

Chapter 2

Thermodynamic Concepts and Processes

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We introduce the concepts of temperature, energy, work, heating, entropy, engines, and the laws of thermodynamics and related macroscopic concepts.

2.1 Introduction

In this chapter we will discuss ways of thinking about macroscopic systems and introduce the basic concepts of thermodynamics. Because these ways of thinking are very different from the ways that we think about microscopic systems, most students of thermodynamics initially find it difficult to apply the abstract principles of thermodynamics to concrete problems. However, the study of thermodynamics has many rewards as was appreciated by Einstein:

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made to me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.¹

The essence of thermodynamics can be summarized by two laws:² (1) Energy is conserved and (2) entropy increases. These statements of the laws are deceptively simple. What is energy? You are probably familiar with the concept of energy from other courses, but can you define it?

¹A. Einstein, *Autobiographical Notes*, Open Court Publishing Company (1991).

²The nature of thermodynamics is summarized in the song “First and Second Law” by Michael Flanders and Donald Swann.

Abstract concepts such as energy and entropy are not easily defined nor understood. However, as you apply these concepts in a variety of contexts, you will gradually come to understand them.

Because thermodynamics describes the macroscopic properties of macroscopic systems without appeal to arguments based on the nature of their microscopic constituents, the concepts of energy and entropy in this context are very abstract. So why bother introducing thermodynamics as a subject in its own right, when we could more easily introduce energy and entropy from microscopic considerations? Besides the intellectual challenge, an important reason is that the way of thinking required by thermodynamics can be applied in other contexts where the microscopic properties of the system are poorly understood or very complex. However, there is no need to forget the general considerations that we discussed in Chapter 1. And you are also encouraged to read ahead, especially in Chapter 4 where the nature of entropy is introduced from first principles.

2.2 The System

The first step in applying thermodynamics is to select the appropriate part of the universe of interest. This part of the universe is called the *system*. In this context the term system is simply anything that we wish to consider. The system is defined by a closed surface called the boundary (see Figure 2.1). The boundary may be real or imaginary and may or may not be fixed in shape or size. The system might be as obvious as a block of steel, water in a container, or the gas in a balloon. Or the system might be defined by an imaginary fixed boundary within a flowing liquid.

The *surroundings* are the rest of the universe that can in any significant way affect or be affected by the system. For example, if an ice cube is placed in a glass of water, we might take the ice to be the system and the water to be the surroundings. In this example we would usually ignore the interaction of the ice cube with the air in the room and the interaction of the glass with the table on which the glass is set. However, if the size of the ice cube and the amount of water were about the same, we would need to consider the ice cube and water to be the system and the air in the room to be the surroundings. The choice depends on the questions of interest. The surroundings need not surround the system. An *open system* can exchange matter with its surroundings; a *closed system* cannot.

2.3 Thermodynamic Equilibrium

Macroscopic systems often exhibit some memory of their recent history. A stirred cup of tea continues to swirl for a while after we stop stirring. A hot cup of coffee cools and takes on the temperature of its surroundings regardless of its initial temperature. The final macrostates of such systems are called *equilibrium* states, which are characterized by their time independence, history independence, and relative simplicity.

Time independence means that the measurable macroscopic properties (such as the temperature, pressure, and density) of equilibrium systems do not change with time except for very small fluctuations that we can observe only under special conditions. In contrast, nonequilibrium macrostates change with time. The time scale for changes may be seconds or years, and cannot be determined from thermodynamic arguments alone. We can say for sure that a system is not in equilibrium if its properties change with time, but time independence during our observation

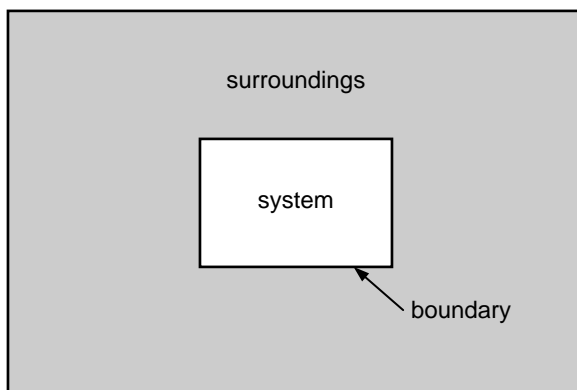


Figure 2.1: Schematic of a thermodynamic system.

time is not sufficient to determine if a system is in equilibrium. It is possible that we just did not observe the system long enough.

As we discussed in Chapter 1 the *macrostate* of a system refers to bulk properties such as temperature and pressure. Only a few quantities are needed to specify the macrostate of a system in equilibrium. For example, if you drop an ice cube into a cup of coffee, the temperature immediately afterward will vary throughout the coffee until the coffee reaches equilibrium. Before equilibrium is reached, we must specify the temperature everywhere in the coffee. Once equilibrium is reached, the temperature will be uniform throughout and only one number is needed to specify the temperature.

History independence implies that a system can go to the same final equilibrium macrostate through an infinity of possible ways. The final macrostate has lost all memory of how it was produced. For example, if we put several cups of coffee in the same room, they will all reach the same final temperature, regardless of their different initial temperatures or how much milk was added. However, there are many cases where the history of the system is important. For example, a metal cooled quickly may contain defects that depend on the detailed history of how the metal was cooled.

It is difficult to know for certain whether a system is in equilibrium because the time it takes a system to reach equilibrium may be very long and our measurements might not indicate whether a system's macroscopic properties are changing. In practice, the criterion for equilibrium is circular. Operationally, a system is in equilibrium if its properties can be consistently described by the laws of thermodynamics.

The circular nature of thermodynamics is not fundamentally different from that of other fields of physics. For example, the law of conservation of energy can never be disproved, because we can always make up new forms of energy to make it true. If we find that we are continually making up new forms of energy for every new system we find, then we would discard the law of conservation of energy as not being useful. For example, if we were to observe a neutron at rest decay into an electron and proton (beta decay) and measure the energy and momentum of the decay products, we would find an apparent violation of energy conservation in the vast majority of decays. Historically, Pauli did not reject energy conservation, but instead suggested that a third particle (the neutrino) is also emitted. Pauli's suggestion was made in 1930, but the (anti)neutrino

was not detected until 1956. In this example our strong belief in conservation of energy led to a new prediction and discovery.

The same is true for thermodynamics. We find that if we use the laws of thermodynamics for systems that experimentally appear to be in equilibrium, then everything works out fine. In some systems such as glasses that we suspect are not in thermal equilibrium, we must be very careful in interpreting our measurements according to the laws of thermodynamics.

2.4 Temperature

The concept of temperature plays a central role in thermodynamics and is related to the physiological sensation of hot and cold. Because such a sensation is an unreliable measure of temperature, we will develop the concept of temperature by considering what happens when two bodies are placed so that they can exchange energy. The most important property of the temperature is its tendency to become equal. For example, if we put a hot and a cold body into *thermal contact*, the temperature of the hot body decreases and the temperature of the cold body increases until both bodies are at the same temperature and the two bodies are in *thermal equilibrium*.

Problem 2.1. Physiological sensation of temperature

- (a) Suppose you are blindfolded and place one hand in a pan of warm water and the other hand in a pan of cold water. Then your hands are placed in another pan of water at room temperature. What temperature would each hand perceive?
- (b) What are some other examples of the subjectivity of our perception of temperature? □

To define temperature more carefully, consider two systems separated by an *insulating* wall.³ A wall is said to be *insulating* if there is no energy transfer through the wall due to temperature differences between regions on both sides of the wall. If the wall between the two systems were *conducting*, then such energy transfer would be possible. Insulating and conducting walls are idealizations. A good approximation to the former is the wall of a thermos bottle; a thin sheet of copper is a good approximation to the latter.

Consider two systems surrounded by insulating walls, except for a wall that allows energy transfer. For example, suppose that one system is a cup of coffee in a vacuum flask and the other system is alcohol enclosed in a glass tube. The glass tube is in thermal contact with the coffee. If energy is added to the alcohol in the tube, the fluid will expand, and if the tube is sufficiently narrow, the change of the column height of the alcohol will be noticeable. The alcohol column height will reach a time-independent value, and hence the coffee and the alcohol are in equilibrium. Next suppose that we dip the alcohol-filled tube into a cup of tea in another vacuum flask. If the height of the alcohol column remains the same, we say that the coffee and tea are at the same temperature. This conclusion can be generalized as follows:

If two bodies are in thermal equilibrium with a third body, they are in thermal equilibrium with each other (zeroth law of thermodynamics).

³An insulating wall is sometimes called an *adiabatic wall*.

This conclusion is sometimes called the *zeroth law of thermodynamics*. The zeroth law implies the existence of a universal property of systems in thermal equilibrium and allows us to identify this property as the temperature of a system without a direct comparison to some standard. This conclusion is not a logical necessity, but an empirical fact. If person A is a friend of B and B is a friend of C , it does not follow that A is a friend of C .

Problem 2.2. Describe some other properties that also satisfy a law similar to the zeroth law. \square

Any body whose macroscopic properties change in a well-defined manner can be used to measure temperature. A *thermometer* is a system with some convenient macroscopic property that changes in a simple way as the equilibrium macrostate changes. Examples of convenient macroscopic properties include the length of an iron rod and the electrical resistance of gold. In these cases we need to measure only a single quantity to indicate the temperature.

Problem 2.3. Why are thermometers relatively small devices in comparison to the system of interest? \square

To use different thermometers, we need to make them consistent with one another. To do so, we choose a standard thermometer that works over a wide range of temperatures and define reference temperatures which correspond to physical processes that always occur at the same temperature. The familiar gas thermometer is based on the fact that the temperature T of a dilute gas is proportional to its pressure P at constant volume. The temperature scale that is based on the gas thermometer is called the *ideal gas temperature scale*. The unit of temperature is called the *kelvin* (K). We need two points to define a linear function. We write

$$T(P) = aP + b, \quad (2.1)$$

where a and b are constants. We may choose the magnitude of the unit of temperature in any convenient way. The gas temperature scale has a natural zero — the temperature at which the pressure of an ideal gas vanishes — and hence we take $b = 0$. The second point is established by the *triple point* of water, the unique temperature and pressure at which ice, water, and water vapor coexist. The temperature of the triple point is *defined* to be exactly 273.16 K. Hence, the temperature of a fixed volume gas thermometer is given by

$$T = 273.16 \frac{P}{P_{\text{tp}}} \quad (\text{ideal gas temperature scale}), \quad (2.2)$$

where P is the pressure of the ideal gas thermometer, and P_{tp} is its pressure at the triple point. Equation (2.2) holds for a fixed amount of matter in the limit $P \rightarrow 0$. From (2.2) we see that the kelvin is defined as the fraction $1/273.16$ of the temperature of the triple point of water.

At low pressures all gas thermometers read the same temperature regardless of the gas that is used. The relation (2.2) holds only if the gas is sufficiently dilute that the interactions between the molecules can be ignored. Helium is the most useful gas because it liquefies at a temperature lower than any other gas.

The historical reason for the choice of 273.16 K for the triple point of water is that it gave, to the accuracy of the best measurements then available, 100 K for the difference between the ice point

triple point	273.16 K	definition
steam point	373.12 K	experiment
ice point	273.15 K	experiment

Table 2.1: Fixed points of the ideal gas temperature scale.

(the freezing temperature at standard pressure⁴) and the steam point (the boiling temperature at the standard pressure of water). However, more accurate measurements now give the difference as 99.97 K (see Table 2.1).

It is convenient to define the *Celsius* scale:

$$T_{\text{celsius}} = T - 273.15, \quad (2.3)$$

where T is the ideal gas temperature. Note that the Celsius and ideal gas temperatures differ only by the shift of the zero. By convention the degree sign is included with the C for Celsius temperature ($^{\circ}\text{C}$), but no degree sign is used with K for kelvin.

Problem 2.4. Temperature scales

- (a) The Fahrenheit scale is defined such that the ice point is at 32°F and the steam point is 212°F . Derive the relation between the Fahrenheit and Celsius temperature scales.
- (b) What is body temperature (98.6°F) on the Celsius and Kelvin scales?
- (c) A meteorologist in Canada reports a temperature of 30°C . How does this temperature compare to 70°F ?
- (d) The *centigrade* temperature scale is defined as

$$T_{\text{centigrade}} = (T - T_{\text{ice}}) \frac{100}{T_{\text{steam}} - T_{\text{ice}}}, \quad (2.4)$$

where T_{ice} and T_{steam} are the ice and steam points of water (see Table 2.1). By definition, there are 100 centigrade units between the ice and steam points. How does the centigrade unit defined in (2.4) compare to the Kelvin or Celsius unit? The centigrade scale has been superseded by the Celsius scale. \square

Problem 2.5. What is the range of temperatures that is familiar to you from your everyday experience and from your prior studies? \square

2.5 Pressure Equation of State

As we have discussed, the equilibrium macrostates of a thermodynamic system are much simpler to describe than nonequilibrium macrostates. For example, the pressure P of a simple fluid (a gas

⁴Standard atmospheric pressure is the pressure of the Earth's atmosphere under normal conditions at sea level and is defined to be $1.013 \times 10^5 \text{ N/m}^2$. The SI unit of pressure is N/m^2 ; this unit has been given the name *pascal* (Pa).

or a liquid) consisting of a single species is uniquely determined by its (number) density $\rho = N/V$, and temperature T , where N is the number of particles and V is the volume of the system. That is, the quantities P , T , and ρ are not independent, but are connected by a relation of the general form

$$P = f(T, \rho). \quad (2.5)$$

This relation is called the *pressure equation of state*. Each of these three quantities can be regarded as a function of the other two, and the macrostate of the system is determined by any two of the three. Note that we have implicitly assumed that the thermodynamic properties of a fluid are independent of its shape.

The pressure equation of state must be determined either empirically or from a simulation or from a theoretical calculation (an application of statistical mechanics). As discussed in Section 1.9 the *ideal gas* represents an idealization in which the potential energy of interaction between the molecules is very small in comparison to their kinetic energy and the system can be treated classically. For an ideal gas, we have for fixed temperature the empirical relation $P \propto 1/V$, or

$$PV = \text{constant} \quad (\text{fixed temperature}). \quad (2.6)$$

The relation (2.6) is sometimes called Boyle's law and was published by Robert Boyle in 1660. Note that the relation (2.6) is not a law of physics, but an empirical relation. An equation such as (2.6), which relates different macrostates of a system all at the same temperature, is called an *isotherm*.

We also have for an ideal gas the empirical relation

$$V \propto T \quad (\text{fixed pressure}). \quad (2.7)$$

Some textbooks refer to (2.7) as Charles's law, but it should be called the *law of Gay-Lussac*.⁵

We can express the empirical relations (2.6) and (2.7) as $P \propto T/V$. In addition, if we hold T and V constant and introduce more gas into the system, we find that the pressure increases in proportion to the amount of gas. If N is the number of gas molecules, we can write

$$PV = NkT \quad (\text{ideal gas pressure equation of state}), \quad (2.8)$$

where the constant of proportionality k in (2.8) is found experimentally to have the same value for all gases in the limit $P \rightarrow 0$. The value of k is

$$k = 1.38 \times 10^{-23} \text{ J/K} \quad (\text{Boltzmann's constant}), \quad (2.9)$$

and is called *Boltzmann's constant*. The equation of state (2.8) will be derived using statistical mechanics in Section 4.5.

Because the number of particles in a typical gas is very large, it sometimes is convenient to measure this number relative to the number of particles in one (gram) mole of gas.⁶ A mole of any substance consists of Avogadro's number $N_A = 6.022 \times 10^{23}$ of that substance. If there are ν moles, then $N = \nu N_A$, and the ideal gas equation of state can be written as

$$PV = \nu N_A k T = \nu R T, \quad (2.10)$$

⁵See Bohren and Albrecht, pages 51–53.

⁶A mole is defined as the quantity of matter that contains as many objects (for example, atoms or molecules) as the number of atoms in exactly 12 g of ^{12}C .

where

$$R = N_A k = 8.314 \text{ J/K mole} \quad (2.11)$$

is the gas constant.

Real gases do not satisfy the ideal gas equation of state except in the limit of low density. For now we will be satisfied with considering a simple phenomenological⁷ equation of state of a real gas with an interparticle interaction similar to the Lennard-Jones potential (see Figure 1.1, page 6). A simple phenomenological pressure equation of state for real gases that is more accurate at moderate densities is due to van der Waals and has the form

$$(P + \frac{N^2}{V^2}a)(V - Nb) = NkT \quad (\text{van der Waals equation of state}), \quad (2.12)$$

where a and b are empirical constants characteristic of a particular gas. The parameter b takes into account the nonzero size of the molecules by decreasing the effective available volume to any given molecule. The parameter a is associated with the attractive interactions between the molecules. We will derive this approximate equation of state in Section 8.2.

2.6 Some Thermodynamic Processes

A change from one equilibrium macrostate of a system to another is called a *thermodynamic process*. Thermodynamics does not determine how much time such a process will take, and the final macrostate is independent of the amount of time it takes to reach the equilibrium macrostate. To describe a process in terms of thermodynamics, the system must be in thermodynamic equilibrium. However, for any process to occur, the system cannot be exactly in thermodynamic equilibrium because at least one thermodynamic variable must change. If the change can be done so that the system can be considered to be in a succession of equilibrium macrostates, then the process is called *quasistatic*. A *quasistatic process* is an idealized concept. Although no physical process is quasistatic, we can imagine real processes that approach the limit of quasistatic processes. Usually, quasistatic processes are accomplished by making changes very slowly. That is, a quasistatic process is defined as a succession of equilibrium macrostates. The name thermodynamics is a misnomer because thermodynamics treats only equilibrium macrostates and not dynamics.

Some thermodynamic processes can go only in one direction and others can go in either direction. For example, a scrambled egg cannot be converted to a whole egg. Processes that can go only in one direction are called *irreversible*. A process is *reversible* if it is possible to restore the system and its surroundings to their original condition. (The surroundings include any body that was affected by the change.) That is, if the change is reversible, the status quo can be restored everywhere.

Processes such as stirring the cream in a cup of coffee or passing an electric current through a resistor are irreversible because, once the process is done, there is no way of reversing the process. But suppose we make a small and very slow frictionless change of a constraint such as an increase in the volume, which we then reverse. Because there is no “friction,” we have not done any net work in this process. At the end of the process, the constraints and the energy of the system

⁷We will use the word *phenomenological* often. It means a description of phenomena that is not derived from first principles.

return to their original values and the macrostate of the system is unchanged. In this case we can say that this process is reversible. No real process is truly reversible because it would require an infinite time to occur. The relevant question is whether the process approaches reversibility.

Problem 2.6. Are the following processes reversible or irreversible?

- (a) Squeezing a plastic bottle.
- (b) Ice melting in a glass of water.
- (c) Movement of a real piston (where there is friction) to compress a gas.
- (d) Pumping of air into a tire. □

2.7 Work

During a process the surroundings can do work on the system of interest or the system can do work on its surroundings. We now obtain an expression for the mechanical work done on a system in a quasistatic process. For simplicity, we assume the system to be a fluid. Because the fluid is in equilibrium, we can characterize it by a uniform pressure P . For simplicity, we assume that the fluid is contained in a cylinder of cross-sectional area A fitted with a movable piston (see Figure 2.2). The piston allows no gas or liquid to escape. We can add weights to the piston causing it to compress the fluid. Because the pressure is defined as the force per unit area, the magnitude of the force exerted by the fluid on the piston is given by PA , which also is the force exerted by the piston on the fluid. If the piston is displaced quasistatically by an amount dx , then the work done *on* the fluid by the piston is given by⁸

$$dW = -(PA) dx = -P(Adx) = -PdV. \quad (2.13)$$

The negative sign in (2.13) is present because, if the volume of the fluid is decreased, the work done by the piston is positive.

If the volume of the fluid changes quasistatically from an initial volume V_1 to a final volume V_2 , the system remains very nearly in equilibrium, and hence its pressure at any stage is a function of its volume and temperature. Hence, the total work is given by the integral

$$W_{1 \rightarrow 2} = - \int_{V_1}^{V_2} P(T, V) dV \quad (\text{quasistatic process}). \quad (2.14)$$

Note that the work done on the fluid is positive if $V_2 < V_1$ and negative if $V_2 > V_1$.

⁸Equation (2.13) can be written as

$$dW/dt = -P(dV/dt),$$

if you wish to avoid the use of differentials (see Section 2.24.1, page 88).

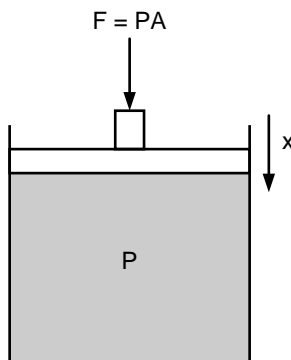


Figure 2.2: Example of work done on a fluid enclosed within a cylinder fitted with a piston when the latter moves a distance Δx .

For the special case of an ideal gas, the work done on a gas that is compressed at constant temperature (an *isothermal process*) is given by

$$W_{1 \rightarrow 2} = -NkT \int_{V_1}^{V_2} \frac{dV}{V} \quad (2.15)$$

$$= -NkT \ln \frac{V_2}{V_1} \quad (\text{ideal gas at constant temperature}). \quad (2.16)$$

We have noted that the pressure P must be uniform throughout the fluid when it is in equilibrium. If compression occurs, then pressure gradients are present. To move the piston from its equilibrium position, we must add (remove) a weight from it. Then for a brief time the total weight on the piston will be greater (less) than PA . This difference is necessary if the piston is to move and do work on the gas. If the movement is sufficiently slow, the pressure departs only slightly from its equilibrium value. What does “sufficiently slow” mean? To answer this question, we have to go beyond the macroscopic reasoning of thermodynamics and consider the molecules that comprise the fluid. If the piston is moved a distance Δx , then the density of the molecules near the piston becomes greater than in the bulk of the fluid. Consequently, there is a net movement of molecules away from the piston until the density again becomes uniform. The time τ for the fluid to return to equilibrium is given by $\tau \approx \Delta x/v_s$, where v_s is the mean speed of the molecules. For comparison, the characteristic time τ_p for the process is $\tau_p \approx \Delta x/v_p$, where v_p is the speed of the piston. If the process is quasistatic, we require that $\tau \ll \tau_p$ or $v_p \ll v_s$. That is, the speed of the piston must be much less than the mean speed of the molecules, a condition that is easy to satisfy in practice.

