

# Chapter 18

## Entropy



**Movie Undive**

The focus of the last chapter was the thermal energy of the atoms and molecules around us. While the thermal energy of an individual molecule is not large, the thermal energy in a reasonable collection of molecules, like a mole, is a noticeable amount. Suppose, for example, you could extract all the thermal energy in a mole of helium atoms at room temperature. How much would that energy be worth at a rate of 10 cents per kilowatt hour?

This is an easy calculation to do. The atoms in helium gas at room temperature have an average kinetic energy of  $3/2 kT$  per molecule, thus the energy of a mole is  $N_A(3/2 kT) = 3/2 RT$ , where  $N_A$  is Avagadro's number and  $R = N_A K$ . Since ice melts at 273 K and water boils at 373 K, a reasonable value for room temperature is 300 K, about one quarter of the way up from freezing to boiling. Thus the total thermal energy in a mole of room temperature helium gas is

$$\left. \begin{array}{l} \text{thermal energy} \\ \text{in a mole of} \\ \text{room temperature} \\ \text{helium gas} \end{array} \right\} = \frac{3}{2} RT$$

$$= \frac{3}{2} \times 8 \frac{\text{joules}}{\text{mole K}} \times 300 K$$

$$= 3600 \text{ joules}$$

This is enough energy to lift 1 kilogram to a height of 360 feet!

To calculate the monetary value of this energy, we note that a kilowatt hour is 1000 watts of electric power for

3600 seconds, or  $1000 \times 3600$  joules. Thus at a rate of 10 cents per kilowatt hour, the thermal energy of a mole of helium gas is worth only .01 cents.

The value .01 cents does not sound like much, but that was the value of the energy in only one mole of helium. Most substances have a greater molar heat capacity than helium due to the fact that energy is stored in internal motions of the molecule. Water at room temperature, for example, has a molar heat capacity six times greater than that of helium. Thus we would expect that the thermal energy in a mole of water should be of the order of 6 times greater than that of helium, or worth about .06 cents.

A mole of water is only 18 grams. A kilogram of water, 1000 grams of it, is 55 moles, thus the thermal energy in a kilogram or liter of water should have a value in the neighborhood of  $.06 \text{ cents/mole} \times 55 \text{ moles} = 3.3 \text{ cents}$ . Now think about the amount of water in a swimming pool that is 25 meters long, 10 meters wide, and 2 meters deep. This is  $500 \text{ m}^3$  or  $500 \times 10^3$  liters, their being  $1000 \text{ liters/m}^3$ . Thus the commercial value of the heat energy in a swimming pool of water at room temperature is  $5 \times 10^5 \times 3.3 \text{ cents}$  or over \$16,000.

The point of this discussion is that there is a lot of thermal energy in the matter around us, energy that would have enormous value if we could get at it. The question is why don't we use this thermal energy rather than getting energy by burning oil and polluting the atmosphere in the process?

## INTRODUCTION

A simple lecture demonstration helps provide insight into why we cannot easily get at, and use, the \$16,000 of thermal energy in the swimming pool. In this demonstration, illustrated in Figure (1), water is pumped up through a hose and squirted down onto a flat plate placed in a small bucket as shown. If you use a vibrator pump, then the water comes out as a series of droplets rather than a continuous stream.

To make the individual water droplets visible, and to slow down the apparent motion, the water is illuminated by a strobe. If the time between strobe flashes is just a bit longer than the time interval which the drops are ejected, the drops will appear to move very slowly. This allows you to follow what appears to be an individual drop as it moves down toward the flat plate.

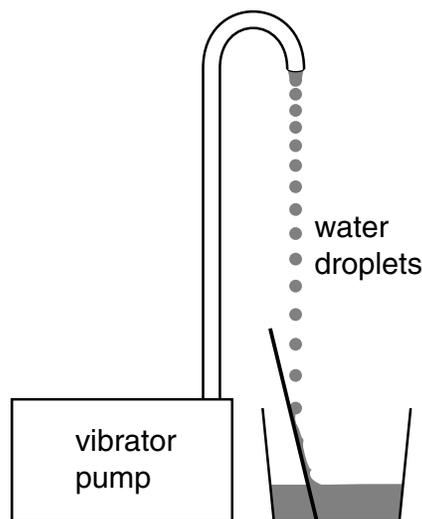
For our discussion, we want to focus on what happens to the drop as it strikes the plate. As seen in the series of pictures in Figure (2), when the drop hits it flattens out, creating a wave that spreads out from where the drop hits. The wave then moves down the plate into the pool of water in the bucket. [In Figure (1) we see several waves flowing down the plate. Each was produced by a separate drop.]

Let us look at this process from the point of view of the energy involved. Before the drop hits, it has kinetic energy due to falling. When it hits, this kinetic energy goes into the kinetic energy of wave motion. The waves then flow into the bucket, eventually dissipate, and all the kinetic energy becomes thermal energy of the water molecules in the bucket. This causes a slight, almost undetectable, increase in the temperature of the water in the bucket (if the water drop had the same temperature as the water in the bucket, and we neglect cooling from evaporation).

We have selected this demonstration for discussion, because with a slight twist of the knob on the strobe, we can make the process appear to run backwards. If the time interval between flashes is just a bit shorter than the pulse interval of the pump, the drops appear to rise from the plate and go back into the hose. The situation looks funny, but it makes a good ending to the demonstration. Everyone knows that what they see couldn't possibly happen—or could it?

Does this reverse flow violate any laws of physics? Once a drop has left the plate it moves like a ball thrown up in the air. From the point of view of the laws of physics, nothing is peculiar about the motion of the drop from the time it leaves the plate until it enters the hose.

**Figure 1**  
*Water droplets are created by a vibrator pump. If you illuminate the drops with a strobe light, you can make them appear to fall or rise.*

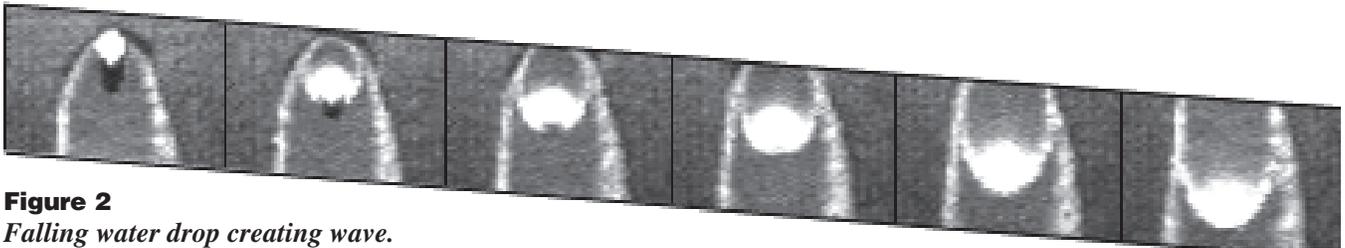


Where the situation looks funny is in the launching of the drop from the plate. But it turns out that none of the laws of physics we have discussed so far is violated there either. Let us look at this launching from the point of view of the energy involved. Initially the water in the bucket is a bit warm. This excess thermal energy becomes organized into a wave that flows up the plate. As seen in Figure (3) the wave coalesces into a drop that is launched up into the air. No violation of the law of conservation of energy is needed to describe this process.

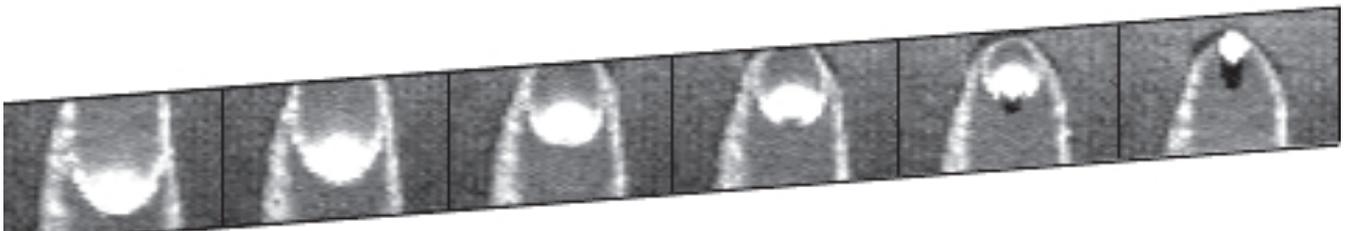
While the launching of the drop in this reversed picture may not violate the laws of physics we have studied, it still looks funny, and we do not see such things happen in the real world. There has to be some reason why we don't. The answer lies in the fact that in the reversed process we have converted thermal energy, the disorganized kinetic energy of individual molecules, into the organized energy of the waves, and finally into the more concentrated kinetic energy of the upward travelling drop. We have converted a disorganized form of energy into an organized form in a way that nature does not seem to allow.

It is not impossible to convert thermal energy into organized kinetic energy or what we call useful work. Steam engines do it all the time. In a modern electric power plant, steam is heated to a high temperature by burning some kind of fuel, and the steam is sent through turbines to produce electricity. A certain fraction of the thermal energy obtained from burning the fuel ends up as electrical energy produced by the electric generators attached to the turbines. This electric energy can then be used to do useful work running motors.

The important point is that power stations cannot simply suck thermal energy out of a reservoir like the ocean and turn it into electrical energy. That would correspond to our water drop being launched by the thermal energy of the water in the bucket.



**Figure 2**  
*Falling water drop creating wave.*



**Figure 3**  
*Rising wave launching water drop.*

Even more discouraging is the fact that power plants do not even use all the energy they get from burning fuel. A typical high efficiency power plant ends up discarding, into the atmosphere or the ocean, over 2/3 of the energy it gets from burning fuel. Less than 1/3 of the energy from the fuel is converted into useful electrical energy. Car engines are even worse. Less than 1/5 of the energy from the gasoline burned goes into powering the car; most of the rest comes out the exhaust pipe.

Why do we tolerate these low efficiency power plants and even lower efficiency car engines? The answer lies in the problem of *converting a disorganized form of energy into an organized one*. Or to state the problem more generally, of trying to create order from chaos.

The basic idea is that a disorganized situation does not naturally organize itself—in nature, things go the other way. For example, if you have a box of gas, and initially the atoms are all nicely localized on one side of the box, a short time later they will be flying around throughout the whole volume of the box. On their own, there is almost no chance that they will all move over to that one side again. If you want them over on one side, you have to do some work, like pushing on a piston, to get them over there. It takes work to create order from disorder.

At first, it seems that the concepts of order and disorder, and the related problems of converting thermal energy into useful work should be a difficult subject to deal with. If you wished to formulate a physical law, how do you go about even defining the concepts. What, for example, should you use as an experimental definition of disorder? It turns out, surprisingly, that there is a precise definition of a quantity called *entropy* which represents the amount of disorder contained in a system. Even more surprising, the concept of entropy was discovered before the true nature of heat was understood.

The basic ideas related to entropy were discovered in 1824 by the engineer Sadi Carnot who was trying to figure out how to improve the efficiency of steam engines. Carnot was aware that heat was wasted in the operation of a steam engine, and was studying the problem in an attempt to reduce the waste of heat. In

his studies Carnot found that there was a *theoretically maximum efficient engine whose efficiency depended upon the temperature of the boiler relative to the temperature of the boiler's surroundings*.

To make his analysis, Carnot had to introduce a new assumption not contained in Newton's law of mechanics. Carnot's assumption is equivalent to the idea that *you cannot convert thermal energy into useful work in a process involving only one temperature*. This is why you cannot sell the \$16,000 worth of thermal energy in the swimming pool—you cannot get it out.

This law is known as the *Second Law of Thermodynamics*. (The first law is the law of conservation of energy itself.) The second law can also be expressed in terms of entropy which we now know represents the disorder of a system. The second law states that in any process, the total entropy (disorder) of a system either stays the same or increases. Put another way, it states that in any process, the total order of a system cannot increase; it can only stay the same, or the system can become more disordered.

To develop his formulas for the maximum efficiency of engines, Carnot invented the concept known as a *Carnot engine*, based on what is called the *Carnot cycle*. The Carnot engine is not a real engine, no one has ever built one. Instead, you should think of it as a *thought experiment*, like the ones we used in Chapter 1 to figure out what happened to moving clocks if the principle of relativity is correct.

The question we wish to answer is, how efficient can you make an engine or a power plant, if the second law of thermodynamics is correct? If you cannot get useful work from thermal energy at one temperature, how much work can you get if you have more than one temperature? It turns out that there is a surprisingly simple answer, but we are going to have to do quite a bit of analysis of Carnot's thought experiment before we get the answer. During the discussion of the Carnot engine, one should keep in mind that we are making this effort to answer one basic question—what are the consequences of the second law of thermodynamics—what are the consequences of the idea that order does not naturally arise from disorder.

