



Steam engines, similar to the one shown here powering a tractor, were a key component of the Industrial Revolution. A steam engine is a heat engine. In a heat engine, energy is extracted at a relatively high temperature, and some of that energy is used to do useful work. As we will learn in this chapter, by the laws of thermodynamics, some fraction of the energy also has to be wasted.

The same basic principles of heat engines are exploited today in modern car engines and in power plants that generate electricity. In this chapter, we will examine the principles of physics on which such devices are based.

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Chapter 15 – The Laws of Thermodynamics

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Thermodynamics is the branch of physics that deals with systems in which energy is in the form of heat, work, and internal energy. Such systems have a wide variety of practical applications, ranging from gasoline-fueled car engines to refrigerators and air conditioners. Some of these devices are rather complex; however, underlying their operation are some basic rules known as the laws of thermodynamics. Understanding these rules will be the theme of the chapter.

15-1 The First Law of Thermodynamics

Consider a cylinder of ideal gas sealed with a piston, a system we examined in Chapter 14. Let's explore what happens to the system's energy when the temperature increases.

EXPLORATION 15.1 – Adding heat to a cylinder

A cylinder of ideal gas, as in Figure 15.1, is sealed with a piston that can move up or down without friction. The top of the piston is exposed to the atmosphere. The ideal gas in the cylinder is initially at room temperature, 20°C . The cylinder is then placed in a water bath that is maintained at a constant temperature of 90°C .

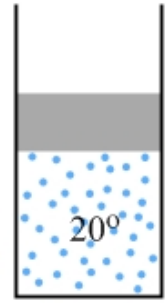


Figure 15.1: A cylinder sealed with a piston that can move up or down without friction. The cylinder is initially at room temperature, 20°C .

Step 1 – Describe qualitatively what happens to this gas system when it is placed in the water bath.

Because the temperature of the gas in the cylinder is lower than that of the water bath, heat will be transferred from the water into the gas. This is shown in Figure 15.2. This transfer of energy will continue until the gas in the cylinder reaches 90°C , the same temperature as the water bath. At that point, thermal equilibrium will be reached and the energy transfer will stop.

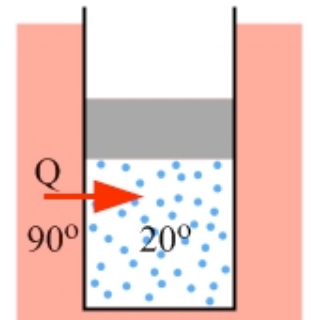


Figure 15.2: When the cylinder is placed in a water bath that is maintained at a temperature higher than the gas, heat is naturally transferred from the water bath into the cylinder until thermal equilibrium is reached.

Step 2 – Describe what happens to the energy transferred as heat from the water bath to the ideal gas. Increasing the temperature of the gas means increasing the internal energy of the gas. Thus, some of the heat Q transferred to the gas causes a change in internal energy, ΔE_{int} . However, something else must change for the gas to satisfy the condition set by the ideal gas law, $PV = nRT$. As we discussed in Chapter 14, in a cylinder in which the piston is free to move, the pressure is determined by the forces on the piston's free-body diagram (see Figure 15.3).

When the gas temperature reaches 90°C , the piston is at a new equilibrium position, but the pressure in the cylinder is the same as it was before – nothing has changed on the free-body diagram. Thus, to satisfy the ideal gas law, the volume occupied by the gas increases when the pressure increases. This is shown in Figure 15.4. The expanding gas does a positive amount of work W , exerting an upward force and causing an upward displacement of the piston. Like the change in internal energy, the work W comes from the heat Q transferred from the water bath into the gas. Thus, some of the transferred heat goes into raising the internal energy of the system, and some goes into doing work.

Figure 15.3: Applying Newton's second law to the free-body diagram tells us that, with the piston at equilibrium, the pressure of the gas is given by $P = P_{\text{atm}} + mg / A$, where A is the area of the top or bottom of the piston.

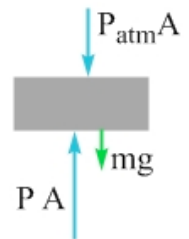
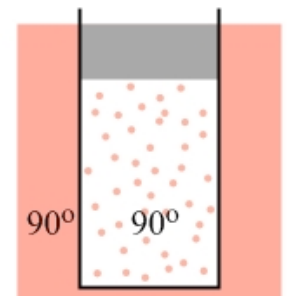


Figure 15.4: When thermal equilibrium is reached, the gas occupies a larger volume because the temperature is higher, maintaining a constant pressure.



Key Idea: Heat transferred between a system and its surroundings can be transformed into two other forms of energy. Some (or even all, in certain cases) of the heat goes into changing the internal energy of the gas (corresponding to a temperature change) while the remaining heat goes into doing work. This statement of energy conservation is the first law of thermodynamics, which is defined more formally below. **Related End-of-Chapter Exercises: 1 and 13.**

The first law of thermodynamics is a statement of energy conservation as it relates to a thermodynamic system. Heat, which is energy transferred into or out of a system, can be transformed into (or come from) some combination of a change in internal energy of the system and the work done by (or on) the system.

$$Q = \Delta E_{\text{int}} + W \quad . \quad (\text{Equation 15.1: The First Law of Thermodynamics})$$

Q is positive when heat is added to a system, and negative when heat is removed.

ΔE_{int} is positive when the temperature of a system increases, and negative when it decreases.

W is positive when a system expands and does work, and negative when the system is compressed.

EXAMPLE 15.1 – Some numerical calculations

Let's do two numerical calculations related to Exploration 15.1. Let's say that 3500 J is transferred to the cylinder as heat. The work done by the gas while the heat is being transferred is 1400 J. (a) Calculate the change in internal energy experienced by the gas in the cylinder. (b) If the change in internal energy can be calculated, in this case, using the equation $\Delta E_{\text{int}} = (3/2)nR\Delta T$, calculate the number of moles of gas in the cylinder.

SOLUTION

(a) We can calculate the change in internal energy by re-arranging the equation for the first law.

$$\Delta E_{\text{int}} = Q - W = 3500 \text{ J} - 1400 \text{ J} = 2100 \text{ J} .$$

(b) Now, we can solve for the number of moles by re-arranging the equation that was given for the change in internal energy.

$$n = \frac{(2/3)\Delta E_{\text{int}}}{R\Delta T} = \frac{(2/3) 2100 \text{ J}}{(8.31 \text{ J/mol K})(+70\text{K})} = \frac{1400 \text{ J}}{(8.31 \text{ J/mol K})(+70\text{K})}$$

$$n = \frac{20 \text{ J/K}}{8.31 \text{ J/mol K}} = 2.4 \text{ moles}$$

Essential Question 15.1: Figure 15.5 shows two cylinders containing equal amounts of the same ideal gas in the same initial state – the gas in the two cylinders has the same pressure, volume, and temperature. The difference between them is that, in cylinder 1, the piston sealing the cylinder is free to move up or down without friction, while the piston in cylinder 2 is fixed so the volume occupied by the gas is constant. Both cylinders are initially at 20°C, but are then placed in a water bath that is maintained at a constant temperature of 80°C and allowed to come to equilibrium. In this process, which cylinder has more heat transferred to it? Which cylinder experiences a larger change in internal energy?

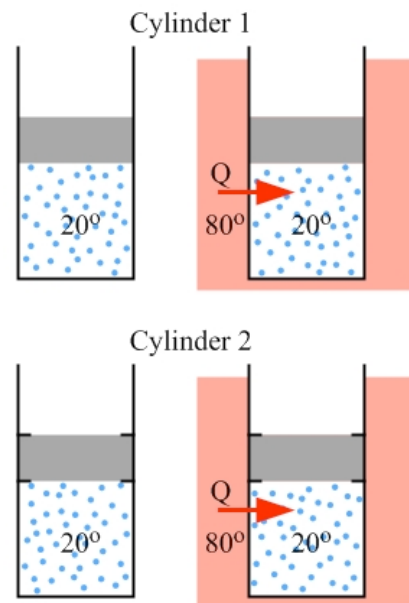


Figure 15.5: The piston in cylinder 1 is free to move without friction, while the piston in cylinder 2 is fixed in place so the gas occupies a constant volume.

Answer to Essential Question 15.1: Coming to equilibrium means reaching the same temperature as the water bath. Thus, both cylinders will experience the same change in temperature, $+60^{\circ}\text{C}$. Internal energy is directly related to temperature. Because the same number of moles of the same type of gas experiences the same temperature change, the change in internal energy is the same in both cases. The difference between the cylinders is that the gas in cylinder 1 will expand when the temperature increases, so the gas does work moving the piston. No work is done by the gas in cylinder 2. Thus $Q_1 = \Delta E_{\text{int}} + W$ is larger than $Q_2 = \Delta E_{\text{int}}$. More heat needs to be added to cylinder 1 than cylinder 2, the difference corresponding to the work done by the gas in cylinder 1.

15-2 Work, and Internal Energy

The first law involves three parameters. Heat (Q) involves a transfer of energy into or out of a system. Let's now explore the ideas of work (W) and change in internal energy (ΔE_{int}).

For the case of the cylinder in section 15-1, the work done by the gas on the piston is the magnitude of the force the gas exerts on the piston multiplied by the magnitude of the piston's displacement, Δh . Using the fact that $F = PA$, and that the volume and height are related by area:

$$W = F\Delta h = (PA)\Delta h = P(A\Delta h) = P\Delta V.$$

Thus, for a constant pressure process we have:

$$W = P\Delta V. \quad (\text{Eq. 15.2: Work done at constant pressure})$$

If the pressure changes, Equation 15.2 does not apply. Is there a general method of finding work that is valid in all cases? Consider now the two processes shown in the P-V diagram in Figure 15.6.

For the constant pressure process, in which the system expands from state 1 to state 2, Equation 15.2 tells us that the work done by the gas in that process is $P\Delta V$. This is the area under the curve defining the process. For the expansion from state 2 to state 3, which is not at constant pressure, the work is still equal to the area under the curve defining the process. This gives us our general method of finding work. The two shaded areas shown in Figure 15.7 represent the work done by the gas in the two processes.

Work: A practical way to calculate the work done by a gas in a particular thermodynamic process is to find the area under the curve for that process on the P-V diagram.

$$W = \text{area under the curve on the P-V diagram.}$$

$$(\text{Equation 15.3: Work done by a gas})$$

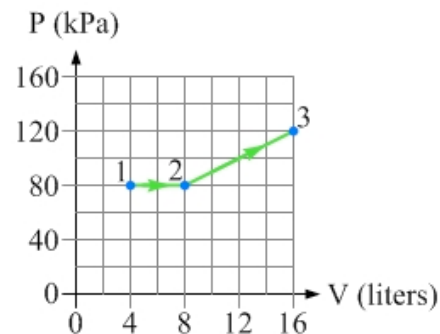


Figure 15.6: The P-V diagram shows an expansion from state 1 to state 2 at constant pressure, followed by another expansion that takes the system to state 3 along the path indicated.

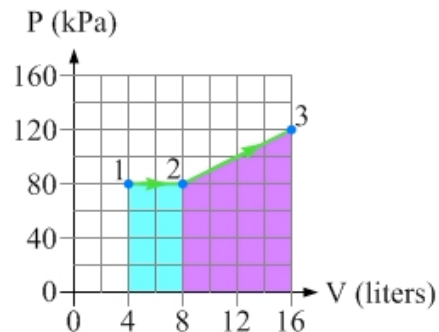


Figure 15.7: The area of the rectangular region under the 1 to 2 process is the work done by the gas in the expansion from state 1 to state 2. The area of the region under the 2 to 3 process is the work done by the gas in moving from state 2 to state 3.

EXAMPLE 15.2A – Calculating the work

Find the work done by the gas in the two processes shown in Figure 15.6.

