Chapter 19 Thermodynamics

“We can express the fundamental laws of the universe which correspond to the two fundamental laws of the mechanical theory of heat in the following simple form.
1. The energy of the universe is a constant. 2. The entropy of the universe tends toward a maximum.”

Rudolf Clausius

19.1 Introduction

Thermodynamics is the study of the relationships between heat, internal energy, and the mechanical work performed by a system. The system considered is usually a heat engine of some kind, although the term can also be applied to living systems such as plants and animals. There are two laws of thermodynamics. The first law of thermodynamics is the law of conservation of energy as applied to a thermodynamic system. We will apply the first law of thermodynamics to a heat engine and study its ramifications. The second law of thermodynamics tells us what processes are, and are not, possible in the operation of a heat engine. The second law is also responsible for telling us in which direction a particular physical process may go. For example a block can slide across a desk and have all of its kinetic energy converted to thermal energy by the work the block does against friction as it is slowed to a stop. However, the reverse process does not happen, that is, the thermal energy in the block does not convert itself into mechanical energy and cause the block to slide across the desk. Using the thermal energy in the block to cause mechanical motion is not a violation of the law of conservation of energy but it is a violation of the second law of thermodynamics.

19.2 The Concept of Work Applied to a Thermodynamic System

Consider what happens to an ideal gas in a cylinder when it is compressed by a constant external force $F$, as shown in figure 19.1(a). The constant force exerted on top of the piston causes it to be displaced a small distance $dy$, thereby compressing the gas in the cylinder. The work done on the gas by the external force in compressing it is

$$W = \int F\,dy$$  \hspace{1cm} (19.1)

This work by the external agent is positive because the external force and the displacement are in the same direction. The external force $F$ and the external pressure $p$ exerted on the gas by the piston are related by
where $A$ is the cross-sectional area of the piston. Substituting equation 19.2 into equation 19.1 gives

$$W = |pA dy$$  \hspace{1cm} (19.3)$$

which is the work done on the gas by the external agent. If the compression takes place very slowly, the constant external pressure exerted by the piston on the gas is equal to the internal pressure exerted by the gas throughout the process. Thus, equation 19.3 can also be interpreted as the work done by the gas rather than the external agent. This is a departure from the usual way we have analyzed the concept of work. Previously, we have always considered the work as being done by the external agent. Our new approach will be to consider all the work to be done on or by the gas itself, not the external agent. The product of the area of the cylinder and the displacement of the gas is equal to the change in volume of the gas. That is,

$$Ady = dV$$  \hspace{1cm} (19.4)$$

the decrease in the volume of the gas. Substituting equation 19.4 into 19.3 gives

$$W = |pdV$$  \hspace{1cm} (19.5)$$

Equation 19.5 represents the amount of work done by the gas when a constant force compresses it by an amount $dV$.

This entire process can be shown on a pressure-volume ($p$-$V$) diagram as in figure 19.1(b). The original state of the gas is represented as the point $B$ in the diagram, where it has the volume $V_B$ and the pressure $p_A$. As the piston moves at constant pressure, the system, the gas in the cylinder, moves from the state at point $B$ to the state at point $A$. The work done on the gas by the external agent is represented by the area under the curve $AB$ on the $p$-$V$ diagram.
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B to the state at point A [figure 19.1(b)] along a horizontal line indicating that the process is occurring at the constant pressure $p_A$. At point A in the figure, the gas has been compressed to the volume $V_A$. The total work done by the gas in compressing it from the point B to the point A, found from equations 19.5, is

$$W_{BA} = \int_{V_B}^{V_A} p_A dV = p_A (V_A - V_B)$$

It is important to note here that the product of $p_A$ and $V_A - V_B$ represents the area of the rectangle cross-hatched in figure 19.1(b). Thus, the area under the curve in a $p$-$V$ diagram always represents a quantity of work. When the area is large, it represents a large quantity of work, and when the area is small the quantity of work likewise is small.

Because $V_A$ is less than $V_B$, the quantity $V_A - V_B$ is negative. Thus, when work is done by a gas in compressing it, that work is always negative. Notice that there are two distinct agents here. The work done by the external agent in compressing the gas is positive, but the work done by the gas in a compression is negative.

If the gas in the cylinder of figure 19.1(a) is allowed to expand back to the original volume $V_B$, then the process can be represented on the same $p$-$V$ diagram of figure 19.1(b) as the same straight line, now going from point A to the point B. The work done by the gas in the expansion from A to B is

$$W_{AB} = \int_{V_A}^{V_B} p_A dV = p_A (V_B - V_A)$$

But now note that since $V_B$ is greater than $V_A$, the quantity $V_B - V_A$ is now a positive quantity. Thus, when a gas expands, the work done by the gas is positive. (The work done on the gas by an external agent during the expansion would be negative. From this point on let us consider only the work done by the gas and forget any external agent.) Thus, the work done by a gas during expansion is positive and the work done by a gas during compression is negative. In either case, the work done is still the area under the line $AB$ given by the product of the sides of the rectangle $p_A$ and $V_B - V_A$. The areas are the same in both cases, however we consider the area positive when the gas expands and negative when the gas is compressed.

Let us now consider the work done along the different paths of the cyclic process shown in the $p$-$V$ diagram of figure 19.2. A cyclic process is a process that runs in a cycle eventually returning to where it started from. Thus, in figure 19.2(a) the cycle goes from A to B, B to C, C to D, and D back to A. The total work done by the system as it goes through the cycle is simply

$$W_{total} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

where

- $W_{AB}$ is the work done on the path $AB$
- $W_{BC}$ is the work done on the path $BC$
- $W_{CD}$ is the work done on the path $CD$
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$W_{DA}$ is the work done on the path $DA$

![Diagram of cyclic process with paths AB, BC, CD](image)

**Figure 19.2** Work done in a cyclic process.

Let us consider the work done along each path separately.

The work done along the path $AB$ is

$$W_{AB} = \int_{V_A}^{V_B} p_A dV = p_A(V_B - V_A)$$  \hspace{1cm} (19.7)

Because the path $AB$ represents an expansion, positive work is done by the gas, as is evidenced by the fact that $V_B - V_A$ is a positive quantity. The work done along the path $AB$ is shown as the area under the line $AB$ in figure 19.2(b).

To find the work done along the path $BC$ we notice that this path represents a process that is performed at the constant volume $V_B$. Therefore, $dV = 0$, and no work is performed along $BC$. Formally,

$$W_{BC} = \int p dV = 0$$  \hspace{1cm} (19.8)

The work done along the path $CD$ is
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\[ W_{CD} = \int_{V_B}^{V_A} p_D dV = p_D(V_A - V_B) \]  \hfill (19.9)

Since the path \( CD \) represents a compression, work is done on the gas. This work is considered negative, as we can see from the fact that \( V_A - V_B \), in equation 19.9, is negative. The work done on the gas is shown as the area under the line \( CD \) in figure 19.2(c).

For the work done along the path \( DA \), we again notice that the volume is a constant and therefore \( dV \) is again zero, and hence the work done must also be zero. Formally,

\[ W_{DA} = \int p dV = 0 \]  \hfill (19.10)

Since the work is given by \( pdV \), whenever \( V \) is a constant in a process, \( dV \) is always zero and the work is also zero along that path in the \( p-V \) diagram.

The net work done by the gas in the cyclic process \( ABCDA \), found from equation 19.6 with the help of equations 19.7 through 19.10, is

\[ W_{\text{total}} = W_{AB} + W_{BC} + W_{CD} + W_{DA} \]  \hfill (19.6)

\[ W_{\text{total}} = p_A(V_B - V_A) + 0 + p_D(V_A - V_B) + 0 \]

We can rewrite this to show that the work along \( CD \) is negative, that is, \( V_A - V_B = -(V_B - V_A) \). Hence,

\[ W_{\text{total}} = p_A(V_B - V_A) - p_D(V_B - V_A) \]

or

\[ W_{\text{total}} = (p_A - p_D)(V_B - V_A) \]  \hfill (19.11)

Thus, equation 19.11 represents the net work done by the gas in this particular cyclic process. Note that \( p_A - p_D \) is one side of the rectangular path of figure 19.2(a) while \( V_B - V_A \) is the other side of that rectangle. Hence, their product in equation 19.11 represents the entire area of the rectangle enclosed by the thermodynamic path \( ABCDA \) and is shown as the cross-hatched area in figure 19.2(d). Another way to visualize this total area, and hence total work, is to subtract the area in figure 19.2(c), the negative work, from the area in figure 19.2(b), the positive work, and we again get the area bounded by the path \( ABCDA \). Although this result was derived for a simple rectangular thermodynamic path, it is true in general. Thus, in any cyclic process, the net work done by the system is equal to the area enclosed by the cyclic thermodynamic path in a \( p-V \) diagram. Therefore, to get as much work as possible out of a system, the enclosed area must be as large as possible. The net work is positive if the cycle proceeds clockwise, in the \( p-V \) diagram, and negative if the cycle proceeds counterclockwise. Finally, we should note that the process \( AB \) takes place at the constant pressure \( p_A \). A process that takes place at a constant pressure is called an isobaric process. Hence, the process \( CD \) is also an isobaric process because it takes place at the constant pressure \( p_D \). Process \( BC \) takes place at the constant volume \( V_B \), and process \( DA \) takes place at the constant volume \( V_A \).
process that takes place at constant volume is called an isochoric or isometric process.

**Example 19.1**

*Work done in a thermodynamic cycle.* One mole of an ideal gas goes through the thermodynamic cycle shown in figure 19.2(a). If \( p_A = 2.00 \times 10^4 \) Pa, \( p_D = 1.00 \times 10^4 \) Pa, \( V_A = 0.250 \) m\(^3\), and \( V_B = 0.500 \) m\(^3\), find the work done along the path (a) \( AB \), (b) \( BC \), (c) \( CD \), (d) \( DA \), and (e) \( ABCDA \).

**Solution**

a. The work done along the path \( AB \), found from equation 19.7, is

\[
W_{AB} = p_A(V_B - V_A) \\
= (2.00 \times 10^4 \text{ Pa})(0.500 \text{ m}^3 - 0.250 \text{ m}^3) \\
= 5.00 \times 10^3 \text{ N m} \\
= 5.00 \times 10^3 \text{ J}
\]

b. The work done along the path \( BC \), found from equation 19.8, is

\[
W_{BC} = p(V_B - V_B) = 0
\]

c. The work done along path \( CD \), given by equation 19.9, is

\[
W_{CD} = p_D(V_A - V_B) \\
= (1.00 \times 10^4 \text{ Pa})(0.250 \text{ m}^3 - 0.500 \text{ m}^3) \\
= -2.50 \times 10^3 \text{ J}
\]

Note that the work done in compressing the gas is negative.

d. The work done along path \( DA \), given by equation 19.10, is

\[
W_{DA} = p(V_A - V_A) = 0
\]

e. The total work done along the entire path \( ABCDA \), found from equation 19.6, is

\[
W_{\text{total}} = W_{AB} + W_{BC} + W_{CD} + W_{DA} \\
= 5.00 \times 10^3 \text{ J} + 0 - 2.50 \times 10^3 \text{ J} + 0 \\
= 2.50 \times 10^3 \text{ J}
\]

19-6
In the cases consider so far, the paths chosen to determine the work done were very simple in that either the pressure \( p \) was a constant along the path and could be removed from under the integral sign, or even when the pressure \( p \) was a variable along the path, the process took place at a constant volume and hence there was no change in the volume \( V \), hence \( dV \) was equal to zero and the work done was equal to zero. For the general case shown in figure 19.3, the path is a curve along which the pressure and volume are constantly changing. The work done in going from the initial state \( f \) to the final state \( i \), is the sum, or integral, of all the small elements of volume \( dV \) multiplied by the average pressure \( p \) in each of these intervals \( dV \), and is given by equation 19.5 as

\[
W = \int_{V_i}^{V_f} pdV
\]  

(19.12)

In this general case, the pressure \( p \) is not a constant but varies with the volume \( V \) as seen in figure 19.3. The functional relationship between \( p \) and \( V \) must be introduced into equation 19.12 to solve for the work done. In any case, the work done will still be equal to the area under the curve in the \( p-V \) diagram. We will now show how this type of problem is solved.

Let us consider another type of process that is very important in thermodynamic systems, the isothermal process. An **isothermal process** is a process that occurs at a constant temperature, that is, \( dT = 0 \) for the process. A picture of an isotherm can be drawn on a \( p-V \) diagram by using the equation of state for an ideal gas, the working substance in the system. Thus, the ideal gas equation, given by equation 17.32, is

\[
pV = nRT
\]
Because \( n \) and \( R \) are constants, if \( T \) is also a constant, then the entire right-hand side of equation 15.23 is a constant. We can then write equation 17.32 as

\[
pV = \text{constant} \quad \text{(19.13)}
\]

If we plot equation 19.13 on a \( p-V \) diagram, we obtain the hyperbolic curves of figure 19.4. Each curve is called an isotherm and in the figure, \( T_3 \) is greater than \( T_2 \), which in turn is greater than \( T_1 \).

![Figure 19.4 Isotherms on a \( p-V \) diagram.](image)

Let us now consider the new cyclic process shown in figure 19.5, in which an ideal gas in a cylinder expands against a piston isothermally. This is shown as the path \( AC \) in the \( p-V \) diagram. To physically carry out the isothermal process along

![Figure 19.5 Cyclic process with an isothermal expansion.](image)

the path \( AC \), the cylinder is surrounded by a constant temperature heat reservoir. The cylinder either absorbs heat from, or liberates heat to, the reservoir in order to maintain the constant temperature. When the isothermal process is finished the heat reservoir is removed. The gas is then compressed at the constant pressure \( p_D \)
at point \( C \) until it reaches the point \( D \). The pressure of the gas is then increased from \( p_D \) to \( p_A \) while the volume of the gas in the cylinder is kept constant. This is shown as the path \( DA \) in the \( p-V \) diagram. Now let us assume that the points \( A, C, \) and \( D \) are the same points that were considered in figure 19.2(a). Recall that the net work done by the system is equal to the area enclosed by the cyclic path. Thus, the net work done in this process is equal to the cross-hatched area within the path \( ACDA \) shown in figure 19.5.