## WORK DONE BY AN EXPANDING GAS

The Carnot thought experiment is based on an analysis of several processes involving the ideal piston and cylinder we discussed in the last chapter. We will discuss each of these processes separately, and then put them together to complete the thought experiment.

The ideal piston and cylinder is shown in Figure (4). A gas, at a pressure  $p$ , is contained in the cylinder by a frictionless piston of cross-sectional area  $A$ . (Since no one has yet built a piston that can seal the gas inside the cylinder and still move frictionlessly, we are now already into the realm of a thought experiment.) A force  $F$  is applied to the outside of the piston as shown to keep the piston from moving. The gas, at a pressure  $p$ , exerts an outward force

$$p \left( \frac{\text{newtons}}{\text{meter}^2} \right) \times A (\text{meter}^2) = pA (\text{newtons})$$

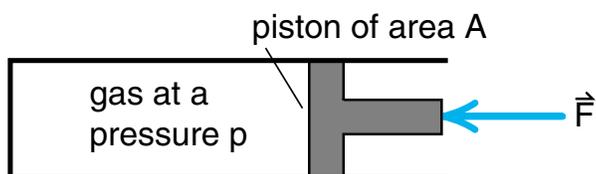
on the cylinder, thus  $F$  must be given by

$$F = pA \quad (1)$$

to keep the cylinder from moving.

If we decrease the force  $F$  just a bit to allow the gas in the cylinder to expand, the expanding gas will do work on the piston. This is because the gas is exerting a force  $pA$  on the cylinder, while the cylinder is moving in the direction of the force exerted by the gas. If the piston moves out a distance  $\Delta x$  as shown in Figure (5), the work  $\Delta W$  done by the gas is the force  $pA$  it exerts times the distance  $\Delta x$

$$\Delta W = (pA)\Delta x \quad (2)$$



**Figure 4**  
In the ideal piston and cylinder, the piston confines the gas and moves frictionlessly.

After this expansion, the volume of the gas has increased by an amount  $\Delta V = A\Delta x$ . Thus Equation 2 can be written in the form  $\Delta W = pA\Delta x$  or

$$\Delta W = p\Delta V \quad (3)$$

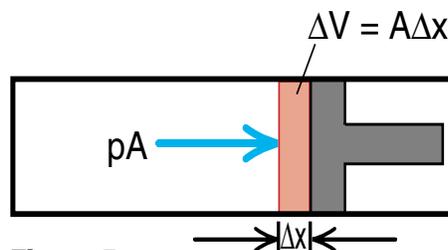
Equation 3 is more general than our derivation indicates. Any time a gas expands its volume by an amount  $\Delta V$ , the work done by the gas is  $(p\Delta V)$  no matter what the shape of the container. For example, if you heat the gas in a balloon and the balloon expands a bit, the work done by the gas is  $(p\Delta V)$  *where  $\Delta V$  is the increase in the volume of the balloon.*

### Exercise 1

In our introduction to the concept of pressure, we dipped a balloon in liquid nitrogen until the air inside became a puddle of liquid air (see Figure 17-19). When we took the balloon out of the liquid nitrogen, the air slowly expanded until the balloon returned to its original size. During the expansion, the rubber of the balloon was relatively loose, which means that the air inside the balloon remained at or very near to atmospheric pressure during the entire time the balloon was expanding.

(a) If the final radius of the balloon is 30 cm, how much work did the gas inside the balloon do as the balloon expanded? (You may neglect the volume of the liquid air present when the expansion started.) (Answer:  $1.1 \times 10^4$  joules.)

(b) Where did the gas inside the balloon get the energy required to do this work?



**Figure 5**  
The work done by an expanding gas is equal to the force  $pA$  it exerts, times the distance  $\Delta x$  the piston moves.

## SPECIFIC HEATS $C_V$ AND $C_p$

In our earlier discussion of specific heat, we dealt exclusively with the “molar” specific heat at constant volume  $C_V$ . We always assumed that we kept the gas at constant volume so that all the energy we added would go into the internal energy of the gas. If we had allowed the gas to expand, then some of the energy would have gone into the work the gas did to expand its volume, and we would not have had an accurate measure of the amount of energy that went into the gas itself.

Sometimes it is convenient to heat a gas while keeping the gas *pressure*, rather than *volume*, constant. This is more or less the case when we heat the gas in a balloon. The balloon expands, but the pressure does not change very much if the expansion is small.

Earlier we defined the molar heat capacity  $C_V$  as the amount of energy required to heat one mole of a substance one kelvin, if the volume of the substance is kept constant. Let us now define the molar heat capacity  $C_p$  as the amount of energy required to heat one mole of a substance one kelvin if the pressure is kept constant. For gases  $C_p$  is always larger than  $C_V$ . This is because, when we heat the gas at constant pressure, the energy goes both into heating and expanding the gas. When we heat the gas at constant volume, the energy goes only into heating the gas. We can write this out as an equation as follows

$$\begin{aligned}
 \text{energy required} & \\
 \text{to heat 1 mole} & \\
 \text{of a gas 1K at} & \\
 \text{constant pressure} & \\
 C_p = & \left( \begin{array}{l} \text{increase in thermal} \\ \text{energy of the gas} \\ \text{when the temperature} \\ \text{increases 1K} \end{array} \right) \\
 & + \left( \begin{array}{l} \text{work done} \\ \text{by the} \\ \text{expanding} \\ \text{gas} \end{array} \right) \quad (4)
 \end{aligned}$$

Noting that since  $C_V$  is equal to the increase in thermal energy of the gas, and that the work done is  $p\Delta V$ , we get

$$C_p = C_V + p\Delta V \quad (5)$$

In the special case of an ideal gas, we can use the ideal gas law  $pV = nRT$ , setting  $n = 1$  for 1 mole

$$pV = RT \quad (1 \text{ mole of gas}) \quad (6)$$

If we let the gas expand a bit at constant pressure, we get differentiating Equation 6, keeping  $p$  constant\*\*

$$p\Delta V = R\Delta T \quad (\text{if } p \text{ is constant}) \quad (7)$$

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\*\* By differentiating the equation ( $pV = RT$ ), we mean that we wish to equate the *change* in ( $pV$ ) to the *change* in ( $RT$ ). To determine the change in ( $pV$ ), for example, we let ( $p$ ) go to ( $p + \Delta p$ ) and ( $V$ ) go to ( $V + \Delta V$ ), so that the product ( $pV$ ) becomes

$$\begin{aligned}
 pV & \rightarrow (p + \Delta p)(V + \Delta V) \\
 & = pV + (\Delta p)V + p\Delta V + (\Delta p)\Delta V
 \end{aligned}$$

If we neglect the second order term  $(\Delta p)\Delta V$  then

$$pV \rightarrow pV + (\Delta p)V + p\Delta V$$

Then if we hold the pressure constant ( $\Delta p = 0$ ), we see that the change in ( $pV$ ) is simply  $(p\Delta V)$ . Since  $R$  is constant, the change in  $RT$  is simply  $R\Delta T$ .

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If the temperature increase is  $\Delta T = 1$  kelvin, then Equation 7 becomes

$$p\Delta V = R \quad (1 \text{ mole, } p \text{ constant, } \Delta T = 1\text{K}) \quad (8)$$

Using Equation 8 in Equation 5 we get the simple result

$$\boxed{C_p = C_v + R} \quad (9)$$

The derivation of Equation 9 illustrates the kind of steps we have to carry out to calculate what happens to the heat we add to substances. For example, in going from Equation 6 to Equation 7, we looked at the change in volume when the temperature but not the pressure was varied. When we make infinitesimal changes of some quantities in an equation while holding the quantities constant, the process is called *partial differentiation*. In this text we will not go into a formal discussion of the ideas of partial differentiation. When we encounter the process, the steps should be fairly obvious as they were in Equation 7.

*(The general subject that deals with changes produced by adding or removing heat from substances is called thermodynamics. The full theory of thermodynamics relies heavily on the mathematics of partial derivatives. For our discussion of Carnot's thought experiments, we need only a small part of thermodynamics theory.)*

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### Exercise 2

(a) Back in Table 2 on page 31 of Chapter 17, we listed the values of the molar specific heats for a number of gases. While the experimental values of did not agree in most cases with the values predicted by the equipartition of energy, you can use the experimental values of  $C_v$  to accurately predict the values of  $C_p$  for these gases. Do that now.

(b) Later in this chapter, in our discussion of what is called the *adiabatic* expansion of a gas (an expansion that allows no heat to flow in), we will see that the ratio of  $C_p/C_v$  plays an important role in the theory. It is common practice to designate this ratio by the Greek letter  $\gamma$

$$\boxed{\gamma \equiv C_p/C_v} \quad (10)$$

- (i) Explain why, for an ideal gas,  $\gamma$  is always greater than 1.
- (ii) Calculate the value of  $\gamma$  for the gases, listed in Table 2 of Chapter 17.

Answers:

gas	$\gamma$
helium	1.66
argon	1.66
nitrogen	1.40
oxygen	1.40
CO <sub>2</sub>	1.28
NH <sub>4</sub>	1.29

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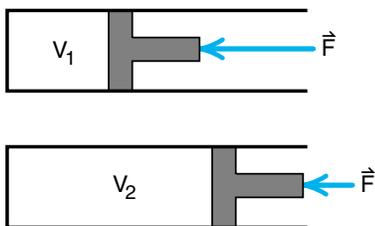
## ISOTHERMAL EXPANSION AND PV DIAGRAMS

In the introduction, we pointed out that while a swimming pool of water may contain \$16,000 of thermal energy, we could not extract this energy to do useful work. To get useful energy, we have to burn fuel to get heat, and convert the heat to useful work. What seemed like an insult is that even the most efficient power plants turn only about 1/3 of the heat from the fuel into useful work, the rest being thrown away, expelled either into the atmosphere or the ocean.

We are now going to discuss a process in which heat is converted to useful work with 100% efficiency. This involves letting the gas in a piston expand at constant temperature, in a process called an *isothermal expansion*. (The prefix “iso” is from the Greek meaning “equal,” thus, isothermal means equal or constant temperature.) This process cannot be used by power plants to make them 100% efficient, because the process is not repetitive. Some work is required to get the piston back so that the expansion can be done over again.

Suppose we start with a gas in a cylinder of volume  $V_1$  and let the gas slowly expand to a volume  $V_2$  as shown in Figure (6). We control the expansion by adjusting the force  $\vec{F}$  exerted on the back side of the piston.

While the gas is expanding, it is doing work on the piston. For each  $\Delta V$  by which the volume of the gas increases, the amount of work done by the gas is  $p\Delta V$ . The energy required to do this work must come from somewhere. If we did not let any heat into the cylinder, the energy would have to come from thermal energy, and the temperature would drop. (This is one way to get work out of thermal energy.)



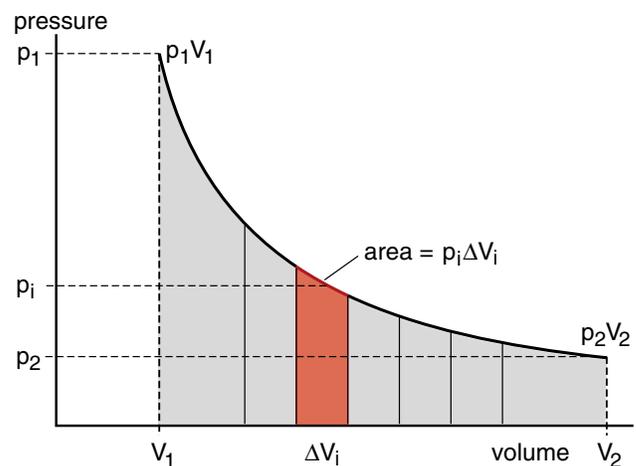
**Figure 6**  
*Isothermal expansion of the gas in a cylinder. The force  $\vec{F}$  on the cylinder is continually adjusted so that the gas expands slowly at constant temperature.*

However, we wish to study the process in which the gas expands at constant temperature. To keep the temperature from dropping, we have to let heat flow into the gas. Since the temperature of the gas is constant, there is no change in the thermal energy of the gas. Thus *all the heat that flows in goes directly into the work done by the gas*.

To calculate the amount of work done, we have to add up all the  $p\Delta V$ 's as the gas goes from a volume  $V_1$  to a volume  $V_2$ . If we graph pressure as a function of volume, in what is called a *pV diagram*, we can easily visualize these increments of work  $p\Delta V$  as shown in Figure (7).

Suppose the pressure of the gas is initially  $p_1$  when the volume of the cylinder is  $V_1$ . As the cylinder moves out and the gas expands, its pressure will drop as shown in Figure (7), reaching the lower value  $p_2$  when the cylinder volume reaches  $V_2$ . At each step  $\Delta V_i$ , when the pressure is  $p_i$ , the amount of work done by the gas is  $p_i\Delta V_i$ . The total work, the sum of all the  $p_i\Delta V_i$ , is just the total area under the pressure curve, as seen in Figure (7).