SOLUTION

For the constant-pressure 1 to 2 process, the work is the area of a rectangle, as in Figure 15.7.

$$W_{1 \rightarrow 2} = P\Delta V = (80 \text{ kPa})(8.0 \text{ L} - 4.0 \text{ L}) = (80 \times 10^3 \text{ Pa})(4.0 \times 10^{-3} \text{ m}^3) = +320 \text{ J}.$$

For the expansion from state 2 to 3, the work is the area under the 2 to 3 line in Figure 15.7. This is equal to the area of a rectangle, with the top of the rectangle at the average pressure.

$$W_{2 \rightarrow 3} = P_{av}\Delta V = (100 \text{ kPa})(16 \text{ L} - 8.0 \text{ L}) = (100 \times 10^3 \text{ Pa})(8.0 \times 10^{-3} \text{ m}^3) = +800 \text{ J}.$$

Let's turn now to the change in internal energy. The change in internal energy is independent of the process that moves a system from one state to another. Thus, if we know what the change in internal energy is for one process, we can apply that to all processes.

Change in internal energy: If the temperature of an ideal gas changes, the change in internal energy of the gas is proportional to the change in temperature. If there is no change in temperature, there is no change in internal energy (as long as the number of moles of gas remains constant).

$$\Delta E_{\text{int}} = n C_V \Delta T . \quad (\text{Equation 15.4: Change in internal energy})$$

Monatomic: $C_V = \frac{3}{2}R$

Diatomic: $C_V = \frac{5}{2}R$

Polyatomic: $C_V = 3R$

C_V is the heat capacity at constant volume, which we will examine in Section 15-3.

If we just want the internal energy, we remove the deltas.

$$E_{\text{int}} = n C_V T . \quad (\text{Equation 15.5: Internal energy of an ideal gas})$$

EXAMPLE 15.2B – Calculating the change in internal energy

Consider again the P-V diagram shown in Figure 15.6. If the gas is diatomic, find the change in internal energy associated with the two processes shown on the diagram.

SOLUTION

To do this, we will combine the ideal gas law with the information on the graph.

$$\Delta E_{\text{int}} = \frac{5}{2} n R \Delta T = \frac{5}{2} n R (T_2 - T_1) = \frac{5}{2} (n R T_2 - n R T_1) = \frac{5}{2} (P_2 V_2 - P_1 V_1).$$

Plugging in the values for the pressures and volumes shown on the P-V diagram gives:

$$\Delta E_{\text{int},1 \rightarrow 2} = \frac{5}{2} [(80 \text{ kPa})(8.0 \text{ L}) - (80 \text{ kPa})(4.0 \text{ L})] = 1600 \text{ J} - 800 \text{ J} = +800 \text{ J}.$$

Using a similar process for the expansion from state 2 to state 3 gives:

$$\Delta E_{\text{int},2 \rightarrow 3} = \frac{5}{2} [(120 \text{ kPa})(16.0 \text{ L}) - (80 \text{ kPa})(8.0 \text{ L})] = 3800 \text{ J} - 1600 \text{ J} = +2200 \text{ J}.$$

Related End-of-Chapter Exercises: 14, 16, 46, 47.

Essential Question 15.2: If we did not know the path taken on the P-V diagram, in Figure 15.6, from state 2 to state 3, could we still find the work or the change in internal energy? Explain.

Answer to Essential Question 15.2: An important distinction between work and the change in internal energy is that the work depends on the process involved in taking a system from one state to another, while the change in internal energy depends only on the initial and final states. Thus, if we do not know the path taken on the P-V diagram, we can not find the work – different processes have different amounts of work associated with them. On the other hand, we can find the change in internal energy, because we know the pressure and volume of the initial and final states. No matter what the process, for a diatomic ideal gas the change in internal energy in moving from state 2 to state 3 will be the +2200 J we calculated in Example 15.2B.

15-3 Constant Volume and Constant Pressure Processes

Let's consider once again two different thermodynamic processes, one in which heat is added to a system at constant volume, and the other when heat is added at constant pressure.

EXPLORATION 15.3A – A constant-volume process

A sample of monatomic ideal gas is initially at a temperature of 200 K. The gas occupies a constant volume. Heat is then added to the gas until the temperature reaches 400 K. This process is shown on the P-V diagram in Figure 15.8, where the system moves from state 1 to state 2 by the process indicated. The diagram also shows the cylinder in state 1 and again in state 2. The figure also shows the 200 K isotherm (lower) and the 400 K isotherm (higher).

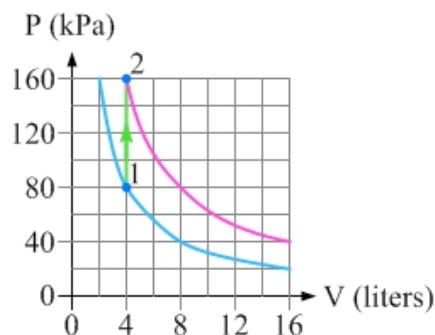


Figure 15.8: A P-V diagram showing a constant-volume process that moves a system of monatomic ideal gas from state 1 to state 2.

Step 1 – Find the number of moles of gas in the cylinder.

Applying the ideal gas law to state 1 gives:

$$n = \frac{PV}{RT} = \frac{(80 \text{ kPa})(4.0 \text{ L})}{(8.31 \text{ J/mol K})(200 \text{ K})} = 0.19 \text{ moles}.$$

Step 2 – Find the work done in this process.

The work done is the area under the curve for the process. Because there is no area under the curve in a constant-volume process the work done by the gas is zero: $W = 0$.

Step 3 – Find the change in internal energy for this process.

In a constant-volume process all the heat added goes into changing the internal energy of the gas. Because the gas is monatomic we have $C_V = 3R/2$. This gives:

$$\Delta E_{\text{int}} = \frac{3}{2} n R \Delta T = \frac{3}{2} (0.19 \text{ moles})(8.31 \text{ J/mol K})(400 \text{ K} - 200 \text{ K}) = +480 \text{ J}.$$

Step 4 – Find the heat added to the gas in this process. The First Law of Thermodynamics tells us that $Q = \Delta E_{\text{int}} + W$, but if the work done by the gas is zero we have $Q = \Delta E_{\text{int}}$. In this case we have $Q = +480 \text{ J}$.

Key ideas for a constant-volume process: There is no work done by the gas: $W = 0$.

The heat added to the gas is equal to the change in internal energy: $Q = n C_V \Delta T$.

Related End-of-Chapter Exercises: 17, 18.

EXPLORATION 15.3B – A constant-pressure process

The system from the previous Exploration is now taken from state 1 to state 3 (in which, like state 2, the system is at 400 K) by the constant-pressure process indicated in Figure 15.9.

Step 1 – Find the work done in this process. The work done by the gas in this process is the area under the curve on the P-V diagram. Because the pressure is constant we can use Equation 15.2:

$$W = P\Delta V = (80 \text{ kPa})(8.0 \text{ L} - 4.0 \text{ L}) = (80 \text{ kPa})(+4.0 \text{ L}) = +320 \text{ J}.$$

Step 2 – Find the change in internal energy for this process.

Because the temperature change is the same, the change in internal energy is the same as it is in the constant-volume process:

$$\Delta E_{\text{int}} = \frac{3}{2}nR\Delta T = \frac{3}{2}(0.19 \text{ moles})(8.31 \text{ J/mol K})(400 \text{ K} - 200 \text{ K}) = +480 \text{ J}.$$

Step 3 – Find the heat added to the gas. Applying the First Law of Thermodynamics gives:

$$Q = \Delta E_{\text{int}} + W = +480 \text{ J} + 320 \text{ J} = +800 \text{ J}$$

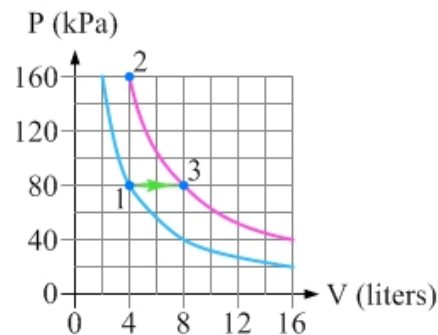


Figure 15.9: A P-V diagram showing a constant-pressure process that moves a system of monatomic ideal gas from state 1 to state 3.

Key ideas for a constant-pressure process: The work done by the gas is given by Equation 15.2: $W = P\Delta V$. **Related End-of-Chapter Exercises: 3, 19 – 21.**

Heat Capacity

In Chapter 13, we used $Q = mc\Delta T$ to find the heat needed to change the temperature of a substance of mass m and specific heat c . For gases, a more convenient equation is $Q = nC\Delta T$, where C is known as the heat capacity. The value of the heat capacity depends on the process the gas follows when the heat is added. At constant volume, when the work done is zero:

$$Q = \Delta E_{\text{int}} = nC_V\Delta T, \quad (\text{Eq. 15.6: Heat needed to change temperature at constant volume})$$

where C_V is the heat capacity at constant volume. As mentioned in Section 15-2, we apply $\Delta E_{\text{int}} = nC_V\Delta T$ to all processes, because the change in internal energy is process independent.

$$\text{Monatomic: } C_V = \frac{3}{2}R \qquad \text{Diatomic: } C_V = \frac{5}{2}R \qquad \text{Polyatomic: } C_V = 3R$$

In contrast, the **heat needed to change temperature at constant pressure** is given by:

$$Q = W + \Delta E_{\text{int}} = P\Delta V + nC_V\Delta T = nR\Delta T + nC_V\Delta T = n(R + C_V)\Delta T = nC_P\Delta T, \quad (\text{Eq. 15.7})$$

where $C_P = R + C_V$ is the heat capacity at constant pressure.

$$\text{Monatomic: } C_P = \frac{5}{2}R \qquad \text{Diatomic: } C_P = \frac{7}{2}R \qquad \text{Polyatomic: } C_P = 4R$$

Essential Question 15.3: In Exploration 15.3B, 800 J of heat added to the system of monatomic ideal gas at 200 K increases the system's temperature to 400 K via a constant-pressure process. If the same 800 J of heat is added to the system, starting in state 1, but the volume is kept constant what will the final temperature of the system be? What about the final pressure?

Answer to Essential Question 15.3: In a constant-volume process, for a monatomic ideal gas:

$$Q = \Delta E_{\text{int}} = \frac{3}{2} n R \Delta T = \frac{3}{2} (0.19 \text{ moles})(8.31 \text{ J/mol K})(400 \text{ K} - 200 \text{ K}) = +480 \text{ J} .$$

Solving for the temperature change when 800 J of heat is added, we get:

$$\Delta T = \frac{2Q}{3nR} = \frac{2 \times 800 \text{ J}}{3(0.19 \text{ moles})(8.31 \text{ J/mol K})} = +333 \text{ K} .$$

Because the initial temperature is 200 K, the final temperature is 200 K + 333 K = 533 K.

Applying the ideal gas law, gives the corresponding pressure:

$$P = \frac{nRT}{V} = \frac{(0.19 \text{ moles})(8.31 \text{ J/mol K})(533 \text{ K})}{4.0 \text{ L}} = 213 \text{ kPa} .$$

15-4 Constant Temperature and Adiabatic Processes

Let's now consider two more thermodynamic processes, the constant temperature (also known as isothermal) process and the adiabatic process.

A constant-temperature (isothermal process: Because the temperature is constant there is no change in internal energy. The First Law of Thermodynamics tells us that, in this case, $Q = W$, and it can be shown (using calculus is the most straightforward way to prove this) that:

$$Q = W = nRT \ln \left(\frac{V_f}{V_i} \right) . \quad (\text{Eq. 15.8: Heat and work for an isothermal process})$$

EXAMPLE 15.4A – Add heat at constant temperature

700 J of heat is added to a system of ideal gas, while the temperature is kept constant at 400 K. The system initially has a pressure of 160 kPa and occupies a volume of 4.0 liters.