Problem 2.7. Work

To refresh your understanding of work in the context of mechanics, look at Figure 2.3 and explain whether the following quantities are positive, negative, or zero:

- (a) The work done on the block by the hand.

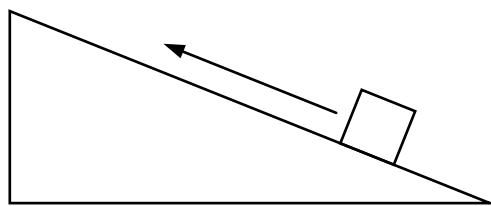


Figure 2.3: A block on an frictionless incline. The arrow indicates the direction of motion. The figure is adapted from Loverude et al. (see references)

- (b) The work done on the block by the Earth.
- (c) The work done on the hand by the block (if there is no such work, state so explicitly). □

Work depends on the path. The solution of the following example illustrates that the work done on a system depends not only on the initial and final macrostates, but also on the intermediate macrostates, that is, on the path.

Example 2.1. Cyclic processes

Figure 2.4 shows a cyclic path in the P - V diagram of an ideal gas. How much work is done on the gas during this cyclic process? (Look at the figure before you attempt to answer the question.)

Solution. During the isobaric (constant pressure) expansion $1 \rightarrow 2$, the work done on the gas is

$$W_{1 \rightarrow 2} = -P_{\text{high}}(V_{\text{high}} - V_{\text{low}}). \quad (2.17)$$

No work is done from $2 \rightarrow 3$ and from $4 \rightarrow 1$. The work done on the gas from $3 \rightarrow 4$ is

$$W_{3 \rightarrow 4} = -P_{\text{low}}(V_{\text{low}} - V_{\text{high}}). \quad (2.18)$$

The net work done on the gas is

$$W_{\text{net}} = W_{1 \rightarrow 2} + W_{3 \rightarrow 4} = -P_{\text{high}}(V_{\text{high}} - V_{\text{low}}) - P_{\text{low}}(V_{\text{low}} - V_{\text{high}}) \quad (2.19a)$$

$$= -(P_{\text{high}} - P_{\text{low}})(V_{\text{high}} - V_{\text{low}}) < 0. \quad (2.19b)$$

The result is that the net work done on the gas is the negative of the area enclosed by the path. If the cyclic process were carried out in the reverse order, the net work done on the gas would be positive. ◇

Problem 2.8. Work in a cyclic process

Consider the cyclic process as described in Example 2.1.

- (a) Because the system was returned to its original pressure and volume, why is the net amount of work done on the system not zero?

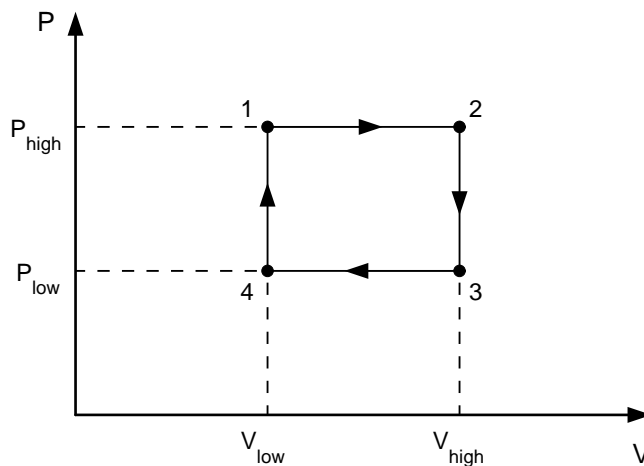


Figure 2.4: A simple cyclic process from $1 \rightarrow 2 \rightarrow 3 \rightarrow 4 \rightarrow 1$. The magnitude of the net work done on the gas equals the enclosed area.

- (b) What would be the work done on the gas if the gas were taken from $1 \rightarrow 2 \rightarrow 3$ and then back to 1 along the diagonal path connecting 3 and 1? \square

Example 2.2. Work changes the total energy

Consider two blocks sitting on a table that are connected by a spring. Initially the spring is unstretched. The two blocks are pushed together by a force on *each* block of magnitude F through a distance d . What is the net work done on the two blocks plus spring system. How much does the energy of the system change? How much does the kinetic energy of the system change? How much does the potential energy of the system change?

Solution. Your initial thought might be that because there is no net force on the system, the work done is zero. That answer is incorrect – understanding mechanics isn’t easy. To calculate the work you need to add the work done by each force separately. In this case each force does an amount of work equal to Fd , and thus the total work done on the system is $2Fd$. You might think that the change in the kinetic energy of the system is equal to $2Fd$ from the work-kinetic energy theorem that you learned in mechanics. That’s also incorrect because the work-kinetic energy theorem is applicable only to a single particle, not to a composite system as we have here. All we can say in this case is that the total energy of the two blocks plus spring system changes by $2Fd$. We cannot answer questions about the change in kinetic or potential energies because not enough information is given.

This example is analogous to a system of many particles. When we do work on it, the total energy of the system changes, but we cannot say anything about how the internal kinetic energy or potential energy changes. It is important to realize that systems of many particles contain both kinetic and potential energy. \diamond

2.8 The First Law of Thermodynamics

If we think of a macroscopic system as consisting of many interacting particles, we know that it has a well defined total energy which satisfies a conservation principle. This simple justification of the existence of a thermodynamic energy function is very different from the historical development because thermodynamics was developed before the atomic theory of matter was well accepted. Historically, the existence of a macroscopic conservation of energy principle was demonstrated by purely macroscopic observations as outlined in the following.⁹

Consider a system enclosed by insulating walls. Such a system is *thermally isolated*. An *adiabatic process* is one in which the macrostate of the system is changed only by work done on the system. That is, no energy is transferred to or from the system by temperature differences. We know from overwhelming empirical evidence that the amount of work needed to change the macrostate of a thermally isolated system depends only on the initial and final macrostates and not on the intermediate states through which the system passes. This independence of the path under these conditions implies that we can define a function E such that for a change from macrostate 1 to macrostate 2, the work done on a thermally isolated system equals the change in E :

$$W = E_2 - E_1 = \Delta E \quad (\text{adiabatic process}). \quad (2.20)$$

The quantity E is called the internal energy of the system.¹⁰ The internal energy in (2.20) is measured with respect to the center of mass and is the same as the total energy of the system in a reference frame in which the center of mass velocity of the system is zero.¹¹ The energy E is an example of a *state* function, that is, it characterizes the state of a macroscopic system and is independent of the path.

If we choose a convenient reference macrostate as the zero of energy, then E has a unique value for each macrostate of the system because the work done on the system W is independent of the path for an adiabatic process. (Remember that in general W depends on the path.)

If we relax the condition that the change be adiabatic and allow the system to interact with its surroundings, we find in general that $\Delta E \neq W$. (The difference between ΔE and W is zero for an adiabatic process.) We know that we can increase the energy of a system by doing work on it or by heating it as a consequence of a temperature difference between it and its surroundings. In general, the change in the (internal) energy of a closed system (fixed number of particles) is given by

$$\boxed{\Delta E = W + Q} \quad (\text{first law of thermodynamics}). \quad (2.21)$$

The quantity Q is the change in the system's energy due to heating ($Q > 0$) or cooling ($Q < 0$) and W is the work done *on* the system. Equation (2.21) expresses the law of conservation of energy and is known as the *first law of thermodynamics*. This equation is equivalent to saying that there are two macroscopic ways of changing the internal energy of a system: doing work and heating (cooling).

⁹These experiments were done by Joseph Black (1728–1799), Benjamin Thompson (Count Rumford) (1753–1814), Robert Mayer (1814–1878), and James Joule (1818–1889). Mayer and Joule are now recognized as the co-discoverers of the first law of thermodynamics, but Mayer received little recognition at the time of his work.

¹⁰Another common notation for the internal energy is U .

¹¹Microscopically, the internal energy of a system of particles equals the sum of the kinetic energy in a reference frame in which the center of mass velocity is zero and the potential energy arising from the interactions of the particles.

One consequence of the first law of thermodynamics is that ΔE is independent of the path, even though the amount of work W depends on the path. And because W depends on the path and ΔE does not, the amount of heating also depends on the path. From one point of view, the first law of thermodynamics expresses what seems obvious to us today, namely, conservation of energy. From another point of view, the first law implies that, although the work done and the amount of heating depend on the path, their sum is independent of the path.

Problem 2.9. Pumping air

A bicycle pump contains one mole of a gas. The piston fits tightly so that no air escapes and friction is negligible between the piston and the cylinder walls. The pump is thermally insulated from its surroundings. The piston is quickly pressed inward. What happens to the temperature of the gas? Explain your reasoning. \square

So far we have considered two classes of thermodynamic quantities. One class consists of *state functions* because they have a specific value for each macrostate of the system. An example of such a function is the internal energy E . As we have discussed, there are other quantities, such as work done on a system and energy transfer due to heating that are not state functions and depend on the thermodynamic process by which the system changed from one macrostate to another.

The energy of a system is a state function. The mathematical definition of a state function goes as follows. Suppose that $f(x)$ is a state function that depends on the parameter x . If x changes from x_1 to x_2 , then the change in f is

$$\Delta f = \int_{x_1}^{x_2} df = f(x_2) - f(x_1). \quad (2.22)$$

That is, the change in f depends only on the end points x_1 and x_2 . We say that df is an exact differential. State functions have exact differentials. Examples of inexact and exact differentials are given in Section 2.24.1.

Originally, many scientists thought that there was a fluid called *heat* in all substances which could flow from one substance to another. This idea was abandoned many years ago, but it is still used in everyday language. Thus, people talk about adding heat to a system. We will avoid this use and whenever possible we will avoid the use of the noun “heat” altogether. Instead, we will refer to heating or cooling processes. These processes occur whenever two bodies at different temperatures are brought into thermal contact. In everyday language we say that heat flows from the hot to the cold body. In the context of thermodynamics we will say that energy is transferred from the hotter to the colder body. There is no need to invoke the noun “heat,” and it is misleading to say that heat “flows” from one body to another.

To understand better that there is no such thing as the amount of heat in a body, consider the following simple analogy adapted from Callen. A farmer owns a pond, fed by one stream and drained by another. The pond also receives water from rainfall and loses water by evaporation. The pond is the system of interest, the water within it is analogous to the internal energy, the process of transferring water by the streams is analogous to doing work, the process of adding water by rainfall is analogous to heating, and the process of evaporation is analogous to cooling. The only quantity of interest is the amount of water, just as the only quantity of interest is energy in the thermal case. An examination of the change in the amount of water in the pond cannot

tell us how the water got there. The terms rain and evaporation refer only to methods of water transfer, just as the terms work, heating, and cooling refer only to methods of energy transfer.

Another example is due to Bohren and Albrecht. Take a small plastic container and add just enough water to it so that its temperature can be conveniently measured. Let the water and the bottle come into equilibrium with their surroundings. Measure the temperature of the water, cap the bottle, and shake it until you are too tired to continue further. Then uncap the bottle and measure the water temperature again. If there were a “whole lot of shaking going on,” you would find the temperature had increased a little.

In this example, the temperature of the water increased without heating. We did work on the water, which resulted in an increase in its internal energy as manifested by a rise in its temperature. The same increase in temperature could have been obtained by bringing the water into contact with a body at a higher temperature. It is impossible to determine by making measurements on the water whether shaking or heating was responsible for taking the system from its initial to its final macrostate. (To silence someone who objects that you heated the water with “body heat,” wrap the bottle with an insulating material.)

Problem 2.10. Distinguishing different types of water transfer

How could the owner of the pond distinguish between the different types of water transfer assuming that the owner has flow meters, a tarpaulin, and a vertical pole? \square

Problem 2.11. Convert the statement “I am cold, please turn on the heat,” to the precise language of physics. \square

Before the equivalence of heating and energy transfer was well established, a change in energy by heating was measured in calories. One calorie is the amount of energy needed to raise the temperature of one gram of water from 14.5°C to 15.5°C. We now know that one calorie is equivalent to 4.186 J, but the use of the calorie for energy transfer by heating and the joule for work still persists. Just to cause confusion, the calorie we use to describe the energy content of foods is actually a kilocalorie.

2.9 Energy Equation of State

In (2.8) we gave the pressure equation of state for an ideal gas. Now that we know that the internal energy is a state function, we need to know how E depends on two of the three variables, T , ρ , and N (for a simple fluid). The form of the *energy equation of state* for an ideal gas must also be determined empirically or calculated from first principles using statistical mechanics (see Section 4.5, page 194). From these considerations the energy equation of state for a monatomic gas is given by

$$E = \frac{3}{2}NkT \quad (\text{ideal gas energy equation of state}). \quad (2.23)$$

Note that the energy of an ideal gas is independent of its density (for a fixed number of particles).

An approximate energy equation of state of a gas corresponding to the pressure equation of state (2.12) is given by

$$E = \frac{3}{2}NkT - N\frac{N}{V}a \quad (\text{van der Waals energy equation of state}). \quad (2.24)$$

Note that the energy depends on the density $\rho = N/V$ if the interactions between particles are included.

Example 2.3. Work done on an ideal gas at constant temperature

Work is done on an ideal gas at constant temperature. What is the change in the energy of the gas?¹²

Solution. Because the energy of an ideal gas depends only on the temperature [see (2.23)], there is no change in its internal energy for an isothermal process. Hence, $\Delta E = 0 = Q + W$, and from (2.15) we have

$$Q = -W = NkT \ln \frac{V_2}{V_1} \quad (\text{isothermal process, ideal gas}). \quad (2.25)$$

We see that if work is done on the gas ($V_2 < V_1$), then the gas must give energy to its surroundings so that its temperature does not change. \diamond

Extensive and intensive variables. The thermodynamic variables that we have introduced so far may be divided into two classes. Quantities such as the density ρ , the pressure P , and the temperature T are *intensive* variables and are *independent* of the size of the system. Quantities such as the volume V and the internal energy E are *extensive* variables and are *proportional* to the number of particles in the system (at fixed density). As we will see in Section 2.10, it often is convenient to convert extensive quantities to a corresponding intensive quantity by defining the ratio of two extensive quantities. For example, the energy per particle and the energy per unit mass are intensive quantities.

2.10 Heat Capacities and Enthalpy

We know that the temperature of a macroscopic system usually increases when we transfer energy to it by heating.¹³ The magnitude of the increase in temperature depends on the nature of the body and how much of it there is. The amount of energy transfer due to heating required to produce a unit temperature rise in a given substance is called the *heat capacity* of the substance. Here again we see the archaic use of the word “heat.” But because the term “heat capacity” is common, we will use it. If a body undergoes an increase of temperature from T_1 to T_2 due to an energy transfer Q , then the average heat capacity is given by the ratio

$$\text{average heat capacity} = \frac{Q}{T_2 - T_1}. \quad (2.26)$$

The value of the heat capacity depends on what constraints are imposed. We introduce the heat capacity at constant volume by the relation

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V. \quad (2.27)$$

¹²We mean the internal energy, as should be clear from the context. In the following we will omit the term internal and simply refer to the energy.

¹³ What is a common counterexample?

Note that, if the volume V is held constant, the change in energy of the system is due only to the energy transferred by heating. We have adopted the common notation in thermodynamics of enclosing partial derivatives in parentheses and using subscripts to denote the variables that are held constant. In this context, it is clear that the differentiation in (2.27) is at constant volume, and we will write $C_V = \partial E / \partial T$ if there is no ambiguity.¹⁴ (See Section 2.24.1 for a discussion of the mathematics of thermodynamics.)

Equation (2.27) together with (2.23) can be used to obtain the heat capacity at constant volume of a monatomic ideal gas:

$$C_V = \frac{3}{2}Nk \quad (\text{monatomic ideal gas}). \quad (2.28)$$

Note that the heat capacity at constant volume of an ideal gas is independent of the temperature.

The heat capacity is an extensive quantity, and it is convenient to introduce the *specific heat* which depends only on the nature of the material, not on the amount of the material. The conversion to an intensive quantity can be achieved by dividing the heat capacity by the amount of the material expressed in terms of the number of moles, the mass, or the number of particles. We will use lower case c for specific heat; the distinction between the various kinds of specific heats will be clear from the context and the units of c .

The enthalpy. The combination of thermodynamic variables $E + PV$ occurs sufficiently often to acquire its own name. The *enthalpy* H is defined as

$$\boxed{H = E + PV} \quad (\text{enthalpy}). \quad (2.29)$$

We can use (2.29) to find a simple expression for C_P , the heat capacity at constant pressure. From (2.13) and (2.21), we have $dE = dQ - PdV$ or $dQ = dE + PdV$. From the identity $d(PV) = PdV + VdP$, we can write $dQ = dE + d(PV) - VdP$. At constant pressure $dQ = dE + d(PV) = d(E + PV) = dH$. Hence, we can define the heat capacity at constant pressure as

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P. \quad (2.30)$$

We will learn that the enthalpy is another state function which often makes the analysis of a system simpler. At this point, we see that C_P can be expressed more simply in terms of the enthalpy.

We can find C_P for an ideal gas by writing $H = E + PV = \frac{3}{2}NKT + NkT$ and using the relation (2.30) to find that $C_P = \frac{5}{2}Nk$, and thus

$$C_P = C_V + Nk \quad (\text{ideal gas}). \quad (2.31)$$

Note that we used the two equations of state, (2.8) and (2.23), to obtain C_P , and we did not have to make an independent measurement or calculation.

Why is C_P greater than C_V ? Unless we prevent it from doing so, a system normally expands as its temperature increases. The system has to do work on its surroundings as it expands. Hence, when a system is heated at constant pressure, energy is needed both to increase the temperature of

¹⁴Although the number of particles also is held constant, we will omit the subscript N in (2.27) and in other partial derivatives to reduce the number of subscripts.

the system and to do work on its surroundings. In contrast, if the volume is kept constant, no work is done on the surroundings and the heating only has to supply the energy required to raise the temperature of the system. We will derive the general relation $C_P > C_V$ for any thermodynamic system in Section 2.22.

Problem 2.12. Heat capacities large and small

Give some examples of materials that have either a small or a large heat capacity relative to that of water. You can find values of the heat capacity in books on materials science and on the internet. \square

Example 2.4. Heating water

A water heater holds 150 kg of water. How much energy is required to raise the water temperature from 18°C to 50°C?

Solution. The (mass) specific heat of water is $c = 4184 \text{ J/kg K}$. (The difference between the specific heats of water at constant volume and constant pressure is negligible at room temperatures.) The energy required to raise the temperature by 32°C is

$$Q = mc(T_2 - T_1) = 150 \text{ kg} \times (4184 \text{ J/kg K}) \times (50^\circ\text{C} - 18^\circ\text{C}) = 2 \times 10^7 \text{ J}. \quad (2.32)$$

We have assumed that the specific heat is constant in this temperature range. \diamond

Note that, when calculating temperature *differences*, it is often more convenient to express temperatures in Celsius, because the kelvin is exactly the same magnitude as a degree Celsius.

Example 2.5. Cooling a brick

A 1.5 kg glass brick is heated to 180°C and then plunged into a cold bath containing 10 kg of water at 20°C. Assume that none of the water boils and there is no heating of the surroundings. What is the final temperature of the water and the glass? The specific heat of glass is approximately 750 J/kg K.

Solution. Conservation of energy implies that

$$\Delta E_{\text{glass}} + \Delta E_{\text{water}} = 0, \quad (2.33a)$$

or

$$m_{\text{glass}}c_{\text{glass}}(T - T_{\text{glass}}) + m_{\text{water}}c_{\text{water}}(T - T_{\text{water}}) = 0. \quad (2.33b)$$

The final equilibrium temperature T is the same for both. We solve for T and obtain

$$T = \frac{m_{\text{glass}}c_{\text{glass}}T_{\text{glass}} + m_{\text{water}}c_{\text{water}}T_{\text{water}}}{m_{\text{glass}}c_{\text{glass}} + m_{\text{water}}c_{\text{water}}} \quad (2.34a)$$

$$= \frac{(1.5 \text{ kg})(750 \text{ J/kg K})(180^\circ\text{C}) + (10 \text{ kg})(4184 \text{ J/kg K})(20^\circ\text{C})}{(1.5 \text{ kg})(750 \text{ J/kg K}) + (10 \text{ kg})(4184 \text{ J/kg K})} \quad (2.34b)$$

$$= 24.2^\circ\text{C}. \quad (2.34c)$$

\square

Example 2.6. Energy needed to increase the temperature

The temperature of two moles of helium gas is increased from 10°C to 30°C at constant volume. How much energy is needed to accomplish this temperature change?

Solution. Because the amount of He gas is given in moles, we need to know its molar specific heat. Helium gas can be well approximated by an ideal gas so we can use (2.28). The molar specific heat is given by [see (2.11)] $c_V = 3R/2 = 1.5 \times 8.314 = 12.5 \text{ J/mole K}$. Because c_V is constant, we have

$$\Delta E = Q = \int C_V dT = \nu c_V \int dT = 2 \text{ mole} \times 12.5 \frac{\text{J}}{\text{mole K}} \times 20 \text{ K} = 500 \text{ J}. \quad (2.35)$$

◇

Example 2.7. A solid at low temperatures

At very low temperatures the heat capacity of an insulating solid is proportional to T^3 . If we take $C = AT^3$ for a particular solid, what is the energy needed to raise the temperature from T_1 to T_2 ? The difference between C_V and C_P can be ignored at low temperatures. (In Section 6.9, we will use the Debye theory to express the constant A in terms of the speed of sound and other parameters and find the range of temperatures for which the T^3 behavior is a reasonable approximation.)