The work done along the path \( AC \), found from equation 19.12, is

\[
W_{AC} = \int_{V_A}^{V_C} p dV
\]  

(19.14)

The pressure \( p \) varies along the path \( AC \), but is given by the ideal gas equation as

\[
p = \frac{nRT}{V}
\]

Substituting this back into equation 19.14 gives

\[
W_{AC} = \int_{V_A}^{V_C} p dV = \int_{V_A}^{V_C} \frac{nRT}{V} dV
\]

But the temperature \( T \) is a constant along path \( AC \) and can be taken outside of the integral to yield

\[
W_{AC} = nRT \int_{V_A}^{V_C} \frac{dV}{V} = nRT \ln \frac{V_C}{V_A}
\]

Hence,

\[
W_{AC} = nRT \ln \frac{V_C}{V_A}
\]  

(19.15)

*Equation 19.15 gives the work done along the isothermal path.*

The work done along the path \( CD \) is

\[
W_{CD} = \int_{V_C}^{V_A} p dV = p_D (V_A - V_C)
\]

Since the path \( CD \) represents a compression, work is done on the gas. This work is considered negative, as we can see from the fact that \( V_A - V_B \) is negative.

For the work done along the path \( DA \), we observe that the volume is a constant and therefore \( dV \) is again zero, and hence the work done must also be zero, that is

\[
W_{DA} = \int p dV = 0
\]

The net work done by the gas in the cyclic process \( ACDA \), found from equation 19.6, is

\[
W_{\text{total}} = W_{AC} + W_{CD} + W_{DA}
\]

(19-9)
Example 19.2

Work done in another thermodynamic cycle. One mole of an ideal gas goes through the thermodynamic cycle shown in figure 19.5. If \( p_A = 2.00 \times 10^4 \) Pa, \( p_D = 1.00 \times 10^4 \) Pa, \( V_A = 0.250 \) m\(^3\), and \( V_C = 0.500 \) m\(^3\), find the work done along the path (a) AC, (b) CD, (c) DA, and (e) ACDA.

Solution

a. The work done along the path AC is found from equation 19.15. However, before we can do that we must first determine the temperature at the point A. This is done with the ideal gas law as

\[ p_A V_A = nRT_A \]

and

\[ T_A = \frac{p_A V_A}{nR} \]

\[ T_A = \frac{(2.00 \times 10^4 \text{ N/m}^2)(0.250 \text{ m}^3)}{(1 \text{ mole})(8.314 \text{ J/(mole K)})} = 601 \text{ K} \]

The work done is now found as

\[ W_{AC} = nRT_A \ln \frac{V_C}{V_A} \]

\[ W_{AC} = (1 \text{ mole})\left(8.314 \frac{\text{ J}}{\text{ mole K}}\right)(601 \text{ K}) \ln \frac{0.500 \text{ m}^3}{0.250 \text{ m}^3} = 3460 \text{ J} \]

b. The work done along path CD is

\[ W_{CD} = p_D (V_A - V_C) \]

\[ = (1.00 \times 10^4 \text{ Pa})(0.250 \text{ m}^3 - 0.500 \text{ m}^3) = -2500 \text{ J} \]

Note that the work done in compressing the gas is negative.

c. The work done along path DA is

\[ W_{DA} = p (V_A - V_A) = 0 \]

d. The total work done along the entire path ACDA, found from equation 19.6, is

\[ W_{total} = W_{AC} + W_{CD} + W_{DA} \]

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To go to this Interactive Example click on this sentence.

It is important to compare example 19.1 with 19.2, and figure 19.2(d) with 19.5. Remember the points A, C, and D in figure 19.5 are the same as the points A, C, and D in figure 19.2(d). But the area under the enclosed curve in figure 19.2(d) is greater than the enclosed area in figure 19.5. Hence, a greater amount of work is done by the system in following the cyclic path ABCDA than the cyclic path ACDA. In fact we found the work done along path ABCDA to be 2500 J while the work done along path ACDA to be 960 J. Thus, the work that the system does depends on the thermodynamic path taken. Even though both processes started at point A and returned to the same point A, the work done by the system is different in each case. This result is succinctly stated as: the work done depends on the path taken, and work is a path dependent quantity.

19.3 Heat Added to or Removed from a Thermodynamic System

We saw in chapter 16 that the amount of heat added or removed from a body is given by equation 16.6 as

\[ Q = mc\Delta T \]  \hspace{1cm} (16.6)

Equation 16.6 was essentially an empirical equation based upon experiments, and really said nothing about the different heat processes that could give rise to this equation. To remedy this we rewrite this equation in the differential form

\[ dQ = mcdT \]  \hspace{1cm} (19.16)

and then the total heat absorbed or liberated in any process is found from integrating equation 19.16 as

\[ Q = \int dQ = \int mcdT \]  \hspace{1cm} (19.17)

This equation can now be applied to the heat added to, or removed from, a gas, if two stipulations are made. First, we saw in chapter 17 that it is more convenient to express the mass \( m \) of a gas in terms of the number of moles \( n \) of the gas. The total mass \( m \) of the gas is the sum of the masses of all the molecules of the gas. That is, \( m \) is equal to the mass of one molecule times the total number of molecules in one mole of the substance, times the total number of moles. That is
where \( m_0 \) is the mass of one molecule; \( N_A \) is Avogadro's number, the number of molecules in one mole of a substance; and \( n \) is the number of moles of the gas. Notice in equation 17.66, the product of the mass of one molecule times Avogadro's number is called the **molecular mass** of the substance \( M \), that is,

\[
M = m_0 N_A
\]  

(19.19)

The molecular mass is thus the mass of one mole of the gas. Substituting equation 19.19 into equation 19.18 gives for the mass of the gas

\[
m = nM
\]  

(19.20)

Equation 19.20 says that the mass of the gas is equal to the number of moles of the gas times the molecular mass of the gas. Substituting equation 19.20 for the mass \( m \) of the gas into equation 19.17, gives

\[
Q = \int nM c dT
\]  

(19.21)

The product \( M c \) is defined as the **molar specific heat** of the gas, or molar heat capacity, and is represented by the capital letter \( C \). Hence,

\[
C = M c
\]  

(19.22)

The heat absorbed or lost by a gas undergoing a thermodynamic process is found by substituting equation 19.22 into equation 19.21. Thus,

\[
Q = \int nC dT
\]  

(19.23)

The second stipulation for applying equation 19.16 to gases has to do with the specific process to which the gas is subjected. Equation 16.6 was based on the heat absorbed or liberated from a solid or a liquid body that was under constant atmospheric pressure. In applying equation 19.23, which is the modified equation 19.16, we must specify the process whereby the temperature change \( dT \) occurs. Figure 19.6 shows some possible processes. Let us start at the point \( A \) in the \( p-V \) diagram of figure 19.6. The temperature at point \( A \) is \( T_0 \) because point \( A \) is on the \( T_0 \) isotherm. Heat can be added to the system such that the temperature of the gas rises to \( T_1 \). But, as we can see from figure 19.6, there are many different ways to get to the isotherm \( T_1 \). The thermodynamic paths \( AB, AC, AD, AE \), or an infinite number of other possible paths can be followed to arrive at \( T_1 \). Therefore, there can be an infinite number of specific heats for gases. Let us restrict ourselves to only
two paths, and hence only two specific heats. The first path we consider is the path AB, which represents a process taking place at constant volume. The second path is path AE, which represents a process taking place at constant pressure. We designate the molar specific heat for a process occurring at constant volume by \( C_v \), whereas we designate the molar specific heat for a process occurring at a constant pressure by \( C_p \).

It is found experimentally that for a monatomic ideal gas such as helium or argon, \( C_v = 12.5 \text{ J/mole K} \), whereas \( C_p = 20.8 \text{ J/mole K} \).

The heat absorbed by the gas as the system moves along the thermodynamic path AB in figure 19.6 is

\[
Q_{AB} = \int_{T_0}^{T_1} nC_v dT = nC_v(T_1 - T_0)
\]  

(19.24)

The heat absorbed by the gas as the system moves along the path AE is given by

\[
Q_{AE} = \int_{T_0}^{T_1} nC_p dT = nC_p(T_1 - T_0)
\]  

(19.25)

Although the system ends up at the same temperature \( T_1 \) whether the path AB or AE is traveled, the heat that is absorbed along each path is different because \( C_p \) and \( C_v \) have different values. Thus, the heat absorbed or liberated in a thermodynamic process depends on the path that is followed. That is, heat like work is path dependent. Although demonstrated for a gas, this statement is true in general.

**Example 19.3**

The heat absorbed along two different thermodynamic paths. Compute the amount of heat absorbed by 1 mole of He gas along path (a) AB and (b) AE, of figure 19.6, if \( T_1 = 400 \text{ K} \) and \( T_0 = 300 \text{ K} \).
Solution

a. The heat absorbed along path AB, given by equation 19.24, is

\[ Q_{AB} = \int_{T_0}^{T_1} nC_v \, dT = nC_v(T_1 - T_0) \]
\[ = (1 \text{ mole})(12.5 \text{ J/mole K})(400 \text{ K} - 300 \text{ K}) \]
\[ = 1250 \text{ J} \]

b. The heat absorbed along the path AE, given by equation 19.25, is

\[ Q_{AE} = \int_{T_0}^{T_1} nC_p \, dT = nC_p(T_1 - T_0) \]
\[ = (1 \text{ mole})(20.8 \text{ J/mole K})(400 \text{ K} - 300 \text{ K}) \]
\[ = 2080 \text{ J} \]

Thus, a greater quantity of heat is absorbed in the process that occurs at constant pressure. This is because at constant pressure the volume expands and some of the heat energy is used to do work, but at constant volume no work is accomplished.

To go to this Interactive Example click on this sentence.

19.4 The First Law of Thermodynamics

Recall from the kinetic theory of gases studied in chapter 17 that the mean kinetic energy of a molecule, found from equation 17.64, is

\[ KE_{avg} = \frac{1}{2} m \nu_{avg}^2 = 3kT \]

Thus, a change in the absolute temperature of a gas shows up as a change in the average energy of a molecule. If the average kinetic energy of one molecule of the gas is multiplied by \( N \), the total number of molecules of the gas present in the thermodynamic system (i.e., the cylinder filled with gas), then this product represents the total internal energy of this quantity of gas. Recall that the internal energy of a body was defined in chapter 16 as the sum of the kinetic energies and potential energies of all the molecules of the body. Because the molecules of a gas are moving so rapidly and are widely separated on the average, only a few are near to each other at any given time and it is unnecessary to consider any intermolecular forces, and hence potential energies of the molecules. Thus, the total kinetic energy
of all the molecules of a gas constitutes the total **internal energy of the gas**. We designate this internal energy of the gas by the symbol $U$. The internal energy of the gas is given by

$$U = (\text{total number of molecules})(\text{mean KE of each molecule})$$

$$= N \text{KE}_{\text{avg}}$$

$$U = N \left( \frac{3}{2} kT \right)$$  \hspace{1cm} (19.26)

But recall from equation 17.63 that

$$k = \frac{R}{N_A}$$

Substituting equation 17.63 into equation 19.26 gives for the internal energy of an ideal gas

$$U = N \left( \frac{3}{2} \frac{R}{N_A} T \right)$$

But the total number of molecules $N$ was given by

$$N = nN_A$$  \hspace{1cm} (17.33)

Thus,

$$U = nN_A \left( \frac{3}{2} \frac{R}{N_A} T \right)$$

and

$$U = \frac{3}{2} nRT$$  \hspace{1cm} (19.27)

From equation 19.27 we see that a change in temperature is thus associated with a change in the internal energy of the gas, that is,

$$dU = \frac{3}{2} nRdT$$  \hspace{1cm} (19.28)

Let us now consider the thermodynamic system shown in the $p$-$V$ diagram of figure 19.7. The isotherm going through point $B$ is labeled $T_B$, whereas the one that goes through points $A$ and $C$ is labeled $T_{AC}$, and finally, the isotherm that goes through point $D$ is called $T_D$. Before the entire system is considered, let us first consider a process that proceeds isothermally from $A$ to $C$. Since the path $AC$ is an isotherm, the temperature is constant and thus $dT = 0$. But from equation 19.28, the change in internal energy $dU$ must also be zero. That is, an **isothermal expansion occurs at constant internal energy**. But how can this be? As the gas expands along $AC$ it is doing work. If the internal energy is constant, where does the energy come from to perform the work that is being done by the gas? Obviously energy must somehow be supplied in order for the gas to do work. **Thus, a quantity**
of heat $dQ$ must be supplied to the system in order for the system to do work along an isothermal path. Hence, for an isothermal process,

$$dQ = dW \quad (19.29)$$

Let us now consider the portion of the process that is along path $BC$ in figure 19.7. The process $BC$ is performed at constant volume, thus, $dV = 0$ along this path. Because the amount of work done by the gas is given as $W = \int pdV$, if $dV = 0$, then the work done along the path $BC$ must also be zero. But the temperature $T_{AC}$ at point $C$ is less than the temperature $T_B$ at the point $B$. There has been a drop in temperature between points $B$ and $C$ and hence a decrease in the internal energy of the system. Since the loss of energy didn’t go into work, because $dV = 0$, heat must have been taken away from the system along path $BC$. The decrease in the internal energy of the system along an isometric path is caused by the heat removed from the system along $BC$, that is,

$$dU = dQ \quad (19.30)$$

But the heat removed from the system during a constant volume process was shown in equation 19.24 to be

$$dQ = nC_v dT \quad (19.31)$$

Since the heat removed is equal to the loss in internal energy by equation 19.30, we can write the change in internal energy from equations 19.30 and 19.31 as

$$dU = nC_v dT \quad (19.32)$$

Equation 19.32 is a general statement governing the change in internal energy during any process, not only the one at constant volume from which equation 19.32
was derived. Recall from equation 19.27, a result from the kinetic theory of gases, that $U$, the internal energy, is only a function of temperature. In fact if $dU$ from equation 19.28 is equated to $dU$ from equation 19.32, we get

$$3nRdT = nC_vdT$$

Solving for $C_v$, the theoretical value of the molar specific heat capacity at constant volume is found to be

$$C_v = \frac{3}{2}R$$

Using the value of $R = 8.314$ J/mole K found in chapter 17, the value of $C_v$, calculated from equation 19.33, is $C_v = 12.5$ J/mole K, which agrees with the experimental value.

The two special cases given by equations 19.29 and 19.30 can be combined into one general equation that contains 19.29 and 19.30 as special cases. This general equation is

$$dQ = dU + dW$$

and is called the first law of thermodynamics. Thus, we can derive equation 19.29 from 19.34 for an isothermal path because then the change in internal energy $dU = 0$. We can derive equation 19.30 from equation 19.34 for a constant volume thermodynamic path, because then $dV = 0$, and hence $dW = 0$. The first law of thermodynamics, equation 19.34, says that the heat $dQ$, added to a system will show up either as a change in internal energy $dU$ of the system and/or as work $dW$ performed by the system. From this analysis we can see that the first law of thermodynamics is just the law of conservation of energy. Equation 19.34 is quite often written in the slightly different form:

$$dU = dQ - dW$$

which is also called the first law of thermodynamics. The first law of thermodynamics can be also stated as the change in the internal energy of the system equals the heat added to the system minus the work done by the system on the outside environment. Perhaps the best way to see the application of the first law to a thermodynamic system is in an example.

