

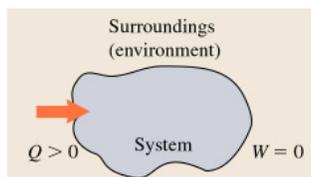
# Chapter 19

## The First Law of Thermodynamics

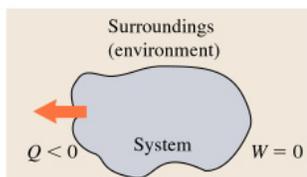
The first law of thermodynamics is an extension of the principle of *conservation of energy*. It includes the transfer of both mechanical and thermal energy. First of all we need to define the concept of a thermodynamic system. Next, we will describe how “heat” and “work” are the two means of transferring energy into or out of the system.

### 1 Thermodynamic Systems

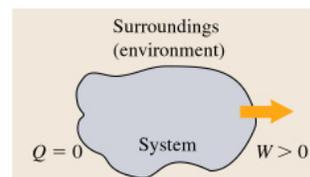
We have separately studied the two forms of energy—work and heat. In this chapter will will combine these two properties to see how they can change the *state* of a thermodynamic system. In general, a **thermodynamic system** is any collection of objects having the potential to exchange energy (mechanical or thermal) with its surroundings. A **thermodynamic process** describes the changes in state of a *thermodynamic system* (i.e., changes in  $p$ ,  $V$ ,  $T$ , and  $n$ ).



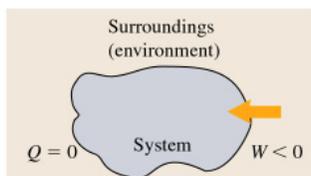
(a) When heat is added *to* the system,  $Q$  is positive



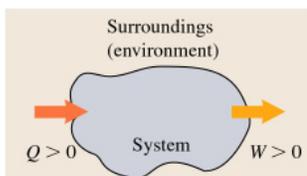
(b) When heat is transferred *out* of the system,  $Q$  is negative



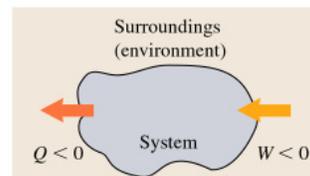
(c) When work is done *by* the system,  $W$  is positive



(d) When work is done *on* the system,  $W$  is negative



(e) Heat is added to the system and work is done by the system

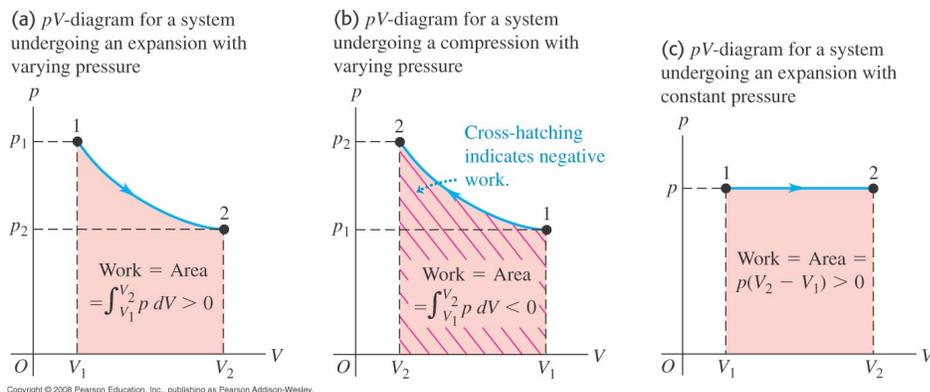


(f) Heat is transferred out of the system and work is done on the system

## 2 Work Done During Volume Changes

In this section, we investigate the amount of work done by a gas (i.e., by the system).

- Positive work – piston moves resulting in an expanding volume.
- Negative work – piston moves resulting in a decreasing volume.



The work done by the gas depends on the force it applies to the piston and the distance the piston moves.