- Is this possible? Can temperature remain constant while heat is added? Explain.
- Sketch this process on a P-V diagram, keeping in mind the following question: When heat is added at constant temperature does the gas pressure increase, as in a constant-volume process, or does the volume increase, as in a constant-pressure process?
- What are the final values of the gas pressure and the volume of the gas?

SOLUTION

(a) This is possible. The first law of thermodynamics tells us that heat Q is converted into some combination of internal energy and/or work. When the temperature is constant we have the special case of no change in internal energy, so all the heat is converted into work.

(b) The temperature is constant so the process proceeds along an isotherm, shown in Figure 15.10. Because Q is positive, and $Q = W$, the work is also positive. Positive work means that the volume must increase, so the pressure drops to keep the temperature constant.

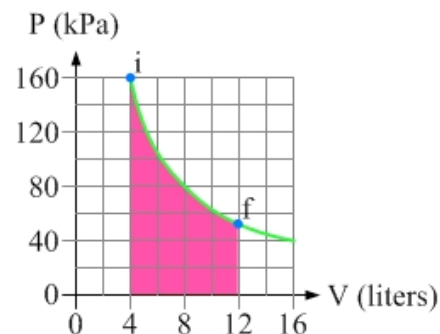


Figure 15.10: A P-V diagram corresponding to heat being added to a system at constant temperature. The final pressure and volume are calculated in part (c). The area corresponding to the work done by the gas is shown shaded.

(c) First, let's re-write Eq. 15.8 using the ideal gas law: $Q = nRT \ln\left(\frac{V_f}{V_i}\right) = P_i V_i \ln\left(\frac{V_f}{V_i}\right)$.

Isolating the logarithm on the right side gives: $\frac{Q}{P_i V_i} = \ln\left(\frac{V_f}{V_i}\right)$.

Taking the exponential of both sides: $e^{Q/(P_i V_i)} = e^{\ln(V_f/V_i)} = \frac{V_f}{V_i}$.

The final volume is thus: $V_f = V_i e^{Q/(P_i V_i)} = (4.0 \text{ L}) e^{700 \text{ J}/(160 \text{ kPa} \times 4.0 \text{ L})} = 11.9 \text{ L}$.

Solving for the final pressure gives: $P_f = \frac{nRT}{V_f} = \frac{P_i V_i}{V_f} = \frac{(160 \text{ kPa})(4.0 \text{ L})}{11.94 \text{ L}} = 54 \text{ kPa}$.

An adiabatic process: In an adiabatic process no heat is added to or removed from the gas (i.e., $Q = 0$). Examples include systems insulated so no heat is exchanged with the surroundings, and systems in which processes happen so fast that there is no time to add or remove heat. Because $Q = 0$ for an adiabatic process the First Law of Thermodynamics tells us that $\Delta E_{\text{int}} = -W$. The energy for any work done comes from the change in the system's internal energy.

$P V^\gamma = \text{constant}$, (Equation 15.9: **Equation for an adiabatic process on the P-V diagram**)

where γ is the ratio of the heat capacity at constant pressure to the heat capacity at constant volume:

$$\gamma = \frac{C_P}{C_V} \quad (\text{Equation 15.10: The constant } \gamma \text{ for an adiabatic process.})$$

EXAMPLE 15.4B – Analyzing an adiabatic process

A system of monatomic ideal gas experiences an adiabatic expansion that moves it from an initial state, at 400 K, to a final state at a temperature of 200 K. The process is shown on the P-V diagram in Figure 15.11. Calculate the values of the final pressure and volume.

SOLUTION

Because the gas is monatomic, we have: $\gamma = \frac{C_P}{C_V} = \frac{5R/2}{3R/2} = \frac{5}{3}$.

From Equation 15.9, we know that: $P_f V_f^\gamma = P_i V_i^\gamma$

From the ideal gas law, we have $P_f = nRT_f/V_f$, as well as $n = P_i V_i/(RT_i)$.

Combining these results leads to $T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}$. (Equation 15.11)

Solving for the final volume gives: $V_f = V_i (T_i/T_f)^{1/(\gamma-1)} = (4.0 \text{ L})(2)^{3/2} = 11.3 \text{ L}$.

The final pressure is thus: $P_f = P_i (V_i/V_f)^\gamma = (160 \text{ kPa}) \left(\frac{4.0 \text{ L}}{11.31 \text{ L}}\right)^{5/3} = 28 \text{ kPa}$.

Related End-of-Chapter Exercises for this section: 4, 22 – 27.

Essential Question 15.4: How much work is done by the gas in Example 15.4B?

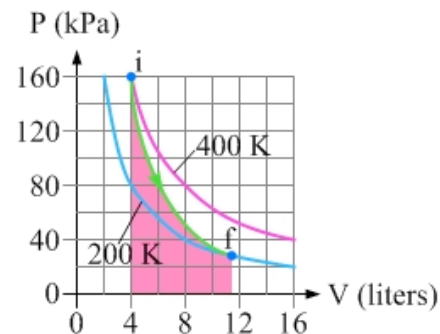


Figure 15.11: The P-V diagram for the adiabatic expansion.

Answer to Essential Question 15.4: The work done by the gas in the expansion is shown by the area shaded in red in Figure 15.11. We can find a numerical value for the work done by applying the First Law of Thermodynamics, $Q = \Delta E_{\text{int}} + W$. Because $Q = 0$, we have:

$$W = -\Delta E_{\text{int}} = -nC_V \Delta T = -\frac{3}{2}nR(T_f - T_i) = -\frac{3}{2}nRT_f + \frac{3}{2}nRT_i.$$

We could solve for the number of moles of gas, but let's instead apply the ideal gas law:

$$W = -\frac{3}{2}P_f V_f + \frac{3}{2}P_i V_i = \frac{3}{2}(P_i V_i - P_f V_f) = \frac{3}{2}(160 \text{ kPa} \times 4.0 \text{ L} - 28.3 \text{ kPa} \times 11.31 \text{ L}) = 480 \text{ J}$$

15-5 A Summary of Thermodynamic Processes

There is no single step-by-step strategy that can be applied to solve every problem involving a thermodynamic process. Instead let's summarize the tools we have to work with. These tools can be applied in whatever order is appropriate to solve a particular problem.

Tools for Solving Thermodynamics Problems

- The P-V diagram can help us to visualize what is going on. In addition, the work done by a gas in a process is the area under the curve defining that process on the P-V diagram.
- The ideal gas law, $PV = nRT$.
- The first law of thermodynamics, $Q = \Delta E_{\text{int}} + W$.
- The general expression for the change in internal energy, $\Delta E_{\text{int}} = nC_V \Delta T$.
- In specific special cases (see the summary in Figure 15.14), there are additional relationships that can be used to relate the different parameters.

EXAMPLE 15.5 – Applying the tools

A system of monatomic ideal gas is taken through the process shown in Figure 15.12. For this process find (a) the work done by the gas, (b) the change in internal energy, and (c) the heat added to the gas.

SOLUTION

(a) The area under the curve has been split into two parts in Figure 15.13, a $\frac{1}{4}$ -circle and a rectangle. Each box on the P-V diagram measures $20 \text{ kPa} \times 2.0 \text{ L}$, representing an area of 40 J . The rectangular area covers 8 boxes, for a total of 320 J of work. The radius of the quarter-circle is four boxes, so the area of that quarter circle is given by:

$$W_{1/4} = \frac{1}{4}\pi r^2 = \frac{1}{4}\pi (4 \text{ units})^2 = 4\pi \text{ boxes} = 4\pi \text{ boxes} \times 40 \text{ J/box} = 500 \text{ J}.$$

Thus, the total work done by the gas is $320 \text{ J} + 500 \text{ J} = 820 \text{ J}$.

(b) The gas is monatomic, so $C_V = 3R/2$.

Combining Eq. 15.4 with the ideal gas law:

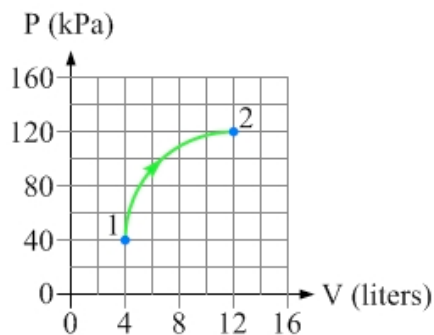


Figure 15.12: The process that moves the system from state 1 to state 2 follows a circular arc on the P-V diagram that covers $\frac{1}{4}$ of a circle.

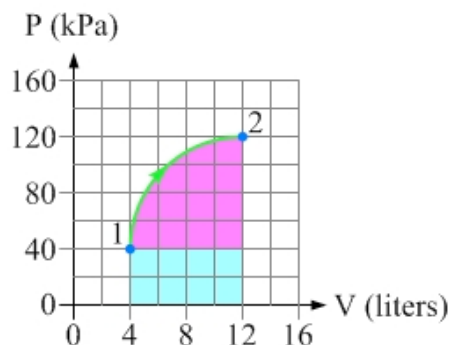


Figure 15.13: To find the work done by the gas here, it is simplest to split the area under the curve into two pieces, a $\frac{1}{4}$ -circle and a rectangle.

$$\Delta E_{\text{int}} = \frac{3}{2} nR\Delta T = \frac{3}{2} (nRT_f - nRT_i) = \frac{3}{2} (P_f V_f - P_i V_i) = \frac{3}{2} (120 \text{ kPa} \times 12 \text{ L} - 4.0 \text{ kPa} \times 4.0 \text{ L}) = 1920 \text{ J}$$

(c) Using the first law of thermodynamics: $Q = \Delta E_{\text{int}} + W = 1920 \text{ J} + 820 \text{ J} = 2740 \text{ J}$.

