The First Law: Expansion and Engines

LEARNING OBJECTIVES

After reading this chapter, you will be able to do the following:

1. Predict the transfer of energy as work and as heat in reversible and irreversible expansions and compressions.
2. Predict the direction of a temperature change in a sample undergoing a Joule-Thomson expansion, based on the relative importance of the intermolecular forces.
3. Calculate the maximum efficiency for a Carnot heat engine, and calculate the heat and work at each stage of the cycle.

GOAL Why Are We Here?

The goal of this chapter is to describe how we use thermodynamic quantities to predict the properties of fundamental processes involving expansion and also to demonstrate how crucial features of these processes depend on the molecular properties of the system. The examples in this chapter focus on how the energy evolves during expansion and contraction and on the conversion of heat into work by means of an engine. The treatment of these processes allows us to demonstrate several fundamental points in classical thermodynamics, as well as prepare the groundwork for our later discussion of phase transitions and chemical reactions.

CONTEXT Where Are We Now?

Chapter 7 assembled a small toolkit for dealing with problems in thermodynamics, and demonstrated how statistical mechanics can predict some of the numerical values—in that case, heat capacities—that those tools use in finding a solution. We saw how to use the heat capacity to predict the relationship between the changes in energy and temperature for heating and cooling.

Now, to extend our use of those tools, we’re going to follow the energy as it moves around during different fundamental processes: expansion and contraction. Whereas the processes in Chapter 7 focus primarily on the heat $q$, much of our attention in this chapter will be invested in the work $w$. There are at least two reasons these processes are of interest in chemistry. First, temperature changes are often accompanied by work arising from changes in the volume of the system as it expands or contracts, and so a proper accounting of the energy requires that we understand the work component as well as the heat. Second, a primary motivating factor for the study of chemical thermodynamics has long been the conversion of heat released by combustion into work by means of an engine. We will examine...
the energy flow during one-step expansions first and then combine steps to make
an engine cycle at the end of the chapter. Our toolkit from Chapter 7 is all we will
need analyze the basic (and remarkable) operation of engines.

**SUPPORTING TEXT** How Did We Get Here?

The main qualitative result we will draw on for the work in this chapter is the
notion from Chapter 2 that the entropy drives a sample to expand when it can
and to exchange energy with another sample when it can to equalize their tem-
peratures. For a more detailed background, we will draw on the following
equations and sections of text to support the ideas developed in this chapter:

- From Chapter 7, we will need the first law of thermodynamics,

\[ dE = dq + dw, \]  

(7.5)

which divides the change in energy into incremental components that we
will use to obtain the contributions to \( \Delta E \) from the heat \( q \) and the work \( w \)
during an expansion.

- For processes that involve a temperature change, we will also need the
  relationship between energy and temperature as expressed using the heat
  capacity at constant volume:

\[ CV = \frac{\partial E}{\partial T}_{V,n}, \]  

(7.44)

### 8.1 Expansion of Gases

Although our primary interest will be in the transfer of energy as heat, this is
often inseparable—or inconvenient to separate—from energy transfer in the
form of work, such as thermal expansion. Therefore, we will take a look at
the thermodynamics of systems in which work is also done. To take advantage
of the ideal gas law, we will stick for now to \( PV \) work.

For problems involving gases in closed systems, it is often informative to plot
the process on a \( P \) versus \( V \) (or \( "P-V" \)) graph. The temperature is specified by the
pressure and volume according to the ideal gas law or one of its non-ideal cousins
(e.g., the van der Waals equation), and the energy by the temperature; therefore,
every point on a \( P-V \) graph corresponds to a unique thermodynamic state. Any
quasistatic process may then be drawn on the graph as a curve, because each point
along the path of a quasistatic process must correspond to a thermodynamic state.
For example, the quasistatic heating of a monatomic ideal gas at constant pressure
would correspond to a single horizontal line (Fig. 8.1), indicating that the pressure
was fixed but the volume was increasing linearly with \( T \). Such plots, and their
relatives, are especially useful for more complex problems, as we will see shortly.

#### Isothermal Expansion

Consider the work done in the reversible expansion between two thermody-
namic states of a gas with volumes \( V_1 \) and \( V_2 \), where \( V_2 > V_1 \). Going back to
our version of the first law (Eq. 7.5) and combining it with Eq. 7.11:

\[ dE = dq + dw = TdS - PdV + \mu dn, \]
and restricting ourselves to a closed system (so that \( dn = 0 \)) and a reversible process, our finding that \( dq_{rev} = TdS \) (Eq. 7.43) means that our incremental work is what’s left over:

\[
\delta w_{rev} = -PdV.
\]

We choose the system illustrated in Fig. 8.2: a cylindrical chamber containing 1.00 mole of a compressed gas at an initial volume of 2.478 L, initial pressure of 10.0 bar, and initial temperature of 298 K. Outside the chamber, the pressure is 1.00 bar and the temperature is 298 K. One wall of the chamber consists of a piston, which can be pushed in (reducing the volume and compressing the gas further) or can be released (allowing the gas to expand). For the following expansion problems, we will permit the gas to expand until the pressure inside the chamber is equal to the external pressure of 1.00 bar.

To simplify matters further, we shall assume that the temperature stays constant, making this an isothermal expansion. In the terminology developed earlier, we perform the expansion with the gas in contact with a temperature reservoir through diathermal walls so that heat can flow freely between the sample and the reservoir. Even so, there are always several ways of proceeding from one thermodynamic state to another, and although the energy and other parameters are fixed for each state, the heat and work during the transition depend on the path between the states as well as the states themselves.

A reversible expansion (Fig. 8.3a) is possible only if the gas is allowed to expand slowly, maintaining equal pressure on both sides of the piston at all times. If the gas pressure differed significantly from the pressure exerted by the walls, then the sample would expand or contract suddenly, not quasistatically. An irreversible expansion (Fig. 8.3b) would take place, pushing rapidly on the surrounding gas and therefore heating it up. For irreversible processes, we must acknowledge that these pressures are not necessarily equal and return to the more general form of (Eq. 7.41) \( \delta w = -P_{\text{min}}dV \). For a reversible process, the change in entropy of the sample \( dS \) need not be zero. The change in the total

\[\begin{align*}
\text{Initial state} & \quad \text{Final state} \\
P_1 &= 10.0 \text{ bar} \\
n &= 1.00 \text{ mol} \\
T &= 298 \text{ K} \\
V_1 &= 2.478 \text{ L} \\

P_2 &= 1.00 \text{ bar} \\
n &= 1.00 \text{ mol} \\
T &= 298 \text{ K} \\
V_2 &= 24.78 \text{ L}
\end{align*}\]

\[\begin{align*}
\text{FIGURE 8.2} & \quad \text{The expansion apparatus.} \quad \text{The walls of the chamber are diathermal for the isothermal expansions.}
\end{align*}\]

\[\begin{align*}
\text{(a)} & \quad P_{\text{ext}} \approx P \\
\text{(b)} & \quad P_{\text{ext}} \ll P
\end{align*}\]

\[\begin{align*}
\text{FIGURE 8.3} & \quad \text{Reversible and irreversible expansion.} \quad \text{(a) The reversible expansion occurs when the pressure } P \text{ of the sample and the external pressure } P_{\text{ext}} \text{ differ by an infinitesimal amount } (P = P_{\text{ext}} = P_{\text{min}}). \quad \text{(b) If } P \text{ is much greater than } P_{\text{ext}} \text{ then the expansion occurs rapidly and irreversibly } (P > P_{\text{ext}} = P_{\text{min}}).
\end{align*}\]
entropy must be zero, and that’s no easy trick. The entropy of the sample may increase during a reversible process only if it is balanced by a decrease in the entropy of a reservoir or some other component of the system.

For the reversible isothermal expansion, we plot the initial and final states on a \( P-V \) graph and draw the reversible isothermal expansion as the curve \( P = \frac{nRT}{V} \) joining the two points. This is done in curve a of Fig. 8.4. Non-quasistatic processes may involve states in which pressure and volume are poorly defined.

