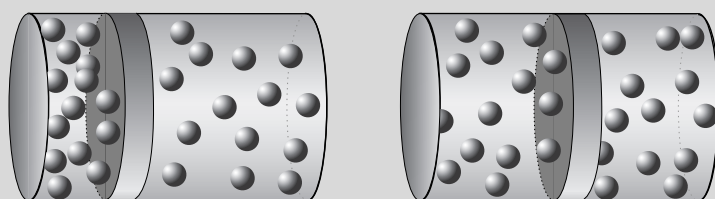


7 Thermodynamic Driving Forces



Thermodynamics Is Two Laws and a Little Calculus

Thermodynamics is a set of tools for reasoning about energies and entropies. It enables you to predict the tendencies of atoms and molecules to react; to bind, absorb, or partition; to dissolve or change phase; or to change their shapes or chemical bonds. The three basic tools of thermodynamics are: the First Law for the conservation of energy (see Chapter 3), the maximum entropy principle, also called the Second Law of thermodynamics (Chapters 2 and 6), and multivariate calculus (Chapter 5). Thermodynamics gives definitions of the forces that act in material systems—pressure, the tendency to exchange volume; temperature, the tendency to exchange energy; and chemical potential, the tendency to exchange matter. In this chapter, we combine these tools to create the machinery of thermodynamics and to explore the principles of equilibria.

What Is a Thermodynamic System?

A thermodynamic system is a collection of matter in any form, delineated from its surroundings by real or imaginary boundaries. The system may be a biological cell, the contents of a test tube, the gas in a piston, a thin film, or a can of soup. How you define a system depends on the problem that you want to solve. In thermodynamics, defining the boundaries is important, because boundaries determine what goes in or out. Much of thermodynamics is bookkeeping, accounting for energy or matter exchange across the boundaries,

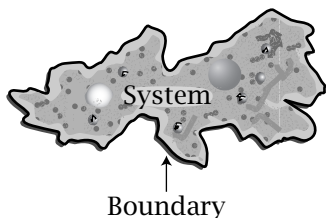


Figure 7.1 An amoeba is an open system.

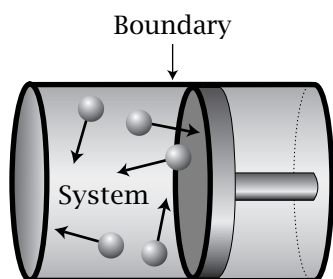


Figure 7.2 A piston can be a closed system.

or volume changes. For a biochemical experiment, the boundary might be the walls of a test tube, or a cell membrane. For a steam engine, the interior of the piston might be the most convenient definition of the system. The boundary need not be fixed in space. It need not even surround a fixed number of molecules. The system might contain subsystems, and the subsystems might also be delineated by real or imaginary boundaries. Systems are defined by the nature of their boundaries:

OPEN SYSTEM. An open system can exchange energy, volume, and matter with its surroundings. The earth and living organisms are open systems (see Figure 7.1).

CLOSED SYSTEM. Energy can cross the boundary of a closed system, but matter cannot. The boundaries can be stationary, as in a light bulb or the walls of a house that loses heat, or movable, as in a balloon or a piston (see Figure 7.2).

ISOLATED SYSTEM. Energy and matter cannot cross the boundaries of an isolated system. Also the volume does not change: the boundaries do not move. The total internal energy of an isolated system is constant. In reality, there is never complete isolation. This kind of idealization is common in thermodynamics.

SEMI-PERMEABLE MEMBRANE. A semipermeable membrane is a boundary that restricts the flow of some kinds of particle, while allowing others to cross. Dialysis is performed with semipermeable membranes. Biological membranes are semipermeable.

ADIABATIC BOUNDARY. An adiabatic boundary allows no heat to flow between a system and its surroundings. Thermos bottles have adiabatic boundaries, more or less. Adiabatic walls permit you to measure work by prohibiting heat flow.

PHASE. A phase is a homogeneous part of a system that is mechanically separable from the rest of the system. Homogeneous means that the pressure, temperature, and concentration are uniform, or continuous functions of position within a phase. In a simple system, a phase can be solid, liquid, gaseous, liquid crystalline, or other.

SIMPLE SYSTEM. A simple system is defined as homogeneous, with only a single phase. It must be uncharged, large enough so that surface effects can be neglected, and not subject to changes due to electric, magnetic, or gravitational fields.

These definitions, like much of thermodynamics, involve idealizations and approximations to reality. In this chapter and Chapter 8, we will focus on simple systems.