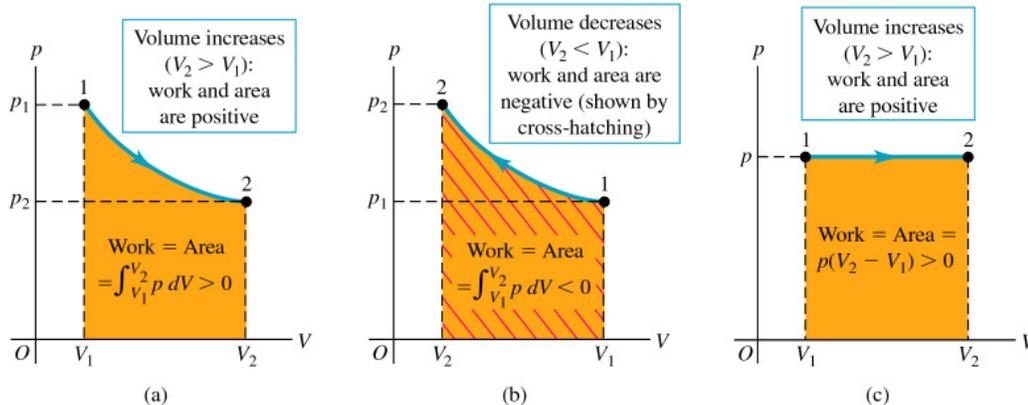
$$dW = F dx \quad \Rightarrow \quad dW = p A dx$$

where  $A dx = dV$ , the differential change in the volume of the system. Thus, the *differential work* done by the gas is proportional to the *differential change in volume* (i.e.,  $dW = p dV$ ).

The work done by the gas when its volume changes from  $V_1 \rightarrow V_2$  is:

$$W = \int_{V_1}^{V_2} p dV \quad (\text{work done in a volume change}) \quad (1)$$

Notice that this equation describes the *area* under the  $p$ - $V$  curve between  $V_1$  and  $V_2$ . The manner and method by which a system moves from state “1” to state “2” is shown as a **thermodynamic path** on the  $p$ - $V$  diagram. We assume that when a system changes from state “1” to state “2”, it does so quasistatically, that is to say, that the state variables ( $p$ ,  $V$ ,  $T$ , and  $n$ ) are well defined quantities describing the “system” (i.e., the gas) on every part of the thermodynamic path.



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## 2.1 Work done by an isothermal expansion

Let's look at the work done by the isothermal expansion of a gas as the volume changes from  $V_1$  to  $V_2$ .

$$W = \int_{V_1}^{V_2} p \, dV = \int_{V_1}^{V_2} \frac{nRT}{V} \, dV = nRT \ln \left( \frac{V_2}{V_1} \right) \quad (\text{isothermal})$$

**Ex. 3** Two moles of an ideal gas are compressed in a cylinder at a constant temperature of  $65.0^\circ\text{C}$  until the original pressure has tripled. (a) Sketch a  $pV$ -diagram for this process. (b) Calculate the amount of work done by the gas.

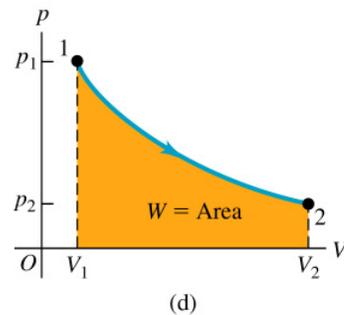
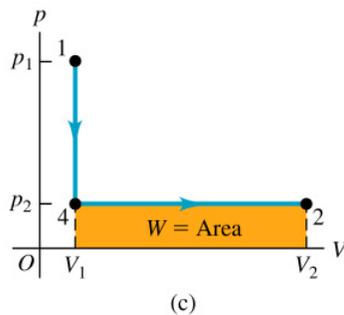
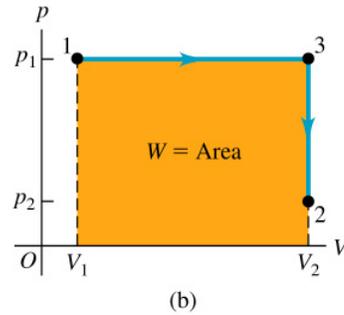
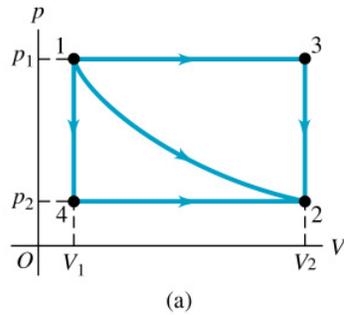
## 3 Paths Between Thermodynamic States