The nice feature of a graph of pressure versus volume like that shown in Figure (7), is *the work done by the gas is always the area under the pressure curve*, no matter what the conditions of the expansion are. If we had allowed the temperature to change, the shape of the pressure curve would have been different, but the work done by the gas would still be the area under the pressure curve.



**Figure 7**  
*The work done by an expanding gas is equal to the sum of all  $p\Delta V$ 's, which is the area under the pressure curve.*

## Isothermal Compression

If we shoved the piston back in, from a volume  $V_2$  to a volume  $V_1$  in Figure (7), we would have to do work on the gas. If we kept the temperature constant, then the pressure would increase along the curve shown in Figure (7) and the work we did would be precisely equal to the area under the curve. In this case work is done on the gas (we could say that during the compression the gas does negative work). When work is done on the gas, the temperature of the gas will rise unless we let heat flow out of the cylinder. Thus if we have an isothermal compression, where there is no increase in the thermal energy of the gas, then we have the pure conversion of useful work into the heat expelled by the piston. This is the opposite of what we want for a power plant.

## Isothermal Expansion of an Ideal Gas

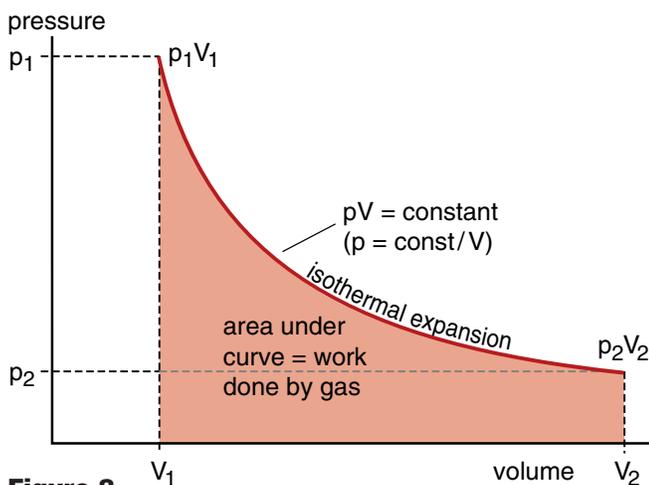
If we have one mole of an ideal gas in our cylinder, and keep the temperature constant at a temperature  $T_1$ , then the gas will obey the ideal gas equation.

$$pV = RT_1 = \text{constant} \quad (11)$$

Thus the equation for the pressure of an ideal gas during an isothermal expansion is

$$p = \frac{\text{constant}}{V} \quad (11a)$$

and we see that the pressure decreases as  $1/V$ . This decrease is shown in the  $pV$  diagram of Figure (8).



**Figure 8**  
In the isothermal expansion of an ideal gas, we have  $pV = \text{constant}$ . Thus the pressure decreases as  $1/V$ .

## ADIABATIC EXPANSION

We have seen that we can get useful work from heat during an isothermal expansion of a gas in a cylinder. As the gas expands, it does work, getting energy for the work from heat that flows into the cylinder. This represents the conversion of heat energy at one temperature into useful work. The problem is that there is a limited amount of work we can get this way. If we shove the piston back in so that we can repeat the process and get more work, it takes just as much work to shove the piston back as the amount of work we got out during the expansion. The end result is that we have gotten nowhere. We need something besides isothermal expansions and compressions if we are to end up with a net conversion of heat into work.

Another kind of expansion is to let the cylinder expand without letting any heat in. This is called an *adiabatic expansion*, where *adiabatic* is from the Greek (*a*-not + *dia*-through + *bainein*-to go). If the gas does work during the expansion, and we let no heat energy in, then *all the work must come from the thermal energy* of the gas. The result is that the gas will cool during the expansion. In an adiabatic expansion, we are converting the heat energy *contained in the gas* into useful work. If we could keep this expansion going we could suck all the thermal energy out of the gas and turn it into useful work. The problem, of course, getting the piston back to start the process over again.

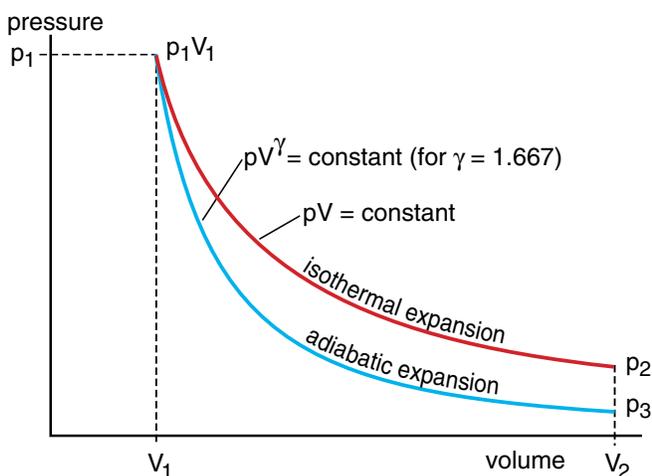
It is instructive to compare an isothermal expansion to an adiabatic expansion of a gas. In either case the pressure drops. But in the adiabatic expansion, the pressure drops faster because the gas cools. In Figure (9), we compare the isothermal and adiabatic expansion curves for an ideal gas. Because the adiabatic curve drops faster in the  $pV$  diagram, there is less area under the adiabatic curve, and the gas does less work. This is not too surprising, because less energy was available for the adiabatic expansion since no heat flowed in.

For an ideal gas, the equation for an adiabatic expansion is

$$pV^\gamma = \text{constant}; \quad \gamma = \frac{C_p}{C_v} \quad (12)$$

a result we derive in the appendix. (You calculated the value of  $\gamma$  for various gases in Exercise 2.) The important point now is not so much this formula, as the fact that the adiabatic curve drops faster than the isothermal curve.

If we compress a gas adiabatically, all the work we do goes into the thermal energy of the gas, and the temperature rises. Thus with an adiabatic expansion we can lower the temperature of the gas, and with an adiabatic compression raise it.



**Figure 9**  
*Comparison of isothermal and adiabatic expansions. In an adiabatic expansion the gas cools, and thus the pressure drops faster.*

### Exercise 3

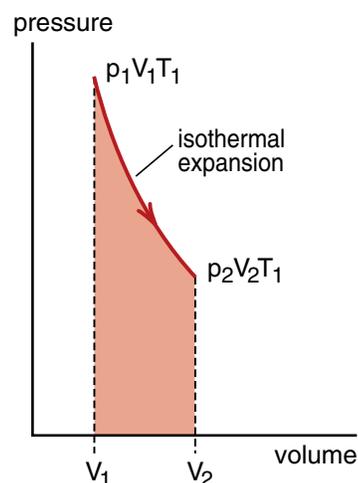
In the next section, we will discuss a way of connecting adiabatic and isothermal expansions and compressions in such a way that we form a complete cycle (get back to the starting point), and get a net amount of work out of the process. Before reading the next section, it is a good exercise to see if you can do this on your own.

In order to see whether or not you are getting work out or putting it in, it is useful to graph the process in a  $pV$  diagram, where the work is simply the area under the curve.

To get you started in this exercise, suppose you begin with an ideal gas at a pressure  $p_1$ , volume  $V_1$ , and temperature  $T_1$ , and expand it isothermally to  $p_2, V_2, T_1$  as shown in Figure (10a). The work you get out is the area under the curve.

If you then compressed the gas isothermally back to  $p_1, V_1, T_1$ , this would complete the cycle (get you back to where you started), but it would take just as much work to compress the gas as you got from the expansion. Thus there is no net work gained from this cycle. A more complex cycle is needed to get work out.

If we add an adiabatic expansion to the isothermal expansion as shown in Figure (10b) we have the start of something more complex. See if you can complete this cycle, i.e., get back to  $p_1, V_1, T_1$ , using adiabatic and isothermal expansions or compressions, and get some net work in the process. See if you can get the answer before we give it to you in the next section. Also show graphically, on Figure (10b) how much work you do get out.



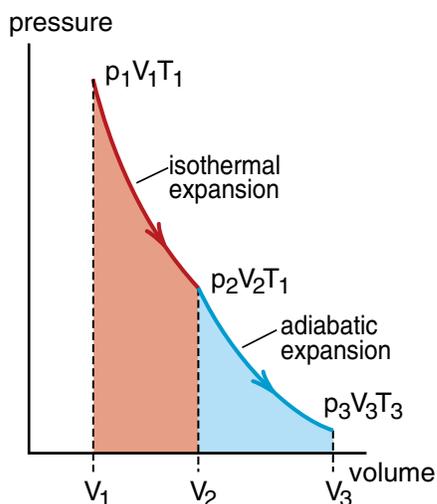
**Figure 10a**  
 *$pV$  diagram for an isothermal expansion from volume  $V_1$  to volume  $V_2$ .*

## THE CARNOT CYCLE

With the isothermal and adiabatic expansion and compression of an ideal gas in a frictionless cylinder, we now have the pieces necessary to construct a Carnot cycle, the key part of our thought experiment to study the second law of thermodynamics.

The goal is to construct a device that continually converts heat energy into work. Such a device is called an *engine*. Both the isothermal and adiabatic expansions of the gas converted heat energy into work, but the expansions alone could not be used as an engine because the piston was left expanded. Carnot's requirement for an engine was that after a complete cycle all the working parts had to be back in their original condition ready for another cycle. Somehow the gas in the cylinder has to be compressed again to get the piston back to its original position. And the compression cannot use up all the work we got from the expansion, in order that we get some net useful work from the cycle.

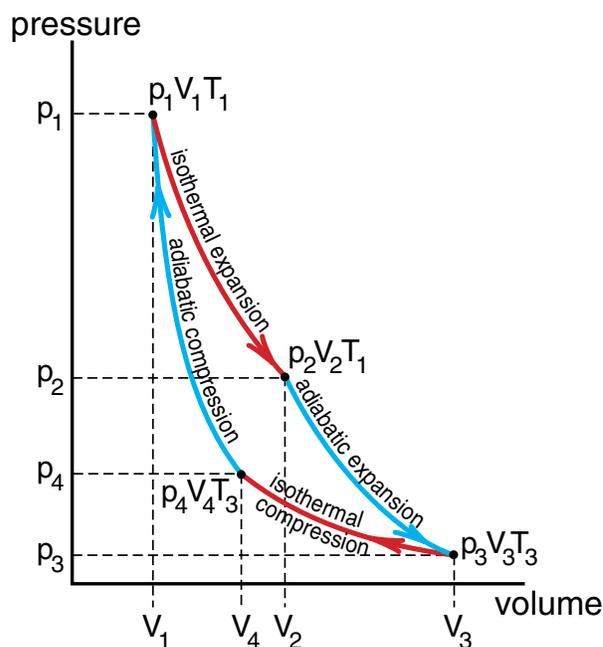
The idea for Carnot's cycle that does give a net amount of useful work is the following. Start off with the gas in the cylinder at a high temperature and let the gas expand isothermally. We will get a certain amount of work from the gas. Then rather than trying to compress the hot gas, which would use up all the work we got, cool the gas to reduce its pressure. Then isothermally compress the cool gas. It should take less work to compress the low pressure cool gas than the work we got from the high pressure hot gas. Then finish the



**Figure 10b**  
*pV diagram for an isothermal expansion followed by an adiabatic expansion.*

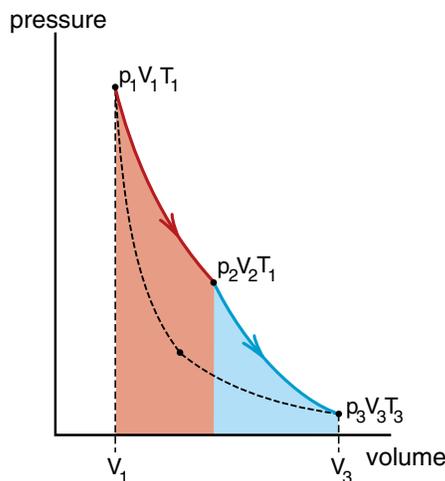
cycle by heating the cool gas back up to its original temperature. In this way you get back to the original volume and temperature (and therefore pressure) of the cylinder; you have a complete cycle, and hopefully you have gotten some useful work from the cycle.

