the engine in one day is still the same at 2.50×10^{14} J. (a) How much more electrical energy is produced due to the upgrade? (b) How much less heat transfer occurs to the environment due to the upgrade?

This problem compares the energy output and heat transfer to the environment by two different types of nuclear power stations—one with the normal efficiency of 34.0%, and another with an improved efficiency of 40.0%. Suppose both have the same heat transfer into the engine in one day, 2.50×10^{14} J. (a) How much more electrical energy is produced by the more efficient power station? (b) How much less heat transfer occurs to the environment by the more efficient power station? (One type of more efficient nuclear power station, the gas-cooled reactor, has not been reliable enough to be economically feasible in spite of its greater efficiency.)

Glossary

irreversible process

any process that depends on path direction

second law of thermodynamics

heat transfer flows from a hotter to a cooler object, never the reverse, and some heat energy in any process is lost to available work in a cyclical process

cyclical process

a process in which the path returns to its original state at the end of every cycle

Otto cycle

a thermodynamic cycle, consisting of a pair of adiabatic processes and a pair of isochoric processes, that converts heat into work, e.g., the four-stroke engine cycle of intake, compression, ignition, and exhaust



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□

Carnot's Perfect Heat Engine: The Second Law of Thermodynamics Restated

- Identify a Carnot cycle.
- Calculate maximum theoretical efficiency of a nuclear reactor.
- Explain how dissipative processes affect the ideal Carnot engine.



This novelty toy, known as the drinking bird, is an example of Carnot's engine. It contains methylene chloride (mixed with a dye) in the abdomen, which boils at a very low temperature—about (100 °F). To operate, one gets the bird's head wet. As the water evaporates, fluid moves up into the head, causing the bird to become top-heavy and dip forward back into the water. This cools down the methylene chloride in the head, and it moves back into the abdomen, causing the bird to become bottom heavy and tip up. Except for a very small input of energy—the original head-wetting—the bird becomes a perpetual motion machine of sorts. (credit: Arabesk.nl, Wikimedia Commons)

We know from the second law of thermodynamics that a heat engine cannot be 100% efficient, since there must always be some heat transfer $Q_c Q_e$ to the environment, which is often called waste heat. How efficient, then, can a heat engine be? This question was answered at a theoretical level in 1824 by a young French engineer, Sadi Carnot (1796–1832), in his study of the then-emerging heat engine technology crucial to the Industrial Revolution. He devised a theoretical cycle, now called the **Carnot cycle**, which is the most efficient cyclical process possible. The second law of thermodynamics can be restated in terms of the Carnot cycle, and so what Carnot actually discovered was this fundamental law. Any heat engine employing the Carnot cycle is called a **Carnot engine**.

What is crucial to the Carnot cycle—and, in fact, defines it—is that only reversible processes are used. Irreversible processes involve dissipative factors, such as friction and turbulence. This increases heat transfer $Q_c Q_e$ to the environment and reduces the efficiency of the engine. Obviously, then, reversible processes are superior.

Carnot Engine

Stated in terms of reversible processes, the **second law of thermodynamics** has a third form:

A Carnot engine operating between two given temperatures has the greatest possible efficiency of any heat engine operating between these two temperatures. Furthermore, all engines employing only reversible processes have this same maximum efficiency when operating between the same given temperatures.

[Figure 2] shows the PV diagram for a Carnot cycle. The cycle comprises two isothermal and two adiabatic processes. Recall that both isothermal and adiabatic processes are, in principle, reversible.

Carnot also determined the efficiency of a perfect heat engine—that is, a Carnot engine. It is always true that the efficiency of a cyclical heat engine is given by:

$$\text{Eff} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

$$\text{Eff} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}$$

What Carnot found was that for a perfect heat engine, the ratio $Q_c/Q_h Q_e / Q_h$ equals the ratio of the absolute temperatures of the heat reservoirs. That is, $Q_c/Q_h = T_c/T_h$ $Q_e / Q_h = T_e / T_h$ for a Carnot engine, so that the maximum or ** Carnot efficiency** Eff_{C} is given by

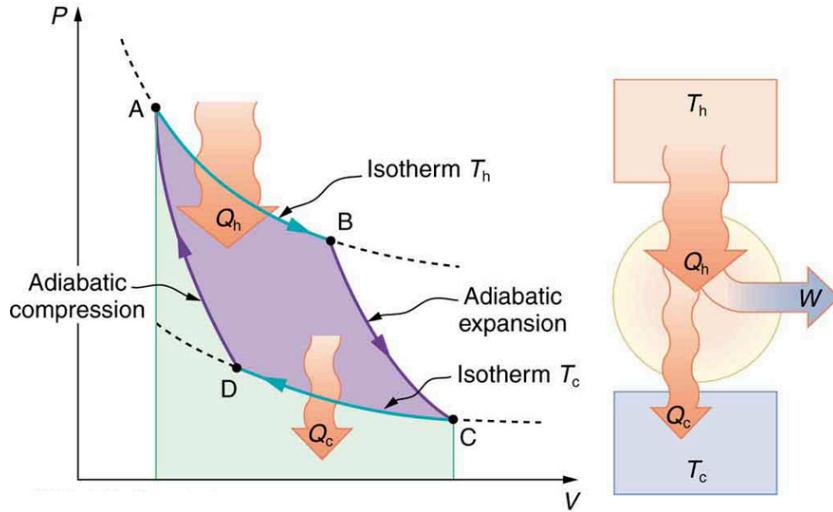
$$\text{EffC} = 1 - \frac{T_c}{T_h}$$

$$\text{Eff}_C = 1 - \frac{T_c}{T_h}$$

where $T_h T_h$ and $T_c T_c$ are in kelvins (or any other absolute temperature scale). No real heat engine can do as well as the Carnot efficiency. But the ideal Carnot engine, like the drinking bird above, while a fascinating novelty, has zero power. This makes it unrealistic for any applications.

Carnot's interesting result implies that 100% efficiency would be possible only if $T_c = 0K$ —that is, only if the cold reservoir were at absolute zero, a practical and theoretical impossibility. But the physical implication is this—the only way to have all heat transfer go into doing work is to remove *all* thermal energy, and this requires a cold reservoir at absolute zero.

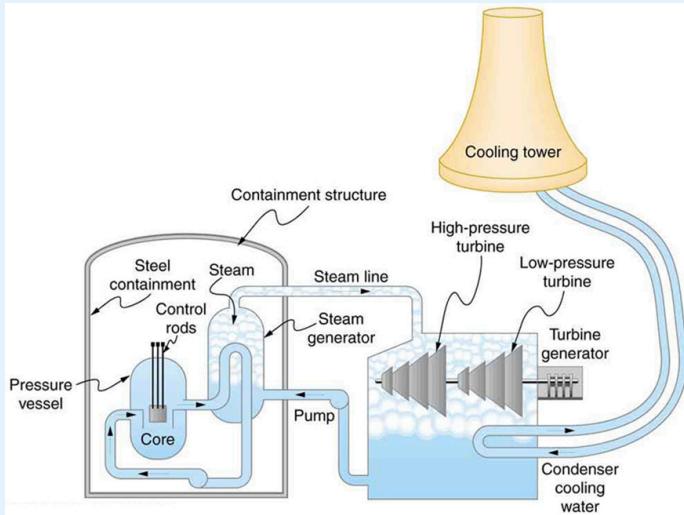
It is also apparent that the greatest efficiencies are obtained when the ratio $T_c/T_h T_c / T_h$ is as small as possible. Just as discussed for the Otto cycle in the previous section, this means that efficiency is greatest for the highest possible temperature of the hot reservoir and lowest possible temperature of the cold reservoir. (This setup increases the area inside the closed loop on the PV diagram; also, it seems reasonable that the greater the temperature difference, the easier it is to divert the heat transfer to work.) The actual reservoir temperatures of a heat engine are usually related to the type of heat source and the temperature of the environment into which heat transfer occurs. Consider the following example.



(PV) diagram for a Carnot cycle, employing only reversible isothermal and adiabatic processes. Heat transfer ($Q_{(h)}$) occurs into the working substance during the isothermal path AB , which takes place at constant temperature ($T_{(h)}$). Heat transfer ($Q_{(c)}$) occurs out of the working substance during the isothermal path CD , which takes place at constant temperature ($T_{(c)}$). The net work output (W) equals the area inside the path $ABCDA$. Also shown is a schematic of a Carnot engine operating between hot and cold reservoirs at temperatures ($T_{(h)}$) and ($T_{(c)}$). Any heat engine using reversible processes and operating between these two temperatures will have the same maximum efficiency as the Carnot engine.

Maximum Theoretical Efficiency for a Nuclear Reactor

A nuclear power reactor has pressurized water at 300°C/300°C. (Higher temperatures are theoretically possible but practically not, due to limitations with materials used in the reactor.) Heat transfer from this water is a complex process (see [Figure 3]). Steam, produced in the steam generator, is used to drive the turbine-generators. Eventually the steam is condensed to water at 27°C/27°C and then heated again to start the cycle over. Calculate the maximum theoretical efficiency for a heat engine operating between these two temperatures.



Schematic diagram of a pressurized water nuclear reactor and the steam turbines that convert work into electrical energy. Heat exchange is used to generate steam, in part to avoid contamination of the generators with radioactivity.

Strategy
 Two turbines are used because this is less expensive than operating a single generator that produces the same amount of electrical energy. The steam is condensed to liquid before being returned to the heat exchanger, to keep exit steam pressure low and aid the flow of steam through the turbines (equivalent to using a lower-temperature cold reservoir). The considerable energy associated with condensation must be dissipated into the environment, in the Carnot (maximum theoretical) efficiency. Those temperatures must first be converted to kelvins. Direct heat transfer to an aquatic environment. (Note that the water going to the cooling tower does not come into contact with the steam flowing over the turbines.)

Solution

The hot and cold reservoir temperatures are given as 300°C/300°C and 27.0°C/27.0°C, respectively. In kelvins, then, $T_h = 573K$, $T_c = 300K$, and $T_c = 273K$, so that the maximum efficiency is

$$\text{Eff}_C = 1 - \frac{T_c}{T_h}$$

Thus,

$$\begin{aligned} \text{Eff}_C &= 1 - \frac{300K}{573K} = 0.476, \text{ or } 47.6\% \\ \text{Eff}_C &= 1 - \frac{273K}{573K} \\ &= 0.476, \text{ or } 47.6\% \end{aligned}$$

Discussion

A typical nuclear power station's actual efficiency is about 35%, a little better than 0.7 times the maximum possible value, a tribute to superior engineering. Electrical power stations fired by coal, oil, and natural gas have greater actual efficiencies (about 42%), because their boilers can reach higher temperatures and pressures. The cold reservoir temperature in any of these power stations is limited by the local environment. [Figure 4] shows (a) the exterior of a nuclear power station and (b) the exterior of a coal-fired power station. Both have cooling towers into which water from the condenser enters the tower near the top and is sprayed downward, cooled by evaporation.



