3 | THE FIRST LAW OF THERMODYNAMICS

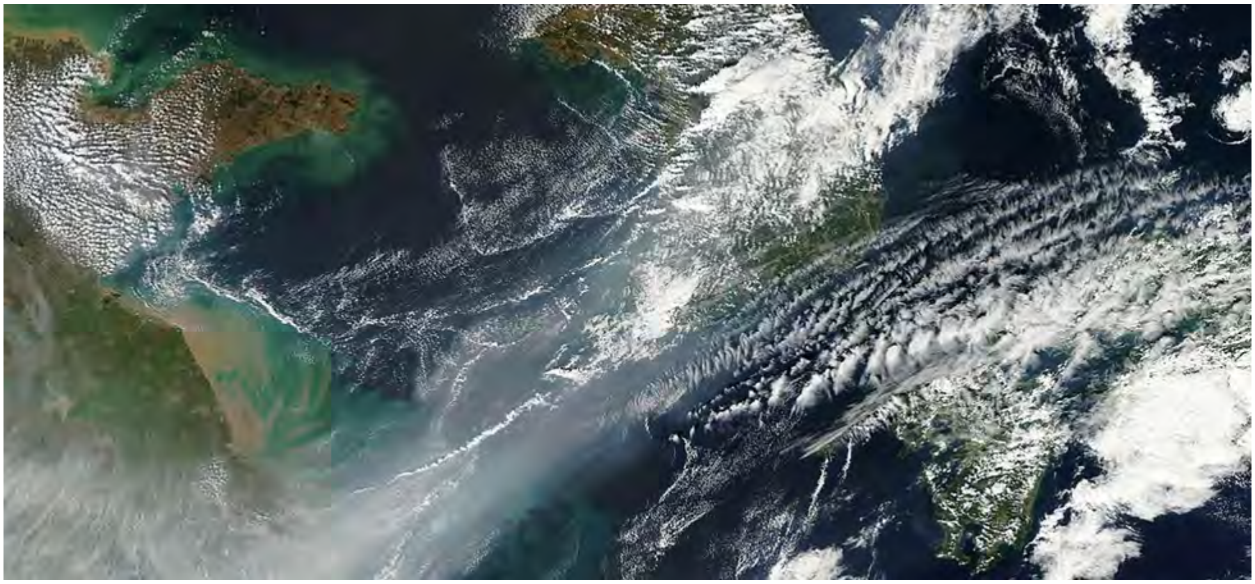


Figure 3.1 A weak cold front of air pushes all the smog in northeastern China into a giant smog blanket over the Yellow Sea, as captured by NASA's Terra satellite in 2012. To understand changes in weather and climate, such as the event shown here, you need a thorough knowledge of thermodynamics. (credit: modification of work by NASA)

Chapter Outline

Introduction

Heat is energy in transit, and it can be used to do work. It can also be converted into any other form of energy. A car engine, for example, burns gasoline. Heat is produced when the burned fuel is chemically transformed into mostly CO_2 and H_2O, which are gases at the combustion temperature. These gases exert a force on a piston through a displacement, doing work and converting the piston's kinetic energy into a variety of other forms—into the car's kinetic energy; into electrical energy to run the spark plugs, radio, and lights; and back into stored energy in the car's battery.

Energy is conserved in all processes, including those associated with thermodynamic systems. The roles of heat transfer and internal energy change vary from process to process and affect how work is done by the system in that process. We will see that the first law of thermodynamics puts a limit on the amount of work that can be delivered by the system when the amount of internal energy change or heat transfer is constrained. Understanding the laws that govern thermodynamic processes and the relationship between the system and its surroundings is therefore paramount in gaining scientific knowledge of energy and energy consumption.

3.1 | Thermodynamic Systems

Learning Objectives

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

- Define a thermodynamic system, its boundary, and its surroundings
- Explain the roles of all the components involved in thermodynamics
- Define thermal equilibrium and thermodynamic temperature
- Link an equation of state to a system

A **thermodynamic system** includes anything whose thermodynamic properties are of interest. It is embedded in its **surroundings** or **environment**; it can exchange heat with, and do work on, its environment through a **boundary**, which is the imagined wall that separates the system and the environment (**Figure 3.2**). In reality, the immediate surroundings of the system are interacting with it directly and therefore have a much stronger influence on its behavior and properties. For example, if we are studying a car engine, the burning gasoline inside the cylinder of the engine is the thermodynamic system; the piston, exhaust system, radiator, and air outside form the surroundings of the system. The boundary then consists of the inner surfaces of the cylinder and piston.

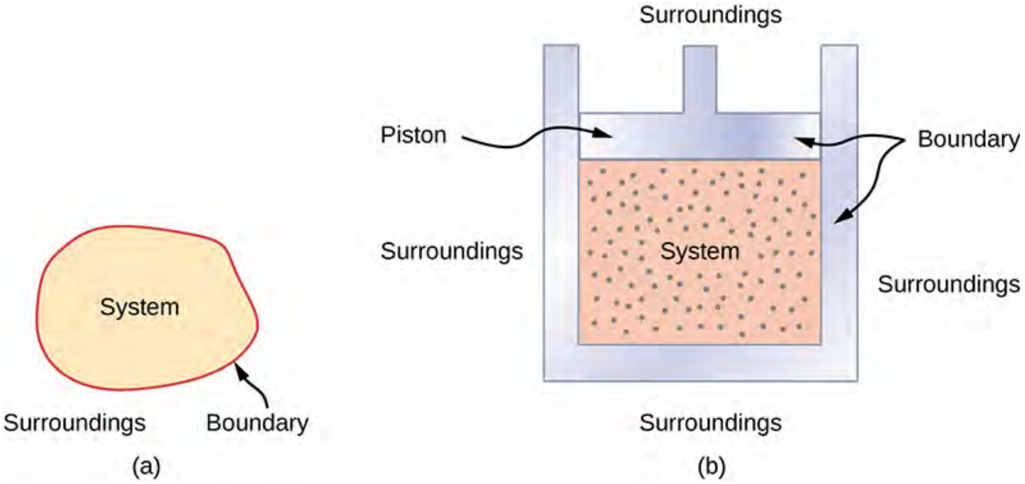


Figure 3.2 (a) A system, which can include any relevant process or value, is self-contained in an area. The surroundings may also have relevant information; however, the surroundings are important to study only if the situation is an open system. (b) The burning gasoline in the cylinder of a car engine is an example of a thermodynamic system.

Normally, a system must have some interactions with its surroundings. A system is called an isolated or **closed system** if it is completely separated from its environment—for example, a gas that is surrounded by immovable and thermally insulating walls. In reality, a closed system does not exist unless the entire universe is treated as the system, or it is used as a model for an actual system that has minimal interactions with its environment. Most systems are known as an **open system**, which can exchange energy and/or matter with its surroundings (**Figure 3.3**).

Figure 3.3 (a) This boiling tea kettle is an open thermodynamic system. It transfers heat and matter (steam) to its surroundings. (b) A pressure cooker is a good approximation to a closed system. A little steam escapes through the top valve to prevent explosion. (credit a: modification of work by Gina Hamilton)

When we examine a thermodynamic system, we ignore the difference in behavior from place to place inside the system for a given moment. In other words, we concentrate on the macroscopic properties of the system, which are the averages of the microscopic properties of all the molecules or entities in the system. Any thermodynamic system is therefore treated as a continuum that has the same behavior everywhere inside. We assume the system is in **equilibrium**. You could have, for example, a temperature gradient across the system. However, when we discuss a thermodynamic system in this chapter, we study those that have uniform properties throughout the system.

Before we can carry out any study on a thermodynamic system, we need a fundamental characterization of the system. When we studied a mechanical system, we focused on the forces and torques on the system, and their balances dictated the mechanical equilibrium of the system. In a similar way, we should examine the heat transfer between a thermodynamic system and its environment or between the different parts of the system, and its balance should dictate the thermal equilibrium of the system. Intuitively, such a balance is reached if the temperature becomes the same for different objects or parts of the system in thermal contact, and the net heat transfer over time becomes zero.

Thus, when we say two objects (a thermodynamic system and its environment, for example) are in thermal equilibrium, we mean that they are at the same temperature, as we discussed in **Temperature and Heat**. Let us consider three objects at temperatures $T_1,\ T_2,$ and $T_3,$ respectively. How do we know whether they are in thermal equilibrium? The governing principle here is the zeroth law of thermodynamics, as described in **Temperature and Heat** on temperature and heat:

If object 1 is in thermal equilibrium with objects 2 and 3, respectively, then objects 2 and 3 must also be in thermal equilibrium.

Mathematically, we can simply write the zeroth law of thermodynamics as

$$\text{If } T_1 = T_2 \text{ and } T_1 = T_3, \text{ then } T_2 = T_3. \tag{3.1}$$

This is the most fundamental way of defining temperature: Two objects must be at the same temperature thermodynamically if the net heat transfer between them is zero when they are put in thermal contact and have reached a thermal equilibrium.

The zeroth law of thermodynamics is equally applicable to the different parts of a closed system and requires that the temperature everywhere inside the system be the same if the system has reached a thermal equilibrium. To simplify our discussion, we assume the system is uniform with only one type of material—for example, water in a tank. The measurable properties of the system at least include its volume, pressure, and temperature. The range of specific relevant variables depends upon the system. For example, for a stretched rubber band, the relevant variables would be length, tension, and temperature. The relationship between these three basic properties of the system is called the **equation of state** of the system and is written symbolically *for a closed system* as

$$f(p,\ V,\ T) = 0, \tag{3.2}$$

where V, p, and T are the volume, pressure, and temperature of the system at a given condition.

In principle, this equation of state exists for any thermodynamic system but is not always readily available. The forms of $f(p,\ V,\ T) = 0$ for many materials have been determined either experimentally or theoretically. In the preceding chapter, we saw an example of an equation of state for an ideal gas, $f(p,\ V,\ T) = pV - nRT = 0.$

We have so far introduced several physical properties that are relevant to the thermodynamics of a thermodynamic system, such as its volume, pressure, and temperature. We can separate these quantities into two generic categories. The quantity associated with an amount of matter is an **extensive variable**, such as the volume and the number of moles. The other properties of a system are **intensive variables**, such as the pressure and temperature. An extensive variable doubles its value if the amount of matter in the system doubles, provided all the intensive variables remain the same. For example, the volume or total energy of the system doubles if we double the amount of matter in the system while holding the temperature and pressure of the system unchanged.

3.2 | Work, Heat, and Internal Energy

Learning Objectives

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

- Describe the work done by a system, heat transfer between objects, and internal energy change of a system
- Calculate the work, heat transfer, and internal energy change in a simple process

We discussed the concepts of work and energy earlier in mechanics. Examples and related issues of heat transfer between different objects have also been discussed in the preceding chapters. Here, we want to expand these concepts to a thermodynamic system and its environment. Specifically, we elaborated on the concepts of heat and heat transfer in the previous two chapters. Here, we want to understand how work is done by or to a thermodynamic system; how heat is transferred between a system and its environment; and how the total energy of the system changes under the influence of the work done and heat transfer.

Work Done by a System

A force created from any source can do work by moving an object through a displacement. Then how does a thermodynamic system do work? **Figure 3.4** shows a gas confined to a cylinder that has a movable piston at one end. If the gas expands against the piston, it exerts a force through a distance and does work on the piston. If the piston compresses the gas as it is moved inward, work is also done—in this case, on the gas. The work associated with such volume changes can be determined as follows: Let the gas pressure on the piston face be p. Then the force on the piston due to the gas is pA, where A is the area of the face. When the piston is pushed outward an infinitesimal distance dx, the magnitude of the work done by the gas is

$$dW = F\,dx = pA\,dx.$$

Since the change in volume of the gas is $dV = A\,dx,$ this becomes

$$dW = pdV. \tag{3.3}$$

For a finite change in volume from V_1 to $V_2,$ we can integrate this equation from V_1 to V_2 to find the net work:

$$W = \int_{V_1}^{V_2} pdV. \tag{3.4}$$

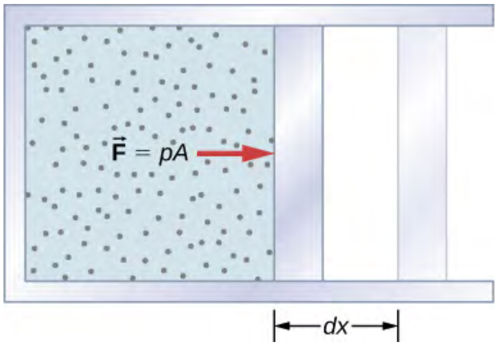


Figure 3.4 The work done by a confined gas in moving a piston a distance dx is given by $dW = Fdx = pdV$.