Solution. Because C is temperature dependent, we have to express the energy transferred as an integral:

$$Q = \int_{T_1}^{T_2} C(T) dT. \quad (2.36)$$

In this case we have

$$Q = A \int_{T_1}^{T_2} T^3 dT = \frac{A}{4} (T_2^4 - T_1^4). \quad (2.37)$$

◇

Problem 2.13. In Example 2.1 we showed that the net work done on the gas in the cyclic process shown in Figure 2.4 is nonzero. Assume that the gas is ideal with N particles and calculate the energy transfer by heating in each step of the process. Then explain why the net work done on the gas is negative and show that the net change of the internal energy is zero. □

2.11 Quasistatic Adiabatic Processes

So far we have considered processes at constant temperature, constant volume, and constant pressure.¹⁵ We have also considered *adiabatic processes* which occur when the system does not exchange energy with its surroundings due to a temperature difference. Note that an adiabatic process need not be isothermal.

Problem 2.14. Give some examples of adiabatic processes. □

¹⁵These processes are called *isothermal*, *isochoric*, and *isobaric*, respectively.

We now show that the pressure of an ideal gas changes more for a given change of volume in a quasistatic adiabatic process than it does in an isothermal process. For an adiabatic process the first law reduces to

$$dE = dW = -PdV \quad (\text{adiabatic process}). \quad (2.38)$$

In an adiabatic process the energy can change due to a change in temperature or volume and thus

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV. \quad (2.39)$$

The first derivative in (2.39) is equal to C_V . Because $(\partial E/\partial V)_T = 0$ for an ideal gas, (2.39) reduces to

$$dE = C_V dT = -PdV \quad (\text{adiabatic process, ideal gas}), \quad (2.40)$$

where we have used (2.38). The easiest way to proceed is to eliminate P in (2.40) using the ideal gas law $PV = NkT$:

$$C_V dT = -NkT \frac{dV}{V}. \quad (2.41)$$

We next eliminate Nk in (2.41) in terms of $C_P - C_V$ and express (2.41) as

$$\frac{C_V}{C_P - C_V} \frac{dT}{T} = \frac{1}{\gamma - 1} \frac{dT}{T} = -\frac{dV}{V}. \quad (2.42)$$

The symbol γ is the ratio of the heat capacities:

$$\gamma = \frac{C_P}{C_V}. \quad (2.43)$$

For an ideal gas C_V and C_P and hence γ are independent of temperature, and we can integrate (2.42) to obtain

$$TV^{\gamma-1} = \text{constant} \quad (\text{quasistatic adiabatic process}). \quad (2.44)$$

For an ideal monatomic gas, we have from (2.28) and (2.31) that $C_V = 3Nk/2$ and $C_P = 5Nk/2$, and hence

$$\gamma = 5/3 \quad (\text{ideal monatomic gas}). \quad (2.45)$$

Problem 2.15. Use (2.44) and the ideal gas pressure equation of state in (2.8) to show that in a quasistatic adiabatic processes P and V are related as

$$PV^\gamma = \text{constant}. \quad (2.46)$$

Also show that T and P are related as

$$TP^{(1-\gamma)/\gamma} = \text{constant}. \quad (2.47)$$

□

The relations (2.44)–(2.47) hold for a quasistatic adiabatic process of an ideal gas.¹⁶ Because $\gamma > 1$, the relation (2.46) implies that for a given volume change, the pressure changes more for an adiabatic process than it does for a comparable isothermal process for which $PV = \text{constant}$. We

¹⁶An easier derivation is suggested in Problem 2.24.

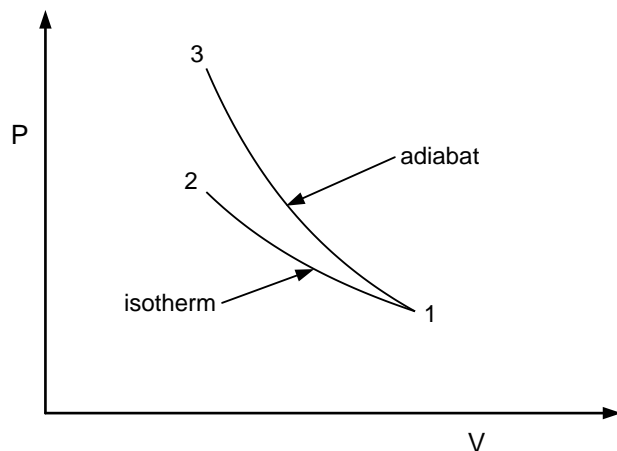


Figure 2.5: Comparison of an isothermal and an adiabatic process. The two processes begin at the same volume V_1 , but the adiabatic process has a steeper slope and ends at a higher pressure.

can understand the reason for this difference as follows. For an isothermal compression the pressure increases and the internal energy of an ideal gas does not change. For an adiabatic compression the energy increases because we have done work on the gas and no energy can be transferred by heating or cooling by the surroundings. The increase in the energy causes the temperature to increase. Hence, in an adiabatic compression, both the decrease in the volume and the increase in the temperature cause the pressure to increase more.

In Figure 2.5 we show the P - V diagram for both isothermal and adiabatic processes. The adiabatic curve has a steeper slope than the isothermal curves at any point. From (2.46) we see that the slope of an adiabatic curve for an ideal gas is

$$\left(\frac{\partial P}{\partial V}\right)_{\text{adiabatic}} = -\gamma \frac{P}{V}, \quad (2.48)$$

in contrast to the slope of an isothermal curve for an ideal gas:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}. \quad (2.49)$$

How can the ideal gas relations $PV^\gamma = \text{constant}$ and $PV = NkT$ both be correct? The answer is that $PV = \text{constant}$ only for an isothermal process. A quasistatic ideal gas process cannot be both adiabatic and isothermal. During an adiabatic process, the temperature of an ideal gas must change. Note that $PV = NkT$ is valid for an ideal gas during any process, but care must be exercised in using this relation because any of the four variables P , V , N , and T can change in a given process.

Problem 2.16. Although we do work on an ideal gas when we compress it isothermally, why does the energy of the gas not increase? \square

Example 2.8. Adiabatic and isothermal expansion

Two identical systems each contain $\nu = 0.1$ mole of an ideal gas at $T = 300$ K and $P = 2.0 \times 10^5$ Pa. The pressure in the two systems is reduced by a factor of 2, allowing the systems to expand, one adiabatically and one isothermally. What are the final temperatures and volumes of each system? Assume that $\gamma = 5/3$.

Solution. The initial volume V_1 is given by

$$V_1 = \frac{\nu RT_1}{P_1} = \frac{0.1 \text{ mole} \times 8.3 \text{ J/(K mole)} \times 300 \text{ K}}{2.0 \times 10^5 \text{ Pa}} = 1.245 \times 10^{-3} \text{ m}^3. \quad (2.50)$$

For the isothermal system, PV remains constant, so the volume doubles as the pressure decreases by a factor of 2, and hence $V_2 = 2.49 \times 10^{-3} \text{ m}^3$. Because the process is isothermal, the temperature remains at 300 K.

For adiabatic compression we have

$$V_2^\gamma = \frac{P_1 V_1^\gamma}{P_2}, \quad (2.51)$$

or

$$V_2 = \left(\frac{P_1}{P_2}\right)^{1/\gamma} V_1 = 2^{3/5} \times 1.245 \times 10^{-3} \text{ m}^3 = 1.89 \times 10^{-3} \text{ m}^3. \quad (2.52)$$

We see that for a given pressure change the volume change for the isothermal process is greater. We leave it as an exercise to show that $T_2 = 250$ K. \diamond

Problem 2.17. Compression of air

Air initially at 20°C is compressed by a factor of 15.

- (a) What is the final temperature assuming that the compression is adiabatic and $\gamma \approx 1.4$,¹⁷ the value of γ for air in the relevant range of temperatures? By what factor does the pressure increase?
- (b) By what factor does the pressure increase if the compression is isothermal?
- (c) For which process does the pressure change more? \square

How much work is done in a quasistatic adiabatic process? Because $Q = 0$, $\Delta E = W$. For an ideal gas, $\Delta E = C_V \Delta T$ for any process. Hence for a quasistatic adiabatic process

$$W = C_V(T_2 - T_1) \quad (\text{quasistatic adiabatic process, ideal gas}). \quad (2.53)$$

In Problem 2.18 you are asked to show that (2.53) can be expressed in terms of the pressure and volume as

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}. \quad (2.54)$$

¹⁷The ratio γ equals 5/3 for an ideal gas of particles when only translational motion is important. We will learn in Section 6.2.1 how to calculate γ for molecules with rotational and vibrational contributions to the energy.

Problem 2.18. Work done in a quasistatic adiabatic process

(a) Use the result that we derived in (2.53) to obtain the alternative form (2.54).

(b) Show that another way to derive (2.54) is to use the relations (2.14) and (2.46). \square

Example 2.9. Compression ratio of a diesel engine

Compression in a diesel engine occurs quickly enough so that very little heating of the environment occurs, and thus the process may be considered adiabatic. If a temperature of 500°C is required for ignition, what is the compression ratio? Assume that the air can be treated as an ideal gas with $\gamma = 1.4$, and the temperature is 20°C before compression.

Solution. Equation (2.44) gives the relation between T and V for a quasistatic adiabatic process. We write T_1 and V_1 and T_2 and V_2 for the temperature and volume at the beginning and the end of the piston stroke. Then (2.46) becomes

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}. \quad (2.55)$$

Hence the compression ratio V_1/V_2 is

$$\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{1/(\gamma-1)} = \left(\frac{773\text{ K}}{293\text{ K}}\right)^{1/0.4} = 11. \quad (2.56)$$

It is only an approximation to assume that the compression is quasistatic in a diesel engine. \diamond

2.12 The Second Law of Thermodynamics

The consequences of the first law of thermodynamics are that energy is conserved in thermal processes and heating is a form of energy transfer. We also noted that the internal energy of a system can be identified with the sum of the potential and kinetic energies of the particles.

As was discussed in Chapter 1, there are many processes that do not occur in nature, but whose occurrence would be consistent with the first law. For example, the first law does not prohibit energy from being transferred spontaneously from a cold body to a hot body, yet it has never been observed. There is another property of systems that must be taken into account, and this property is called the *entropy*.¹⁸

Entropy is another example of a state function. One of the remarkable achievements of the nineteenth century was the reasoning that such a state function must exist without any idea of how to measure its value directly. In Chapter 4 we will learn about the relation between the entropy and the number of possible microscopic states, but for now we will follow a logic that does not depend on any knowledge of the microscopic behavior.

It is not uncommon to use heating as a means of doing work. For example, power plants burn oil or coal to turn water into steam, which in turn turns a turbine in a magnetic field, creating electricity which then can do useful work in your home. Can we completely convert all the energy

¹⁸This thermodynamic variable was named by Rudolf Clausius in 1850 who formed the word *entropy* (from the Greek word for transformation) so as to be as similar as possible to the word energy.

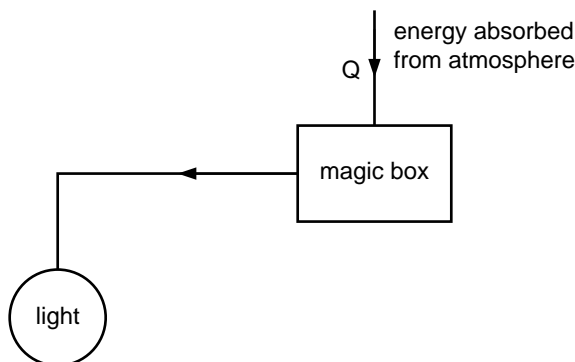


Figure 2.6: A machine that converts energy transferred by heating into work with 100% efficiency violates the Kelvin statement of the second law of thermodynamics.

created by chemical reactions into work? Can we cool a system and use *all* the energy lost by the system to do work? Our everyday experience tells us that we cannot. If it were possible, we could power a boat to cross the Atlantic by cooling the sea and transferring energy from the sea to drive the propellers. We would need no fuel and travel would be much cheaper. Or instead of heating a fluid by doing electrical work on a resistor, we could consider a process in which a resistor cools the fluid and produces electrical energy at its terminals. The fact that these processes do not occur is summarized in one of the statements of the second law of thermodynamics:

It is impossible to construct an engine which, operating in a cycle, will produce no other effect than the extraction of energy from a reservoir and the performance of an equivalent amount of work (Kelvin-Planck statement).¹⁹

This form of the second law implies that a *perpetual motion machine of the second kind* does not exist. Such a machine would convert energy completely into work (see Figure 2.6).

What about the isothermal expansion of an ideal gas? Does this process violate the second law? When the gas expands, it does work on the piston which causes the gas to lose energy. Because the process is isothermal, the gas must absorb energy so that its internal energy remains constant. (The internal energy of an ideal gas depends only on the temperature.) We have

$$\Delta E = Q + W = 0. \quad (2.57)$$

We see that $W = -Q$, that is, the work done on the gas is $-Q$ and the work done by the gas is Q . We conclude that we have completely converted the absorbed energy into work. However, this conversion does not violate the Kelvin-Planck statement because the macrostate of the gas is different at the end than at the beginning; that is, the isothermal expansion of an ideal gas is not a cyclic process. We cannot use this process to make an engine.

¹⁹The original statement by Kelvin is "It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects." Planck wrote "It is impossible to construct an engine, which working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir." See Zemansky and Dittman, p. 147.

Another statement of the second law based on the empirical observation that energy does not spontaneously go from a colder to a hotter body can be stated as follows:

No process is possible whose sole result is cooling a colder body and heating a hotter body (Clausius statement).

The Kelvin-Planck and the Clausius statements of the second law look different, but each statement and the first law implies the other so their consequences are identical.

We will adopt a more abstract version of the second law that is not based directly on experimental observations, but is more convenient in many contexts:

There exists an additive function of state known as the entropy S that can never decrease in an isolated system.

Because the entropy cannot decrease in an isolated system, we conclude that the entropy is a *maximum* for an isolated system in equilibrium.²⁰ The term *additive* means that if the entropy of two systems is S_A and S_B , respectively, the total entropy of the combined system is $S = S_A + S_B$. In the following we show that the Kelvin and Clausius statements follow from this version of the second law.

The statement of the second law in terms of the entropy is applicable only to isolated systems (a system enclosed by insulating, rigid, and impermeable walls). Most systems of interest can exchange energy with their surroundings. In many cases the surroundings may be idealized as a large body that does not interact with the rest of the universe. For example, we can take the surroundings of a cup of hot water to be the air in the room. In this case we can treat the *composite* system, system plus surroundings, as isolated. For the composite system, we have for any process

$$\Delta S_{\text{composite}} \geq 0, \quad (2.58)$$

where $S_{\text{composite}}$ is the entropy of the system plus its surroundings.

If a change is reversible, we cannot have $\Delta S_{\text{composite}} > 0$, because if we reverse the change, we would have $\Delta S_{\text{composite}} < 0$, a violation of the Clausius statement as we shall soon see. Hence, the only possibility is that

$$\Delta S_{\text{composite}} = 0 \quad (\text{reversible process}). \quad (2.59)$$

To avoid confusion, we will use the term reversible to be equivalent to a constant entropy process. The condition for a process to be reversible requires only that the total entropy of a closed system is constant; the entropies of its parts may increase or decrease.

2.13 The Thermodynamic Temperature

The Clausius and Kelvin-Planck statements of the second law arose from the importance of heat engines to the development of thermodynamics. A seemingly different purpose of thermodynamics

²⁰Maximum and minimum principles are ubiquitous in physics. Leonhard Euler wrote that “Nothing whatsoever takes place in the universe in which some relation of maximum and minimum does not appear.”

is to determine the conditions of equilibrium. These two purposes are linked by the fact that whenever there is a difference of temperature, work can be done.

In the following we derive the properties of the thermodynamic temperature from the second law. In Section 2.16 we will show that this temperature is the same as the ideal gas scale temperature introduced in Section 2.2.

Consider an isolated composite system that is partitioned into two *subsystems* A and B by a fixed, impermeable, insulating wall. For the composite system we have

$$E = E_A + E_B = \text{constant}, \quad (2.60)$$

$V = V_A + V_B = \text{constant}$, and $N = N_A + N_B = \text{constant}$. Because the entropy is additive, we can write the total entropy as

$$S(E_A, V_A, N_A, E_B, V_B, N_B) = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B). \quad (2.61)$$

Most divisions of the energy E_A and E_B between subsystems A and B do not correspond to thermal equilibrium.

For thermal equilibrium to be established we replace the fixed, impermeable, *insulating* wall by a fixed, impermeable, *conducting* wall so that the two subsystems are in thermal contact and energy transfer by heating or cooling may occur. We say that we have removed an *internal constraint*. According to our statement of the second law, the values of E_A and E_B will be such that the entropy of the composite system becomes a maximum. To find the value of E_A that maximizes S as given by (2.61), we calculate

$$dS = \left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} dE_A + \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} dE_B. \quad (2.62)$$

Because the total energy of the system is conserved, we have $dE_B = -dE_A$, and hence

$$dS = \left[\left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} - \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} \right] dE_A. \quad (2.63)$$

The condition for equilibrium is that $dS = 0$ for arbitrary values of dE_A , and hence

$$\left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} = \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B}. \quad (2.64)$$

Because the temperatures of the two systems are equal in thermal equilibrium, we conclude that the derivative $\partial S / \partial E$ must be associated with the temperature. We will find that it is convenient to define the thermodynamic temperature T as

$$\boxed{\frac{1}{T} \equiv \left(\frac{\partial S}{\partial E} \right)_{V, N}} \quad (\text{thermodynamic temperature}), \quad (2.65)$$

which implies that the condition for thermal equilibrium is

$$\frac{1}{T_A} = \frac{1}{T_B}, \quad (2.66)$$

or $T_A = T_B$.

We have found that, if two systems are separated by a conducting wall, energy will be transferred until the systems reach the same temperature. Now suppose that the two systems are initially separated by an insulating wall and that the temperatures of the two systems are almost equal with $T_A > T_B$. If this constraint is removed, we know that energy will be transferred across the conducting wall and the entropy of the composite system will increase. From (2.63) we can write the change in entropy of the composite system as

$$\Delta S \approx \left[\frac{1}{T_A} - \frac{1}{T_B} \right] \Delta E_A > 0, \quad (2.67)$$

where T_A and T_B are the initial values of the temperatures. The condition that $T_A > T_B$ requires that $\Delta E_A < 0$ in order for $\Delta S > 0$ in (2.67) to be satisfied. Hence, we conclude that the definition (2.65) of the thermodynamic temperature implies that energy is transferred from a system with a higher value of T to a system with a lower value of T .

We can express (2.67) as follows: *No process exists in which a cold body becomes cooler while a hotter body becomes still hotter and the constraints on the bodies and the state of its surroundings are unchanged.* We recognize this statement as the Clausius statement of the second law.

Note that the inverse temperature can be interpreted as the response of the entropy to a change in the energy of the system. In Section 2.17 we will derive the condition for *mechanical equilibrium*, and in Chapter 7 we will discuss the condition for *chemical equilibrium*. These two conditions complement the condition for thermal equilibrium. All three conditions must be satisfied for *thermodynamic equilibrium* to be established.

The definition (2.65) of T is not unique, and we could have replaced $1/T$ by other functions of temperature such as $1/T^2$ or $1/\sqrt{T}$. However, we will find in Section 2.16 that the definition (2.65) implies that the thermodynamic temperature is identical to the ideal gas scale temperature.

2.14 The Second Law and Heat Engines

A body that can change the temperature of another body without changing its own temperature and without doing work is known as a *heat bath*. The term is archaic, but we will adopt it because of its common usage.²¹ A heat bath can be either a heat source or a heat sink. Examples of a heat source and a heat sink, depending on the circumstances, are the Earth's ocean and atmosphere. If we want to measure the electrical conductivity of a small block of copper at a certain temperature, we can place it into a large body of water that is at the desired temperature. The temperature of the copper will become equal to the temperature of the large body of water, whose temperature will be unaffected by the copper.

For pure heating or cooling the increase in the entropy is given by

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V,N} dE. \quad (2.68)$$

In this case $dE = dQ$ because no work is done. If we express the partial derivative in (2.68) in terms of T , we can rewrite (2.68) as

$$dS = \frac{dQ}{T} \quad (\text{pure heating}). \quad (2.69)$$

²¹The terms thermal bath and heat reservoir are also used.

We emphasize that the relation (2.69) holds only for quasistatic changes. Note that (2.69) implies that *the entropy does not change in a quasistatic, adiabatic process*.

We now use (2.69) to discuss the problem that motivated the development of thermodynamics – the efficiency of heat engines. We know that an engine converts energy from a heat source to work and returns to its initial state. According to (2.69), the transfer of energy from a heat source lowers the entropy of the source. If the energy transferred is used to do work, the work done must be done on some other system. Because the process of doing this work may be quasistatic and adiabatic, the work done need not involve a change of entropy. But if all of the energy transferred were converted into work, the total entropy would decrease, and we would violate the entropy statement of the second law. Hence, we arrive at the conclusion summarized in the Kelvin-Planck statement of the second law: no process is possible whose sole result is the complete conversion of energy into work. We need to do something with the energy that was not converted to work.

The simplest possible engine works in conjunction with a heat source at temperature T_{high} and a heat sink at temperature T_{low} . In a cycle the heat source transfers energy Q_{high} to the engine, and the engine does work W and transfers energy Q_{low} to the heat sink (see Figure 2.7). At the end of one cycle, the energy and entropy of the engine are unchanged because they return to their original values.