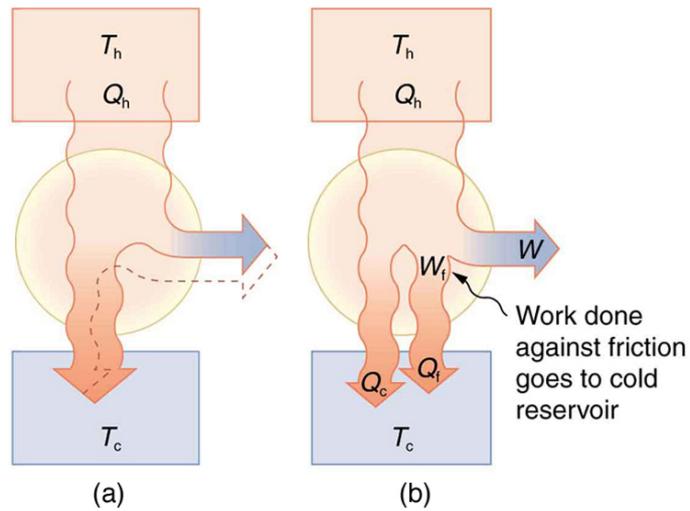
(a)



(b)

(a) A nuclear power station (credit: BlatantWorld.com) and (b) a coal-fired power station. Both have cooling towers in which water evaporates into the environment, representing ($Q_{\{c\}}$). The nuclear reactor, which supplies ($Q_{\{h\}}$), is housed inside the dome-shaped containment buildings. (credit: Robert & Mihaela Vicol, publicphoto.org)

Since all real processes are irreversible, the actual efficiency of a heat engine can never be as great as that of a Carnot engine, as illustrated in [Figure 5](a). Even with the best heat engine possible, there are always dissipative processes in peripheral equipment, such as electrical transformers or car transmissions. These further reduce the overall efficiency by converting some of the engine's work output back into heat transfer, as shown in [Figure 5](b).



Real heat engines are less efficient than Carnot engines. (a) Real engines use irreversible processes, reducing the heat transfer to work. Solid lines represent the actual process; the dashed lines are what a Carnot engine would do between the same two reservoirs. (b) Friction and other dissipative processes in the output mechanisms of a heat engine convert some of its work output into heat transfer to the environment.

Section Summary

- The Carnot cycle is a theoretical cycle that is the most efficient cyclical process possible. Any engine using the Carnot cycle, which uses only reversible processes (adiabatic and isothermal), is known as a Carnot engine.
- Any engine that uses the Carnot cycle enjoys the maximum theoretical efficiency.
- While Carnot engines are ideal engines, in reality, no engine achieves Carnot's theoretical maximum efficiency, since dissipative processes, such as friction, play a role. Carnot cycles without heat loss may be possible at absolute zero, but this has never been seen in nature.

Conceptual Questions

Think about the drinking bird at the beginning of this section ([Figure 1]). Although the bird enjoys the theoretical maximum efficiency possible, if left to its own devices over time, the bird will cease "drinking." What are some of the dissipative processes that might cause the bird's motion to cease?

Can improved engineering and materials be employed in heat engines to reduce heat transfer into the environment? Can they eliminate heat transfer into the environment entirely?

Does the second law of thermodynamics alter the conservation of energy principle?

Problem Exercises

A certain gasoline engine has an efficiency of 30.0%. What would the hot reservoir temperature be for a Carnot engine having that efficiency, if it operates with a cold reservoir temperature of 200°C ?

A gas-cooled nuclear reactor operates between hot and cold reservoir temperatures of 700°C and 27.0°C . (a) What is the maximum efficiency of a heat engine operating between these temperatures? (b) Find the ratio of this efficiency to the Carnot efficiency of a standard nuclear reactor (found in [Example 1](#)).

(a) What is the hot reservoir temperature of a Carnot engine that has an efficiency of 42.0% and a cold reservoir temperature of 27.0°C ? (b) What must the hot reservoir temperature be for a real heat engine that achieves 0.700 of the maximum efficiency, but still has an efficiency of 42.0% (and a cold reservoir at 27.0°C)? (c) Does your answer imply practical limits to the efficiency of car gasoline engines?

Steam locomotives have an efficiency of 17.0% and operate with a hot steam temperature of 425°C . (a) What would the cold reservoir temperature be if this were a Carnot engine? (b) What would the maximum efficiency of this steam engine be if its cold reservoir temperature were 150°C ?

Practical steam engines utilize 450°C steam, which is later exhausted at 270°C . (a) What is the maximum efficiency that such a heat engine can have? (b) Since 270°C steam is still quite hot, a second steam engine is sometimes operated using the exhaust of the first. What is the maximum efficiency of the second engine if its exhaust has a temperature of 150°C ? (c) What is the overall efficiency of the two engines? (d) Show that this is the same efficiency as a single Carnot engine operating between 450°C and 150°C . Explicitly show how you follow the steps in the [Problem-Solving Strategies for Thermodynamics](#).

A coal-fired electrical power station has an efficiency of 38%. The temperature of the steam leaving the boiler is 550°C. What percentage of the maximum efficiency does this station obtain? (Assume the temperature of the environment is 20°C.)

Would you be willing to financially back an inventor who is marketing a device that she claims has 25 kJ of heat transfer at 600 K, has heat transfer to the environment at 300 K, and does 12 kJ of work? Explain your answer.

Unreasonable Results

(a) Suppose you want to design a steam engine that has heat transfer to the environment at 270°C and has a Carnot efficiency of 0.800. What temperature of hot steam must you use? (b) What is unreasonable about the temperature? (c) Which premise is unreasonable?

Unreasonable Results

Calculate the cold reservoir temperature of a steam engine that uses hot steam at 450°C and has a Carnot efficiency of 0.700. (b) What is unreasonable about the temperature? (c) Which premise is unreasonable?

Glossary

Carnot cycle

a cyclical process that uses only reversible processes, the adiabatic and isothermal processes

Carnot engine

a heat engine that uses a Carnot cycle

Carnot efficiency

the maximum theoretical efficiency for a heat engine



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Applications of Thermodynamics: Heat Pumps and Refrigerators

- Describe the use of heat engines in heat pumps and refrigerators.
- Demonstrate how a heat pump works to warm an interior space.
- Explain the differences between heat pumps and refrigerators.
- Calculate a heat pump's coefficient of performance.



Almost every home contains a refrigerator. Most people don't realize they are also sharing their homes with a heat pump.

(credit: Id1337x, Wikimedia Commons)

Heat pumps, air conditioners, and refrigerators utilize heat transfer from cold to hot. They are heat engines run backward. We say backward, rather than reverse, because except for Carnot engines, all heat engines, though they can be run backward, cannot truly be reversed. Heat transfer occurs from a cold reservoir Q_c and into a hot one. This requires work input W

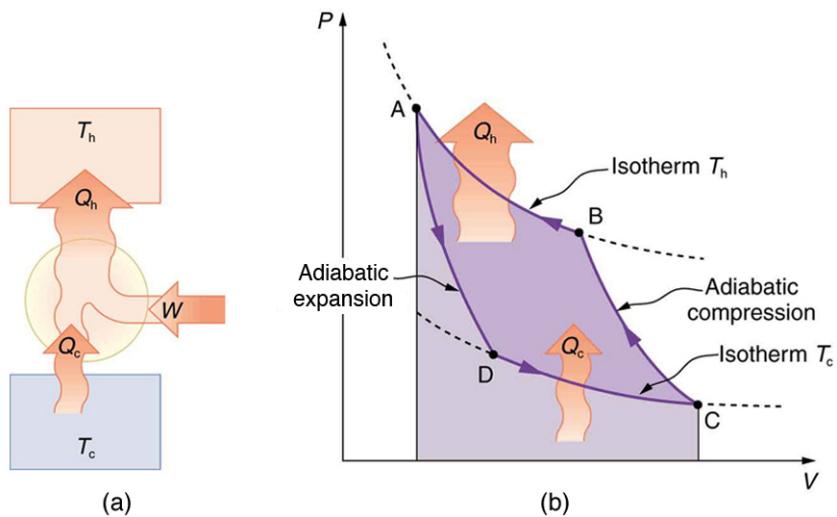
, which is also converted to heat transfer. Thus the heat transfer to the hot reservoir is, which is also converted to heat transfer. Thus the heat transfer to the hot reservoir is $Q_h = (Q_c + W)$. (Note that Q_h is positive, and W

are positive, with their directions indicated on schematics rather than by sign.) A heat pump's mission is for heat transfer

are positive, with their directions indicated on schematics rather than by sign. A heat pump's mission is for heat transfer Q_h

to occur into a warm environment, such as a home in the winter. The mission of air conditioners and refrigerators is for heat transfer

to occur into a warm environment, such as a home in the winter. The mission of air conditioners and refrigerators is for heat transfer Q_c to occur from a cool environment, such as chilling a room or keeping food at lower temperatures than the environment. (Actually, a heat pump can be used both to heat and cool a space. It is essentially an air conditioner and a heating unit all in one. In this section we will concentrate on its heating mode.)

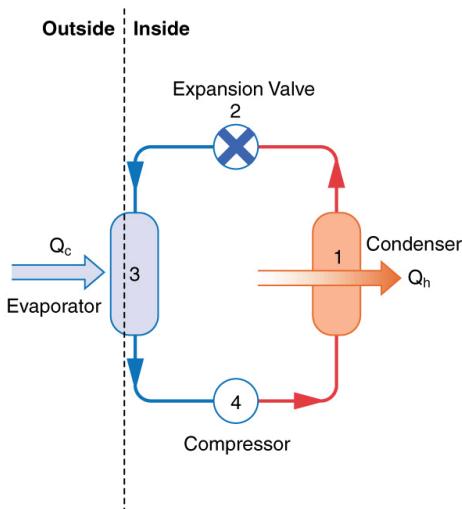


Heat pumps, air conditioners, and refrigerators are heat engines operated backward. The one shown here is based on a Carnot (reversible) engine. (a) Schematic diagram showing heat transfer from a cold reservoir to a warm reservoir with a heat pump. The directions of WW , Q_hQ_h , and Q_cQ_c are opposite what they would be in a heat engine. (b) PV diagram for a Carnot cycle similar to that in [Figure 3](#Figure3) but reversed, following path ADCBA. The area inside the loop is negative, meaning there is a net work input. There is heat transfer Q_cQ_c into the system from a cold reservoir along

Heat Pumps

The great advantage of using a heat pump to keep your home warm, rather than just burning fuel, is that a heat pump supplies $Q_h = Q_c + WQ_h = Q_c + W$. Heat transfer is from the outside air, even at a temperature below freezing, to the indoor space. You only pay for WW , and you get an additional heat transfer of Q_cQ_c from the outside at no cost; in many cases, at least twice as much energy is transferred to the heated space as is used to run the heat pump. When you burn fuel to keep warm, you pay for all of it. The disadvantage is that the work input (required by the second law of thermodynamics) is sometimes more expensive than simply burning fuel, especially if the work is done by electrical energy.