To cool the gas, and then later heat it up again, Carnot used an adiabatic expansion and then an adiabatic compression. We can follow the steps of the Carnot cycle on the  $pV$  diagram shown in Figure (11). The gas starts out at the upper left hand corner at a high temperature  $T_1$ , volume  $V_1$ , pressure  $p_1$ . It then goes through an isothermal expansion from a volume  $V_1$  to a volume  $V_2$ , remaining at the initial temperature  $T_1$ . The hot gas is then cooled down to a low temperature  $T_3$  by an adiabatic expansion to a volume  $V_3$ . The cool, low pressure gas is then compressed isothermally to a volume  $V_4$ , where it is then heated back to a higher temperature  $T_1$  by an adiabatic compression. The volume  $V_4$  is chosen just so that the adiabatic compression will bring the temperature back to  $T_1$  when the volume gets back to  $V_1$ .

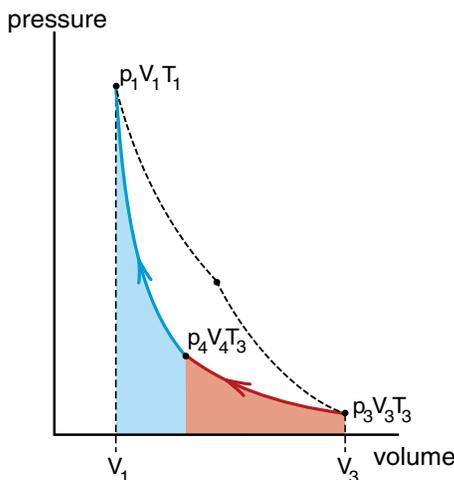


**Figure 11**  
*The Carnot Cycle. The gas first expands at a high temperature  $T_1$ . It is then cooled to a lower temperature  $T_3$  by an adiabatic expansion. Then it is compressed at this lower temperature, and finally heated back to the original temperature  $T_1$  by an adiabatic compression. We get a net amount of work from the process because it takes less work to compress the cool low pressure gas than we got from the expansion of the hot high pressure gas.*

In this set of 4 processes, we get work out of the two expansions, but put work back in during the two compressions. Did we really get some net work out? We can get the answer immediately from the  $pV$  diagram. In Figure (12a), we see the amount of work we got out of the two expansions. It is the total area under the expansion curves. In Figure (12b) we see how much work went back in during the two compressions. It is the total area under the two compression curves. Since there is more area under the expansion curves than the compression curves, we got a net amount of work out. The net work out is, in fact, just equal to the 4 sided area between the curves, seen in Figure (13).



**Figure 12a**  
The work we get out of the two expansions is equal to the area under the expansion curves.



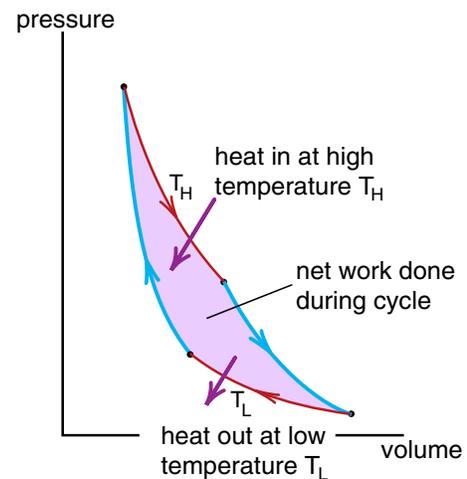
**Figure 12b**  
The work required to compress the gas back to its original volume is equal to the area under the compression curves.

## Thermal Efficiency of the Carnot Cycle

The net effect of the Carnot cycle is the following. During the isothermal expansion while the cylinder is at the high temperature  $T_H$ , a certain amount of thermal or heat energy, call it  $Q_H$ , flows into the cylinder.  $Q_H$  must be equal to the work the gas is doing during the isothermal expansion *since the gas' own thermal energy does not change at the constant temperature.* (Here, all the heat in becomes useful work.)

During the isothermal compression, while the cylinder is at the lower temperature  $T_L$ , (the gas having been cooled by the adiabatic expansion), an amount of heat  $Q_L$  is expelled from the cylinder. Heat must be expelled because we are doing work on the gas by compressing it, and *none of the energy we supply can go into the thermal energy of the gas because its temperature is constant.* (Here all the work done becomes expelled heat.)

Since no heat enters or leaves the cylinder during the adiabatic expansion or compression, all flows of heat have to take place during the isothermal processes. Thus the net effect of the process is that an amount of thermal energy or heat  $Q_H$  flows into the cylinder at the high temperature  $T_H$ , and an amount of heat  $Q_L$  flows out at the low temperature  $T_L$ , and we get a net amount of useful work  $W$  out equal to the 4-sided area seen in Figure (13). By the law of conservation of energy, the



**Figure 13**  
The net work we get out of one complete cycle is equal to the area bounded by the four sided shape that lies between the expansion and compression curves.

work  $W$  must be equal to the difference between  $Q_H$  in and  $Q_L$  out

$$W = Q_H - Q_L \quad (13)$$

We see that the Carnot engine suffers from the same problem experienced by power plants and automobile engines. They take in heat  $Q_H$  at a high temperature (produced by burning fuel) and do some useful work  $W$ , but they expel heat  $Q_L$  out into the environment. To be 100% efficient, the engine should use all of  $Q_H$  to produce work, and not expel any heat  $Q_L$ . But the Carnot cycle does not appear to work that way.

One of the advantages of the Carnot cycle is that we can calculate  $Q_H$  and  $Q_L$ , and see just how efficient the cycle is. It takes a couple of pages of calculations, which we do in the appendix, but we obtain a remarkably simple result. The ratio of the heat in,  $Q_H$ , to the heat out,  $Q_L$ , is simply equal to the ratio of the high temperature  $T_H$  to the low temperature  $T_L$ .

$$\boxed{\frac{Q_H}{Q_L} = \frac{T_H}{T_L}} \quad \text{for a Carnot cycle based on an ideal gas} \quad (14)$$

One suspects that if you do a lot of calculation involving integration, logarithms, and quantities like the specific heat ratio, and almost everything cancels to leave such a simple result as Equation 14, then there might be a deeper significance to the result than expected. Equation 14 was derived for a Carnot cycle operating with an ideal gas. It turns out that *the result is far more general* and has broad applications.

#### Exercise 4

A particular Carnot engine has an efficiency of 26.8%. That means that only 26.8% of  $Q_H$  comes out as useful work  $W$  and the rest, 73.2% is expelled at the low temperature  $T_L$ . The difference between the high and low temperature is 100 K ( $T_H - T_L = 100$  K). What are the values of  $T_H$  and  $T_L$ ? First express your answer in kelvins, then in degrees centigrade. (The answer should be familiar temperatures.)

#### Exercise 5

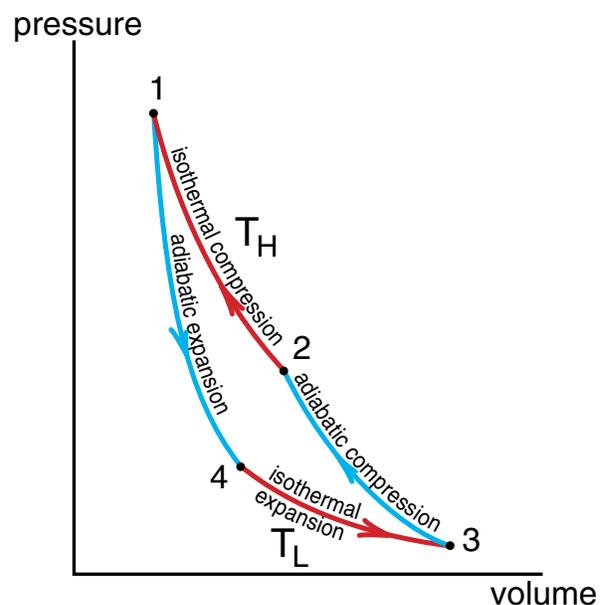
If you have a 100% efficient Carnot engine, what can you say about  $T_H$  and  $T_L$ ?

## Reversible Engines

In our discussion of the principle of relativity, it was immediately clear why we developed the light pulse clock thought experiment. You could immediately see that moving clocks should run slow, and why that was a consequence of the principle of relativity.

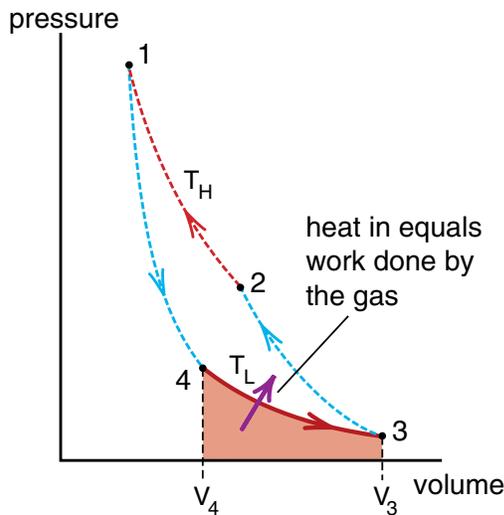
We now have a new thought experiment, the Carnot engine, which is about as idealized as our light pulse clock. We have been able to calculate the efficiency of a Carnot engine, but it is not yet obvious what that has to do either with real engines, or more importantly with the second law of thermodynamics which we are studying. It is not obvious because we have not yet discussed one crucial feature of the Carnot engine.

*The Carnot engine is explicitly designed to be reversible.* As shown in Figure (14), we could start at point 1 and go to point 4 by an adiabatic expansion of the gas. During this expansion the gas would do work but no heat is allowed to flow in. Thus the work energy would come from thermal energy and the gas would cool from  $T_H$  to  $T_L$ .

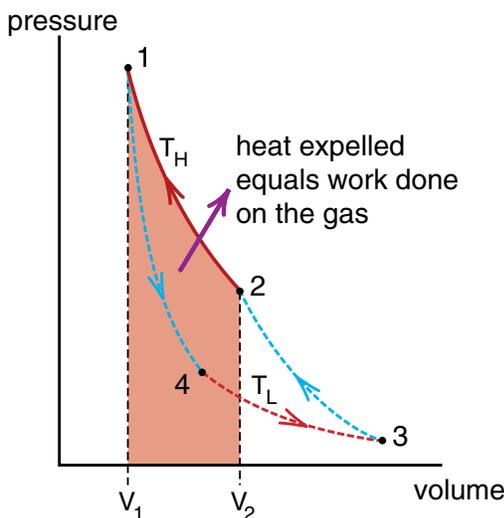


**Figure 14**  
*The Carnot cycle run backward.*

The next step of the reverse Carnot cycle is an isothermal expansion from a volume  $V_4$  to a volume  $V_3$ . During this expansion, the gas does an amount of work equal to the area under the curve as shown in Figure (15a). Since there is no change in the internal energy of a gas when the temperature of the gas remains constant, the heat flowing in equals the work done by the gas. This is the same amount of heat  $Q_L$  that flowed out when the engine ran forward.



a) During the isothermal expansion, some heat flows into the gas to supply the energy needed for the work done by the gas.



b) A lot more work is required, and a lot more heat is expelled when we compress the hot gas isothermally.

**Figure 15**  
Heat flow when the Carnot cycle runs backward. Since more heat flows out than in, some work  $W$  is required for the cycle. The net effect is that the work  $W$  pumps heat out of the gas, giving us a refrigerator.

In going from point 3 to point 2, we adiabatically compress the gas to heat it from the lower temperature  $T_L$  to the higher temperature  $T_H$ . Since the compression is adiabatic, no heat flows in or out.

In the final step from point 2 to point 1, we isothermally compress the gas back to its original volume  $V_1$ . Since the gas temperature remains constant at  $T_H$ , there is no change in thermal energy and all the work we do, shown as the area under the curve in Figure (15b), must be expelled in the form of heat flowing out of the cylinder. The amount of heat expelled is just  $Q_H$ , the amount that previously flowed in when the engine was run forward.

We have gone through the reverse cycle in detail to emphasize the fact that the engine should run equally well both ways. In the forward direction the engine takes in a larger amount of heat  $Q_H$  at the high temperature  $T_H$ , expels a smaller amount of heat  $Q_L$  at the lower temperature  $T_L$ , and produces an amount of useful work  $W$  equal to the difference  $Q_H - Q_L$ .

In the reverse process, the engine takes in a smaller amount of heat  $Q_L$  at the low temperature  $T_L$ , and expels a larger amount  $Q_H$  at the higher temperature  $T_H$ . Since more heat energy is expelled than taken in, an amount of work  $W = Q_H - Q_L$  must now be supplied to run the engine. When we have to supply work to pump out heat, we do not usually call the device an engine. The common name is a *refrigerator*. In a refrigerator, the refrigerator motor supplies the work  $W$ , a heat  $Q_L$  is sucked out of the freezer box, and a total amount of energy  $Q_L + W = Q_H$  is expelled into the higher room temperature of the kitchen. If we have a Carnot refrigerator running on an ideal gas, then the heats  $Q_L$  and  $Q_H$  are still given by Equation 14

$$\frac{Q_L}{Q_H} = \frac{T_L}{T_H} \quad (14 \text{ repeated})$$

where  $T_L$  and  $T_H$  are the temperatures on a scale starting from absolute zero such as in the kelvin scale.