We will learn the properties of 4 thermodynamic paths in this chapter.

1. Isothermal – no change in temperature ( $\Delta T = 0$ )
2. Isobaric – no change in pressure ( $\Delta p = 0$ )

3. Isochoric – no change in volume ( $\Delta V = 0$ )
4. Adiabatic – no exchange of thermal energy ( $Q = 0$ )

We will discuss the *adiabatic* process in more detail later.



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## 4 Internal Energy and the First Law of Thermodynamics

In order to understand the concept of “internal energy,” we must begin with the fact that matter consists of atoms and molecules that contain *kinetic* and *potential* energies. The **internal energy** of a system is the sum of kinetic energies of all of its constituent particles, plus the sum of all the potential energies of interaction among these particles.

Let’s imagine that we introduce some thermal energy  $Q$  into a system. How can it respond to the increase of energy? It can either raise the temperature of the gas (i.e., increase its internal energy), or it can cause the system to do mechanical work  $W$  on the external environment, or both. This simple *conservation of energy* principle can be written as:

$$Q = \Delta U + W \quad (\text{first law of thermodynamics}) \quad (2)$$

where  $\Delta U$  is the change in internal energy, and  $W$  is the *work* done by the system.

Another way of looking at the *first law of thermodynamics* is to rewrite the previous equation as:

$$\Delta U = Q - W \quad (3)$$

*The change in internal energy of a system during any thermodynamic process depends only on the initial and final states, not on the thermodynamic path leading from one state to another.* The thermal energy  $Q$  and the work  $W$  will depend on the thermodynamic path, however, the change in internal energy  $\Delta U$  is independent of the thermodynamic path. As we will see later, the change in internal energy  $\Delta U$  depends only on the change in temperature  $\Delta T$  (i.e.,  $\Delta U \sim \Delta T$ ).

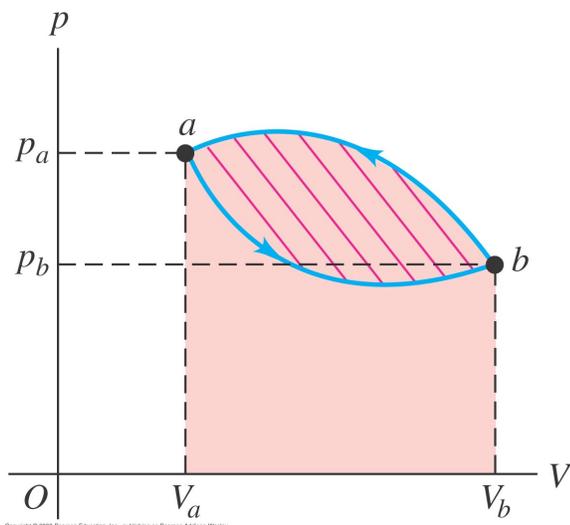
**Ex. 9** A gas in a cylinder expands from a volume of  $0.110 \text{ m}^3$  to  $0.320 \text{ m}^3$ . Heat flows into the gas just rapidly enough to keep the pressure constant at  $1.65 \times 10^5 \text{ Pa}$  during the expansion. The total heat added is  $1.15 \times 10^5 \text{ J}$ . (a) Find the work done by the gas. (b) Find the change in internal energy of the gas. (c) Does it matter whether the gas is ideal? Why or why not?