**Example 19.4**

Applying the first law of thermodynamics. Two moles of an ideal gas are carried around the thermodynamic path $ABCDA$ in figure 19.7. Here $T_D = 150$ K, $T_{AC} = 300$ K, $T_B = 600$ K, and $p_A = 2.00 \times 10^4$ Pa, while $p_D = 1.00 \times 10^4$ Pa. The volume $V_A = 0.250$ m$^3$, while $V_B = 0.500$ m$^3$. Find the work done, the heat lost or absorbed, and
the internal energy of the system for the thermodynamic paths (a) \( AB \), (b) \( BC \), (c) \( CD \), (d) \( DA \), and (e) \( ABCDA \).

**Solution**

a. The work done by the expanding gas along the path \( AB \) is

\[
W_{AB} = \int_{V_A}^{V_B} p \, dV = p_A (V_B - V_A) \\
= \left( 2.00 \times 10^4 \, \text{N/m}^2 \right) (0.500 \, \text{m}^3 - 0.250 \, \text{m}^3) \\
= 5.00 \times 10^3 \, \text{J}
\]

The heat absorbed by the gas along path \( AB \) is

\[
Q_{AB} = \int_{T_{AC}}^{T_B} nC_p \, dT = nC_p (T_B - T_{AC}) \\
= (2 \, \text{moles}) \left( 20.8 \, \text{J/mole K} \right) (600 \, \text{K} - 300 \, \text{K}) \\
= 1.25 \times 10^4 \, \text{J}
\]

The change in internal energy along path \( AB \), found from the first law equation 19.35, is

\[
\Delta U_{AB} = Q_{AB} - W_{AB} \\
= 1.25 \times 10^4 \, \text{J} - 5.00 \times 10^3 \, \text{J} \\
= 7.50 \times 10^3 \, \text{J}
\]

Thus, there is a gain of internal energy along the path \( AB \).

b. The work done along path \( BC \) is

\[
W_{BC} = \int_{V_B}^{V_B} p \, dV \\
W_{BC} = p (V_B - V_B) = 0
\]

The heat lost along path \( BC \) is

\[
Q_{BC} = \int_{T_B}^{T_{AC}} nC_v \, dT = nC_v (T_{AC} - T_B) \\
= (2 \, \text{moles}) \left( 12.5 \, \text{J/mole K} \right) (300 \, \text{K} - 600 \, \text{K}) \\
= -7.50 \times 10^3 \, \text{J}
\]

The loss of internal energy in dropping from 600 K at \( B \) to 300 K at \( C \) is found from the first law as

\[
\Delta U_{BC} = Q_{BC} - W_{BC} \\
= -7.50 \times 10^3 \, \text{J} - 0 \\
= -7.50 \times 10^3 \, \text{J}
\]

c. The work done during the compression along the path \( CD \) is
\[ W_{CD} = \int_{V_B}^{V_A} p \, dV = p_F(V_A - V_B) \]
\[ = \left(1.00 \times 10^4 \text{ N/m}^2\right)(0.250 \text{ m}^3 - 0.500 \text{ m}^3) \]
\[ = -2.50 \times 10^{-3} \text{ J} \]

The heat lost along the path \(CD\) is
\[ Q_{CD} = \int_{T_{AC}}^{T_D} nC_p \, dT = nC_p(T_D - T_{AC}) \]
\[ = (2 \text{ moles}) \left(20.8 \frac{\text{ J}}{\text{ mole K}}\right)(150 \text{ K} - 300 \text{ K}) \]
\[ = -6.24 \times 10^3 \text{ J} \]

The change in internal energy along the path \(CD\), found from the first law, is
\[ \Delta U_{CD} = Q_{CD} - W_{CD} \]
\[ = -6.24 \times 10^3 \text{ J} - (-2.50 \times 10^3 \text{ J}) \]
\[ = -3.74 \times 10^3 \text{ J} \]

Note that the internal energy decreased, as expected, since the temperature decreased from 300 K to 150 K.

d. The work done along the path \(DA\) is
\[ W_{DA} = \int_{V_A}^{V_A} p \, dV \]
\[ W_{DA} = p(V_A - V_A) = 0 \]

The heat added along the path \(DA\) is
\[ Q_{DA} = \int_{T_D}^{T_{AC}} nC_v \, dT = nC_v(T_{AC} - T_D) \]
\[ = (2 \text{ moles}) \left(12.5 \frac{\text{ J}}{\text{ mole K}}\right)(300 \text{ K} - 150 \text{ K}) \]
\[ = 3.74 \times 10^3 \text{ J} \]

The change in internal energy along \(DA\) is
\[ \Delta U_{DA} = Q_{DA} - W_{DA} \]
\[ = 3.74 \times 10^3 \text{ J} - 0 \]
\[ = 3.74 \times 10^3 \text{ J} \]

e. The net work done throughout the cycle \(ABCD\) is
\[ W_{ABCD} = W_{AB} + W_{BC} + W_{CD} + W_{DA} \]
The net heat added throughout the cycle ABCDA is

\[ Q_{ABCDA} = Q_{AB} + Q_{BC} + Q_{CD} + Q_{DA} \]

\[ = 1.25 \times 10^4 J - 7.50 \times 10^3 J - 6.24 \times 10^3 J + 3.74 \times 10^3 J \]

\[ = 2.50 \times 10^3 J \]

Note that \( Q_{AB} \) and \( Q_{DA} \) are positive quantities, which means that heat is being added to the system along these two paths. Also note that \( Q_{BC} \) and \( Q_{CD} \) are negative quantities, which means that heat is being taken away from the system along these two paths. In general, \( Q \) is always positive when heat is added to the system and negative when heat is removed from the system.

This effect is seen in figure 19.7 by drawing lines entering the enclosed thermodynamic path when heat is added to the system, and lines emanating from the enclosed path when heat is taken away from the system. This is a characteristic of all engines operating in a cycle, that is, heat is always added and some heat is always rejected. The net change in internal energy throughout the cycle ABCDA is

\[ \Delta U_{ABCDA} = \Delta U_{AB} + \Delta U_{BC} + \Delta U_{CD} + \Delta U_{DA} \]  

\[ = 7.50 \times 10^3 J - 7.50 \times 10^3 J - 3.74 \times 10^3 J + 3.74 \times 10^3 J \]

\[ = 0 \]

Note that the total change in internal energy around the entire cycle is equal to zero. This is a very reasonable result because the internal energy of a system depends only on the temperature of the system. If we go completely around the cycle, we end up at the same starting point with the same temperature. Since \( dT = 0 \) around the cycle, \( dU = nC_v dT \) must also equal zero around the cycle.

Applying the first law to the entire cycle we have

\[ \Delta U_{ABCDA} = Q_{ABCDA} - W_{ABCDA} \]

But as just seen, \( \Delta U_{ABCDA} = 0 \), therefore,

\[ Q_{ABCDA} = W_{ABCDA} \]  

(19.37)

That is, the energy for the net work done by the system comes from the net heat applied to the system. Looking at the calculations, we see that this is indeed the case since

\[ Q_{ABCDA} = 2.50 \times 10^3 J \]

while

\[ W_{ABCDA} = 2.50 \times 10^3 J \]
Another very interesting thing can be learned from this example. Look at the change in internal energy from the point A to the point C, and note that regardless of the path chosen, the change in internal energy is the same. Thus, from our calculations,

$$\Delta U_{AC} = \Delta U_{AB} + \Delta U_{BC} = 7.50 \times 10^3 \text{ J} - 7.50 \times 10^3 \text{ J} = 0$$

and

$$\Delta U_{AC} = -\Delta U_{AD} - \Delta U_{DC} = -3.74 \times 10^3 \text{ J} + 3.74 \times 10^3 \text{ J} = 0$$

Along the isothermal path AC

$$\Delta U_{AC} = 0$$

because if $T$ is constant, $U$ is constant. Thus, regardless of the path chosen between two points on a p-V diagram, $\Delta U$ is always the same. (It will not always be zero, as in this case where the points A and C happen to lie along the same isotherm, but whatever its numerical value, $\Delta U$ is always the same.)

What is especially interesting about this fact is that the work done depends on the path taken, the heat absorbed or liberated depends on the path taken, but their difference $Q - W$, which is equal to $\Delta U$ is independent of the path taken. That is, $\Delta U$ depends only on the initial and final states of the thermodynamic system and not the path between the initial and final states.

Thus, the internal energy is to a thermodynamic system what the potential energy is to a mechanical system. (Recall from chapter 7, section 7.8 that the work done, and hence the potential energy, was the same whether an object was lifted to a height $h$, or moved up a frictionless inclined plane to the same height $h$. That is, the potential energy was independent of the path taken.)

The thermodynamic system considered in figure 19.7 represents an engine of some kind. That is, heat is added to the engine and the engine does work. To compare one engine with another it is desirable to know how efficient each engine is. The efficiency of an engine can be defined in terms of what we get out of the system compared to what we put into the system. Heat, $Q_{in}$, is put into the engine, and work, $W$, is performed by the engine, hence the efficiency of an engine can be defined as

$$\text{Eff} = \frac{\text{Work out}}{\text{Heat in}} = \frac{W}{Q_{in}}$$

(19.38)

Example 19.5

The efficiency of an engine. In example 19.4, $2.50 \times 10^3$ J of work was done by the
system, whereas the heat added to the system was the heat added along paths $AB$ and $DA$, which is equal to $1.25 \times 10^4 \text{ J} + 3.74 \times 10^3 \text{ J}$, which is equal to $1.62 \times 10^4 \text{ J}$. Find the efficiency of that engine.

**Solution**

The efficiency of the engine, found from equation 19.38, is

\[
\text{Eff} = \frac{W}{Q_{in}} = \frac{2.50 \times 10^3 \text{ J}}{1.62 \times 10^4 \text{ J}} = 0.15
\]

Thus, the efficiency of the engine represented by the thermodynamic cycle of figure 19.7 is only 15%. This is not a very efficient engine. We will discuss the maximum possible efficiency of an engine when we study the Carnot cycle in section 19.8.

Before leaving this section, however, let us take one more look at the change in the internal energy of the system along the path $ABC$. We have already seen that since the initial and final states lie on the same isotherm, the change in internal energy is zero. There is still, however, some more important physics to be obtained by further considerations of this path. The change in internal energy along the path $ABC$ is given by

\[
\Delta U_{ABC} = \Delta U_{AB} + \Delta U_{BC}
\]

But from the first law we can write this as

\[
\Delta U_{ABC} = Q_{AB} - W_{AB} + Q_{BC} - W_{BC}
\]

But as we have already seen

\[
Q_{AB} = nC_p(T_B - T_{AC})
\]
\[
W_{AB} = p_A(V_B - V_A)
\]
\[
Q_{BC} = nC_v(T_{AC} - T_B)
\]
\[
W_{BC} = p(V_B - V_B) = 0
\]

Substituting all these terms into equation 19.39, gives

\[
\Delta U_{ABC} = nC_p(T_B - T_{AC}) - p_A(V_B - V_A) + nC_v(T_{AC} - T_B)
\]
\[
\Delta U_{ABC} = nC_p(T_B - T_{AC}) - nC_v(T_B - T_{AC}) - p_A V_B + p_A V_A
\]

But from the ideal gas equation,
p_AV_A = nRT_{AC} \quad (19.41)

and

p_AV_B = p_BV_B = nRT_B \quad (19.42)

Substituting equations 19.41 and 19.42 back into equation 19.40, we get

\[ \Delta U_{ABC} = nC_p(T_B - T_{AC}) - nC_v(T_B - T_{AC}) - nRT_B + nRT_{AC} \]

\[ \Delta U_{ABC} = (C_p - C_v - R)n(T_B - T_{AC}) \quad (19.43) \]

However, we have already determined that \( \Delta U_{ABC} \) is equal to zero. Hence, equation 19.43 implies that

\[ C_p - C_v - R = 0 \]

or

\[ C_p - C_v = R \quad (19.44) \]

Thus we have determined a theoretical relation between the molar specific heat capacities and the universal gas constant \( R \). Since it has already been shown that \( C_v = \frac{3}{2}R \) in equation 19.33, \( C_p \) can now be solved for in equation 19.44 to obtain

\[ C_p = C_v + R \]

\[ = \frac{3}{2}R + R \]

\[ = \frac{5}{2}R \quad (19.45) \]

Using the value of \( R = 8.314 \text{ J/mole K} \) found in chapter 17, the value of \( C_p \) is 20.8 J/mole K, which agrees with the experimental value of \( C_p \) for a monatomic gas.