This integral is only meaningful for a **quasi-static process**, which means a process that takes place in infinitesimally small steps, keeping the system at thermal equilibrium. (We examine this idea in more detail later in this chapter.) Only then does a well-defined mathematical relationship (the equation of state) exist between the pressure and volume. This relationship can be plotted on a pV diagram of pressure versus volume, where the curve is the change of state. We can approximate such a process as one that occurs slowly, through a series of equilibrium states. The integral is interpreted graphically as the area under the pV curve (the shaded area of **Figure 3.5**). Work done by the gas is positive for expansion and negative for compression.

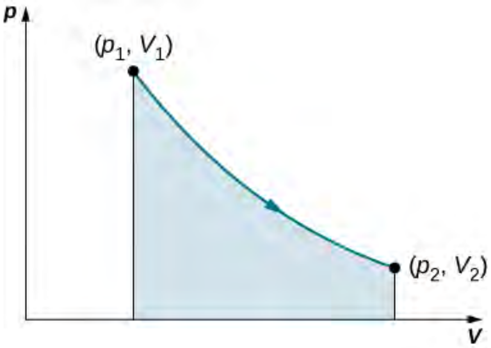


Figure 3.5 When a gas expands slowly from V_1 to V_2, the work done by the system is represented by the shaded area under the pV curve.

Consider the two processes involving an ideal gas that are represented by paths AC and ABC in **Figure 3.6**. The first process is an isothermal expansion, with the volume of the gas changing its volume from V_1 to V_2. This isothermal process is represented by the curve between points A and C. The gas is kept at a constant temperature T by keeping it in thermal equilibrium with a heat reservoir at that temperature. From **Equation 3.4** and the ideal gas law,

$$W = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \left(\frac{nRT}{V}\right) dV.$$

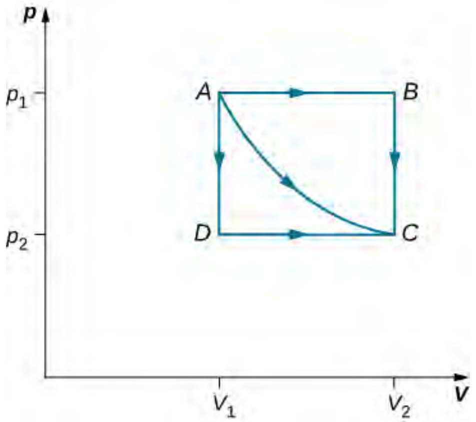


Figure 3.6 The paths *ABC*, *AC*, and *ADC* represent three different quasi-static transitions between the equilibrium states *A* and *C*.

The expansion is isothermal, so *T* remains constant over the entire process. Since *n* and *R* are also constant, the only variable in the integrand is *V*, so the work done by an ideal gas in an isothermal process is

$$W = nRT\int_{V_1}^{V_2}\frac{dV}{V} = nRT\ln\frac{V_2}{V_1}.$$

Notice that if $V_2 > V_1$ (expansion), *W* is positive, as expected.

The straight lines from *A* to *B* and then from *B* to *C* represent a different process. Here, a gas at a pressure p_1 first expands isobarically (constant pressure) and quasi-statically from V_1 to V_2, after which it cools quasi-statically at the constant volume V_2 until its pressure drops to p_2. From *A* to *B*, the pressure is constant at *p*, so the work over this part of the path is

$$W = \int_{V_1}^{V_2} p dV = p_1\int_{V_1}^{V_2} dV = p_1(V_2 - V_1).$$

From *B* to *C*, there is no change in volume and therefore no work is done. The net work over the path *ABC* is then

$$W = p_1(V_2 - V_1) + 0 = p_1(V_2 - V_1).$$

A comparison of the expressions for the work done by the gas in the two processes of **Figure 3.6** shows that they are quite different. This illustrates a very important property of thermodynamic work: It is *path dependent*. We cannot determine the work done by a system as it goes from one equilibrium state to another unless we know its thermodynamic path. Different values of the work are associated with different paths.

Example 3.1

Isothermal Expansion of a van der Waals Gas

Studies of a van der Waals gas require an adjustment to the ideal gas law that takes into consideration that gas molecules have a definite volume (see **The Kinetic Theory of Gases**). One mole of a van der Waals gas has an equation of state

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT,$$

where *a* and *b* are two parameters for a specific gas. Suppose the gas expands isothermally and quasi-statically from volume V_1 to volume V_2. How much work is done by the gas during the expansion?

Strategy

Because the equation of state is given, we can use **Equation 3.4** to express the pressure in terms of V and T. Furthermore, temperature T is a constant under the isothermal condition, so V becomes the only changing variable under the integral.

Solution

To evaluate this integral, we must express p as a function of V. From the given equation of state, the gas pressure is

$$p = \frac{RT}{V - b} - \frac{a}{V^2}.$$

Because T is constant under the isothermal condition, the work done by 1 mol of a van der Waals gas in expanding from a volume V_1 to a volume V_2 is thus

$$\begin{aligned} W &= \int_{V_1}^{V_2} \left(\frac{RT}{V - b} - \frac{a}{V^2} \right) = \left| RT\ln(V - b) + \frac{a}{V} \right|_{V_1}^{V_2} \\ &= RT\ln\left(\frac{V_2 - b}{V_1 - b} \right) + a\left(\frac{1}{V_2} - \frac{1}{V_1} \right). \end{aligned}$$

Significance

By taking into account the volume of molecules, the expression for work is much more complex. If, however, we set $a = 0$ and $b = 0$, we see that the expression for work matches exactly the work done by an isothermal process for one mole of an ideal gas.

3.1 Check Your Understanding How much work is done by the gas, as given in **Figure 3.6**, when it expands quasi-statically along the path ADC?

Internal Energy

The **internal energy** E_{int} of a thermodynamic system is, by definition, the sum of the mechanical energies of all the molecules or entities in the system. If the kinetic and potential energies of molecule i are K_i and U_i, respectively, then the internal energy of the system is the average of the total mechanical energy of all the entities:

$$E_{\text{int}} = \sum_i (\bar{K}_i + \bar{U}_i), \tag{3.5}$$

where the summation is over all the molecules of the system, and the bars over K and U indicate average values. The kinetic energy K_i of an individual molecule includes contributions due to its rotation and vibration, as well as its translational energy $m_i v_i^2/2$, where v_i is the molecule's speed measured relative to the center of mass of the system. The potential energy U_i is associated only with the interactions between molecule i and the other molecules of the system. In fact, neither the system's location nor its motion is of any consequence as far as the internal energy is concerned. The internal energy of the system is not affected by moving it from the basement to the roof of a 100-story building or by placing it on a moving train.

In an ideal monatomic gas, each molecule is a single atom. Consequently, there is no rotational or vibrational kinetic energy and $K_i = m_i v_i^2/2$. Furthermore, there are no interatomic interactions (collisions notwithstanding), so $U_i = \text{constant}$, which we set to zero. The internal energy is therefore due to translational kinetic energy only and

$$E_{\text{int}} = \sum_i \bar{K}_i = \sum_i \frac{1}{2} m_i \overline{v_i^2}.$$

From the discussion in the preceding chapter, we know that the average kinetic energy of a molecule in an ideal monatomic gas is

$$\frac{1}{2} m_i \overline{v_i^2} = \frac{3}{2} k_{\text{B}} T,$$

where T is the Kelvin temperature of the gas. Consequently, the average mechanical energy per molecule of an ideal monatomic gas is also $3k_{\text{B}}T/2,$ that is,

$$\overline{K_i + U_i} = \bar{K}_i = \frac{3}{2} k_{\text{B}} T.$$

The internal energy is just the number of molecules multiplied by the average mechanical energy per molecule. Thus for n moles of an ideal monatomic gas,

$$E_{\text{int}} = nN_{\text{A}}\left(\frac{3}{2} k_{\text{B}} T\right) = \frac{3}{2} nRT. \tag{3.6}$$

Notice that the internal energy of a given quantity of an ideal monatomic gas depends on just the temperature and is completely independent of the pressure and volume of the gas. For other systems, the internal energy cannot be expressed so simply. However, an increase in internal energy can often be associated with an increase in temperature.

We know from the zeroth law of thermodynamics that when two systems are placed in thermal contact, they eventually reach thermal equilibrium, at which point they are at the same temperature. As an example, suppose we mix two monatomic ideal gases. Now, the energy per molecule of an ideal monatomic gas is proportional to its temperature. Thus, when the two gases are mixed, the molecules of the hotter gas must lose energy and the molecules of the colder gas must gain energy. This continues until thermal equilibrium is reached, at which point, the temperature, and therefore the average translational kinetic energy per molecule, is the same for both gases. The approach to equilibrium for real systems is somewhat more complicated than for an ideal monatomic gas. Nevertheless, we can still say that energy is exchanged between the systems until their temperatures are the same.

3.3 | First Law of Thermodynamics

Learning Objectives

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

- State the first law of thermodynamics and explain how it is applied
- Explain how heat transfer, work done, and internal energy change are related in any thermodynamic process

Now that we have seen how to calculate internal energy, heat, and work done for a thermodynamic system undergoing change during some process, we can see how these quantities interact to affect the amount of change that can occur. This interaction is given by the first law of thermodynamics. British scientist and novelist C. P. Snow (1905–1980) is credited with a joke about the four laws of thermodynamics. His humorous statement of the first law of thermodynamics is stated “you can’t win,” or in other words, you cannot get more energy out of a system than you put into it. We will see in this chapter how internal energy, heat, and work all play a role in the first law of thermodynamics.

Suppose Q represents the heat exchanged between a system and the environment, and W is the work done by or on the system. The first law states that the change in internal energy of that system is given by $Q - W$. Since added heat increases the internal energy of a system, Q is positive when it is added to the system and negative when it is removed from the system.

When a gas expands, it does work and its internal energy decreases. Thus, W is positive when work is done by the system and negative when work is done on the system. This sign convention is summarized in **Table 3.1**. The **first law of**

thermodynamics is stated as follows:

First Law of Thermodynamics

Associated with every equilibrium state of a system is its internal energy E_{int}. The change in E_{int} for any transition between two equilibrium states is

$$\Delta E_{\text{int}} = Q - W \tag{3.7}$$

where Q and W represent, respectively, the heat exchanged by the system and the work done by or on the system.

Thermodynamic Sign Conventions for Heat and Work

Process	Convention
Heat added to system	$Q > 0$
Heat removed from system	$Q < 0$
Work done by system	$W > 0$
Work done on system	$W < 0$

Table 3.1

The first law is a statement of energy conservation. It tells us that a system can exchange energy with its surroundings by the transmission of heat and by the performance of work. The net energy exchanged is then equal to the change in the total mechanical energy of the molecules of the system (i.e., the system's internal energy). Thus, if a system is isolated, its internal energy must remain constant.

Although Q and W both depend on the thermodynamic path taken between two equilibrium states, their difference $Q - W$ does not. **Figure 3.7** shows the pV diagram of a system that is making the transition from A to B repeatedly along different thermodynamic paths. Along path 1, the system absorbs heat Q_1 and does work W_1; along path 2, it absorbs heat Q_2 and does work W_2, and so on. The values of Q_i and W_i may vary from path to path, but we have

$$Q_1 - W_1 = Q_2 - W_2 = \cdots = Q_i - W_i = \cdots,$$

or

$$\Delta E_{\text{int1}} = \Delta E_{\text{int2}} = \cdots = \Delta E_{\text{int}i} = \cdots.$$

That is, the change in the internal energy of the system between A and B is path independent. In the chapter on potential energy and the conservation of energy, we encountered another path-independent quantity: the change in potential energy between two arbitrary points in space. This change represents the negative of the work done by a conservative force between the two points. The potential energy is a function of spatial coordinates, whereas the internal energy is a function of thermodynamic variables. For example, we might write $E_{\text{int}}(T, p)$ for the internal energy. Functions such as internal energy and potential energy are known as *state functions* because their values depend solely on the state of the system.

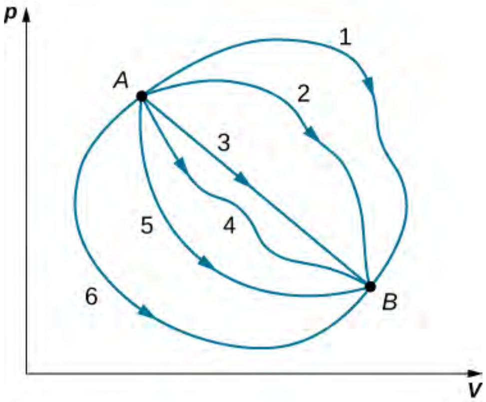


Figure 3.7 Different thermodynamic paths taken by a system in going from state *A* to state *B*. For all transitions, the change in the internal energy of the system $\Delta E_{\text{int}} = Q - W$ is the same.

Often the first law is used in its differential form, which is

$$dE_{\text{int}} = dQ - dW. \tag{3.8}$$

Here dE_{int} is an infinitesimal change in internal energy when an infinitesimal amount of heat dQ is exchanged with the system and an infinitesimal amount of work dW is done by (positive in sign) or on (negative in sign) the system.