## 4.1 Cyclic Processes

In a cyclic process, a thermodynamic system exchanges heat and work as described by a thermodynamic process going from state  $a$  to state  $b$ .

In a cyclic process:

1. The work done *by* the gas going from  $a \rightarrow b$  is the area under the curve (+)
2. The work done *by* the gas going from  $b \rightarrow a$  is the area under the curve (-)
3. The total work done by the gas going from  $a \rightarrow b \rightarrow a$  is the *shaded* area between the two curves.



4. The total change in internal energy  $\Delta U$  is zero going from  $a \rightarrow b \rightarrow a$  because you start at temperature  $T_a$  and you finish at temperature  $T_a$  (i.e.,  $\Delta T = 0$ ).

**Q 19.24** A thermodynamic system undergoes a cyclic process as shown in **Fig. Q19.24**. The cycle consists of two closed loops: I and II. (a) Over one complete cycle, does the system do positive or negative work? (b) In each loop, is the net work done by the system positive or negative? (c) Over one complete cycle, does heat flow into or out of the system? (d) In each loop, does heat flow into or out of the system? Explain.

**Ex. 13** The  $pV$  diagram in Fig. E19.13 shows a process  $abc$  involving 0.450 mol of an ideal gas. (a) What was the temperature of this gas at points  $a$ ,  $b$ , and  $c$ ? (b) How much work was done “by” or “on” the gas in this process? (c) How much heat had to be added during the process to increase the internal energy of the gas by 15,000 J?