### 19.5 An Adiabatic Process

An **adiabatic process** is a process that occurs without an exchange of heat between the system and its environment. That is, heat is neither added to nor taken away from the system during the process. Thus,

\[ dQ = 0 \quad (19.46) \]

in an adiabatic process. The first law of thermodynamics for an adiabatic process becomes

\[ dU = dQ - dW \]

\[ dU = -dW \quad (19.47) \]

Thus, in an adiabatic process, the energy for the work done by the gas comes from a loss in the internal energy of the gas.
Let us now analyze the adiabatic process in more detail. The change in internal energy $dU$ is given by equation 19.32 as

$$dU = nC_vdT$$

while the change in work is given by

$$dW = pdV$$

Equation 19.46 can now be written as

$$nC_vdT = -pdV$$

Upon integrating we get

$$\int_{T_i}^{T_f} nC_vdT = -\int_{V_i}^{V_f} pdV \quad (19.48)$$

Since the pressure $p$ of the gas is not a constant, we substitute for it from the ideal gas equation as

$$pV = nRT$$

and

$$p = \frac{nRT}{V}$$

Substituting this into equation 19.48 gives

$$\int_{T_i}^{T_f} nC_vdT = -\int_{V_i}^{V_f} \frac{nRT}{V}dV$$

$$\int_{T_i}^{T_f} C_v \frac{dT}{T} = -R \int_{V_i}^{V_f} \frac{dV}{V}$$

$$C_v \ln T \bigg|_{T_i}^{T_f} = -R \ln V \bigg|_{V_i}^{V_f}$$

$$C_v [\ln T_f - \ln T_i] = -R[\ln V_f - \ln V_i]$$

$$C_v \ln \frac{T_f}{T_i} = -R \ln \frac{V_f}{V_i}$$

From the characteristics of the natural logarithm, this can also be written as

$$\ln \left( \frac{T_f}{T_i} \right)^{C_v} = -R \ln \left( \frac{V_f}{V_i} \right)$$

and upon taking the exponential of both sides of the equation, this becomes

$$\left( \frac{T_f}{T_i} \right)^{C_v} = \left( \frac{V_f}{V_i} \right)^{-R}$$

$$\left( \frac{T_f}{T_i} \right)^{C_v} = \left( \frac{V_i}{V_f} \right)^{R}$$

Taking the $C_v$ root of both sides of the equation, this becomes

$$\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\frac{R}{C_v}} \quad (19.49)$$
But we showed in equation 19.44 that

\[ R = C_p - C_v \]

Substituting this into equation 19.49 gives

\[
\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right) \frac{C_p - C_v}{C_v} = \left( \frac{V_i}{V_f} \right) \frac{C_p}{C_v} \quad (19.50)
\]

We now define the ratio of the specific heats to be the new constant

\[
\gamma = \frac{C_p}{C_v} \quad (19.51)
\]

Equation 19.50 now becomes

\[
\frac{T_f}{T_i} = \left( \frac{V_i}{V_f} \right)^{\gamma - 1} \quad (19.52)
\]

and finally

\[
T_i V_i^{\gamma - 1} = T_f V_f^{\gamma - 1} \quad (19.53)
\]

*Equation 19.53 gives the first law of thermodynamics for an ideal gas for an adiabatic process. It gives the relation between the initial temperature and volume of the gas to the final temperature and volume of the gas. It is sometimes desirable to express the adiabatic process in terms of the pressure and volume of the gas. We can do this by solving the ideal gas equation for the temperature \( T \) as

\[
T = \frac{pV}{nR}
\]

and then substituting this into equation 19.53 to obtain

\[
\frac{p_i V_i^{\gamma - 1}}{nR} = \frac{p_f V_f^{\gamma - 1}}{nR} \]

\[
p_i V_i = p_f V_f \quad (19.54)
\]

*Equation 19.54 also gives the first law of thermodynamics for an ideal gas for an adiabatic process. It gives the relation between the initial pressure and volume of the gas to the final pressure and volume of the gas. Equation 19.54 can also be written in the simplified form

\[
p V^\gamma = \text{constant} \quad (19.55)
\]

Using equation 19.55 an adiabatic process can be drawn as the dashed line on a \( p-V \) diagram as shown in figure 19.8. Note that the adiabatic line has a steeper slope than the isotherm.
Finally, we can express the adiabatic process in terms of the temperature and pressure of the gas by substituting for the volume $V$ by the ideal gas law into equation 19.54 as follows.

$$V = nRT$$

$$p_iV_i^\gamma = p_i\left(\frac{nRT_i}{p_i}\right)^\gamma = p_fV_f^\gamma = p_f\left(\frac{nRT_f}{p_f}\right)^\gamma$$

$$p_i\left(\frac{T_i}{p_i}\right)^\gamma = p_f\left(\frac{T_f}{p_f}\right)^\gamma$$

$$\frac{p_i}{p_i^\gamma} = \frac{p_f}{p_f^\gamma}$$

$$p_i^{1-\gamma}T_i^{\gamma} = p_f^{1-\gamma}T_f^{\gamma}$$

Taking the $\gamma$ root of both sides of the equation gives

$$T_i^{1-\gamma}p_i^{1-\gamma} = T_f^{1-\gamma}p_f^{1-\gamma}$$

Equation 19.56 also gives the first law of thermodynamics for an ideal gas for an adiabatic process. It gives the relation between the initial temperature and pressure of the gas to the final temperature and pressure of the gas. The first law for the adiabatic process is used in either the form of equation 19.53, 19.54, or 19.56 depending upon the particular problem.

**Example 19.6**

The adiabatic expansion of rising air. A parcel of air at the surface of the earth, where the pressure is 1000 mb, occupies a volume of 3.00 m$^3$. The parcel of air rises.
in the atmosphere to a level where the pressure is 500 mb. What is the new volume of this parcel of air.

**Solution**

The ratio of the specific heats $\gamma$ is found from equation 19.51 as

$$\gamma = \frac{C_p}{C_v} = \frac{20.8 \text{ J/mole K}}{12.5 \text{ J/mole K}} = 1.66$$

The final volume of the air is found from rearranging equation 19.54 to

$$V_f = V_i \left(\frac{P_i}{P_f}\right)^{\frac{1}{\gamma}}$$

$$V_f = \left(\frac{1000 \text{ mb}}{500 \text{ mb}}\right)^{\frac{1}{1.66}} \cdot (3.00 \text{ m}^3)$$

$$V_f = 4.55 \text{ m}^3$$

Notice that as the air rises in the atmosphere to a region of lower pressure the air expands.

To go to this Interactive Example click on this sentence.

**Example 19.7**

The adiabatic cooling of rising air. A parcel of air at the surface of the earth, where the pressure is 1000 mb, is at a temperature of 30.0 °C = 303 K. The parcel of air rises in the atmosphere to a level where the pressure is 500 mb. What is the new temperature of this parcel of air.

**Solution**

The ratio of the specific heats $\gamma$ is found from equation 19.51 as

$$\gamma = \frac{C_p}{C_v} = \frac{20.8 \text{ J/mole K}}{12.5 \text{ J/mole K}} = 1.66$$

The final temperature of the air is found from rearranging equation 19.56 to
This adiabatic process of the cooling of rising air is responsible for the formation of clouds in the atmosphere, which we will discuss in the section “Have you ever wondered” at the end of this chapter.

**To go to this Interactive Example click on this sentence.**

The adiabatic process is essential to the study of the Carnot cycle which we will study in section 19.9. Some processes that are not strictly speaking adiabatic can be treated as adiabatic processes because the process occurs so rapidly that there is not enough time for the system to exchange any significant quantities of heat with its environment.

### 19.6 Some Special Cases of the First Law of Thermodynamics

Although we have already discussed the first law of thermodynamics pretty thoroughly, let us summarize some of the results into special cases.

**An Isothermal Process**

An isothermal process is a process that occurs at constant temperature. Therefore,

\[
dT = 0
\]

But \(dU = nC_v dT\). Therefore, if \(dT = 0\), then \(dU = 0\). The first law then becomes

\[
dU = 0 = dQ - dW
\]

\[
dQ = dW
\]

In an isothermal process, heat added to the system shows up as mechanical work done by the system.
An Adiabatic Process

An **adiabatic process** is a process that occurs without an exchange of heat between the system and its environment. That is, heat is neither added to nor taken away from the system during the process. Thus,

\[ dQ = 0 \]

*in an adiabatic process*. The first law of thermodynamics for an adiabatic process becomes

\[ dU = dQ - dW \]

\[ dU = -dW \quad \text{(19.47)} \]

Thus, *in an adiabatic process, the energy for the work done by the gas comes from a loss in the internal energy of the gas.*

Isochoric Process or Isometric Process

An **isochoric process** is a process that occurs at constant volume, that is,

\[ dV = 0 \]

Since the work done, \( dW \), is equal to \( pdV = 0 \), then \( dW \) must also be zero. The first law of thermodynamics for an isochoric process therefore becomes

\[ dQ = dU \quad \text{(19.58)} \]

Thus, the heat added to a system during an isochoric process shows up as an increase in the internal energy of the system.

An Isobaric Process

An **isobaric process** is a process that occurs at constant pressure, therefore,

\[ dp = 0 \]

Since the pressure is a constant for an isobaric process, the work done in an isobaric process is given by the product of the constant pressure \( p \) and the change in volume \( \Delta V \). That is,

\[ W = p\Delta V = p(V_f - V_i) \]

If the process is not an isobaric one then the pressure must be determined by the integration shown in equation 19.12

\[ W = \int_{V_i}^{V_f} pdV \]
A Cyclic Process

A cyclic process is one that always returns to its initial state. The process studied as $ABCDA$ in figure 19.7 is an example of a cyclic process. Because the system always returns to the original state it will have the same energy, hence, $dU$ is always equal to zero for a cyclic process. That is,

$$dU = 0$$

Hence, the first law of thermodynamics for a cyclic process becomes

$$W = Q$$

(19.59)

Thus, the work done by the system in the cyclic process is equal to the heat added to the system on a portion of the cycle minus the heat removed on the remainder of the cycle.

19.7 The Gasoline Engine

The thermodynamic system studied so far is somewhat idealistic. In order to be more specific, let us consider the thermodynamic process that occurs in the gasoline engine of an automobile. The engine usually consists of four, six, or eight cylinders. Each cylinder has an inlet valve, an exhaust valve, a spark plug, and a movable piston, which is connected to the crankshaft by a piston rod. The operation of one of these cylinders is shown schematically in figure 19.9. The gasoline engine is approximated by an Otto cycle and is shown on the $p-V$ diagram of figure 19.10.

Figure 19.9(a) shows the first stroke of the engine, which is called the intake stroke. The inlet valve opens and a mixture of air and gasoline is drawn into the cylinder as the piston moves downward. Because the inlet valve is open during this first stroke, the air pressure inside the cylinder is the same constant value as atmospheric pressure and is thus shown as the isobaric path $OA$ in figure 19.10. When the cylinder is completely filled to the volume $V_A$ with the air and gasoline mixture, point $A$, the inlet valve, closes and the compression stroke starts, figure 19.9(b). The piston moves upward very rapidly causing an adiabatic compression of the air-gas mixture. This is shown as the adiabatic path $AB$ in figure 19.10. When the piston is at its highest point (its smallest volume $V_B$), a spark is applied to the mixture by the spark plug. This spark causes ignition of the air-gas mixture (a small explosion of the mixture), and a great deal of heat is supplied to the mixture by the explosion. This supply of heat is shown as $Q_H$ on the path $BC$ of figure 19.10. The explosion occurs so rapidly that it takes a while to overcome the inertia of the piston to get it into motion. Hence, for this small time period, the pressure and temperature in the cylinder rises very rapidly at approximately constant volume. This is shown as the path $BC$ in figure 19.10. At the point $C$ the force of the air-gas mixture is now able to overcome the inertia of the piston, and the piston moves downward very rapidly during the power stroke, figure 19.9(d). Because the piston
moves very rapidly, this portion of the process can be approximated by the adiabatic expansion of the gas shown as $CD$ in figure 19.10. As the piston moves down rapidly this downward motion of the piston is transferred by the piston rod to the crankshaft of the engine causing the crankshaft to rotate. That is, the piston rod is connected off-center to the crankshaft. Thus, when the piston rod moves downward it creates a torque that causes the crankshaft to rotate. The rotating crankshaft is connected by a series of gears to the rear wheels of the car thus causing the wheels to turn and the car to move. At the end of this power stroke the piston has moved down to the greatest volume $V_A$. At this point $D$, the exhaust valve of the cylinder opens and the higher pressure at $D$ drops very rapidly to the outside pressure at $A_1$ and a good deal of heat $Q_C$ is exhausted out through the exhaust valve. As the
piston now moves upward in figure 19.9(f) all the remaining used gas-air mixture is dumped out through the exhaust valve. This is shown as the path \( AO \) in figure 19.10. At the position \( O \), the exhaust valve closes and the inlet valve opens allowing a new mixture of air and gasoline to enter the cylinder. The process now starts over again as the same cycle \( OABCDAO \) of figure 19.10. The net result of the entire cycle is that heat \( Q_H \) is added along path \( BC \), work is done equal to the area enclosed by the cyclic path, and heat \( Q_C \) is exhausted out of the system. Thus, heat has been added to the system and the system performed useful work. Four, six, or eight of these cylinders are ganged together with the power stroke of each cylinder occurring at a different time for each cylinder. This has the effect of smoothing out the torque on the crankshaft, causing a more constant rotation of the crankshaft. Unfortunately practical limitations, such as compression ratio, friction, cooling, and so on, cause the efficiency of the gasoline engine, which uses the Otto cycle, to be limited to about 20% to 25%.

19.8 The Ideal Heat Engine

There are many heat engines in addition to the gasoline engine, but they all have one thing in common: every engine absorbs heat from a source at high temperature, performs some amount of mechanical work, and then rejects some heat at a lower temperature. This process can be visualized with the schematic diagram for an ideal heat engine, and is shown in figure 19.11. The engine is represented by the circle in the diagram. The engine absorbs the quantity of heat \( Q_H \) from a hot-temperature reservoir, at a temperature \( T_H \). (In the gasoline engine, the quantity of heat \( Q_H \) was supplied by the combustion of the air-gasoline mixture.) Some of this absorbed heat
energy is converted to work, which is shown as the pipe coming out of the engine at the right. This corresponds to the work done during the power stroke of the gasoline engine. The rest of the original absorbed heat energy is dumped as exhaust heat $Q_C$ into the low-temperature reservoir. (In the gasoline engine this is the hot exhaust gas that is rejected to the cooler environment outside the engine.)

Because the engine operates in a cycle, $\Delta U = 0$, and as we have already seen, the net work done is equal to the net heat absorbed by the engine, that is,

$$W = Q$$

But the net heat absorbed is equal to the difference between the total heat absorbed $Q_H$ at the hot reservoir, and the heat rejected $Q_C$ at the cold reservoir, that is,

$$Q = Q_H - Q_C$$

Thus, the work done by the engine is equal to the difference between the heat absorbed from the hot reservoir and the heat rejected to the cold reservoir

$$W = Q_H - Q_C$$ \hspace{1cm} (19.60)

The efficiency of a heat engine can also be defined from equation 19.38 as

$$Eff = \frac{W}{Q_{in}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$ \hspace{1cm} (19.61)

$$Eff = 1 - \frac{Q_C}{Q_H}$$ \hspace{1cm} (19.62)

Thus, to make any heat engine as efficient as possible it is desirable to make $Q_H$ as large as possible and $Q_C$ as small as possible. It would be most desirable to have $Q_C = 0$, then the engine would be 100% efficient. Note that this would not be a
violation of the first law of thermodynamics. However, as we will see in section 19.11, such a process is not possible.

Before leaving this section we should note that a refrigerator, or a heat pump, is a heat engine working in reverse. A refrigerator is represented schematically in figure 19.12, where the refrigerator is represented as the circle in the diagram. Work $W$ is done on the refrigerator, thereby extracting a quantity of heat $Q_C$ from the low-temperature reservoir and exhausting the large quantity of heat $Q_H$ to the hot reservoir. The total heat energy exhausted to the high-temperature reservoir $Q_H$ is the sum of the work done on the engine plus the heat $Q_C$ extracted from the low-temperature reservoir. Thus,

$$Q_H = W + Q_C$$

We define the equivalent of an efficiency for a refrigerator, the coefficient of performance, as

Coefficient of performance = \frac{\text{Heat removed}}{\text{Work done}}

Coefficient of performance = \frac{Q_C}{W} \quad (19.63)

Coefficient of performance = \frac{Q_C}{Q_H - Q_C} \quad (19.64)

19.9 The Carnot Cycle
As we saw in section 19.7, it is desirable to get the maximum possible efficiency from a heat engine. Sadi Carnot (1796-1832) showed that the maximum efficiency of any heat engine must follow a cycle consisting of the isothermal and adiabatic paths shown in the $p-V$ diagram in figure 19.13, and now called the Carnot cycle. The cycle begins at point $A$. Let us now consider each path individually.
**Path AB:** An ideal gas is first compressed isothermally along the path AB. Since AB is an isotherm, \(dT = 0\) and hence \(dU = 0\). The first law therefore says that \(Q = W\) along path AB. That is, the work \(W_{AB}\) done on the gas is equal to the heat removed from the gas \(Q_C\), at the low temperature, \(T_C\).