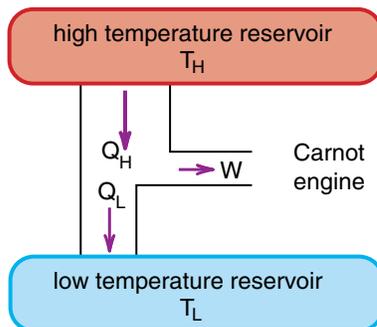
### Exercise 6

How much work must a Carnot refrigerator do to remove 1000 joules of energy from its ice chest at  $0^\circ\text{C}$  and expel the heat into a kitchen at  $27^\circ\text{C}$ ?

## ENERGY FLOW DIAGRAMS

Because of energy conservation, we can view the flow of energy in much the same way as the flow of some kind of a fluid. In particular we can construct flow diagrams for energy that look much like plumbing diagrams for water. Figure (16) is the energy flow diagram for a Carnot engine running forward. At the top and the bottom are what are called *thermal reservoirs*—large sources of heat at constant temperature (like swimming pools full of water). At the top is a thermal reservoir at the high temperature  $T_H$  (it could be kept at the high temperature by burning fuel) and at the bottom is a thermal reservoir at the low temperature  $T_L$ . For power plants, the low temperature reservoir is often the ocean or the cool water in a river. Or it may be the cooling towers like the ones pictured in photographs of the nuclear power plants at Three Mile Island.

In the energy flow diagram for the forward running Carnot engine, an amount of heat  $Q_H$  flows out of the high temperature reservoir, a smaller amount  $Q_L$  is expelled into the low temperature reservoir, and the difference comes out as useful work  $W$ . If the Carnot engine is run on an ideal gas,  $Q_H$  and  $Q_L$  are always related by  $Q_H/Q_L = T_H/T_L$ .



**Figure 16**

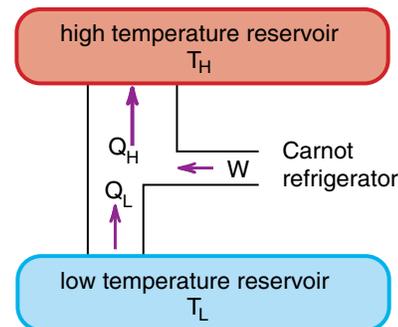
*Energy flow diagram for a Carnot engine. Since energy is conserved, we can construct a flow diagram for energy that resembles a plumbing diagram for water. In a Carnot cycle,  $Q_H$  flows out of a “thermal reservoir” at a temperature  $T_H$ . Some of this energy goes out as useful work  $W$  and the rest,  $Q_L$ , flows into the low temperature thermal reservoir at a temperature  $T_L$ .*

Figure (17) is the energy flow diagram for a Carnot refrigerator. A heat  $Q_L$  is sucked out of the low temperature reservoir, an amount of work  $W$  is supplied (by some motor), and the total energy  $Q_H = Q_L + W$  is expelled into the high temperature reservoir.

## Maximally Efficient Engines

We are now ready to relate our discussion of the Carnot cycles to the second law of thermodynamics. The statement of the second law we will use is that you cannot extract useful work from thermal energy at one temperature. (The colloquial statement of the first law of thermodynamics—conservation of energy—is that you can’t get something for nothing. The second law says that you can’t break even.)

Up until now we have had to point out that our formula for the efficiency of a Carnot engine was based on the assumption that we had an ideal gas in the cylinder. If we use the second law of thermodynamics, we can show that it is impossible to construct any engine, by any means, that is more efficient than the Carnot engine we have been discussing. This will be the main result of our thought experiment.



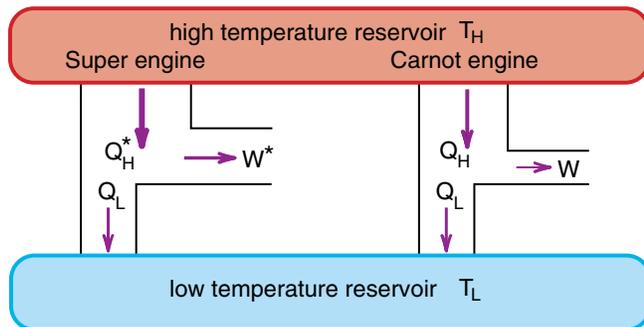
**Figure 17**

*The Carnot refrigerator is a Carnot engine run backwards. The work  $W$  plus the heat  $Q_L$  equals the heat  $Q_H$  pumped up into the high temperature reservoir.*

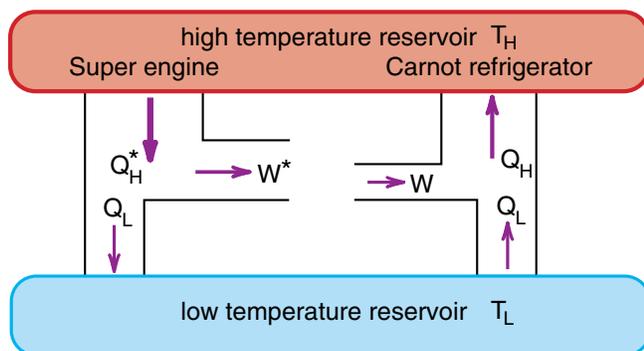
Let us suppose that you have constructed a Super engine that takes in more heat  $Q_H^*$  from the high temperature reservoir, and does more work  $W^*$ , while rejecting the same amount of heat  $Q_L$  as a Carnot engine. In the comparison of the two engines in Figure (18) you can immediately see that your Super engine is more efficient than the Carnot engine because you get more work out for the same amount of heat lost to the low temperature reservoir.

Now let us run the Carnot engine backwards as a refrigerator as shown in Figure (19). The Carnot refrigerator requires an amount of work  $W$  to suck the heat  $Q_L$  out of the low temperature reservoir and expel the total energy  $Q_H = W + Q_L$  into the high temperature reservoir.

You do not have to look at Figure (19) too long before you see that you can use some of the work  $W^*$  that your Super engine produces to run the Carnot refrigerator. Since your engine is more efficient than the Carnot cycle,  $W^* > W$  and you have some work left over.



**Figure 18**  
*Comparison of the Super engine with the Carnot engine.*

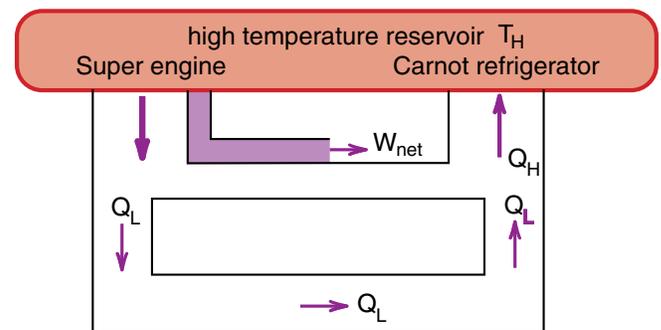


**Figure 19**  
*Now run the Carnot engine backward as a refrigerator.*

The next thing you notice is that you do not need the low temperature reservoir. All the heat expelled by your Super engine is taken in by the Carnot refrigerator. The low temperature reservoir can be replaced by a pipe and the new plumbing diagram for the combined Super engine and Carnot refrigerator is shown in Figure (20). The overall result of combining the super engine and Carnot refrigerator is that a net amount of work  $W_{net} = W^* - W$  is extracted from the high temperature reservoir. The net effect of this combination is to produce useful work from thermal energy at a single temperature, *which is a violation of the second law of thermodynamics.*

### Exercise 7

Suppose you build a Super engine that takes the same amount of heat from the high temperature reservoir as a Carnot engine, but rejects less heat  $Q_L^* < Q_L$  than a Carnot engine into the low temperature. Using energy flow diagrams show what would happen if this Super engine were connected to a Carnot refrigerator. (You would still be getting useful work from thermal energy at some temperature. From what temperature reservoir would you be getting this work?)



**Figure 20**  
*If you connect the Super engine to the Carnot refrigerator, you can eliminate the low temperature reservoir and still get some work  $W_{net}$  out. This machine extracts work from a single temperature, in violation of the second law of thermodynamics.*

## Reversibility

We have just derived the rather sweeping result that if the second law of thermodynamics is correct, you cannot construct an engine that is more efficient than a Carnot engine based on an ideal gas. You may wonder why the cycles based on an ideal gas are so special. It turns out that they are not special. What was special about the Carnot engine is that it was reversible, that it could be run backwards as a refrigerator. You can use precisely the same kind of arguments we just used to show that *all reversible engines must have precisely the same efficiency as a Carnot engine*. It is a requirement of the second law of thermodynamics.

There were two reasons we went through the detailed steps of constructing a Carnot engine using an ideal gas in a frictionless piston. The first was to provide one example of how an engine can be constructed. It is not a very practical example, commercial engines are based on different kinds of cycles. But the Carnot engine illustrates the basic features of all engines. In all engines the process must be repetitive, at least two temperatures must be involved, and only some of the heat extracted from the high temperature reservoir can be converted to useful work. Some heat must be expelled at a lower temperature.

While all reversible engines have the same efficiency, we have to work out at least one example to find out what that efficiency is. You might as well choose the simplest possible example, and the Carnot cycle using an ideal gas is about as simple as they get. Because of the second law of thermodynamics, you know that even though you are working out a very special example, the answer  $Q_H/Q_L = T_H/T_L$  applies to all reversible engines operating between two temperature reservoirs. This is quite a powerful result from the few pages of calculations in the appendix.

## APPLICATIONS OF THE SECOND LAW

During the oil embargo in the middle 1970s, there was a sudden appreciation of the consequences of the second law of thermodynamics, for it finally became clear that we had to use energy efficiently. Since that time there has been a growing awareness that there is a cost to producing energy that considerably exceeds what we pay for it. Burning oil and coal depletes natural limited resources and adds carbon dioxide to the atmosphere which may contribute to global climate changes. Nuclear reactors, which were so promising in the 1950s, pose unexpected safety problems, both now as in the example of Chernobyl, and in the very distant future when we try to deal with the storage of spent reactor parts. Hydroelectric power floods land that may have other important uses, and can damage the agricultural resources of an area as in the case of the Aswan Dam on the Nile River. More efficient use of energy from the sun is a promising idea, but technology has not evolved to the point where solar energy can supply much of our needs. What we have learned is that, for now, the first step is to use energy as efficiently as possible, and in doing this, the second law of thermodynamics has to be our guide.

During the 1950s and 60s, one of the buzz words for modern living was the *all electric house*. These houses were heated electrically, electric heaters being easy and inexpensive to install and convenient to use. And it also represents one of the most stupid ways possible to use energy. In terms of a heat cycle, it represents the 100% conversion of work energy into thermal energy, what we would have called in the last section, a 0% efficient engine. There are better ways of using electric power than converting it all into heat.

You can see where the waste of energy comes in when you think of the processes involved in producing electric power. In an electric power plant, the first step is to heat some liquid or gas to a high temperature by burning fuel. In a common type of coal or oil fired power plant, mercury vapor is heated to temperatures of 600 to 700 degrees centigrade. The mercury vapor is then used to run a mercury vapor turbine which cools the mercury vapor to around 200° C. This cooler mercury vapor then heats steam which goes through a steam turbine to a steam condenser at temperatures

around 100° C. In a nuclear reactor, the first step is often to heat liquid sodium by having it flow through pipes that pass through the reactor. The hot sodium can then be used to heat mercury vapor which runs turbines similar to those in a coal fired plant. The turbines are attached to generators which produce the electric power.

Even though there are many stages, and dangerous and exotic materials used in power stations, we can estimate the maximum possible efficiency of a power plant simply by knowing the highest temperature  $T_H$  of the boiler, and the lowest temperature  $T_L$  of the condenser. If the power plant were a reversible cycle running between these two temperatures, it would take in an amount of heat  $Q_H$  at the high temperature and reject an amount of heat  $Q_L$  at the low temperature, where  $Q_H$  and  $Q_L$  are related by  $Q_H/Q_L = T_H/T_L$  (Eq. 14). The work we got out would be

$$W = Q_H - Q_L \quad \begin{array}{l} \text{amount of work from} \\ \text{a reversible cycle} \end{array} \quad (15)$$

We would naturally define the efficiency of the cycle as the ratio of the work out to the heat energy in

$$\text{efficiency} = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} \quad (16)$$

If we solve Equation 14 for  $Q_L$

$$Q_L = Q_H \frac{T_L}{T_H}$$

and use this in Equation 16, we get

$$\text{efficiency} = \frac{Q_H - Q_L}{Q_H} = \frac{Q_H(1 - T_L/T_H)}{Q_H}$$

$$\text{efficiency} = \frac{T_H - T_L}{T_H} \quad \begin{array}{l} \text{efficiency of a} \\ \text{reversible cycle} \end{array} \quad (17)$$

Since by the second law of thermodynamics no process can be more efficient than a reversible cycle, Equation 17 represents the maximum possible efficiency of a power plant.