Example 3.2

Changes of State and the First Law

During a thermodynamic process, a system moves from state *A* to state *B*, it is supplied with 400 J of heat and does 100 J of work. (a) For this transition, what is the system's change in internal energy? (b) If the system then moves from state *B* back to state *A*, what is its change in internal energy? (c) If in moving from *A* to *B* along a different path, $W'_{AB} = 400\,\text{J}$ of work is done on the system, how much heat does it absorb?

Strategy

The first law of thermodynamics relates the internal energy change, work done by the system, and the heat transferred to the system in a simple equation. The internal energy is a function of state and is therefore fixed at any given point regardless of how the system reaches the state.

Solution

a. From the first law, the change in the system's internal energy is

$$\Delta E_{\text{int}AB} = Q_{AB} - W_{AB} = 400\,\text{J} - 100\,\text{J} = 300\,\text{J}.$$

b. Consider a closed path that passes through the states *A* and *B*. Internal energy is a state function, so ΔE_{int} is zero for a closed path. Thus

$$\Delta E_{\text{int}} = \Delta E_{\text{int}AB} + \Delta E_{\text{int}BA} = 0,$$

and

$$\Delta E_{\text{int}AB} = -\Delta E_{\text{int}BA}.$$

This yields

$$\Delta E_{\text{int}BA} = -300\,\text{J}.$$

c. The change in internal energy is the same for any path, so

$$\begin{aligned}\Delta E_{\text{int}AB} &= \Delta E'_{\text{int}AB} = Q'_{AB} - W'_{AB};\\ 300\,\text{J} &= Q'_{AB} - (-400\,\text{J}),\end{aligned}$$

and the heat exchanged is

$$Q'_{AB} = -100\,\text{J}.$$

The negative sign indicates that the system loses heat in this transition.

Significance

When a closed cycle is considered for the first law of thermodynamics, the change in internal energy around the whole path is equal to zero. If friction were to play a role in this example, less work would result from this heat added. **Example 3.3** takes into consideration what happens if friction plays a role.

Notice that in **Example 3.2**, we did not assume that the transitions were quasi-static. This is because the first law is not subject to such a restriction. It describes transitions between equilibrium states but is not concerned with the intermediate states. The system does not have to pass through only equilibrium states. For example, if a gas in a steel container at a well-defined temperature and pressure is made to explode by means of a spark, some of the gas may condense, different gas molecules may combine to form new compounds, and there may be all sorts of turbulence in the container—but eventually, the system will settle down to a new equilibrium state. This system is clearly not in equilibrium during its transition; however, its behavior is still governed by the first law because the process starts and ends with the system in equilibrium states.

Example 3.3

Polishing a Fitting

A machinist polishes a 0.50-kg copper fitting with a piece of emery cloth for 2.0 min. He moves the cloth across the fitting at a constant speed of 1.0 m/s by applying a force of 20 N, tangent to the surface of the fitting. (a) What is the total work done on the fitting by the machinist? (b) What is the increase in the internal energy of the fitting? Assume that the change in the internal energy of the cloth is negligible and that no heat is exchanged between the fitting and its environment. (c) What is the increase in the temperature of the fitting?

Strategy

The machinist's force over a distance that can be calculated from the speed and time given is the work done on the system. The work, in turn, increases the internal energy of the system. This energy can be interpreted as the heat that raises the temperature of the system via its heat capacity. Be careful with the sign of each quantity.

Solution

a. The power created by a force on an object or the rate at which the machinist does frictional work on the fitting is $\vec{\mathbf{F}} \cdot \vec{\mathbf{v}} = -Fv$. Thus, in an elapsed time Δt (2.0 min), the work done on the fitting is

$$\begin{aligned}W &= -Fv\Delta t = -(20\,\text{N})(0.1\,\text{m/s})(1.2 \times 10^2\ \text{s})\\ &= -2.4 \times 10^3\ \text{J}.\end{aligned}$$

b. By assumption, no heat is exchanged between the fitting and its environment, so the first law gives for the change in the internal energy of the fitting:

$$\Delta E_{\text{int}} = -W = 2.4 \times 10^3\ \text{J}.$$

c. Since ΔE_{int} is path independent, the effect of the $2.4 \times 10^3\ \text{J}$ of work is the same as if it were supplied at atmospheric pressure by a transfer of heat. Thus,

$$2.4 \times 10^3\ \text{J} = mc\Delta T = (0.50\,\text{kg})(3.9 \times 10^2\ \text{J/kg} \cdot {}^\circ\text{C})\Delta T,$$

and the increase in the temperature of the fitting is

$$\Delta T = 12\ °\text{C},$$

where we have used the value for the specific heat of copper, $c = 3.9 \times 10^2\ \text{J/kg} \cdot °\text{C}$.

Significance

If heat were released, the change in internal energy would be less and cause less of a temperature change than what was calculated in the problem.

3.2 Check Your Understanding The quantities below represent four different transitions between the same initial and final state. Fill in the blanks.

Q **(J)**	***W*** **(J)**	ΔE_{int}**(J)**
–80	–120	
90		
	40	
	–40	

Table 3.2

Example 3.4

An Ideal Gas Making Transitions between Two States

Consider the quasi-static expansions of an ideal gas between the equilibrium states *A* and *C* of Figure 3.6. If 515 J of heat are added to the gas as it traverses the path *ABC*, how much heat is required for the transition along *ADC*? Assume that $p_1 = 2.10 \times 10^5\ \text{N/m}^2$, $p_2 = 1.05 \times 10^5\ \text{N/m}^2$, $V_1 = 2.25 \times 10^{-3}\ \text{m}^3$, and $V_2 = 4.50 \times 10^{-3}\ \text{m}^3$.

Strategy

The difference in work done between process *ABC* and process *ADC* is the area enclosed by *ABCD*. Because the change of the internal energy (a function of state) is the same for both processes, the difference in work is thus the same as the difference in heat transferred to the system.

Solution

For path *ABC*, the heat added is $Q_{ABC} = 515\ \text{J}$ and the work done by the gas is the area under the path on the *pV* diagram, which is

$$W_{ABC} = p_1(V_2 - V_1) = 473\ \text{J}.$$

Along *ADC*, the work done by the gas is again the area under the path:

$$W_{ADC} = p_2(V_2 - V_1) = 236\ \text{J}.$$

Then using the strategy we just described, we have

$$Q_{ADC} - Q_{ABC} = W_{ADC} - W_{ABC},$$

which leads to

$$Q_{ADC} = Q_{ABC} + W_{ADC} - W_{ABC} = (515 + 236 - 473)\ \text{J} = 278\ \text{J}.$$

Significance

The work calculations in this problem are made simple since no work is done along *AD* and *BC* and along *AB* and

DC; the pressure is constant over the volume change, so the work done is simply $p\Delta V$. An isothermal line could also have been used, as we have derived the work for an isothermal process as $W = nRT\ln\frac{V_2}{V_1}$.

Example 3.5

Isothermal Expansion of an Ideal Gas

Heat is added to 1 mol of an ideal monatomic gas confined to a cylinder with a movable piston at one end. The gas expands quasi-statically at a constant temperature of 300 K until its volume increases from *V* to 3*V*. (a) What is the change in internal energy of the gas? (b) How much work does the gas do? (c) How much heat is added to the gas?

Strategy

(a) Because the system is an ideal gas, the internal energy only changes when the temperature changes. (b) The heat added to the system is therefore purely used to do work that has been calculated in **Work, Heat, and Internal Energy**. (c) Lastly, the first law of thermodynamics can be used to calculate the heat added to the gas.

Solution

a. We saw in the preceding section that the internal energy of an ideal monatomic gas is a function only of temperature. Since $\Delta T = 0$, for this process, $\Delta E_{\text{int}} = 0$.

b. The quasi-static isothermal expansion of an ideal gas was considered in the preceding section and was found to be

$$\begin{aligned} W &= nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{3V}{V} \\ &= (1.00\ \text{mol})(8.314\ \text{J/K}\cdot\text{mol})(300\ \text{K})(\ln 3) = 2.74 \times 10^3\ \text{J}. \end{aligned}$$

c. With the results of parts (a) and (b), we can use the first law to determine the heat added:

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

which leads to

$$Q = W = 2.74 \times 10^3\ \text{J}.$$

Significance

An isothermal process has no change in the internal energy. Based on that, the first law of thermodynamics reduces to $Q = W$.

☑ **3.3 Check Your Understanding** Why was it necessary to state that the process of **Example 3.5** is quasi-static?

Example 3.6

Vaporizing Water

When 1.00 g of water at 100 °C changes from the liquid to the gas phase at atmospheric pressure, its change in volume is $1.67 \times 10^{-3}\ \text{m}^3$. (a) How much heat must be added to vaporize the water? (b) How much work is done by the water against the atmosphere in its expansion? (c) What is the change in the internal energy of the water?

Strategy

We can first figure out how much heat is needed from the latent heat of vaporization of the water. From the volume change, we can calculate the work done from $W = p\Delta V$ because the pressure is constant. Then, the first law of thermodynamics provides us with the change in the internal energy.

Solution

a. With L_v representing the latent heat of vaporization, the heat required to vaporize the water is

$$Q = mL_v = (1.00\text{ g})(2.26 \times 10^3\text{ J/g}) = 2.26 \times 10^3\text{ J}.$$

b. Since the pressure on the system is constant at $1.00\text{ atm} = 1.01 \times 10^5\text{ N/m}^2$, the work done by the water as it is vaporized is

$$W = p\Delta V = (1.01 \times 10^5\text{ N/m}^2)(1.67 \times 10^{-3}\text{ m}^3) = 169\text{ J}.$$

c. From the first law, the thermal energy of the water during its vaporization changes by

$$\Delta E_{\text{int}} = Q - W = 2.26 \times 10^3\text{ J} - 169\text{ J} = 2.09 \times 10^3\text{ J}.$$

Significance

We note that in part (c), we see a change in internal energy, yet there is no change in temperature. Ideal gases that are not undergoing phase changes have the internal energy proportional to temperature. Internal energy in general is the sum of all energy in the system.

3.4 Check Your Understanding When 1.00 g of ammonia boils at atmospheric pressure and $-33.0\,°\text{C}$, its volume changes from 1.47 to 1130 cm^3. Its heat of vaporization at this pressure is $1.37 \times 10^6\text{ J/kg}$. What is the change in the internal energy of the ammonia when it vaporizes?

View this **site (https://openstaxcollege.org/l/211stlawthermo)** to learn about how the first law of thermodynamics. First, pump some heavy species molecules into the chamber. Then, play around by doing work (pushing the wall to the right where the person is located) to see how the internal energy changes (as seen by temperature). Then, look at how heat added changes the internal energy. Finally, you can set a parameter constant such as temperature and see what happens when you do work to keep the temperature constant (*Note:* You might see a change in these variables initially if you are moving around quickly in the simulation, but ultimately, this value will return to its equilibrium value).

3.4 | Thermodynamic Processes

Learning Objectives

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

- Define a thermodynamic process
- Distinguish between quasi-static and non-quasi-static processes
- Calculate physical quantities, such as the heat transferred, work done, and internal energy change for isothermal, adiabatic, and cyclical thermodynamic processes

In solving mechanics problems, we isolate the body under consideration, analyze the external forces acting on it, and then use Newton's laws to predict its behavior. In thermodynamics, we take a similar approach. We start by identifying the part of the universe we wish to study; it is also known as our system. (We defined a system at the beginning of this chapter as anything whose properties are of interest to us; it can be a single atom or the entire Earth.) Once our system is selected, we determine how the environment, or surroundings, interact with the system. Finally, with the interaction understood, we study the thermal behavior of the system with the help of the laws of thermodynamics.

The thermal behavior of a system is described in terms of *thermodynamic variables*. For an ideal gas, these variables are pressure, volume, temperature, and the number of molecules or moles of the gas. Different types of systems are generally characterized by different sets of variables. For example, the thermodynamic variables for a stretched rubber band are tension, length, temperature, and mass.

The state of a system can change as a result of its interaction with the environment. The change in a system can be fast or slow and large or small. The manner in which a state of a system can change from an initial state to a final state is called a **thermodynamic process**. For analytical purposes in thermodynamics, it is helpful to divide up processes as either *quasi-static* or *non-quasi-static*, as we now explain.

Quasi-static and Non-quasi-static Processes

A quasi-static process refers to an idealized or imagined process where the change in state is made infinitesimally slowly so that at each instant, the system can be assumed to be at a thermodynamic equilibrium with itself and with the environment. For instance, imagine heating 1 kg of water from a temperature $20\,°\text{C}$ to $21\,°\text{C}$ at a constant pressure of 1 atmosphere. To heat the water very slowly, we may imagine placing the container with water in a large bath that can be slowly heated such that the temperature of the bath can rise infinitesimally slowly from $20\,°\text{C}$ to $21\,°\text{C}$. If we put 1 kg of water at $20\,°\text{C}$ directly into a bath at $21\,°\text{C}$, the temperature of the water will rise rapidly to $21\,°\text{C}$ in a non-quasi-static way.