We have defined the work W done on a system as positive. However, in the context of engines, it is more natural to define the work done by the system as positive because that work is the output of the system. Hence, in this section we will take Q_{high} , Q_{low} , and W to be positive quantities, and explicitly put in minus signs where needed. From the arrows in Figure 2.7 we see that the input to the engine is Q_{high} and the output is W and Q_{low} . Hence, we have $Q_{\text{high}} = W + Q_{\text{low}}$, or $W = Q_{\text{high}} - Q_{\text{low}}$. From the second law we have that

$$\Delta S_{\text{total}} = \Delta S_{\text{high}} + \Delta S_{\text{low}} = -\frac{Q_{\text{high}}}{T_{\text{high}}} + \frac{Q_{\text{low}}}{T_{\text{low}}} \geq 0. \quad (2.70)$$

We rewrite (2.70) as

$$\frac{Q_{\text{low}}}{Q_{\text{high}}} \geq \frac{T_{\text{low}}}{T_{\text{high}}}. \quad (2.71)$$

The *thermal efficiency* η of the engine is defined as

$$\eta = \frac{\text{what you obtain}}{\text{what you pay for}} \quad (2.72)$$

$$= \frac{W}{Q_{\text{high}}} = \frac{Q_{\text{high}} - Q_{\text{low}}}{Q_{\text{high}}} = 1 - \frac{Q_{\text{low}}}{Q_{\text{high}}}. \quad (2.73)$$

From (2.73) we see that the engine is most efficient when the ratio $Q_{\text{low}}/Q_{\text{high}}$ is as small as possible. Equation (2.71) shows that $Q_{\text{low}}/Q_{\text{high}}$ is a minimum when the cycle is reversible or

$$\Delta S_{\text{total}} = 0, \quad (2.74)$$

and

$$\frac{Q_{\text{low}}}{Q_{\text{high}}} = \frac{T_{\text{low}}}{T_{\text{high}}}. \quad (2.75)$$

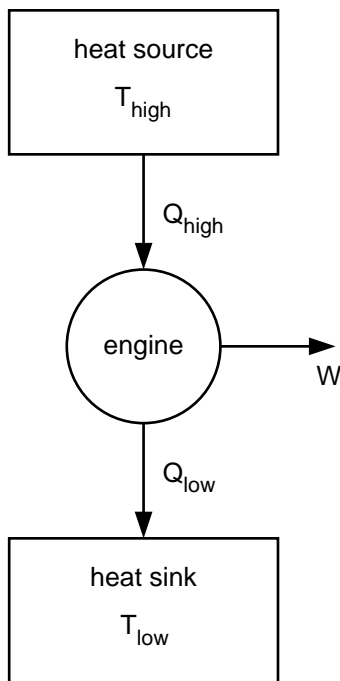


Figure 2.7: Schematic energy transfer diagram for an ideal heat engine. The convention when analyzing energy transfers in the context of engines is that the quantities Q_{high} , Q_{low} , and W are taken to be positive.

For these conditions we find that the maximum thermal efficiency is

$$\eta = 1 - \frac{T_{\text{low}}}{T_{\text{high}}} \quad (\text{maximum thermal efficiency}). \quad (2.76)$$

Note that the temperature in (2.76) is the thermodynamic temperature. A reversible engine of this type is known as a *Carnot engine*.

The result (2.76) illustrates the remarkable power of thermodynamics. We have concluded that all reversible engines operating between a heat source and a heat sink with the same pair of temperatures have the same efficiency and that no irreversible engine working between the same pair of temperatures may have a greater efficiency. This statement is known as *Carnot's principle*. We have been able to determine the maximum efficiency of a reversible engine without knowing anything about the details of the engine.

Real engines never reach the maximum thermodynamic efficiency because of the presence of mechanical friction and because the processes cannot really be quasistatic. For these reasons, real engines seldom attain more than 30–40% of the maximum thermodynamic efficiency. Nevertheless, the basic principles of thermodynamics are an important factor in their design.

Example 2.10. A Carnot engine

A Carnot engine extracts 250 J from a heat source and rejects 100 J to a heat sink at 15°C in one cycle. How much work does the engine do in one cycle? What is its efficiency? What is the temperature of the heat source?

Solution. From the first law we have

$$W = 250 \text{ J} - 100 \text{ J} = 150 \text{ J}. \quad (2.77)$$

The efficiency is given by

$$\eta = \frac{W}{Q_{\text{high}}} = \frac{150}{250} = 0.6 = 60\%. \quad (2.78)$$

We can use this result for η and the general relation (2.76) to solve for T_{high} :

$$T_{\text{high}} = \frac{T_{\text{low}}}{1 - \eta} = \frac{288 \text{ K}}{1 - 0.6} = 720 \text{ K}. \quad (2.79)$$

Note that we must use the thermodynamic temperature to calculate the efficiency. \diamond

Example 2.11. The efficiency of a hypothetical engine

The cycle of a hypothetical engine is illustrated in Figure 2.8. Let $P_{\text{low}} = 1 \times 10^6 \text{ Pa}$, $P_{\text{high}} = 2 \times 10^6 \text{ Pa}$, $V_{\text{low}} = 5 \times 10^{-3} \text{ m}^3$, and $V_{\text{high}} = 25 \times 10^{-3} \text{ m}^3$. If the energy absorbed by heating the engine is $5 \times 10^4 \text{ J}$, what is the efficiency of the engine?

Solution. The magnitude of the work done by the engine equals the area enclosed:

$$W = \frac{1}{2}(P_{\text{high}} - P_{\text{low}})(V_{\text{high}} - V_{\text{low}}). \quad (2.80)$$

(Recall that the convention in the treatment of heat engines is that all energy transfers are taken to be positive.) Confirm that $W = 1 \times 10^4 \text{ J}$. The efficiency is given by

$$\eta = \frac{W}{Q_{\text{absorbed}}} = \frac{1 \times 10^4}{5 \times 10^4} = 0.20. \quad (2.81)$$

Note that, even if the engine operated reversibly, we cannot use the Carnot efficiency because we have no assurance that the engine is operating between two heat baths. \diamond

The maximum efficiency of a Carnot engine depends on the temperatures T_{high} and T_{low} in a simple way and not on the details of the cycle or working substance. The *Carnot cycle* is a particular sequence of idealized processes that yields the maximum thermodynamic efficiency given in (2.76). The four steps of the Carnot cycle (two adiabatic and two isothermal steps) are illustrated in Figure 2.9. The initial state is at 1. The system is in contact with a heat bath at temperature T_{high} so that the temperature of the system also is T_{high} . The system volume is small and its pressure is high.

$1 \rightarrow 2$, *isothermal expansion*. The system expands while it is in contact with the heat source. During the expansion the high pressure gas pushes on the piston and the piston turns a crank. This step is a power stroke of the engine and the engine does work. To keep the system at the same temperature, the engine must absorb energy from the heat source.

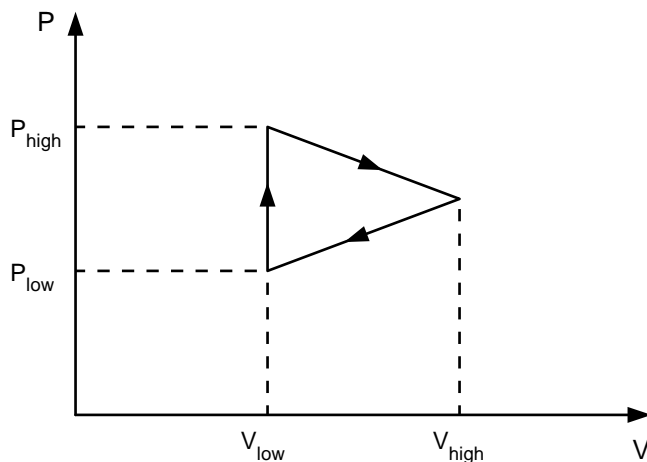


Figure 2.8: The cycle of the hypothetical engine considered in Example 2.11. Take $P_{\text{low}} = 1 \times 10^6 \text{ Pa}$, $P_{\text{high}} = 2 \times 10^6 \text{ Pa}$, $V_{\text{low}} = 5 \times 10^{-3} \text{ m}^3$, and $V_{\text{high}} = 25 \times 10^{-3} \text{ m}^3$.

We could compress the system isothermally and return the system to its initial state. Although this step would complete the cycle, exactly the same amount of work would be needed to push the piston back to its original position and hence no net work would be done. To make the cycle useful, we have to choose a cycle so that not all the work of the power stroke is lost in restoring the system to its initial pressure, temperature, and volume. The idea is to reduce the pressure of the system so that during the compression step less work has to be done. One way of reducing the pressure is to lower the temperature of the system by doing an adiabatic expansion.

$2 \rightarrow 3$, *adiabatic expansion*. We remove the thermal contact of the system with the hot bath and allow the volume to continue to increase so that the system expands adiabatically. Both the pressure and the temperature of the system decrease. The step $2 \rightarrow 3$ is also a power stroke, but now we are cashing in on the energy stored in the system, because it can no longer take energy from the heat source.

$3 \rightarrow 4$, *isothermal compression*. We now begin to restore the system to its initial condition. At 3 the system is placed in contact with the heat sink at temperature T_{low} to ensure that the pressure remains low. Work is done on the system by pushing on the piston and compressing the system. As the system is compressed, the temperature of the system would rise, but the thermal contact with the heat sink ensures that the temperature remains at T_{low} . The extra energy is dumped into the heat sink.

$4 \rightarrow 1$, *adiabatic compression*. At 4 the volume is almost what it was initially, but the temperature of the system is too low. Before the piston returns to its initial state, we remove the contact with the heat sink and allow the work of adiabatic compression to increase the temperature of the system to T_{high} .

These four steps represent a complete cycle, and the idealized engine is ready to go through another cycle. Note that a net amount of work has been done, because more work was done *by* the system during its power strokes than was done *on* the system while it was compressed. The reason is that the work done during the compression steps was against a lower pressure. The result is

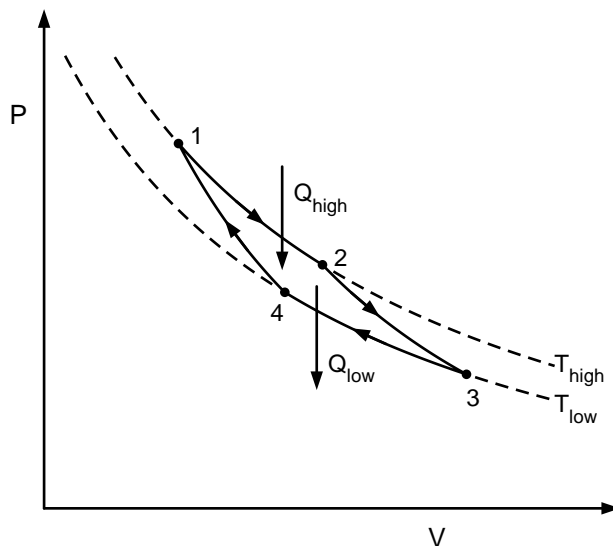


Figure 2.9: The four steps of the Carnot cycle.

that we have extracted useful work, and some of the energy of the system was discarded into the heat sink while the system was being compressed. The price we have had to pay to do work by having the system heated by the heat source is to throw away some of the energy to the heat sink.

Example 2.12. The Carnot cycle for an ideal gas

Determine the changes in the various thermodynamic quantities of interest during each step of the Carnot cycle and show that the efficiency of a Carnot cycle whose working substance is an ideal gas is given by $\eta = 1 - T_{\text{low}}/T_{\text{high}}$.

Solution. We will use the P - V diagram for the engine shown in Figure 2.9. During the isothermal expansion $1 \rightarrow 2$, energy Q_{high} is absorbed by the gas by heating at temperature T_{high} . The expanding gas does positive work against its environment, which lowers the energy of the gas. However, $\Delta E = 0$ for an ideal gas along an isotherm and thus the gas must receive energy by heating given by

$$Q_{\text{high}} = |W_{1 \rightarrow 2}| = NkT_{\text{high}} \ln \frac{V_2}{V_1}, \quad (2.82)$$

where $W_{1 \rightarrow 2} = -\int_{V_1}^{V_2} P dV$ is the work done on the gas, which is negative. The work done by the gas is thus positive.

During the adiabatic expansion $2 \rightarrow 3$, $Q_{2 \rightarrow 3} = 0$ and $W_{2 \rightarrow 3} = |C_V(T_{\text{low}} - T_{\text{high}})|$. Similarly, $W_{3 \rightarrow 4} = -NkT_{\text{low}} \ln V_4/V_3$, and because Q_{low} is positive by convention, we have

$$Q_{\text{low}} = \left| NkT_{\text{low}} \ln \frac{V_4}{V_3} \right| = NkT_{\text{low}} \ln \frac{V_3}{V_4}. \quad (2.83)$$

Finally, during the adiabatic compression $4 \rightarrow 1$, $Q_{4 \rightarrow 1} = 0$ and $W_{4 \rightarrow 1} = |C_V(T_{\text{low}} - T_{\text{high}})|$. We also have $W_{\text{net}} = Q_{\text{high}} - Q_{\text{low}}$, where W_{net} , Q_{high} , and Q_{low} are positive quantities.

Because the product $TV^{\gamma-1}$ is a constant in a quasistatic adiabatic process, we have

$$T_{\text{high}}V_2^{\gamma-1} = T_{\text{low}}V_3^{\gamma-1} \quad (2.84a)$$

$$T_{\text{low}}V_4^{\gamma-1} = T_{\text{high}}V_1^{\gamma-1}, \quad (2.84b)$$

which implies that

$$\frac{V_2}{V_1} = \frac{V_3}{V_4}. \quad (2.85)$$

The net work is given by

$$W_{\text{net}} = Q_{\text{high}} - Q_{\text{low}} = Nk(T_{\text{high}} - T_{\text{low}}) \ln \frac{V_3}{V_4}. \quad (2.86)$$

The efficiency is given by

$$\eta = \frac{W_{\text{net}}}{Q_{\text{high}}} = \frac{T_{\text{high}} - T_{\text{low}}}{T_{\text{high}}} = 1 - \frac{T_{\text{low}}}{T_{\text{high}}}, \quad (2.87)$$

as we found previously by general arguments. \diamond

Problem 2.19. A Carnot refrigerator

A refrigerator cools a closed container and heats the outside room surrounding the container. According to the second law of thermodynamics, work must be done by an external body for this process to occur. Suppose that the refrigerator extracts the amount Q_{cold} from the container at temperature T_{cold} and transfers energy Q_{hot} at temperature T_{hot} to the room. The external work supplied is W (see Figure 2.10). We define the *coefficient of performance* (COP) as

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{\text{cold}}}{W}. \quad (2.88)$$

Show that the maximum value of the COP corresponds to a reversible refrigerator and is given by

$$\text{COP} = \frac{T_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}}. \quad (2.89)$$

Note that a refrigerator is more efficient for smaller temperature differences. \square

Problem 2.20. Heat pump

A heat pump works on the same principle as a refrigerator, but the goal is to heat a room by cooling its cooler surroundings. For example, we could heat a building by cooling a nearby body of water. If we extract energy Q_{cold} from the surroundings at T_{cold} , do work W , and deliver Q_{hot} to the room at T_{hot} , the coefficient of performance is given by

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{\text{hot}}}{W}. \quad (2.90)$$

What is the maximum value of COP for a heat pump in terms of T_{cold} and T_{hot} ? What is the COP when the outside temperature is 0°C and the interior temperature is 23°C ? Is it more effective to operate a heat pump during the winters in New England where the winters are cold or in the Pacific Northwest where the winters are relatively mild? (It is too bad that the maximum efficiency of a heat pump occurs when it is needed least.) \square

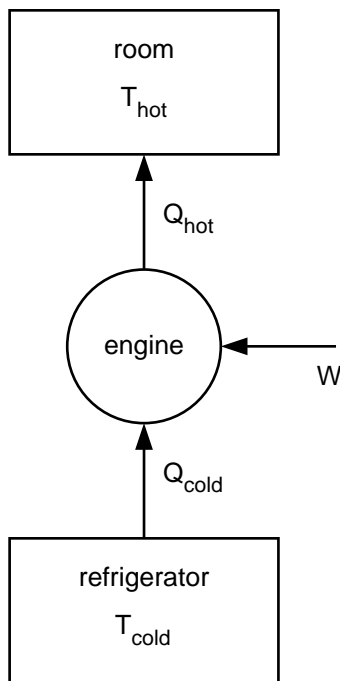


Figure 2.10: The transfer of energy in an idealized refrigerator (see Problem 2.19).

2.15 Entropy Changes

The impetus for developing thermodynamics was the industrial revolution and the efficiency of engines. The key to thermodynamics is understanding the role of entropy changes. In this section we apply the techniques of thermodynamics to calculating entropy changes to a variety of macroscopic systems. We begin with an example.

Example 2.13. Change in entropy of a solid

The heat capacity of water and solids at room temperatures is independent of temperature to a good approximation. A solid with the constant heat capacity C is taken from an initial temperature T_1 to a final temperature T_2 . What is its change in entropy? (Ignore the small difference in the heat capacities at constant volume and constant pressure.)

Solution. We assume that the temperature of the solid is increased by putting the solid in contact with a succession of heat baths at temperatures separated by a small amount such that we can use the quasistatic result $dS = dQ/T$. Then the entropy change is given by

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} C(T) \frac{dT}{T}. \quad (2.91)$$

Because the heat capacity C is assumed to be constant, we find

$$\Delta S = S_2 - S_1 = C \int_{T_1}^{T_2} \frac{dT}{T} = C \ln \frac{T_2}{T_1}. \quad (2.92)$$

Even though we used a specific quasistatic process, the change in entropy would be the same for any process that took the solid from the same initial state to the same final state. Note that if $T_2 < T_1$, the entropy of the solid is decreased. In Example 2.15 we consider the change in entropy of a larger composite system consisting of a liquid and a heat bath. \diamond

How can we measure the entropy of a solid? We know how to measure the temperature and the energy, but we have no entropy meter. Instead we have to determine the entropy *indirectly*. If the volume is held constant, we can determine the *entropy difference* between two temperatures by doing many successive measurements of the heat capacity and by doing the integral in (2.91). Note that such a determination gives only the entropy difference. We will discuss how to determine the absolute value of the entropy under certain conditions in Section 2.20.

Example 2.14. Entropy change due to thermal contact

A solid with heat capacity C_A at temperature T_A is placed in contact with another solid with heat capacity C_B at a lower temperature T_B . What is the change in entropy of the system after the two bodies have reached thermal equilibrium?

Solution. Assume that the heat capacities are independent of temperature and the two solids are isolated from their surroundings.

From Example 2.5 we know that the final equilibrium temperature is given by

$$T = \frac{C_A T_A + C_B T_B}{C_A + C_B}. \quad (2.93)$$

Although the process is irreversible, we can calculate the entropy change by considering any process that takes a body from one temperature to another. For example, we can imagine that a body is brought from its initial temperature T_B to the temperature T in many successive infinitesimal steps by placing it in successive contact with a series of heat baths at infinitesimally greater temperatures. At each contact the body is arbitrarily close to equilibrium and has a well-defined temperature. For this reason, we can apply the result (2.92), which yields $\Delta S_A = C_A \ln T/T_A$. The total change in the entropy of the system is given by

$$\Delta S = \Delta S_A + \Delta S_B = C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B}, \quad (2.94)$$

where T is given by (2.109). Substitute real numbers for T_A , T_B , C_A , and C_B and convince yourself that $\Delta S \geq 0$. Does the sign of ΔS depend on whether $T_A > T_B$ or $T_A < T_B$? \diamond

Example 2.15. Entropy change of water in contact with a heat bath

One kilogram of water at $T_A = 0^\circ\text{C}$ is brought into contact with a heat bath at $T_B = 50^\circ\text{C}$. What is the change of entropy of the water, the heat bath, and the combined system consisting of the water and the heat bath?

Solution. The change in entropy of the water is given by

$$\Delta S_A = C \ln \frac{T_B}{T_A} = 4184 \text{ J/K} \ln \frac{273 + 50}{273 + 0} = 704 \text{ J/K}. \quad (2.95)$$

Why does the number 273 enter in (2.95)? The amount of energy transferred to the water from the heat bath is

$$Q = C(T_B - T_A) = 4184 \text{ J/K} \times 50 \text{ K} = 209,200 \text{ J}. \quad (2.96)$$

The change in entropy of the heat bath is

$$\Delta S_B = \frac{-Q}{T_B} = -\frac{209,200 \text{ J}}{323 \text{ K}} = -648 \text{ J/K}. \quad (2.97)$$

Hence the total change in the entropy is

$$\Delta S = \Delta S_A + \Delta S_B = 704 \text{ J/K} - 648 \text{ J/K} = 56 \text{ J/K}. \quad (2.98)$$

Note that ΔS is positive. \diamond

Problem 2.21. Water in contact with two heat baths in succession

The temperature of 1 kg of water at 0°C is increased to 50°C by first bringing it into contact with a heat bath at 25°C and then with a heat bath at 50°C . What is the change in entropy of the entire system? How does this change in entropy compare with the change that was found in Example 2.15? \square

Example 2.16. More on the nature of a heat bath

A heat bath is a large system whose temperature remains unchanged when energy is added to or subtracted from it. As an example we first consider two systems with constant volume heat capacities C_A and C_B that are initially at different temperatures T_A and T_B . What happens when the two systems are placed in thermal contact (and are isolated from their surroundings)? The volume of the two systems is fixed and the heat capacities are independent of temperature. We will consider the general case and then take the limit $C_B \rightarrow \infty$.

From (2.93) the final temperature T can be written as

$$T = \frac{C_A}{C_A + C_B} T_A + \frac{C_B}{C_A + C_B} T_B. \quad (2.99)$$

We define the ratio

$$\lambda = \frac{C_A}{C_B}, \quad (2.100)$$

and rewrite (2.99) as

$$T = \frac{C_A}{C_B(1 + C_A/C_B)} T_A + \frac{1}{(1 + C_A/C_B)} T_B \quad (2.101a)$$

$$= \frac{1}{1 + \lambda} (\lambda T_A + T_B). \quad (2.101b)$$

In the limit $\lambda \rightarrow 0$ corresponding to system B becoming a heat bath we see from (2.101b) that $T = T_B$.