The basic components of a heat pump in its heating mode are shown in [Figure 3]. A working fluid such as a non-CFC refrigerant is used. In the outdoor coils (the evaporator), heat transfer Q_cQ_c occurs to the working fluid from the cold outdoor air, turning it into a gas. In the indoor coils (the condenser), heat transfer Q_hQ_h occurs from the working fluid to the heated space, turning it back into a liquid.



A simple heat pump has four basic components: (1) condenser, (2) expansion valve, (3) evaporator, and (4) compressor. In the heating mode, heat transfer Q_cQ_c occurs to the working fluid in the evaporator (3) from the colder outdoor air, turning it into a gas. The electrically driven compressor (4) increases the temperature and pressure of the gas and forces it into the condenser coils that are inside the heated space.

The electrically driven compressor (4) increases the temperature and pressure of the gas and forces it into the condenser coils that are inside the heated space. Because the temperature of the gas is higher than the temperature inside the room, heat transfer in the room occurs and the gas condenses to a liquid. The liquid then flows back through a pressure-reducing valve (the outdoor expansion valve, labeled (2) in the diagram) to the evaporator (3). (In the cooling cycle, the evaporator and condenser coils exchange roles and the flow direction of the fluid is reversed.)

The quality of a heat pump is judged by how much heat transfer Q_hQ_h occurs into the warm space compared with how much work input WW is required. In the spirit of taking the ratio of what you get to what you spend, we define a **heat pump's coefficient of performance** (COP_{hp}) to be

$$\text{COP}_{\text{hp}} = \frac{Q_h}{W}$$

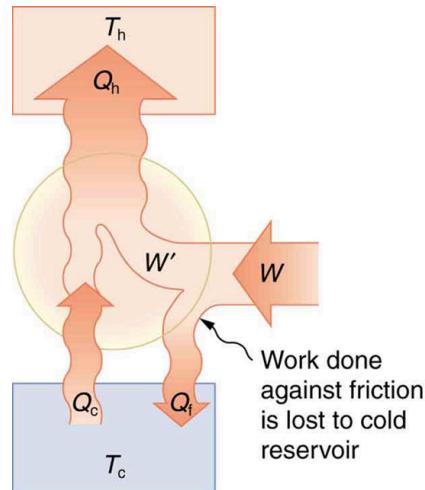
$$\text{COP}_{\text{hp}} = \frac{Q_h}{W}.$$

Since the efficiency of a heat engine is $\text{Eff} = W/Q_h$, we see that $\text{COP}_{\text{hp}} = 1/\text{Eff}$, an important and interesting fact. First, since the efficiency of any heat engine is less than 1, it means that $\text{COP}_{\text{hp}}/\text{COP}_{\text{hp}}$ is always greater than 1—that is, a heat pump always has more heat transfer Q_h/Q_c than work put into it.

Second, it means that heat pumps work best when temperature differences are small. The efficiency of a perfect, or Carnot, engine is $\text{Eff}_C = 1 - (T_c/T_h)$.

$\text{Eff}_C = 1 - (T_c/T_h)$; thus, the smaller the temperature difference, the smaller the efficiency and the greater the $\text{COP}_{\text{hp}}/\text{COP}_{\text{hp}}$ ** (because $\text{COP}_{\text{hp}} = 1/\text{Eff}$, $\text{COP}_{\text{hp}} = 1/\text{Eff}$). In other words, heat pumps do not work as well in very cold climates as they do in more moderate climates.

Friction and other irreversible processes reduce heat engine efficiency, but they do **not** benefit the operation of a heat pump—instead, they reduce the work input by converting part of it to heat transfer back into the cold reservoir before it gets into the heat pump.



When a real heat engine is run backward, some of the intended work input WW goes into heat transfer before it gets into the heat engine, thereby reducing its coefficient of performance $\text{COP}_{\text{hp}}/\text{COP}_{\text{hp}}$. In this figure, $W'W'$ represents the portion of WW that goes into the heat pump, while the remainder of WW is lost in the form of frictional heat Q_f to the cold reservoir. If all of WW had gone into the heat pump, then Q_h/Q_c would have been greater. The best heat pump uses adiabatic and isothermal processes, since, in theory, there would be no dissipative processes to reduce the heat transfer to the hot reservoir.

The Best COP_{hp} of a Heat Pump for Home Use

A heat pump used to warm a home must employ a cycle that produces a working fluid at temperatures greater than typical indoor temperature so that heat transfer to the inside can take place. Similarly, it must produce a working fluid at temperatures that are colder than the outdoor temperature so that heat transfer occurs from outside. Its hot and cold reservoir temperatures therefore cannot be too close, placing a limit on its COP_{hp}. (See [Figure 2].) What is the best coefficient of performance possible for such a heat pump, if it has a hot reservoir temperature of 45.0°C/45.0°C and a cold reservoir temperature of -15.0°C/-15.0°C?

Strategy

A Carnot engine reversed will give the best possible performance as a heat pump. As noted above, $COP_{hp} = 1/EffCOP_{hp} = 1 / Eff$, so that we need to first calculate the Carnot efficiency to solve this problem.

Solution

Carnot efficiency in terms of absolute temperature is given by :

$$Eff_C = 1 - \frac{T_c}{T_h}$$

The temperatures in kelvins are $T_h = 318K$, $T_c = 258K$, so that

$$Eff_C = 1 - \frac{258K}{318K} = 0.1887.$$

Thus, from the discussion above,

$$COP_{hp} = \frac{1}{Eff} = \frac{1}{0.1887} = 5.30,$$

or

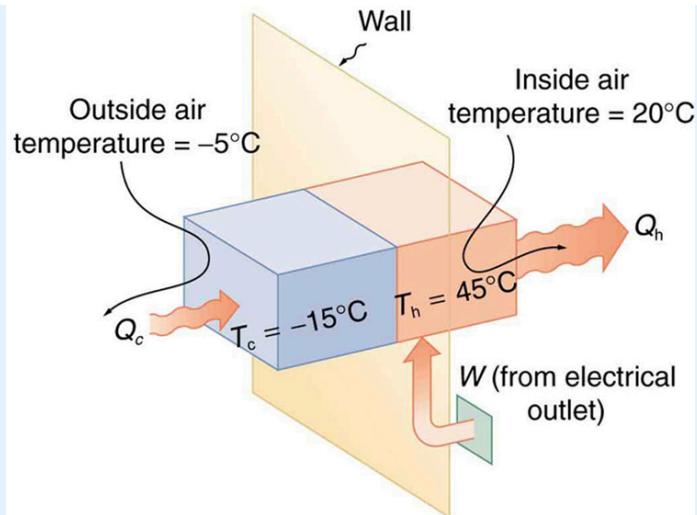
$$COP_{hp} = \frac{Q_h}{W} = 5.30,$$

so that

$$Q_h = 5.30W.$$

Discussion

This result means that the heat transfer by the heat pump is 5.30 times as much as the work put into it. It would cost 5.30 times as much for the same heat transfer by an electric room heater as it does for that produced by this heat pump. This is not a violation of conservation of energy. Cold ambient air provides 4.3 J per 1 J of work from the electrical outlet.



Heat transfer from the outside to the inside, along with work done to run the pump, takes place in the heat pump of the example above. Note that the cold temperature produced by the heat pump is lower than the outside temperature, so that heat transfer into the working fluid occurs. The pump's compressor produces a temperature greater than the indoor temperature in order for heat transfer into the house to occur.

Real heat pumps do not perform quite as well as the ideal one in the previous example; their values of $\text{COP}_{\text{hp}}/\text{COP}_{\text{lp}}$ range from about 2 to 4. This range means that the heat transfer $Q_h Q_h$ from the heat pumps is 2 to 4 times as great as the work WW put into them. Their economical feasibility is still limited, however, since WW is usually supplied by electrical energy that costs more per joule than heat transfer by burning fuels like natural gas. Furthermore, the initial cost of a heat pump is greater than that of many furnaces, so that a heat pump must last longer for its cost to be recovered. Heat pumps are most likely to be economically superior where winter temperatures are mild, electricity is relatively cheap, and other fuels are relatively expensive. Also, since they can cool as well as heat a space, they have advantages where cooling in summer months is also desired. Thus some of the best locations for heat pumps are in warm summer climates with cool winters. [Figure 6] shows a heat pump, called a “reverse cycle” or “split-system cooler” in some countries.



In hot weather, heat transfer occurs from air inside the room to air outside, cooling the room. In cool weather, heat transfer occurs from air outside to air inside, warming the room. This switching is achieved by reversing the direction of flow of the working fluid.

Air Conditioners and Refrigerators

Air conditioners and refrigerators are designed to cool something down in a warm environment. As with heat pumps, work input is required for heat transfer from cold to hot, and this is expensive. The quality of air conditioners and refrigerators is judged by how much heat transfer $Q_c Q_c$ occurs from a cold environment compared with how much work input WW is required. What is considered the benefit in a heat pump is considered waste heat in a refrigerator. We thus define the **coefficient of performance** (COP_{ref}) of an air conditioner or refrigerator to be

$$\text{COP}_{\text{ref}} = Q_c W.$$

$$\text{COP}_{\text{ref}} = \frac{Q_c}{W}.$$

Noting again that $Q_h = Q_c + W$, we can see that an air conditioner will have a lower coefficient of performance than a heat pump, because $COP_{hp} = Q_h/W$ and $COP_{hp} = Q_h / W$ and Q_h/Q_c is greater than Q_c/Q_c . In this module's Problems and Exercises, you will show that

$$\begin{aligned} COP_{ref} &= COP_{hp} - 1 \\ COP_{ref} &= COP_{hp} - 1 \end{aligned}$$

for a heat engine used as either an air conditioner or a heat pump operating between the same two temperatures. Real air conditioners and refrigerators typically do remarkably well, having values of COP_{ref} ranging from 2 to 6. These numbers are better than the COP_{hp} values for the heat pumps mentioned above, because the temperature differences are smaller, but they are less than those for Carnot engines operating between the same two temperatures.

A type of COP rating system called the “energy efficiency rating” (EER) has been developed. This rating is an example where non-SI units are still used and relevant to consumers. To make it easier for the consumer, Australia, Canada, New Zealand, and the U.S. use an Energy Star Rating out of 5 stars—the more stars, the more energy efficient the appliance. EERs are expressed in mixed units of British thermal units (Btu) per hour of heating or cooling divided by the power input in watts. Room air conditioners are readily available with EERs ranging from 6 to 12. Although not the same as the COPs just described, these EERs are good for comparison purposes—the greater the EER, the cheaper an air conditioner is to operate (but the higher its purchase price is likely to be).