The important thing to remember about Equation 17 is that the temperatures  $T_H$  and  $T_L$  start from absolute zero. The only way we could get a completely efficient engine or power plant would be to have the low

temperature at absolute zero, which is not only impossible to achieve but even difficult to approach. You can see from this equation why many power plants are located on the shore of an ocean or on the bank of a large river. These bodies are capable of soaking up large quantities of heat at relatively low temperatures. If an ocean or river is not available, the power plant will have large cooling towers to condense steam. Condensing steam at atmospheric pressure provides a low temperature of  $T_L = 100^\circ \text{C}$  or 373 K.

Equation 15 also tells you why power plants run their boilers as hot as possible, using exotic substances like mercury vapor or liquid sodium. Here one of the limiting factors is how high a temperature turbine blades can handle without weakening. Temperatures as high as 450° C or around 720 K are about the limit of current technology. Thus we can estimate the maximum efficiency of power plants simply by knowing how high a temperature turbine blades can withstand, and that the plant uses water for cooling. You do not have to know the details of what kind of fuel is used, what kind of exotic materials are involved, or how turbines and electric generators work, as long as they are efficient. Using the numbers  $T_H = 720 \text{ k}$ ,  $T_L = 373 \text{ k}$  we find that the maximum efficiency is about

$$\begin{aligned} \text{maximum efficiency} &= \frac{T_H - T_L}{T_H} = \frac{720 - 373}{720} \\ &= .48 \end{aligned} \quad (18)$$

Thus about 50% represents a theoretical upper limit to the efficiency of power plants using current technology. In practice, well designed power plants reach only about 33% efficiency due to small inefficiencies in the many steps involved.

You can now see why the all electric house was such a bad idea. An electric power plant consumes three times as much fuel energy as it produces electric energy. Then the electric heater in the all electric house turns this electric energy back into thermal energy. If the house had a modern oil furnace, somewhere in the order of 85% of the full energy can go into heating the house and hot water. This is far better than the 33% efficiency from heating directly by electricity.

## Electric Cars

One of the hot items in the news these days is the electric car. It is often touted as the pollution free solution to our transportation problems. There are advantages to electric cars, but not as great an advantage as some new stories indicate.

When you plug in your electric car to charge batteries, you are not eliminating the pollution associated with producing useful energy. You are just moving the pollution from the car to the power plant, which may, however, be a good thing to do. A gasoline car may produce more harmful pollutants than a power station, and car pollutants tend to concentrate in places where people live creating smog in most major cities on the earth. (Some power plants also create obnoxious smog, like the coal fired plants near the Grand Canyon that are harming some of the most beautiful scenery in the country.)

In addition to moving and perhaps improving the nature of pollution, power plants have an additional advantage over car engines—they are more efficient. Car engines cannot handle as high a temperature as a power plant, and the temperature of the exhaust from a car is not as low as condensing steam or ocean water. Car engines seldom have an efficiency as high as 20%; in general, they are less than half as efficient as a power plant. Thus there will be a gain in efficiency in the use of fuel when electric cars come into more common use.

(One way electric cars have for increasing their efficiency is to replace brakes with generators. When going down a hill, instead of breaking and dissipating energy by heating the brake shoes, the gravitational potential energy being released is turned into electric energy by the generators attached to the wheels. This energy is then stored as chemical energy in the batteries as the batteries are recharged.)

## The Heat Pump

There is an intelligent way to heat a house electrically, and that is by using a heat pump. The idea is to use the electric energy to pump heat from the colder outside temperature to the warmer inside temperature. Pumping heat from a cooler temperature to a warmer temperature is precisely what a refrigerator does, while taking heat from the freezer chest and exhausting it into the kitchen. The heat pump takes heat from the cooler outside and exhausts it into the house.

As we saw in our discussion, it takes work to pump heat from a cooler to a higher temperature. The ratio of the heat  $Q_L$  taken in at the low temperature, to the heat  $Q_H$  expelled at the higher temperature, is  $Q_H/Q_L = T_H/T_L$  for a maximally efficient refrigerator. The amount of work  $W$  required is  $W = Q_H - Q_L$ . The efficiency of this process is the ratio of the amount of heat delivered to the work required.

$$\begin{aligned} \text{efficiency of} \\ \text{heat pump} &= \frac{Q_H}{W} = \frac{Q_H}{Q_H - Q_L} \\ &= \frac{T_H}{T_H - T_L} \end{aligned} \quad (19)$$

where the last step in Equation 19 used  $Q_L = Q_H T_L / T_H$ .

---

### Exercise 8

Derive the last formula in Equation 19.

---

When the temperature difference  $T_H - T_L$  is small, we can get very high efficiencies, i.e., we can pump a lot of heat using little work. In the worst case, where  $T_L = 0$  and we are trying to suck heat from absolute zero, the efficiency of a heat pump is 1—heat delivered equals the work put in—and the heat pump is acting like a resistance heater.

To illustrate the use of a heat pump let us assume that it is freezing outside ( $T_L = 0^\circ\text{C} = 273\text{K}$ ) and you want the inside temperature to be  $27^\circ\text{C} = 300\text{K}$ . Then a heat pump could have an efficiency of

$$\begin{aligned} \text{efficiency of heat} \\ \text{pump running from} \\ 0^\circ\text{C to } 27^\circ\text{C} &= \frac{T_H}{T_H - T_L} \\ &= \frac{300\text{ k}}{300\text{ k} - 273\text{ k}} \\ &= 11.1 \end{aligned}$$

In other words, as far as the second law of thermodynamics is concerned, we should be able to pump eleven times as much heat into a house, when it is just freezing outside, as the amount of electrical energy required to pump the heat. Even if the electrical energy is produced at only 30% efficiency, we should still get  $.30 \times 11.1 = 3.3$  times as much heat into the house as by burning the fuel in the house at 100% conversion of fuel energy into heat.

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### Exercise 9

This so-called “heat of fusion” of water is 333kJ/kg. What that means is that when a kilogram (1 liter) of water freezes (going from  $0^\circ\text{C}$  water to  $0^\circ\text{C}$  ice), 333 kilojoules of heat are released. Thus to freeze a liter of  $0^\circ\text{C}$  water in your refrigerator, the refrigerator motor has to pump  $333 \times 10^3$  joules of heat energy out of the refrigerator into the kitchen. The point of the problem is to estimate how powerful a refrigerator motor is required if you want to be able to freeze a liter of water in 10 minutes.

Assume that the heat is being removed at a temperature of  $0^\circ\text{C}$  and being expelled into a kitchen whose temperature is  $30^\circ\text{C}$ , and that the refrigerator equipment is 100% efficient. (We will account for a lack of efficiency at the end of this problem.)

In the United States, the power of motors is generally given in “horsepower”, a familiar but archaic unit. The conversion factor is 1 horsepower = 746 watts, and a power of 1 watt is 1 joule per second.

Calculate the horsepower required, then double the answer to account for lack of efficiency. (Answer: 0.16 horsepower.)

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### Exercise 10

Here is a problem that should give you some practice with the concepts of efficiency. You have the choice of buying a furnace that converts heat energy of oil into heat in the house with 85% efficiency. I.e., 85% of the heat energy of the oil goes into the house, and 15% goes up the chimney. Or you can buy a heat pump which is half as efficient as a Carnot refrigerator. (This is a more realistic estimate of the current technology of refrigeration equipment.) At very low temperatures outside, heat pumps are not as efficient, and burning oil in your own furnace is more efficient. But if it does not get too cold outside, heat pumps are more efficient. At what outside temperature will the heat pump and the oil furnace have the same efficiency? Assume that the electric energy you use is produced by a power plant that is 30% efficient. (Answer:  $-26^\circ\text{C}$ .)

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## The Internal Combustion Engine

We finish this section on practical applications with a brief discussion of the internal combustion engine. The main point is to give an example of an engine that runs on a cycle that is different from a Carnot cycle. It is more difficult to apply the second law of thermodynamics to an internal combustion engine because it does not take heat in or expel heat at constant temperatures like the Carnot engine, but we can still analyze the work we get out using a  $pV$  diagram.

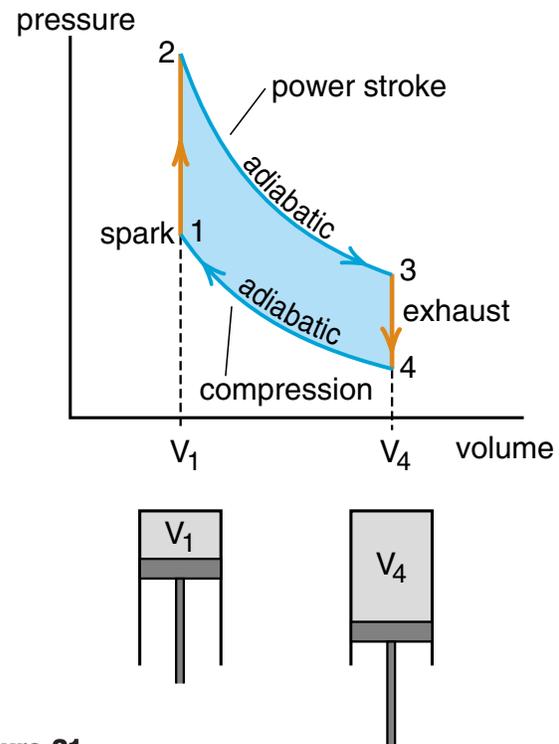
The  $pV$  diagram for an internal combustion engine is shown in Figure (21). At position 1, a fuel and air mixture have been compressed to a small volume  $V_1$  by the piston which is at the top of the cylinder. If it is a gasoline engine, the fuel air mixture is ignited by a spark from a sparkplug. If it is a diesel engine, the mixture of diesel fuel and air have been heated to the point of combustion by the adiabatic compression from point 4 to point 1 that has just taken place. One of the advantages of a diesel engine is that an electrical system to produce the spark is not needed. This is particularly important for boat engines where electric systems give all sorts of problems. (We said this was a section on practical applications.)

After ignition, the pressure and temperature of the gas rise rapidly to  $p_2, T_2$  before the piston has had a chance to move. Thus the volume remains at  $V_1$  and the  $pV$  curve goes straight up to point 2. The heated gas then expands adiabatically, and cools some, driving the piston down to the bottom of the cylinder. This is the stroke from which we get work from the engine.

We now have a cylinder full of hot burned exhaust gases. In a 4 cycle engine, a valve at the top of the cylinder is opened, and a piston is allowed to rise, pushing the hot exhaust gases out into the exhaust pipes. Not much work is required to do this. This is the part of the cycle where (relatively) low temperature thermal energy is exhausted to the environment.

While the piston goes back down, the valves are set so that a mixture of air and fuel are sucked into the piston. When the cylinder is at the bottom of the piston, we have a cool, low pressure fuel air mixture filling the full volume  $V_4$ . We are now at the position labeled (4) in Figure (21). It took two strokes (up and down) of the piston to go from position 3 to position 4.

In the final stroke, the valves are shut and the rising piston adiabatically compresses the gas back to the starting point  $p_1, V_1, T_1$ . While the increase in temperature during this compression is what is needed to ignite the diesel fuel, you do not want the temperature to rise enough to ignite the air gasoline mixture in a gasoline engine. This can sometimes happen in a gasoline engine, causing a knock in the engine, or sometimes allowing the engine to run for a while after you have shut off the ignition key and stopped the spark plug from functioning.



**Figure 21**

*$PV$  diagram for an internal combustion engine. When the piston is all the way up in the cylinder the volume is  $V_1$ . When it is all the way down, the volume has increased to  $V_2$ .*

## ENTROPY

The second law of thermodynamics provided us with the remarkable result that the efficiency of all reversible engines is the same. Detailed calculation of this efficiency using a Carnot engine based on an ideal gas gave us a surprisingly simple formula for this efficiency, namely  $Q_H/Q_L = T_H/T_L$ . Our preceding examples involving car engines, power plants, refrigerators and heat pumps illustrate how important this simple relationship is to mankind.