Quasi-static processes are done slowly enough that the system remains at thermodynamic equilibrium at each instant, despite the fact that the system changes over time. The thermodynamic equilibrium of the system is necessary for the system to have well-defined values of macroscopic properties such as the temperature and the pressure of the system at each instant of the process. Therefore, quasi-static processes can be shown as well-defined paths in state space of the system.

Since quasi-static processes cannot be completely realized for any finite change of the system, all processes in nature are non-quasi-static. Examples of quasi-static and non-quasi-static processes are shown in **Figure 3.8**. Despite the fact that all finite changes must occur essentially non-quasi-statically at some stage of the change, we can imagine performing infinitely many quasi-static process corresponding to every quasi-static process. Since quasi-static processes can be analyzed analytically, we mostly study quasi-static processes in this book. We have already seen that in a quasi-static process the work by a gas is given by pdV.

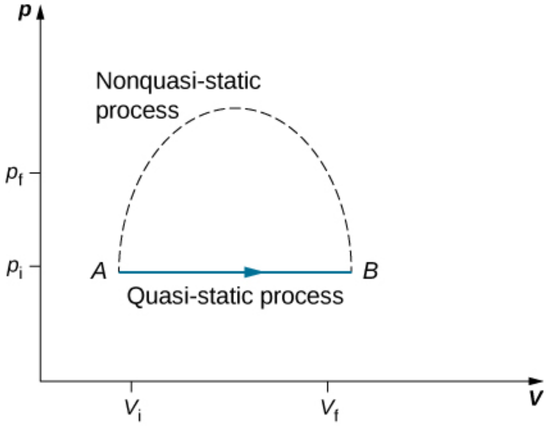


Figure 3.8 Quasi-static and non-quasi-static processes between states *A* and *B* of a gas. In a quasi-static process, the path of the process between *A* and *B* can be drawn in a state diagram since all the states that the system goes through are known. In a non-quasi-static process, the states between *A* and *B* are not known, and hence no path can be drawn. It may follow the dashed line as shown in the figure or take a very different path.

Isothermal Processes

An **isothermal process** is a change in the state of the system at a constant temperature. This process is accomplished by keeping the system in thermal equilibrium with a large heat bath during the process. Recall that a heat bath is an idealized "infinitely" large system whose temperature does not change. In practice, the temperature of a finite bath is controlled by either adding or removing a finite amount of energy as the case may be.

As an illustration of an isothermal process, consider a cylinder of gas with a movable piston immersed in a large water tank whose temperature is maintained constant. Since the piston is freely movable, the pressure inside P_{in} is balanced by the pressure outside P_{out} by some weights on the piston, as in **Figure 3.9**.

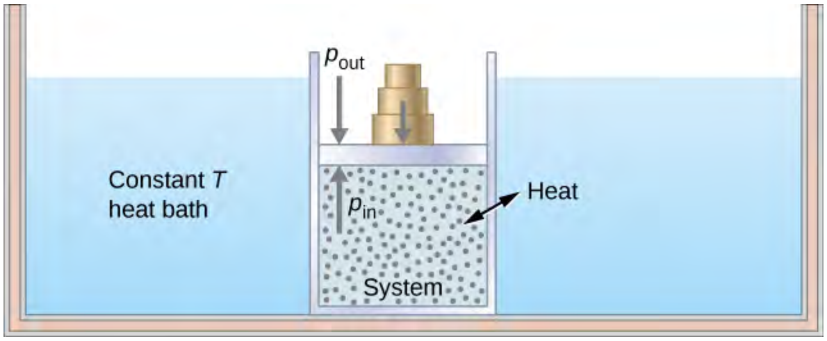


Figure 3.9 Expanding a system at a constant temperature. Removing weights on the piston leads to an imbalance of forces on the piston, which causes the piston to move up. As the piston moves up, the temperature is lowered momentarily, which causes heat to flow from the heat bath to the system. The energy to move the piston eventually comes from the heat bath.

As weights on the piston are removed, an imbalance of forces on the piston develops. The net nonzero force on the piston would cause the piston to accelerate, resulting in an increase in volume. The expansion of the gas cools the gas to a lower temperature, which makes it possible for the heat to enter from the heat bath into the system until the temperature of the gas is reset to the temperature of the heat bath. If weights are removed in infinitesimal steps, the pressure in the system decreases infinitesimally slowly. This way, an isothermal process can be conducted quasi-statically. An isothermal line on a (*p*, *V*) diagram is represented by a curved line from starting point *A* to finishing point *B*, as seen in **Figure 3.10**. For an ideal gas, an isothermal process is hyperbolic, since for an ideal gas at constant temperature, $p \propto \frac{1}{V}$.

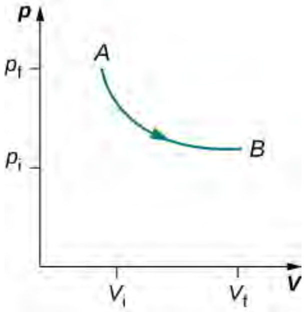


Figure 3.10 An isothermal expansion from a state labeled *A* to another state labeled *B* on a *pV* diagram. The curve represents the relation between pressure and volume in an ideal gas at constant temperature.

An isothermal process studied in this chapter is quasi-statically performed, since to be isothermal throughout the change of volume, you must be able to state the temperature of the system at each step, which is possible only if the system is in thermal equilibrium continuously. The system must go out of equilibrium for the state to change, but for quasi-static processes, we imagine that the process is conducted in infinitesimal steps such that these departures from equilibrium can be made as brief and as small as we like.

Other quasi-static processes of interest for gases are isobaric and isochoric processes. An **isobaric process** is a process where the pressure of the system does not change, whereas an **isochoric process** is a process where the volume of the system does not change.

Adiabatic Processes

In an **adiabatic process**, the system is insulated from its environment so that although the state of the system changes, no heat is allowed to enter or leave the system, as seen in **Figure 3.11**. An adiabatic process can be conducted either quasi-statically or non-quasi-statically. When a system expands adiabatically, it must do work against the outside world, and therefore its energy goes down, which is reflected in the lowering of the temperature of the system. An adiabatic expansion leads to a lowering of temperature, and an adiabatic compression leads to an increase of temperature. We discuss adiabatic expansion again in **Adiabatic Processes for an ideal Gas**.

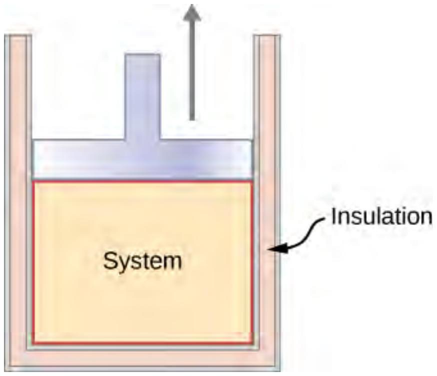


Figure 3.11 An insulated piston with a hot, compressed gas is released. The piston moves up, the volume expands, and the pressure and temperature decrease. The internal energy goes into work. If the expansion occurs within a time frame in which negligible heat can enter the system, then the process is called adiabatic. Ideally, during an adiabatic process no heat enters or exits the system.

Cyclic Processes

We say that a system goes through a **cyclic process** if the state of the system at the end is same as the state at the beginning. Therefore, state properties such as temperature, pressure, volume, and internal energy of the system do not change over a complete cycle:

$$\Delta E_{\text{int}} = 0.$$

When the first law of thermodynamics is applied to a cyclic process, we obtain a simple relation between heat into the system and the work done by the system over the cycle:

$$Q = W \,(\text{cyclic process}).$$

Thermodynamic processes are also distinguished by whether or not they are reversible. A **reversible process** is one that can be made to retrace its path by differential changes in the environment. Such a process must therefore also be quasi-static. Note, however, that a quasi-static process is not necessarily reversible, since there may be dissipative forces involved. For example, if friction occurred between the piston and the walls of the cylinder containing the gas, the energy lost to friction would prevent us from reproducing the original states of the system.

We considered several thermodynamic processes:

1. An isothermal process, during which the system’s temperature remains constant
2. An adiabatic process, during which no heat is transferred to or from the system
3. An isobaric process, during which the system’s pressure does not change
4. An isochoric process, during which the system’s volume does not change

Many other processes also occur that do not fit into any of these four categories.

View this **site (https://openstaxcollege.org/l/21idegaspvdiag)** to set up your own process in a pV diagram. See if you can calculate the values predicted by the simulation for heat, work, and change in internal energy.

3.5 | Heat Capacities of an Ideal Gas

Learning Objectives

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

- Define heat capacity of an ideal gas for a specific process
- Calculate the specific heat of an ideal gas for either an isobaric or isochoric process
- Explain the difference between the heat capacities of an ideal gas and a real gas
- Estimate the change in specific heat of a gas over temperature ranges

We learned about specific heat and molar heat capacity in **Temperature and Heat**; however, we have not considered a process in which heat is added. We do that in this section. First, we examine a process where the system has a constant volume, then contrast it with a system at constant pressure and show how their specific heats are related.

Let's start with looking at **Figure 3.12**, which shows two vessels *A* and *B*, each containing 1 mol of the same type of ideal gas at a temperature *T* and a volume *V*. The only difference between the two vessels is that the piston at the top of *A* is fixed, whereas the one at the top of *B* is free to move against a constant external pressure *p*. We now consider what happens when the temperature of the gas in each vessel is slowly increased to $T + dT$ with the addition of heat.

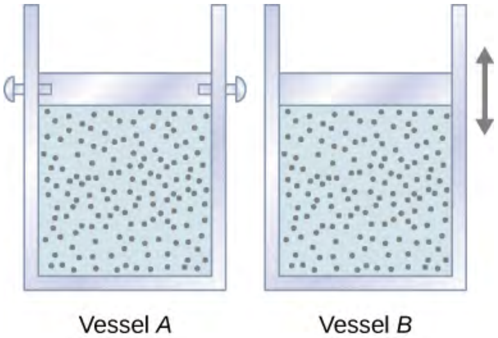


Figure 3.12 Two vessels are identical except that the piston at the top of *A* is fixed, whereas that atop *B* is free to move against a constant external pressure *p*.

Since the piston of vessel *A* is fixed, the volume of the enclosed gas does not change. Consequently, the gas does no work, and we have from the first law

$$dE_{\text{int}} = dQ - dW = dQ.$$

We represent the fact that the heat is exchanged at constant volume by writing

$$dQ = C_V\,dT,$$

where C_V is the **molar heat capacity at constant volume** of the gas. In addition, since $dE_{\text{int}} = dQ$ for this particular process,

$$dE_{\text{int}} = C_V\,dT. \tag{3.9}$$

We obtained this equation assuming the volume of the gas was fixed. However, internal energy is a state function that depends on only the temperature of an ideal gas. Therefore, $dE_{\text{int}} = C_V\,dT$ gives the change in internal energy of an ideal gas for any process involving a temperature change *dT*.

When the gas in vessel *B* is heated, it expands against the movable piston and does work $dW = pdV$. In this case, the heat is added at constant pressure, and we write

$$dQ = C_p\,dT,$$

where C_p is the **molar heat capacity at constant pressure** of the gas. Furthermore, since the ideal gas expands against a constant pressure,

$$d(pV) = d(RT)$$

becomes

$$pdV = RdT.$$

Finally, inserting the expressions for dQ and pdV into the first law, we obtain

$$dE_{\text{int}} = dQ - pdV = (C_p - R)dT.$$

We have found dE_{int} for both an isochoric and an isobaric process. Because the internal energy of an ideal gas depends only on the temperature, dE_{int} must be the same for both processes. Thus,

$$C_V dT = (C_p - R)dT,$$

and

$$C_p = C_V + R. \tag{3.10}$$

The derivation of **Equation 3.10** was based only on the ideal gas law. Consequently, this relationship is approximately valid for all dilute gases, whether monatomic like He, diatomic like O_2, or polyatomic like CO_2 or NH_3.

In the preceding chapter, we found the molar heat capacity of an ideal gas under constant volume to be

$$C_V = \frac{d}{2}R,$$

where d is the number of degrees of freedom of a molecule in the system. **Table 3.3** shows the molar heat capacities of some dilute ideal gases at room temperature. The heat capacities of real gases are somewhat higher than those predicted by the expressions of C_V and C_p given in **Equation 3.10**. This indicates that vibrational motion in polyatomic molecules is significant, even at room temperature. Nevertheless, the difference in the molar heat capacities, $C_p - C_V$, is very close to R, even for the polyatomic gases.