The EER of an air conditioner or refrigerator can be expressed as

$$\begin{aligned} EER &= Q_c/t_1 W/t_2, \\ EER &= \frac{Q_c / t_1}{W / t_2}, \end{aligned}$$

where Q_c is the amount of heat transfer from a cold environment in British thermal units, t_1 is time in hours, W is the work input in joules, and t_2 is time in seconds.

Problem-Solving Strategies for Thermodynamics

1. **Examine the situation to determine whether heat, work, or internal energy are involved.** Look for any system where the primary methods of transferring energy are heat and work. Heat engines, heat pumps, refrigerators, and air conditioners are examples of such systems.
2. **Identify the system of interest and draw a labeled diagram of the system showing energy flow.**
3. **Identify exactly what needs to be determined in the problem (identify the unknowns).** A written list is useful. Maximum efficiency means a Carnot engine is involved. Efficiency is not the same as the coefficient of performance.
4. **Make a list of what is given or can be inferred from the problem as stated (identify the knowns).** Be sure to distinguish heat transfer into a system from heat transfer out of the system, as well as work input from work output. In many situations, it is useful to determine the type of process, such as isothermal or adiabatic.
5. **Solve the appropriate equation for the quantity to be determined (the unknown).**
6. **Substitute the known quantities along with their units into the appropriate equation and obtain numerical solutions complete with units.**
7. **Check the answer to see if it is reasonable: Does it make sense?** For example, efficiency is always less than 1, whereas coefficients of performance are greater than 1.

Section Summary

- An artifact of the second law of thermodynamics is the ability to heat an interior space using a heat pump. Heat pumps compress cold ambient air and, in so doing, heat it to room temperature without violation of conservation principles.
- To calculate the heat pump's coefficient of performance, use the equation $COP_{hp} = Q_h/W$.
- A refrigerator is a heat pump; it takes warm ambient air and expands it to chill it.

Conceptual Questions

Explain why heat pumps do not work as well in very cold climates as they do in milder ones. Is the same true of refrigerators?

In some Northern European nations, homes are being built without heating systems of any type. They are very well insulated and are kept warm by the body heat of the residents. However, when the residents are not at home, it is still warm in these houses. What is a possible explanation?

Why do refrigerators, air conditioners, and heat pumps operate most cost-effectively for cycles with a small difference between $T_h T_h$ and $T_c T_c$? (Note that the temperatures of the cycle employed are crucial to its COPCOP .)

Grocery store managers contend that there is **less** total energy consumption in the summer if the store is kept at a **low** temperature. Make arguments to support or refute this claim, taking into account that there are numerous refrigerators and freezers in the store.

Can you cool a kitchen by leaving the refrigerator door open?

Problem Exercises

What is the coefficient of performance of an ideal heat pump that has heat transfer from a cold temperature of -25.0°C to a hot temperature of 40.0°C ?

Suppose you have an ideal refrigerator that cools an environment at -20.0°C and has heat transfer to another environment at 50.0°C . What is its coefficient of performance?

What is the best coefficient of performance possible for a hypothetical refrigerator that could make liquid nitrogen at -200°C and has heat transfer to the environment at 35.0°C ?

In a very mild winter climate, a heat pump has heat transfer from an environment at 5.00°C to one at 35.0°C . What is the best possible coefficient of performance for these temperatures? Explicitly show how you follow the steps in the [Problem-Solving Strategies for Thermodynamics](#).

(a) What is the best coefficient of performance for a heat pump that has a hot reservoir temperature of 50.0°C and a cold reservoir temperature of -20.0°C ? (b) How much heat transfer occurs into the warm environment if $3.60 \times 10^7 \text{ J}$ of work ($10.0 \text{ kW} \cdot \text{h}$) is put into it? (c) If the cost of this work input is 10.0 cents/kW · h, how does its cost compare with the direct heat transfer achieved by burning natural gas at a cost of 85.0 cents per therm. (A therm is a common unit of energy for natural gas and equals $1.055 \times 10^8 \text{ J}$.)

(a) What is the best coefficient of performance for a refrigerator that cools an environment at -30.0°C – 30.0°C and has heat transfer to another environment at 45.0°C ? (b) How much work in joules must be done for a heat transfer of 4186 kJ from the cold environment? (c) What is the cost of doing this if the work costs 10.0 cents per $3.60 \times 10^6 \text{ J}$ (a kilowatt-hour)? (d) How many kJ of heat transfer occurs into the warm environment? (e) Discuss what type of refrigerator might operate between these temperatures.

Suppose you want to operate an ideal refrigerator with a cold temperature of -10.0°C – 10.0°C , and you would like it to have a coefficient of performance of 7.00. What is the hot reservoir temperature for such a refrigerator?

An ideal heat pump is being considered for use in heating an environment with a temperature of 22.0°C . What is the cold reservoir temperature if the pump is to have a coefficient of performance of 12.0?

A 4-ton air conditioner removes $5.06 \times 10^7 \text{ J}$ (48 000 British thermal units) from a cold environment in 1.00 h. (a) What energy input in joules is necessary to do this if the air conditioner has an energy efficiency rating (EER) of 12.0? (b) What is the cost of doing this if the work costs 10.0 cents per $3.60 \times 10^6 \text{ J}$ (one kilowatt-hour)? (c) Discuss whether this cost seems realistic. Note that the energy efficiency rating (EER) of an air conditioner or refrigerator is defined to be the number of British thermal units of heat transfer from a cold environment per hour divided by the watts of power input.

Show that the coefficients of performance of refrigerators and heat pumps are related by $\text{COP}_{\text{ref}} = \text{COP}_{\text{hp}} - 1$.

Start with the definitions of the COPs and the conservation of energy relationship between Q_h , Q_c , and W .

Glossary

heat pump

a machine that generates heat transfer from cold to hot

coefficient of performance

for a heat pump, it is the ratio of heat transfer at the output (the hot reservoir) to the work supplied; for a refrigerator or air conditioner, it is the ratio of heat transfer from the cold reservoir to the work supplied



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Entropy and the Second Law of Thermodynamics: Disorder and the Unavailability of Energy

- Define entropy and calculate the increase of entropy in a system with reversible and irreversible processes.
- Explain the expected fate of the universe in entropic terms.
- Calculate the increasing disorder of a system.



The ice in this drink is slowly melting. Eventually the liquid will reach thermal equilibrium, as predicted by the second law of thermodynamics. (credit: Jon Sullivan, PDPhoto.org)

There is yet another way of expressing the second law of thermodynamics. This version relates to a concept called **entropy**. By examining it, we shall see that the directions associated with the second law—heat transfer from hot to cold, for example—are related to the tendency in nature for systems to become disordered and for less energy to be available for use as work. The entropy of a system can in fact be shown to be a measure of its disorder and of the unavailability of energy to do work.

Making Connections: Entropy, Energy, and Work

Recall that the simple definition of energy is the ability to do work. Entropy is a measure of how much energy is not available to do work. Although all forms of energy are interconvertible, and all can be used to do work, it is not always possible, even in principle, to convert the entire available energy into work. That unavailable energy is of interest in thermodynamics, because the field of thermodynamics arose from efforts to convert heat to work.

We can see how entropy is defined by recalling our discussion of the Carnot engine. We noted that for a Carnot cycle, and hence for any reversible processes, $Q_c/Q_h = T_c/T_h$. Rearranging terms yields

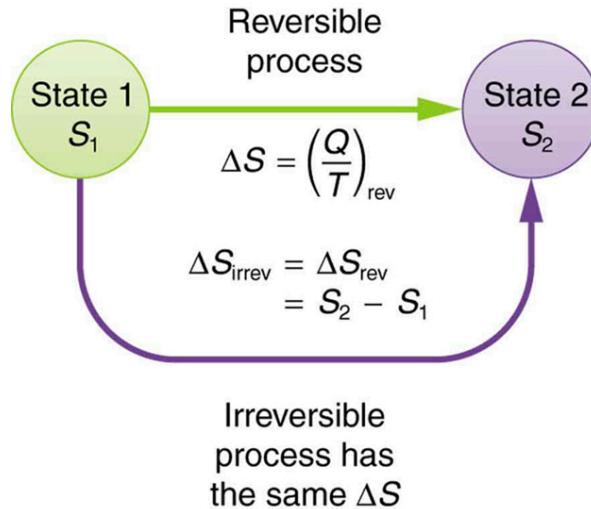
$$\frac{Q_c}{T_c} = \frac{Q_h}{T_h}$$

for any reversible process. $Q_c Q_h$ and $Q_h Q_h$ are absolute values of the heat transfer at temperatures $T_c T_c$ and $T_h T_h$, respectively. This ratio of Q/TQ is defined to be the **change in entropy** ΔS for a reversible process,

$$\Delta S = \frac{Q}{T} \text{ rev},$$

where Q is the heat transfer, which is positive for heat transfer into and negative for heat transfer out of, and T is the absolute temperature at which the reversible process takes place. The SI unit for entropy is joules per kelvin (J/K). If temperature changes during the process, then it is usually a good approximation (for small changes in temperature) to take T to be the average temperature, avoiding the need to use integral calculus to find ΔS .

The definition of $\Delta S \Delta S$ is strictly valid only for reversible processes, such as used in a Carnot engine. However, we can find $\Delta S \Delta S$ precisely even for real, irreversible processes. The reason is that the entropy S of a system, like internal energy U , depends only on the state of the system and not how it reached that condition. Entropy is a property of state. Thus the change in entropy $\Delta S \Delta S$ of a system between state 1 and state 2 is the same no matter how the change occurs. We just need to find or imagine a reversible process that takes us from state 1 to state 2 and calculate $\Delta S \Delta S$ for that process. That will be the change in entropy for any process going from state 1 to state 2. (See [Figure 2].)



When a system goes from state 1 to state 2, its entropy changes by the same amount (ΔS), whether a hypothetical reversible path is followed or a real irreversible path is taken.

Now let us take a look at the change in entropy of a Carnot engine and its heat reservoirs for one full cycle. The hot reservoir has a loss of entropy $\Delta S_h = -Q_h/T_h$, because heat transfer occurs out of it (remember that when heat transfers out, then Q has a negative sign). The cold reservoir has a gain of entropy $\Delta S_c = Q_c/T_c \Delta S_c = Q_c/T_c$, because heat transfer occurs into it. (We assume the reservoirs are sufficiently large that their temperatures are constant.) So the total change in entropy is

$$\Delta S_{\text{tot}} = \Delta S_h + \Delta S_c.$$

$$\Delta S_{\text{tot}} = \Delta S_h + \Delta S_c.$$

Thus, since we know that $Q_h/T_h = Q_c/T_c Q_h = Q_c/T_c$ for a Carnot engine,

$$\Delta S_{\text{tot}} = -Q_h/T_h + Q_c/T_c = 0.$$

$$\Delta S_{\text{tot}} = -\frac{Q_h}{T_h} + \frac{Q_c}{T_c} = 0.$$

This result, which has general validity, means that *the total change in entropy for a system in any reversible process is zero*.