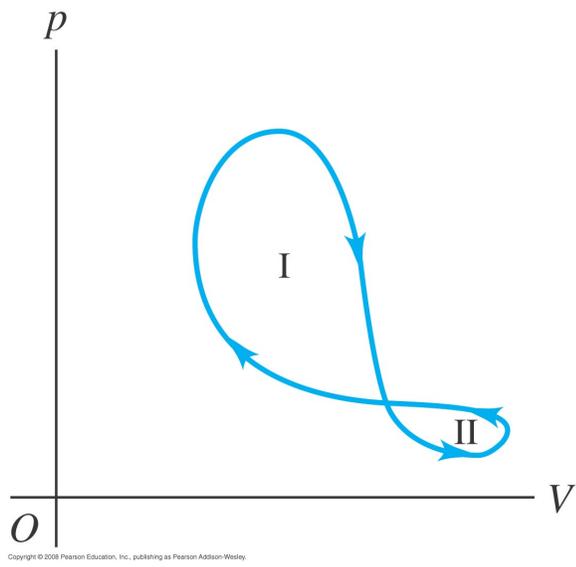


Figure 1: University Physics–Figure Q19.24

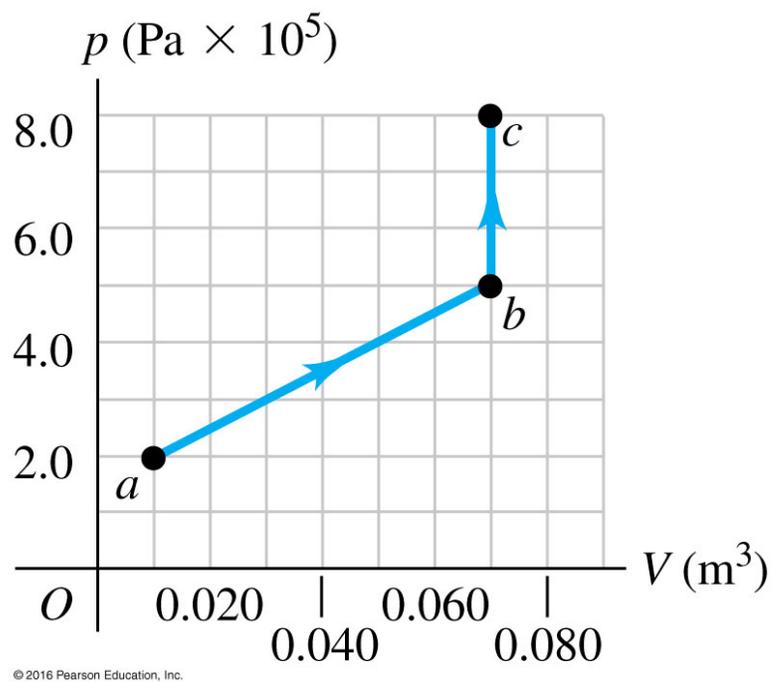
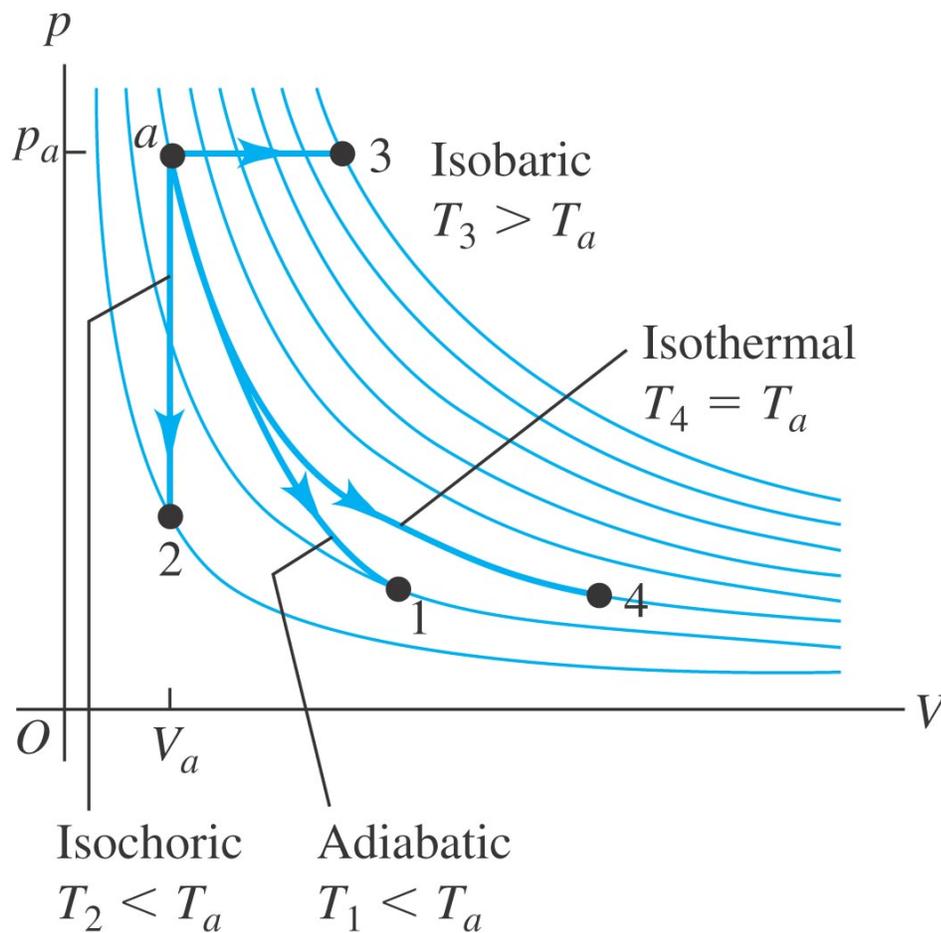


Figure 2: University Physics–Figure E19.13

## 5 Kinds of Thermodynamic Processes

What does the *first law of thermodynamics* reveal for each of the following processes?

1. Adiabatic –  $Q = 0$ .       $\Delta U = -W$
2. Isochoric –  $\Delta V = 0$ .       $\Delta U = Q$       because  $W = 0$
3. Isobaric –  $\Delta P = 0$ .      None of the three quantities  $\Delta U$ ,  $Q$ , and  $W$  is zero. However, we can easily calculate the work.  $W = p(V_2 - V_1)$ .
4. Isothermal –  $\Delta T = 0$ .       $\Delta U = 0$  and  $Q = W = nRT \ln(V_2/V_1)$ .