The total change in the entropy is given by (2.94). The first term gives

$$\Delta S_A = C_A \ln \frac{T}{T_A} \rightarrow C_A \ln \frac{T_B}{T_A}, \quad (2.102)$$

in the limit that system B is treated as a heat bath. To evaluate the second term in (2.94) we write

$$\frac{T}{T_B} = \frac{1}{1+\lambda} \left(1 + \lambda \frac{T_A}{T_B} \right) \approx (1-\lambda) \left(1 + \lambda \frac{T_A}{T_B} \right) \quad (2.103a)$$

$$\approx 1 + \lambda \left(\frac{T_A}{T_B} - 1 \right), \quad (2.103b)$$

where we have used the approximation $(1+x)^{-1} \approx 1-x$, and kept terms through order λ . We have

$$\Delta S_B = C_B \ln \frac{T}{T_B} \rightarrow C_A \frac{1}{\lambda} \ln \left[1 + \lambda \left(\frac{T_A}{T_B} - 1 \right) \right] \rightarrow C_A \left(\frac{T_A}{T_B} - 1 \right), \quad (2.104)$$

where we have used the approximation $\ln(1+x) \approx x$. Hence, the total change in the entropy of the system is given by

$$\Delta S = C_A \left[\ln \frac{T_B}{T_A} + \frac{T_A}{T_B} - 1 \right]. \quad (2.105)$$

In Problem 2.61 you will be asked to show that ΔS in (2.105) is always greater than zero for $T_A \neq T_B$. \diamond

Problem 2.22. Use the numerical values for various quantities from Example 2.15 to show that (2.105) gives the same numerical result as (2.98). \square

Example 2.17. Melting of ice

A beaker contains a 0.1 kg block of ice at 0°C. Suppose that we wait until the ice melts and then comes to room temperature. What is the change of entropy of the ice to water? (It takes 334 kJ to melt 1 kg of ice.)

Solution. If we add energy to ice by heating at its melting temperature $T = 273.15$ K at atmospheric pressure, the effect is to melt the ice rather than to raise its temperature.

We melt the ice by supplying $0.1 \text{ kg} \times 334 \text{ kJ/kg} = 33,400 \text{ J}$ from a heat bath at 273.15 K, assuming that the ice is in equilibrium with the air in the room which acts as a heat bath. Hence, the entropy increase due to the melting of the ice is given by $\Delta S = 33,400/273.15 = 122.2 \text{ J/K}$.

The change in the entropy to bring the water from 0°C to room temperature, which we take to be 22°C, is $(0.1 \times 4184) \ln 295/273 = 32.4 \text{ J/K}$. Thus, the total change in entropy of the ice to water at room temperature is $122.2 + 32.4 = 154.6 \text{ J/K}$. \diamond

Example 2.18. Entropy change in a free expansion

Consider an ideal gas of N particles in a closed, insulated container that is divided into two chambers by an impermeable partition (see Figure 2.11). The gas is initially confined to one

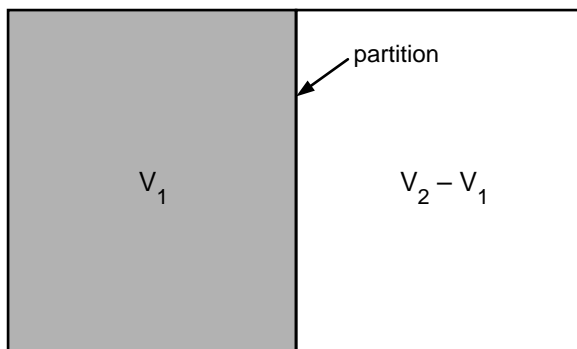


Figure 2.11: The free expansion of an isolated ideal gas. The second chamber is initially a vacuum and the total volume of the two chambers is V_2 .

chamber of volume V_1 at a temperature T . The gas is then allowed to expand freely into a vacuum to fill the entire container of volume V_2 . What is the change in entropy?

Solution. Because the composite system of two chambers has rigid impermeable walls, no energy leaves or enters the composite system either by heating or by work. Hence, there is no change in the internal energy of the gas. It might be argued that $\Delta S = Q/T = 0$ because $Q = 0$. However, this conclusion would be incorrect because the relation $dS = dQ/T$ holds only for a quasistatic process.

The expansion from V_1 to V_2 is an irreversible process. Left to itself, the system will not return spontaneously to its original state with all the particles in the left container. Because the entropy is a state function, we can consider another process that takes the system to the same final state. This process should be quasistatic so that we can use thermodynamics, and also should take place at constant energy because there is no change in energy during the free expansion of an ideal gas. Suppose that the two chambers are separated by a movable partition with a nonzero mass. Because the partition has mass, the gas does work on the partition to increase its volume by an amount ΔV ; that is, work $-P\Delta V$ is done on the gas. Because we want the final state of the gas to have the same energy as the initial state, we need to simultaneously add energy to the gas by heating. Because the gas is ideal, the internal energy depends only on the temperature, and hence the temperature of the ideal gas is unchanged. Hence, $dE = TdS - PdV = 0$, or

$$\Delta S = \frac{1}{T} \int_{V_1}^{V_2} P dV = \frac{1}{T} \int_{V_1}^{V_2} \frac{NkT}{V} dV = Nk \ln \frac{V_2}{V_1}. \quad (2.106)$$

Hence, the entropy increases as expected. \diamond

The discussion of the free expansion of an ideal gas illustrates two initially confusing aspects of thermodynamics. As mentioned, the name thermodynamics is a misnomer because thermodynamics treats only equilibrium states and not dynamics. Nevertheless, thermodynamics discusses processes that must happen over some interval of time. It is also confusing that we can consider processes that did not actually happen. In this case the calculation of ΔS in Example 2.18 is identical to what we would do for an isothermal nonadiabatic quasistatic process where the gas

does work, even though in the actual process no work was done by the gas and no heating or cooling occurred. However, the initial and final states and the change in the entropy are the same for the actual process and the calculated process.

Quasistatic adiabatic processes. We have already discussed that quasistatic adiabatic processes have the special property that the entropy does not change, but we repeat this statement here to emphasize its importance. If a process is adiabatic, then $Q = 0$, and if the process is also quasistatic, then $\Delta S = Q/T = 0$, and there is no change in the entropy.

Quasistatic processes are subtle. Consider again the free expansion of an ideal gas. Initially the gas is confined to one chamber and then allowed to expand freely into the second chamber to fill the entire container. It is certainly not quasistatic, and thus $\Delta S > 0$, even though $Q = 0$. Suppose that we imagine this process to be performed very slowly by dividing the second chamber into many small chambers separated by partitions and puncturing each partition in turn, allowing the expanded gas to come into equilibrium. It might seem that in the limit of an infinite number of partitions that such a process would be quasistatic. However, this conclusion is incorrect because it would imply that $dS = dQ/T = 0$.

Note that an infinitesimal process is not necessarily quasistatic. The puncture of a partition would cause the wall to move suddenly, thus creating turbulence and causing changes that are not near equilibrium. Also the work done by the gas in a quasistatic process is $dW = PdV$, but no work is done even though $PdV \neq 0$. The expansion of a gas into a vacuum is not quasistatic no matter how slowly it is performed, and the process is not reversible, because the gas will never return to its original volume.

Example 2.19. Maximum work

When two bodies are placed in thermal contact, no work is done, that is, $W = 0$ and $\Delta E = Q_A + Q_B = 0$. How can we extract the maximum work possible from the two bodies?

Solution. From our discussion of heat engines, we know that we should not place them in thermal contact. Instead we run a Carnot (reversible) engine between the two bodies. However, unlike the heat baths considered in the Carnot engine, here the heat capacities of the two bodies are finite, and hence the temperature of each body changes as energy is transferred from one body to the other.

To extract the maximum work we assume that the process is reversible and write

$$\Delta S = \Delta S_A + \Delta S_B = 0. \quad (2.107)$$

If we assume that the heat capacities are constant, it follows using (2.91) that

$$C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B} = 0. \quad (2.108)$$

We solve (2.108) for T and find that

$$T = T_A^{C_A/(C_A+C_B)} T_B^{C_B/(C_A+C_B)}. \quad (2.109)$$

We see that the final temperature for a reversible process is the geometrical average of T_A and T_B weighted by their respective heat capacities. \diamond

Problem 2.23. More work

- (a) Show that the work performed
- by*
- the heat engine in Example 2.19 is given by

$$W = C_A(T_A - T) + C_B(T_B - T), \quad (2.110)$$

where C_A and C_B are constants and T is given by (2.109) if the process is reversible. (Recall that our convention is to consider the work done on a system, except when we are discussing heat engines.)

- (b) Suppose that $C_A = C_B = C$ (a constant independent of T) in (2.93) and (2.109). Compare the form of the expressions for the final temperature.
- (c) Suppose that $T_A = 256\text{ K}$ and $T_B = 144\text{ K}$. What are the relative values of the final temperatures in (2.93) and (2.109) assuming that the heat capacities of the two bodies are equal? For which process is the final temperature lower? Why?
- (d) Suppose that the heat capacities of both bodies depend linearly on the temperature T rather than being constant; that is, $C_A = AT$ and $C_B = BT$, where A and B are constants. What is the final temperature assuming that the two bodies are placed in thermal contact? What is the final temperature for the case when the maximum work is extracted? What is the maximum work done? \square

Are all forms of energy equivalent? If you were offered 100 J of energy, would you choose to have it delivered as compressed gas at room temperature or as a hot brick at 400 K? If you are not sure what you want to do with the energy, you should take the form of the energy that can be most directly converted into work, because there is no restriction on the efficiency of using stored energy for heating. What is different is the *quality* of the energy, which we take to be a measure of its ability to do work. We can readily convert energy from higher to lower quality, but the second law of thermodynamics prevents us from going in the opposite direction with 100% efficiency.

As an example consider the adiabatic free expansion of an ideal gas from volume V_1 to volume V_2 . As we found in Example 2.18, the entropy increase is $\Delta S = Nk \ln V_2/V_1$. If we had instead let the gas undergo a quasistatic isothermal expansion, the work done by the gas would have been $W = NkT \ln V_2/V_1$, which is the same as $T\Delta S$ for the adiabatic free expansion. Thus, an increase in entropy implies that some energy has become unavailable to do work.

2.16 Equivalence of Thermodynamic and Ideal Gas Scale Temperatures

So far we have assumed that the ideal gas scale temperature that we introduced in Section 2.4 is the same as the thermodynamic temperature defined by (2.65). We now show that the two temperatures are proportional and can be made equal if we choose the units of S appropriately.

The ideal gas temperature scale, which we denote as θ in this section to distinguish it from the thermodynamic temperature T , is defined by the relation

$$\theta = PV/Nk. \quad (2.111)$$

That is, θ is proportional to the pressure of a gas at a fixed low density and is equal to 273.16 K at the triple point of water. The fact that $\theta \propto P$ for a dilute gas is a matter of definition. Another important property of ideal gases is that the internal energy depends only on θ and is independent of the volume.

To show the equivalence between T and θ we need to consider a process for which we have a general result involving the thermodynamic temperature that is independent of the nature of the system involved in the process. We can then specialize to the ideal gas. The only example we have so far is the Carnot cycle. At every stage of the cycle we have

$$\frac{dQ}{\theta} = \frac{dE - dW}{\theta} = \frac{dE + PdV}{\theta}, \quad (2.112)$$

or

$$\frac{dQ}{\theta} = \frac{dE}{\theta} + Nk \frac{dV}{V}. \quad (2.113)$$

The first term on the right-hand side of (2.113) depends only on θ and the second term depends only on the volume. If we integrate (2.113) around one cycle, both θ and V return to their starting values, and hence the loop integral of the right-hand side of (2.113) is zero. We conclude that

$$\oint \frac{dQ}{\theta} = 0. \quad (2.114)$$

Because the only places where Q is nonzero are at the hot and cold heat baths which are held at constant temperatures, we have

$$0 = \frac{Q_{\text{cold}}}{\theta_{\text{cold}}} - \frac{Q_{\text{hot}}}{\theta_{\text{hot}}} = 0. \quad (2.115)$$

In Section 2.14 we showed that $Q_{\text{cold}}/Q_{\text{hot}} = T_{\text{cold}}/T_{\text{hot}}$ for a Carnot engine [see (2.75)]. If we combine this result with (2.115), we find that

$$\frac{T_{\text{cold}}}{T_{\text{hot}}} = \frac{\theta_{\text{cold}}}{\theta_{\text{hot}}}. \quad (2.116)$$

It follows that the thermodynamic temperature T is proportional to the ideal gas scale temperature θ . From now on we shall assume that we have chosen suitable units for S so that $T = \theta$.

2.17 The Thermodynamic Pressure

In Section 2.13 we showed that the thermodynamic definition of temperature follows by considering the condition for the thermal equilibrium of two subsystems. In the following, we show that the pressure can be defined in an analogous way and that the pressure can be interpreted as a response of the entropy to a change in the volume.

As before, consider an isolated composite system that is partitioned into two subsystems. The subsystems are separated by a movable, insulating wall so that the energies and volumes of the subsystems can adjust themselves, but N_A and N_B are fixed. For simplicity, we assume that E_A and E_B have already changed so that thermal equilibrium has been established. For fixed total

volume V we have one independent variable, which we take to be V_A ; V_B is given by $V_B = V - V_A$. The value of V_A that maximizes $S = S_A + S_B$ is given by

$$dS = \frac{\partial S_A}{\partial V_A} dV_A + \frac{\partial S_B}{\partial V_B} dV_B = 0. \quad (2.117)$$

Because $dV_A = -dV_B$, we can use (2.117) to write the condition for *mechanical equilibrium* as

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}. \quad (2.118)$$

We define the thermodynamic pressure P as

$$\boxed{\frac{P}{T} \equiv \left(\frac{\partial S}{\partial V} \right)_{E,N}} \quad (\text{definition of thermodynamic pressure}). \quad (2.119)$$

Note that the presence of $1/T$ in the definition of pressure makes the units come out correctly. We will see in the next section that the factor of $1/T$ is needed for consistency with the relation $dE = TdS - PdV$.

For completeness, we define the *chemical potential* as the response of the entropy to a change in the number of particles:

$$\boxed{\frac{\mu}{T} \equiv - \left(\frac{\partial S}{\partial N} \right)_{E,V}} \quad (\text{definition of the chemical potential}). \quad (2.120)$$

We will discuss the interpretation of μ in Section 4.12. You probably won't be surprised to learn that if two systems can exchange particles, then the equality of the chemical potential μ is the condition for *chemical equilibrium*.

We will sometimes distinguish between thermal equilibrium, mechanical equilibrium, and chemical equilibrium for which the temperatures, pressures, and chemical potentials are equal, respectively. When all three conditions are satisfied, a system is in thermodynamic equilibrium.

2.18 The Fundamental Thermodynamic Relation

The first law of thermodynamics implies that the internal energy E is a function of state. For *any* change of state, the change in E is given by (2.21)

$$\Delta E = Q + W \quad (\text{any process}). \quad (2.121)$$

To separate the contributions to E due to heating and work, the constraints on the system have to be known. If the change is quasistatic, then the infinitesimal work done is

$$dW = -PdV, \quad (\text{quasistatic process}) \quad (2.122)$$

and

$$dQ = TdS. \quad (\text{quasistatic process}) \quad (2.123)$$

Thus, for an infinitesimal quasistatic change in the energy we have

$$dE = TdS - PdV. \quad (2.124)$$

There are two ways of thinking about (2.124). As our derivation suggests this equation tells us the relation between changes in the energy, entropy, and volume. Alternatively, we can interpret (2.124) as the differential form (for fixed N) of the fundamental equation $E = E(S, V, N)$. Because $S = S(E, V, N)$ is also a state function and because we defined T , P , and μ in terms of derivatives of S , we may rewrite (2.124) as

$$dS = \frac{1}{T}dE + \frac{P}{T}dV. \quad (2.125)$$

We also have

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN. \quad (2.126)$$

A comparison of (2.125) and (2.126) gives the familiar results $1/T = (\partial S/\partial E)_{V,N}$ and $P/T = (\partial S/\partial V)_{E,N}$ [see (2.65) and (2.119)]. If we allow N to vary we can use (2.120) and write

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN. \quad (2.127)$$

If we know the entropy S as a function of E , V , and N , we can determine the corresponding responses T , P , and μ . For this reason we shall refer to E , V , and N as the natural variables in which S should be expressed. In this context S can be interpreted as a *thermodynamic potential* because its various partial derivatives yield the equations of state of the system. In Section 2.21 we shall discuss thermodynamic potentials that have different sets of natural variables.

We can alternatively consider E as a function of S , V , and N and rewrite (2.127) as

$$\boxed{dE = TdS - PdV + \mu dN} \quad (\text{fundamental thermodynamic relation}). \quad (2.128)$$

Equation (2.128) is a mathematical statement of the combined first and second laws of thermodynamics. There are very few equations in thermodynamics that are necessary to memorize, but (2.128) is one of the few equations that you should know without thinking.

Many useful thermodynamic relations can be derived using (2.128). For example, if we regard E as a function of S , V , and N , we can write

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN. \quad (2.129)$$

If we compare (2.128) and (2.129), we see that

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N}, \quad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N}, \quad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}. \quad (2.130)$$

Note that $E(S, V, N)$ also can be interpreted as a thermodynamic potential.

2.19 The Entropy of an Ideal Classical Gas

Because we know two equations of state of an ideal gas, (2.8) and (2.23), we can find the entropy of an ideal classical gas as a function of various combinations of E , T , P , and V for fixed N . If we substitute $1/T = \frac{3}{2}Nk/E$ and $P/T = Nk/V$ into (2.127), we obtain

$$dS = \frac{3}{2}Nk \frac{dE}{E} + Nk \frac{dV}{V}. \quad (2.131)$$

We can integrate (2.131) to obtain the change in the entropy from state E_1, V_1 to state E_2, V_2 :

$$\Delta S = \frac{3}{2}Nk \ln \frac{E_2}{E_1} + Nk \ln \frac{V_2}{V_1}. \quad (2.132)$$

We see that S is an additive quantity as we have assumed; that is, S is proportional to N .

Frequently it is more convenient to express S in terms of T and V or T and P . To obtain $S(T, V)$ we substitute $E = \frac{3}{2}NkT$ into (2.132) and obtain

$$\Delta S = \frac{3}{2}Nk \ln \frac{T_2}{T_1} + Nk \ln \frac{V_2}{V_1} \quad (\text{ideal gas}). \quad (2.133)$$

Problem 2.24. Applications of (2.133)

- (a) Use (2.133) to derive the relation (2.44) between T and V for a quasistatic adiabatic process.
- (b) An ideal gas of N particles is confined to a box of chamber V_1 at temperature T . The gas is then allowed to expand freely into a vacuum to fill the entire container of volume V_2 . The container is thermally insulated. What is the change in entropy of the gas?
- (c) Find $\Delta S(T, P)$ for an ideal classical gas. □

2.20 The Third Law of Thermodynamics

Only differences in the entropy can be calculated using purely thermodynamic relations as we did in Section 2.19. We can define the absolute value of the entropy by using the third law of thermodynamics which states that

$$\lim_{T \rightarrow 0} S = 0 \quad (\text{third law of thermodynamics}). \quad (2.134)$$

The statistical basis of this law is discussed in Section 4.6. In the context of thermodynamics, the third law can be understood only as a consequence of empirical observations.

The most important consequence of the third law is that all heat capacities must go to zero as the temperature approaches zero. For changes at constant volume, we know that [see (2.91)]

$$S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT. \quad (2.135)$$

The condition (2.134) implies that in the limit $T_1 \rightarrow 0$, the integral in (2.135) must be finite, and hence we require that $C_V(T) \rightarrow 0$ as $T \rightarrow 0$. Similarly, we can argue that $C_P \rightarrow 0$ as $T \rightarrow 0$. Note that these conclusions about the low temperature behavior of C_V and C_P are independent of the nature of the system. Such is the power of thermodynamics. The low temperature behavior of the heat capacity was first established experimentally in 1910–1912.

As we will find in Section 4.6, the third law is a consequence of the fact that the most fundamental description of nature at the microscopic level is quantum mechanical. We have already seen that the heat capacity is a constant for an ideal gas. Hence, the thermal equation of state, $E = \frac{3}{2}NkT$, as well as the pressure equation of state, $PV = NkT$, must cease to be applicable at sufficiently low temperatures.

Example 2.20. Low temperature entropy of an insulating solid

At very low temperature T , the heat capacity C of an insulating solid is proportional to T^3 . If we take $C = AT^3$ for a particular solid, what is the entropy of the solid at temperature T ?

Solution. As before, the entropy is given by [see (2.91)]

$$S(T) = \int_0^T \frac{C_V(T)}{T} dT, \quad (2.136)$$

where we have used the fact that $S(T=0) = 0$. We can integrate the right-hand side of (2.136) from $T = 0$ to the desired value of T to find the absolute value of S . The result in this case is $S = AT^3/3$. \diamond

2.21 Free Energies

We know that the entropy of an isolated system can never decrease. However, an isolated system is of little experimental interest, and we wish to consider the more typical case where the system of interest is connected to a much larger system, a heat bath, whose properties do not change significantly. In the following we will consider a heat bath whose temperature and pressure are unchanged by interactions with a much smaller system.

If a system is connected to a heat bath, then the entropy of the system may increase or decrease. The only thing we can say for sure is that the entropy of the system plus the heat bath must increase or remain unchanged. Because the entropy is additive, we have²²

$$S_{\text{composite}} = S + S_{\text{bath}} \quad (2.137)$$

and

$$\Delta S_{\text{composite}} = \Delta S + \Delta S_{\text{bath}} \geq 0. \quad (2.138)$$

The properties of the system of interest are denoted by the absence of a subscript. Our goal is to determine if there is a property of the system alone (not the composite system) that is a maximum

²²The following discussion is adapted from Mandl, pp. 89–92.

or a minimum. We begin by writing the change ΔS_{bath} in terms of the properties of the system. Because energy can be transferred between the system and heat bath, we have

$$\Delta S_{\text{bath}} = \frac{-Q}{T_{\text{bath}}}, \quad (2.139)$$

where Q is the amount of energy transferred to the system by heating, and $-Q$ is the amount of energy transferred to the heat bath. If we use (2.139), we can rewrite (2.138) as

$$\Delta S_{\text{composite}} = \Delta S - \frac{Q}{T_{\text{bath}}}. \quad (2.140)$$

The application of the first law to the system gives

$$\Delta E = Q + W, \quad (2.141)$$

where ΔE is the change in the energy of the system and W is the work done on it. If the work done on the system is due to the heat bath, then $W = -P_{\text{bath}}\Delta V$, where ΔV is the change in volume of the system. Then we can write

$$\Delta S_{\text{composite}} = \Delta S - \frac{\Delta E - W}{T_{\text{bath}}} = \Delta S - \frac{\Delta E + P_{\text{bath}}\Delta V}{T_{\text{bath}}} \geq 0. \quad (2.142)$$

A little algebra leads to

$$\Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S \leq 0. \quad (2.143)$$

This result suggests that we define the *availability* by

$$A = E + P_{\text{bath}}V - T_{\text{bath}}S, \quad (2.144)$$

so that (2.143) becomes

$$\Delta A = \Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S \leq 0. \quad (2.145)$$

The availability includes properties of both the system and the heat bath. The significance of the availability will be discussed in the following.