The entropy of various parts of the system may change, but the total change is zero. Furthermore, the system does not affect the entropy of its surroundings, since heat transfer between them does not occur. Thus the reversible process changes neither the total entropy of the system nor the entropy of its surroundings. Sometimes this is stated as follows: *Reversible processes do not affect the total entropy of the universe*. Real processes are not reversible, though, and they do change total entropy. We can, however, use hypothetical reversible processes to determine the value of entropy in real, irreversible processes. The following example illustrates this point.

Entropy Increases in an Irreversible (Real) Process

Spontaneous heat transfer from hot to cold is an irreversible process. Calculate the total change in entropy if 4000 J of heat transfer occurs from a hot reservoir at $T_h = 600\text{K}$ (327°C) to a cold reservoir at $T_c = 250\text{K}$ (-23°C) , assuming there is no temperature change in either reservoir. (See [Figure 2].)

Strategy

How can we calculate the change in entropy for an irreversible process when $\Delta S_{\text{tot}} = \Delta S_h + \Delta S_c$ $\Delta S_{\text{tot}} = \Delta S_h + \Delta S_c$ is valid only for reversible processes?

Remember that the total change in entropy of the hot and cold reservoirs will be the same whether a reversible or irreversible process is involved in heat transfer from hot to cold. So we can calculate the change in entropy of the hot reservoir for a hypothetical reversible process in which 4000 J of heat transfer occurs from it; then we do the same for a hypothetical reversible process in which 4000 J of heat transfer occurs to the cold reservoir. This produces the same changes in the hot and cold reservoirs that would occur if the heat transfer were allowed to occur irreversibly between them, and so it also produces the same changes in entropy.

Solution

We now calculate the two changes in entropy using $\Delta S_{\text{tot}} = \Delta S_h + \Delta S_c$ $\Delta S_{\text{tot}} = \Delta S_h + \Delta S_c$. First, for the heat transfer from the hot reservoir,

$$\Delta S_h = -Q_h/T_h = -4000\text{J}/600\text{K} = -6.67\text{J/K.}$$

$$\Delta S_h = \frac{-Q_h}{T_h} = \frac{-4000\text{J}}{600\text{K}} = -6.67\text{J/K.}$$

And for the cold reservoir,

$$\Delta S_c = Q_c/T_c = 4000\text{J}/250\text{K} = 16.0\text{J/K.}$$

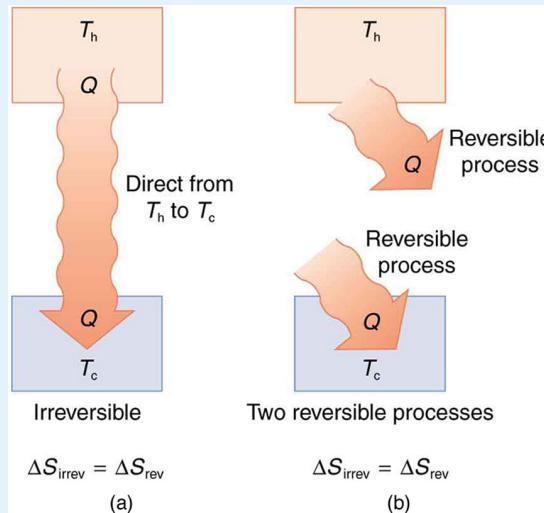
$$\Delta S_c = \frac{Q_c}{T_c} = \frac{4000\text{J}}{250\text{K}} = 16.0\text{J/K.}$$

Thus the total is

$$\begin{aligned} \Delta S_{\text{tot}} &= \Delta S_h + \Delta S_c &= (-6.67 + 16.0)\text{J/K} &= 9.33\text{J/K.} \\ \Delta S_{\text{tot}} &= \Delta S_h + \Delta S_c \\ &= (-6.67 + 16.0)\text{J/K} \\ &= 9.33\text{J/K.} \end{aligned}$$

Discussion

There is an *increase* in entropy for the system of two heat reservoirs undergoing this irreversible heat transfer. We will see that this means there is a loss of ability to do work with this transferred energy. Entropy has increased, and energy has become unavailable to do work.



(a) Heat transfer from a hot object to a cold one is an irreversible process that produces an overall increase in entropy. (b) The same final state and, thus, the same change in entropy is achieved for the objects if reversible heat transfer processes occur between the two objects whose temperatures are the same as the temperatures of the corresponding objects in the irreversible process.

It is reasonable that entropy increases for heat transfer from hot to cold. Since the change in entropy is Q/T , there is a larger change at lower temperatures. The decrease in entropy of the hot object is therefore less than the increase in entropy of the cold object, producing an overall increase, just as in the previous example. This result is very general:

There is an increase in entropy for any system undergoing an irreversible process.

With respect to entropy, there are only two possibilities: entropy is constant for a reversible process, and it increases for an irreversible process. There is a fourth version of **the second law of thermodynamics stated in terms of entropy**:

The total entropy of a system either increases or remains constant in any process; it never decreases.

For example, heat transfer cannot occur spontaneously from cold to hot, because entropy would decrease.

Entropy is very different from energy. Entropy is *not* conserved but increases in all real processes. Reversible processes (such as in Carnot engines) are the processes in which the most heat transfer to work takes place and are also the ones that keep entropy constant. Thus we are led to make a connection between entropy and the availability of energy to do work.

Entropy and the Unavailability of Energy to Do Work

What does a change in entropy mean, and why should we be interested in it? One reason is that entropy is directly related to the fact that not all heat transfer can be converted into work. The next example gives some indication of how an increase in entropy results in less heat transfer into work.

Less Work is Produced by a Given Heat Transfer When Entropy Change is Greater

(a) Calculate the work output of a Carnot engine operating between temperatures of 600 K and 100 K for 4000 J of heat transfer to the engine. (b) Now suppose that the 4000 J of heat transfer occurs first from the 600 K reservoir to a 250 K reservoir (without doing any work, and this produces the increase in entropy calculated above) before transferring into a Carnot engine operating between 250 K and 100 K. What work output is produced? (See [Figure 3].)

Strategy

In both parts, we must first calculate the Carnot efficiency and then the work output.

Solution (a)

The Carnot efficiency is given by

$$\text{Eff}_C = 1 - \frac{T_c}{T_h}$$

Substituting the given temperatures yields

$$\text{Eff}_C = 1 - \frac{100\text{K}}{600\text{K}} = 0.833.$$

Now the work output can be calculated using the definition of efficiency for any heat engine as given by

$$\text{Eff} = \frac{W}{Q_h}$$

Solving for W and substituting known terms gives

$$\begin{aligned} W &= \text{Eff}_C Q_h = (0.833)(4000\text{J}) = 3333\text{J}. \\ W &= \text{Eff}_C Q_h \\ &= (0.833) (4000\text{J}) = 3333\text{J}. \end{aligned}$$

Solution (b)

Similarly,

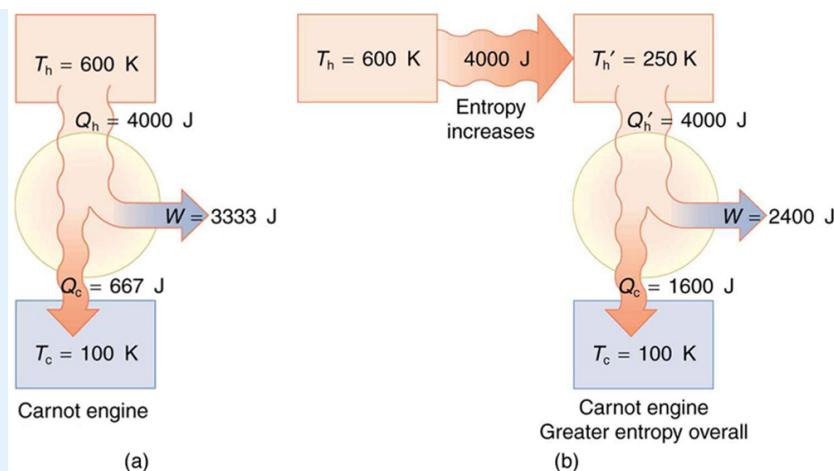
$$\begin{aligned} \text{Eff}'_C &= 1 - \frac{T_c}{T'_c} = 1 - \frac{100\text{K}}{250\text{K}} = 0.600, \\ \text{Eff}'_C &= 1 - \frac{T_c}{T'_c} = 1 - \frac{100\text{K}}{250\text{K}} = 0.600, \end{aligned}$$

so that

$$\begin{aligned} W &= \text{Eff}'_C Q_h = (0.600)(4000\text{J}) = 2400\text{J}. \\ W &= \text{Eff}'_C Q_h \\ &= (0.600) (4000\text{J}) = 2400\text{J}. \end{aligned}$$

Discussion

There is 933 J less work from the same heat transfer in the second process. This result is important. The same heat transfer into two perfect engines produces different work outputs, because the entropy change differs in the two cases. In the second case, entropy is greater and less work is produced. Entropy is associated with the *unavailability* of energy to do work.



(a) A Carnot engine working at between 600 K and 100 K has 4000 J of heat transfer and performs 3333 J of work.
 (b) The 4000 J of heat transfer occurs first irreversibly to a 250 K reservoir and then goes into a Carnot engine. The increase in entropy caused by the heat transfer to a colder reservoir results in a smaller work output of 2400 J. There is a permanent loss of 933 J of energy for the purpose of doing work.

When entropy increases, a certain amount of energy becomes *permanently* unavailable to do work. The energy is not lost, but its character is changed, so that some of it can never be converted to doing work—that is, to an organized force acting through a distance. For instance, in the previous example, 933 J less work was done after an increase in entropy of 9.33 J/K occurred in the 4000 J heat transfer from the 600 K reservoir to the 250 K reservoir. It can be shown that the amount of energy that becomes unavailable for work is

$$W_{\text{unavail}} = \Delta S \cdot T_0,$$

$$W_{\text{unavail}} = \Delta S \cdot T_0,$$

where T_0 is the lowest temperature utilized. In the previous example,

$$W_{\text{unavail}} = (9.33 \text{ J/K})(100 \text{ K}) = 933 \text{ J}$$

$$W_{\text{unavail}} = (9.33 \text{ J/K}) (100 \text{ K}) = 933 \text{ J}$$

as found.

Heat Death of the Universe: An Overdose of Entropy

In the early, energetic universe, all matter and energy were easily interchangeable and identical in nature. Gravity played a vital role in the young universe. Although it may have *seemed* disorderly, and therefore, superficially entropic, in fact, there was enormous potential energy available to do work—all the future energy in the universe.

As the universe matured, temperature differences arose, which created more opportunity for work. Stars are hotter than planets, for example, which are warmer than icy asteroids, which are warmer still than the vacuum of the space between them.