Properties Are Extensive and Intensive

Some properties of matter are *extensive*. An extensive property P of a system is the sum of the properties $P_1 + P_2 + P_3 + \dots$ of its component subsystems. For example, the volume of a glass of water is the sum of volumes of two half

glasses of water. Alternatively, properties can be *intensive*, or independent of the size of a system. Temperature is intensive: the temperature of a glass of water is not the sum of the temperatures of two half glasses. Pressures and concentrations are also intensive quantities. Extensive properties include:

SPATIAL EXTENT. A system has volume, area, or length determined by the positions of its boundaries. We will usually consider the volume V , but with films or surfaces you might be interested in the area. When you stretch rubber bands, you might be interested in the length.

NUMBER OF PARTICLES. A system is composed of some number of particles such as atoms, molecules or other microscopic units. For a gas in a piston, a chemical reaction, or for ice in water, a natural microscopic unit is the atom or molecule. The particles of a system can belong to different species. For example, the gases in a piston can include O_2 , N_2 , CO , etc. You can have N_i molecules of species i , that is N_1 molecules of species 1, N_2 molecules of species 2, and so on. Rather than the number of molecules, we sometimes specify the numbers of moles, $n_i = N_i/\mathcal{N}$, where $\mathcal{N} = 6.022045 \times 10^{23}$ molecules per mole is Avogadro's number. We use bold type to denote the set of all species: $\mathbf{n} = n_1, n_2, \dots, n_M$ or $\mathbf{N} = N_1, N_2, \dots, N_M$, where M is the number of species.

INTERNAL ENERGY. The internal energy U of a system is extensive. For a system of independent particles, the internal energy is the sum of the particle energies, according to Equation (3.8):

$$U = \sum_{i=1}^t N_i \varepsilon_i,$$

where t is the number of energy levels, N_i is the number of particles in energy level i , and ε_i is the energy at level i .

ENTROPY. The entropy of a system is the sum of the entropies of its independent subsystems (see Chapter 6).

The Fundamental Thermodynamic Equations, $S = S(U, V, \mathbf{N})$ or $U = U(S, V, \mathbf{N})$, Predict Equilibria

In Chapters 2 and 3 we used simple models to illustrate how the tendency toward maximum multiplicity W (and maximum entropy S) can account for some tendencies of physical systems. When the volume can change, the tendency toward maximum entropy $S(V)$ predicts the expansion of gases. When particle numbers can change, maximizing $S(N)$ predicts mixing. And when the energy can exchange, maximizing $S(U)$ predicts the tendency for heat to flow. However, many problems of interest involve multiple degrees of freedom. With the tools of multivariate calculus, you can predict more complex processes. If the energy, volume, and particle number are all free to change, then the **fundamental thermodynamic equation for entropy** is multivariate:

$$S = S(U, V, \mathbf{N}).$$

$S = S(U, V, \mathbf{N})$ is just a statement that we are taking $U, V, N_1, N_2, \dots, N_M$ to be independent of each other, and that the entropy is dependent on them.

It is an inconvenient quirk of history (for us) that thermodynamics evolved instead with the arrangement of variables known as the **fundamental thermodynamic equation for energy**:

$$U = U(S, V, \mathbf{N}).$$

We will see that the fundamental definitions of pressure, chemical potential, and temperature are based on the form $U = U(S, V, \mathbf{N})$. Unfortunately, while the main definitions of thermodynamics originate from the energy equation, the microscopic driving forces are better understood in terms of the entropy equation $S = S(U, V, \mathbf{N})$. So we need to switch back and forth between $S = S(U, V, \mathbf{N})$ and $U = U(S, V, \mathbf{N})$. For example, in Chapter 2 we illustrated how $S(U)$ accounts for the tendency for heat to flow, but temperature is defined in terms of $U(S)$. This small inconvenience adds a few steps to our logic.

Either equation, $S = S(U, V, \mathbf{N})$ or $U = U(S, V, \mathbf{N})$, will completely specify the state of a simple system. Thermodynamics does not tell you the specific mathematical dependence of S on (U, V, \mathbf{N}) or U on (S, V, \mathbf{N}) . *Equations of state*, such as the ideal gas law, specify interrelations among these variables. Equations of state must come either from experiments or from microscopic models. They are imported into thermodynamics, which gives additional useful relationships.