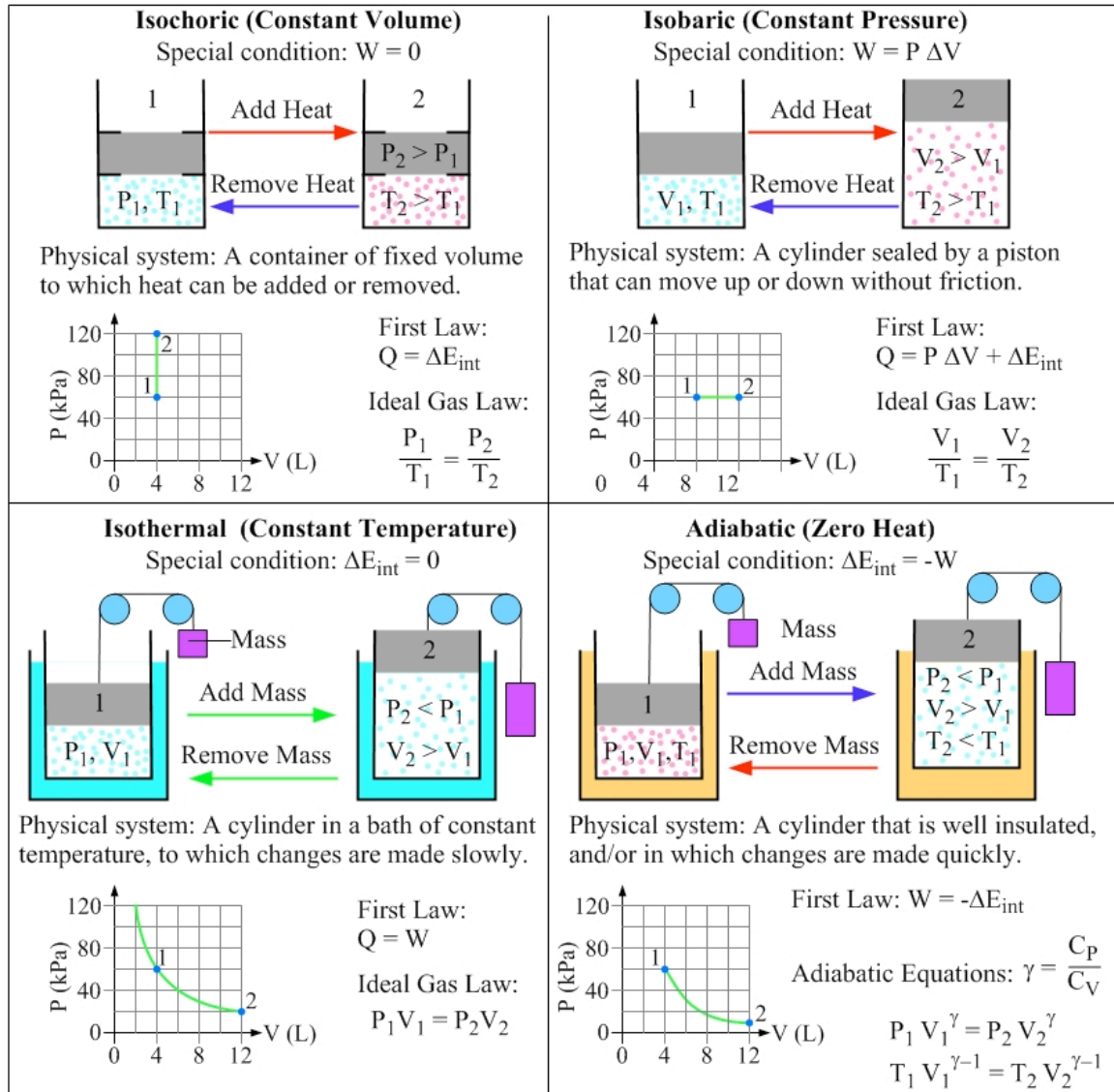


Figure 15.14: A summary of four special-case thermodynamic processes. For each, we see the special condition associated with that process; a pictorial representation and description in words of a corresponding physical system; a P-V diagram for the process; and equations we can apply to solve problems associated with the process.

Related End-of-Chapter Exercises for this section: 6, 7, 28 – 31.

Essential Question 15.5: Compare the P-V diagrams for the isochoric and isobaric processes in Figure 15.14. Assuming these pertain to the same system, and state 1 is the same in both cases, in which case is the change in internal energy larger? In which case is more heat involved?

Answer to Essential Question 15.5: The ideal gas law tells us that temperature is proportional to PV . $P_2V_2 = 480 \text{ J}$ for state 2 in both processes we are considering, so the temperature in state 2 is the same in both cases. $\Delta E_{\text{int}} = nC_V \Delta T$, and all three factors on the right-hand side are the same for the two processes, so the change in internal energy is the same (+360 J, in fact). Because the gas does no work in the isochoric process, and a positive amount of work in the isobaric process, the First Law tells us that more heat is required for the isobaric process (+600 J versus +360 J).

15-6 Thermodynamic Cycles

Many devices, such as car engines and refrigerators, involve taking a thermodynamic system through a series of processes before returning the system to its initial state. Such a cycle allows the system to do work (e.g., to move a car) or to have work done on it so the system can do something useful (e.g., removing heat from a fridge). Let's investigate this idea.

EXPLORATION 15.6 – Investigate a thermodynamic cycle

One cycle of a monatomic ideal gas system is represented by the series of four processes in Figure 15.15. The process taking the system from state 4 to state 1 is an isothermal compression at a temperature of 400 K. Complete Table 15.1 to find Q , W , and ΔE_{int} for each process, and for the entire cycle.

Process	Special process?	Q (J)	W (J)	ΔE_{int} (J)
1 → 2	No	+1360		
2 → 3	Isobaric			
3 → 4	Isochoric		0	
4 → 1	Isothermal			0
Entire Cycle	No			0

Table 15.1: Table to be filled in to analyze the cycle. See Step 1 for a justification of the 0's in the table.

Step 1 – Fill in any zeroes in the table. There is no work done in the 3 → 4 process, and the change in internal energy is zero in the 4 → 1 process. However, ΔE_{int} for the entire cycle is also zero (this is always true), because the system returns to its original state, and therefore its original temperature.

Step 2 – Analyze the 1 → 2 process. The work done by the gas is

$$W_{1 \rightarrow 2} = P_{\text{av}} \Delta V = 100 \text{ kPa} \times (8.0 \text{ L} - 4.0 \text{ L}) = 400 \text{ J}.$$

From the ideal gas law, PV is proportional to temperature. Because $P_1 V_1 = 320 \text{ J}$ corresponds to $T_1 = 400 \text{ K}$ (so $nR = 0.80 \text{ J/K}$ in this case), then $P_2 V_2 = 960 \text{ J} = 3(P_1 V_1)$ corresponds to a tripling of the temperature to $T_2 = 1200 \text{ K}$. We know that $C_V = 3R/2$, so:

$$\Delta E_{\text{int},1 \rightarrow 2} = \frac{3}{2} nR \Delta T = \frac{3}{2} nR (T_2 - T_1) = \frac{3}{2} (0.80 \text{ J/K}) (1200 \text{ K} - 400 \text{ K}) = +960 \text{ J}.$$

Using the first law: $Q_{1 \rightarrow 2} = \Delta E_{\text{int},1 \rightarrow 2} + W_{1 \rightarrow 2} = +960 \text{ J} + 400 \text{ J} = +1360 \text{ J}$.

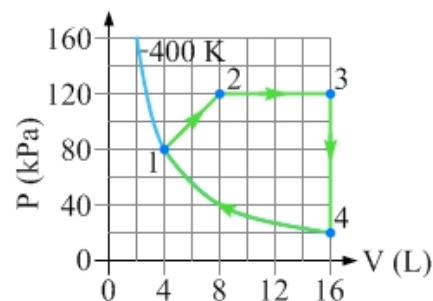


Figure 15.15: The series of four processes making up the cycle.

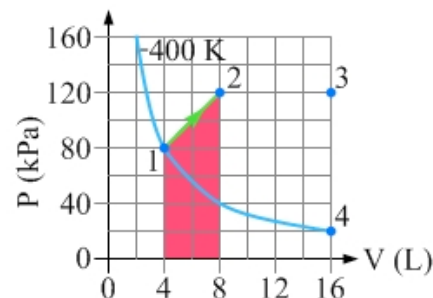


Figure 15.16: The work done by the gas in the 1 → 2 process equals the area under the curve, shown shaded.

Step 3 – Analyze the 2 → 3 process. The work done by the gas in the 2 → 3 process is the area of the shaded region in Figure 15.17:

$$W_{2 \rightarrow 3} = P\Delta V = 120 \text{ kPa} \times (16.0 \text{ L} - 8.0 \text{ L}) = 960 \text{ J}.$$

Doubling the volume while keeping the pressure constant doubles the absolute temperature. Thus $T_3 = 2T_2 = 2400 \text{ K}$, and:

$$\Delta E_{\text{int},2 \rightarrow 3} = nC_V\Delta T = \frac{3}{2}nR(T_3 - T_2) = \frac{3}{2}(0.80 \text{ J/K})(2400 \text{ K} - 1200 \text{ K}) = +1440 \text{ J}.$$

Applying the first law tells us that

$$Q_{2 \rightarrow 3} = \Delta E_{\text{int},2 \rightarrow 3} + W_{2 \rightarrow 3} = +1440 \text{ J} + 960 \text{ J} = +2400 \text{ J}.$$

Step 4 – Analyze the 3 → 4 process. With no work done in this process:

$$Q_{3 \rightarrow 4} = \Delta E_{\text{int},3 \rightarrow 4} = \frac{3}{2}nR(T_4 - T_3) = \frac{3}{2}(0.80 \text{ J/K})(400 \text{ K} - 2400 \text{ K}) = -2400 \text{ J}.$$

Step 5 – Analyze the 4 → 1 process. $\Delta E_{\text{int}} = 0$ for an isothermal process.

The work done by the gas is the area of the shaded region in Figure 15.18, in blue to remind us that it is negative. Using Equation 15.8:

$$Q_{4 \rightarrow 1} = W_{4 \rightarrow 1} = nRT \ln(V_f/V_i) = (0.80 \text{ J/K})(400 \text{ K}) \ln(4.0 \text{ L}/16 \text{ L}) = -444 \text{ J}.$$

Step 6 – Complete the table. Each process, and the entire cycle, satisfies the first law, and values in each column sum to the value for the cycle.

Process	Special process?	Q (J)	W (J)	ΔE_{int} (J)
1 → 2	No	+1360	+400	+960
2 → 3	Isobaric	+2400	+960	+1440
3 → 4	Isochoric	-2400	0	-2400
4 → 1	Isothermal	-444	-444	0
Entire Cycle	No	+916	+916	0

Table 15.2: The completed table. Check that each row satisfies the first law and each column adds up.

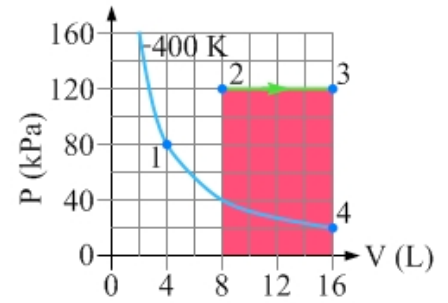


Figure 15.17: The work done by the gas in the 2 → 3 process equals the shaded area under the curve.

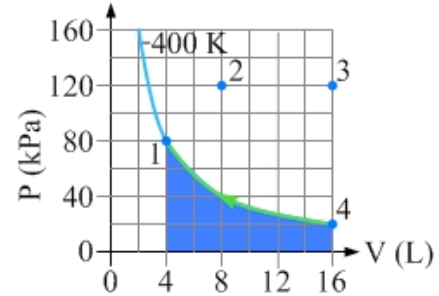


Figure 15.18: The work done by the gas in the 4 → 1 is negative, and is the shaded area under the curve.

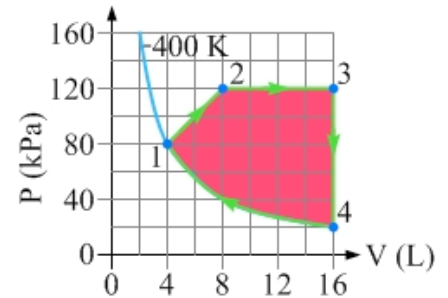


Figure 15.19: The enclosed area is the net work done in the cycle.

Key Ideas for a Thermodynamic Cycle: The cycle satisfies the first law of thermodynamics, as does each of its processes. The change in internal energy for any cycle is always zero because the system returns to its original state, and the area of the enclosed region on the P-V diagram is the net work done by the gas in the cycle. **Related End-of-Chapter Exercises: 32 – 38.**

Essential Question 15.6: Complete Table 15.3, for a cycle consisting of three processes. The process taking the system from state 1 to state 2 is adiabatic.

Process	Q (J)	W (J)	ΔE_{int} (J)
1 → 2			-300
2 → 3	+800	0	
3 → 1			
Entire Cycle		-200	

Table 15.3: Fill in the missing values.

Answer to Essential Question 15.6: We can immediately fill in the following values: $Q_{1\rightarrow 2} = 0$ because there is no heat in an adiabatic process; $\Delta E_{\text{int},2\rightarrow 3} = +800 \text{ J}$ so the $2 \rightarrow 3$ process satisfies the first law; and $\Delta E_{\text{int,cycle}} = 0$ because that is always true (the system returns to its initial state, with no change in temperature). With those three values in the table it is straightforward to fill in the remaining values by (a) making sure that each row satisfies the first law ($Q = W + \Delta E_{\text{int}}$) and, (b) that in every column the sum of the values for the individual processes is equal to the value for the entire cycle. The completed table is shown in Table 15.4.