Most of these are cooling down from their usually violent births, at which time they were provided with energy of their own—nuclear energy in the case of stars, volcanic energy on Earth and other planets, and so on. Without additional energy input, however, their days are numbered.

As entropy increases, less and less energy in the universe is available to do work. On Earth, we still have great stores of energy such as fossil and nuclear fuels; large-scale temperature differences, which can provide wind energy; geothermal energies due to differences in temperature in Earth's layers; and tidal energies owing to our abundance of liquid water. As these are used, a certain fraction of the energy they contain can never be converted into doing work. Eventually, all fuels will be exhausted, all temperatures will equalize, and it will be impossible for heat engines to function, or for work to be done.

Entropy increases in a closed system, such as the universe. But in parts of the universe, for instance, in the Solar system, it is not a locally closed system. Energy flows from the Sun to the planets, replenishing Earth's stores of energy. The Sun will continue to supply us with energy for about another five billion years. We will enjoy direct solar energy, as well as side effects of solar energy, such as wind power and biomass energy from photosynthetic plants. The energy from the Sun will keep our water at the liquid state, and the Moon's gravitational pull will continue to provide tidal energy. But Earth's geothermal energy will slowly run down and won't be replenished.

But in terms of the universe, and the very long-term, very large-scale picture, the entropy of the universe is increasing, and so the availability of energy to do work is constantly decreasing. Eventually, when all stars have died, all forms of potential energy have been utilized, and all temperatures have equalized (depending on the mass of the universe, either at a very high temperature following a universal contraction, or a very low one, just before all activity ceases) there will be no possibility of doing work.

Either way, the universe is destined for thermodynamic equilibrium—maximum entropy. This is often called the *heat death of the universe*, and will mean the end of all activity. However, whether the universe contracts and heats up, or continues to expand and cools down, the end is not near. Calculations of black holes suggest that entropy can easily continue for at least $10^{100} 10^{100}$ years.

Order to Disorder

Entropy is related not only to the unavailability of energy to do work—it is also a measure of disorder. This notion was initially postulated by Ludwig Boltzmann in the 1800s. For example, melting a block of ice means taking a highly structured and orderly system of water molecules and converting it into a disorderly liquid in which molecules have no fixed positions. (See [Figure 5].) There is a large increase in entropy in the process, as seen in the following example.

Entropy Associated with Disorder

Find the increase in entropy of 1.00 kg of ice originally at 0°C that is melted to form water at 0°C .

Strategy

As before, the change in entropy can be calculated from the definition of ΔS once we find the energy Q needed to melt the ice.

Solution

The change in entropy is defined as:

$$\Delta S = QT.$$

$$\Delta S = \frac{Q}{T}.$$

Here Q is the heat transfer necessary to melt 1.00 kg of ice and is given by

$$Q = mL_f,$$

where m is the mass and L_f is the latent heat of fusion. $L_f = 334 \text{ kJ/kg}$ for water, so that

$$Q = (1.00 \text{ kg}) (334 \text{ kJ/kg}) = 3.34 \times 10^5 \text{ J}.$$

$$Q = (1.00 \text{ kg}) (334 \text{ kJ/kg}) = 3.34 \times 10^5 \text{ J}.$$

Now the change in entropy is positive, since heat transfer occurs into the ice to cause the phase change; thus,

$$\Delta S = QT = 3.34 \times 10^5 \text{ J} \cdot \frac{1}{T}.$$

$$\Delta S = \frac{Q}{T} = \frac{3.34 \times 10^5 \text{ J}}{T}.$$

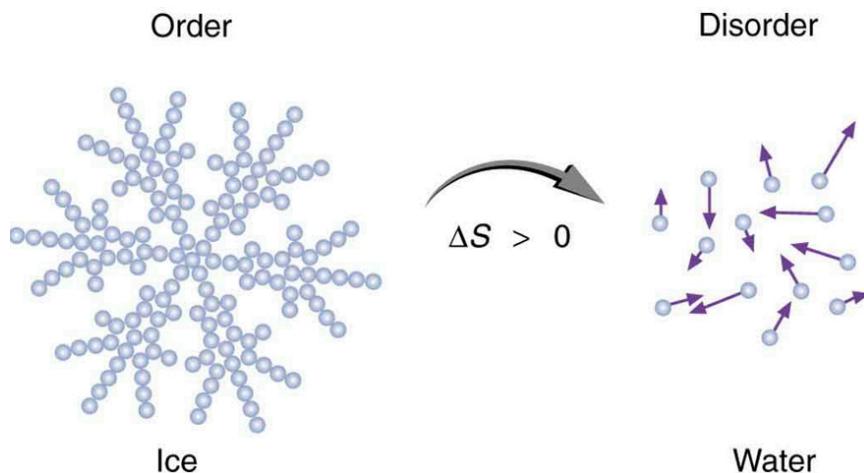
T is the melting temperature of ice. That is, $T = 0^{\circ}\text{C} = 273\text{K}$. So the change in entropy is

$$\Delta S = 3.34 \times 10^5 \text{ J} / 273\text{K} = 1.22 \times 10^3 \text{ J/K}.$$

$$\Delta S = \frac{3.34 \times 10^5 \text{ J}}{273\text{K}} = 1.22 \times 10^3 \text{ J/K}.$$

Discussion

This is a significant increase in entropy accompanying an increase in disorder.



When ice melts, it becomes more disordered and less structured. The systematic arrangement of molecules in a crystal structure is replaced by a more random and less orderly movement of molecules without fixed locations or orientations. Its entropy increases because heat transfer occurs into it. Entropy is a measure of disorder.

In another easily imagined example, suppose we mix equal masses of water originally at two different temperatures, say 20.0°C 20.0°C and 40.0°C 40.0°C. The result is water at an intermediate temperature of 30.0°C 30.0°C. Three outcomes have resulted: entropy has increased, some energy has become unavailable to do work, and the system has become less orderly. Let us think about each of these results.

First, entropy has increased for the same reason that it did in the example above. Mixing the two bodies of water has the same effect as heat transfer from the hot one and the same heat transfer into the cold one. The mixing decreases the entropy of the hot water but increases the entropy of the cold water by a greater amount, producing an overall increase in entropy.

Second, once the two masses of water are mixed, there is only one temperature—you cannot run a heat engine with them. The energy that could have been used to run a heat engine is now unavailable to do work.

Third, the mixture is less orderly, or to use another term, less structured. Rather than having two masses at different temperatures and with different distributions of molecular speeds, we now have a single mass with a uniform temperature.

These three results—entropy, unavailability of energy, and disorder—are not only related but are in fact essentially equivalent.

Life, Evolution, and the Second Law of Thermodynamics

Some people misunderstand the second law of thermodynamics, stated in terms of entropy, to say that the process of the evolution of life violates this law. Over time, complex organisms evolved from much simpler ancestors, representing a large decrease in entropy of the Earth's biosphere. It is a fact that living organisms have evolved to be highly structured, and much lower in entropy than the substances from which they grow. But it is *always* possible for the entropy of one part of the universe to decrease, provided the total change in entropy of the universe increases. In equation form, we can write this as

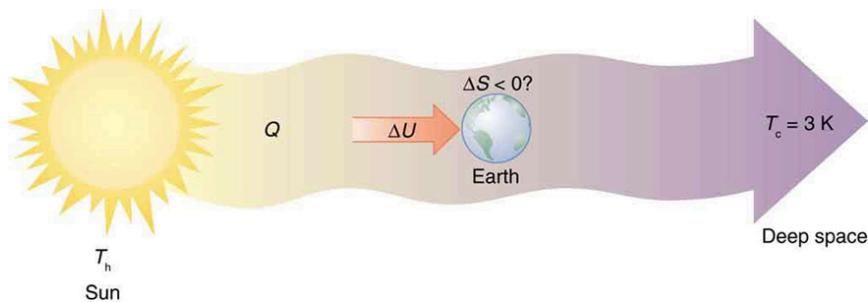
$$\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{envir}} > 0.$$

$$\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{envir}} > 0.$$

Thus ΔS_{syst} can be negative as long as ΔS_{envir} is positive and greater in magnitude.

How is it possible for a system to decrease its entropy? Energy transfer is necessary. If I pick up marbles that are scattered about the room and put them into a cup, my work has decreased the entropy of that system. If I gather iron ore from the ground and convert it into steel and build a bridge, my work has decreased the entropy of that system. Energy coming from the Sun can decrease the entropy of local systems on Earth—that is, ΔS_{syst} is negative. But the overall entropy of the rest of the universe increases by a greater amount—that is, ΔS_{envir} is positive and greater in magnitude. Thus, $\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{envir}} > 0$ and $\Delta S_{\text{tot}} = \Delta S_{\text{syst}} + \Delta S_{\text{envir}} > 0$, and the second law of thermodynamics is *not* violated.

Every time a plant stores some solar energy in the form of chemical potential energy, or an updraft of warm air lifts a soaring bird, the Earth can be viewed as a heat engine operating between a hot reservoir supplied by the Sun and a cold reservoir supplied by dark outer space—a heat engine of high complexity, causing local decreases in entropy as it uses part of the heat transfer from the Sun into deep space. There is a large total increase in entropy resulting from this massive heat transfer. A small part of this heat transfer is stored in structured systems on Earth, producing much smaller local decreases in entropy. (See [Figure 6].)



Earth's entropy may decrease in the process of intercepting a small part of the heat transfer from the Sun into deep space.

Entropy for the entire process increases greatly while Earth becomes more structured with living systems and stored energy in various forms.

PhET Explorations: Reversible Reactions

Watch a reaction proceed over time. How does total energy affect a reaction rate? Vary temperature, barrier height, and potential energies. Record concentrations and time in order to extract rate coefficients. Do temperature dependent studies to extract Arrhenius parameters. This simulation is best used with teacher guidance because it presents an analogy of chemical reactions.

Section Summary

- Entropy is the loss of energy available to do work.
- Another form of the second law of thermodynamics states that the total entropy of a system either increases or remains constant; it never decreases.
- Entropy is zero in a reversible process; it increases in an irreversible process.
- The ultimate fate of the universe is likely to be thermodynamic equilibrium, where the universal temperature is constant and no energy is available to do work.
- Entropy is also associated with the tendency toward disorder in a closed system.

Conceptual Questions

A woman shuts her summer cottage up in September and returns in June. No one has entered the cottage in the meantime. Explain what she is likely to find, in terms of the second law of thermodynamics.

Consider a system with a certain energy content, from which we wish to extract as much work as possible. Should the system's entropy be high or low? Is this orderly or disorderly? Structured or uniform? Explain briefly.

Does a gas become more orderly when it liquefies? Does its entropy change? If so, does the entropy increase or decrease? Explain your answer.

Explain how water's entropy can decrease when it freezes without violating the second law of thermodynamics. Specifically, explain what happens to the entropy of its surroundings.

Is a uniform-temperature gas more or less orderly than one with several different temperatures? Which is more structured? In which can heat transfer result in work done without heat transfer from another system?