**Path BC:** Path BC is an adiabatic compression and hence \(dQ = 0\) along this path. The first law therefore becomes \(\Delta U = W\). That is, the work \(W_{BC}\) done on the gas during the compression is equal to the increase in the internal energy of the gas as the temperature increases from \(T_C\) to \(T_H\).

**Path CD:** Path CD is an isothermal expansion. Hence, \(dT = 0\) and \(dU = 0\). Therefore, the first law becomes \(W = Q\). That is, the heat added to the gas \(Q_H\) at the high temperature \(T_H\) is equal to the work \(W_{CD}\) done by the expanding gas.

**Path DA:** Path DA is an adiabatic expansion, hence \(dQ = 0\) along this path. The first law becomes \(\Delta U = W\). Thus, the energy necessary for the work \(W_{DA}\) done by the expanding gas comes from the decrease in the internal energy of the gas. The gas decreases in temperature from \(T_H\) to \(T_C\).

The net effect of the Carnot cycle is that heat \(Q_H\) is absorbed at a high temperature \(T_H\), mechanical work \(W\) is done by the engine, and waste heat \(Q_C\) is exhausted to the low-temperature reservoir at a temperature \(T_C\). The net work done by the Carnot engine is

\[ W = Q_H - Q_C \]

The efficiency is given by the same equations 19.61 and 19.62 as we derived before. That is,

\[ \text{Eff} = 1 - \frac{Q_C}{Q_H} \quad (19.62) \]
Lord Kelvin proposed that the ratio of the heat rejected to the heat absorbed could serve as a temperature scale. Kelvin then showed that for a Carnot engine

\[
\frac{Q_C}{Q_H} = \frac{T_C}{T_H}
\]

(19.65)

where \(T_C\) and \(T_H\) are the Kelvin or absolute temperatures of the gas. With the aid of equation 19.65, we can express the efficiency of a Carnot engine as

\[
\text{Eff} = 1 - \frac{T_C}{T_H}
\]

(19.66)

The importance of equation 19.66 lies in the fact that the Carnot engine is the most efficient of all engines. If the efficiency of a Carnot engine can be determined, then the maximum efficiency possible for an engine operating between the high temperature \(T_H\) and the low temperature \(T_C\) is known.

**Example 19.8**

*Efficiency of a Carnot engine.* In examples 19.4 and 19.5 the engine operated between a maximum temperature of 600 K and a minimum temperature of 150 K. The efficiency of that particular engine was 15%. What would the efficiency of a Carnot engine be, operating between these same temperatures?

**Solution**

The efficiency of the Carnot engine, found from equation 19.66, is

\[
\text{Eff} = 1 - \frac{T_C}{T_H} = 1 - \frac{150 \text{ K}}{600 \text{ K}} = 0.75
\]

Therefore, the maximum efficiency for any engine operating between these temperatures cannot be higher than 75%. Obviously the efficiency of 15% for the previous cycle is not very efficient.

*To go to this Interactive Example click on this sentence.*

19.10 The Second Law of Thermodynamics

There are several processes that occur regularly in nature, but their reverse processes never occur. For example, we can convert the kinetic energy of a moving car to heat in the brakes of the car as the car is braked to a stop. However, we
cannot heat up the brakes of a stopped car and expect the car to start moving. That is, we cannot convert the heat in the brakes to kinetic energy of the car. Thus, mechanical energy can be converted into heat energy but heat energy cannot be completely converted into mechanical energy. As another example, a hot cup of coffee left to itself always cools down to room temperature, never the other way around. There is thus a kind of natural direction followed by nature. That is, processes will proceed naturally in one direction, but not in the opposite direction. Yet in any of these types of processes there is no violation of the first law of thermodynamics regardless of which direction the process occurs. This unidirectionality of nature is expressed as the second law of thermodynamics and tells which processes will occur in nature. The second law will first be described in terms of the ideal heat engine and refrigerator studied in section 19.8.

The Kelvin-Planck Statement of the Second Law
No process is possible whose sole result is the absorption of heat from a reservoir at a single temperature and the conversion of this heat energy completely into mechanical work. This statement is shown schematically in figure 19.14. That is, the diagram in figure 19.14 cannot occur in nature. Observe from figure 19.14 that heat $Q_H$ is absorbed from the hot reservoir and converted completely into work. In figure 19.11 we saw that there had to be an amount of heat $Q_C$ exhausted into the cold reservoir. Thus the Kelvin-Planck statement of the second law of thermodynamics says that there must always be a quantity of heat $Q_C$ exhausted from the engine into a lower temperature reservoir.

![Figure 19.14 Kelvin-Planck violation of the second law.](image)

The Clausius Statement of the Second Law of Thermodynamics
No process is possible whose sole result is the transfer of heat from a cooler to a hotter body. The Clausius statement of the second law of thermodynamics can best be described by the refrigerator of figure 19.12. Work was done on the refrigerator to draw heat $Q_C$ out of the cold reservoir to then deliver it to the hot
reservoir. The Clausius statement says that work must always be done to do this. The violation of this Clausius statement of the second law is shown in figure 19.15.

![Figure 19.15](image)

**Figure 19.15** Clausius violation of the second law.

This statement of the second law of thermodynamics is essentially an observation of nature. Thermal energy flows from hot reservoirs (hot bodies) to cold reservoirs (cold bodies). The reverse process where heat flows from a cold body to a hot body without the application of some kind of work does not occur in nature. Thus, the second law of thermodynamics says that such processes are impossible, and the diagram in figure 19.15 cannot occur in nature.

### 19.11 Entropy

The second law of thermodynamics has been described in terms of statements about which processes are possible and which are not possible. It would certainly be more desirable to put the second law on a more quantitative basis. In 1865, Clausius introduced the concept of entropy to indicate what processes are possible and what ones are not. When a thermodynamic system changes from one equilibrium state to another in a series of small increments such that the system always moves through a series of equilibrium states, the system is said to go through a **reversible process**. A reversible process can be drawn as a continuous line on a *p-V* diagram. All the processes that have been considered are reversible processes. When a thermodynamic system changes from one equilibrium state to another along a reversible path, there is a change in entropy, $\Delta S$ of the system given by

$$\Delta S = \int_{S_i}^{S_f} dS = S_f - S_i = \int \frac{dQ}{T}$$

(19.67)

where $dQ$ is the heat added to the system, and $T$ is the absolute temperature of the system.
Example 19.9

Change in entropy. Find the change in entropy (a) when 5.00 kg of ice at −5.00 °C is warmed to 0.00 °C, (b) when 5.00 kg of ice at 0.00 °C is converted into water at 0.00 °C, and (c) for the entire process.

Solution

a. The change in entropy in heating the ice is found from equation 19.67 as

\[
\Delta S = \int_{T_i}^{T_f} \frac{dQ}{T} = \int_{T_i}^{T_f} \frac{mc dT}{T}
\]

where \(dQ = mc dT\) is the energy added to heat the ice. Thus

\[
\Delta S = mc \ln \frac{T_f}{T_i} = mc\left[\ln T_f - \ln T_i\right]
\]

\[
= (5.00 \text{ kg}) \left(\frac{2093 \text{ J}}{\text{kg K}}\right) \ln \left(\frac{273 \text{ K}}{268 \text{ K}}\right)
\]

\[
= 193 \text{ J/K}
\]

b. The change in entropy in melting the ice is also found from equation 19.67. But the melting process takes place at the constant temperature of \(T = 0.00 \text{ °C} = 273 \text{ K}\). Hence the temperature \(T\) can be removed from under the integral sign to yield

\[
\Delta S = \int \frac{dQ}{T} = \frac{1}{T} \int dQ = \frac{Q}{T}
\]

where \(Q\) is the heat absorbed by the ice in melting and is found from \(Q = mL_f\).

Therefore the change in entropy is

\[
\Delta S = \frac{Q}{T} = \frac{mL_f}{T}
\]

\[
= (5.00 \text{ kg})(3.34 \times 10^5 \text{ J/kg})
\]

\[
= 6.12 \times 10^5 \text{ J/K}
\]

c. The total change in entropy for the entire process is the sum of the change in entropy for the two processes. Therefore,

\[
\Delta S = \Delta S_1 + \Delta S_2
\]

\[
= 193 \text{ J/K} + 6.12 \times 10^5 \text{ J/K}
\]

\[
= 6.31 \times 10^5 \text{ J/K}
\]
Whenever heat is added to a system, \( dQ \) is positive, and hence, \( \Delta S \) is also positive. If heat is removed from a system, \( dQ \) is negative, and therefore, \( \Delta S \) is also negative. When the ice melts there is a positive increase in entropy.

Entropy is a very different concept than the concept of energy. For example, in a gravitational system, a body always falls from a region of high potential energy to low potential energy, thereby losing potential energy. In contrast, in an isolated thermodynamic system, the system always changes from values of low entropy to values of high entropy, thereby increasing the entropy of the system. Therefore, the concept of entropy can tell us in which direction a process will proceed. For example, if an isolated thermodynamic system is in a state \( A \), and we wish to determine if it can naturally go to state \( B \) by itself, we first measure the initial value of the entropy at \( A \), \( S_i \), and the final value of the entropy at \( B \), \( S_f \). The system will move from \( A \) to \( B \) only if there is an increase in the entropy in moving from \( A \) to \( B \). That is, the process is possible if

\[
\Delta S = S_f - S_i > 0
\]

If \( \Delta S \) is negative for the proposed process, the system will not proceed to the point \( B \). The second law of thermodynamics can also be stated as: the entropy of an isolated system increases in every natural process, and only those processes are possible for which the entropy of the system increases or remains a constant. The entropy of a nonisolated system may either increase, or decrease, depending on whether heat is added to or taken away from the system. If \( dQ \) is equal to zero, such as in an adiabatic process, then \( dS \) also equals zero. Hence, an adiabatic process is also an isentropic process. Just as the change in internal energy of a system from state \( A \) to state \( B \) is independent of the path taken to get from \( A \) to \( B \), the entropy of a system is also independent of the path taken.

### Example 19.10

The change in entropy in a thermodynamic process. Find the change in entropy of the system for the thermodynamic paths (a) \( AB \), (b) \( BC \), (c) \( CD \), (d) \( DA \), and (e) \( ABCDA \) in example 19.4 and figure 19.7. Recall that two moles of an ideal gas were carried around the thermodynamic path \( ABCDA \), where \( T_D = 150 \text{ K} \), \( T_{AC} = 300 \text{ K} \), \( T_B = 600 \text{ K} \), \( p_A = 2.00 \times 10^4 \text{ Pa} \), \( p_D = 1.00 \times 10^4 \text{ Pa} \), \( V_A = 0.250 \text{ m}^3 \), and \( V_B = 0.500 \text{ m}^3 \).

**Solution**

a. The change in entropy along the path \( AB \) is found as
\[\Delta S_{AB} = \int_{T_{AC}}^{T_{B}} \frac{dQ}{T} = \int_{T_{AC}}^{T_{B}} \frac{nC_p dT}{T} = nC_p \ln T \mid_{T_{AC}}^{T_{B}} = nC_p [\ln T_B - \ln T_{AC}] \]
\[\Delta S_{AB} = nC_p \ln \frac{T_B}{T_{AC}}\]
\[\Delta S_{AB} = (2 \text{ moles}) \left(20.8 \frac{\text{J}}{\text{mole K}}\right) \ln \left(\frac{600 \text{ K}}{300 \text{ K}}\right)\]
\[\Delta S_{AB} = 28.8 \text{ J/K} \]

b. The change in entropy along the path BC is found as
\[\Delta S_{BC} = \int_{T_{AC}}^{T_{B}} \frac{dQ}{T} = \int_{T_{AC}}^{T_{B}} \frac{nC_v dT}{T} = nC_v \ln T \mid_{T_{AC}}^{T_{B}} = nC_v [\ln T_{AC} - \ln T_B] \]
\[\Delta S_{BC} = nC_v \ln \frac{T_B}{T_{AC}}\]
\[\Delta S_{BC} = (2 \text{ moles}) \left(12.5 \frac{\text{J}}{\text{mole K}}\right) \ln \left(\frac{300 \text{ K}}{600 \text{ K}}\right)\]
\[\Delta S_{BC} = -17.3 \text{ J/K} \]

c. The change in entropy along the path CD is found as
\[\Delta S_{CD} = \int_{T_{AC}}^{T_{D}} \frac{dQ}{T} = \int_{T_{AC}}^{T_{D}} \frac{nC_p dT}{T} = nC_p \ln T \mid_{T_{AC}}^{T_{D}} = nC_p [\ln T_D - \ln T_{AC}] \]
\[\Delta S_{CD} = nC_p \ln \frac{T_D}{T_{AC}}\]
\[\Delta S_{CD} = (2 \text{ moles}) \left(20.8 \frac{\text{J}}{\text{mole K}}\right) \ln \left(\frac{150 \text{ K}}{300 \text{ K}}\right)\]
\[\Delta S_{CD} = -28.8 \text{ J/K} \]

d. The change in entropy along the path DA is found as
\[\Delta S_{DA} = \int_{T_{AC}}^{T_{D}} \frac{dQ}{T} = \int_{T_{AC}}^{T_{D}} \frac{nC_v dT}{T} = nC_v \ln T \mid_{T_{AC}}^{T_{D}} = nC_v [\ln T_D - \ln T_{AC}] \]
\[\Delta S_{DA} = nC_v \ln \frac{T_D}{T_{AC}}\]
\[\Delta S_{DA} = (2 \text{ moles}) \left(12.5 \frac{\text{J}}{\text{mole K}}\right) \ln \left(\frac{300 \text{ K}}{150 \text{ K}}\right)\]
\[\Delta S_{DA} = 17.3 \text{ J/K} \]

e. The change in entropy along the path ABCDA is found as
\[\Delta S_{ABCD} = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA}\]
\[\Delta S_{ABCD} = 28.8 \text{ J/K} - 17.3 \text{ J/K} - 28.8 \text{ J/K} + 17.3 \text{ J/K}\]
\[\Delta S_{ABCD} = 0\]

The change in entropy around the entire cyclic process is equal to zero.