Process	Q (J)	W (J)	ΔE_{int} (J)
1 \rightarrow 2	0	+300	-300
2 \rightarrow 3	+800	0	+800
3 \rightarrow 1	-1000	-500	-500
Entire Cycle	-200	-200	0

Table 15.4: The completed table.

15-7 Entropy and the Second Law of Thermodynamics

A system of ideal gas in a particular state has an entropy, just as it has a pressure, a volume, and a temperature. Unlike pressure, volume, and temperature, which are easy to determine, the entropy of a system can be difficult to find. On the other hand, changes in entropy can be quite straightforward to calculate.

Entropy: Entropy is in some sense a measure of disorder. The symbol for entropy is S , and the units are J/K.

Change in entropy: In certain cases the change in entropy, ΔS , is easy to determine. An example is in an isothermal process in which an amount of heat Q is transferred to a system:

$$\Delta S = \frac{Q}{T} \quad \text{(Equation 15.12: Change in entropy for an isothermal process)}$$

In cases where heat is transferred while the temperature changes, the change in entropy can be approximated if the temperature change is small compared to the absolute temperature. In this case:

$$\Delta S \approx \frac{Q}{T_{\text{av}}}, \quad \text{(Equation 15.13: Approximate change in entropy)}$$

where T_{av} is the average temperature of the system while the heat is being transferred.

EXAMPLE 15.7 – Mixing water

You have two containers of water. In one container there is 1.0 kg of water at 17°C, while in the second container there is 1.0 kg of water at 37°C. You then pour the water in one container into the other container and allow the system to come to equilibrium. Assuming no heat is transferred from the water to the container or the surroundings, determine the change in entropy for (a) the water that is initially cooler, (b) the water that is initially warmer, and (c) the system.

SOLUTION

Because the two samples of water have equal mass the equilibrium temperature will be 27°C, halfway between the initial temperatures of the two samples. Thus, while heat is being transferred from the warmer water to the cooler water the average temperature of the cooler water will be 22°C, or 295K, and the average temperature of the warmer water will be 32°C (305K).

(a) Because a temperature change of 10° is small compared to the absolute temperature of about 300K, we can use Equation 15.13 to find the change in entropy. To find the heat, use:

$$Q = mc\Delta T = (1.0 \text{ kg})(4186 \text{ J/kg } ^\circ\text{C})(10^\circ\text{C}) = 41860 \text{ J} .$$

This heat is added to the cooler water, so the heat is a positive quantity. Thus:

$$\Delta S_1 \approx \frac{Q}{T_{av}} = \frac{+41860 \text{ J}}{295\text{K}} = +141.90 \text{ J/K} .$$

(b) The heat added to the cooler water comes from the warmer water, so the heat involved for the warmer water is also 41860 J, but negative because it is removed. Thus:

$$\Delta S_2 \approx \frac{Q}{T_{av}} = \frac{-41860 \text{ J}}{305\text{K}} = -137.25 \text{ J/K} .$$

(c) Although the entropy of the warmer water decreases, on the whole, the system's entropy increases by an amount:

$$\Delta S = \Delta S_1 + \Delta S_2 = +141.90 \text{ J/K} - 137.25 \text{ J/K} = +4.7 \text{ J/K} .$$

The situation above is an example of an irreversible process. Even though energy in the 2.0 kg of water at 27°C after mixing is equal to the total energy in the two separate containers before mixing, the entropy of the mixture at one temperature is larger than that of the system of two separate containers at different temperatures. The mixture will not spontaneously separate back into two halves with a 20°C difference, making the process irreversible. This leads us to the second law of thermodynamics.

The Second Law of Thermodynamics: The entropy of a closed system never decreases as time goes by. Reversible processes do not change the entropy of a system, while irreversible processes increase a system's entropy.
 $\Delta S \geq 0$. (Equation 15.14: **The Second Law of Thermodynamics**)

Entropy is sometimes referred to as time's arrow – time proceeds in the direction of increasing entropy. Imagine watching a science fiction movie in which a spacecraft in deep space explodes into a million pieces. Then you play the film backwards, and see the million pieces magically come together to form the spacecraft. You know without a doubt that the film is running backwards – what is it that gives it away? Both momentum and energy are conserved in the explosion, whether you view it forwards or backwards. What gives it away that you are viewing the film backwards is that the process of the million pieces coming together to form the spacecraft decreases the entropy of the system. Our experience is that systems obey the second law of thermodynamics, and proceed in a direction that tends to increase entropy.

What if you view a film forwards and backwards and you can not tell which direction corresponds to time moving forwards? An example would be an elastic collision between two objects. In such a case, the process on film is most likely reversible, with no change (or negligible change) in entropy, giving us nothing to go by to determine the direction of increasing time.

Related End-of-Chapter Exercises: 39, 40, and 57.

Essential Question 15.7: When you were younger, you were probably asked to clean up your room. Let's say that you cleaned your room up on Saturday, and over the course of the next week it gradually got messy again – the second law of thermodynamics at work! The next Saturday you had to clean your room again. What happened to the entropy of your room when you cleaned it up? Does this violate the second law of thermodynamics? Explain.

Answer to Essential Question 15.7: Decreasing the disorder of the room decreases its entropy. If the cleaning up process happened spontaneously that would violate the Second Law. However, in the system of you and the room, the decrease in entropy of the room is more than offset by the increase in entropy in your body, as measured by things like waste products that accumulated in your muscles as you did work. The room does not represent a closed system; examining a closed system (you and the room) we see that the Second Law of Thermodynamics is satisfied.

15-8 Heat Engines

Heat engines use heat to do work. Examples are car engines and heat engines that run in reverse, such as refrigerators and air conditioners. All heat engines require two temperatures. Adding heat at a higher temperature expands the system, while removing it at a lower temperature contracts the system, re-setting the engine so that a new cycle can occur.

Diagrams of the energy flow in a heat engine are shown in Figure 15.20. Q_H is the magnitude of the heat added or removed at a higher temperature, while Q_L is the magnitude of the heat added or removed at a lower temperature. W is the magnitude of the work involved, which is negative for a cooling device.

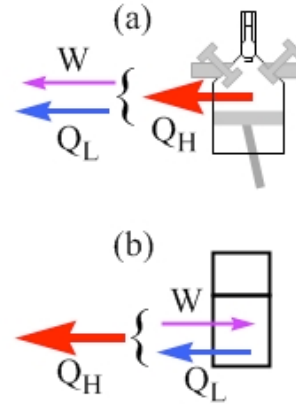


Figure 15.20: Energy flow diagrams. In (a), some heat from the cylinder of a car engine does useful work and the rest is discarded into the atmosphere. In (b), the combination of the heat removed from inside a refrigerator, and the work needed to extract it, is discarded into the room by the refrigerator's cooling coils.

The energy equation to accompany the diagram above (which is simply the First Law of Thermodynamics applied to a cycle, or a number of cycles) is:

$$Q_H - Q_L = W . \quad (\text{Eq. 15.15: Energy equation for a heat engine or cooling device})$$

The efficiency, e , of a heat engine is the work done by the engine divided by the heat added to cause that work to be done:

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H} . \quad (\text{Equation 15.16: Efficiency for a heat engine})$$

Can an ideal engine have an efficiency of 1, by eliminating losses from things like friction? No, in fact, as was proved by the French mathematician Sadi Carnot (1796 – 1832).

EXPLORATION 15.8 – An ideal (Carnot) engine

Carnot showed that an engine runs at maximum efficiency when it operates on the four-process cycle described in Table 15.5, and shown in the P-V diagram in Figure 15.21.

Process	Description	Heat	ΔS
1 \rightarrow 2	Isothermal expansion at T_H	$+Q_H$	$+Q_H/T_H$
2 \rightarrow 3	Adiabatic expansion to T_L	0	0
3 \rightarrow 4	Isothermal compression at T_L	$-Q_L$	$-Q_L/T_L$
4 \rightarrow 1	Adiabatic compression to T_H	0	0
Cycle	The Carnot Cycle	$Q_H - Q_L$	0

Table 15.5: The sequence of processes in a Carnot cycle.

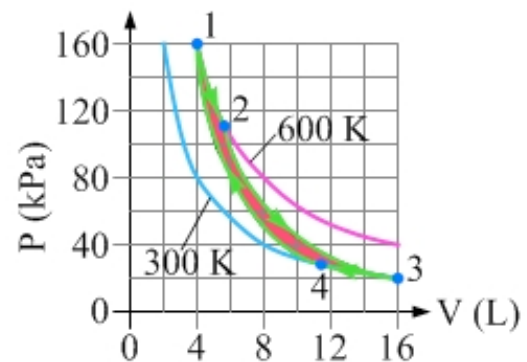


Figure 15.21: The P-V diagram for the Carnot cycle.

Step 1 – Equate the sum of the individual changes in entropy to the change in entropy for the cycle. Entropy is a state function. Because the cycle returns the system to its initial state the system returns to its original entropy. The change in entropy for a complete cycle is always zero:

$$\Sigma \Delta S = 0 \quad \text{which gives, in this case:} \quad \frac{Q_H}{T_H} = \frac{Q_L}{T_L} .$$

This gives: $\frac{T_L}{T_H} = \frac{Q_L}{Q_H} .$ (Equation 15.17: **The Carnot relationship for an ideal engine**)

Step 2 – Write the efficiency equation in terms of temperatures. Substituting Equation 15.17 into the efficiency equation, Equation 15.16 gives the efficiency of an ideal engine:

$$e_{ideal} = 1 - \frac{T_L}{T_H} . \text{ (Equation 15.18: Efficiency for an ideal engine)}$$

Key ideas for an ideal engine: The maximum efficiency of an engine is determined by the two temperatures the engine operates between. The third law of thermodynamics states that it is impossible to reach absolute zero, so even an ideal engine can never achieve 100% efficiency.
Related End-of-Chapter Exercises: 41 – 43 and 58.

EXAMPLE 15.8 – A heat pump

If you heat your home using electric heat, 1000 J of electrical energy can be transformed into 1000 J of heat. An alternate heating system is a heat pump, which extracts heat from a lower-temperature region (outside the house) and transfers it to a higher-temperature region (inside the house). The work done by the heat pump is 1000 J, and the temperatures are $T_H = 17^\circ\text{C} = 290\text{K}$ and $T_L = -23^\circ\text{C} = 250\text{K}$. (a) Predict whether the maximum amount of heat delivered to the house in this situation is more than, less than, or equal to 1000 J. (b) Calculate this maximum heat.

SOLUTION

(a) Many people predict that the heat pump delivers less than 1000 J of heat to the house, perhaps because of the condition that the efficiency is less than 1. However, the heat pump can be viewed as a cooling device because it is cooling the outside – it acts like an air conditioner in reverse. The heat delivered to the house is Q_H , which from the energy-flow diagram in Figure 15.20 (b) is larger than W . Thus, the pump delivers more than 1000 J of heat to the house.

(b) To find the maximum possible amount of heat we will treat the heat pump as an ideal device, and apply the Carnot relationship (Equation 15.17). Re-arranging this equation gives:

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

Substituting this into Equation 15.15, $Q_H - Q_L = W$, gives:

$$Q_H - \frac{T_L}{T_H} Q_H = W$$

Solving for Q_H , the heat delivered to the house, gives:

$$Q_H = \frac{T_H}{T_H - T_L} W = \frac{290\text{K}}{290\text{K} - 250\text{K}} (1000 \text{ J}) = 7250 \text{ J} .$$

Thus, 1000 J of work extracts 6250 J of heat from the outside air, delivering a total of 7250 J of heat to the indoors. This is why heat pumps are far superior to electric heaters!

Related End-of-Chapter Exercises: 44, 45, 59, 60.

Chapter Summary

Essential Idea: Heat can be used to do work.

In this chapter we looked at the connection between heat, work, and the change in internal energy, and we saw how the laws of thermodynamics can be applied to understand the basic operation of practical devices such as engines, refrigerators, and air conditioners.