## 6 Internal Energy of an Ideal Gas

When studying the properties of *free expansion*, we see that the temperature  $T$  is constant. This means that the internal energy  $U$  is constant even though  $p$  and  $V$  do change. Many experiments have shown that when a low-density gas undergoes a free expansion, its temperature *does not* change. Therefore  $U \sim T$  and does not depend on  $p$  and  $V$ .

**Conclusion:** The internal energy of an ideal gas depends only on its temperature, not on its pressure or volume.  $U \sim T$

## 7 Heat Capacities of an Ideal Gas

In this section, we want to identify the thermal energy  $Q$  transferred in each of the 4 thermodynamic processes. We already know that  $Q = 0$  for an adiabatic process. Secondly, we know that  $Q = W = nRT \ln(V_2/V_1)$  for an isothermal process. As a result, we only need to identify the heat exchanged for *isobaric* and *isochoric* processes. We appeal to our knowledge of heat exchange as described in the previous chapter, namely,  $Q = nC \Delta T$ .

The thermal energy transferred in an *isobaric* process is:

$$Q_p = nC_p \Delta T \quad (4)$$

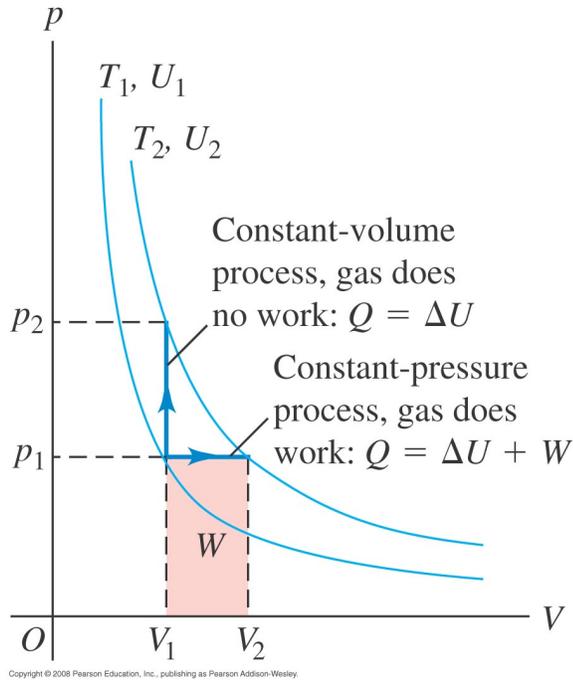
The thermal energy transferred in an *isochoric* process is:

$$Q_V = nC_V \Delta T \quad (5)$$

While  $C_p$  and  $C_V$  have the same units [J/(mol·K)], they are *not equal* to each other. However, there is a relationship between  $C_p$  and  $C_V$ . Let's see what it is. First of all, notice that in Eq. 5, that  $W = 0$ , so  $\Delta U = Q_V = nC_V \Delta T$ .

$$\Delta U = Q_V = nC_V \Delta T \quad (\text{for an isochoric process}) \quad (6)$$

$$\begin{aligned} \Delta U &= Q_p - W = nC_p \Delta T - p \Delta V \\ \Delta U &= nC_p \Delta T - nR \Delta T \quad (\text{for an isobaric process}) \end{aligned} \quad (7)$$



The  $\Delta U$ 's in Eqs. 6 and 7 are equal to each other (see the diagram above). Both paths “begin” and “end” on the same isotherm ( $\Delta U_{\text{isochoric}} = \Delta U_{\text{isobaric}}$ ).