For the reversible isothermal process, we will write the work as \( w_{T, \text{rev}} \), where the \( T \) indicates that \( T \) is held constant. The work can be evaluated as

\[
\begin{align*}
  w_{T, \text{rev}} &= \int_{V_1}^{V_2} P dV \\
  &= \int_{V_1}^{V_2} \frac{nRT}{V} dV \\
  &= -nRT \ln \left( \frac{V_2}{V_1} \right) \\
  &= \frac{nRT \ln \left( \frac{V_2}{V_1} \right)}{V_1}.
\end{align*}
\]

(8.1)

where the pressure \( P \) is a state function determined by the other parameters, such as \( T \) and \( V \). The magnitude of this integral is the area under the curve \( P \) between the two points representing the initial and final states. The sign of \( w \) is determined by which state is the upper limit and which is the lower limit of the integral; expansion requires work to be done by the system, whereas compression requires work be done to the system. We can solve the integral by recognizing that

\[
V_2 = \frac{nRT}{P_2} = \frac{(1.00 \text{ mol})(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{1.00 \text{ bar}} \approx 24.8 \text{ L},
\]

and by expressing the pressure in terms of the parameter \( V \) and the constants \( n \) and \( T \):

\[
P = \frac{nRT}{V}.
\]

For the reversible isothermal expansion,

\[
\begin{align*}
  w_{T, \text{rev}} &= -\int_{V_1}^{V_2} P dV = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \\
  &= -nRT \ln \left( \frac{V_2}{V_1} \right).
\end{align*}
\]

(8.2)

This is a general result for the work obtained from the reversible isothermal expansion of an ideal gas. Substituting in the values from Fig. 8.2 gives

\[
w_{T, \text{rev}} = -(1.00 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})\ln \left( \frac{24.78}{2.478} \right) \\
= -5.71 \times 10^3 \text{ J} = -5.71 \text{ kJ}.
\]

The integral in Eq. 8.1 cannot be used for irreversible processes, for which the pressure need not be a continuous function at all. When we introduced Eq. 7.41, we used \( P_{\text{min}} \) instead of \( P \) for the sample to express the work, because the amount of work done depends on the force opposing the work. In any case, this is the convenient way to write the equation for cases where the external pressure is well-known but the pressure of the gas itself is not a smooth function of \( T \) and \( V \). For example, if the tension on our piston is released completely, the expansion of...
8.1 Expansion of Gases

Expansion of Gases

We find the work done by the system when we integrate Eq. 7.41, where $P_{\text{min}}$ in this case is the constant external pressure of 1.00 bar:

$$w_{T,\text{irr}} = \int_{V_1}^{V_2} P_{\text{min}} dV$$

$$= -P_{\text{min}} (V_2 - V_1),$$

and for our case that gives

$$w_{T,\text{irr}} = -(1.00 \text{ bar})(24.78 \text{ L} - 2.478 \text{ L})$$

$$= -22.3 \text{ bar L} = -2.23 \text{ kJ}.$$
This process is plotted as curve b in Fig. 8.4. Again, acknowledging the sign
convention, \( w \) gives the energy lost through work done by the sample, so it is
negative.

Of these examples, the reversible expansion does the most work, and this
result holds for all processes. This is because in the reversible expansion, the
forces that oppose each other must be as evenly matched as possible at every
point during the process. In our irreversible expansions, \( P_{\text{min}} \) is significantly
lower than \( P \), and therefore the integral of \( P_{\text{min}}dV \) is lower. The system does less
work because it doesn’t have to push as hard.

The energy \( E \) for a monatomic ideal gas is just
\[ \frac{3}{2}nRT \] (Eq. 3.59), a function
only of the number of moles and the temperature. Therefore, in the isothermal
expansion of an ideal gas, \( \Delta E = q + w \) is zero because the temperature of the gas
doesn’t change. Since the sample does work during the expansion, meaning \( w \) is
negative, then heat must be absorbed from the reservoir in order to keep the sample
temperature the same, with the total heat influx equaling the amount of work
done (Fig. 8.6). So, for example, in our reversible isothermal expansion, the heat
flow is
\[ q_{T,\text{rev}} \ll nRT \ln \left( \frac{V_2}{V_1} \right) \],
(8.4)
and for the irreversible isothermal expansion as just given,
\[ q_{T,\text{irr}} = P_{\text{min}}(V_2 - V_1) \].
(8.5)
In either case, heat flows from the reservoir while the temperature doesn’t
change. The reservoir is so vast that heat can flow constantly in and out of it,
without measurably affecting the properties of the reservoir itself.

Also worth noticing is that even though this is a reversible process, the
entropy of the sample does change: \( dq_{\text{rev}} \neq 0 \) and \( dS = dq_{\text{rev}}/T \). This requires
the reservoir to respond with its own entropy change that exactly cancels the
sample’s change in entropy.

**Adiabatic Expansion**

So can we keep the total entropy and the system entropy constant? Consider now
the case when the expanding gas is contained within adiabatic walls, which
forbid the transfer of heat from the outside. Again we carry out the reversible
expansion, from the same initial conditions until the final pressure equals the
external pressure of 1.00 bar. For such an adiabatic expansion, \( dS = 0 \) because
\( dq_{\text{rev}} = TdS \), so the change in energy comes from work alone:

reversible adiabatic process: \[ dE = dw_{S,\text{rev}} = -PdV \],
(8.6)
where now the subscript \( S \) indicates that this is the work for the adiabatic process,
where \( S \) of the sample is constant. We are continuing to assume a closed sample
(meaning \( dn = 0 \)), so the only work done is \( PV \) work.

We assume furthermore that the ideal gas law still applies:
\[ dE = -PdV = -\frac{nRTdV}{V} \].
(8.7)
If we want only to solve for the work during this process, Eq. 8.7 may look
sufficient; we could integrate it from \( V_1 \) to \( V_2 \) to get \( \Delta E \), and that would be
the work. There are two problems with that: (i) because the sample is thermally insulated from the surroundings, its temperature no longer needs to be constant and therefore \( T \) cannot be factored out of the integral; and (ii) with the temperature changing, we no longer know what the final volume \( V_2 \) is. Somehow we ended up with not enough equations for the number of unknowns we have.

**TOOLS OF THE TRADE**  **Bomb Calorimetry**

The distinction between heat and temperature was not well established until the end of the 19th century, and consequently there was no consistent theory to describe the release or absorption of heat by chemical processes such as phase changes or chemical reactions. Around 1780, Antoine Lavoisier and Pierre Laplace together developed an instrument for measuring heats of various processes, which they gauged by the amount of ice melted, but the work was ahead of its time. Nearly a century later, Marcellin Berthelot developed the first modern device for measuring the heat flow in a chemical reaction: the bomb calorimeter.

What is a bomb calorimeter? A calorimeter is any device that measures the heat flow during a process. Calorimeters are the chief diagnostic tool in thermodynamics, and we will draw on many results from calorimetry in the chapters ahead. A bomb calorimeter is any calorimeter that operates with the sample at a fixed volume.

Why do we use a bomb calorimeter? Standard bench-top conditions in the laboratory allow us to maintain a constant temperature of the system (using a water bath or heating mantle) and a constant pressure (by exposure to the atmosphere or—for air-sensitive compounds—by working in a glove-box filled with an inert gas at fixed pressure).

Why is fixed pressure important? Keeping the pressure fixed reduces the number of changing variables, which is convenient for record keeping alone, but it also simplifies the thermodynamics whenever we can set one parameter to a constant. By fixing the pressure, we ensure that the enthalpy change during a process is equal to the heat:

\[
\Delta H = \int dH = \int (TdS + VdP)
\]

\[
(\Delta H)_P = \int (TdS + VdP)_P = \int (TdS) = q \text{ if } dP = 0,
\]

where the subscript \( P \) indicates that the pressure is kept constant. The enthalpy was invented to make this relationship true.

But we have a more general definition—and a more intuitive understanding—of the energy \( E \). If we want to measure \( \Delta E \) instead of \( \Delta H \), however, the experiment can be much more challenging. The combustion of sucrose, for example,

\[
C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O
\]
We can figure out what that missing equation is. Whenever we want to find $\Delta E$ for a sample while $T$ varies, we will need the heat capacity because that defines the relationship between $\Delta E$ and $\Delta T$. So the equation we are missing must involve the heat capacity. For an ideal gas, the energy from the equipartition principle is (Eq. 3.20)

$$E = \frac{1}{2} N_e p_n R T.$$  

For a closed sample of an ideal gas, $E$ is a function only of the temperature. Now we can find the final thermodynamic state of our reversible adiabatic expansion:

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT = C_V dT$$  

(8.8)

$$C_V dT = -\frac{n R T dV}{V}.$$  

combine Eqs. 8.7 and 8.8

$$\int_{T_1}^{T_2} \frac{C_V dT}{T} = -\int_{V_1}^{V_2} \frac{n R dV}{V}$$  

isolate like variables and integrate

$$C_V \ln \frac{T_2}{T_1} = -n R \ln \frac{V_2}{V_1} \int (dx/x) = \ln x + C$$  

(8.9)

$$C_V \ln \frac{P_2 V_2/(nR)}{P_1 V_1/(nR)} = C_V \ln \frac{P_2 V_2}{P_1 V_1} = -n R \ln \frac{V_2}{V_1}$$  

$$PV = nRT$$  

$$C_V \left[ \ln \frac{P_2}{P_1} + \ln \frac{V_2}{V_1} \right] = -n R \ln \frac{V_2}{V_1}$$  

$$\ln xy = \ln x + \ln y$$

liberates roughly 6000 kJ of heat per mole of sucrose and forms 23 product molecules for every 13 reactant molecules. In order to directly measure the $\Delta E$ of the reaction, we would choose to carry it out at constant volume rather than constant pressure. In that case, the heat measured by the calorimeter is equal to the change in energy:

$$\Delta E = \int dE = \int (T dS - P dV)$$

$$\langle\Delta E\rangle_V = \int (T dS - P dV)_V = \int (T dS) = q.$$  

A bomb calorimeter yields the energy change during a reaction directly, and as such provides a more direct link between the heat released or absorbed by a reaction and our understanding of chemical bond energies. What’s not to like?