The First Law of Thermodynamics

The first law of thermodynamics is a statement of energy conservation as it relates to a thermodynamic system. Heat, Q , can be transformed into (or come from) some combination of a change in internal energy, ΔE_{int} , of the system and the work, W , done by the system.

$$Q = \Delta E_{\text{int}} + W \quad . \quad (\text{Equation 15.1: The First Law of Thermodynamics})$$

Q is positive when heat is added to a system, and negative when heat is removed.

ΔE_{int} is positive when the temperature of a system increases, and negative when it decreases.

W is positive when a system expands and does work, and negative when the system is compressed.

Work, and Change in Internal Energy

The work done by a system during a thermodynamic process is equal to the area under the curve corresponding to that process on a P-V diagram.

Change in internal energy: If the temperature of an ideal gas changes the change in internal energy of the gas is proportional to the change in temperature.

$$\Delta E_{\text{int}} = n C_V \Delta T \quad . \quad (\text{Equation 15.4: Change in internal energy})$$

Heat Capacity

C_V is known as the heat capacity at constant volume.

$$\text{Monatomic: } C_V = \frac{3}{2}R \quad \quad \text{Diatomic: } C_V = \frac{5}{2}R \quad \quad \text{Polyatomic: } C_V = 3R$$

$C_p = R + C_V$ is the heat capacity at constant pressure.

$$\text{Monatomic: } C_p = \frac{5}{2}R \quad \quad \text{Diatomic: } C_p = \frac{7}{2}R \quad \quad \text{Polyatomic: } C_p = 4R$$

Special Thermodynamic Processes (see also Figure 15.14 in Section 15-5)

1. **An isochoric (constant volume) process.** There is no work done by the gas: $W = 0$. The heat added to the gas is equal to the change in internal energy: $Q = \Delta E_{\text{int}} = n C_V \Delta T$.
2. **An isobaric (constant pressure) process.** The work done by the gas is $W = P\Delta V$.
3. **An isothermal (constant temperature) process.** There is no change in internal energy, $\Delta E_{\text{int}} = 0$, so $Q = W$. The work done by the gas is given by:

$$Q = W = nRT \ln\left(\frac{V_f}{V_i}\right) \quad (\text{Eq. 15.8: Heat and work for an isothermal process})$$

4. **An adiabatic process.** Such a process is characterized by no heat transfer: $Q = 0$. On the P-V diagram an adiabatic process moves along a line given by:

$$PV^\gamma = \text{constant} \quad (\text{Eq. 15.9: Equation for an adiabatic process on the P-V diagram})$$

$$\gamma = \frac{C_P}{C_V} \quad (\text{Equation 15.10: The constant } \gamma \text{ for an adiabatic process})$$

$$\text{Another useful equation in an adiabatic situation is: } T_f V_f^{\gamma-1} = T_i V_i^{\gamma-1}. \quad (\text{Eq. 15.11})$$

Tools for Solving Thermodynamics Problems

- The P-V diagram can help us to visualize what is going on. In addition, the work done by a gas in a process is the area under the curve defining that process on the P-V diagram.
- The ideal gas law, $PV = nRT$, and the first law of thermodynamics, $Q = \Delta E_{\text{int}} + W$.
- The general expression for the change in internal energy, $\Delta E_{\text{int}} = nC_V \Delta T$.
- In specific special cases (see Figure 15.14, and the preceding section in this summary), there are additional relationships that can be used to relate the different parameters.

A Thermodynamic Cycle

A cycle is a sequence of processes that returns a system to its original state. The cycle as a whole satisfies the first law of thermodynamics, as does each of its processes. The change in internal energy for any cycle is always zero, because the system returns to its initial state, and the area of the enclosed region on the P-V diagram is the net work done in the cycle.

Entropy and the Second Law of Thermodynamics

Entropy is in some sense a measure of disorder. The symbol for entropy is S , and the units are J/K. Entropy is sometimes called time's arrow, because entropy tends to increase with time.

$$\Delta S \approx \frac{Q}{T_{av}}, \quad (\text{Equation 15.13: Approximate change in entropy})$$

where T_{av} is the average temperature of the system while the heat is being transferred.

$$\Delta S \geq 0. \quad (\text{Equation 15.14: The Second Law of Thermodynamics})$$

The entropy of a closed system tends to increase as time goes by.

Heat Engines

A heat engine, such as a car engine, uses a thermodynamic cycle to do work. Cooling devices such as refrigerators and air conditioners are heat engines run in reverse, having work done on them to pump heat from a cooler place to a warmer place.

$$Q_H - Q_L = W. \quad (\text{Eq. 15.15: Energy equation for a heat engine or cooling device})$$

$$e = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}. \quad (\text{Equation 15.16: Efficiency for a heat engine})$$

$$\frac{T_L}{T_H} = \frac{Q_L}{Q_H}. \quad (\text{Equation 15.17: The Carnot relationship for an ideal engine})$$

$$e_{\text{ideal}} = 1 - \frac{T_L}{T_H}. \quad (\text{Equation 15.18: Efficiency for an ideal engine})$$

End-of-Chapter Exercises

Exercises 1 – 12 are conceptual questions that are designed to see if you have understood the main concepts of the chapter.

- Two cylinders of ideal gas are initially identical (same pressure, volume, number of moles, and temperature) except that, in cylinder 1, the piston is free to move up or down without friction while, in cylinder 2, the piston is fixed in place so the volume occupied by the gas is constant. The same amount of heat is then added to both cylinders. Rank the cylinders based on (a) the final temperature of the gas, (b) the change in internal energy for the gas, and (c) the final pressure of the gas.

- A system of ideal gas can be taken from state 3 to state 4 by three different paths labeled A, B, and C on the P-V diagram in Figure 15.22. Rank these paths based on (a) the work done by the gas; (b) the change in internal energy of the gas; (c) the heat transferred to the gas.

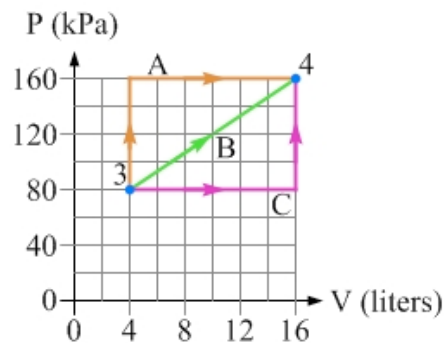


Figure 15.22: A system is taken from state 3 to state 4 by one of three possible paths. For Exercise 2.

- Consider two systems, each containing the same number of moles of ideal gas at the same initial pressure, volume, and temperature. In system A, the temperature is then doubled by adding heat at constant volume. In system B, the temperature is doubled by adding heat at constant pressure. (a) Under these conditions, which system would you expect to need more heat to be transferred to it, to achieve the doubling of the temperature? Why? (b) It turns out that exactly the same amount of heat is added to each system to double the temperature. Upon closer inspection, you find that the gases are different in the two systems. In what way are they different?
- A system of monatomic ideal gas is in a particular initial state. You now have a choice between three different processes, each of which double the volume occupied by the gas. Process A is an isothermal (constant temperature) expansion, process B is an adiabatic expansion, and process C is an isobaric (constant pressure) expansion. Rank these three processes, from most positive to most negative, based on (a) the work done by the gas, (b) the change in internal energy of the gas, and (c) the heat transferred to the gas during the process.
- Is it possible to accomplish any of the following with a sample of ideal gas? If so, explain how you would do it. If not, explain why not. (a) Add heat to a system without changing the system's temperature. (b) Increase the temperature of a system without adding heat. (c) Add heat to a system while decreasing the temperature. (d) Change the temperature of a system that is so well-insulated that no heat is transferred between the system and its surroundings.
- A system of ideal gas is in a particular initial state, and you will add a particular amount of heat Q to the system.
 - Process A: Add the heat at constant temperature.
 - Process B: Add the heat at constant volume.
 - Process C: Add the heat at constant pressure.
 Which process should you use if you want the system to end up (a) doing the most work? (b) with the maximum possible final temperature? (c) with the maximum possible final volume? (d) with the maximum possible final pressure?

7. Return to the situation described in Exercise 6. Rank the three processes based on (a) the work done by the gas in the process. (b) the final temperature of the system. (c) the final volume of the system. (d) the final pressure of the system.
8. A system of ideal gas is in a particular initial state, and you want the system to do a particular amount of work, W . You have three different processes to choose from. Process A is a constant pressure process; process B is done at constant temperature; while process C is an adiabatic process. (a) Sketch a P-V diagram showing the three different processes. Which process should you use if you want the system to end up (b) using the smallest amount of heat? (c) with the maximum possible final temperature? (d) with the maximum possible final volume? (e) with the minimum possible final pressure?
9. Return to the situation described in Exercise 8. Rank the three processes based on (a) the heat required by the process. (b) the final temperature of the system. (c) the final volume of the system. (d) the final pressure of the system.
10. A system of ideal gas is in a particular initial state, and you want to double the absolute temperature of the system. You have three different processes to choose from. Process A is a constant pressure process; process B is done at constant volume; while process C is an adiabatic process. (a) Sketch a P-V diagram showing the three different processes. Which process should you use if you want the system to end up (b) with the maximum possible final volume? (c) with the minimum possible final pressure?
11. Return to the situation described in Exercise 10. Rank the three processes based on (a) the heat required by the process. (b) the final temperature of the system. (c) the final volume of the system. (d) the final pressure of the system.
12. On a hot day, you decide to open your fridge door to be cooled by the cold air inside the fridge. In the short term, this is effective for cooling you down. If you left the fridge door open for a long time, however, with the refrigerator running, would the room end up warmer, cooler, or the same temperature as it was when you first opened the door? Explain.

Exercises 13 – 16 deal with heat, change in internal energy, and work, the three parameters that are connected by the first law of thermodynamics.

13. Two cylinders of ideal gas are initially identical (same pressure, volume, number of moles, and temperature) except that in cylinder 1 the piston is free to move up or down without friction, while in cylinder 2 the piston is fixed in place so the volume occupied by the gas is constant. The temperature in each cylinder is initially 50°C . Each cylinder is then placed in a container of ice water that is maintained at 0°C , and allowed to come to equilibrium. (a) Which cylinder has more heat removed from it in this process? (b) Which cylinder experiences the larger change in internal energy in this process? Justify your answers.
14. (a) How much work is done by the gas in the process shown in Figure 15.23? (b) If the gas is monatomic, what is the change in internal energy associated with the process? (c) How much heat is involved in this process? (d) Is heat transferred into the gas or transferred out of the gas?

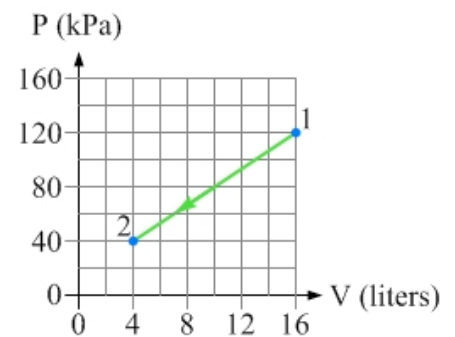


Figure 15.23: A system is taken from state 1 to state 2 by the process shown. For Exercise 14.

15. A system of ideal gas can be taken from state 3 to state 4 by three different paths labeled A, B, and C on the P-V diagram in Figure 15.24. Assume the gas is diatomic. For each of the three paths, calculate (a) the work done by the gas; (b) the change in internal energy of the gas; (c) the heat transferred to the gas.