We now look at some typical experimental situations and introduce a quantity that depends only on the properties of the system. First, we assume that its volume and number of particles is fixed, and that its temperature equals the temperature of the heat bath; that is, we set $T_{\text{bath}} = T$ and $\Delta V = 0$. In this case we have

$$\Delta A = \Delta E - T\Delta S = \Delta F \leq 0, \quad (2.146)$$

where we have defined the *Helmholtz free energy* as

$$\boxed{F \equiv E - TS}. \quad (2.147)$$

The inequality in (2.146) implies that if a constraint within the system is removed, then the system's Helmholtz free energy will *decrease*. Just as $\Delta S \geq 0$ and $S(E, V, N)$ is a maximum at equilibrium, $\Delta F \leq 0$ and $F(T, V, N)$ is a minimum at equilibrium. Thus, F plays the analogous role for systems at constant T and V that was played by the entropy for an isolated system (constant E and V).

What are the natural variables for F ? From our discussion it should be clear that these variables are T , V , and N . The answer can be found by taking the differential of (2.147) and using (2.128). The result is

$$dF = dE - SdT - TdS \quad (2.148a)$$

$$= (TdS - PdV + \mu dN) - SdT - TdS \quad (2.148b)$$

$$= -SdT - PdV + \mu dN. \quad (2.148c)$$

We substituted $dE = TdS - PdV + \mu dN$ to go from (2.148a) to (2.148c). From (2.148) we see that $F = F(T, V, N)$ and that S , P , and μ can be obtained by taking appropriate partial derivatives of F . For example,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad (2.149)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \quad (2.150)$$

and

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}. \quad (2.151)$$

The Helmholtz free energy is an example of a free energy or *thermodynamic potential*.²³

We can relax the condition of a fixed volume by requiring that the pressure be specified. In this case mechanical equilibrium requires that the pressure of the system equal the pressure of the bath. This case is common in experiments with fluids where the pressure is fixed at atmospheric pressure. We write $P_{\text{bath}} = P$ and express (2.143) as

$$\Delta A = \Delta E + P\Delta V - T\Delta S = \Delta G \leq 0, \quad (2.152)$$

where we have defined the Gibbs free energy as

$$\boxed{G \equiv E - TS + PV = F + PV}. \quad (2.153)$$

The natural variables of G can be found in the same way as we did for F . We find that $G = G(T, P, N)$ and

$$dG = dE - SdT - TdS + PdV + VdP \quad (2.154a)$$

$$= (TdS - PdV + \mu dN) - SdT - TdS + PdV + VdP \quad (2.154b)$$

$$= -SdT + VdP + \mu dN. \quad (2.154c)$$

We can use similar reasoning to conclude that G is a minimum at fixed temperature, pressure, and number of particles.

We can also relate G to the chemical potential by noting that G and N are extensive variables (see Section 2.9), but T and P are not. Thus, G must be proportional to N :

$$G = Ng(T, P), \quad (2.155)$$

²³A more formal way of obtaining the various thermodynamic potentials is given in Section 2.24.2.

where $g(T, P)$ is the Gibbs free energy per particle. This function must be the chemical potential because $\partial G/\partial N = g(T, P)$ from (2.155) and $\partial G/\partial N = \mu$ from (2.154). Thus, the chemical potential is the Gibbs free energy per particle:

$$\mu(T, P) = \frac{G}{N} = g(T, P). \quad (2.156)$$

Because g depends only on T and P , we have

$$dg = d\mu = \left(\frac{\partial g}{\partial P}\right)_T dP + \left(\frac{\partial g}{\partial T}\right)_P dT \quad (2.157)$$

$$= v dP - s dT, \quad (2.158)$$

where $v = V/N$ and $s = S/N$. Equation (2.158) is called the *Gibbs-Duhem equation*. The properties of G and the relation (2.158) will be important when we discuss processes involving a change of phase (see Section 7.3).

Another common thermodynamic potential is the *enthalpy* H which we defined in (2.29). This potential is similar to $E(S, V, N)$ except for the requirement of fixed P rather than fixed V .

Problem 2.25. The enthalpy

(a) Given the definition of the enthalpy in (2.29) show that

$$dH = T dS + V dP + \mu dN, \quad (2.159)$$

and

$$T = \left(\frac{\partial H}{\partial S}\right)_{P, N}, \quad (2.160)$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S, N}, \quad (2.161)$$

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S, P}. \quad (2.162)$$

(b) Show that H is a minimum for an equilibrium system at fixed entropy. \square

Landau potential. A very useful thermodynamic potential is one for which the variables T , V , and μ are specified. This potential has no generally recognized name or symbol, but is sometimes called the *Landau potential* and is usually, but not always, denoted by Ω . Another common name is simply the *grand potential*. We will adopt the notation Ω and refer to Ω as the Landau potential in honor of Lev Landau. The Landau potential is the thermodynamic potential for which the variables T , V , and μ are specified and is given by

$$\boxed{\Omega(T, V, \mu) = F - \mu N}. \quad (2.163)$$

If we take the derivative of Ω and use the fact that $dF = -SdT - PdV + \mu dN$ (see (2.148)), we find that

$$d\Omega = dF - \mu dN - Nd\mu \quad (2.164a)$$

$$= -SdT - PdV - Nd\mu. \quad (2.164b)$$

Name	Potential	Differential Form
Internal energy	$E(S, V, N)$	$dE = TdS - PdV + \mu dN$
Entropy	$S(E, V, N)$	$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN$
Enthalpy	$H(S, P, N) = E + PV$	$dH = TdS + VdP + \mu dN$
Helmholtz free energy	$F(T, V, N) = E - TS$	$dF = -SdT - PdV + \mu dN$
Gibbs free energy	$G(T, P, N) = F + PV$	$dG = -SdT + VdP + \mu dN$
Landau potential	$\Omega(T, V, \mu) = F - \mu N$	$d\Omega = -SdT - PdV - Nd\mu$

Table 2.2: Summary of the common thermodynamic potentials, their natural variables, and their differential form. From the differential forms we can easily write down various thermodynamic quantities as partial derivatives of the appropriate potential. For example, $N = -(\partial\Omega/\partial\mu)_{T,V}$.

From (2.164b) we have

$$S = -\left(\frac{\partial\Omega}{\partial T}\right)_{V,\mu}, \quad (2.165)$$

$$P = -\left(\frac{\partial\Omega}{\partial V}\right)_{T,\mu}, \quad (2.166)$$

$$N = -\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,V}. \quad (2.167)$$

Because $G = N\mu$, we can write $\Omega = F - G$. Hence, if we use the definition $G = F + PV$, we obtain

$$\Omega(T, V, \mu) = F - \mu N = F - G = -PV. \quad (2.168)$$

The relation (2.168) will be very useful for obtaining the equation of state of various systems (see Section 6.8).

Table 2.2 summarizes the important thermodynamic potentials and their natural variables.

***Useful work and availability.** The free energies that we have introduced are useful for understanding the maximum amount of useful work, W_{useful} , that can be done *by* a system when it is connected to a heat bath. The system is not necessarily in thermal or mechanical equilibrium with its surroundings. In addition to the system of interest and its surroundings (the bath), we include a third body, namely, the body on which the system does useful work. The third body is thermally insulated. The total work W_{by} done *by* the system is the work done against its surroundings, $P_{\text{bath}}\Delta V$ plus the work done on the body, W_{useful} :

$$W_{\text{by}} = P_{\text{bath}}\Delta V + W_{\text{useful}}. \quad (2.169)$$

Because W_{by} is the work done by the system when its volume changes by ΔV , the first term in (2.169) does not contain a negative sign. This term is the work that is necessarily and uselessly performed by the system in changing its volume and thus also the volume of its surroundings. The second term is the useful work done by the system. In (2.143) we replace the work done on the heat bath, $P_{\text{bath}}\Delta V$, by the total work done by the system $P_{\text{bath}}\Delta V + W_{\text{useful}}$ to obtain

$$\Delta E + P_{\text{bath}}\Delta V + W_{\text{useful}} - T_{\text{bath}}\Delta S \leq 0. \quad (2.170)$$

That is, the useful work done is

$$W_{\text{useful}} \leq -(\Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S) = -\Delta A. \quad (2.171)$$

Note that the maximum amount of useful work that can be done by the system is equal to $-\Delta A$. This relation explains the meaning of the terminology *availability* because only $-\Delta A$ is available for useful work. The rest of the work is wasted on the surroundings.

Problem 2.26. Maximum useful work and free energy changes

- (a) Show that if the change in volume of the system is zero, $\Delta V = 0$, and the initial and final temperatures are that of the heat bath, then the maximum useful work is $-\Delta F$.
- (b) Show that if the initial and final temperature and pressure are that of the bath, then the maximum useful work is $-\Delta G$. \square

2.22 Thermodynamic Derivatives

All thermodynamic measurements can be expressed in terms of partial derivatives. For example, the pressure P can be expressed as $P = -\partial F/\partial V$. Let us suppose that we make several thermodynamic measurements, for example, C_V , C_P , and κ , the isothermal compressibility. The latter is defined as

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \quad (\text{isothermal compressibility}). \quad (2.172)$$

Suppose that we wish to know the (isobaric) thermal expansion coefficient α , which is defined as

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (\text{thermal expansion coefficient}). \quad (2.173)$$

(The number of particles N is assumed to be held constant in the above derivatives.) Do we need to make an independent measurement of α or can we determine α by knowing the values of C_V , C_P , and κ ? To answer this question and related ones, we first need to know how to manipulate partial derivatives. This aspect of thermodynamics can be confusing when first encountered.

Thermodynamic systems normally have two or more independent variables. For example, we can choose the combination E , V , N or T , P , N . Because there are many choices of combinations of independent variables, it is important to be explicit about which variables are independent and which variables are being held constant in any partial derivative. We suggest that you read Section 2.24.1 to review some of the properties of partial derivatives. The following example illustrates the power of purely thermodynamic arguments based on the manipulation of thermodynamic derivatives.

Example 2.21. Thermodynamics of blackbody radiation

In Section 6.7 we show from first principles some of the basic results of blackbody radiation. In particular, we show that u , the energy per unit volume, is proportional to T^4 [see (6.139a)]. In the following we obtain this result using thermodynamic arguments and two reasonable assumptions. The arguments might be difficult to follow if you are not familiar with blackbody radiation. The

point of the example in this context is that the formalism of thermodynamics plus a few assumptions can lead to new results. The following derivation was first given by Boltzmann in 1884.

Solution. The two assumptions are that u depends only on T and the radiation exerts a pressure on the walls of the cavity given by

$$P = \frac{1}{3}u(T). \quad (2.174)$$

Equation (2.174) follows directly from Maxwell's electromagnetic theory and is obtained in Section 6.7 from first principles (see Problem 6.25).

We start from the fundamental thermodynamic relation $dE = TdS - PdV$, and write it as

$$dS = \frac{dE}{T} + \frac{P}{T}dV. \quad (2.175)$$

We let $E = Vu$, substitute $dE = Vdu + u dV$ and the relation (2.174) into (2.175), and write

$$dS = \frac{V}{T}du + \frac{u}{T}dV + \frac{1}{3}\frac{u}{T}dV = \frac{V}{T}\frac{du}{dT}dT + \frac{4}{3}\frac{u}{T}dV. \quad (2.176)$$

From (2.176) we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{4}{3}\frac{u}{T}, \quad (2.177a)$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{V}{T}\frac{du}{dT}. \quad (2.177b)$$

Because the order of the derivatives is irrelevant, $\partial^2 S / \partial V \partial T$ and $\partial^2 S / \partial T \partial V$ are equal. Hence, we obtain

$$\frac{4}{3}\frac{\partial}{\partial T}\left(\frac{u}{T}\right) = \frac{\partial}{\partial V}\left(\frac{V}{T}\right)\frac{du}{dT}. \quad (2.178)$$

Next we assume that u depends only on T and perform the derivatives in (2.178) to find

$$\frac{4}{3}\left[\frac{1}{T}\frac{du}{dT} - \frac{u}{T^2}\right] = \frac{1}{T}\frac{du}{dT}, \quad (2.179)$$

which reduces to

$$\frac{du}{dT} = 4\frac{u}{T}. \quad (2.180)$$

If we assume the form $u(T) = aT^n$ and substitute it in (2.180), we find that this form is a solution for $n = 4$:

$$u(T) = aT^4. \quad (2.181)$$

The constant a in (2.181) cannot be determined by thermodynamic arguments.

We can obtain the entropy by using the first partial derivative in (2.177a). The result is

$$S = \frac{4}{3T}Vu(T) + \text{constant}. \quad (2.182)$$

The constant of integration in (2.182) must be set equal to zero to make S proportional to V . Hence, we conclude that $S = 4aVT^3/3$. \diamond

Example 2.21 illustrates the power of thermodynamic arguments and indicates that it would be useful to relate various thermodynamic derivatives to one another. The *Maxwell relations*, which we derive in the following, relate the various thermodynamic derivatives of E , F , G , and H to one another and are useful for eliminating quantities that are difficult to measure in favor of quantities that can be measured directly. We will see that the Maxwell relations can be used to show that the internal energy and enthalpy of an ideal gas depend only on the temperature. We also will answer the question posed in Section 2.22 and relate the coefficient of thermal expansion to other thermodynamic derivatives.

We start with the thermodynamic potential $E(S, V, N)$ and write

$$dE = TdS - PdV + \mu dN. \quad (2.183)$$

In the following we will assume that N is a constant for simplicity. From (2.183) we have that

$$T = \left(\frac{\partial E}{\partial S} \right)_V \quad (2.184)$$

and

$$P = - \left(\frac{\partial E}{\partial V} \right)_S. \quad (2.185)$$

Because the order of differentiation is irrelevant, we obtain from (2.184) and (2.185)

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}, \quad (2.186)$$

or

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V. \quad (2.187)$$

Equation (2.187) is one of the Maxwell relations. The other Maxwell relations are obtained in Problem 2.27.

Problem 2.27. More Maxwell relations

From the differentials of the thermodynamic potentials

$$dF = -SdT - PdV, \quad (2.188)$$

$$dG = -SdT + VdP, \quad (2.189)$$

$$dH = TdS + VdP, \quad (2.190)$$

derive the Maxwell relations

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V, \quad (2.191)$$

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P, \quad (2.192)$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P. \quad (2.193)$$

Also consider a variable number of particles to derive the Maxwell relations

$$\left(\frac{\partial V}{\partial N}\right)_P = \left(\frac{\partial \mu}{\partial P}\right)_N, \quad (2.194)$$

and

$$\left(\frac{\partial \mu}{\partial V}\right)_N = -\left(\frac{\partial P}{\partial N}\right)_V. \quad (2.195)$$

□

The Maxwell relations depend on our identification of $(\partial E/\partial S)_V$ with the temperature, a relation that follows from the second law of thermodynamics. The Maxwell relations are not purely mathematical in content, but are different expressions of the second law. In the following, we use these relations to derive some useful relations between various thermodynamic quantities.

Internal energy of an ideal gas. We first show that the internal energy E of an ideal gas is a function only of T given the pressure equation of state, $PV = NkT$. That is, if we consider E as a function of T and V , we want to show that $(\partial E/\partial V)_T = 0$. From the fundamental thermodynamic relation, $dE = TdS - PdV$, we see that $(\partial E/\partial V)_T$ can be expressed as

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P. \quad (2.196)$$

Note the importance of specifying which quantity is being held constant when taking a partial derivative. The quantity $(\partial E/\partial V)_S = -P$ is clearly different from $(\partial E/\partial V)_T$. To show that E is a function of T only, we need to show that the right-hand side of (2.196) is zero. The term involving the entropy in (2.196) can be rewritten using the Maxwell relation (2.191):

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \quad (2.197)$$

Because $(\partial P/\partial T)_V = P/T$ for an ideal gas, we see that the right-hand side of (2.197) is zero.

Problem 2.28. Show that the enthalpy of an ideal gas is a function of T only. □

Relation between heat capacities. As we have seen, it is much easier to calculate the heat capacity at constant volume than at constant pressure. However, it is usually easier to measure the heat capacity at constant pressure. For example, most solids expand when heated, and hence it is easier to make measurements at constant pressure. In the following, we derive a thermodynamic relation that relates C_V and C_P . Recall that

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad (2.198a)$$

and

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P. \quad (2.198b)$$

We consider S as a function of T and P , and write

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP, \quad (2.199)$$

and take the partial derivative with respect to temperature at constant volume of both sides of (2.199):

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V. \quad (2.200)$$

We then use (2.198) to rewrite (2.200) as

$$\frac{C_V}{T} = \frac{C_P}{T} + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V. \quad (2.201)$$

Because we would like to express $C_P - C_V$ in terms of measurable quantities, we use the Maxwell relation (2.192) to eliminate $(\partial S/\partial P)$ and rewrite (2.201) as

$$C_P - C_V = T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V. \quad (2.202)$$

We next use the identity [see (2.238)]

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1 \quad (2.203)$$

to eliminate $(\partial P/\partial T)_V$ and write

$$C_P - C_V = -T \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2. \quad (2.204)$$

If we substitute the definitions (2.172) of the isothermal compressibility κ and (2.173) for the thermal expansion coefficient α , we obtain the desired general relation

$$C_P - C_V = V \frac{T}{\kappa} \alpha^2. \quad (2.205)$$

For an ideal gas we have $\kappa = 1/P$ and $\alpha = 1/T$ and (2.205) reduces to [see (2.31)]

$$C_P - C_V = Nk. \quad (2.206)$$

Although we will not derive these conditions here, it is plausible that the heat capacity and compressibility of equilibrium thermodynamic systems must be positive. Given these assumptions, we see from (2.205) that $C_P > C_V$ in general.

2.23 *Applications to Irreversible Processes

Although the thermodynamic quantities of a system can be defined only when the system is in equilibrium, we have found that it is possible to obtain useful results for systems that pass through nonequilibrium states if the initial and final states are in equilibrium. In the following, we will consider some well-known thermodynamic processes.

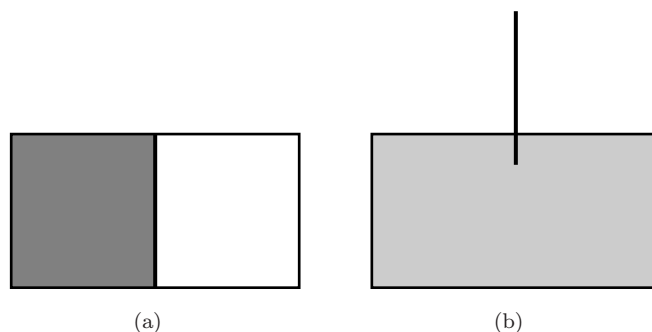


Figure 2.12: (a) A gas is kept in the left half of a box by a partition. The right half is evacuated. (b) The partition is removed and the gas expands irreversibly to fill the entire box.

2.23.1 Joule or free expansion process

In a Joule or free expansion the system expands into a vacuum while the entire system is thermally isolated (see Figure 2.12). The quantity of interest is the temperature change that is produced. Although this process is irreversible, we have learned that it can be treated by thermodynamics. Because $dQ = 0$ and $dW = 0$, the energy is a constant so that $dE(T, V) = 0$. This condition can be written as

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = 0. \quad (2.207)$$

Hence, we obtain

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V} \quad (2.208)$$

$$= -\frac{1}{C_V} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right]. \quad (2.209)$$

Equation (2.209) follows from the definition of C_V and from (2.197). The partial derivative $(\partial T/\partial V)_E$ is known as the Joule coefficient. For a finite change in volume, the total temperature change is found by integrating (2.209):

$$\Delta T = - \int_{V_1}^{V_2} \frac{1}{C_V} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV. \quad (2.210)$$

Because $(\partial P/\partial T)_V = P/T$ for an ideal gas, we conclude that the temperature of an ideal gas is unchanged in a free expansion. If the gas is not dilute, we expect that the intermolecular interactions are important and that the temperature will change in a free expansion.

Problem 2.29. Free expansion of a van der Waals gas

Calculate $(\partial T/\partial V)_E$ for the van der Waals energy equation of state (2.24) and show that a free expansion results in cooling. \square

The cooling of a gas during a free expansion can be understood by the following qualitative argument. In a real gas there is an attractive force between the molecules or atoms, which leads to the total potential energy of a dilute gas being negative. As the gas expands, the attractive force becomes weaker, and the total potential energy becomes less negative, that is, it increases. As a result, the kinetic energy must decrease to keep the total energy constant. Because the temperature is proportional to the kinetic energy per particle, the temperature will also decrease. This free expansion process is used in refrigeration.

2.23.2 Joule-Thomson process

The Joule-Thomson (or Joule-Kelvin²⁴ or porous plug) process is a steady state process in which a gas is forced through a porous plug or expansion valve from a region of high pressure P_1 to a region of lower pressure P_2 [see Figure 2.13]. The gas is thermally isolated from its surroundings. The process is irreversible because the gas is not in equilibrium. We will see that a real gas is either cooled or heated by passing through the plug.

Consider a given amount (for example, one mole) of a gas that occupies a volume V_1 at pressure P_1 on the left-hand side of the valve and a volume V_2 at pressure P_2 when the gas arrives on the right-hand side. The work done on the gas is given by

$$W = -\int_{V_1}^0 P dV - \int_0^{V_2} P dV. \quad (2.211)$$

The pressure on each side of the porous plug is constant, and hence we obtain

$$W = P_1 V_1 - P_2 V_2. \quad (2.212)$$

Because the process takes place in an isolated tube, there is no energy transfer due to heating, and the change in the internal energy is given by

$$\Delta E = E_2 - E_1 = W = P_1 V_1 - P_2 V_2. \quad (2.213)$$

Hence, we obtain

$$E_2 + P_2 V_2 = E_1 + P_1 V_1, \quad (2.214)$$

which can be written as

$$H_2 = H_1. \quad (2.215)$$

That is, the Joule-Thomson process occurs at constant enthalpy. All we can say is that the final enthalpy equals the initial enthalpy; the intermediate states of the gas are nonequilibrium states for which the enthalpy is not defined.