To go to this Interactive Example click on this sentence.
The fact that the change in entropy around the entire cyclic process in example 19.10 is equal to zero is a characteristic of entropy and is usually written as

\[ \oint ds = \oint \frac{dQ}{T} = 0 \]  

*(Equation 19.69)*

Equation 19.69 says that when a system is carried around a reversible cycle the sum of all the ds’s is equal to zero.

### 19.12 Statistical Interpretation of Entropy

As we have seen in sections 19.10 and 19.11, the second law of thermodynamics is described in terms of statements about which processes in nature are possible and which are not possible. Clausius introduced the concept of entropy to put the second law on a more quantitative basis. He stated the second law as: *the entropy of an isolated system increases in every natural process, and only those processes are possible for which the entropy of the system increases or remains a constant.* But this analysis was done on a macroscopic level, that is, a large-scale level, where concepts of temperature, pressure, and volume were employed. But the gas, the usual working substance discussed, is made up of billions of molecules, as shown in the kinetic theory of gases. Ludwig Boltzmann’s approach to the second law of thermodynamics is a further extension of the kinetic theory, and is called *statistical mechanics.* Boltzmann looked at the molecules of the gas and asked what the most probable distribution of these molecules is. There is a certain order to the distribution of the molecules, with some states more probable than others. Thus, statistical mechanics deals with probabilities.

As an example, let us consider the gas molecules in figure 19.16(a). The molecules are contained in the left-hand side of a box by a partition located in the center of the box. When the partition is removed some of the molecules move to the right-hand side of the box until an equilibrium condition is reached whereby there

![Figure 19.16](image-url) *Gas molecules in a partitioned box.*
are the same number of molecules in both sides of the box, figure 19.16(b). We now ask, can all the gas molecules in the entire box of figure 19.16(b) move to the left and be found in the original state shown in figure 19.16(a)? We know from experience that this never happens. This would be tantamount to all the gas molecules in the room that you are now sitting in moving completely to the other side of the room, leaving you in a vacuum. This just does not happen in life. However, if it did it would not violate the first law of thermodynamics. But the second law says some processes do not occur. This is certainly one of them. Notice that the first case in which all the molecules are in the left-hand side of the box is more orderly than the second case where the molecules are distributed over the entire box. (If the volume of the box is larger, there are more random paths for the molecules to follow and hence more disorder.)

As another example of order and disorder, let us drop a piece of clay. When the clay is dropped, superimposed over the thermal motion of the molecules of the clay is the velocity of the clay toward the ground. That is, all the molecules have a motion toward the ground, which is an ordered motion. When the clay hits the ground and sticks to it, the kinetic energy of the falling molecules shows up as thermal energy of the clay molecules, which is a random or disordered motion of the molecules. Hence there is a transformation from order to disorder in the natural process of a collision of a falling object. Now as we know, the clay cannot gather together all the random thermal motion of the clay molecules and convert them to ordered translational motion upward, and hence the clay by itself cannot move upward. Thus the concept of which processes can occur in nature can also be measured by the amount of order or disorder between the initial and final states of the system. Using the concept of order, the second law of thermodynamics can also be stated as: an isolated system in a state of relative order will always pass to a state of relative disorder until it reaches the state of maximum disorder, which is thermal equilibrium.

Let us return to our example of the gas molecules in a box. Although normally there are billions of molecules in the box, to simplify our discussion let us assume that there are only four molecules present. They are numbered consecutively 1, 2, 3, and 4. Let us ask how many ways we can distribute these four molecules between the left- and right-hand sides of the box. First we could place the four molecules all in the left-hand side of the box as shown in table 19.1. Thus there is only one way we can place the four molecules into the left-hand side of the box. Let us designate the number of ways that the four molecules can be distributed as \(N_i\) and note that \(N_1 = 1\). Next we see how many ways we can place one molecule in the right-hand side of the box and three in the left-hand side. That is, first we place molecule 1 in the right-hand side of the box, and see that that leaves molecules 2, 3,4, in the left-hand side. Then we place molecule 2 in the right-hand side and see that we then have molecules 1, 3, 4 in the left-hand side. Continuing in this way we see from the table that there are four ways to do this. Thus, we designate the number of ways we can place one molecule in the right-hand side of the box and
three in the left-hand side as \( N_2 \) and see that this is equal to 4. Next we see how many ways we can place two molecules in the right-hand side of the box and two in

<table>
<thead>
<tr>
<th>Left</th>
<th>Right</th>
<th>( N_i )</th>
<th>( P_i = N_i/N )</th>
<th>( S = k \ln P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2 3 4</td>
<td></td>
<td>1</td>
<td>1/16 = 6.25%</td>
<td>2.53 \times 10^{-23} J/K</td>
</tr>
<tr>
<td>2 3 4</td>
<td>1</td>
<td>4</td>
<td>4/16 = 25%</td>
<td>4.44 \times 10^{-23} J/K</td>
</tr>
<tr>
<td>1 2 3 4</td>
<td>1 2 3</td>
<td>6</td>
<td>6/16 = 37.5%</td>
<td>5.00 \times 10^{-23} J/K</td>
</tr>
<tr>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
<td>4</td>
<td>4/16 = 25%</td>
<td>4.44 \times 10^{-23} J/K</td>
</tr>
<tr>
<td>1 2 3 4</td>
<td>1 2 3 4</td>
<td>1</td>
<td>1/16 = 6.25%</td>
<td>2.53 \times 10^{-23} J/K</td>
</tr>
</tbody>
</table>

\[ \sum N_i = N = 16 ; \sum P_i = 100\% \]

the left-hand side. From the table we see that there are six ways, and we call this \( N_3 = 6 \). Next we see how many ways we can place one molecule in the left-hand side of the box and three in the right-hand side. Again from the table we see that there are four ways to do this, and we call this \( N_4 = 4 \). Finally we ask how many ways can the four molecules be placed in the right-hand side of the box and again we see from the table there is only one way. We call this \( N_5 = 1 \). Thus there are five possible ways (for a total of 16 possible states) that the four molecules could be distributed between the left- and right-hand sides of the box.

But which of all these possibilities is the most probable? The probability that the molecules are in the state that they are in compared with all the possible states they could be in is given by

\[ P = \frac{N_i}{N} \times 100\% \]  \hspace{1cm} (19.70)

where \( N_i \) is the number of states that the molecules could be in for a particular distribution and \( N \) is the total number of possible states. As we see from the table, there are 16 possible states that the four molecules could be in. Hence the
probability that the molecules are in the state where all four are on the left-hand side is

\[ P = \frac{N_1 \times 100\%}{N} = \frac{1}{16} \times 100\% = 6.25\% \]

That is, there is a 6.25% probability that all four molecules will be found in the left-hand side of the box.

The probability that the distribution of the four molecules has three molecules in the left-hand side and one in the right-hand side is found by observing that there are four possible ways that the molecules can be distributed and hence \( N_2 = 4 \). Therefore,

\[ P = \frac{N_2 \times 100\%}{N} = \frac{4}{16} \times 100\% = 25\% \]

Thus there is a 25% probability that there are three molecules in the left-hand side and one molecule in the right-hand side. Continuing in this way the probabilities that the molecules will have the particular distribution is shown in table 19.1. Thus there is a 37.5% probability that the distribution has two molecules in each half of the box, a 25% probability that the distribution has one molecule in the left half of the box and three in the right half of the box, and finally a 6.25% probability that the distribution has no molecules in the left half of the box and four in the right half of the box.

Notice that the first and last distributions (all molecules either on the left side or on the right side), are the most ordered and they have the lowest probability, 6.25%, for the distribution of the molecules. Also notice that the third distribution where there are two molecules on each side of the box has the greatest disorder and also the highest probability that this is the way that the molecules will be distributed. Notice that the distribution with the greatest possible number of states gives the highest probability. These ideas led Boltzmann to define the entropy of a state as

\[ S = k \ln P \]  

(19.71)

where \( k \) is a constant, that later turned out to be the Stefan-Boltzmann constant, which is equal to \( 1.38 \times 10^{-23} \text{ J/K} \); \( \ln \) is the natural logarithm; and \( P \) is the probability that the system is in the state specified. Thus in our example, the entropy of the first distribution is computed as

\[ S = k \ln P = (1.38 \times 10^{-23} \text{ J/K})(\ln 6.25) = 2.53 \times 10^{-23} \text{ J/K} \]

The entropy for each possible distribution is computed and shown in table 19.1. Notice that the most disordered state (two molecules on each side of the box) has the highest value of entropy. If we were to start the system with the four molecules in the left-hand box, entropy \( = 2.53 \times 10^{-23} \text{ J/K} \), the system would move in the
direction of maximum entropy, $5.00 \times 10^{-23} \text{ J/K}$, the state with two molecules on each side of the box. As before, natural processes move in the direction of maximum entropy. The actual values of the computed entropy for this example are extremely small, because we are dealing with only four molecules. If we had only one mole of a gas in the box we would have $6.02 \times 10^{23}$ molecules in the box, an enormous number compared with our four molecules. In such a case the numerical values of the entropy would be much higher. However, there would still be the same type of distributions. The state with the greatest disorder, the same number of molecules on each side of the box, would be the state with the greatest value of the entropy. The state with all the molecules on one side of the box would have a finite but vanishingly small value of probability.

Hence the original problem we stated in figure 19.16(a), with the gas in the left partition has the smallest entropy while the gas on both sides of the box in figure 19.16(b), has the greatest entropy. The process flows from the state of lowest entropy to the one of highest entropy. It is interesting to note that it is not impossible for the gas molecules on both sides of the box to all move to the left-hand side of the box, but the probability is so extremely small that it would take a time greater than the age of the universe for it to happen. Hence, effectively it will not happen.

The state of maximum entropy is the state of maximum disorder and is the state where all the molecules are moving in a completely random motion. This state is, of course, the state of thermal equilibrium. We have seen throughout our study of heat that whenever two objects at different temperatures are brought together, the hot body will lose thermal energy to the cold body until the hot and cold body are at the same equilibrium temperature. Thus, as all bodies tend to equilibrium they all approach a state of maximum entropy. Hence, the universe itself tends toward a state of maximum entropy, which is a state of thermal equilibrium of all the molecules of the universe. This is a state of uniform temperature and density of all the atoms and molecules in the universe. No physical, chemical, or biological processes would be capable of occurring, however, because a state of total disorder cannot do any additional work. This ultimate state of the universe is sometimes called the heat death of the universe.

One final thought about entropy, and that is the idea of a direction for time. All the laws of physics, except for the second law of thermodynamics, are invariant to a change in the direction of time. That is, for example, Newton’s laws of motion would work equally well if time were to run backward. If a picture were taken of a swinging pendulum with a video camera, and then played first forward and then backward, we could not tell from the picture which picture is running forward in time and which is running backward in time. They would both appear the same. On the other hand, if we take a video of a dropped coffee cup that hits the ground and shatters into many pieces we can certainly tell the difference between running the video forward or backward. When the video is run backward we would see a shattered coffee cup on the floor come together and repair itself and then jump upward onto the table. Nature does not work this way, so we know the picture must
be running backward. Now before the coffee cup is dropped, we have a situation of order. When the cup is dropped and shattered we have a state of disorder. Since natural processes run from a state of order (low entropy) to one of disorder (high entropy), we can immediately see the time sequence that must be followed in the picture. The correct sequence to view the video picture is to start where the coffee cup has its lowest entropy (on the table initially at rest) and end where the cup has its maximum entropy (on the floor broken into many pieces). Hence the concept of entropy gives us a direction for time. In any natural process, the initial state has the lowest entropy, and the final state has the greatest entropy. Thus time flows in the direction of the increase in entropy. Stated another way, the past is the state of lowest entropy and the future is the state of highest entropy. Thus entropy is sometimes said to be time’s arrow, showing its direction.

Because of this, there have been many speculative ideas attributed to time. What happens to time when the universe reaches its state of maximum entropy? Since time flows from low entropy to high entropy, what happens when there is no longer a change in entropy? Would there be an infinite present? An eternity?

### Have you ever wondered?

#### An Essay on the Application of Physics

**Meteorology -- The Physics of the Atmosphere**

Have you ever wondered, while watching the weather forecast on your local TV station, what all those lines and arrows were on those maps? It looked something like figure 1.

If we were to look at the television screen more closely we would see a map of the United States. At every weather station throughout the United States, the atmospheric pressure is measured and recorded on a weather map. On that map, a series of lines, connecting those pressures that are the same, are drawn. These lines are called **isobars** and can be seen in figure 2. An isobar is a line along which the pressure is constant. An isobar is analogous to a contour line that is drawn on a topographical map to indicate a certain height above mean sea level. As an example, consider the mountain and valley shown in figure 3(a). A series of contour lines are drawn around the mountain at constant heights above sea level. The first line is drawn at a height $H = 200\, \text{m}$ above sea level. Everywhere on this line the height is exactly $200\, \text{m}$ above sea level. The next contour line is drawn at $H = 400\, \text{m}$. Everywhere on this line the height is exactly $400\, \text{m}$ above sea level. Between the $200\, \text{m}$ contour and the $400\, \text{m}$ contour line the height varies between $200\, \text{m}$ and $400\, \text{m}$. The contour line for $600\, \text{m}$ is also drawn in the figure. The very top of the mountain is greater than the $600\, \text{m}$ and is the highest point of the mountain. The contour lines showing the valley are drawn at $-200\, \text{m}$, $-400\, \text{m}$, and $-600\, \text{m}$. The $-200\, \text{m}$ contour line shows that every point on this line is $200\, \text{m}$ below sea level. The bottom of the valley is the lowest point in the valley. If we were to look down on
the mountain and valley from above, we would see a series of concentric circles representing the contour lines as they are shown in figure 3(b). (On a real mountain and valley the contours would probably not be true circles.)