Molar Heat Capacities of Dilute Ideal Gases at Room Temperature

Type of Molecule	Gas	C_p (J/mol K)	C_V (J/mol K)	$C_p - C_V$ (J/mol K)
Monatomic	Ideal	$\frac{5}{2}R = 20.79$	$\frac{3}{2}R = 12.47$	$R = 8.31$
Diatomic	Ideal	$\frac{7}{2}R = 29.10$	$\frac{5}{2}R = 20.79$	$R = 8.31$
Polyatomic	Ideal	$4R = 33.26$	$3R = 24.94$	$R = 8.31$

Table 3.3

3.6 | Adiabatic Processes for an Ideal Gas

Learning Objectives

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

- Define adiabatic expansion of an ideal gas
- Demonstrate the qualitative difference between adiabatic and isothermal expansions

When an ideal gas is compressed adiabatically $(Q = 0)$, work is done on it and its temperature increases; in an adiabatic expansion, the gas does work and its temperature drops. Adiabatic compressions actually occur in the cylinders of a car, where the compressions of the gas-air mixture take place so quickly that there is no time for the mixture to exchange heat with its environment. Nevertheless, because work is done on the mixture during the compression, its temperature does rise significantly. In fact, the temperature increases can be so large that the mixture can explode without the addition of a spark. Such explosions, since they are not timed, make a car run poorly—it usually "knocks." Because ignition temperature rises with the octane of gasoline, one way to overcome this problem is to use a higher-octane gasoline.

Another interesting adiabatic process is the free expansion of a gas. **Figure 3.13** shows a gas confined by a membrane to one side of a two-compartment, thermally insulated container. When the membrane is punctured, gas rushes into the empty side of the container, thereby expanding freely. Because the gas expands "against a vacuum" $(p = 0)$, it does no work, and because the vessel is thermally insulated, the expansion is adiabatic. With $Q = 0$ and $W = 0$ in the first law, $\Delta E_{\text{int}} = 0,$ so $E_{\text{int}\ i} = E_{\text{int}\ f}$ for the free expansion.

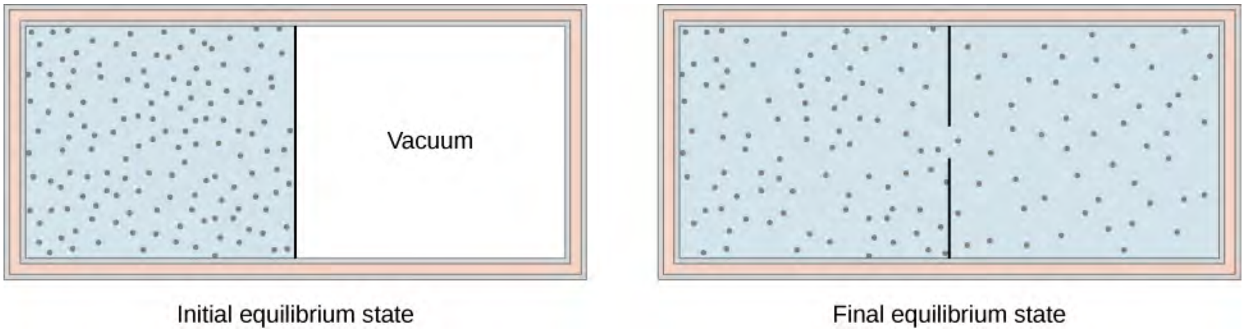


Figure 3.13 The gas in the left chamber expands freely into the right chamber when the membrane is punctured.

If the gas is ideal, the internal energy depends only on the temperature. Therefore, when an ideal gas expands freely, its temperature does not change.

A quasi-static, adiabatic expansion of an ideal gas is represented in **Figure 3.14**, which shows an insulated cylinder that contains 1 mol of an ideal gas. The gas is made to expand quasi-statically by removing one grain of sand at a time from the top of the piston. When the gas expands by dV, the change in its temperature is dT. The work done by the gas in the expansion is $dW = pdV$; $dQ = 0$ because the cylinder is insulated; and the change in the internal energy of the gas is, from **Equation 3.9**, $dE_{\text{int}} = C_V dT$. Therefore, from the first law,

$$C_V dT = 0 - pdV = -pdV,$$

so

$$dT = -\frac{pdV}{C_V}.$$

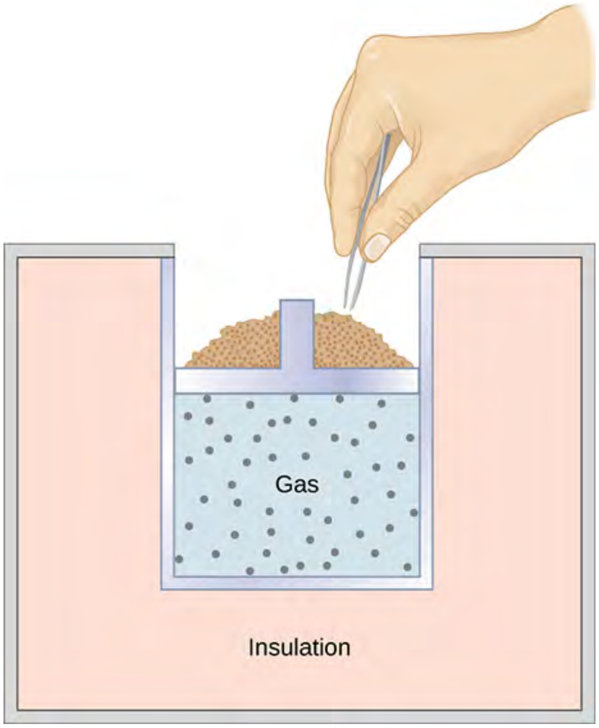


Figure 3.14 When sand is removed from the piston one grain at a time, the gas expands adiabatically and quasi-statically in the insulated vessel.

Also, for 1 mol of an ideal gas,

$$d(pV) = d(RT),$$

so

$$pdV + Vdp = RdT$$

and

$$dT = \frac{pdV + Vdp}{R}.$$

We now have two equations for dT. Upon equating them, we find that

$$C_V Vdp + (C_V + R)pdV = 0.$$

Now, we divide this equation by pV and use $C_p = C_V + R$. We are then left with

$$C_V \frac{dp}{p} + C_p \frac{dV}{V} = 0,$$

which becomes

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0,$$

where we define γ as the ratio of the molar heat capacities:

$$\gamma = \frac{C_p}{C_V}. \quad (3.11)$$

Thus,

$$\int \frac{dp}{p} + \gamma \int \frac{dV}{V} = 0$$

and

$$\ln p + \gamma \ln V = \text{constant.}$$

Finally, using $\ln(A^x) = x \ln A$ and $\ln AB = \ln A + \ln B$, we can write this in the form

$$pV^{\gamma} = \text{constant.} \tag{3.12}$$

This equation is the condition that must be obeyed by an ideal gas in a quasi-static adiabatic process. For example, if an ideal gas makes a quasi-static adiabatic transition from a state with pressure and volume p_1 and V_1 to a state with p_2 and V_2, then it must be true that $p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$.

The adiabatic condition of **Equation 3.12** can be written in terms of other pairs of thermodynamic variables by combining it with the ideal gas law. In doing this, we find that

$$p^{1-\gamma} T^{\gamma} = \text{constant} \tag{3.13}$$

and

$$TV^{\gamma - 1} = \text{constant.} \tag{3.14}$$

A reversible adiabatic expansion of an ideal gas is represented on the *pV* diagram of **Figure 3.15**. The slope of the curve at any point is

$$\frac{dp}{dV} = \frac{d}{dV}\left(\frac{\text{constant}}{V^{\gamma}}\right) = -\gamma \frac{p}{V}.$$

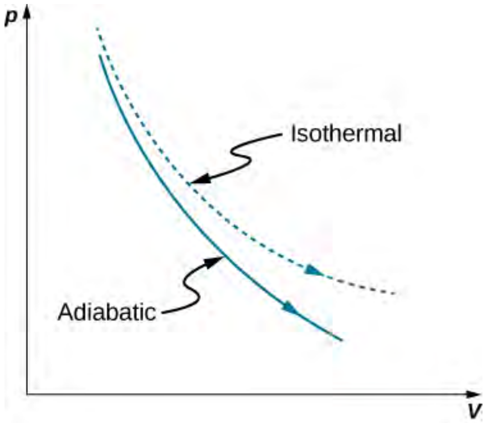


Figure 3.15 Quasi-static adiabatic and isothermal expansions of an ideal gas.

The dashed curve shown on this *pV* diagram represents an isothermal expansion where *T* (and therefore *pV*) is constant. The slope of this curve is useful when we consider the second law of thermodynamics in the next chapter. This slope is

$$\frac{dp}{dV} = \frac{d}{dV}\frac{nRT}{V} = -\frac{p}{V}.$$

Because $\gamma > 1$, the isothermal curve is not as steep as that for the adiabatic expansion.

Example 3.7

Compression of an Ideal Gas in an Automobile Engine

Gasoline vapor is injected into the cylinder of an automobile engine when the piston is in its expanded position. The temperature, pressure, and volume of the resulting gas-air mixture are $20\,°\text{C}$, $1.00 \times 10^5\ \text{N/m}^2$, and $240\,\text{cm}^3$, respectively. The mixture is then compressed adiabatically to a volume of $40\,\text{cm}^3$. Note that in the actual operation of an automobile engine, the compression is not quasi-static, although we are making that assumption here. (a) What are the pressure and temperature of the mixture after the compression? (b) How much work is done by the mixture during the compression?

Strategy

Because we are modeling the process as a quasi-static adiabatic compression of an ideal gas, we have $pV^\gamma =$ constant and $pV = nRT$. The work needed can then be evaluated with $W = \int_{V_1}^{V_2} p dV$.

Solution

a. For an adiabatic compression we have

$$p_2 = p_1 \left(\frac{V_1}{V_2}\right)^\gamma,$$

so after the compression, the pressure of the mixture is

$$p_2 = (1.00 \times 10^5\ \text{N/m}^2)\left(\frac{240 \times 10^{-6}\ \text{m}^3}{40 \times 10^{-6}\ \text{m}^3}\right)^{1.40} = 1.23 \times 10^6\ \text{N/m}^2.$$

From the ideal gas law, the temperature of the mixture after the compression is

$$\begin{aligned} T_2 &= \left(\frac{p_2 V_2}{p_1 V_1}\right) T_1 \\ &= \frac{(1.23 \times 10^6\ \text{N/m}^2)(40 \times 10^{-6}\ \text{m}^3)}{(1.00 \times 10^5\ \text{N/m}^2)(240 \times 10^{-6}\ \text{m}^3)} \cdot 293\ \text{K} \\ &= 600\ \text{K} = 328\ °\text{C}. \end{aligned}$$

b. The work done by the mixture during the compression is

$$W = \int_{V_1}^{V_2} p dV.$$

With the adiabatic condition of **Equation 3.12**, we may write p as K/V^γ, where $K = p_1 V_1^\gamma = p_2 V_2^\gamma$. The work is therefore

$$\begin{aligned}
W &= \int_{V_1}^{V_2} \frac{K}{V^{\gamma}} dV \\
&= \frac{K}{1-\gamma}\left(\frac{1}{V_2{}^{\gamma-1}} - \frac{1}{V_1{}^{\gamma-1}}\right) \\
&= \frac{1}{1-\gamma}\left(\frac{p_2 V_2^{\gamma}}{V_2{}^{\gamma-1}} - \frac{p_1 V_1^{\gamma}}{V_1{}^{\gamma-1}}\right) \\
&= \frac{1}{1-\gamma}(p_2 V_2 - p_1 V_1) \\
&= \frac{1}{1-1.40}[(1.23 \times 10^6 \text{ N/m}^2)(40 \times 10^{-6} \text{ m}^3) \\
&-(1.00 \times 10^5 \text{ N/m}^2)(240 \times 10^{-6} \text{ m}^3)] \\
&= -63 \text{ J}.
\end{aligned}$$

Significance

The negative sign on the work done indicates that the piston does work on the gas-air mixture. The engine would not work if the gas-air mixture did work on the piston.