**Recall:** The internal energy of an ideal gas depends only on its temperature, not on its pressure or volume.

$$\Delta U = nC_V \Delta T \quad (\text{for all thermodynamical paths})$$

Using this equation, we find:

$$nC_V \Delta T = nC_p \Delta T - nR \Delta T$$

Finally, we have:

$$C_p = C_V + R \quad (\text{molar heat capacities of an ideal gas}) \quad (8)$$

**Table 19.1** Molar Heat Capacities of Gases at Low Pressure

Type of Gas	Gas	$C_V$ (J/mol · K)	$C_p$ (J/mol · K)	$C_p - C_V$ (J/mol · K)	$\gamma = C_p/C_V$
Monatomic	He	12.47	20.78	8.31	1.67
	Ar	12.47	20.78	8.31	1.67
Diatomic	H <sub>2</sub>	20.42	28.74	8.32	1.41
	N <sub>2</sub>	20.76	29.07	8.31	1.40
	O <sub>2</sub>	20.85	29.17	8.31	1.40
	CO	20.85	29.16	8.31	1.40
Polyatomic	CO <sub>2</sub>	28.46	36.94	8.48	1.30
	SO <sub>2</sub>	31.39	40.37	8.98	1.29
	H <sub>2</sub> S	25.95	34.60	8.65	1.33

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**Ex. 19** In an experiment to simulate conditions within an automobile engine, 0.185 mol of air at a temperature of 780 K and a pressure of  $3.00 \times 10^6$  Pa is contained in a cylinder of volume 40.0 cm<sup>3</sup>. Then 645 J of heat is transferred to the cylinder. (a) If the volume of the cylinder is constant while the heat is added, what is the final temperature of the air? Assume that the air is essentially nitrogen gas, and use the data in Table 19.1 even though the pressure is not low. Draw a  $pV$ -diagram for this process. b) If instead the volume of the cylinder is allowed to increase while the pressure remains constant, repeat part (a). Draw a  $pV$ -diagram for this process.

**Ex. 22** Three moles of an ideal monatomic gas expands at a constant pressure of 2.50 atm; the volume of the gas changes from  $3.20 \times 10^{-2}$  m<sup>3</sup> to  $4.50 \times 10^{-2}$  m<sup>3</sup>. Calculate (a) the initial and final temperatures of the gas; (b) the amount of work the gas does in expanding; (c) the amount of heat added to the gas; (d) the change in internal energy of the gas.

## 7.1 The ratio of heat capacities

The definition of  $\gamma$ , the ratio of heat capacities:

$$\gamma = \frac{C_P}{C_V}$$

For monatomic gases:

$$\gamma = \frac{5}{3}$$

For diatomic gases:

$$\gamma = \frac{7}{5}$$

Remember,  $\Delta U = nC_V \Delta T$ , *whether the volume is constant or not.*

## 8 Adiabatic Processes for an Ideal Gas

An adiabatic process is a process in which no heat transfer takes place between the system (i.e., the working gas), and the environment. In short,  $Q = 0$ , and from the first law of thermodynamics we have  $\Delta U = -W$ . From the first law of thermodynamics we can write  $\Delta U = -W$ , or  $dU = -dW$ :

$$nC_V dT = -p dV = -\frac{nRT dV}{V}$$

$$nC_V dT + nRT \frac{dV}{V} = 0$$

$$\frac{dT}{T} + \frac{R}{C_V} \frac{dV}{V} = 0$$

$$\frac{R}{C_V} = \frac{C_P - C_V}{C_V} = \gamma - 1$$

where  $\gamma = C_P/C_V$ , the ratio of specific heats. Integrating both sides, we obtain

$$TV^{\gamma-1} = \text{constant} \quad \text{or} \quad PV^\gamma = (\text{constant})$$

### Work done along an adiabat

$$W = \int_{V_1}^{V_2} p dV = \frac{1}{\gamma - 1} (P_1 V_1 - P_2 V_2)$$

or

$$W = -\Delta U = -n C_V \Delta T = n C_V (T_1 - T_2)$$

**Ex. 28** Five moles of monatomic ideal gas have initial pressure  $2.50 \times 10^3$  Pa and initial volume  $2.10 \text{ m}^3$ . While undergoing an adiabatic expansion, the gas does 1480 J of work. What is the final pressure of the gas after the expansion?