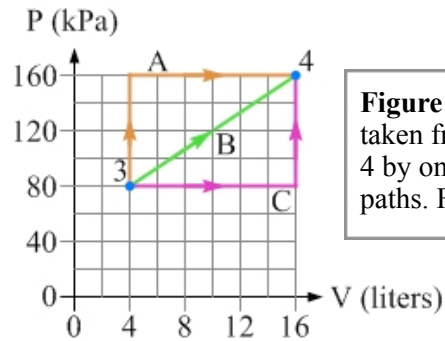


Figure 15.24: A system is taken from state 3 to state 4 by one of three possible paths. For Exercise 15.

16. A system of monatomic ideal gas contains a certain number of moles of gas so that $nR = 0.200 \text{ J/K}$. The system is taken from state 5 to state 6 (see Figure 15.25) by an unknown sequence of processes. (a) What is the temperature of the system in state 6? (b) What is the work done by the gas as the system moves from state 5 to state 6? (c) What is the change in internal energy of the gas as it moves from state 5 to state 6?

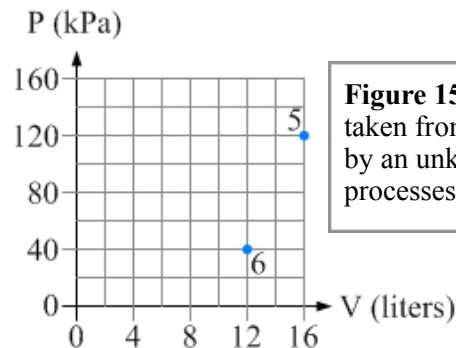


Figure 15.25: A system is taken from state 5 to state 6 by an unknown sequence of processes. For Exercise 16.

Exercises 17 – 21 deal with constant volume and constant pressure processes.

17. A cylinder of diatomic ideal gas is sealed in a cylinder by a piston that is fixed in place so the gas occupies a constant volume of 2.0 L. The pressure is initially 100 kPa, and the temperature is 400 K. The temperature is then decreased to 200 K by means of a constant volume process. (a) Sketch this process on a P-V diagram, and mark the final state of the system accurately on the diagram. (b) Find the work done by the gas in this process. (c) Find the change in internal energy of the gas in this process. (d) Find the amount of heat removed from the gas in this process. (e) Find the final internal energy of the gas.

18. Repeat Exercise 17, but this time the gas is monatomic instead of diatomic.

19. Repeat Exercise 17, but this time the piston is free to move without friction, and the decrease in temperature from 400 K to 200 K is done via a process in which the pressure remains constant at 100 kPa.

20. Four different processes are shown on the P-V diagram in Figure 15.26. The processes are carried out on a system of diatomic ideal gas. Rank these processes, from most positive to most negative, based on (a) the work done by the gas during the process, and (b) the change in internal energy of the gas during the process. Express your rankings in a form like $2 > 1 = 3 > 4$.

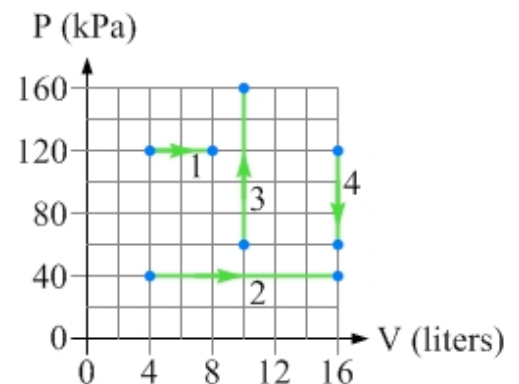


Figure 15.26: A P-V diagram showing four different processes, for Exercises 20 and 21.

21. Return to the situation described in Exercise 20 and shown in Figure 15.26. (a) For the process in which the work done by the gas is most positive, calculate the work. (b) For the process in which the internal energy of the gas increases by the largest amount, calculate that change in internal energy.

Exercises 22 – 27 deal with constant temperature and adiabatic processes.

22. A cylinder of monatomic ideal gas is sealed in a cylinder by a piston. The gas occupies a volume of 2.0 L. The pressure is initially 100 kPa, and cylinder is placed in an oven that maintains the temperature at 400 K. 100 J of work is then done on the piston, compressing the gas (in other words, the gas does -100 J of work). The work is done very slowly so that the gas maintains a constant temperature. (a) Sketch this process on a P-V diagram, shading in the region corresponding to the work done by the gas. (b) Find the change in internal energy of the gas in this process. (c) Find the final volume occupied by the gas. (d) Find the final pressure of the gas.
23. Repeat Exercise 22, but now the compression of the system is done very quickly so there is no time for heat to be transferred between the system and its surroundings. In other words, the process is adiabatic.
24. A system of diatomic ideal gas is in an initial state such that the pressure is 80 kPa and the volume occupied by the gas is 6.0 L. The system then experiences a compression at constant temperature that raises the pressure to 150 kPa. (a) Find the final volume occupied by the gas. (b) Find the work done by the gas in this process. (c) Find the ratio of the final temperature to the initial temperature.
25. Repeat Exercise 24, but now the compression that raises the pressure of the system to 150 kPa is an adiabatic process.
26. A system of monatomic ideal gas is in an initial state such that the pressure is 120 kPa and the volume occupied by the gas is 3.0 L. The system then experiences an expansion at constant temperature that increases the volume occupied by the gas to 8.0 L. (a) Find the final pressure of the gas. (b) Find the work done by the gas in this process. (c) Find the ratio of the final temperature to the initial temperature.
27. Repeat Exercise 26, but now the expansion that increases the volume to 8.0 L is an adiabatic process.

Exercises 28 – 31 deal with thermodynamic processes in general. Make use of the various tools for solving thermodynamic problems, outlined in section 15-5.

28. A system of diatomic ideal gas with an initial temperature of 500K is taken from an initial state i to a final state f by the process shown on the P-V diagram in Figure 15.27. Determine (a) the work done by the gas in the process. (b) the final temperature of the system. (c) the change in internal energy of the gas. (d) the heat associated with the process.
29. A system of monatomic ideal gas has an initial pressure of 100 kPa, a temperature of 400K, and a number of moles such that the product $nR = 2.0$ J/K. 1000 J of heat is then added to the system, while the pressure remains constant. Determine (a) the work done by the gas in the process, and (b) the final temperature of the gas. (c) Sketch an accurate P-V diagram for this process.

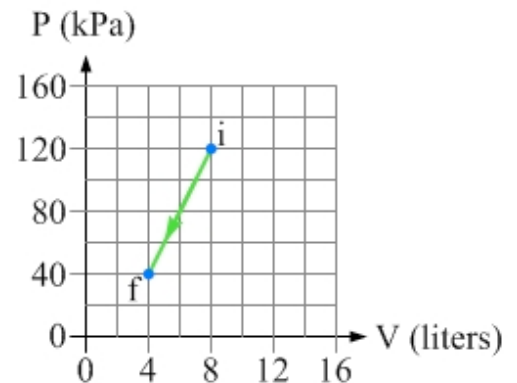


Figure 15.27: A process carried out on a system of diatomic ideal gas, for Exercise 28.

30. A system of monatomic ideal gas has an initial volume of 12 liters, a temperature of 600K, and a number of moles such that the product $nR = 0.50 \text{ J/K}$. 200 J of heat is then removed from the system at constant temperature. Determine (a) the work done by the gas in the process, and (b) the final volume occupied by the gas. (c) Sketch an accurate P-V diagram for this process.
31. A system of diatomic ideal gas is taken through the process shown in Figure 15.28. The process has the shape of a $\frac{1}{4}$ -circle on the P-V diagram. For this process, find (a) the work done by the gas, (b) the change in internal energy, and (c) the heat added to the gas.

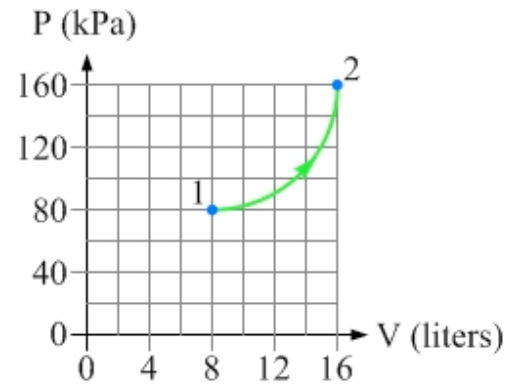


Figure 15.28: P-V diagram for a process taking a diatomic ideal gas from state 1 to state 2, for Exercise 31.

Exercises 32 – 38 deal with thermodynamic cycles.

32. Complete Table 15.6, where the process taking the system from state 2 to state 3 is isothermal.

Process	Q (J)	W (J)	ΔE_{int} (J)
1 \rightarrow 2			-300
2 \rightarrow 3	+200		
3 \rightarrow 1		+100	
Entire Cycle	+500		

Table 15.6: A table for a three-process cycle, for Exercise 32.

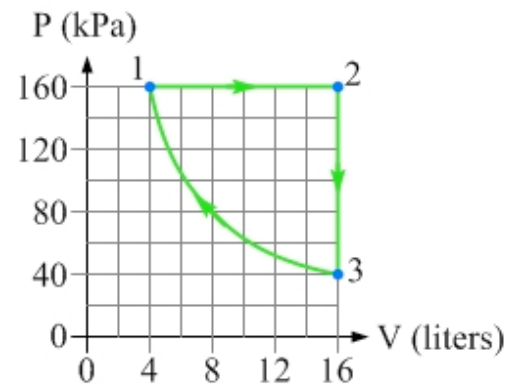


Figure 15.29: A three-process cycle, for Exercises 33 and 34.

33. Consider the P-V diagram for a three-process cycle in Figure 15.29. The cycle consists of a constant pressure process, a constant volume process, and an isothermal process at a temperature of 500 K. The system consists of a particular amount of a diatomic ideal gas. For this cycle, construct a table like that shown in Table 15.6.
34. Consider again the situation described in Exercise 33, and shown in Figure 15.29. What happens to all the values in the table when the cycle is carried out in the direction opposite to that shown in the P-V diagram, going from state 1 to 3 to 2 to 1?
35. Consider the following four-process cycle that is carried out on a system of monatomic ideal gas, starting from state 1 in which the pressure is 120 kPa and the volume is 4.0 liters. Process A is a constant-pressure process that doubles the volume; process B is an isothermal process, doubling the volume from the previous state; process C is a constant volume process that returns the system to its initial temperature; and process D is an isothermal process that returns the system to state 1. (a) Sketch a P-V diagram for this cycle. (b) Calculate the net work done by the gas in this cycle.

36. Consider the following four-process cycle that is carried out on a system of monatomic ideal gas, starting from state 1 in which the pressure is 80 kPa and the volume is 4.0 liters. Process A is an isothermal process that triples the volume; process B is a constant volume process that returns the system to a pressure of 80 kPa; process C is an isothermal process that returns the system to a volume of 4.0 liters; and process D is a constant volume process that returns the system to state 1. (a) Sketch a P-V diagram for this cycle. (b) For this cycle, construct a table like that shown in Table 15.6.
37. Consider the four-process cycle shown in the P-V diagram in Figure 15.30. (a) What does the area of the enclosed region, shown in red, represent? (b) What is the area of one of the boxes on the P-V diagram? (c) Estimate how many such boxes it would take to equal the area of the enclosed region. (d) Estimate the work done by the gas in one cycle.
38. Consider the four-process cycle shown in the P-V diagram in Figure 15.30. Find the work done by the gas in the process taking the system from (a) state 1 to state 2, (b) state 2 to state 3, (c) state 3 to state 4, (d) state 4 to state 1. For the entire cycle determine (e) the net work done by the gas, (f) the net change in internal energy of the gas, and (g) the net heat added to the gas.