CHAPTER 3 REVIEW

KEY TERMS

adiabatic process process during which no heat is transferred to or from the system

boundary imagined walls that separate the system and its surroundings

closed system system that is mechanically and thermally isolated from its environment

cyclic process process in which the state of the system at the end is same as the state at the beginning

environment outside of the system being studied

equation of state describes properties of matter under given physical conditions

equilibrium thermal balance established between two objects or parts within a system

extensive variable variable that is proportional to the amount of matter in the system

first law of thermodynamics the change in internal energy for any transition between two equilibrium states is $\Delta E_{\text{int}} = Q - W$

intensive variable variable that is independent of the amount of matter in the system

internal energy average of the total mechanical energy of all the molecules or entities in the system

isobaric process process during which the system's pressure does not change

isochoric process process during which the system's volume does not change

isothermal process process during which the system's temperature remains constant

molar heat capacity at constant pressure quantifies the ratio of the amount of heat added removed to the temperature while measuring at constant pressure

molar heat capacity at constant volume quantifies the ratio of the amount of heat added removed to the temperature while measuring at constant volume

open system system that can exchange energy and/or matter with its surroundings

quasi-static process evolution of a system that goes so slowly that the system involved is always in thermodynamic equilibrium

reversible process process that can be reverted to restore both the system and its environment back to their original states together

surroundings environment that interacts with an open system

thermodynamic process manner in which a state of a system can change from initial state to final state

thermodynamic system object and focus of thermodynamic study

KEY EQUATIONS

Equation of state for a closed system	$f(p, V, T) = 0$
Net work for a finite change in volume	$W = \int_{V_1}^{V_2} p\,dV$
Internal energy of a system (average total energy)	$E_{\text{int}} = \sum_i (\bar{K}_i + \bar{U}_i),$
Internal energy of a monatomic ideal gas	$E_{\text{int}} = nN_{\text{A}}\left(\frac{3}{2}k_{\text{B}}T\right) = \frac{3}{2}nRT$
First law of thermodynamics	$\Delta E_{\text{int}} = Q - W$

Molar heat capacity at constant pressure	$C_p = C_V + R$
Ratio of molar heat capacities	$\gamma = C_p / C_V$
Condition for an ideal gas in a quasi-static adiabatic process	$pV^{\gamma} = \text{ constant}$

SUMMARY

3.1 Thermodynamic Systems

- A thermodynamic system, its boundary, and its surroundings must be defined with all the roles of the components fully explained before we can analyze a situation.
- Thermal equilibrium is reached with two objects if a third object is in thermal equilibrium with the other two separately.
- A general equation of state for a closed system has the form $f(p, V, T) = 0,$ with an ideal gas as an illustrative example.

3.2 Work, Heat, and Internal Energy

- Positive (negative) work is done by a thermodynamic system when it expands (contracts) under an external pressure.
- Heat is the energy transferred between two objects (or two parts of a system) because of a temperature difference.
- Internal energy of a thermodynamic system is its total mechanical energy.

3.3 First Law of Thermodynamics

- The internal energy of a thermodynamic system is a function of state and thus is unique for every equilibrium state of the system.
- The increase in the internal energy of the thermodynamic system is given by the heat added to the system less the work done by the system in any thermodynamics process.

3.4 Thermodynamic Processes

- The thermal behavior of a system is described in terms of thermodynamic variables. For an ideal gas, these variables are pressure, volume, temperature, and number of molecules or moles of the gas.
- For systems in thermodynamic equilibrium, the thermodynamic variables are related by an equation of state.
- A heat reservoir is so large that when it exchanges heat with other systems, its temperature does not change.
- A quasi-static process takes place so slowly that the system involved is always in thermodynamic equilibrium.
- A reversible process is one that can be made to retrace its path and both the temperature and pressure are uniform throughout the system.
- There are several types of thermodynamic processes, including (a) isothermal, where the system’s temperature is constant; (b) adiabatic, where no heat is exchanged by the system; (c) isobaric, where the system’s pressure is constant; and (d) isochoric, where the system’s volume is constant.
- As a consequence of the first law of thermodymanics, here is a summary of the thermodymaic processes: (a) isothermal: $\Delta E_{\text{int}} = 0, Q = W;$ (b) adiabatic: $Q = 0, \Delta E_{\text{int}} = -W;$ (c) isobaric: $\Delta E_{\text{int}} = Q - W;$ and (d) isochoric: $W = 0, \Delta E_{\text{int}} = Q.$

3.5 Heat Capacities of an Ideal Gas

- For an ideal gas, the molar capacity at constant pressure C_p is given by $C_p = C_V + R = dR/2 + R$, where d is the number of degrees of freedom of each molecule/entity in the system.
- A real gas has a specific heat close to but a little bit higher than that of the corresponding ideal gas with

$$C_p \simeq C_V + R.$$

3.6 Adiabatic Processes for an Ideal Gas

- A quasi-static adiabatic expansion of an ideal gas produces a steeper pV curve than that of the corresponding isotherm.
- A realistic expansion can be adiabatic but rarely quasi-static.

CONCEPTUAL QUESTIONS

3.1 Thermodynamic Systems

1. Consider these scenarios and state whether work is done by the system on the environment (SE) or by the environment on the system (ES): (a) opening a carbonated beverage; (b) filling a flat tire; (c) a sealed empty gas can expands on a hot day, bowing out the walls.

3.2 Work, Heat, and Internal Energy

2. Is it possible to determine whether a change in internal energy is caused by heat transferred, by work performed, or by a combination of the two?

3. When a liquid is vaporized, its change in internal energy is not equal to the heat added. Why?

4. Why does a bicycle pump feel warm as you inflate your tire?

5. Is it possible for the temperature of a system to remain constant when heat flows into or out of it? If so, give examples.

3.3 First Law of Thermodynamics

6. What does the first law of thermodynamics tell us about the energy of the universe?

7. Does adding heat to a system always increase its internal energy?

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

3.4 Thermodynamic Processes

9. When a gas expands isothermally, it does work. What is the source of energy needed to do this work?

10. If the pressure and volume of a system are given, is the temperature always uniquely determined?

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

3.5 Heat Capacities of an Ideal Gas

12. How can an object transfer heat if the object does not possess a discrete quantity of heat?

13. Most materials expand when heated. One notable exception is water between $0\ °C$ and $4\ °C$, which actually decreases in volume with the increase in temperature. Which is greater for water in this temperature region, C_p or C_V ?

14. Why are there two specific heats for gases C_p and C_V, yet only one given for solid?

3.6 Adiabatic Processes for an Ideal Gas

15. Is it possible for γ to be smaller than unity?

16. Would you expect γ to be larger for a gas or a solid? Explain.

17. There is no change in the internal energy of an ideal gas undergoing an isothermal process since the internal energy depends only on the temperature. Is it therefore correct to say that an isothermal process is the same as an adiabatic process for an ideal gas? Explain your answer.

18. Does a gas do any work when it expands adiabatically? If so, what is the source of the energy needed to do this work?

PROBLEMS

3.1 Thermodynamic Systems

19. A gas follows $pV = bp + c_T$ on an isothermal curve, where p is the pressure, V is the volume, b is a constant, and c is a function of temperature. Show that a temperature scale under an isochoric process can be established with this gas and is identical to that of an ideal gas.

20. A mole of gas has isobaric expansion coefficient $dV/dT = R/p$ and isochoric pressure-temperature coefficient $dp/dT = p/T$. Find the equation of state of the gas.

21. Find the equation of state of a solid that has an isobaric expansion coefficient $dV/dT = 2cT - bp$ and an isothermal pressure-volume coefficient $dV/dp = -bT$.

3.2 Work, Heat, and Internal Energy

22. A gas at a pressure of 2.00 atm undergoes a quasi-static isobaric expansion from 3.00 to 5.00 L. How much work is done by the gas?

23. It takes 500 J of work to compress quasi-statically 0.50 mol of an ideal gas to one-fifth its original volume. Calculate the temperature of the gas, assuming it remains constant during the compression.

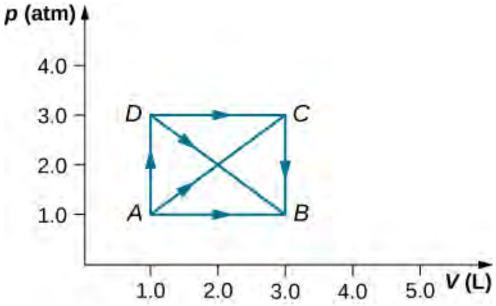
24. It is found that, when a dilute gas expands quasi-statically from 0.50 to 4.0 L, it does 250 J of work. Assuming that the gas temperature remains constant at 300 K, how many moles of gas are present?

25. In a quasi-static isobaric expansion, 500 J of work are done by the gas. If the gas pressure is 0.80 atm, what is the fractional increase in the volume of the gas, assuming it was originally at 20.0 L?

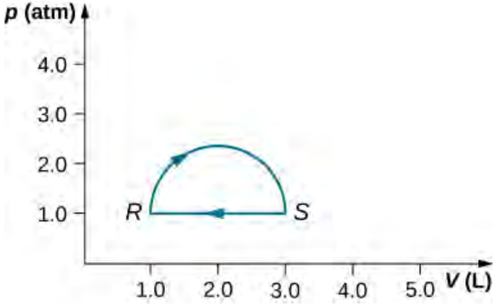
26. When a gas undergoes a quasi-static isobaric change in volume from 10.0 to 2.0 L, 15 J of work from an external source are required. What is the pressure of the gas?

27. An ideal gas expands quasi-statically and isothermally from a state with pressure p and volume V to a state with volume 4V. Show that the work done by the gas in the expansion is pV(ln 4).

28. As shown below, calculate the work done by the gas in the quasi-static processes represented by the paths (a) AB; (b) ADB; (c) ACB; and (d) ADCB.



29. (a) Calculate the work done by the gas along the closed path shown below. The curved section between R and S is semicircular. (b) If the process is carried out in the opposite direction, what is the work done by the gas?



30. An ideal gas expands quasi-statically to three times its original volume. Which process requires more work from the gas, an isothermal process or an isobaric one? Determine the ratio of the work done in these processes.

31. A dilute gas at a pressure of 2.0 atm and a volume of 4.0 L is taken through the following quasi-static steps: (a) an isobaric expansion to a volume of 10.0 L, (b) an isochoric change to a pressure of 0.50 atm, (c) an isobaric compression to a volume of 4.0 L, and (d) an isochoric change to a pressure of 2.0 atm. Show these steps on a pV diagram and determine from your graph the net work done by the gas.

32. What is the average mechanical energy of the atoms of an ideal monatomic gas at 300 K?

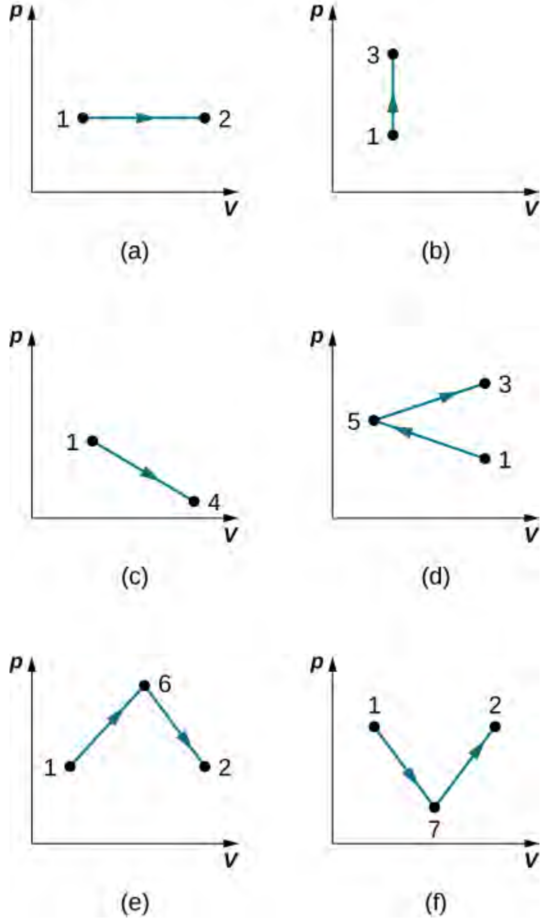
33. What is the internal energy of 6.00 mol of an ideal monatomic gas at $200\ °C$?

34. Calculate the internal energy of 15 mg of helium at a temperature of $0\ °C$.

35. Two monatomic ideal gases A and B are at the same temperature. If 1.0 g of gas A has the same internal energy as 0.10 g of gas B, what are (a) the ratio of the number of moles of each gas and (b) the ration of the atomic masses of the two gases?

36. The van der Waals coefficients for oxygen are $a = 0.138\ \text{J} \cdot \text{m}^3/\text{mol}^2$ and $b = 3.18 \times 10^{-5}\ \text{m}^3/\text{mol}$. Use these values to draw a van der Waals isotherm of oxygen at 100 K. On the same graph, draw isotherms of one mole of an ideal gas.

37. Find the work done in the quasi-static processes shown below. The states are given as (p, V) values for the points in the pV plane: 1 (3 atm, 4 L), 2 (3 atm, 6 L), 3 (5 atm, 4 L), 4 (2 atm, 6 L), 5 (4 atm, 2 L), 6 (5 atm, 5 L), and 7 (2 atm, 5 L).



(a) (b)

(c) (d)

(e) (f)

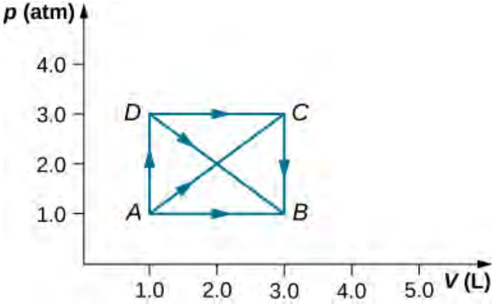
3.3 First Law of Thermodynamics

38. When a dilute gas expands quasi-statically from 0.50 to 4.0 L, it does 250 J of work. Assuming that the gas temperature remains constant at 300 K, (a) what is the change in the internal energy of the gas? (b) How much heat is absorbed by the gas in this process?