When you do a calculation and a lot of stuff cancels out, it suggests that your result may have a simpler interpretation than you originally expected. This turns out to be true for our calculations of the heat flow in a Carnot engine. To get a new perspective on our equation for heat flow, let us write the equation in the form

$$\frac{Q_H}{T_H} = \frac{Q_L}{T_L} \quad (20)$$

In this form the equation for heat flow is beginning to look like a conservation law for the quantity  $Q/T$ . During the isothermal expansion, an amount  $Q_H/T_H$  of this quantity flowed into the piston. During the isothermal compression,  $Q_L/T_L$  flowed out. We find that if the engine is reversible, the amount of  $Q/T$  that flowed in is equal to the amount of  $Q/T$  that flowed out. The net effect is that there was no change in  $Q/T$  during the cycle.

To get a better insight into what this quantity  $Q/T$  may be, consider a nonreversible engine operating between  $T_H$  and  $T_L$ , an engine that would be less efficient than the Carnot engine. Assume that the less efficient engine and the Carnot engine both take in the same amount of heat  $Q_H$  at the high temperature  $T_H$ . Then the less efficient engine must do less work and expel more heat at the low temperature  $T_L$ . Thus  $Q_L$  for the less efficient engine is bigger than  $Q_L$  for the Carnot engine. Since  $Q_L/T_L = Q_H/T_H$  for the Carnot engine,  $Q_L/T_L$  must be greater than  $Q_H/T_H$  for the less efficient engine

$$\frac{Q_L}{T_L} > \frac{Q_H}{T_H} \quad \text{for an engine that is less efficient than a Carnot engine} \quad (21)$$

We see that the inefficient engine expelled more  $Q/T$  than it took in. The inefficient, non reversible, engine creates  $Q/T$  while reversible engines do not.

As we have done throughout the course, whenever we encounter a quantity that is conserved, or sometimes conserved, we give it a name. We did this for linear momentum, angular momentum, and energy. Now we have a quantity  $Q/T$  that is unchanged by reversible engines, but created or increased by irreversible inefficient ones. We are on the verge of defining the quantity physicists call *entropy*. We say on the verge of defining entropy, because  $Q/T$  is not entropy itself; it represents the *change in entropy*. We can say that when the gas expanded, the entropy of the gas *increased* by  $Q_H/T_H$ . And when the gas was compressed, the entropy decreased by  $Q_L/T_L$ .

For a reversible engine there is no net change in entropy as we go around the cycle. But for an irreversible, inefficient engine, more entropy comes out than goes in during each cycle. The net effect of an inefficient engine is to create entropy.

What is this thing called entropy that is created by inefficient irreversible engine? Consider the most inefficient process we can imagine—the electric heater which converts useful work in the form of electrical energy into heat. From one point of view, the device does nothing but create entropy. If the heater is at a temperature  $T$ , and the electric power into the heater is  $W$  watts, all this energy is converted to heat and entropy is produced at a rate of  $W/T$  in units of entropy per second. (Surprisingly, there is no standard name for a unit of entropy. The units of  $Q/T$  are of course joules/kelvin, the same as Boltzman's constant.)

The process of converting energy in the form of useful work into the random thermal energy of molecules can be viewed as the process of turning order into disorder. Creating entropy seems to be related to creating disorder. But the surprising thing is that we have an explicit formula  $Q/T$  for changes in entropy. How could it be possible to measure disorder, to have an explicit formula for changes in disorder? This question baffled physicists for many generations.

Ludwig Boltzman proposed that entropy was related to the number of ways that a system could be arranged. Suppose, for example, you go into a woodworking shop and there are a lot of nails on the wall with tools hanging on them. In one particular woodworking shop you find that the carpenter has drawn an outline of the tool on the wall behind the nail. You enter her shop you find that the tool hanging from each nail exactly matches the outline behind it. Here we have perfect order, every tool is in its place and there is one and only one way the tools can be arranged. We would say that, as far as locating tools is concerned the shop is in perfect order, it has no disorder or entropy.

On closer inspection, we find that the carpenter has two saws with identical outlines, a crosscut saw and a rip saw. We also see that the nails are numbered, and see the cross cut saw on nail 23 and the rip saw on nail 24. A week later when we come back, the cross cut is on nail 24 and the rip saw on 23. Thus we find that her system is not completely orderly, for there are two different ways the saws can be placed. This way of organizing tools has some entropy.

A month later we come back to the shop and find that another carpenter has taken over and painted the walls. We find that there are still 25 nails and 25 tools, but now there is no way to tell which tool belongs on which nail. Now there are many, many ways to hang up the tools and the system is quite disordered. We have the feeling that this organization, or lack of organization, of the tools has quite high entropy.

To put a numerical value on how disorganized the carpenter shop is, we go to a mathematician who tells us that there are  $N!$  ways to hang  $N$  tools on  $N$  nails. Thus there are  $25! = 1.55 \times 10^{25}$  different ways the 25 tools can be hung on the 25 nails. We could use this number as a measure of the disorder of the system, but the number is very large and increases very rapidly with the number of tools. If, for example, there were 50 tools hung on 50 nails, there would be  $3.04 \times 10^{64}$  different ways of hanging them. Such large numbers are not convenient to work with.

When working with large numbers, it is easier to deal with the logarithm of the number than the number itself. There are approximately  $10^{51}$  protons in the earth. The log to the base 10 of this number is 51 and the natural logarithm,  $\ln(10^{51})$ , is 2.3 times bigger or 117. In discussing the number of protons in the earth, the number 117 is easier to work with than  $10^{51}$ , particularly if you have to write out all the zeros.

If we describe the disorder of our tool hanging system in terms of the logarithm of the number of ways the tools can be hung, we get a much more reasonable set of numbers, as shown in Table 1.

Setup	Number of ways to arrange tools	Logarithm of the number of ways
all tools have unique positions	1	0
two saws can be interchanged	2	.7
25 tools on unmarked nails	$1.5 \times 10^{25}$	58
50 tools on unmarked nails	$3.0 \times 10^{65}$	148

**TABLE 1**

The table starts off well. If there is a unique arrangement of the tools, only one way to arrange them, the logarithm of the number of ways is 0. This is consistent with our idea that there is no disorder. As the number of tools on unmarked nails increases, the number of ways they can be arranged increases at an enormous pace, but the logarithm increases at a reasonable rate, approximately as fast as the number of tools and nails. This logarithm provides a reasonable measure of the disorder of the system.

We could define the entropy of the tool hanging system as the logarithm of the number of ways the tools could be hung. One problem, however, is that this definition of entropy would have different dimensions than the definition introduced earlier in our discussions of engines. There changes in entropy, for example  $Q_H/T_H$ , had dimensions of joules/kelvin, while our logarithm is dimensionless. However, this problem could be fixed by multiplying our dimensionless logarithm by some fundamental constant that has the dimensions of joules/kelvin. That constant, of course, is Boltzman's constant  $k$ , where  $k = 1.38 \times 10^{-23}$  joules/kelvin. We could therefore take as the formula for the entropy (call it  $S$ ) of our tool hanging system as

$$\boxed{S = k \ln(n)} \quad \begin{array}{l} \text{entropy of our tool} \\ \text{hanging system} \end{array} \quad (22)$$

where  $n$  is the number of ways the tools can be hung. Multiplying our logarithm by  $k$  gives us the correct dimensions, but very small values when applied to as few items as 25 or 50 tools.

Equation 22 appears on Boltzman's tombstone as a memorial to his main accomplishment in life. Boltzman believed that Equation 22 should be true in general. That, for example, it should apply to the atoms of the gas inside the cylinder of our heat engine. When heat flows into the cylinder and the entropy increases by an amount  $Q_H/T_H$ , the number of ways that the atoms could be arranged should also increase, by an amount we can easily calculate using Equation 22. Explicitly, if before the heat flowed in there were  $n_{\text{old}}$  ways the atoms could be arranged, and after the heat flowed in  $n_{\text{new}}$  ways, then Equation 22 gives

$$\frac{\text{change in entropy}}{\text{entropy}} = k \ln(n_{\text{new}}) - k \ln(n_{\text{old}}) = \frac{Q_H}{T_H}$$

Since  $\ln(n_{\text{new}}) - \ln(n_{\text{old}}) = \ln(n_{\text{new}}/n_{\text{old}})$ , we get

$$\ln\left(\frac{n_{\text{new}}}{n_{\text{old}}}\right) = \frac{Q_H}{kT_H} \quad (23)$$

Taking the exponent of both sides of Equation 16, using the fact that  $e^{\ln(x)} = x$ , we get

$$\frac{n_{\text{new}}}{n_{\text{old}}} = e^{Q_H/kT_H} \quad (24)$$

Thus Boltzman's equation gives us an explicit formula for the fractional increase in the number of ways the atoms in the gas atoms in the cylinder can be arranged.

Boltzman committed suicide in 1906, despondent over the lack of acceptance of his work on the statistical theory of matter, of which Equation 22 is the cornerstone. And in 1906 it is not too surprising that physicists would have difficulty dealing with Boltzman's equation. What is the meaning of the number of ways you can arrange gas atoms in a cylinder? From a Newtonian perspective, there are an infinite number of ways to place just one atom in a cylinder. You can count them by moving the atoms an infinitesimal distance in any direction. So how could it be that  $10^{24}$  atoms in a cylinder have only a finite way in which they can be arranged?

This question could not be satisfactorily answered in 1906, the answer did not come until 1925 with the discovery of quantum mechanics. In a quantum picture, an atom in a cylinder has only certain energy levels, an idea we will discuss later in Chapter 35. Even when you have  $10^{24}$  atoms in the cylinder, the whole system has only certain allowed energy levels. At low temperatures the gas does not have enough thermal energy to occupy very many of the levels. As a result the number of ways the atoms can be arranged is limited and the entropy is low. As the temperature is increased, the gas atoms can occupy more levels, can be arranged in a greater number of ways, and therefore have a greater entropy.

The concept of entropy provides a new definition of absolute zero. A system of particles is at absolute zero when it has zero entropy, when it has one uniquely defined state. We mentioned earlier that quantum mechanics requires that a confined particle has some kinetic energy. All the kinetic energy cannot be removed by cooling. This gives rise to the so-called *zero point energy* that keeps helium a liquid even at absolute zero. However, a bucket of liquid helium can be at absolute zero as long as it is in a single unique quantum state, even though the atoms have zero point kinetic energy.

In our discussion of temperature in the last chapter, we used the ideal gas thermometer for our experimental definition of temperature. We pointed out, however, that this definition would begin to fail as we approached very low temperatures near absolute zero. At these temperatures we need a new definition which agrees with the ideal gas thermometer definition at higher temperatures. The new definition which is used by the physics community, is based on the efficiency of a reversible engine or heat cycle. You can measure the ratio of two temperatures  $T_H$  and  $T_C$ , by measuring the heats  $Q_H$  and  $Q_C$  that enter and leave the cycle, and use the formula  $T_H/T_C = Q_H/Q_C$ . Since this formula is based on the idea that a reversible cycle creates no entropy ( $Q_H/T_H = Q_C/T_C$ ), we can see that the concept of entropy forms the basis for the definition of temperature.

### The Direction of Time

We began the chapter with a discussion of a demonstration that looked funny. We set the strobe so that the water drops appeared to rise from the plate in the bucket and enter the hose. Before our discussion of the second law of thermodynamics, we could not find any law of physics that this backward process appeared to violate. Now we can see that the launching of the drops from the plate is a direct contradiction of the second law. In that process, heat energy in the bucket converts itself at one temperature into pure useful work that launches the drop.

When you run a moving picture of some action backwards, effectively reversing the direction of time, in most cases the only law of physics that is violated is the second law of thermodynamics. The only thing that appears to go wrong is that disordered systems appear to organize themselves on their own. Scrambled eggs turn into an egg with a whole yoke just by the flick of a fork. Divers pop out of swimming pools propelled, like the drops in our demonstration, by the heat energy in the pool (see movie). All these funny looking things require remarkable coincidences which in real life do not happen.

For a while there was a debate among physicists as to whether the second law of thermodynamics was the only law in nature that could be used to distinguish between time running forward and time running backward.

When you study processes like the decay of one kind of elementary particle into another, the situation is so simple that the concepts of entropy and the second law of thermodynamics do not enter into the analysis. In these cases you can truly study whether nature is symmetric with the respect to the reversal of time. If you take a moving picture of a particle decay, and run the movie backwards, will you see a process that can actually happen? For example if a muon decays into an electron and a neutrino, as happened in our muon lifetime experiment, running that moving picture backward would have neutrinos coming in, colliding with an electron, creating a muon. Thus, if the basic laws of physics are truly symmetric to the reversal of time, it should be possible for a neutrino and an electron to collide and create a muon. This process is observed.

In 1964 Val Fitch and James Cronin discovered an elementary particle process which indicated that nature was not symmetric in time. Fitch found a violation of this symmetry in the decay of a particle called the neutral  $K$  meson. For this discovery, Fitch was awarded the Nobel prize in 1980. Since the so-called “weak interaction” is responsible for the decay of  $K$  mesons, the weak interaction is not fully symmetric to the reversal of time. The second law of thermodynamics is not the only law of physics that knows which way time goes.