The challenge is that the reaction takes place quickly, and therefore the 6000 kJ/mol released by the reaction initially heats the products, raising the temperature and pressure of the system to many times its initial pressure. The calorimeter risks exploding like a bomb.

The distinction between enthalpy and energy in solution-phase chemistry is usually very small, so constant-pressure calorimeters are more common. Bomb calorimeters today are primarily to characterize gas-phase reactions and combustion processes, which may occur so rapidly or violently that the sample needs to be contained. Related processes studied by bomb calorimetry include the incineration of toxic wastes and the metabolism of foods.

**How do they work?** A typical bomb calorimeter consists of a small steel drum (the bomb) submerged in 2 L of water, with a thermometer monitoring the water temperature to high precision. The sample is in a rigid container, so it can do no work, but heat can be transferred between the sample and the surrounding water. By conservation of energy, we can write the energy change of the system as

$$\Delta E_{sys} = -\Delta E_{water} = -q_{water} = -C_V \Delta T_{water}.$$  

From the measured change in the temperature of the water and the known heat capacity of the water, the energy change of the system can be calculated. Bomb calorimeters designed specifically for combustion reactions, such as the one shown in the figure, also include a regulated oxygen supply and a nickel heating coil that ignites the fuel.
Expansion of Gases

\[ \frac{C_V}{R} \ln \frac{P_2}{P_1} = -(C_V + nR) \ln \frac{V_2}{V_1} = -(C_P) \ln \frac{V_2}{V_1} \quad \text{combine terms, Eq. 7.55} \]

\[ V_2 = V_1 \left( \frac{P_2}{P_1} \right)^{-C_V/C_P} \quad \text{solve for } V_2 \ (8.10) \]

Here the heat capacity is assumed constant over the temperature range in the integral, an assumption with limitations illustrated by Fig. 7.5. The accuracy of the approximation is improved by averaging the heat capacity over the temperature range. The Appendix gives heat capacities and other data for various species.

Let’s use again our expansion apparatus, redrawn in Fig. 8.7, but this time we cannot calculate the final volume or the work done until we have a value for the heat capacity \( C_V \). Assume the gas to be an ideal monatomic gas with \( C_{Vm} = 3R/2 \).

When the pressure of the system is lessened reversibly, and the ambient pressure is 1.00 bar, the final volume \( V_2 \) is not 24.78 L but

\[ V_2 = V_1 \left( \frac{P_2}{P_1} \right)^{-C_V/(C_V + nR)} = (2.478 \text{ L}) \left( \frac{1}{10.0} \right)^{-3/5} = 9.87 \text{ L}. \]

This time there is no flow of heat to maintain the same energy, and \( E \) decreases during the expansion because \( \Delta E = w \). With \( E \) directly proportional to the temperature, the temperature of the gas drops also. This in turn affects the product \( PV \) of the gas. In this adiabatic expansion, the gas cannot expand to the final volume of 24.78 L reached in the isothermal expansion, because now the gas cools as it expands, and so it reaches the stipulated final pressure of 1.00 bar at a lower volume. The work done during this expansion is equal to \( \Delta E = C_V \Delta T \), and \( T_2 \) can be found using the ideal gas law:

\[ T_2 = \frac{P_2 V_2}{nR} = \frac{(1.00 \text{ bar})(9.87 \text{ L})}{(1 \text{ mol})(0.083145 \text{ bar L K}^{-1} \text{ mol}^{-1})} = 119 \text{ K}. \]

The work done is

\[ w_{S, \text{rev}} = nC_{Vm}(T_2 - T_1) = (1.00 \text{ mol}) \frac{3R}{2} (119 \text{ K} - 298 \text{ K}) = -2.23 \text{ kJ}. \]

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**CHECKPOINT** Why does the math surrounding the adiabatic expansion seem so much more involved than the math for the isothermal expansion? For the isothermal expansion, \( T \) and \( n \) are fixed and the ideal gas law can then relate \( P \) and \( V \) directly. The adiabatic expansion fixes \( S \) and \( n \), but \( S \) does not appear in the ideal gas law, so we still have three parameters—\( P, V, \) and \( T \)—all varying. That is why we need to introduce an additional equation before we can solve for all the variables.

**FIGURE 8.7** The adiabatic expansion. The walls do not allow heat to flow in, so work done by the expanding gas channels energy out of the sample, lowering the gas temperature.
The $P$-$V$ graph for this expansion is given in curve c of Fig. 8.8.

Rapid, uncontrolled expansions are often approximated to take place under adiabatic conditions because there simply may not be enough time for heat to be transferred into the sample. Combining the expressions we have for $\Delta E$ and for $V_2/V_1$, we can get a common expression for the energy released by our expansion in terms of the initial pressure and volume and the final pressure:

$$w_{S,\text{rev}} = C_V(T_2 - T_1) \quad (8.11)$$

Similarly:

$$= C_V \left[ \frac{P_2V_2}{nR} - \frac{P_1V_1}{nR} \right] \quad PV = nRT$$

$$= \frac{C_V}{nR} \left[ P_2V_1 \left( \frac{P_2}{P_1} \right)^{-C_P/C_V} - P_1V_1 \right] \quad \text{by Eq. 8.10}$$

$$= \frac{C_V}{nR} (P_1V_1) \left[ \frac{P_2}{P_1} \left( \frac{P_2}{P_1} \right)^{-C_P/C_V} - 1 \right] \quad \text{factor out } P_1V_1$$

$$= \frac{C_V}{nR} \left[ \frac{P_2}{P_1} \left( \frac{P_2}{P_1} \right)^{-C_P/C_V} - 1 \right]$$

$$= \frac{1}{(C_P/C_V) - 1} (P_1V_1) \left[ \left( \frac{P_2}{P_1} \right)^{1-(C_P/C_V)} - 1 \right]$$

$$= \frac{P_1V_1}{\gamma - 1} \left[ \left( \frac{P_2}{P_1} \right)^{1-(C_P/C_V)} - 1 \right]. \quad \text{set } \gamma = C_P/C_V \quad (8.12)$$

The heat capacity ratio $\gamma = C_P/C_V$ is at its maximum value of 5/3 for the ideal monatomic gas. As the complexity and mass of the gas molecule increases, the number of available equipartition degrees of freedom $N_{eq}$ also rises, so the ratio of $C_P = C_V + nR$ to $C_V$ approaches 1. For gas molecules, however, the value is rarely less than 1.1.

Equation 8.12 shows—as we might expect—that the work done depends primarily on (i) $P_1V_1$, proportional both to the amount of material $n$ available at the beginning of the expansion and to its temperature $T_1$; and on (ii) the compression ratio $P_2/P_1$ between the final and initial pressures. If we divide $w$ by $n = P_1V_1/(RT_1)$ to get roughly the work per unit of material, then we find that the work done does not vary enormously over the range of likely $\gamma$ values (Fig. 8.9). At low compression ratios, a gas with high heat capacity (smaller $\gamma$) can do more work because it contains more energy at a given temperature than, for example, a monatomic gas. At very high compression ratios, however, a high heat capacity becomes a liability for doing work because the gas loses more energy upon cooling, and it rapidly reaches too low a temperature to continue expanding.

However, the work increases steeply with the compression ratio $P_2/P_1$, so a highly compressed gas can do a lot of work—or a lot of damage—as it expands.


**FIGURE 8.9** Compression ratios and work. The work per mole $w_{\text{rev}}/n$ is graphed as a function of the compression ratio $P_2/P_1$, based on Eq. 8.12 and assuming an initial temperature of $T_1 = 300$ K. The curve for $\gamma = 5/3$ corresponds to the monatomic gas, and $\gamma = 13/12$ corresponds to a 5-atom molecule with all vibrations included (full equipartition in Table 7.2). The two cross at high compression ratio.

### EXAMPLE 8.2 Explosions as Adiabatic Expansions

**CONTEXT** In the latter part of the 19th century, one rapid area of development in chemistry was the synthesis of new explosives, which were needed for mining coal to fuel the industrial revolution. From this period, we learned how to make a number of organic peroxides, such as HMTD (hexamethylene triperoxide diamine). These are compounds which, following a general rule of explosives, combine combustible elements such as carbon and hydrogen with oxygen. This strategy allows the combustion reaction to occur on the time scale of molecular motion, rather than diffusion, and the release of energy propagates through the material faster than the speed of sound. However, the organic peroxides combine this with extremely fragile $\text{O-O}$ bonds, making compounds that may blow up at the slightest shock. A temperamental explosive is a liability in most settings, and HMTD is no longer used for industrial applications. The energy of such an explosion can be channeled into: (a) the energy required to break the container, (b) the energy of the pressure front at the head of the expansion, and (c) the kinetic energy of any projectiles propelled by the expanding gas. If the container is fragile, as much as 80% of the energy released by the explosion is likely to be in the pressure wave.