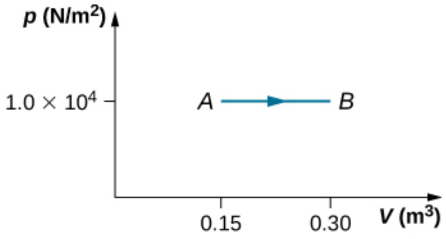
39. In a quasi-static isobaric expansion, 500 J of work are done by the gas. The gas pressure is 0.80 atm and it was originally at 20.0 L. If the internal energy of the gas increased by 80 J in the expansion, how much heat does the gas absorb?

40. An ideal gas expands quasi-statically and isothermally from a state with pressure p and volume V to a state with volume 4V. How much heat is added to the expanding gas?

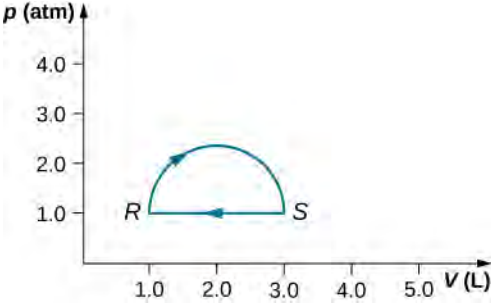
41. As shown below, if the heat absorbed by the gas along AB is 400 J, determine the quantities of heat absorbed along (a) ADB; (b) ACB; and (c) ADCB.



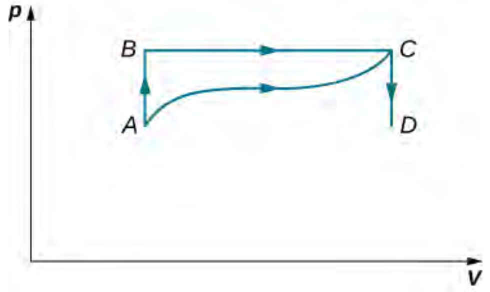
42. During the isobaric expansion from A to B represented below, 130 J of heat are removed from the gas. What is the change in its internal energy?



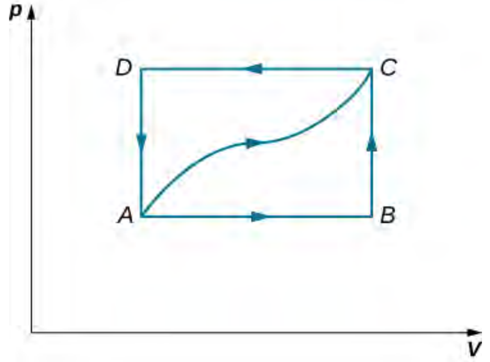
43. (a) What is the change in internal energy for the process represented by the closed path shown below? (b) How much heat is exchanged? (c) If the path is traversed in the opposite direction, how much heat is exchanged?



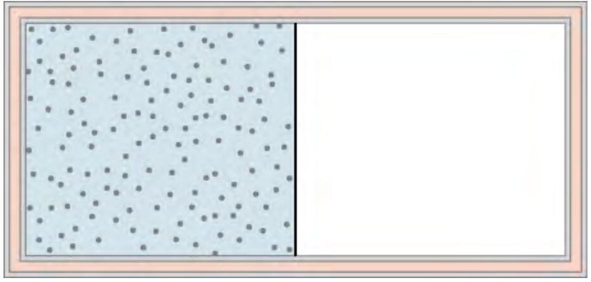
44. When a gas expands along path AC shown below, it does 400 J of work and absorbs either 200 or 400 J of heat. (a) Suppose you are told that along path ABC, the gas absorbs either 200 or 400 J of heat. Which of these values is correct? (b) Give the correct answer from part (a), how much work is done by the gas along ABC? (c) Along CD, the internal energy of the gas decreases by 50 J. How much heat is exchanged by the gas along this path?



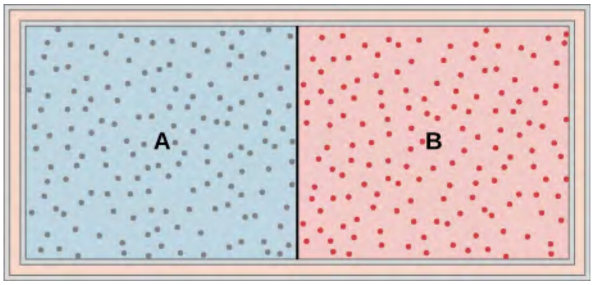
45. When a gas expands along *AB* (see below), it does 500 J of work and absorbs 250 J of heat. When the gas expands along *AC*, it does 700 J of work and absorbs 300 J of heat. (a) How much heat does the gas exchange along *BC*? (b) When the gas makes the transmission from *C* to *A* along *CDA*, 800 J of work are done on it from *C* to *D*. How much heat does it exchange along *CDA*?



46. A dilute gas is stored in the left chamber of a container whose walls are perfectly insulating (see below), and the right chamber is evacuated. When the partition is removed, the gas expands and fills the entire container. Calculate the work done by the gas. Does the internal energy of the gas change in this process?

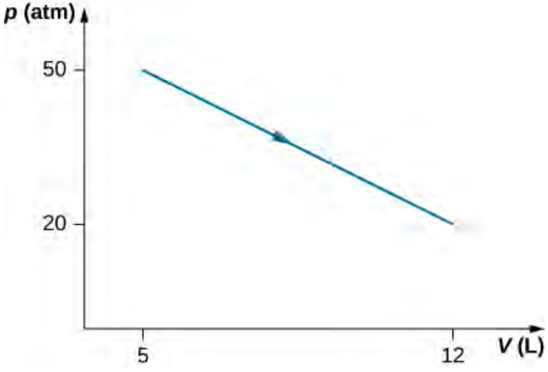


47. Ideal gases A and B are stored in the left and right chambers of an insulated container, as shown below. The partition is removed and the gases mix. Is any work done in this process? If the temperatures of A and B are initially equal, what happens to their common temperature after they are mixed?



48. An ideal monatomic gas at a pressure of $2.0 \times 10^5\ \text{N/m}^2$ and a temperature of 300 K undergoes a quasi-static isobaric expansion from 2.0×10^3 to $4.0 \times 10^3\ \text{cm}^3$. (a) What is the work done by the gas? (b) What is the temperature of the gas after the expansion? (c) How many moles of gas are there? (d) What is the change in internal energy of the gas? (e) How much heat is added to the gas?

49. Consider the process for steam in a cylinder shown below. Suppose the change in the internal energy in this process is 30 kJ. Find the heat entering the system.



50. The state of 30 moles of steam in a cylinder is changed in a cyclic manner from a-b-c-a, where the pressure and volume of the states are: a (30 atm, 20 L), b (50 atm, 20 L), and c (50 atm, 45 L). Assume each change takes place along the line connecting the initial and final states in the pV plane. (a) Display the cycle in the pV plane. (b) Find the net work done by the steam in one cycle. (c) Find the net amount of heat flow in the steam over the course of one cycle.

51. A monatomic ideal gas undergoes a quasi-static process that is described by the function $p(V) = p_1 + 3(V - V_1)$, where the starting state is (p_1, V_1) and the final state (p_2, V_2). Assume the system consists of n moles of the gas in a container that can exchange heat with the environment and whose volume can change freely. (a) Evaluate the work done by the gas during the change in the state. (b) Find the change in internal energy of the gas. (c) Find the heat input to the gas during the change. (d) What are initial and final temperatures?

52. A metallic container of fixed volume of $2.5 \times 10^{-3}\ \text{m}^3$ immersed in a large tank of temperature $27\ °\text{C}$ contains two compartments separated by a freely movable wall. Initially, the wall is kept in place by a stopper so that there are 0.02 mol of the nitrogen gas on one side and 0.03 mol of the oxygen gas on the other side, each occupying half the volume. When the stopper is removed, the wall moves and comes to a final position. The movement of the wall is controlled so that the wall moves in infinitesimal quasi-static steps. (a) Find the final volumes of the two sides assuming the ideal gas behavior for the two gases. (b) How much work does each gas do on the other? (c) What is the change in the internal energy of each gas? (d) Find the amount of heat that enters or leaves each gas.

53. A gas in a cylindrical closed container is adiabatically and quasi-statically expanded from a state *A* (3 MPa, 2 L) to a state *B* with volume of 6 L along the path $1.8\ pV = \text{constant}$. (a) Plot the path in the *pV* plane. (b) Find the amount of work done by the gas and the change in the internal energy of the gas during the process.

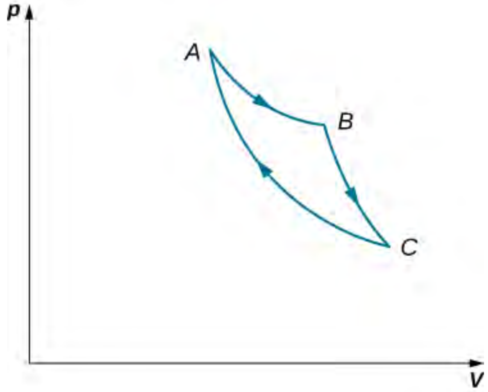
3.4 Thermodynamic Processes

54. Two moles of a monatomic ideal gas at (5 MPa, 5 L) is expanded isothermally until the volume is doubled (step 1). Then it is cooled isochorically until the pressure is 1 MPa (step 2). The temperature drops in this process. The gas is now compressed isothermally until its volume is back to 5 L, but its pressure is now 2 MPa (step 3). Finally, the gas is heated isochorically to return to the initial state (step 4). (a) Draw the four processes in the pV plane. (b) Find the total work done by the gas.

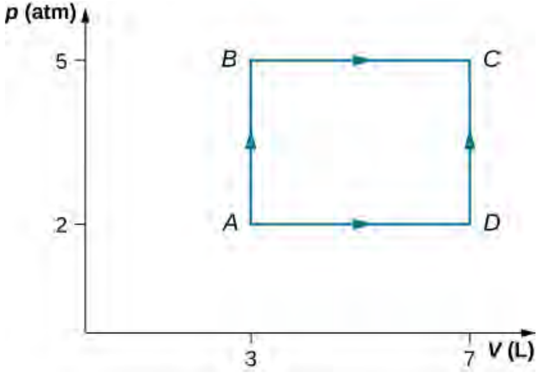
55. Consider a transformation from point *A* to *B* in a two-step process. First, the pressure is lowered from 3 MPa at point *A* to a pressure of 1 MPa, while keeping the volume at 2 L by cooling the system. The state reached is labeled *C*. Then the system is heated at a constant pressure to reach a volume of 6 L in the state *B*. (a) Find the amount of work done on the *ACB* path. (b) Find the amount of heat exchanged by the system when it goes from *A* to *B* on the *ACB* path. (c) Compare the change in the internal energy when the *AB* process occurs adiabatically with the *AB* change through the two-step process on the *ACB* path.

56. Consider a cylinder with a movable piston containing n moles of an ideal gas. The entire apparatus is immersed in a constant temperature bath of temperature T kelvin. The piston is then pushed slowly so that the pressure of the gas changes quasi-statically from p_1 to p_2 at constant temperature T. Find the work done by the gas in terms of n, R, T, p_1, and p_2.

57. An ideal gas expands isothermally along AB and does 700 J of work (see below). (a) How much heat does the gas exchange along AB? (b) The gas then expands adiabatically along BC and does 400 J of work. When the gas returns to A along CA, it exhausts 100 J of heat to its surroundings. How much work is done on the gas along this path?



58. Consider the processes shown below. In the processes AB and BC, 3600 J and 2400 J of heat are added to the system, respectively. (a) Find the work done in each of the processes AB, BC, AD, and DC. (b) Find the internal energy change in processes AB and BC. (c) Find the internal energy difference between states C and A. (d) Find the total heat added in the ADC process. (e) From the information give, can you find the heat added in process AD? Why or why not?



59. Two moles of helium gas are placed in a cylindrical container with a piston. The gas is at room temperature $25\ °\text{C}$ and under a pressure of 3.0×10^5 Pa. When the pressure from the outside is decreased while keeping the temperature the same as the room temperature, the volume of the gas doubles. (a) Find the work the external agent does on the gas in the process. (b) Find the heat exchanged by the gas and indicate whether the gas takes in or gives up heat. Assume ideal gas behavior.