Give an example of a spontaneous process in which a system becomes less ordered and energy becomes less available to do work. What happens to the system's entropy in this process?

What is the change in entropy in an adiabatic process? Does this imply that adiabatic processes are reversible? Can a process be precisely adiabatic for a macroscopic system?

Does the entropy of a star increase or decrease as it radiates? Does the entropy of the space into which it radiates (which has a temperature of about 3 K) increase or decrease? What does this do to the entropy of the universe?

Explain why a building made of bricks has smaller entropy than the same bricks in a disorganized pile. Do this by considering the number of ways that each could be formed (the number of microstates in each macrostate).

Problem Exercises

(a) On a winter day, a certain house loses $5.00 \times 10^8 \text{ J}$ of heat to the outside (about 500 000 Btu). What is the total change in entropy due to this heat transfer alone, assuming an average indoor temperature of 21.0°C and an average outdoor temperature of 5.00°C ? (b) This large change in entropy implies a large amount of energy has become unavailable to do work. Where do we find more energy when such energy is lost to us?

On a hot summer day, $4.00 \times 10^6 \text{ J}$ of heat transfer into a parked car takes place, increasing its temperature from 35.0°C to 45.0°C . What is the increase in entropy of the car due to this heat transfer alone?

A hot rock ejected from a volcano's lava fountain cools from 1100°C to 40.0°C , and its entropy decreases by 950 J/K . How much heat transfer occurs from the rock?

When $1.60 \times 10^5 \text{ J}$ of heat transfer occurs into a meat pie initially at 20.0°C , its entropy increases by 480 J/K . What is its final temperature?

The Sun radiates energy at the rate of $3.80 \times 10^{26} \text{ W}$ from its 5500°C surface into dark empty space (a negligible fraction radiates onto Earth and the other planets). The effective temperature of deep space is -270°C . (a) What is the increase in entropy in one day due to this heat transfer? (b) How much work is made unavailable?

(a) In reaching equilibrium, how much heat transfer occurs from 1.00 kg of water at 40.0°C when it is placed in contact with 1.00 kg of 20.0°C water in reaching equilibrium? (b) What is the change in entropy due to this heat transfer? (c) How much work is made unavailable, taking the lowest temperature to be 20.0°C ? Explicitly show how you follow the steps in the [Problem-Solving Strategies for Entropy](#).

What is the decrease in entropy of 25.0 g of water that condenses on a bathroom mirror at a temperature of 35.0°C , assuming no change in temperature and given the latent heat of vaporization to be 2450 kJ/kg ?

Find the increase in entropy of 1.00 kg of liquid nitrogen that starts at its boiling temperature, boils, and warms to 20.0°C at constant pressure.

A large electrical power station generates 1000 MW of electricity with an efficiency of 35.0%. (a) Calculate the heat transfer to the power station, $Q_h Q_h$, in one day. (b) How much heat transfer $Q_c Q_c$ occurs to the environment in one day? (c) If the heat transfer in the cooling towers is from 35.0°C 35.0°C water into the local air mass, which increases in temperature from 18.0°C 18.0°C to 20.0°C 20.0°C, what is the total increase in entropy due to this heat transfer? (d) How much energy becomes unavailable to do work because of this increase in entropy, assuming an 18.0°C 18.0°C lowest temperature? (Part of $Q_c Q_c$ could be utilized to operate heat engines or for simply heating the surroundings, but it rarely is.)

(a) How much heat transfer occurs from 20.0 kg of 90.0°C 90.0°C water placed in contact with 20.0 kg of 10.0°C 10.0°C water, producing a final temperature of 50.0°C 50.0°C? (b) How much work could a Carnot engine do with this heat transfer, assuming it operates between two reservoirs at constant temperatures of 90.0°C 90.0°C and 10.0°C 10.0°C? (c) What increase in entropy is produced by mixing 20.0 kg of 90.0°C 90.0°C water with 20.0 kg of 10.0°C 10.0°C water? (d) Calculate the amount of work made unavailable by this mixing using a low temperature of 10.0°C 10.0°C, and compare it with the work done by the Carnot engine. Explicitly show how you follow the steps in the [Problem-Solving Strategies for Entropy](#). (e) Discuss how everyday processes make increasingly more energy unavailable to do work, as implied by this problem.

Glossary

entropy

a measurement of a system's disorder and its inability to do work in a system

change in entropy

the ratio of heat transfer to temperature $Q/TQ / T$

second law of thermodynamics stated in terms of entropy

the total entropy of a system either increases or remains constant; it never decreases



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Statistical Interpretation of Entropy and the Second Law of Thermodynamics: The Underlying Explanation

- Identify probabilities in entropy.
- Analyze statistical probabilities in entropic systems.



When you toss a coin a large number of times, heads and tails tend to come up in roughly equal numbers. Why doesn't heads come up 100, 90, or even 80% of the time? (credit: Jon Sullivan, PDPhoto.org)

The various ways of formulating the second law of thermodynamics tell what happens rather than why it happens. Why should heat transfer occur only from hot to cold? Why should energy become ever less available to do work? Why should the universe become increasingly disorderly? The answer is that it is a matter of overwhelming probability. Disorder is simply vastly more likely than order.

When you watch an emerging rainstorm begin to wet the ground, you will notice that the drops fall in a disorganized manner both in time and in space. Some fall close together, some far apart, but they never fall in straight, orderly rows. It is not impossible for rain to fall in an orderly pattern, just highly unlikely, because there are many more disorderly ways than orderly ones. To illustrate this fact, we will examine some random processes, starting with coin tosses.

Coin Tosses

What are the possible outcomes of tossing 5 coins? Each coin can land either heads or tails. On the large scale, we are concerned only with the total heads and tails and not with the order in which heads and tails appear. The following possibilities exist:

5heads, 0 tails	4heads, 1 tail	3heads, 2 tails	2heads, 3 tails	1head, 4 tails	0head, 5 tails
5heads, 0 tails					
4heads, 1 tail					
3heads, 2 tails					
2heads, 3 tails					
1head, 4 tails					
0head, 5 tails					

These are what we call macrostates. A **macrostate** is an overall property of a system. It does not specify the details of the system, such as the order in which heads and tails occur or which coins are heads or tails.

Using this nomenclature, a system of 5 coins has the 6 possible macrostates just listed. Some macrostates are more likely to occur than others. For instance, there is only one way to get 5 heads, but there are several ways to get 3 heads and 2 tails, making the latter macrostate more probable. [Table 1] lists of all the ways in which 5 coins can be tossed, taking into account the order in which heads and tails occur. Each sequence is called a **microstate**—a detailed description of every element of a system.

5-Coin Toss

	Individual microstates	Number of microstates
5 heads, 0 tails	HHHHH	1
4 heads, 1 tail	HHHHT, HHHTH, HHTHH, HTHHH, THHHH	5
3 heads, 2 tails	HTHTH, THTHH, HTHHT, THHTH, THHHT HTHTH, THTHH, HTHHT, THHHT	10
2 heads, 3 tails	TTTHH, TTHHT, THHTT, HHTTT, TTHTH, THTHT, HTHTT, THTTH, HTTHT, HTTTT	10
1 head, 4 tails	TTTTH, TTTHT, TTHTT, THTTT, HTTTT	5
0 heads, 5 tails	TTTTT	1
		Total: 32

The macrostate of 3 heads and 2 tails can be achieved in 10 ways and is thus 10 times more probable than the one having 5 heads. Not surprisingly, it is equally probable to have the reverse, 2 heads and 3 tails. Similarly, it is equally probable to get 5 tails as it is to get 5 heads. Note that all of these conclusions are based on the crucial assumption that each microstate is equally probable. With coin tosses, this requires that the coins not be asymmetric in a way that favors one side over the other, as with loaded dice. With any system, the assumption that all microstates are equally probable must be valid, or the analysis will be erroneous.

The two most orderly possibilities are 5 heads or 5 tails. (They are more structured than the others.) They are also the least likely, only 2 out of 32 possibilities. The most disorderly possibilities are 3 heads and 2 tails and its reverse. (They are the least structured.) The most disorderly possibilities are also the most likely, with 20 out of 32 possibilities for the 3 heads and 2 tails and its reverse. If we start with an orderly array like 5 heads and toss the coins, it is very likely that we will get a less orderly array as a result, since 30 out of the 32 possibilities are less orderly. So even if you start with an orderly state, there is a strong tendency to go from order to disorder, from low entropy to high entropy. The reverse can happen, but it is unlikely.

100-Coin Toss

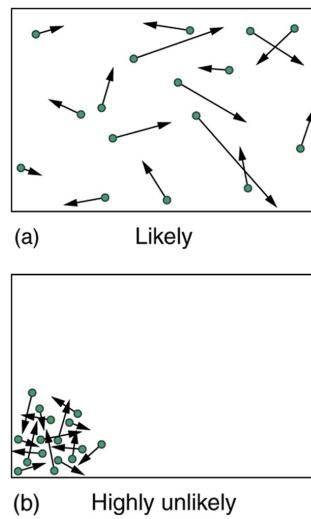
Macrostate		Number of microstates
Heads	Tails	(W)
100	0	1
99	1	1.0×10^2 1.0×10^2
95	5	7.5×10^7 7.5×10^7
90	10	1.7×10^{13} 1.7×10^{13}
75	25	2.4×10^{23} 2.4×10^{23}
60	40	1.4×10^{28} 1.4×10^{28}
55	45	6.1×10^{28} 6.1×10^{28}
51	49	9.9×10^{28} 9.9×10^{28}
50	50	1.0×10^{29} 1.0×10^{29}
49	51	9.9×10^{28} 9.9×10^{28}
45	55	6.1×10^{28} 6.1×10^{28}
40	60	1.4×10^{28} 1.4×10^{28}
25	75	2.4×10^{23} 2.4×10^{23}
10	90	1.7×10^{13} 1.7×10^{13}
5	95	7.5×10^7 7.5×10^7
1	99	1.0×10^2 1.0×10^2
0	100	1
		Total: 1.27×10^{30} 1.27×10^{30}

This result becomes dramatic for larger systems. Consider what happens if you have 100 coins instead of just 5. The most orderly arrangements (most structured) are 100 heads or 100 tails. The least orderly (least structured) is that of 50 heads and 50 tails. There is only 1 way (1 microstate) to get the most orderly arrangement of 100 heads. There are 100 ways (100 microstates) to get the next most orderly arrangement of 99 heads and 1 tail (also 100 to get its reverse). And there are 1.0×10^{29} 1.0×10^{20} ways to get 50 heads and 50 tails, the least orderly arrangement. [Table 2] is an abbreviated list of the various macrostates and the number of microstates for each macrostate. The total number of microstates—the total number of different ways 100 coins can be tossed—is an impressively large 1.27×10^{30} . Now, if we start with an orderly macrostate like 100 heads and toss the coins, there is a virtual certainty that we will get a less orderly macrostate. If we keep tossing the coins, it is possible, but exceedingly unlikely, that we will ever get back to the most orderly macrostate. If you tossed the coins once each second, you could expect to get either 100 heads or 100 tails once in $2 \times 10^{22} \times 10^{22}$ years! This period is 1 trillion ($10^{12} \times 10^{12}$) times longer than the age of the universe, and so the chances are essentially zero. In contrast, there is an 8% chance of getting 50 heads, a 73% chance of getting from 45 to 55 heads, and a 96% chance of getting from 40 to 60 heads. Disorder is highly likely.