![Chemical structure of HMTD](image)

**PROBLEM** If 1.0 L of hexamethylene triperoxide diamine (HMTD) explodes by suddenly decomposing to gases at a pressure of 1.0 kbar at the ambient temperature, calculate the grams of TNT that would release a pressure wave of equal energy, assuming $4680 \text{ J/gTNT}$, and assuming the explosion is reversible. Assume an average value for $\gamma$ of 1.4, an ambient pressure of 1.0 bar, and that 70% of the energy is in the pressure wave.

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1. It has been common practice to model explosions as reversible adiabatic expansions, as shown in this example, although the fast time scale and generation of a shock wave clearly indicate that the process is irreversible. This approximation has the advantage of establishing an upper limit to the power of the explosive so that a reasonable margin of safety can be set, but irreversible models do tend to agree better with experiment. Problem 8.10 offers a simple example of an irreversible adiabatic expansion.
### Joule-Thomson Expansion

There is a special case of the adiabatic expansion in which the enthalpy is held constant, even while \( P, V, \) and \( T \) are all permitted to change. A schematic apparatus for the experiment is shown in Fig. 8.10. A gas is initially at pressure \( P_1 \), volume \( V_1 \), and temperature \( T_1 \), and is separated by a permeable plug from a second container. The plug allows gas to flow, but it prevents the temperatures and pressures of the two containers from equilibrating. We press a piston in container 1 to push the gas into container 2, where a second piston is pulled out to make a volume for the gas to expand into. The critical feature is that the expansion from one container into the other is carried out at constant pressure \( P_1 \) in the first container and a constant pressure \( P_2 \) in the second container. In order for the gas to flow from 1 to 2, \( P_2 \) is always less than \( P_1 \). The experiment ends when all the gas has been pushed from container 1 to container 2. No heat is permitted to flow into the system or between the two containers.

Because no heat could flow, the change in energy in each container is just equal to the work \( w \) in each container, and \( \Delta E \) overall is equal to the sum of the work in container 1 and the work in container 2:

\[
\Delta E = w_2 + w_1.
\]  

(8.13)

Furthermore, because we kept the pressure in each container constant, the work in each container is just \(-P\Delta V\). Therefore,

\[
\Delta E = -P_2(V_2) - P_1(-V_1) = P_1V_1 - P_2V_2.
\]  

(8.14)

---

**SOLUTION** Equation 8.12 allows us to predict the maximum work from the expansion:

\[
w = \frac{P_1V_1}{\gamma - 1} \left( \frac{P_2}{P_1} \right)^{(\gamma - 1)/\gamma} - 1.
\]

\(P_1\) is the initial pressure of the expanding gases (1.0 \( \cdot \) 10³ bar), \( V_1 \) is the initial volume (1.0 L), and \( P_2 \) is the ambient pressure (1.0 bar, the pressure at which the expansion will stop). We substitute these numbers and multiply by the factor of 70% to find

\[
w = (0.70) \left( \frac{1.0 \times 10^3 \text{ bar}}{1.0 \times 10^5} \right)^{1/(1.4)} - 1 = -1.5 \times 10^3 \text{ bar L}
\]

\[m_{\text{TNT}} = (1.5 \times 10^3 \text{ bar L}) \left( \frac{100 \text{ J}}{1 \text{ bar L}} \right) \left( \frac{1.0 \text{ g TNT}}{4680 \text{ J}} \right) = 32 \text{ g TNT}.
\]

**EXTEND** Notice that the initial temperature of the gases was assumed to be ambient, rather than extremely hot. Oddly enough, although we often associate explosions with highly exothermic reactions, the destructive force in the most common explosions is primarily mechanical energy—not chemical energy—generated by the rapid expansion of gases that suddenly find themselves at much higher pressure than their surroundings. It is difficult to study the chemical mechanisms at work in explosions, because the dynamics are so rapid, but HMTD is one example where the molecule may fall apart so quickly that relatively little combustion actually occurs. Because energy is needed for the initial bond breaking, the net reaction is sometimes only weakly exothermic and may even be endothermic. Nonetheless, the mechanical energy released when one solid-phase molecule becomes four or five gas-phase molecules—driven to occupy thousands of times their current volume—can have devastating results.
This difference doesn’t have to be zero, because we can pick $V_1$ and $V_2$ to be almost anything we want, so we can get the energy to change during this process. However, it turns out that these conditions force the enthalpy to be constant, because the change in energy is exactly balanced by the change in $PV$:

$$\Delta H = \Delta(E + PV) = \Delta E + \Delta(PV) = (P_1V_1 - P_2V_2) + (P_2V_2 - P_1V_1) \quad \text{by Eq. 8.14}$$

$$= 0.$$  \hspace{1cm} (8.15)

This is called the **Joule-Thomson expansion**, after James Joule and William Thomson (also known as Lord Kelvin, of absolute temperature fame).

To calculate the actual work and $\Delta E$ values is a task we’ll leave for an exercise, but a simpler question we can answer for now is this: at the plug that separates the two containers, how much does the temperature change as the pressure drops? Mathematically, we are looking for the derivative of $T$ with respect to $P$ at constant enthalpy; this number is called the **Joule-Thomson coefficient**, $(\partial T/\partial P)_H$.

It can be expressed in terms of the heat capacity of the gas by use of the chain rule (Table A.4):

$$\left(\frac{\partial T}{\partial P}\right)_H = -\left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T = -\frac{1}{C_P} \left(\frac{\partial H}{\partial P}\right)_T.$$  \hspace{1cm} (8.16)

The remaining partial derivative in Eq. 8.16 may be written in terms of the coefficient of thermal expansion $\alpha$ as follows:

$$\left(\frac{\partial H}{\partial P}\right)_T = \left(\frac{TdS + VdP}{dP}\right)_T = \frac{dH}{dP} = TdS + VdP$$

$$\quad \quad \quad = T\left(\frac{\partial S}{\partial P}\right)_T + V$$

$$\quad \quad \quad = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -TV\alpha + V.$$  \hspace{1cm} (8.17)

The third step uses one of our Maxwell relations (Eq. 7.30).

The Joule-Thomson coefficient is

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{TV\alpha - V}{C_P}.$$  \hspace{1cm} (8.18)

This formula is valid for any gas in a closed system, ideal or not. For the ideal gas, we have already shown (Eq. 7.54) that $\alpha = 1/T$, which sets the Joule-Thomson coefficient to zero. For the ideal gas, the temperature of the gas does not change during this expansion, so $P_1V_1 = nRT = P_2V_2$, and therefore $\Delta E = 0$ as well.

To estimate how a real gas will deviate from the ideal gas, we add the simplest non-ideal term to the ideal gas law—namely, the second virial coefficient $B_2(T)$ from Eq. 4.39:

$$P = RT\left[ V_m^{-1} + B_2(T)V_m^{-2} \right]$$

The Joule-Thomson coefficient depends on $V$, $T$, $\alpha$, and $C_p$ (Eq. 8.18). We leave the temperature in the expression, temperature being one of the parameters we measure, and we treat the heat capacity $C_p$ as an empirical parameter for the non-ideal gas. The non-ideality appears in $V$ and in $\alpha$. 
To evaluate $V$ and $\alpha$, we want a simple formula for the volume that includes the correction from the virial expansion:

$$V = \frac{nRT}{P} \left( 1 + \frac{n}{V} B_2(T) \right).$$  \hspace{1cm} (8.19)

Taking the derivative of this equation to get $V\alpha$ is straightforward, keeping in mind that $V$ is a function of $T$:

$$V\alpha = \left( \frac{\partial V}{\partial T} \right)_P = \frac{nRT}{P} \left( \frac{\partial B_2}{\partial T} \right)_P \left[ V + \frac{nRT^2}{P} \left( \frac{\partial B_2}{\partial T} \right)_P - V \right]$$

$$= \frac{V}{T} + \frac{nRT}{P} \left[ - n \frac{RT}{V^2} B_2(T) \left( \frac{\partial V}{\partial T} \right)_P + n \left( \frac{\partial B_2}{\partial T} \right)_P \right].$$  \hspace{1cm} (8.20)

We have neglected $nB_2(T)/V$ compared to 1. Because $(\frac{\partial V}{\partial T})_P$ appears on both sides of the equation, we combine both sides to solve for $V\alpha$:

$$V\alpha = \left( \frac{\partial V}{\partial T} \right)_P = \frac{V}{T} + \frac{nRT}{P} \frac{n}{V} \left( \frac{\partial B_2}{\partial T} \right)_P.$$  \hspace{1cm} (8.21)