60. An amount of n moles of a monatomic ideal gas in a conducting container with a movable piston is placed in a large thermal heat bath at temperature T_1 and the gas is allowed to come to equilibrium. After the equilibrium is reached, the pressure on the piston is lowered so that the gas expands at constant temperature. The process is continued quasi-statically until the final pressure is 4/3 of the initial pressure p_1. (a) Find the change in the internal energy of the gas. (b) Find the work done by the gas. (c) Find the heat exchanged by the gas, and indicate, whether the gas takes in or gives up heat.

3.5 Heat Capacities of an Ideal Gas

61. The temperature of an ideal monatomic gas rises by 8.0 K. What is the change in the internal energy of 1 mol of the gas at constant volume?

62. For a temperature increase of $10\,°\text{C}$ at constant volume, what is the heat absorbed by (a) 3.0 mol of a dilute monatomic gas; (b) 0.50 mol of a dilute diatomic gas; and (c) 15 mol of a dilute polyatomic gas?

63. If the gases of the preceding problem are initially at 300 K, what are their internal energies after they absorb the heat?

64. Consider 0.40 mol of dilute carbon dioxide at a pressure of 0.50 atm and a volume of 50 L. What is the internal energy of the gas?

65. When 400 J of heat are slowly added to 10 mol of an ideal monatomic gas, its temperature rises by $10\,°\text{C}$. What is the work done on the gas?

66. One mole of a dilute diatomic gas occupying a volume of 10.00 L expands against a constant pressure of 2.000 atm when it is slowly heated. If the temperature of the gas rises by 10.00 K and 400.0 J of heat are added in the process, what is its final volume?

3.6 Adiabatic Processes for an Ideal Gas

67. A monatomic ideal gas undergoes a quasi-static adiabatic expansion in which its volume is doubled. How is the pressure of the gas changed?

68. An ideal gas has a pressure of 0.50 atm and a volume of 10 L. It is compressed adiabatically and quasi-statically until its pressure is 3.0 atm and its volume is 2.8 L. Is the gas monatomic, diatomic, or polyatomic?

69. Pressure and volume measurements of a dilute gas undergoing a quasi-static adiabatic expansion are shown below. Plot ln p vs. V and determine γ for this gas from your graph.

P (atm)	V (L)
20.0	1.0
17.0	1.1
14.0	1.3
11.0	1.5
8.0	2.0
5.0	2.6
2.0	5.2
1.0	8.4

70. An ideal monatomic gas at 300 K expands adiabatically and reversibly to twice its volume. What is its final temperature?

71. An ideal diatomic gas at 80 K is slowly compressed adiabatically and reversibly to twice its volume. What is its final temperature?

72. An ideal diatomic gas at 80 K is slowly compressed adiabatically to one-third its original volume. What is its final temperature?

73. Compare the charge in internal energy of an ideal gas for a quasi-static adiabatic expansion with that for a quasi-static isothermal expansion. What happens to the temperature of an ideal gas in an adiabatic expansion?

74. The temperature of n moles of an ideal gas changes from T_1 to T_2 in a quasi-static adiabatic transition. Show that the work done by the gas is given by

$$W = \frac{nR}{\gamma - 1}(T_1 - T_2).$$

75. A dilute gas expands quasi-statically to three times its initial volume. Is the final gas pressure greater for an isothermal or an adiabatic expansion? Does your answer depend on whether the gas is monatomic, diatomic, or polyatomic?

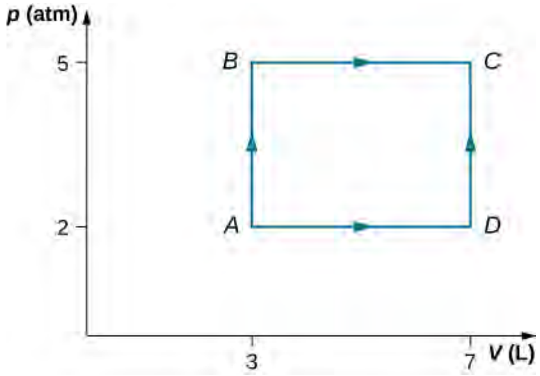
76. (a) An ideal gas expands adiabatically from a volume of $2.0 \times 10^{-3}\ \text{m}^3$ to $2.5 \times 10^{-3}\ \text{m}^3$. If the initial pressure and temperature were 5.0×10^5 Pa and 300 K, respectively, what are the final pressure and temperature of the gas? Use $\gamma = 5/3$ for the gas. (b) In an isothermal process, an ideal gas expands from a volume of $2.0 \times 10^{-3}\ \text{m}^3$ to $2.5 \times 10^{-3}\ \text{m}^3$. If the initial pressure and temperature were 5.0×10^5 Pa and 300 K, respectively, what are the final pressure and temperature of the gas?

77. On an adiabatic process of an ideal gas pressure, volume and temperature change such that pV^{γ} is constant with $\gamma = 5/3$ for monatomic gas such as helium and $\gamma = 7/5$ for diatomic gas such as hydrogen at room temperature. Use numerical values to plot two isotherms of 1 mol of helium gas using ideal gas law and two adiabatic processes mediating between them. Use $T_1 = 500\text{ K},\ V_1 = 1\text{ L},$ and $T_2 = 300\text{ K}$ for your plot.

78. Two moles of a monatomic ideal gas such as helium is compressed adiabatically and reversibly from a state (3 atm, 5 L) to a state with pressure 4 atm. (a) Find the volume and temperature of the final state. (b) Find the temperature of the initial state of the gas. (c) Find the work done by the gas in the process. (d) Find the change in internal energy of the gas in the process.

ADDITIONAL PROBLEMS

79. Consider the process shown below. During steps *AB* and *BC*, 3600 J and 2400 J of heat, respectively, are added to the system. (a) Find the work done in each of the processes *AB*, *BC*, *AD*, and *DC*. (b) Find the internal energy change in processes *AB* and *BC*. (c) Find the internal energy difference between states *C* and *A*. (d) Find the total heat added in the *ADC* process. (e) From the information given, can you find the heat added in process *AD*? Why or why not?



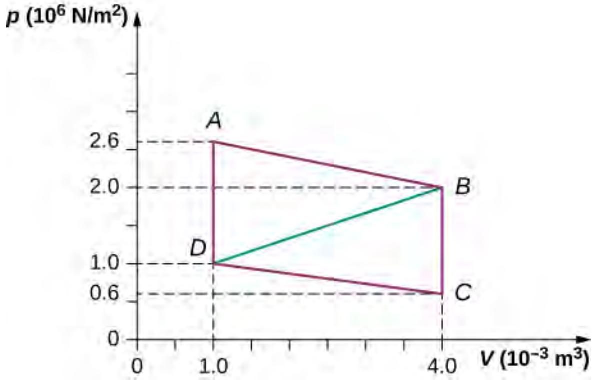
80. A car tire contains 0.0380 m^3 of air at a pressure of 2.20×10^5 Pa (about 32 psi). How much more internal energy does this gas have than the same volume has at zero gauge pressure (which is equivalent to normal atmospheric pressure)?

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

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

83. A hand-driven tire pump has a piston with a 2.50-cm diameter and a maximum stroke of 30.0 cm. (a) How much work do you do in one stroke if the average gauge pressure is $2.4 \times 10^5\text{ N/m}^2$ (about 35 psi)? (b) What average force do you exert on the piston, neglecting friction and gravitational force?

84. Calculate the net work output of a heat engine following path *ABCDA* as shown below.



85. What is the net work output of a heat engine that follows path *ABDA* in the preceding problem with a straight line from *B* to *D*? Why is the work output less than for path *ABCDA*?

86. Five moles of a monatomic ideal gas in a cylinder at 27 °C is expanded isothermally from a volume of 5 L to 10 L. (a) What is the change in internal energy? (b) How much work was done on the gas in the process? (c) How much heat was transferred to the gas?

87. Four moles of a monatomic ideal gas in a cylinder at 27 °C is expanded at constant pressure equal to 1 atm until its volume doubles. (a) What is the change in internal energy? (b) How much work was done by the gas in the process? (c) How much heat was transferred to the gas?

88. Helium gas is cooled from 20 °C to 10 °C by expanding from 40 atm to 1 atm. If there is 1.4 mol of helium, (a) What is the final volume of helium? (b) What is the change in internal energy?

89. In an adiabatic process, oxygen gas in a container is compressed along a path that can be described by the following pressure in atm as a function of volume V, with $V_0 = 1L: \; p = (3.0\,\text{atm})(V/V_0)^{-1.2}$. The initial and final volumes during the process were 2 L and 1.5 L, respectively. Find the amount of work done on the gas.

90. A cylinder containing three moles of a monatomic ideal gas is heated at a constant pressure of 2 atm. The temperature of the gas changes from 300 K to 350 K as a result of the expansion. Find work done (a) on the gas; and (b) by the gas.

91. A cylinder containing three moles of nitrogen gas is heated at a constant pressure of 2 atm. The temperature of the gas changes from 300 K to 350 K as a result of the expansion. Find work done (a) on the gas, and (b) by the gas by using van der Waals equation of state instead of ideal gas law.

92. Two moles of a monatomic ideal gas such as oxygen is compressed adiabatically and reversibly from a state (3 atm, 5 L) to a state with a pressure of 4 atm. (a) Find the volume and temperature of the final state. (b) Find the temperature of the initial state. (c) Find work done by the gas in the process. (d) Find the change in internal energy in the process. Assume $C_V = 5R$ and $C_p = C_V + R$ for the diatomic ideal gas in the conditions given.

93. An insulated vessel contains 1.5 moles of argon at 2 atm. The gas initially occupies a volume of 5 L. As a result of the adiabatic expansion the pressure of the gas is reduced to 1 atm. (a) Find the volume and temperature of the final state. (b) Find the temperature of the gas in the initial state. (c) Find the work done by the gas in the process. (d) Find the change in the internal energy of the gas in the process.

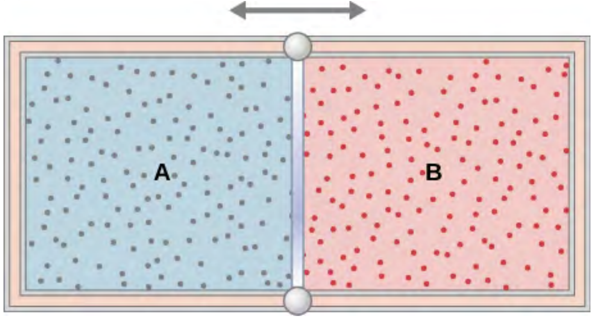
CHALLENGE PROBLEMS

94. One mole of an ideal monatomic gas occupies a volume of $1.0 \times 10^{-2}\ \text{m}^3$ at a pressure of $2.0 \times 10^5\ \text{N/m}^2$. (a) What is the temperature of the gas? (b) The gas undergoes a quasi-static adiabatic compression until its volume is decreased to $5.0 \times 10^{-3}\ \text{m}^3$. What is the new gas temperature? (c) How much work is done on the gas during the compression? (d) What is the change in the internal energy of the gas?

95. One mole of an ideal gas is initially in a chamber of volume $1.0 \times 10^{-2}\ \text{m}^3$ and at a temperature of $27\,°\text{C}$. (a) How much heat is absorbed by the gas when it slowly expands isothermally to twice its initial volume? (b) Suppose the gas is slowly transformed to the same final state by first decreasing the pressure at constant volume and then expanding it isobarically. What is the heat transferred for this case? (c) Calculate the heat transferred when the gas is transformed quasi-statically to the same final state by expanding it isobarically, then decreasing its pressure at constant volume.

96. A bullet of mass 10 g is traveling horizontally at 200 m/s when it strikes and embeds in a pendulum bob of mass 2.0 kg. (a) How much mechanical energy is dissipated in the collision? (b) Assuming that C_v for the bob plus bullet is 3R, calculate the temperature increase of the system due to the collision. Take the molecular mass of the system to be 200 g/mol.

97. The insulated cylinder shown below is closed at both ends and contains an insulating piston that is free to move on frictionless bearings. The piston divides the chamber into two compartments containing gases A and B. Originally, each compartment has a volume of $5.0 \times 10^{-2}\ \text{m}^3$ and contains a monatomic ideal gas at a temperature of $0\,°\text{C}$ and a pressure of 1.0 atm. (a) How many moles of gas are in each compartment? (b) Heat Q is slowly added to A so that it expands and B is compressed until the pressure of both gases is 3.0 atm. Use the fact that the compression of B is adiabatic to determine the final volume of both gases. (c) What are their final temperatures? (d) What is the value of Q?



98. In a diesel engine, the fuel is ignited without a spark plug. Instead, air in a cylinder is compressed adiabatically to a temperature above the ignition temperature of the fuel; at the point of maximum compression, the fuel is injected into the cylinder. Suppose that air at $20\,°\text{C}$ is taken into the cylinder at a volume V_1 and then compressed adiabatically and quasi-statically to a temperature of $600\,°\text{C}$ and a volume V_2. If $\gamma = 1.4$, what is the ratio V_1/V_2? (Note: In an operating diesel engine, the compression is not quasi-static.)