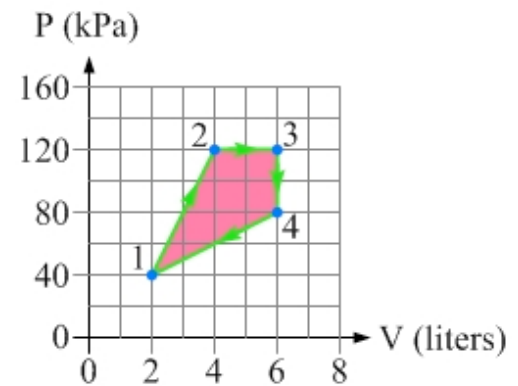


Figure 15.30: The P-V diagram for a four-process cycle, for Exercises 37 and 38.

Exercises 39 – 45 deal with entropy, the second law of thermodynamics, and heat engines.

39. You have two containers of water. In one container there is 1.0 kg of water at 7.0°C , while in the second container there is 5.0 kg of water at 27°C . You then pour the water in the first container into the second container and allow the system to come to equilibrium. Assuming no heat is transferred from the water to the container or the surroundings, determine the change in entropy for (a) the water that is initially cooler, (b) the water that is initially warmer, and (c) the system.
40. You have two containers of water. In one container there is 5.0 kg of water at 7.0°C , while in the second container there is 1.0 kg of water at 27°C . You then pour the water in the first container into the second container and allow the system to come to equilibrium. Assuming no heat is transferred from the water to the container or the surroundings, determine the change in entropy for (a) the water that is initially cooler, (b) the water that is initially warmer, and (c) the system.
41. In Section 15-8, we discussed the Carnot cycle, the cycle for a Carnot engine. Let's now examine the Stirling cycle, the cycle for a Stirling engine. The four processes are:
 Process A: Expansion at constant temperature T_H .
 Process B: Removing heat at a constant volume V_2 .
 Process C: Contraction at constant temperature T_L (say $T_H = 2T_L$).
 Process D: Adding heat at constant volume V_1 (say $V_2 = 2V_1$).
 Process D returns the system to its initial state. (a) Sketch a P-V diagram for this cycle. (b) Create a table to show, for each process and the entire cycle, whether the heat, work, change in internal energy, and change in entropy, is positive, negative, or zero.

42. Return to the situation described in Exercise 41. Let's say the system uses monatomic ideal gas, that $V_1 = 8.0 \text{ L}$, $T_L = 300 \text{ K}$, and the pressure in the initial state is $P_1 = 150 \text{ kPa}$. (a) Determine the net work done by the engine in one cycle. (b) Calculate the efficiency of the engine by dividing the net work done by the total amount of heat added to the system during processes A and D. (c) Compare your answer in part (b) to the ideal efficiency of an engine operating between temperatures of T_L and T_H .
43. A particular car engine operates between temperatures of $T_H = 400^\circ\text{C}$ (inside the cylinders of the engine) and $T_L = 20^\circ\text{C}$ (the temperature of the surroundings). (a) Given these two temperatures, what is the maximum possible efficiency the car can have? (b) With this maximum efficiency, determine how much heat must be obtained by burning fuel in the car's engine to accelerate a 1500 kg car from rest to a speed of 100 km/h (neglect resistive forces).
44. A refrigerator is characterized by a number called the coefficient of performance (COP), which is defined as the heat removed from the cool place (inside the fridge) divided by the work required to remove that heat: $COP = Q_L / W$. (a) If you are buying a new fridge is it better to buy one with a higher COP or a lower COP? Let's say that a fridge operates between temperatures of $T_L = 4^\circ\text{C}$ and $T_H = 30^\circ\text{C}$. A particular fridge has a COP of 6.0. (b) If 500 J of work is done by the compressor in the fridge to extract heat from inside the fridge, how much heat is removed from inside the fridge? (c) How much heat is dumped by the fridge into the surroundings, in this case? (d) What is the maximum possible COP that would be achieved by an ideal fridge operating between the two temperatures specified above?
45. An air conditioner and a refrigerator operate on the same principles, so the definition of coefficient of performance given in the previous exercise applies to air conditioners as well as refrigerators. Let's say a particular air conditioner has a COP of 7.5 when operating between temperatures of $T_L = 20^\circ\text{C}$ (inside your house) and $T_H = 30^\circ\text{C}$ (outside your house). (a) Is this an ideal device? Explain. (b) If the outside temperature increased to 35°C , would you expect this to change the coefficient of performance? Explain.

General problems and conceptual questions

46. In Section 15-2, we calculated the work done by the gas, and the change in internal energy of the gas, for a system of diatomic ideal gas that went from state 1 to state 2 and then to state 3 (see Figure 15.6). Determine the heat Q associated with the process that takes the system from (a) state 1 to state 2 (b) state 2 to state 3.
47. In section 15-2, we examined a system of diatomic ideal gas that was moved from state 1 to state 3 via state 2. Let's now bring the same system from state 1 to state 3 via state 4, as shown in Figure 15.31. Draw your own version of the P-V diagram, and then shade in the region that corresponds to the work done in moving the system from (a) state 1 to state 4 (b) state 4 to state 3. (c) Calculate the work done by the gas in these two processes.

48. Consider the system of diatomic ideal gas described in Exercise 47, and the processes shown on the P-V diagram in Figure 15.31. For the two processes shown, calculate (a) the change in internal energy of the gas, and (b) the heat added to the gas.

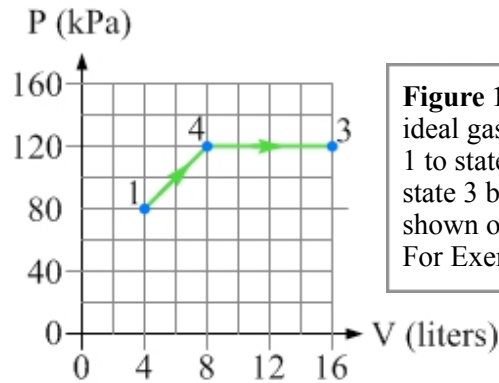


Figure 15.31: A system of ideal gas is moved from state 1 to state 4 and then on to state 3 by the processes shown on the P-V diagram. For Exercises 47 – 49.

49. Re-do Exercise 48. This time, the gas is monatomic instead of diatomic.

50. A system of monatomic ideal gas is moved from state 1 to state 2 by the process shown in Figure 15.32. (a) Determine the work done by the gas in this process. (b) Determine the change in internal energy for this process. (c) Determine the amount of heat associated with this process, and state whether heat was transferred into the gas or out of the gas.

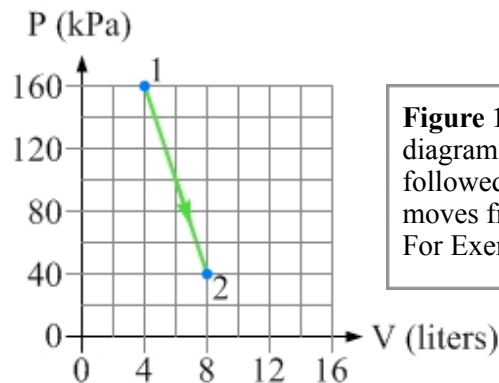


Figure 15.32: The P-V diagram shows the process followed by a system as it moves from state 1 to state 2. For Exercise 50.

51. A system of monatomic ideal gas is initially in state i , as shown in Figure 15.33. Compare the following situations, in which the system starts in the initial state i in each case. In case 1, the system's volume is increased by 4.0 L in a constant-pressure process. In case 2, the volume is decreased by 4.0 L in a constant-pressure process. (a) Sketch these two cases on a P-V diagram. (b) In which case is the magnitude of the work done by the gas larger? Explain your answer. (c) Calculate the work done by the gas in case 2.

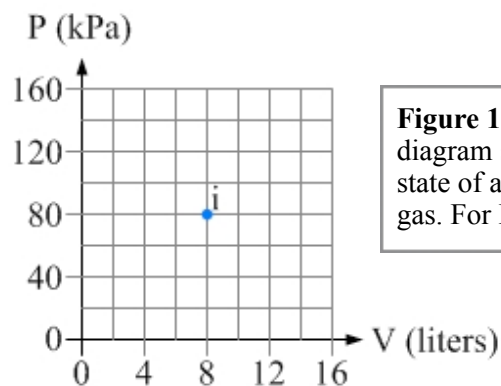


Figure 15.33: The P-V diagram shows the initial state of a system of ideal gas. For Exercises 51 – 53.

52. Repeat Exercise 51, but this time the changes in volume occur at constant temperature instead of at constant pressure.
53. Repeat Exercise 51 but, this time, the changes in volume have magnitudes of 2.0 L and occur during adiabatic processes.
54. (a) Why does a bicycle pump get hot as you pump it? (b) The pump is first filled with air, which we can approximate as a diatomic ideal gas, at room temperature and atmospheric pressure. You then quickly compress the gas, increasing the pressure by a factor of 5. Estimate the final temperature of the gas in this process.

55. A system of ideal gas has an initial pressure of 100 kPa and occupies a volume of 8.0 liters. Doubling the system's absolute temperature by means of a constant pressure process would require an amount of work W . Instead, you decide to double the absolute temperature by carrying out two processes in sequence, a constant volume process followed by a constant pressure process. Find the final pressure and volume of the system if the total work done in the sequence of processes is (a) $W/2$, or (b) $1.5 W$.
56. Repeat Exercise 55 but, this time, the sequence of processes used to double the temperature is done in reverse order. First, you do a constant pressure process, and then you do a constant volume process.
57. Consider what happens to entropy when a house is built. The construction involves taking a large number of bricks, pieces of wood, nails, cans of paint, wires, pipes, etc., and putting them together into a well-ordered system. Does this process violate the second law of thermodynamics? Explain.

58. Return to the description of the Carnot cycle in Section 15-8. The P-V diagram for the Carnot cycle can be hard to follow, because none of the processes is a straight line. Let's consider the T-S (temperature-entropy) diagram for the Carnot cycle instead, shown in Figure 15.34. For the Carnot cycle, the T-S diagram is a rectangle. (a) The area under the curve on a P-V diagram represents the work done by the gas. What does the area under the curve represent on the T-S diagram? (b) The area of the region enclosed by a cycle on a P-V diagram represents the net work done by the gas in one cycle. What does the area of the region enclosed by a cycle on the T-S diagram represent?

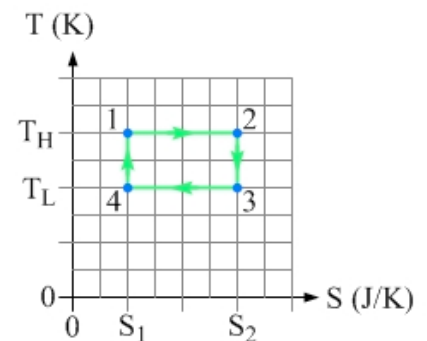


Figure 15.34: T-S (temperature-entropy) diagram for the Carnot cycle.

59. Ocean Thermal Energy Conversion (OTEC) generates electricity using the difference between the temperatures at the surface of the ocean, where the water is warm, and far below the surface, where the water is cool. A test system off Hawaii operated between temperatures of 80°F (the water temperature at the surface) and 40°F (the temperature far below the surface), and operated with an efficiency of about 2.3%. (a) What is the maximum efficiency we could expect from this system? (b) At the maximum efficiency, let's say the plant generates electricity at the rate of 100 MW. At what rate is energy being removed from the warm surface water? (c) At what rate is energy being deposited into the cooler sub-surface water?
60. Do some research on the Ocean Thermal Energy Conversion process described in Exercise 59, and write a paragraph or two describing how it works. Comment, in particular, on whether this idea is feasible for generating electricity, as well as on the environmental impact of such a system.
61. Comment on each statement in the following conversation between two students.

Jesse: This question talks about a thermodynamic system that is so well insulated that no heat is transferred between the system and the surrounding environment. That must mean that the temperature of the system stays constant, right?

Scott: I think so. That's the way it works in your house - the more insulation you have, the more constant the temperature of your house is.

Jesse: So, because the temperature is constant, there is no change in internal energy, and with no heat transferred there must also be no work done, right?