Finally, we go back to the Joule-Thomson coefficient,

$$\left( \frac{\partial T}{\partial P} \right)_H = \frac{TV\alpha - V}{C_p}$$

$$= \frac{1}{C_p} \left[ \frac{nRT^2}{P} \frac{n}{V} \left( \frac{\partial B_2}{\partial T} \right)_P - \frac{nRT}{P} \frac{n}{V^2} B_2(T) \right]$$

$$= \frac{1}{C_p} \left[ \frac{nRT^2}{PV} \left( \frac{\partial B_2}{\partial T} \right)_P - B_2(T) \right]$$

$$= \frac{1}{C_p} \left[ \frac{PV}{nRT} \left( \frac{\partial B_2}{\partial T} \right)_P - B_2(T) \right]$$

$$= \frac{1}{C_p} \left[ \frac{PV}{nRT} \left( \frac{\partial B_2}{\partial T} \right)_P \right]$$

$$= \frac{1}{C_p} \left[ \frac{PV}{n^2RT} + B_2(T) \right]$$

$$= \frac{1}{C_p} \left[ \frac{PV}{n^2RT} + \frac{B_2(T)}{V} \right]$$

$$= \left( \frac{\partial T}{\partial P} \right)_H \text{ cancel like factors}$$

$$= \frac{PV}{nRT} = 1$$
Expansion of Gases

\[ V_m \ll B_2(T) \]

so \( 1/n = V_m/V \ll B_2(T)/V \)

The final expression, Eq. 8.22, is simple, but not terribly informative yet. We need only one more step to pull out predictions, however, and that is to rewrite \( B_2(T) \) and \( (\Delta\mu/\Delta T)_P \) in terms of the van der Waals coefficients \( a \) and \( b \) (Table 4.2):

\[ B_2(T) = b - \frac{a}{RT} \left( \frac{\partial B_2}{\partial T} \right)_P = \frac{a}{RT^2}. \]  

(8.23)

Now we can write

\[ \left( \frac{\partial T}{\partial P} \right)_H = \frac{a}{RT^2} - \frac{b - \frac{a}{RT}}{C_{P_m}} \]  

(8.24)

Recall that \( b \) represents the excluded volume—roughly the volume of the container occupied by the molecules themselves—and \( a \) represents the strength of the intermolecular attraction. Both are positive. We consider two limits:

at high \( T \): \[ \left( \frac{\partial T}{\partial P} \right)_H = \frac{-b}{C_{P_m}} \]  

(8.25)

at low \( T \): \[ \left( \frac{\partial T}{\partial P} \right)_H = \frac{2a}{RTC_{P_m}} \]  

(8.26)

Although we have not considered the exact form of \( C_{P_m} \), it’s safe to say that it is always positive. When the temperature is high, therefore, the Joule-Thomson coefficient is negative—which means that the temperature decreases as the pressure increases. For our adiabatic expansion, the temperature would rise as the gas expands and the pressure drops. At low temperature, on the other hand, the \( a \) term dominates, and the coefficient is positive—meaning that the gas cools off as it expands.

Consider the following qualitative pictures of what happens. Gas-phase molecules that share a large \( a \) coefficient tend to form weakly bonded complexes, easily dissociated by the impact of another molecule. When this sample expands rapidly into a vacuum, the density decreases. Many of the weakly bonded complexes are dissociated by collisions with other molecules and are not replaced, because the formation of weakly bonded complexes is unlikely at low densities. Therefore, the sample goes from a state in which many of the molecules are weakly bound, at low potential energy, to a state in which nearly all the molecules are unbound, and therefore at higher potential energy. This requires a conversion of kinetic energy into potential energy (collisions lose energy to the breaking of the van der Waals bonds), which lowers the temperature (Fig. 8.11a).
On the other hand, molecules with very low \( a \) coefficients, or at very high temperatures, form no significant number of complexes. Instead, the chief interaction between the molecules involves only the repulsive wall of the intermolecular potential. At high densities, the molecules spend much of their time in regions of high potential energy next to other molecules. When such a sample expands, it is like spilling a jar of marbles; the potential energy required to keep the molecules stored next to each other is converted to kinetic energy as the molecules roll away from each other (Fig. 8.11b). The sample heats up.

A compressed gas cylinder of helium or methane typically gets filled to a pressure of over 100 bar. Compared to this, 1 bar is negligible, and the liberation of a gas from one of these high-pressure cylinders—to fill a balloon or fuel a methane torch, for example—is approximately a Joule-Thomson expansion. Most gases at room temperature are still in the low temperature limit, and the gas cools as it expands. For \( \text{H}_2 \) and He gas, however, the molecules are so non-polarizable and the intermolecular forces so weak that the \( a \) constant is extremely small, and even at room temperature the Joule-Thomson coefficient is negative. These gases warm up as they expand against a low pressure. The temperature at which the Joule-Thomson coefficient changes sign is called the **Joule-Thomson inversion temperature**, and it tells us where the gas crosses the boundary from the dominance of attractive intermolecular forces to dominance by the repulsions.

### Example 8.3 Joule-Thomson Coefficients

**Context** Joule-Thomson cooling occurs in many applications, and understanding the process may be critical to the success of some ventures. For example, one proposal for the reduction of carbon dioxide in the atmosphere is CO\(_2\) sequestration: pumping the CO\(_2\) into gas-tight pockets deep underground, left vacant by the extraction of petroleum.\(^2\) One concern, however, is that the nearly enthalpy-free expansion of CO\(_2\) from a transfer tube into the pocket might lead to substantial Joule-Thomson cooling, potentially leading the CO\(_2\) to freeze and clog the line. The first step toward understanding these dynamics is calculation of the Joule-Thomson coefficient.

**Problem** Use the van der Waals constants to estimate the Joule-Thomson coefficients for He, \( \text{H}_2 \), \( \text{N}_2 \), and CO\(_2\) at 300. K.

<table>
<thead>
<tr>
<th></th>
<th>( a ) (L(^2) bar mol(^{-2}))</th>
<th>( b ) (L mol(^{-1}))</th>
<th>( C_{pm} ) (J K(^{-1}) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>0.034</td>
<td>0.0237</td>
<td>20.88</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>0.247</td>
<td>0.0266</td>
<td>28.58</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>1.37</td>
<td>0.0387</td>
<td>24.09</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>3.66</td>
<td>0.0429</td>
<td>37.11</td>
</tr>
</tbody>
</table>

**Solution** The Joule-Thomson coefficient is approximately equal to

\[
\left( \frac{\partial T}{\partial P} \right)_H = \frac{2a}{RT} - \frac{b}{C_{pm}},
\]

\(^2\)In fact, one idea is that pumping carbon dioxide into these pockets will enhance the removal of methane from the pockets, and the methane can then be sold in order to help finance the sequestration. You might reasonably wonder just what’s supposed to happen with the methane that we would sell to finance the removal of greenhouse gases from the atmosphere.
where $R = 0.083145 \text{bar L K}^{-1} \text{mol}^{-1}$ and $T = 300 \text{K}$. This equation gives the Joule-Thomson coefficient $(\frac{\partial T}{\partial P})_H$ in the awkward units L K$^{-1}$, so we convert $L \text{J}^{-1}$ to bar$^{-1}$ by multiplying by $(10^{-3} \text{ m}^3/\text{L})^3 (10^3 \text{ Pa/bar})$, which increases the value by a factor of 100.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\frac{2a}{RT} (\text{L mol}^{-1})$</th>
<th>$(\frac{\partial T}{\partial P})_H$ (from Eq. 8.24) (K bar$^{-1}$)</th>
<th>$(\frac{\partial T}{\partial P})_H$ (experiment) (K bar$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>$2.8 \cdot 10^{-3}$</td>
<td>$-0.100$</td>
<td>$-0.062$</td>
</tr>
<tr>
<td>H$_2$</td>
<td>$2.01 \cdot 10^{-2}$</td>
<td>$-0.024$</td>
<td>$-0.03$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>$0.110$</td>
<td>$0.24$</td>
<td>$0.27$</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>$0.293$</td>
<td>$0.675$</td>
<td>$1.11$</td>
</tr>
</tbody>
</table>

**EXAMPLE 8.4 The Joule-Thomson Inversion Temperature**

**CONTEXT** Gases in industrial applications suffer from one inconvenient characteristic: at STP, a gas occupies a thousand times the volume of the same substance in liquid form. Numerous chemicals that are gases under normal conditions are liquefied to save shipping costs (since the liquid weighs just as much as the gas, but takes up a lot less space), or to take advantage of the cryogenic properties of liquids with very low boiling points (especially liquid N$_2$, which boils at 77 K, and liquid helium, which boils at 4 K). One standard method for liquefying a gas is to compress it to a high pressure and then let it cool by Joule-Thomson expansion down to its boiling point, where some of the gas will condense. But this backfires if the gas heats up as it expands, if the Joule-Thomson coefficient is negative. A basic liquefier design compresses the gas at ambient temperature, lowers the temperature using a heat exchanger, carries out a Joule-Thomson expansion to convert some of the gas into liquid, and then sends the remaining gas back through the heat exchanger (to cool the incoming gas) whereupon it will cycle through the compressor again. For gases where the Joule-Thomson inversion temperature is very low, it is necessary to pre-cool the gas below its Joule-Thomson inversion temperature. Otherwise, the compressed gas heats up when expanding and doesn't liquefy.