Disorder in a Gas

The fantastic growth in the odds favoring disorder that we see in going from 5 to 100 coins continues as the number of entities in the system increases. Let us now imagine applying this approach to perhaps a small sample of gas. Because counting microstates and macrostates involves statistics, this is called **statistical analysis**. The macrostates of a gas correspond to its macroscopic properties, such as volume, temperature, and pressure; and its microstates correspond to the detailed description of the positions and velocities of its atoms. Even a small amount of gas has a huge number of atoms: 1.0cm^3 of an ideal gas at 1.0 atm and 0°C has 2.7×10^{19} atoms. So each macrostate has an immense number of microstates. In plain language, this means that there are an immense number of ways in which the atoms in a gas can be arranged, while still having the same pressure, temperature, and so on.

The most likely conditions (or macrostates) for a gas are those we see all the time—a random distribution of atoms in space with a Maxwell-Boltzmann distribution of speeds in random directions, as predicted by kinetic theory. This is the most disorderly and least structured condition we can imagine. In contrast, one type of very orderly and structured macrostate has all of the atoms in one corner of a container with identical velocities. There are very few ways to accomplish this (very few microstates corresponding to it), and so it is exceedingly unlikely ever to occur. (See [Figure 2](b).) Indeed, it is so unlikely that we have a law saying that it is impossible, which has never been observed to be violated—the second law of thermodynamics.



(a) The ordinary state of gas in a container is a disorderly, random distribution of atoms or molecules with a Maxwell-Boltzmann distribution of speeds. It is so unlikely that these atoms or molecules would ever end up in one corner of the container that it might as well be impossible. (b) With energy transfer, the gas can be forced into one corner and its

The disordered condition is one of **high entropy** and the ordered one has **low entropy**. With a transfer of energy from another system, we could force all of the atoms into one corner and have a local decrease in entropy, but at the cost of **an overall increase in entropy of the universe**. If the atoms start out in one corner, they will quickly disperse and become uniformly distributed and will never return to the orderly original state ([Figure 2](b)). Entropy will increase. With such a large sample of atoms, it is possible—but unimaginably unlikely—for entropy to decrease. Disorder is vastly more likely than order.

The arguments that disorder and high entropy are the most probable states are quite convincing. The great Austrian physicist Ludwig Boltzmann (1844–1906)—who, along with Maxwell, made so many contributions to kinetic theory—proved that the entropy of a system in a given state (a macrostate) can be written as

$$S = k_B \ln W, \\ S = k_B \ln W,$$

where $k_B = 1.38 \times 10^{-23} \text{J/K}$ is Boltzmann's constant, and $\ln W$ is the natural logarithm of the number of microstates W corresponding to the given macrostate. W is proportional to the probability that the macrostate will occur. Thus entropy is directly related to the probability of a state—the more likely the state, the greater its entropy. Boltzmann proved that this expression for S is equivalent to the definition $\Delta S = Q/T\Delta S = Q/T$, which we have used extensively.

Thus the second law of thermodynamics is explained on a very basic level: entropy either remains the same or increases in every process. This phenomenon is due to the extraordinarily small probability of a decrease, based on the extraordinarily larger number of microstates in systems with greater entropy. Entropy *can* decrease, but for any macroscopic system, this outcome is so unlikely that it will never be observed.

Entropy Increases in a Coin Toss

Suppose you toss 100 coins starting with 60 heads and 40 tails, and you get the most likely result, 50 heads and 50 tails. What is the change in entropy?

Strategy

Noting that the number of microstates is labeled WW in [Table 2] for the 100-coin toss, we can use $\Delta S = S_f - S_i = k_B \ln W_f - k_B \ln W_i$ to calculate the change in entropy.

Solution

The change in entropy is

$$\Delta S = S_f - S_i = k_B \ln W_f - k_B \ln W_i$$

$$\Delta S = S_f - S_i = k_B \ln W_f - k_B \ln W_i$$

where the subscript i stands for the initial 60 heads and 40 tails state, and the subscript f for the final 50 heads and 50 tails state. Substituting the values for WW from [Table 2] gives

$$\begin{aligned} \Delta S &= (1.38 \times 10^{-23} \text{ J/K}) [\ln(1.0 \times 10^{29}) - \ln(1.4 \times 10^{28})] &= 2.7 \times 10^{-23} \text{ J/K} \\ \Delta S &= (1.38 \times 10^{-23} \text{ J/K}) [\ln(1.0 \times 10^{29}) - \ln(1.4 \times 10^{28})] \\ &= 2.7 \times 10^{-23} \text{ J/K} \end{aligned}$$

Discussion

This increase in entropy means we have moved to a less orderly situation. It is not impossible for further tosses to produce the initial state of 60 heads and 40 tails, but it is less likely. There is about a 1 in 90 chance for that decrease in entropy ($-2.7 \times 10^{-23} \text{ J/K} - 2.7 \times 10^{-23} \text{ J/K}$) to occur. If we calculate the decrease in entropy to move to the most orderly state, we get $\Delta S = -92 \times 10^{-23} \text{ J/K}$. There is about a 11 in $10^{30} 10^{30}$ chance of this change occurring. So while very small decreases in entropy are unlikely, slightly greater decreases are impossibly unlikely. These probabilities imply, again, that for a macroscopic system, a decrease in entropy is impossible. For example, for heat transfer to occur spontaneously from 1.00 kg of $0^\circ\text{C} 0^\circ\text{C}$ ice to its $0^\circ\text{C} 0^\circ\text{C}$ environment, there would be a decrease in entropy of $1.22 \times 10^3 \text{ J/K}$. Given that a $\Delta S \Delta S$ of $10^{-21} \text{ J/K} 10^{-21} \text{ J/K}$ corresponds to about a 11 in $10^{30} 10^{30}$ chance, a decrease of this size ($10^3 \text{ J/K} 10^3 \text{ J/K}$) is an *utter* impossibility. Even for a milligram of melted ice to spontaneously refreeze is impossible.

Problem-Solving Strategies for Entropy

1. Examine the situation to determine if entropy is involved.
 2. Identify the system of interest and draw a labeled diagram of the system showing energy flow.
 3. Identify exactly what needs to be determined in the problem (identify the unknowns). A written list is useful.
 4. Make a list of what is given or can be inferred from the problem as stated (identify the knowns). You must carefully identify the heat transfer, if any, and the temperature at which the process takes place. It is also important to identify the initial and final states.
 5. Solve the appropriate equation for the quantity to be determined (the unknown). Note that the change in entropy can be determined between any states by calculating it for a reversible process.
 6. Substitute the known value along with their units into the appropriate equation, and obtain numerical solutions complete with units.
 7. To see if it is reasonable: Does it make sense? For example, total entropy should increase for any real process or be constant for a reversible process.
- Disordered states should be more probable and have greater entropy than ordered states.

Section Summary

- Disorder is far more likely than order, which can be seen statistically.
- The entropy of a system in a given state (a macrostate) can be written as

$$S = k_B \ln W$$

$$S = k_B \ln W$$

where $k_B = 1.38 \times 10^{-23} \text{ J/K}$, $k_B = 1.38 \times 10^{-23} \text{ J/K}$ is Boltzmann's constant, and $\ln W$ is the natural logarithm of the number of microstates WW corresponding to the given macrostate.

Conceptual Questions

Explain why a building made of bricks has smaller entropy than the same bricks in a disorganized pile. Do this by considering the number of ways that each could be formed (the number of microstates in each macrostate).

Problem Exercises

Using [Table 2], verify the contention that if you toss 100 coins each second, you can expect to get 100 heads or 100 tails once in 2×10^{22} years; calculate the time to two-digit accuracy.

What percent of the time will you get something in the range from 60 heads and 40 tails through 40 heads and 60 tails when tossing 100 coins? The total number of microstates in that range is 1.22×10^{30} . (Consult [Table 2].)

(a) If tossing 100 coins, how many ways (microstates) are there to get the three most likely macrostates of 49 heads and 51 tails, 50 heads and 50 tails, and 51 heads and 49 tails? (b) What percent of the total possibilities is this? (Consult [Table 2].)

(a) What is the change in entropy if you start with 100 coins in the 45 heads and 55 tails macrostate, toss them, and get 51 heads and 49 tails? (b) What if you get 75 heads and 25 tails? (c) How much more likely is 51 heads and 49 tails than 75 heads and 25 tails? (d) Does either outcome violate the second law of thermodynamics?

(a) What is the change in entropy if you start with 10 coins in the 5 heads and 5 tails macrostate, toss them, and get 2 heads and 8 tails? (b) How much more likely is 5 heads and 5 tails than 2 heads and 8 tails? (Take the ratio of the number of microstates to find out.) (c) If you were betting on 2 heads and 8 tails would you accept odds of 252 to 45? Explain why or why not.

10-Coin Toss

Macrostate		Number of Microstates (W)
Heads	Tails	
10	0	1
9	1	10
8	2	45
7	3	120
6	4	210
5	5	252
4	6	210
3	7	120
2	8	45
1	9	10
0	10	1
		Total: 1024

(a) If you toss 10 coins, what percent of the time will you get the three most likely macrostates (6 heads and 4 tails, 5 heads and 5 tails, 4 heads and 6 tails)? (b) You can realistically toss 10 coins and count the number of heads and tails about twice a minute. At that rate, how long will it take on average to get either 10 heads and 0 tails or 0 heads and 10 tails?

(a) Construct a table showing the macrostates and all of the individual microstates for tossing 6 coins. (Use [Table 3] as a guide.) (b) How many macrostates are there? (c) What is the total number of microstates? (d) What percent chance is there of tossing 5 heads and 1 tail? (e) How much more likely are you to toss 3 heads and 3 tails than 5 heads and 1 tail? (Take the ratio of the number of microstates to find out.)

In an air conditioner, 12.65 MJ of heat transfer occurs from a cold environment in 1.00 h. (a) What mass of ice melting would involve the same heat transfer? (b) How many hours of operation would be equivalent to melting 900 kg of ice? (c) If ice costs 20 cents per kg, do you think the air conditioner could be operated more cheaply than by simply using ice? Describe in detail how you evaluate the relative costs.

Glossary

macrostate

an overall property of a system

microstate

each sequence within a larger macrostate

statistical analysis

using statistics to examine data, such as counting microstates and macrostates



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