The isobars are to a weather map as contour lines are to a topographical map. The isobars represent the pressure of the atmosphere. By drawing the isobars, a picture of the pressure field is obtained. Normal atmospheric pressure is 29.92 in. of Hg or 1013.25 mb. But remember that normal is an average of abnormals. At any
given time, the pressure in the atmosphere varies slightly from this normal value. If the atmospheric pressure is greater than normal at your location, then you are in a region of high pressure. If, on the other hand, the atmospheric pressure is less than normal at your location, then you are in a region of low pressure. The isobars indicating high and low pressure are shown in figure 4(a). The high-pressure region can be visualized as a mountain and the low-pressure region as a valley in figure 4(b). Air in the high-pressure region flows down the pressure mountain into the low-pressure valley, just as a ball would roll down a real mountain side into the valley below. This flow of air is called wind. Hence, air always flows out of a high-pressure area into a low-pressure area. The force on a ball rolling down the mountain is the component, acting down the mountain, of the gravitational force on the ball. The force on a parcel of air is caused by the difference in pressure between the higher pressure and the lower pressure. This force is called the pressure gradient force (PGF) per unit mass, and it is directed from the high-pressure area to the low-pressure area. It is effectively the slope of the pressure mountain-valley. A large pressure gradient, corresponding to a steep slope, causes large winds, whereas a small pressure gradient, corresponding to a shallow slope, causes very light winds.

If the earth were not rotating, the air would flow perpendicular to the isobars. However, the earth does rotate, and the rotation of the earth causes air to be deflected to the right of its original path. The deflection of air to the right of its
path in the northern hemisphere is called the Coriolis effect. The Coriolis effect arises because the rotating earth is not an inertial coordinate system. For small-scale motion the rotating earth approximates an inertial coordinate system.

However, for large-scale motion, such as the winds, the effect of the rotating earth must be taken into account. It is taken into account by assuming that there is a fictitious force, called the Coriolis force (CF) that acts to the right of the path of a parcel of air in its motion through the atmosphere. The equation for the Coriolis force is

\[ \text{CF} = 2v\Omega \sin \phi \]  \hspace{1cm} (17H.1)

where CF is the Coriolis force per unit mass of air, \( v \) is the speed of the wind, \( \Omega \) is the angular velocity of the earth, and \( \phi \) is the latitude. Thus, the Coriolis force depends on the speed of the air (the greater the speed the greater the force) and the latitude angle \( \phi \). At the equator, \( \phi = 0 \) and \( \sin \phi = 0 \), and hence there is no force of deflection at the equator. For \( \phi = 90^\circ \), \( \sin \phi = 1 \), hence the maximum force and deflection occur at the pole.

Let us describe the motion of the air as it moves toward the low-pressure area. The air starts on its motion at the point A, figure 5(a), along a path that is perpendicular to the isobars. But the air is deflected to the right of its path by the

**Figure 4** High and low atmospheric pressure.
Coriolis force, and ends up at the position $B$. At $B$, the pressure gradient force is still acting toward the center of the low-pressure area, while the Coriolis force, acting to the right of the path, is opposite to the pressure gradient force. An approximate balance\(^1\) exists between the two forces and the air parcel now moves parallel to the isobars. Notice that the air moves counterclockwise in a low-pressure area.

As the air moves over the ground, there is a frictional force $f$ that acts on the air, is directed opposite to the direction of motion of the air, and is responsible for the slowing down of the air. This is shown in figure 5(b). But, as seen in equation 17H.1, the Coriolis force is a function of the wind speed. If the wind speed decreases

\[^1\text{A more detailed analysis by Newton's second law would give}\]

\[
a = \frac{F}{m} = \text{PGF} + \text{CF}
\]

Since the air parcel is moving in a circle of radius $r$, with a velocity $v$, the acceleration is the centripetal acceleration given by $v^2/r$. Hence Newton’s second law should be written as

\[
\frac{v^2}{r} = \text{PGF} + \text{CF}
\]

But in very large scale motion, such as over a continent, $v^2/r = 0.1 \times 10^{-3}$ m/s\(^2\), while the PGF $= 1.1 \times 10^{-3}$ m/s\(^2\). Thus the centripetal acceleration is about 1/10 of the acceleration caused by the pressure gradient force, and in this simplified analysis is neglected. The second law then becomes

\[
0 = \text{PGF} + \text{CF}
\]

or

\[
\text{PGF} = -\text{CF}
\]

Hence the force on the air parcel is balanced between the pressure gradient force and the Coriolis force. The wind that results from the balance between the PGF and the CF is called the geostrophic wind. For a more accurate analysis and especially in smaller sized pressure systems such as hurricanes and tornadoes this assumption cannot be made and the centripetal acceleration must be taken into account.
because of friction, the Coriolis force also decreases. Hence, there is no longer the balance between the pressure gradient force and the Coriolis force and the air parcel now moves toward the low-pressure area. The combined result of the pressure gradient force, the Coriolis force, and the frictional force, causes the air to spiral into the low-pressure area, as seen in figure 5(b).

The result of the above analysis shows that air spirals counterclockwise into a low-pressure area at the surface of the earth. But where does all this air go? It must go somewhere. The only place for it to go is upward into the atmosphere. Hence, there is vertical motion upward in a low-pressure area.

Now recall from chapter 13 that the pressure of the air in the atmosphere decreases with altitude. Hence, when the air rises in the low-pressure area it finds itself in a region of still lower pressure aloft. Therefore, the rising air from the surface expands into the lower pressure aloft. But as seen in this chapter, for a gas to expand the gas must do work. Since there is no heat added to, or taken away from this rising air, $\Delta Q = 0$, and the air is expanding adiabatically. But as just shown in equation 19.47, the work done in the expansion causes a decrease in the internal energy of the gas. Hence, the rising air cools as it expands because the energy necessary for the gas to expand comes from the internal energy of the gas itself. Hence the temperature of the air decreases as the air expands and the rising air cools.

The amount of water vapor in the air is called humidity. The maximum amount of water vapor that the air can hold is temperature dependent. That is, at high temperatures the air can hold a large quantity of water vapor, whereas at low temperatures it can only hold a much smaller quantity. If the rising air cools down far enough it reaches the point where the air has all the water vapor it can hold. At this point the air is said to be saturated and the relative humidity of the air is 100%. If the air continues to rise and cool, it cannot hold all this water vapor. Hence, some of the water vapor condenses to tiny drops of water. These drops of water effectively float in the air. (They are buoyed up by the rising air currents.) The aggregate of all these tiny drops of water suspended in the air is called a cloud. Hence, clouds are formed when the rising air is cooled to the condensation point. If the rising and cooling continue, more and more water vapor condenses until the water drops get so large that they fall and the falling drops are called rain. In summary, associated with a low-pressure area in the atmosphere is rising air. The cooling of this adiabatically expanding air causes the formation of clouds, precipitation, and general bad weather. Thus, when the weatherman says that low pressure is moving into your area, as a general rule, you can expect bad weather.

Everything we said about the low-pressure area is reversed for a high-pressure area. The pressure gradient force points away from the high-pressure area. As the air starts out of the high-pressure area at the point $A$, figure 6(a), it is moving along a path that is perpendicular to the isobars. The Coriolis force now acts on the air and deflects it to the right of its path. By the time the air reaches the point $B$, the pressure gradient force is approximately balanced by the Coriolis
force\textsuperscript{2} and the air moves parallel to the isobars. Thus, the air flows clockwise around the high-pressure area. The frictional force slows down the air and causes the Coriolis force to decrease in size. The pressure gradient force is now greater than the Coriolis force, and the air starts to spiral out of the high-pressure area, figure 6(b).

From what we have just seen, air spirals out of a high-pressure area at the surface of the earth. But if all the air that was in the high-pressure area spirals out, what is left within the high-pressure area? If the air is not replenished, the area would become a vacuum. But this is impossible. Therefore, air must come from somewhere to replenish the air spiraling out of the high. The only place that it can come from is from the air aloft. That is, air aloft moves downward into the high-pressure area at the surface. Thus, there is vertical motion downward in a high-pressure area.

As the air aloft descends, it finds itself in a region of still higher pressure and is compressed adiabatically. Thus, work is done on the gas by the atmosphere and this increase in energy shows up as an increase in the internal energy of the air, and hence an increase in the temperature of the descending air. Thus, the air warms up adiabatically as it descends. Because warmer air can hold more water vapor than colder air, the water droplets that made up the clouds evaporate into the air. As more and more air descends, more and more water droplets evaporate into the air until any clouds that were present have evaporated, leaving clear skies. Hence, high-pressure areas are associated with clear skies and, in general, good weather. So when the weatherman tells you that high pressure is moving into your area, you can usually expect good weather.

Now when you look at your TV weather map, look for the low- and high-pressure areas. If the low-pressure area is moving into your region, you can expect clouds and deteriorating weather. If the high-pressure area is moving into your region, you can expect improving weather with clear skies.

\textsuperscript{2}The same approximation for the balance between the PGF and the CF used in the analysis of the low-pressure area is also made for the high-pressure area.
Those other lines on the weather map are called fronts. A front is a boundary between two different air masses. An air mass is a large mass of air having uniform properties of temperature and moisture throughout the horizontal. Air sitting over the vast regions of Canada has the characteristic of being cold and dry. This air mass is called a continental polar air mass and is designated as a cP air mass. Air sitting over the southern ocean areas and the Gulf of Mexico has the characteristic of being hot and humid. This air mass is called a maritime tropical, mT, air mass. These two air masses interact at what is called the polar front. Much of your weather is associated with this polar front. If the continental polar air mass is moving forward, the polar front is called a cold front. On a weather map the cold front is shown either as a blue line or, if the presentation is in black and white, a black line with little triangles on its leading edge showing the direction of motion. If the continental polar air mass is retreating northward, the polar front is called a warm front. On a weather map the warm front is shown either as a red line or, if the presentation is in black and white, a black line with little semicircles on its edge showing the direction in which the front is retreating. The center of the polar front is embedded in the low-pressure area.

With all this background, let us now analyze the weather map of figure 2. Notice that there is a large low-pressure area over the eastern half of the United States. In general, the poorer weather will be found in this region. A high-pressure area is found across the western half of the United States. In general, good weather will be found in this region. The polar front can also be seen in figure 2. The cold front is the boundary between the cold continental polar air that came out of Canada and the warm moist maritime tropical air that has moved up from the gulf. The arrows on the map indicate the velocity of the air. The cold dry cP air, being heavier than the warm tropical mT air, pushes underneath the mT air, driving it upward. The moisture in the rising tropical air condenses and forms a narrow band of clouds along the length of the cold front. The precipitation usually associated with the cold front is showery.

The warm front is the boundary of the retreating cool air and the advancing warm moist air. The mT air, being lighter than the retreating cP air, rises above the colder air. The sloping front of the retreating air is much shallower than the slope of the advancing cold front. Therefore, the mT air rises over a very large region and gives a very vast region of clouds and precipitation. Thus the weather associated with a warm front is usually more extensive than the weather associated with a cold front.

Your weather depends on where you are with respect to the frontal systems. If you are north of the warm front in figure 2, such as in Illinois, Ohio, or Pennsylvania, the temperatures will be cool, the winds will be from the southeast, the sky will be cloudy, and you will be getting precipitation. If you are south of the warm front and in advance of the cold front, such as in Alabama, Georgia, South Carolina, and Florida, the temperature will be warm, the humidity high, winds will be from the southwest and you will usually have nice weather. If the cold front has already passed you by, such as in Kansas, Oklahoma, Texas, and Arkansas, the
skies will be clear or at least clearing, the temperature will be cold, the humidity will be low, the winds will be from the northwest, and in general you will have good weather.

All the highs, lows, and fronts, move across the United States from the west toward the east. So the weather that you get today will change as these weather systems move toward you.

The Language of Physics

Thermodynamics
The study of the relationships between heat, internal energy, and the mechanical work performed by a system. The system is usually a heat engine of some kind (p. ).

Work
The work done by a gas during expansion is positive and the work done by a gas during compression is negative. The work done is equal to the area under the curve in a $p$-$V$ diagram. The work done depends on the thermodynamic path taken in the $p$-$V$ diagram (p. ).

Cyclic process
A process that runs in a cycle eventually returning to where it started from. The net work done by the system during a cyclic process is equal to the area enclosed by the cyclic thermodynamic path in a $p$-$V$ diagram. The net work is positive if the cycle proceeds clockwise, and negative if the cycle proceeds counterclockwise on the $p$-$V$ diagram. The total change in internal energy around the entire cycle is equal to zero. The energy for the net work done by the system comes from the net heat applied to the system (p. ).

Isobaric process
A process that takes place at a constant pressure (p. ).

Isochoric or isometric processes
A process that takes place at constant volume. The heat added to a system during an isochoric process shows up as an increase in the internal energy of the system (p. ).

Isothermal process
A process that takes place at constant temperature (p. ).

Molecular mass
The molecular mass of any substance is equal to the mass of one molecule of that substance times the total number of molecules in one mole of the substance
Avogadro’s number. Thus, the molecular mass of any substance is equal to the mass of one mole of that substance. Hence, the mass of a gas is equal to the number of moles of a gas times the molecular mass of the gas (p.).

**Molar specific heat**
The product of the specific heat of a substance and its molecular mass (p.).

**Heat in a thermodynamic process**
The heat absorbed or liberated in a thermodynamic process depends on the path that is followed in a $p$-$V$ diagram. Thus, heat, like work, is path dependent. Heat is always positive when it is added to the system and negative when it is removed from the system (p.).

**Internal energy of a gas**
The internal energy of a gas is equal to the sum of the kinetic energy of all the molecules of a gas. A change in temperature is associated with a change in the internal energy of a gas. Hence, an isothermal expansion occurs at constant internal energy. Regardless of the path chosen between two points in a $p$-$V$ diagram, the change in internal energy is always the same. Thus, the internal energy of the system is independent of the path taken in a $p$-$V$ diagram; it depends only on the initial and final states of the thermodynamic system (p.).

**The first law of thermodynamics**
The heat added to a system will show up either as a change in internal energy of the system or as work performed by the system. It is also stated in the form: the change in the internal energy of the system equals the heat added to the system minus the work done by the system on the outside environment. The first law is really a statement of the law of conservation of energy applied to a thermodynamic system (p.).

**Efficiency**
The efficiency of an engine can be defined in terms of what we get out of the system compared to what we put into the system. It is thus equal to the ratio of the work performed by the system to the heat put into the system. It is desirable to make the efficiency of an engine as high as possible (p.).

**Adiabatic process**
A process that occurs without an exchange of heat between the system and its environment. That is, heat is neither added nor taken away from the system during the process (p.).

**Otto cycle**
A thermodynamic cycle that is approximated in the operation of the gasoline engine (p.).
Ideal heat engine
An idealized engine that shows the main characteristics of all engines, namely, every engine absorbs heat from a source at high temperature, performs some amount of mechanical work, and then rejects some heat at a lower temperature (p. ).

Refrigerator
A heat engine working in reverse. That is, work is done on the refrigerator, thereby extracting a quantity of heat from a low-temperature reservoir and exhausting a large quantity of heat to a hot reservoir (p. ).

Carnot cycle
A thermodynamic cycle of a Carnot engine, consisting of two isothermal and two adiabatic paths in a $p$-$V$ diagram. The Carnot engine is the most efficient of all engines (p. ).