**PROBLEM** Given $a = 0.034 \text{ L}^2 \text{ bar mol}^{-2}$ and $b = 0.0237 \text{ L mol}^{-1}$ for He, and $2.25 \text{ L}^2 \text{ bar mol}^{-2}$ and $0.0428 \text{ L mol}^{-1}$ (respectively) for CH$_4$, calculate the Joule-Thomson inversion temperatures for these gases.
8.2 Engines

We have looked at isolated types of mechanical processes—adiabatic and isothermal expansions in particular. For many applications, however, the interesting cases are when different types of processes are combined. We call a device that continuously converts heat into work a **heat engine**.

Since the heat source can deliver only a finite amount of energy at any given time, practical engines operate by repeating a single cyclic process that performs this conversion, relying on a stable or reproducible heat source.

Let’s consider a couple of general points about these cycles. We’ll keep the assumption that the processes in the engine cycle are quasistatic, because in the gas expansion problems we found that the maximum work was done by the reversible process, and a reversible process must be quasistatic. If all the changes are quasistatic, however, then the cycle must involve more than one type of process. An engine that relied entirely on quasistatic isothermal or adiabatic expansion would never have a net conversion of heat to work because it would only move back and forth along the same path—the same amount of work done by the system would have to be done to the system to get it back to the beginning of the cycle, so the net work would always be zero.

Another way to see this is to recall that the $PV$ work done by or to the system can be represented by the area integral under the $P$ versus $V$ curve of the process:

$$w_{\text{rev}} = -\int_{\text{initial}}^{\text{final}} PdV. \quad (8.27)$$

Whether the work is done by or to the system is determined by the direction of motion along the curve: which is the initial state and which is the final. This determines which point is the upper limit of the area integral and which is...
Richard B. Peterson is professor of mechanical engineering and director of the Advanced Tactical Energy Systems Program at Oregon State University. One of many projects in his research group involving basic thermodynamics is the development of new methods to transfer heat, for example to cool vehicle cabins or protective clothing. It is an ancient problem: how to remove energy from a system that may already be cooler than its surroundings. Opposing the natural flow of heat toward the cooler body requires energy and relies on a series of processes similar to the heat engine cycles described in this chapter. Professor Peterson is investigating mechanical designs based on microchannel components that allow the energy released by a burning hydrocarbon fuel to efficiently pump heat from one location to another, drawing on his expertise in the use of microscopic channels for heat and mass transfer.

If the cycle simply runs back and forth along the same path, the area integrals sum to zero. So to get net work done by the engine, more than one kind of process needs to be used.

**The Carnot Cycle**

One of the simplest such cycles is the *Carnot cycle*, named for Nicolas Carnot, who developed this first model of the heat engine in 1824. (It was Carnot’s model that later inspired Clausius’s studies, eventually leading him to formulate the concept of entropy.) Our system is an idealized steam engine (Fig. 8.12), consisting of an ideal gas in a cylindrical chamber of diathermal walls, trapped by a piston that moves when work is done by the engine. We can heat the gas to some high temperature $T_{\text{hot}}$ by filling a jacket around the chamber with steam, or we can cool the gas down to a much lower temperature $T_{\text{cold}}$ using cold water. The piston is hooked up to a *compressor*, a smaller engine that we can use to compress the gas. We can choose to begin with the piston down (the gas is compressed) and the diathermal wall heating the system to temperature $T_{\text{hot}}$. Call this state A of the engine. (We will label the states by letter and will number the steps that take us from one state to the next.) The cycle then consists of the following four steps (Fig. 8.13):

1. **Isothermal expansion.** The gas expands isothermally at temperature $T_{\text{hot}}$ from pressure $P_A$ and volume $V_A$ to $P_B$ and $V_B$.
2. **Adiabatic expansion.** We expel the steam heating the diathermal wall. Now the system begins to cool off, expanding adiabatically until it reaches temperature $T_{\text{cold}}$ at pressure $P_C$ and volume $V_C$. 

![FIGURE 8.12 Schematic of the Carnot engine.](image)
3. **Isothermal compression.** Now we compress the cooled gas isothermally, using the little engine to push the piston back in, until we get to the conditions $P_D$ and $V_D$, at $T_{\text{cold}}$ (which is maintained by flowing cold water against the wall).

4. **Adiabatic compression.** Finally, we purge the cold water and return to the starting conditions in step 1 by adiabatically compressing the gas until it reaches $T_{\text{hot}}$ as a result of the compression, rather than by heating the diathermal wall again. From here the cycle can begin again by disengaging the compressor and letting the steam back in behind the diathermal wall.

The important point to see in this cycle is that while the gas cycles back and forth between pressure limits of $P_A$ and $P_C$, less work is done on the system in the return half of the cycle (steps 3 and 4) than the system does during the power stroke (steps 1 and 2). From a careful look at Fig. 8.13, we can see why this is so: the return stroke involves compressing the cooled gas, the power stroke is expansion of the heated gas. Heated gas exerts more pressure than cooled gas at the same volume, so it does more work as it expands and requires more work to compress it. The secret of the Carnot cycle is to compress the gas while it is cold and exerts less pressure.

Now let us find the heat and work transferred during each of these stages in terms of the state functions $V$ and $T$. The volumes are all unequal, with $V_A < V_D < V_B < V_C$ and $T_{\text{cold}} < T_{\text{hot}}$.

1. **Isothermal expansion.** The work for step 1 is:

$$w_1 = -\int_{V_A}^{V_B} P(V) dV = -\int_{V_A}^{V_B} \frac{nRT_{\text{hot}}}{V} dV = -nRT_{\text{hot}} \ln \frac{V_B}{V_A},$$

(8.29)

Since the process is isothermal and we are assuming an ideal gas, the energy $E$ is constant. Therefore, $\Delta E = q + w = 0$, and

$$q_1 = -w_1 = nRT_{\text{hot}} \ln \frac{V_B}{V_A},$$

(8.30)

Work is done by the system ($dw_1 < 0$) as it expands against the surroundings, and heat must flow into the system ($dq_1 > 0$) to keep it at constant temperature.
2. **Adiabatic expansion.** For the ideal gas, \( E = C_v T \), so \( \Delta E = C_v \Delta T \). Furthermore, for an adiabatic process \( q = 0 \), so \( \Delta E = w \), giving

\[
w_2 = C_v(T_{\text{cold}} - T_{\text{hot}}) \quad q_2 = 0.
\] (8.31)

Work is still being done by the system, but no heat can flow in to replace the energy lost as work, so the system cools off.

3. **Isothermal compression.** This step is analogous to step 1, but in the opposite direction:

\[
w_3 = - \int_{V_C}^{V_B} P(V)dV = -nRT_{\text{cold}} \ln \frac{V_D}{V_C} \quad q_3 = nRT_{\text{cold}} \ln \frac{V_D}{V_C}.
\] (8.32)

Now work is being done to compress the system \((dW > 0)\), which would heat it up if it were not for the cold temperature reservoir, so heat flows out \((dq < 0)\).

4. **Adiabatic compression.** And this step is analogous to step 2, but in the opposite direction:

\[
w_4 = -C_v(T_{\text{cold}} - T_{\text{hot}}) \quad q_4 = 0.
\] (8.33)

Work is still being done to the system, but now the system heats up since no heat can flow out of the system.

The work done by the system in step 2 exactly cancels the work done to the system in step 4, so the total work over the cycle is

\[
w = w_1 + w_2 + w_3 + w_4 = -nR\left(T_{\text{hot}} \ln \frac{V_B}{V_A} + T_{\text{cold}} \ln \frac{V_D}{V_C}\right).
\] (8.34)

We can simplify this because we learned while working out the properties of the adiabatic expansion that the ratio of the initial and final volumes depends only on the ratio of the initial and final temperatures (Eq. 8.9):

\[
C_v \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1}.
\]

Our steps 2 and 4 are adiabatic expansions at different volumes and pressures, but between the same two temperatures, \(T_{\text{hot}}\) and \(T_{\text{cold}}\). Rewriting Eq. 8.9 for the states in the Carnot cycle, we obtain

\[
C_v \ln \frac{T_{\text{hot}}}{T_{\text{cold}}} = -nR \ln \frac{V_B}{V_C} = -nR \ln \frac{V_A}{V_D}.
\]

Therefore, we can relate the volume ratios \(V_B/V_A\) and \(V_D/V_C\) that appear in Eq. 8.34:

\[
\frac{V_D}{V_A} = \frac{V_C}{V_B}
\]

\[
\frac{V_D}{V_C} = \frac{V_A}{V_B}.
\]

The total work done can then be rewritten:

\[
w = -nR\left(T_{\text{hot}} \ln \frac{V_B}{V_A} + T_{\text{cold}} \ln \frac{V_D}{V_C}\right) = -nR\left(T_{\text{hot}} \ln \frac{V_B}{V_A} + T_{\text{cold}} \ln \frac{V_A}{V_B}\right)
\]

\[
= -nR(T_{\text{hot}} - T_{\text{cold}}) \ln \frac{V_B}{V_A} \quad \ln \frac{V_A}{V_B} = -\ln \left(\frac{V_B}{V_A}\right)
\] (8.35)
This quantity is negative (because \( V_B > V_A \) and \( T_{\text{hot}} > T_{\text{cold}} \)), which implies that over one complete cycle work is done by the system.