The calculation of the temperature change in the Joule-Thomson effect is similar to our calculation of the Joule effect. Because the process occurs at constant enthalpy, it is useful to write

$$dH(T, P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0. \quad (2.216)$$

²⁴William Thomson was later awarded a peerage and became Lord Kelvin.

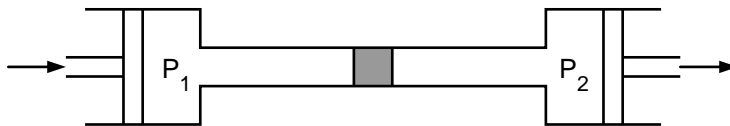


Figure 2.13: Schematic representation of the Joule-Thomson process. The two pistons ensure constant pressures on each side of the porous plug. The porous plug can be made by packing glass wool into a tube. The process can be made continuous by using a pump to return the gas from the region of low pressure to the region of high pressure.

As before, we assume that the number of particles is a constant. From (2.216) we have

$$dT = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P} dP. \quad (2.217)$$

From the relation $dH = TdS + VdP$ (see (2.159)), we have $(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V$. If we substitute this relation in (2.217), use the Maxwell relation (2.192), and the definition $C_P = (\partial H/\partial T)_P$, we obtain

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(T\alpha - 1), \quad (2.218)$$

where the thermal expansion coefficient α is defined by (2.173). Note that the change in pressure dP is negative, that is, the gas goes from a region of high pressure to a region of low pressure. To find the temperature change produced in a finite pressure drop, we integrate (2.218) and find

$$\Delta T = T_2 - T_1 = \int_{P_1}^{P_2} \frac{V}{C_P} (T\alpha - 1) dP. \quad (2.219)$$

For an ideal gas, $\alpha = 1/T$ and $\Delta T = 0$ as expected.

To understand the nature of the temperature change in a real gas, we calculate α for the van der Waals equation of state (2.12). We write the latter in the form

$$P + a\rho^2 = \frac{\rho kT}{1 - b\rho}, \quad (2.220)$$

and take the derivative with respect to T at constant P :

$$2a\rho \left(\frac{\partial \rho}{\partial T}\right)_P = \frac{\rho k}{1 - b\rho} + \left(\frac{\partial \rho}{\partial T}\right)_P \frac{kT}{(1 - b\rho)^2}. \quad (2.221)$$

If we express α as

$$\alpha = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_P, \quad (2.222)$$

we can write (2.221) in the form

$$\left[\frac{kT}{(1 - b\rho)^2} - 2a\rho \right] \alpha = \frac{k}{(1 - b\rho)}. \quad (2.223)$$

Problem 2.30. Low density limit of the thermal expansion coefficient

For simplicity, consider low densities and show that α in (2.223) is given by

$$\alpha = \frac{k(1 - b\rho)}{kT - 2a\rho(1 - b\rho)^2}, \quad (2.224a)$$

$$\approx \frac{1}{T} \left[1 - \rho \left(b - \frac{2a}{kT} \right) \right]. \quad (2.224b)$$

Use the approximation $(1 + x)^n \approx 1 + nx$ for small x to obtain (2.224b). Then show that in this approximation

$$T\alpha - 1 = \rho[(2a/kT) - b]. \quad (2.225)$$

□

We can define an inversion temperature T_{inv} at which the derivative $(\partial T / \partial P)_H$ changes sign. From (2.219) and (2.225) we see that $kT_{\text{inv}} = 2a/b$ for a low density gas. For $T > T_{\text{inv}}$, the gas warms as the pressure falls in the Joule-Thomson expansion; for $T < T_{\text{inv}}$, the gas cools as the pressure falls.

For most gases T_{inv} is well above room temperatures. Although the cooling effect is small, the effect can be made cumulative by using the cooled expanded gas in a heat exchanger to precool the incoming gas.

2.24 Supplementary Notes

2.24.1 The mathematics of thermodynamics

Because the notation of thermodynamics is cumbersome, we have tried to simplify it whenever possible. However, one common simplification can lead to confusion.

Consider the functional relations

$$y = f(x) = x^2 \quad (2.226)$$

and

$$x = g(z) = z^{1/2}. \quad (2.227)$$

If we write x in terms of z , we can write y as

$$y = h(z) = f(g(z)) = z. \quad (2.228)$$

We have given the composite function a different symbol h because this function is different from both f and g . But we would soon exhaust the letters of the alphabet, and we frequently write $y = f(z) = z$, even though $f(z)$ is a different function than $f(x)$.

The notation is even more confusing in thermodynamics. Consider, for example, the entropy S as a function of E , V , and N , which we write as $S(E, V, N)$. However, we frequently consider E as a function of T from which we would obtain another functional relation: $S(E(T, V, N), V, N)$. A mathematician would write the latter function with a different symbol, but physicists usually do not. In so doing we confuse the name of a function with that of a variable and use the same

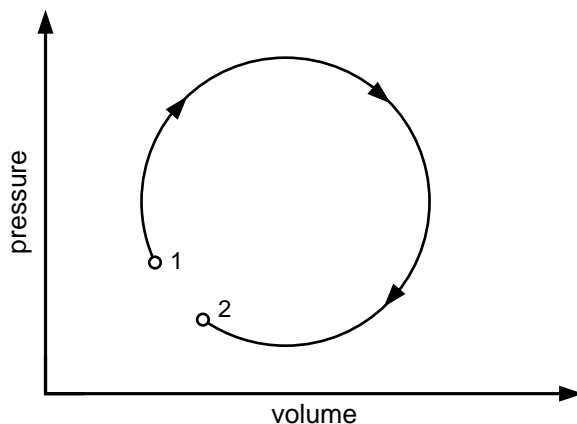


Figure 2.14: The change in internal energy can be made arbitrarily small by making the initial (1) and final (2) states arbitrarily close, but the total work done, which is the area enclosed by the nearly closed curve, is not vanishingly small. Adapted from Bohren and Albrecht.

name (symbol) for the same physical quantity. This sloppiness can cause problems when we take partial derivatives. If we write $\partial S/\partial V$, is E or T to be held fixed? One way to avoid confusion is to write $(\partial S/\partial V)_E$ or $(\partial S/\partial V)_T$, but this notation can become cumbersome.

Another confusing aspect of the mathematics of thermodynamics is the use of differentials. Some authors, including Bohren and Albrecht,²⁵ have criticized their use. These authors and others argue that the first law should be written as

$$\frac{dE}{dt} = \frac{dQ}{dt} + \frac{dW}{dt}, \quad (2.229)$$

rather than

$$dE = dQ + dW, \quad (2.230)$$

An argument for writing the first law in the form (2.229) is that the first law applies to a process, which must occur over an interval of time. Here, dE/dt represents the rate of energy change, dW/dt is the rate of doing work, and dQ/dt is the rate of heating. In contrast, dE in (2.230) is the infinitesimal change in internal energy, dW is the infinitesimal work done on the system, and dQ is the infinitesimal heat added. However, the meaning of an infinitesimal in this context is not clear. For example, for the process shown in Figure 2.14, the energy difference $E_2 - E_1$ is arbitrarily small and hence could be represented by a differential dE , but the work and heating are not infinitesimal. The use of infinitesimals should not cause confusion if you understand that dy in the context $dy/dx = f(x)$ has a different meaning than in the context $dy = f(x) dx$.

Example 2.22. Exact and inexact differentials

Suppose that a system is described by two variables, x and y and $f(x, y) = xy$ (see page 44).²⁶ Then

$$df = d(xy) = ydx + xdy. \quad (2.231)$$

²⁵See Bohren and Albrecht, pp. 93–99.

²⁶This example is taken from Blundell and Blundell [2006], page 105.

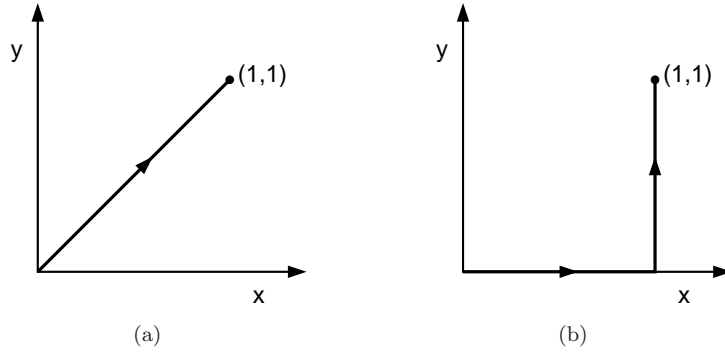


Figure 2.15: Two among many possible paths between the points $(x, y) = (0, 0)$ and $(1, 1)$.

If $f(x, y)$ changes from $(0, 0)$ to $(1, 1)$, the change in f is given by

$$\Delta f = \int_{0,0}^{1,1} df = xy \Big|_{0,0}^{1,1} = (1 \times 1) - (0 \times 0) = 1. \quad (2.232)$$

This result is independent of the path because df is an exact differential.

Now consider $dg = ydx$. The change in g when (x, y) changes from $(0, 0)$ to $(1, 1)$ along the path shown in Figure 2.15(a) is

$$\Delta g = \int_{0,0}^{1,1} y dx = \int_0^1 x dx = 1/2. \quad (2.233)$$

Show that when the integral is along the path shown in Figure 2.15(b), the result is $\Delta g = 0$. Hence the value of Δg depends on the path and dg is an inexact differential. Many textbooks write inexact differentials as $\bar{d}g$. \diamond

Review of partial derivatives. If z is a function of two independent variables x and y , then the total change in $z(x, y)$ due to changes in x and y can be expressed as

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy. \quad (2.234)$$

The cross derivatives $\partial^2 z / \partial x \partial y$ and $\partial^2 z / \partial y \partial x$ are equal, that is, the order of the two derivatives does not matter. We used this property to derive the Maxwell relations in Section 2.22.

The *chain rule* for differentiation holds in the usual way if the *same* variables are held constant in each derivative. For example, we can write

$$\left(\frac{\partial z}{\partial x} \right)_y = \left(\frac{\partial z}{\partial w} \right)_y \left(\frac{\partial w}{\partial x} \right)_y. \quad (2.235)$$

We also can derive a relation whose form is superficially similar to (2.235) when *different* variables are held constant in each term. From (2.234) we set $dz = 0$ and obtain

$$dz = 0 = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy. \quad (2.236)$$

We divide both sides of (2.236) by dx :

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z, \quad (2.237)$$

and rewrite (2.237) as

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z. \quad (2.238)$$

Note that (2.238) involves a relation between the three possible partial derivatives which involve x , y , and z .

Problem 2.31. Consider the function

$$z(x, y) = x^2 y + 2x^4 y^6. \quad (2.239)$$

Calculate $\partial z/\partial x$, $\partial z/\partial y$, $\partial^2 z/\partial x \partial y$, and $\partial^2 z/\partial y \partial x$ and show that $\partial^2 z/\partial x \partial y = \partial^2 z/\partial y \partial x$. \square

2.24.2 Thermodynamic potentials and Legendre transforms

There are many ways of encoding the information in a function. For example Fourier transforms are useful when a function is periodic. In quantum mechanics it is useful to expand a wave function in terms of eigenfunctions. In thermodynamics we usually have more control over certain variables than others. For example, we might prefer to work with the temperature, which is easy to measure and is formally defined as a derivative, rather than the energy or entropy which are more difficult to measure.

Consider a function $f(x)$ of one variable. The *Legendre transform* allows us to replace the independent variable x by the derivative df/dx without sacrificing any of the information in the original relation. In the following we will consider functions of only one variable, but the results can be easily generalized to functions of several variables.

The derivative

$$m(x) \equiv f'(x) \equiv \frac{df(x)}{dx} \quad (2.240)$$

is the slope of $f(x)$ at x . To treat m as the independent variable instead of x , we might be tempted to solve (2.240) for x in terms of m and then simply write f as a function of m . However, this procedure would lead to a loss of some of the mathematical content of the original function $f(x)$. That is, given f as a function of m , we would not be able to reconstruct $f(x)$.

As an example²⁷ suppose that $f(x) = (1/2)e^{2x}$. Hence $m = e^{2x}$ and $f(m) = m/2$. We now try to reconstruct $f(x)$ from $f(m)$ to determine if we still have the same information. Because $m = f'(x)$, we have $f(m) = f(m(x)) = f'(x)/2$ or $f' = 2f$. The solution of the latter differential equation gives $f(x) = Ae^{2x}$, where A is not specified. So this procedure loses information. The problem is that knowing only the slope does not tell us the value of the intercept at $x = 0$.

The goal of the Legendre transformation is to find the function $g(m)$ such that $g(m)$ contains the same information as the function $f(x)$. In Figure 2.16(a) we show three of the infinite number of curves with the same slope $f'(x)$. Our goal is to replace the information in the set of points

²⁷This example is adapted from Chowdhury and Stauffer [2000].

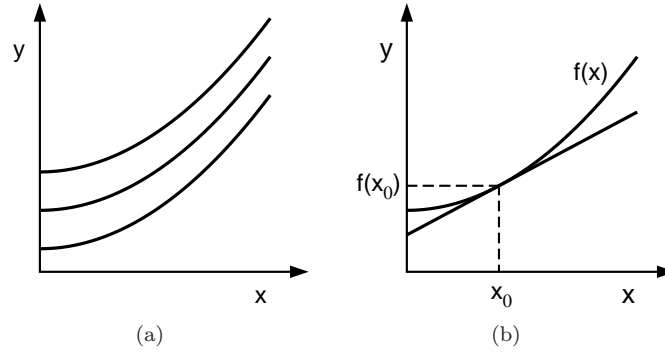


Figure 2.16: (a) Three of the infinite set of curves with the same values of $f'(x)$ for all x . (b) The curve $f(x)$ and the tangent line at a specific value of $x = x_0$ needed to provide enough information to reproduce $f(x)$.

$\{x, f(x)\}$ by the equivalent information specified by the set $\{m, g(m)\}$. To do so we need to choose the specific curve $f(x)$ shown in Figure 2.16(b). At each point x_0 , we can specify a specific curve by giving the value of the $x = 0$ intercept of the tangent line at x_0 .

Consider the tangent line that passes through the point $(x_0, f(x_0))$ with slope m and intercept b at $x = 0$. Because the general equation for a straight line is $y = mx + b$, we can write

$$b = y - mx, \quad (2.241a)$$

or

$$g(m(x_0)) = f(x_0) - f'(x_0)x_0. \quad (2.241b)$$

The slope depends on the particular point x_0 . The function g for an arbitrary point x is given by

$$g(m(x)) = f(x) - xf'(x) = f(x) - xm. \quad (2.242)$$

The function $g(m)$ is the Legendre transform of $f(x)$.

Our goal is to write g only in terms of the variable m . We now show that the right-hand side of (2.242) depends only on m and not on x . From (2.242) we write

$$dg = df - m dx - x dm. \quad (2.243)$$

Because $df = m dx$ [see (2.240)], we have

$$dg = -x dm. \quad (2.244)$$

Hence, g depends only on m , just as $df = m dx$ indicates that f depends only on x .

To calculate $g(m)$ explicitly we have to eliminate x in (2.242) using $m = f'(x)$. We can solve the latter for x only if there is a one-to-one relation between x and m , which holds if the function $f'(x)$ is monotonic or $f(x)$ is always concave up or always concave down.

Example 2.23. Reconstructing $f(x)$

We again consider $f(x) = \frac{1}{2}e^{2x}$ for which $m(x) = e^{2x}$. Then

$$g = f(x) - xm = \frac{1}{2}e^{2x} - xe^{2x}. \quad (2.245)$$

We next invert the relation $m = e^{2x}$ to solve for x in terms of m : $x = \frac{1}{2} \ln m$. Hence the Legendre transform of $f(x)$ is

$$g(m) = \frac{1}{2}m(1 - \ln m). \quad (2.246) \quad \diamond$$

Now suppose that $g(m)$ is given. Can we construct $f(x)$? From (2.244) we have $x = -dg/dm$. From (2.246) we have $x = \frac{1}{2} \ln m$, and hence $m = e^{2x}$ for our example. Hence

$$f = g(m) + xm = \frac{1}{2}m(1 - \ln m) + xm \quad (2.247a)$$

and

$$f(x) = \frac{1}{2}e^{2x}(1 - 2x) + xe^{2x} = \frac{1}{2}e^{2x}, \quad (2.247b)$$

which is the original function.

Problem 2.32. Simple Legendre transforms

- (a) Calculate the Legendre transform of $f(x) = x^3$.
- (b) Calculate the Legendre transforms of the functions $f(x) = x$ and $f(x) = \sin x$ if they exist. \square

Problem 2.33. The Helmholtz free energy as a Legendre transform

Start from the function $E(S, V, N)$ and use the Legendre transform to find the function $F(T, V, N)$. \square

Vocabulary

thermodynamics, system, boundary, surroundings, macrostate

insulator, conductor, adiabatic wall, thermal contact

volume V , pressure P , number of particles N , chemical potential μ

thermometer, thermodynamic temperature T (K), Celsius temperature scale ($^{\circ}\text{C}$), ideal gas temperature scale

W , work done on a system

Q , energy transferred due to a temperature difference only

state function, internal energy E , entropy S

three laws of thermodynamics

intensive and extensive variables

heat capacity C , specific heat c

quasistatic, reversible, irreversible, isothermal, constant volume, adiabatic, quasistatic, and cyclic processes

heat bath, heat source, heat sink, reservoir

Carnot engine, Carnot efficiency, refrigerator, heat pump, efficiency, coefficient of performance

thermal equilibrium, mechanical equilibrium, chemical equilibrium, thermodynamic equilibrium

thermodynamic potential, Helmholtz free energy F , Gibbs free energy G , enthalpy H , Landau potential Ω

ideal gas equation of state, van der Waals equation of state

Boltzmann's constant k , universal gas constant R

Additional Problems

Problem 2.34. Mechanical and thermodynamic equilibrium

Compare the notion of equilibrium in mechanics and thermodynamics. □

Problem 2.35. Meaning of phenomenological

In the text the word phenomenological was used to describe a description of phenomena that is not derived from first principles. In what sense is all of physics phenomenological? □

Problem 2.36. Barometer

Explain how a barometer works to measure pressure. □

Problem 2.37. Is a diamond forever?

Diamond is a metastable form of carbon, which means that it is not in the state with the lowest free energy. That is, diamond is in a local rather than in the global minimum of the free energy. Obviously, the diamond state can stay for a very long time. Is it possible to apply the laws of thermodynamics to diamond? What is the stable form of carbon? □

Problem 2.38. A question of degree

Although you probably learned how to convert between Fahrenheit and Celsius temperatures, you might not remember the details. The fact that 1°C equals $\frac{9}{5}^\circ\text{F}$ is not too difficult to remember, but where does the factor of 32 go? An alternative procedure is to add 40 to the temperature in $^\circ\text{C}$ or $^\circ\text{F}$ and multiply by $\frac{5}{9}$ if going from $^\circ\text{F}$ to $^\circ\text{C}$ or by $\frac{9}{5}$ if going from $^\circ\text{C}$ to $^\circ\text{F}$. Then subtract 40 from the calculated temperature to obtain the desired conversion. Explain why this procedure works. □

Problem 2.39. Historical development of thermodynamics

Discuss the development of our understanding of thermodynamics and the contributions of people such as Count Rumford (Benjamin Thompson), James Joule, Julius Robert von Mayer, Sadi Carnot, William Thomson (Lord Kelvin), Rudolf Clausius, Anders Celsius, and Gabriel Fahrenheit. Choose two people to discuss and use at least two different sources. \square

Problem 2.40. Naming rights

Discuss the meaning of the statement that one of the most important contributions of 19th century thermodynamics was the development of the understanding that heat (and work) are names of *processes* not names of *things*. \square

Problem 2.41. Hot and cold

It is common in everyday language to refer to temperatures as “hot” and “cold.” Why is this use of language misleading? Does it make sense to say that one body is “twice as hot” as another? Does it matter whether the Celsius or Kelvin temperature scale is used? \square

Problem 2.42. Does it make sense to talk about the amount of heat in a room? \square **Problem 2.43.** Heat as a fluid

- (a) In what context can energy transferred by heating be treated as a fluid? Give some examples where this concept of “heat” is used in everyday life. In what context does the concept of “heat” as a fluid break down? Is it possible to isolate “heat” in a bottle or pour it from one object to another?
- (b) *Write a short essay based on at least two sources on the history of the “caloric.” \square

Problem 2.44. Why should we check the pressure in a tire when the tire is cold? \square **Problem 2.45.** Why do we use the triple point of water to calibrate thermometers? Why not use the melting point or the boiling point? \square **Problem 2.46.** Money in the bank

In the text we discussed the analogy of the internal energy to the amount of water in a pond. The following analogy due to Dugdale might also be helpful.²⁸ Suppose that a student has a bank account with a certain amount of money. The student can add to this amount by either depositing or withdrawing cash and by writing or depositing checks from the accounts of others. Does the total amount of money in the student’s account distinguish between cash and check transfers? Discuss the analogies to internal energy, work, and heating. \square

²⁸See Dugdale, pp. 21–22.

Problem 2.47. Common misconceptions

The following excerpt is taken from a text used by one of the author's children when he was in the sixth grade. The title and the author of the text will remain anonymous. Find the conceptual errors in the text.

A. What is heat?

You have learned that all matter is made up of atoms. Most of these atoms combine to form molecules. These molecules are always moving – they have kinetic energy. *Heat* is the energy of motion (kinetic energy) of the particles that make up any piece of matter.

The amount of heat a material has depends on how many molecules it has and how fast the molecules are moving. The greater the number of molecules and the faster they move, the greater the number of collisions between them. These collisions produce a large amount of heat.