The second law of thermodynamics
The second law of thermodynamics tells us which processes are possible and which are not. The concept of entropy is introduced to give a quantitative basis for the second law. It is equal to the ratio of the heat added to the system to the absolute temperature of the system, when a thermodynamic system changes from one equilibrium state to another along a reversible path. In an isolated system, the system always changes from values of low entropy to values of high entropy, and only those processes are possible for which the entropy of the system increases or remains a constant (p. ).

Kelvin-Planck statement of the second law of thermodynamics
No process is possible whose sole result is the absorption of heat from a reservoir at a single temperature and the conversion of this heat energy completely into mechanical work (p. ).

Clausius statement of the second law of thermodynamics
No process is possible whose sole result is the transfer of heat from a cooler to a hotter body (p. ).

Summary of Important Equations

<table>
<thead>
<tr>
<th>Equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W = \int pdV$</td>
<td>Work done by a gas</td>
</tr>
<tr>
<td>$W_{AC} = nRT \ln \frac{V_C}{V_A}$</td>
<td>Work done on an isothermal path</td>
</tr>
<tr>
<td>$m = m_0 N_A n$</td>
<td>Mass of the gas</td>
</tr>
</tbody>
</table>
Chapter 19  Thermodynamics

Molecular mass

\[ M = m_0 N_A \]  \hspace{1cm} (19.19)

Mass of the gas

\[ m = nM \]  \hspace{1cm} (19.20)

Molar specific heat

\[ C = Mc \]  \hspace{1cm} (19.22)

Heat absorbed or liberated by a gas at constant volume

\[ Q = \int_{T_0}^{T_1} nC_v dT = nC_v(T_1 - T_0) \]  \hspace{1cm} (19.24)

Heat absorbed or liberated by a gas at constant pressure

\[ Q = \int_{T_0}^{T_1} nC_p dT = nC_p(T_1 - T_0) \]  \hspace{1cm} (19.25)

Internal energy of an ideal gas

\[ U = \frac{3}{2} nRT \]  \hspace{1cm} (19.27)

Change in internal energy of an ideal gas

\[ dU = \frac{3}{2} nRdT \]  \hspace{1cm} (19.28)

Change in internal energy of an ideal gas

\[ dU = nC_v dT \]  \hspace{1cm} (19.32)

Molar specific heat at constant volume

\[ C_v = \frac{3}{2} R \]  \hspace{1cm} (19.33)

Molar specific heat at constant pressure

\[ C_p = \frac{5}{2} R \]  \hspace{1cm} (19.45)

First law of thermodynamics

\[ dU = dQ - dW \]  \hspace{1cm} (19.35)

Adiabatic process

\[ dQ = 0 \]  \hspace{1cm} (19.46)

First law for adiabatic process

\[ dW = -dU \]  \hspace{1cm} (19.47)

\[ T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \]  \hspace{1cm} (19.53)

\[ \frac{p_i V_i^{\gamma}}{p_f V_f^{\gamma}} = \frac{1}{T_i} \]  \hspace{1cm} (19.54)

\[ T_i p_i^{\gamma-1} = T_f p_f^{\gamma-1} \]  \hspace{1cm} (19.56)

Isothermal process

\[ dT = 0 \]

\[ dU = 0 \]  \hspace{1cm} (19.57)

First law for isothermal process

\[ dQ = dW \]  \hspace{1cm} (19.58)

Isochoric or isometric process

\[ dV = 0 \]

First law for isochoric process

\[ dQ = dU \]  \hspace{1cm} (19.58)

Isobaric process

\[ dp = 0 \]

Cyclic process

\[ dU = 0 \]

First law for cyclic process

\[ W = Q \]  \hspace{1cm} (19.59)

Efficiency of any engine

\[ \text{Eff} = \frac{W}{Q_{in}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} \]  \hspace{1cm} (19.61)

\[ \text{Eff} = 1 - \frac{Q_C}{Q_H} = \frac{T_C}{T_H} \]  \hspace{1cm} (19.62)

Efficiency of a Carnot engine

\[ \text{Eff} = 1 - \frac{T_C}{T_H} \]  \hspace{1cm} (19.66)

Entropy

\[ \Delta S = \int_{S_i}^{S_f} dS = S_f - S_i = \int \frac{dQ}{T} \]  \hspace{1cm} (19.67)

Probability that molecules are in a particular state compared with all the possible states

\[ P = \frac{N_i}{N} \times 100\% \]  \hspace{1cm} (19.70)

Entropy

\[ S = k \ln P \]  \hspace{1cm} (19.71)
Questions for Chapter 19

1. Discuss the difference between the work done by the gas and the work done on the gas in any thermodynamic process.
2. Why is the work done in a thermodynamic process a function of the path traversed in the p-V diagram?
3. Define the following processes: isobaric, isothermal, isochoric, adiabatic, cyclic, and isoentropic.
4. How is it possible that a solid and a liquid have one value for the specific heat and a gas can have an infinite number of specific heats?
5. Discuss the first and second laws of thermodynamics.
6. Describe what is meant by the statement, “the internal energy of a thermodynamic system is conservative.”
7. Figure 19.8 shows a plot of isotherms and adiabats on a p-V diagram. Explain why the adiabats have a steeper slope.
8. Discuss the thermodynamic process in a diesel engine, and draw the process on a p-V diagram.
9. Use the first law of thermodynamics to describe a solar heating system.
10. Can you use a home refrigerator to cool the home in the summer by leaving the door of the refrigerator open?
11. Why is a heat pump not very efficient in very cold climates?
12. Show how equation 19.65 could be used as the basis of a temperature scale.
13. Is it possible to connect a heat engine to a refrigerator such that the work done by the engine is used to drive the refrigerator, and the waste heat from the refrigerator is then given to the engine, to drive the engine thus making a perpetual motion machine?
14. Discuss the concept of entropy and how it can be used to determine if a thermodynamic process is possible.
15. Discuss the statements: (a) entropy is sometimes called time’s arrow and (b) the universe will end in a heat death when it reaches its state of maximum entropy.

Problems for Chapter 19

19.2 The Concept of Work Applied to a Thermodynamic System

1. How much work is done by an ideal gas when it expands at constant atmospheric pressure from a volume of 0.027 m³ to a volume of 1.00 m³?
2. What is the area of the cross-hatched area in the p-V diagram? What is the work done in going from A to B?
3. What is the net work done in the triangular cycle $ABC$?
4. How much work is done in the cycle $ABCDA$ in the diagram below?

5. One mole of an ideal gas goes through the cycle shown. If $p_A = 2.00 \times 10^5$ Pa, $p_D = 5.00 \times 10^4$ Pa, $V_B = 2.00$ m$^3$, and $V_A = 0.500$ m$^3$, find the work done along the paths (a) $AB$, (b) $BC$, (c) $CD$, (d) $DA$, and (e) $ABCDA$.

19.3 Heat Added to or Removed from a Thermodynamic System

6. What is the mass of 4.00 moles of He gas?
7. Find the amount of heat required to raise the temperature of 5.00 moles of He, 10.0 °C, at constant volume.
8. Find the amount of heat required to raise the temperature of 5.00 moles of He, 10.0 °C, at constant pressure.
9. Compute the amount of heat absorbed when one mole of a monatomic gas, at a temperature of 200 K, rises to a temperature of 400 K (a) isochorically and (b) isobarically.

19.4 The First Law of Thermodynamics

10. What is the total internal energy of 3.00 moles of an ideal gas at (a) 273 K and (b) 300 K?
11. What is the change in internal energy of 3.00 moles of an ideal gas when it is heated from 273 K to 293 K?
12. Find the change in the internal energy of 1 mole of an ideal gas when heated from 300 K to 500 K.

13. In a thermodynamic system, 500 J of work are done and 200 J of heat are added. Find the change in the internal energy of the system.

14. In a certain process, the temperature rises from 50.0 °C to 150.0 °C as 1000 J of heat energy are added to 4 moles of an ideal gas. Find the work done by the gas during this process.

15. In a thermodynamic system, 200 J of work are done and 500 J of heat are added. Find the change in the internal energy of the system.

16. In a certain process with an ideal gas, the temperature drops from 120 °C to 80.0 °C as 2000 J of heat energy are removed from the system and 1000 J of work are done by the gas. Find the number of moles of the gas that are present.

17. Four moles of an ideal gas are carried through the cycle ABCDA of figure 19.7. If \( T_D = 100 \) K, \( T_A = T_C = 200 \) K, \( T_B = 400 \) K, \( p_A = 0.500 \times 10^5 \) Pa, and \( p_D = 2.50 \times 10^4 \) Pa, use the ideal gas equation to determine the volumes \( V_A \) and \( V_B \).

*18. In problem 17 find the work done, the heat lost or absorbed, and the change in internal energy of the gas for the paths (a) AB, (b) BC, (c) CD, (d) DA, and (e) ABCDA.

19. In a thermodynamic system, 700 J of work are done by the system while the internal energy drops by 450 J. Find the heat transferred to the gas during this process.

20. If 5.00 J of work are done by a refrigerator and 8.00 J of heat are exhausted into the hot reservoir, how much heat was removed from the cold reservoir?

21. A heat engine is operating at 40.0% efficiency. If 3.00 J of heat are added to the system, how much work is the engine capable of doing?

19.5 An Adiabatic Process

*22. A monatomic gas expands adiabatically to double its original volume. What is its final pressure in terms of its initial pressure?

23. A parcel of air at the surface of the earth, where the pressure is 1000 mb, and its temperature is 20.0 °C. The parcel of air rises in the atmosphere to a level where the pressure is 850 mb. What is the new temperature of this parcel of air?

*24. One mole of He gas at atmospheric pressure is compressed adiabatically from an initial temperature of 20.0 °C to a final temperature of 100 °C. Find the new pressure of the gas.

25. If 50.0 J of work are done on one mole of an ideal gas during an adiabatic compression, what is the temperature change of the gas?

19.6 Some Special Cases of the First Law of Thermodynamics

26. If the temperature of 2.00 moles of an ideal gas increases by 40.0 K during an isochoric process, how much heat was added to the gas?

27. If 800 J of thermal energy are removed from 8 moles of an ideal gas
during an isochoric process, find the change in temperature in degrees (a) Kelvin, (b) Celsius, and (c) Fahrenheit.

28. If 3.00 J of heat are added to a gas during an isothermal expansion, how much work is the system capable of doing during this process?

29. During an isothermal contraction, 55.0 J of work are done on an ideal gas. How much thermal energy was extracted from the gas during this process?

19.7 The Gasoline Engine

*30. The crankshaft of a gasoline engine rotates at 1200 revolutions per minute. The area of each piston is 80.0 cm\(^2\) and the length of the stroke is 13.0 cm. If the average pressure during the power stroke is \(7.01 \times 10^5\) Pa, find the power developed in each cylinder. (Hint: remember that there is only one power stroke for every two revolutions of the crankshaft.)

19.8 The Ideal Heat Engine and 19.9 The Carnot Cycle

31. An engine operates between room temperature of 20.0 °C and a cold reservoir at 5.00 °C. Find the maximum efficiency of such an engine.

32. What is the efficiency of a Carnot engine operating between temperatures of 300 K and 500 K?

33. A Carnot engine is working in reverse as a refrigerator. Find the coefficient of performance if the engine is operating between the temperatures –10.5 °C and 35.0 °C.

34. A Carnot refrigerator operates between –10.0 °C and 25.0 °C. Find how much work must be done per joule of heat extracted.

35. Calculate the efficiency of an engine that absorbs 500 J of thermal energy while it does 250 J of work.

19.11 Entropy

36. Find the change in entropy if 10.0 kg of ice at 0.00 °C is converted to water at +10.0 °C.

37. A gas expands adiabatically from 300 K to 350 K. Find the change in its entropy.

*38. Find the total change in entropy if 2.00 kg of ice at 0.00 °C is mixed with 25.0 kg of water at 20.0 °C.

39. Find the change in entropy when 2.00 kg of steam at 110 °C is converted to water at 90.0 °C.

40. A gas expands isothermally and does 500 J of work. If the temperature of the gas is 35.0 °C, find its change in entropy.

Additional Problems

41. In the thermodynamic system shown in the diagram, (a) 50.0 J of thermal energy are added to the system, and 20.0 J of work are done by the system along path \(abc\). Find the change in internal energy along this path. (b) Along path \(adc\), 10.0 J of work are done by the system. Find the heat absorbed or liberated from the
system along this path. (c) The system returns from state \( c \) to its initial state \( a \) along path \( ca \). If 15.0 J of work are done on the system find the amount of heat absorbed or liberated by the system.

Diagram for problem 41.  
Diagram for problem 43.

42. Draw the following process on a \( p-V \) diagram. First 8.00 m\(^3\) of air at atmospheric pressure are compressed isothermally to a volume of 4.00 m\(^3\). The gas then expands adiabatically to 8.00 m\(^3\) and is then compressed isobarically to 4.00 m\(^3\).

43. In the diagram shown, one mole of an ideal gas is at atmospheric pressure and a temperature of 250 K at position \( a \). (a) Find the volume of the gas at \( a \). (b) The pressure of the gas is then doubled while the volume is kept constant. Find the temperature of the gas at position \( b \). (c) The gas is then allowed to expand isothermally to position \( c \). Find the volume of the gas at \( c \).

*44. Repeat problem 43, but for part (c) let the gas expand adiabatically to atmospheric pressure. Find the volume of the gas at this point. Show this point on the diagram.

45. A lecture hall at 20.0 °C contains 100 students whose basic metabolism generates \( 4.186 \times 10^5 \) J/hr of thermal energy. If the size of the hall is 15.0 m by 30.0 m by 4.00 m, what is the increase in temperature of the air in the hall at the end of 1 hr? It is desired to use an air conditioner to cool the room to 20.0 °C. If the air conditioner is 45.0% efficient, what size air conditioner is necessary?

Interactive Tutorials
46. A thermodynamic cycle. Three moles of an ideal gas are carried around the thermodynamic cycle \( ABCDA \) shown in figure 19.7. Find the work done, the heat lost or absorbed, and the internal energy of the system for the thermodynamic paths (a) \( AB \), (b) \( BC \), (c) \( CD \), (d) \( DA \), and (e) \( ABCDA \). The temperatures are \( T_D = 147 \) K, \( T_{AC} = 250 \) K, and \( T_B = 425 \) K. The pressures are \( p_A = 5.53 \times 10^4 \) Pa and \( p_D = 3.25 \times 10^4 \) Pa. The volumes are \( V_A = 0.113 \) m\(^3\) and \( V_B = 0.192 \) m\(^3\). (f) Find the efficiency of this system.

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