The total heat absorbed by the system is the sum of the heats from steps 1 and 3:

\[
q = nR \left( T_{\text{hot}} \ln \frac{V_B}{V_A} + T_{\text{cold}} \ln \frac{V_D}{V_C} \right) = nR(T_{\text{hot}} - T_{\text{cold}}) \ln \frac{V_B}{V_A}. \tag{8.36}
\]

This is \(-1\) times the work, which is a requirement because we have returned to the original thermodynamic state in step 1 by the end of the cycle, so from beginning to end of the cycle \( \Delta E = q + w \) must be zero, and \( q = -w \).

The feature that measures an engine’s usefulness is its ability to convert fuel, which provides the source of the high temperature reservoir at \( T_{\text{hot}} \), into work.

The cooling temperature reservoir is usually available as some recyclable commodity (unlike the fuel), such as water or air. The efficiency \( \varepsilon \) of the engine is therefore given by the ratio of the work obtained to the heat provided by the fuel, \( q_1 \):

\[
\varepsilon = \frac{-w}{q_1} = \frac{nRT_{\text{hot}} \ln \frac{V_B}{V_A}}{nRT_{\text{hot}} \ln \frac{V_B}{V_A}} = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}}. \tag{8.37}
\]

The efficiency cannot be greater than 1, which is required by the conservation of energy. Its highest value is for a very large temperature difference \( T_{\text{hot}} - T_{\text{cold}} \), or in other words, for a very hot fuel source.

Note that the \( P \) versus \( V \) graph is not always the easiest way to draw these cyclic processes. For the Carnot cycle, it would actually be easier to draw the \( T \) versus \( S \) graph, since the isothermal processes are at constant \( T \) and the adiabatic processes are at constant \( S \). This curve is useful for representing the heat evolved or absorbed at each stage of the cycle, just as the \( P \) versus \( V \) graph is illustrative of the work.

**The Otto Cycle**

We can apply these same methods to a device that is more common today than Carnot’s steam engine: the internal combustion engine. An idealized version of the operation of an internal combustion engine is given by the Otto cycle. The system in this case is an adiabatic cylinder with a piston, again connected to a compression engine. This time instead of two temperature reservoirs we need two material reservoirs: a fuel supply line and an exhaust line. Finally, we need a spark plug, which will ignite the fuel.

The steps in the cycle are as follows:

1. Starting this time before the power stroke at \( P_A \) and \( T_A \), we ignite the compressed fuel at volume \( V_A \). The combustion is much more rapid than any mechanical motion, so the pressure and temperature increase to \( P_B \) and \( T_B \) isochorically (at constant volume).
2. Now comes the power stroke. The pressurized combustion products expand adiabatically to pressure \( P_C \) and volume \( V_C \).
3. The piston stops, and the gas cools isochorically, with pressure dropping to \( P_D \). This is a considerable simplification over real devices.
4. Finally, the compressor returns the system adiabatically to volume $V_A$, pressurizing it in the process. In an internal combustion engine, this coincides with replacement of the exhaust gases with fresh fuel.

This process is more easily drawn on an $S$-$V$ graph, consisting only of horizontal adiabats and vertical isochors. The efficiency of this engine, found the same way as for the Carnot cycle, is given by the equation (Problem 8.28):

$$\eta = \frac{T_{\text{hot}} - T_{\text{cold}}}{T_{\text{hot}}} = 1 - \left(\frac{V_A}{V_B}\right)^{(C_p-C_V)/C_V}.$$  \hspace{1cm} (8.38)

The ratio $V_A/V_B$ is the compression ratio, and it appears with an exponent that is positive (since $C_p > C_V$). The bigger the difference in volumes, therefore, the closer the efficiency comes to the ideal value of 1. Greater compression ratios imply greater fuel efficiency.

Since the maximum work is accomplished when the process is reversible, and a reversible process must be quasistatic, uneven or too rapid combustion reduces the engine efficiency. The combustion rate is a function of the fuel as much as the igniter, and control over this parameter has long been a target of petroleum engineering. Lead anti-knocking agents were promoted in the 1920s to improve engine efficiency but were subsequently outlawed as the highly toxic lead found its way into the environment.

**CONTEXT** Where Do We Go from Here?

In the low-temperature Joule-Thomson expansion, the gas is at lower potential energy before the expansion than after. The property that compels the gas to climb up out of the cylinder, expanding and breaking intermolecular bonds to arrive at a less energetically favored state, is the subject of our next chapter: the entropy.

With this introduction to fundamental processes in thermodynamics, we can now look more closely at the entropy and how it controls the evolution of our systems. In particular, we want to find ways of predicting changes in entropy that take advantage of measurements that are straightforward to make, such as temperature, volume, and pressure measurements. Once we have a feel for how entropy directs processes, we will be able to extend these rather formal case studies in thermodynamics to real chemical problems, such as phase transitions and solvation.

**KEY CONCEPTS AND EQUATIONS**

8.1 Expansion of Gases. During the reversible *isothermal expansion* of an ideal gas from volume $V_1$ to $V_2$ at a constant temperature, the change in energy due to work is

$$w_{T,\text{rev}} = -nRT \ln \left(\frac{V_2}{V_1}\right).$$  \hspace{1cm} (8.2)

For the temperature to remain constant, the energy lost as the sample does work must be replaced by an equal energy transferred as heat from the surroundings:

$$q_{T,\text{rev}} = nRT \ln \left(\frac{V_2}{V_1}\right).$$  \hspace{1cm} (8.4)

The irreversible expansion always does less work. If the expansion opposes a constant pressure $P_{\text{min}}$, the work is

$$w_{T,\text{irr}} = -P_{\text{min}} (V_2 - V_1).$$  \hspace{1cm} (8.3)

In an *adiabatic expansion*, heat cannot flow to replace the energy lost to the PV work, so the temperature drops. The work done can be calculated from the initial and final temperatures or pressures:

$$w_{S,\text{rev}} = C_V (T_2 - T_1) = \frac{P_1 V_1}{\gamma - 1} \left[\frac{P_2}{P_1}\right]^{\gamma/(\gamma - 1)} - 1.$$  \hspace{1cm} (8.12)

The Joule-Thomson expansion is a special case of the adiabatic expansion, carried out at constant enthalpy.
The van der Waals equation of gases allows us to predict that the Joule-Thomson coefficient,

\[
\left( \frac{\partial T}{\partial P} \right)_H = \frac{2a}{RT} - \frac{b}{C_{Pm}},
\]  

(8.24)

will be positive for most real gases, meaning that the gas will cool down as the expansion pulls against the intermolecular attractions. In hydrogen, helium, and other gases with very weak intermolecular attractions, the gas may instead heat up as it expands.

**KEY TERMS**

- A **Joule-Thomson expansion** allows a gas to expand at constant enthalpy by maintaining a constant pressure inside and outside the original container. Under these conditions it is possible to observe the balance between attractive and repulsive intermolecular forces.

- At the **Joule-Thomson inversion temperature** of a gas, the **Joule-Thomson coefficient** \( \left( \frac{\partial T}{\partial P} \right)_H \) goes from a positive value (gas cools upon expansion) to a negative value (gas heats up upon expansion).

- A **heat engine** is a device that converts heat into useful work.

- The **Carnot cycle** is a model for a heat engine that operates on a series of reversible isothermal and adiabatic expansions and compressions, loosely based on the design of a steam engine.

- The **Otto cycle** for a heat engine uses a series of reversible isochoric and adiabatic expansions and compressions. The Otto cycle better represents the operation of an internal combustion engine.

- The **heat capacity ratio** \( \gamma \) for a substance is equal to \( C_P / C_V \).

**OBJECTIVES REVIEW**

1. *Predict the transfer of energy as work and as heat in reversible and irreversible expansions and compressions.* Calculate \( w \) for 0.100 mol of an ideal gas compressed reversibly from 2.00 L to 1.00 L at a constant \( T = 298 \, \text{K} \).

2. *Predict the direction of a temperature change in a sample undergoing a Joule-Thomson expansion, based on the relative importance of the intermolecular forces.* Estimate the Joule-Thomson coefficient of neon at 100 K.

3. *Calculate the maximum efficiency for a Carnot heat engine and calculate the heat and work at each stage of the cycle.* If a Carnot engine has a maximum efficiency of 0.30 and \( T_{\text{cold}} = 298 \, \text{K} \), what is the value of \( T_{\text{hot}} \)?