How is heat measured? Scientists measure heat by using a unit called a *calorie*. A calorie is the amount of heat needed to raise the temperature of 1 gram of water 1 degree centigrade (Celsius).

A gram is a unit used for measuring mass. There are about 454 grams in 1 pound.

Scientists use a *small calorie* and a *large Calorie*. The unit used to measure the amount of heat needed to raise the temperature of 1 gram of water 1 degree centigrade is the *small calorie*. The *large calorie* is used to measure units of heat in food. For example, a glass of milk when burned in your body produces about 125 Calories.

Questions:

1. What is heat?
2. What two things does the amount of heat a substance has depend on?
3. What is a calorie?
4. Explain the following: small calorie; large calorie.

B. What is temperature?

The amount of hotness in an object is called its *temperature*. A *thermometer* is used to measure temperature in units called *degrees*. Most thermometers contain a liquid.

C. Expansion and Contraction

Most solids, liquids and gases *expand* when heated and *contract* when cooled. When matter is heated, its molecules move faster. As they move, they collide with their neighbors very rapidly. The collisions force the molecules to spread farther apart. The farther apart they spread, the more the matter expands.

Air, which is a mixture of gases, expands and becomes lighter when its temperature rises. Warm air rises because the cold, heavier air sinks and pushes up the lighter warm air.

What happens when solids or gases are cooled? The molecules slow down and collide less. The molecules move closer together, causing the material to contract. □

Problem 2.48. Why are the terms heat capacity and specific heat poor choices of names? Suggest more appropriate names. Comment on the statement: “The heat capacity of a body is a measure of how much heat the body can hold.” □

Problem 2.49. The atmosphere of Mars has a pressure that is only 0.007 times that of Earth and an average temperature of 218 K. What is the volume of 1 mole of the Martian atmosphere? Compare your result with the volume of one mole on Earth. □

Problem 2.50. Gasoline burns in an automobile engine and releases energy at the rate of 160 kW. Energy is lost through the car's radiator at the rate of 51 kW and out the exhaust at 50 kW. An additional 23 kW goes to frictional heating within the car. What fraction of the fuel energy is available for moving the car? \square

Problem 2.51. Two moles of an ideal gas at 300 K in a volume of 0.10 m^3 are compressed isothermally by a motor driven piston to a volume of 0.010 m^3 . If this process takes place in 120 s, how powerful a motor is needed? \square

Problem 2.52. Give an example of a process in which a system is not heated, but its temperature increases. Also give an example of a process in which a system is heated, but its temperature is unchanged. \square

Problem 2.53. Expansion of a gas into vacuum

- (a) Suppose that a gas expands adiabatically into a vacuum. What is the work done by the gas?
- (b) Suppose that the total energy of the gas is given by [see (2.24)]

$$E = \frac{3}{2}NkT - N\frac{N}{V}a, \quad (2.248)$$

where a is a positive constant. Initially the gas occupies a volume V_1 at a temperature T_1 . The gas then expands adiabatically into a vacuum so that it occupies a total volume V_2 . What is the final temperature of the gas? \square

Problem 2.54. Black hole thermodynamics

A black hole is created from the collapse of a massive object into one so dense that nothing can escape beyond a certain radius, including light. The measurable properties of a black hole depend only on its mass, charge, and angular momentum. In this problem we estimate the entropy and temperature of a charge neutral nonrotating black hole.

- (a) Because the properties of the black hole depend only on its mass, use dimensional analysis to estimate the radius R of a black hole in terms of its mass M , the gravitational constant G , and the speed of light c . (Black holes are a consequence of the general theory of relativity, and thus we expect that the radius depends only on M , G , and c .)
- (b) Assume that the entropy is of order Nk , where N is the number of particles in the black hole. The maximum entropy occurs when the particles are photons of wavelength λ of the order of the diameter of the black hole. Take $\lambda = 2R$ and determine the entropy S as a function of M (the total energy is Mc^2 and the energy of a photon is hc/λ). More detailed theoretical arguments give the correct relation

$$S = k \frac{8\pi^2 GM^2}{hc}. \quad (2.249)$$

Your approximate result should have the correct dependence on G , M , h , c , and k . Calculate a numerical value for the entropy for a one solar mass black hole using (2.249). (The solar mass $M_\odot \approx 2 \times 10^{30} \text{ kg}$.)

- (c) Express the entropy in terms of the surface area A of the black hole instead of M . Note that the area is a direct measure of the entropy. Does the entropy increase or decrease when two black holes coalesce into one?
- (d) Express S in terms of the total energy E instead of M and determine the temperature for a one solar mass black hole. Use the approximation for R obtained in part (a) to find the temperature in terms of the gravitational field g at the radius R . \square

Problem 2.55. Entropy as a state function

- (a) Suppose that one mole of a monatomic ideal gas expands in a quasistatic adiabatic process from $P_1 = 1 \text{ Pa}$ and $V_1 = 1 \text{ m}^3$ to $V_2 = 8 \text{ m}^3$. What is the change in the pressure and the entropy of the gas?
- (b) What are the initial and final temperatures of the gas?
- (c) Consider a process at constant volume that brings the system to the temperature T_2 which you found in part (b). What is the change in entropy of this process?
- (d) Next increase the volume to V_2 at constant temperature T_2 . What is the change in the entropy in this isothermal process?
- (e) Compare the total change in the entropy to the result that you found in part (a). Does the change of the entropy depend on the path between two equilibrium states? \square

Problem 2.56. Consider the various processes shown in Figure 2.17 and calculate W , the total work done on the system and Q , the total energy absorbed by heating the system. Assume that the system is a monatomic ideal gas. (This problem is adapted from Reif, p. 215.)

- (a) The volume is changed quasistatically along the curved path $1 \rightarrow 3$ while the gas is kept thermally isolated.
- (b) The system is compressed from its original volume of $V_1 = 8 \text{ m}^3$ to its final volume $V_3 = 1 \text{ m}^3$ along the path $1 \rightarrow 2$ and $2 \rightarrow 3$. The pressure is kept constant at $P_1 = 1 \text{ Pa}$ and the system is cooled to maintain constant pressure. The volume is then kept constant and the system is heated to increase the pressure to $P_2 = 32 \text{ Pa}$.
- (c) The pressure is changed at constant volume along the path $1 \rightarrow 4$ and then at constant pressure along $4 \rightarrow 3$. The two steps of the preceding process are performed in opposite order.
- (d) Diagonal path $1 \rightarrow 3$. The volume is decreased and the system is cooled so that the change in the pressure is proportional to the change in volume. \square

Problem 2.57. More work

Consider a system described by the van der Waals equation of state which expands at constant temperature from volume V_1 to volume V_2 . Assume that the density $\rho = N/V \ll 1$ over the range of volumes of interest.

- (a) Calculate the work W_{vdw} done on the gas to the lowest relevant order in ρ .

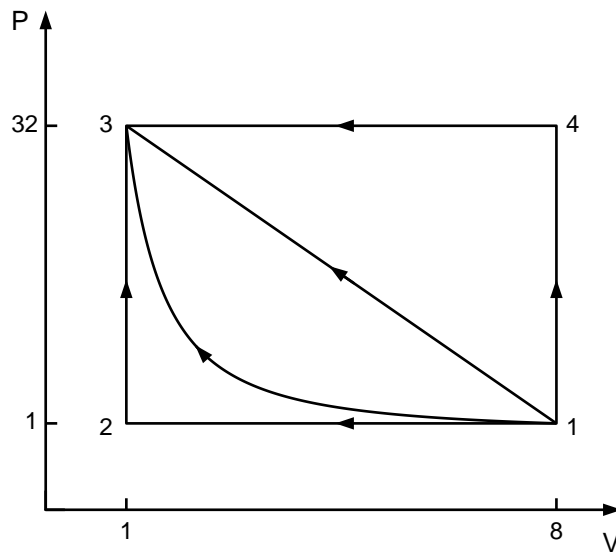


Figure 2.17: Illustration of various thermodynamic processes discussed in Problem 2.56. The units of the pressure P and the volume V are Pa and m^3 , respectively.

- (b) Calculate the work W_{ideal} done on the gas under the same conditions assuming that the gas is ideal.
- (c) Find the difference $W_{\text{vdw}} - W_{\text{ideal}}$ and discuss the reason why this difference is positive or negative as a function of the temperature. \square

Problem 2.58. A 0.5 kg copper block at 80°C is dropped into 1 kg of water at 10°C . What is the final temperature? What is the change in entropy of the system? The specific heat of copper is $386 \text{ J}/(\text{kg K})$. \square

Problem 2.59. Carnot efficiencies

- (a) Surface temperatures in the tropical oceans are approximately 25°C , while hundreds of meters below the surface the temperature is approximately 5°C . What would be the efficiency of a Carnot engine operating between these temperatures?
- (b) What is the efficiency of a Carnot engine operating between the normal freezing and boiling points of water? \square

Problem 2.60. A small sample of material is taken through a Carnot cycle between a heat source of boiling helium at 1.76 K and a heat sink at an unknown lower temperature. During the process, 7.5 mJ of energy is absorbed by heating from the helium and 0.55 mJ is rejected at the lower temperature. What is the lower temperature? \square

Problem 2.61. Positive change of the total entropy

- (a) In Example 2.16 it was shown that the total entropy change when body A is placed in thermal contact with a heat bath at temperature T_B can be written as

$$\Delta S = C_A f\left(\frac{T_B}{T_A}\right), \quad (2.250)$$

where C_A is temperature-independent and T_A is the initial temperature of body A . The function $f(x)$ is given by

$$f(x) = \ln x + \frac{1}{x} - 1, \quad (2.251)$$

where $x = T_B/T_A$. Calculate $f(x = 1)$ and df/dx and show that the total entropy increases when body A is placed in thermal contact with a heat bath at a higher temperature ($x > 1$).

- (b) If the total entropy increases in a heating process, does the total entropy decrease in a cooling process? Use similar considerations to show that the total entropy increases in both cases.
- (c) Plot $f(x)$ as a function of x and confirm that its minimum value is at $x = 1$ and that $f > 0$ for $x < 1$ and $x > 1$. \square

Problem 2.62. Changes in the entropy

Calculate the changes in entropy due to various methods of heating:

- (a) One kilogram of water at 0°C is brought into contact with a heat bath at 90°C . What is the change in entropy of the water? What is the change in entropy of the bath? What is the change in entropy of the entire system consisting of both water and heat bath? (The specific heat of water is approximately 4184 J/kg K .)
- (b) The water is heated from 0°C to 90°C by first bringing it into contact with a heat bath at 45°C and then with a heat bath at 90°C . What is the change in entropy of the entire system?
- (c) Discuss how the water can be heated from 0°C to 90°C without any change in entropy of the entire system. \square

Problem 2.63. The Otto cycle

The Otto cycle is an idealized prototype of most present-day internal combustion engines. The idealization assumes that the working substance is air rather than a mixture of gases and vapor whose composition changes during the cycle. For simplicity, we assume that C_V and C_P are constant and that $\gamma = C_P/C_V = 1.4$, the value for air. The more important approximation is that the processes are assumed to be quasistatic. An idealized cycle that represents the six parts of this cycle is known as the air standard Otto cycle and is illustrated in Figure 2.18.

$5 \rightarrow 1$. *Intake stroke.* The mixture of gasoline and air is drawn into the tube through the intake valve by the movement of the piston. Idealization: A quasistatic isobaric intake of air at pressure P_0 to a volume V_1 .

$1 \rightarrow 2$. *Compression stroke.* The intake valve closes and the air-fuel mixture is rapidly compressed in the tube. The compression is nearly adiabatic and the temperature rises. Idealization: A quasistatic adiabatic compression from V_1 to V_2 ; the temperature rises from T_1 to T_2 .

$2 \rightarrow 3$. *Explosion*. The mixture explodes such that the volume remains unchanged and a very high temperature and pressure is reached. Idealization: A quasistatic and constant volume increase of temperature and pressure due to the absorption of energy from a series of heat baths between T_2 and T_3 .

$3 \rightarrow 4$. *Power stroke*. The hot combustion products expand and do work on the piston. The pressure and temperature decrease considerably. Idealization: A quasistatic adiabatic expansion produces a decrease in temperature.

$4 \rightarrow 1$. *Valve exhaust*. At the end of the power stroke the exhaust valve opens and the combustion products are exhausted to the atmosphere. There is a sudden decrease in pressure. Idealization: A quasistatic constant volume decrease in temperature to T_1 and pressure P_0 due to an exchange of energy with a series of heat baths between T_4 and T_1 .

$1 \rightarrow 5$. *Exhaust stroke*. The piston forces the remaining gases into the atmosphere. The exhaust valve then closes and the intake valve opens for the next intake stroke. Idealization: A quasistatic isobaric expulsion of the air.

Show that the efficiency of the Otto cycle is

$$\eta = 1 - \left(\frac{V_2}{V_1} \right)^{\gamma-1}. \quad (2.252)$$

A compression ratio of about ten can be used without causing knocking. Estimate the theoretical maximum efficiency. In a real engine, the efficiency is about half of this value. \square

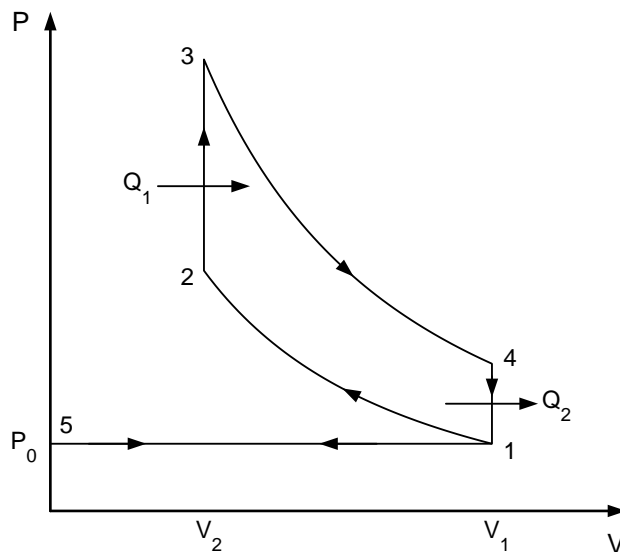


Figure 2.18: The air standard Otto cycle.

Problem 2.64. If S is expressed as a function of T, V or T, P , then it is no longer a thermodynamic potential. That is, the maximum thermodynamic information is contained in S as a function of E and V (for fixed N). Why? \square

Problem 2.65. The enthalpy as a free energy

Show that the enthalpy $H = E + PV$ is the appropriate free energy if the entropy and number of particles is fixed, but the volume can change. In this case we consider a system connected to a larger body such that the pressure of the system equals that of the large body with the constraint that the larger body and the system do not exchange energy. \square

Problem 2.66. The Landau potential

Find the Landau potential for the case where the temperature is fixed by a heat bath, the volume is fixed, and particles can move between the systems and the heat bath. You will need to extend the definition of the availability to allow for the number of particles to vary within the system. Use a similar argument about extensive variables to show that the Landau potential equals $-PV$. \square

Problem 2.67. Joule-Thomson inversion temperature

The inversion temperature for the Joule-Thomson effect is determined by the relation $(\partial T/\partial V)_P = T/V$ [see (2.218)]. In Section 2.23.2 we showed that for low densities and high temperatures (low pressures) the inversion temperature is given by $kT_{\text{inv}} = 2a/b$.

(a) Show that at high pressures T_{inv} is given by

$$kT_{\text{inv}} = \frac{2a}{9b} \left[2 \pm \sqrt{1 - 3b^2 P/a} \right]^2. \quad (2.253)$$

(b) Show that as $P \rightarrow 0$, $kT_{\text{inv}} = 2a/b$.

(c) For $P < a/3b^2$, there are two inversion points between which the derivative $(\partial T/\partial P)_H$ is positive. Outside this temperature interval the derivative is negative. For $P > a/3b^2$ there are no inversion points and $(\partial T/\partial P)_H$ is negative everywhere. Find the pressure dependence of the inversion temperature for the Joule-Thomson effect. \square

Problem 2.68. More thermodynamic identities

(a) Derive the identities

$$\left(\frac{\partial C_P}{\partial P} \right)_T = -T \left(\frac{\partial^2 V}{\partial T^2} \right)_P, \quad (2.254a)$$

and

$$\left(\frac{\partial C_V}{\partial V} \right)_T = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V. \quad (2.254b)$$

(b) Show that

$$\frac{\kappa}{\kappa_S} = \frac{C_P}{C_V}, \quad (2.255)$$

where the isothermal compressibility is given by (2.172) and the adiabatic compressibility κ_S is defined as

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S. \quad (2.256)$$

Use (2.255) and (2.205) to obtain the relation

$$\kappa_T - \kappa_S = \frac{TV}{C_P} \alpha^2. \quad (2.257)$$

□

Suggestions for Further Reading

C. J. Adkins, *Equilibrium Thermodynamics*, third edition, Cambridge University Press (1983).

Ralph Baierlein, *Thermal Physics*, Cambridge University Press, New York (1999).

Robert P. Bauman, *Modern Thermodynamics with Statistical Mechanics*, Macmillan Publishing Company (1992).

Stephen J. Blundell and Katherine M. Blundell, *Thermal Physics*, 2nd ed., Oxford University Press (2009).

Craig F. Bohren and Bruce A. Albrecht, *Atmospheric Thermodynamics*, Oxford University Press (1998). A book that should be read by professors and students alike. In particular, they discuss the history of the ideal gas pressure equation of state and why Charles deserves none of the credit. This chapter has been influenced by their discussion of thermodynamics.

Herbert B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, second edition, John Wiley & Sons (1985). Callen's discussion of the principles of thermodynamics is an example of clarity.

Debashish Chowdhury and Dietrich Stauffer, *Principles of Equilibrium Statistical Mechanics*, Wiley-VCH (2000).

J. S. Dugdale, *Entropy and its Physical Meaning*, Taylor & Francis (1996). An accessible introduction to thermodynamics.

Harvey S. Leff and William D. Teeters, "EER, COP, and the second law efficiency for air conditioners," *Am. J. Phys.* **46**, 19–22 (1978).

Don S. Lemons, *Mere Thermodynamics*, The Johns Hopkins University Press (2009). Highly recommended.

Beth Lindsey, Paula Heron, and Peter Shaffer, "Student ability to apply the concepts of work and energy to extended systems," *Am. J. Phys.* **77**, 999–1009 (2009). This paper inspired our Example 2.2.

Michael E. Loverude, Christian H. Kautz, and Paula R. L. Henon, "Student understanding of the first law of thermodynamics: Relating work to the adiabatic compression of an ideal gas," *Am. J. Phys.* **70**, 137–148 (2002).

Alan Macdonald, “A new statement of the second law of thermodynamics,” *Am. J. Phys.* **63**, 1122–1127 (1995).

F. Mandl, *Statistical Physics*, second edition, John Wiley & Sons (1988).

David E. Meltzer, “Investigation of students’ reasoning regarding heat, work, and the first law of thermodynamics in an introductory calculus-based general physics course,” *Am. J. Phys.* **72**, 1432–1446 (2004).

Barry R. Parker and Robert J. McLeod, “Black hole thermodynamics in an undergraduate thermodynamics course,” *Am. J. Phys.* **48**, 1066–1070 (1980).

F. Reif, *Statistical Physics*, Volume 5 of the Berkeley Physics Series, McGraw-Hill (1965).

Wayne Saslow, “An economic analogy to thermodynamics,” *Am. J. Phys.* **67** 1239–1247 (1999). The author develops several analogies between economic systems and thermodynamics.

Daniel V. Schroeder, *An Introduction to Thermal Physics*, Addison-Wesley (2000).

Daniel F. Styer, “A thermodynamic derivative means an experiment,” *Am. J. Phys.* **67**, 1094–1095 (1999).

Mark W. Zemansky and Richard H. Dittman, *Heat and Thermodynamics*, sixth edition, McGraw-Hill (1981). A classic text on thermodynamics.

R. K. P. Zia, Edward F. Redish, and Susan R. McKay, “Making sense of the Legendre transform,” *Am. J. Phys.* **77**, 614–622 (2009).

The history of thermodynamics and statistical mechanics is fascinating and not one to which we can do justice. We encourage you to read some of the original sources such as the English translation of Sadi Carnot’s paper in *Reflections on the Motive Power of Fire: A Critical Edition with the Surviving Scientific Manuscripts*, edited by Robert Fox, Manchester University Press (1986). Other recommended books are listed in the following.

Stephen G. Brush, *The Kind of Motion We Call Heat: A History of the Kinetic Theory of Gases in the Nineteenth Century*, Elsevier Science (1976). See also *The Kind of Motion We Call Heat: Physics and the Atomists*, Elsevier Science (1986); *The Kind of Motion We Call Heat: Statistical Physics and Irreversible Processes*, Elsevier Science (1986).

Hasok Chang, *Inventing Temperature*, Oxford University Press (2004). An interesting synthesis on the history of the concept of temperature.

Maxwell on Heat and Statistical Mechanics, edited by E. Garber, S. G. Brush, and C. W. F. Everitt, Lehigh University Press (1995).

Peter M. Harman, *Energy, Force, and Matter*, Cambridge University Press (1982).

Martin J. Klein, “Thermodynamics in Einstein’s thought,” *Science* **157**, 509–516 (1967); idem, “Maxwell, his demon, and the second law of thermodynamics,” *Am. Scientist* **58**, 84–97 (1970); idem, “Carnot’s contribution to thermodynamics,” *Physics Today* **27** (8), 23–28 (1974).

Thomas S. Kuhn, “Energy conservation as an example of simultaneous discovery,” in *Critical Problems in the History of Science*, edited by Marshall Clagett, University of Wisconsin Press (1959), pp. 321–356.

Robert D. Purrington, *Physics in the Nineteenth Century*, Rutgers University Press (1997). This monograph discusses the rich and fascinating history of thermodynamics among other developments.

Daniel M. Siegel, “The energy concept: A historical overview,” *Materials and Society* **7**, 411–424 ((1983)).

Crosbie Smith, *The Science of Energy: A Cultural History of Energy Physics in Victorian Britain*, University of Chicago Press (1998).