#### Movie

*Time reversed motion picture of dive*

## APPENDIX: CALCULATION OF THE EFFICIENCY OF A CARNOT CYCLE

The second law of thermodynamics tells us that the efficiency of all reversible heat engines is the same. Thus if we can calculate the efficiency of any one engine, we have the results for all. Since we have based so much of our discussion on the Carnot engine running on an ideal gas, we will calculate the efficiency of that engine.

To calculate the efficiency of the ideal gas Carnot engine, we need to calculate the amount of work we get out of (or put into) isothermal and adiabatic expansions. With these results, we can then calculate the net amount of work we get out of one cycle and then the efficiency of the engine. To simplify the formulas, we will assume that our engine is running on one mole of an ideal gas.

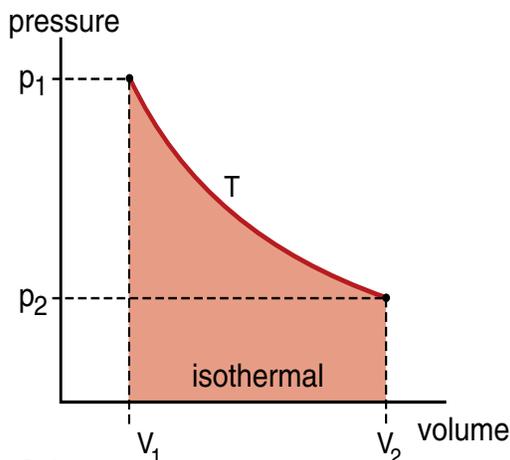
### Isothermal Expansion

Suppose we have a gas at an initial volume  $V_1$ , pressure  $p_1$ , temperature  $T$ , and expand it isothermally to a volume  $V_2$ , pressure  $p_2$ , and of course the same temperature  $T$ .

The P-V diagram for the process is shown in Figure (A-1). The curve is determined by the ideal gas law, which for 1 mole of an ideal gas is

$$pV = RT \quad (\text{A-1})$$

The work we get out of the expansion is the shaded area under the curve, which is the integral of the pressure curve from  $V_1$  to  $V_2$ .



**Figure A-1**  
*Isothermal expansion.*

Using Equation 1, we get

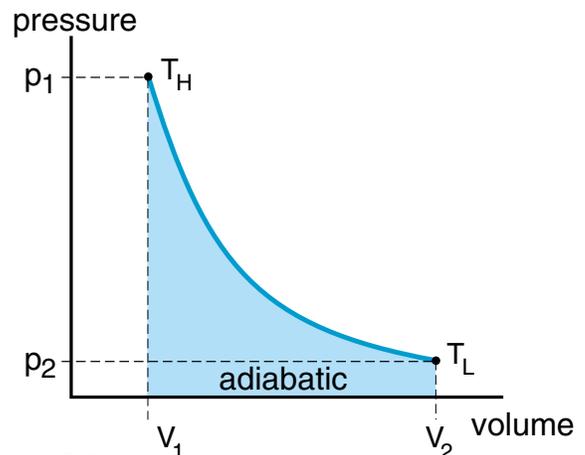
$$\begin{aligned} W &= \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \frac{RT}{V} dV \\ &= RT \int_{V_1}^{V_2} \frac{dV}{V} = RT \ln V \Big|_{V_1}^{V_2} \\ &= RT \left[ \ln(V_2) - \ln(V_1) \right] \quad (\text{A-2}) \\ &= RT \ln \left( \frac{V_2}{V_1} \right) \end{aligned}$$

Thus the work we get out is  $RT$  times the logarithm of the ratio of the volumes.

### Adiabatic Expansion

It is a bit trickier to calculate the amount of work we get out of an adiabatic expansion. If we start with a mole of ideal gas at a volume  $V_1$ , pressure  $p_1$ , and temperature  $T_H$ , the gas will cool as it expands because the gas does work and we are not letting any heat in. Thus when the gas gets to the volume  $V_2$ , at a pressure  $p_2$ , its temperature  $T_C$  will be cooler than its initial temperature  $T_H$ .

The pV diagram for the adiabatic expansion is shown in Figure (A-2). To get an equation for the adiabatic expansion curve shown, let us assume that we change the volume of the gas by an infinitesimal amount  $\Delta V$ . With this volume change, there will be an infinitesimal pressure drop  $\Delta p$ , and an infinitesimal temperature



**Figure A-2**  
*Adiabatic expansion.*

drop  $\Delta T$ . We can find the relationship between these small changes by differentiating the ideal gas equations. Starting with

$$pv = RT$$

and differentiating we get

$$p\Delta V + (\Delta p)V = R\Delta T \quad (\text{A-3})$$

We now have to introduce the idea that the expansion is taking place adiabatically, i.e., that no heat is entering. That means that the work  $p\Delta V$  done by the gas during the infinitesimal expansion  $\Delta V$  must all have come from thermal energy. But the decrease in thermal energy is  $C_V\Delta T$ . Thus we have from conservation of energy

$$p\Delta V + C_V\Delta T = 0$$

or

$$\Delta T = \frac{-p\Delta V}{C_V} \quad (\text{A-4})$$

The  $-$  (minus) sign tells us that the temperature drops as work energy is removed.

Using Equation A-4 for  $\Delta T$  in Equation A-3 gives

$$p\Delta V + \Delta pV = R\left(\frac{-p\Delta V}{C_V}\right)$$

Combining the  $p\Delta V$  terms gives

$$p\Delta V\left(1 + \frac{R}{C_V}\right) + \Delta pV = 0$$

$$p\Delta V\left(\frac{C_V + R}{C_V}\right) + \Delta pV = 0 \quad (\text{A-5})$$

Earlier in the chapter, in Equation 9, we found that for an ideal gas,  $C_V$  and  $C_p$  were related by  $C_p = C_V + R$ . Thus Equation A-5 simplifies to

$$p\Delta V\left(\frac{C_p}{C_V}\right) + \Delta pV = 0 \quad (\text{A-6})$$

It is standard notation to define the ratio of specific heats by the constant  $\gamma$

$$\frac{C_p}{C_V} \equiv \gamma \quad (\text{A-7})$$

thus Equation A-6 can be written in the more compact form

$$\gamma p\Delta V + \Delta pV = 0 \quad (\text{A-8})$$

The next few steps will look like they were extracted from a calculus text. They may or may not be too familiar, but you should be able to follow them step-by-step.

First we will replace  $\Delta V$  and  $\Delta p$  by  $dV$  and  $dp$  to indicate that we are working with calculus differentials. Then dividing through by the product  $pV$  gives

$$\gamma \frac{dV}{V} + \frac{dp}{p} = 0 \quad (\text{A-9})$$

Doing an indefinite integration of this equation gives

$$\gamma \ln(V) + \ln(p) = \text{const} \quad (\text{A-10})$$

The  $\gamma$  can be taken inside the logarithm to give

$$\ln(V^\gamma) + \ln(p) = \text{const} \quad (\text{A-11})$$

Next exponentiate both sides of Equation A-11 to get

$$e^{\ln(V^\gamma) + \ln(p)} = e^{\text{const}} = \text{another const} \quad (\text{A-12})$$

where  $e^{\text{const}}$  is itself a constant. Now use the fact that  $e^{a+b} = e^a e^b$  to get

$$e^{\ln(V^\gamma)} e^{\ln(p)} = \text{const} \quad (\text{A-13})$$

Finally use  $e^{\ln(x)} = x$  to get the final result

$$\boxed{pV^\gamma = \text{const}} \quad \begin{array}{l} \text{adiabatic} \\ \text{expansion} \end{array} \quad (\text{A-14})$$

Equation A-14 is the formula for the adiabatic curve seen in Figure (A-2). During an isothermal expansion, we have  $pV = RT$  where  $T$  is a constant. Thus if we compare the formulas for isothermal and adiabatic expansions, we have for any ideal gas

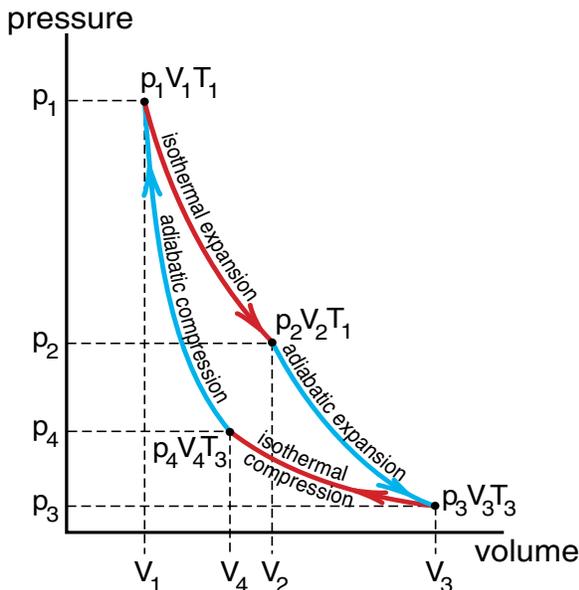
$pV = \text{const}$ <i>isothermal expansion</i>	(A-15)
$pV^\gamma = \text{const}$ <i>adiabatic expansion</i>	
$\gamma = C_p/C_V$ <i>ratio of specific heats</i>	
$C_p = C_V + R$	

### The Carnot Cycle

We now have the pieces in place to calculate the efficiency of a Carnot cycle running on one mole of an ideal gas. The cycle is shown in Figure (11) repeated here as Figure (A-3).

During the isothermal expansion from point 1 to 2, the amount of heat that flows into our mole of gas is equal to the work one by the gas. By Equation A-2, this work is

$$W_{12} = Q_H = RT_H \ln(V_2/V_1) \quad (A-16)$$



**Figure A-3**  
The Carnot cycle.

The heat  $Q_L$  expelled at the low temperature  $T_L$  is equal to the work we do compressing the gas isothermally in going from point 3 to 4. This work is

$$W_{34} = Q_L = RT_C \ln(V_4/V_3) \quad (A-17)$$

Taking the ratio of Equations A-16 to A-17 we get

$$\frac{Q_H}{Q_L} = \frac{T_H \ln(V_2/V_1)}{T_C \ln(V_4/V_3)} \quad (A-18)$$

The next step is to calculate the ratio of the logarithms of the volumes using the adiabatic expansion formula  $pV^\gamma = \text{constant}$ .

In going adiabatically from 2 to 3 we have

$$p_2 V_2^\gamma = p_3 V_3^\gamma \quad (A-19)$$

and in going from 4 to 1 adiabatically we have

$$p_4 V_4^\gamma = p_1 V_1^\gamma \quad (A-20)$$

Finally, use the ideal gas law  $pV = RT$  to express the pressure  $p$  in terms of volume and temperature in Equations A-19 and A-20. Explicitly use

$$\begin{aligned} p_1 &= RT_H / V_1 ; & p_2 &= RT_H / V_2 \\ p_3 &= RT_C / V_3 ; & p_4 &= RT_C / V_4 \end{aligned} \quad (A-21)$$

to get for Equation (19)

$$\begin{aligned} \frac{RT_H}{V_2} V_2^\gamma &= \frac{RT_C}{V_3} V_3^\gamma \\ \text{or} & \\ T_H V_2^{\gamma-1} &= T_C V_3^{\gamma-1} \end{aligned} \quad (A-22)$$

and similarly for Equation (20)

$$T_H V_1^{\gamma-1} = T_C V_4^{\gamma-1} \quad (A-23)$$

as you can check for yourself.

If we divide Equation A-22 by A-23 the temperatures  $T_H$  and  $T_C$  cancel, and we get

$$\frac{V_2^{\gamma-1}}{V_1^{\gamma-1}} = \frac{V_3^{\gamma-1}}{V_4^{\gamma-1}}$$

or

$$\left(\frac{V_2}{V_1}\right)^{\gamma-1} = \left(\frac{V_3}{V_4}\right)^{\gamma-1} \quad (\text{A-24})$$

Taking the  $(\gamma - 1)$ th root of both sides of Equation A-24 gives simply

$$\left(\frac{V_2}{V_1}\right) = \left(\frac{V_3}{V_4}\right) \quad (\text{A-25})$$

Since  $V_2/V_1 = V_3/V_4$ , the logarithms in Equation A-18 cancel, and we are left with the surprisingly simple result

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \quad (\text{14 repeated})$$

which is our Equation 14 for the efficiency of a Carnot cycle. As we mentioned, when you are doing a calculation and a lot of stuff cancels to give a simple result, there is a chance that your result is more general, or has more significance than you expected. In this case, Equation 14 is the formula for the efficiency of any reversible engine, no matter how it is constructed. We happened to get at this formula by calculating the efficiency of a Carnot engine running on one mole of an ideal gas.

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