**PROBLEMS**

**Discussion Problems**

8.1 *Indicate whether each of the following parameters would be positive (“+”), negative (”−”), or zero (“0”) during an irreversible, adiabatic compression of an ideal gas from volume \( V_1 \) to a smaller volume \( V_2 \).*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>+, −, or 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_2 )</td>
<td>( \Delta T )</td>
</tr>
</tbody>
</table>

**Parameter | +, −, or 0**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>+, −, or 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>( q )</td>
<td>( \Delta S )</td>
</tr>
</tbody>
</table>

8.2 *A leak in a container allows an ideal gas to escape our sample irreversibly and isothermally at constant pressure. For each of the following parameters, identify any that stay unchanged (for the sample) during this process, any that decrease, and any that increase.*

8.3 *For the isobaric heating of an ideal gas, indicate whether each of the following would be positive (“+”), negative (“−”), or zero (“0”):*

a. \( \Delta E \) b. \( q \) c. \( \Delta P \) d. \( \Delta T \) e. \( \Delta V \)

**Expansions**

8.4 *The reversible isothermal expansion of an ideal gas does 1.00 kJ of work at 325 K, ending at a final volume \( V_2 = 10.0 \, \text{L} \) and pressure \( P_2 = 1.00 \, \text{bar} \). Find the initial volume \( V_1 \).*

8.5 *A 2.5 L volume of a monatomic ideal gas at 298 K is contained by a piston at a constant pressure of 1.00 bar. The piston is lifted by reversible, isothermal, and isobaric addition of 1.00 mole of the same gas through a port in the container. Calculate the work \( w \) in J for this process.*
8.6 Calculate $\Delta G$ for the reversible isothermal expansion of 2.00 mol of an ideal gas from 1.00 L to 20.0 L at 298 K.

8.7 We repeat the isothermal expansion of 1 mol of an ideal gas from 2.478 L to 24.78 L at 298 K, but this time we have a slowly responding piston, such that the pressure inside the sample $P$ is always equal to $2P_{ex} - (1$ bar). Calculate the work, $w$, for the expansion in kJ.

8.8 An irreversible isothermal expansion is carried out in the following system at a temperature of $T = 298.15$ K. An ideal gas is initially at a pressure $P_1 = 10.00$ bar in the chamber. One wall of the chamber is movable, but expansion of the gas is resisted by a spring on the other side of the wall. The spring has a force constant of 504.0 N/cm, the diameter of the tube is 10 cm, and the initial length $z_1$ of the gas chamber is 3.16 cm. The spring exerts a force $F = k(z - z_1)$. Find the values $P_2$, $V_2$, and $z_2$ for the final state, and $q$, $w$, $\Delta E$, and $\Delta H$ for the entire process.

8.9 A chamber has a piston with a cross-sectional area of 10.0 cm$^2$. How far does the piston move during an isothermal expansion of 0.0020 mole of air from 10.0 bar to 1.0 bar at 298 K?

8.10 Calculate the work in J done during the irreversible process when C$_{Vm} = 3$R at 4000 K in a 10 cm$^3$ volume expand adiabatically during an explosion in air, when the air is at 300 K and 1 bar.

8.11 Find an equation for the rate of change in temperature during an adiabatic expansion, $(\frac{dT}{dV})_{k,n}$, in terms of $V$, $\alpha$, $k_T$, and $k_S$.

8.12 Two thermally insulated gas chambers, A and B, are separated by a freely moving adiabatic wall. The chambers contain ideal gases, both initially at 300 K, 10$^5$ Pa, and 10 L. Combustion occurs in chamber A, causing the temperature to increase instantaneously to 1000 K and the number of molecules to double. The gases in both chambers now obey the equation $E = 6nRT$. Calculate the overall $\Delta E$ and $\Delta H$ for the expansion (do not include the combustion), and the final values of $V_A$, $V_B$, $P_A$, $P_B$, $T_A$, and $T_B$.

8.13 Start from 0.100 mol of a monatomic ideal gas at a volume of 5.00 L at 298 K. Find the final pressure if we change the volume adiabatically to bring the gas to a final temperature of 410 K.

8.14 Give the final values of $P$, $V$, and $T$ for a reversible, adiabatic expansion of 1.00 mol of an ideal gas, starting from 2.00 L and 415 K, if 2.0 kJ of work is done by the expansion. The molar heat capacity at constant volume of the gas is 2.5 $R$.

8.15 For the reversible isobaric expansion of $n$ moles of an ideal gas at pressure $P$ from an initial volume $V_i$ to a final volume $V_f$.

a. find an equation for the work $w$.

b. find an equation for the heat $q$.

Use the molar heat capacity of the gas $C_{p,m}$ where necessary.

8.16 This chapter describes a reversible, adiabatic expansion of 1.00 mol of a monatomic ideal gas with the following initial and final conditions:

<table>
<thead>
<tr>
<th>Initial</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P$</td>
<td>10.00 bar</td>
</tr>
<tr>
<td>$V$</td>
<td>2.478 L</td>
</tr>
<tr>
<td>$T$</td>
<td>298 K</td>
</tr>
</tbody>
</table>

We found that $\Delta E = w = -2.24$ kJ. Find $\Delta H$ for this process.

8.17 Calculate $q$ and $w$ for the reversible, isothermal compression of 0.100 mol of air from 2.50 L to 0.25 L at 298 K.

8.18 In this chapter, we described the reversible, isothermal expansion of 1.00 mol of an ideal gas from 2.48 L at 10.00 bar and 298 K to a final pressure of 1.00 bar. Repeat the process from the same starting point, but this time set the final pressure $P_f$ to 0.100 bar. Calculate the following parameters: $a$. $V_2$ $b$. $\Delta E$ $c$. $w$ $d$. $\Delta S$ $e$. $\Delta F$

8.19 Two 10.0 L samples A and B each of 1.00 mole helium are placed in a rigid 20.0 L container on either side of a movable wall. Initially, sample A is at a temperature of 400 K while sample B is at a temperature of 250 K. A thin wire in the movable wall allows heat to transfer reversibly between the two regions, and the samples come to equilibrium. Find the volumes $V_A$ and $V_B$ at equilibrium and the heat transfer $q_A$ for sample A for the process. For helium, $C_{p,m} = 20.88$ kJ$^{-1}$ mol$^{-1}$.

8.20 Sketch a $P$–$V$ graph of the curve for the following cyclical process for an ideal gas:

a. The sample gas expands adiabatically from $P_1$, $V_1$ to volume $V_2$.

b. The sample is compressed isothermally to volume $V_3$.

c. The sample warms isobarically to the initial state.

This process is graphed while the gas refrigerates a container that is in thermal contact with our sample for only one step of this cycle. Label that step "refrig" on your graph.
8.21 For a monatomic ideal gas, set \( \mu = \frac{3}{2} RT \). We reversibly add \( \Delta n \) moles of a monatomic ideal gas to a sample at constant pressure \( P \) and temperature \( T \). Find an equation for the work \( w \) during this process in terms of \( P, T, \) and/or \( \Delta n \). Because adding the gas involves net motion of the molecular mass, the \( \mu \, dn \) term contributes to the work in this problem.

8.22

a. Find an expression for \( \left( \frac{\partial P}{\partial V} \right)_{S, n} \) of any material in terms of any of \( \alpha, C_P, C_V \), or the compressibilities \( \kappa \), where

\[
\kappa_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \quad \kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S.
\]

b. Evaluate this expression when the material is an ideal gas.

8.23 Prove that the Helmholtz free energy \( F \) decreases during a spontaneous expansion at constant \( P \) and \( T \).

8.24 The system sketched in the following figure consists of two rigid (fixed volume) chambers, A and B, which are connected by a porous, thermally insulated membrane. Initially, chamber A has \( n \) moles of a gas and B is empty. Chamber A is heated at a constant temperature \( T_A \), causing the gas to migrate through the membrane into chamber B, which is maintained at a much lower constant temperature \( T_B \). Prove that one of the thermodynamic potentials remains a constant during this process.

8.25 Compress an ideal gas adiabatically from pressure \( P_1 \), volume \( V_1 \), and temperature \( T_1 \) to one-half the volume. What is the final temperature \( T_2 \) in terms of the initial temperature \( T_1 \) and the molar heat capacities \( C_{V_m} \) and \( C_{P_m} \)?

**Engines**

8.26 Find an expression for the heat and work done during steps 1 and 2 of the Otto cycle.

8.27 Calculate the net heat in J consumed by the Carnot cycle graphed in the following figure:

8.28 Prove that the efficiency \( \varepsilon \) of the Otto cycle is given by

\[
\varepsilon = 1 - \left( \frac{V_1}{V_2} \right)^{(C_p - C_v)/C_v}.
\]

8.29 Consider two engines, one running on the Carnot cycle and one on the Carnot cycle. The adiabatic steps of the power strokes are identical for the two engines. Find which engine is more efficient.

8.30 Find the ratio \( \varepsilon_C / \varepsilon_X \), where \( \varepsilon_C \) is the efficiency of a Carnot engine and \( \varepsilon_X \) is the efficiency of an engine with the following cycle.

8.31 Consider a closed (constant \( n \)) heat engine operating on four steps: (a) isobaric expansion from volume \( V_1 \) to \( V_2 \), (b) isochoric cooling from temperature \( T_2 \) to \( T_3 \), (c) isobaric compression from volume \( V_3 \) to \( V_4 \), (d) isochoric heating from temperature \( T_4 \) to \( T_1 \). Find expressions for the energy transferred as work and heat at each step and the total work per cycle, in terms of \( V_1, V_2, T_1, T_2, T_3, \) and \( n \).

8.32 For the process drawn in the following figure, calculate the net work done in one cycle.