The Fundamental Equations Define the Thermodynamic Driving Forces

The Definitions

The fundamental equation for small changes in entropy $S(U, V, \mathbf{N})$ can be expressed as

$$dS = \left(\frac{\partial S}{\partial U}\right)_{V, \mathbf{N}} dU + \left(\frac{\partial S}{\partial V}\right)_{U, \mathbf{N}} dV + \sum_{j=1}^M \left(\frac{\partial S}{\partial N_j}\right)_{U, V, N_{i \neq j}} dN_j. \quad (7.1)$$

When you use the fundamental energy equation instead, you can describe small changes in energy $U(S, V, \mathbf{N})$ by

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V, \mathbf{N}} dS + \left(\frac{\partial U}{\partial V}\right)_{S, \mathbf{N}} dV + \sum_{j=1}^M \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_{i \neq j}} dN_j. \quad (7.2)$$

Each of the partial derivatives in the fundamental energy Equation (7.2) corresponds to a measurable physical property. For now, take the following to be mathematical definitions: the *temperature* T , the *pressure* p , and the *chemical potential* μ_j , are *defined by* the partial derivatives given in Equation (7.2):

$$T = \left(\frac{\partial U}{\partial S}\right)_{V, \mathbf{N}}, \quad p = -\left(\frac{\partial U}{\partial V}\right)_{S, \mathbf{N}}, \quad \mu_j = \left(\frac{\partial U}{\partial N_j}\right)_{S, V, N_{i \neq j}}. \quad (7.3)$$

We will show, starting on page 110, that these mathematical definitions describe the physical properties that are familiar as temperature, pressure, and chemical potential. According to Equation (7.3), the quantities T , p , and μ are derivatives of the internal energy. In total derivative expressions, each partial derivative term ($\partial U/\partial x$) is described as being *conjugate* to x . Temperature is conjugate to entropy, pressure is conjugate to volume, and chemical potential is conjugate to the number of particles.

Substituting the definitions given in Equation (7.3) into Equation (7.2) gives the **differential form of the fundamental energy equation**:

$$dU = TdS - pdV + \sum_{j=1}^M \mu_j dN_j. \quad (7.4)$$

Alternatively, you can rearrange Equation (7.4) to get a useful **differential form of the fundamental entropy equation**:

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{p}{T}\right) dV - \sum_{j=1}^M \left(\frac{\mu_j}{T}\right) dN_j. \quad (7.5)$$

Comparison of Equations (7.5) and (7.1) gives three more definitions:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{V,N}, \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_{U,N}, \quad \frac{\mu_j}{T} = - \left(\frac{\partial S}{\partial N_j}\right)_{U,V,N_{i \neq j}}. \quad (7.6)$$

Equations (7.4) and (7.5) are completely general statements that there are some functional dependences $S(U, V, \mathbf{N})$ and $U(S, V, \mathbf{N})$, and that these dependences define T , p , and μ . Equations (7.4) and (7.5) are *fundamental* because they completely specify all the changes that can occur in a simple thermodynamic system, and they are the bases for extremum principles that predict states of equilibria. An important difference between these fundamental equations and others that we will write later is that S and U are functions of only the extensive variables. Beginning on page 111 we will show how to use Equations (7.4) and (7.5) to identify states of equilibrium.

Sometimes thermodynamic reasoning enters a problem only by providing a definition. Here is an example in which the ideal gas law is derived from just two ingredients: the definition of pressure given in Equation (7.6), and the simple lattice model of a gas from Example 2.2 (page 32).

EXAMPLE 7.1 The ideal gas law derived from the lattice model. Take the definition of pressure, $p/T = (\partial S/\partial V)_{U,N}$, from Equation (7.6). Into this expression, insert the function $S(V)$ from the lattice model in Example 2.2. For a lattice of M sites with N particles, use the Boltzmann expression for entropy and Equation (2.3) to get

$$\frac{S}{k} = \ln W(N, M) = \ln \left(\frac{M!}{N!(M-N)!} \right).$$

You can convert from $S(N, M)$ to $S(N, V)$ by using the chain rule (see page 77). There are M lattice sites per unit volume V , so $M = (\text{constant}) V$. This gives $(\partial M/\partial V) = M/V$, and

$$\left(\frac{\partial S}{\partial V}\right)_N = \left(\frac{\partial S}{\partial M}\right)_N \left(\frac{dM}{dV}\right) = \left(\frac{\partial S}{\partial M}\right)_N \left(\frac{M}{V}\right). \quad (7.7)$$

To get $S(M)$, apply Stirling's approximation (page 57) to Equation (2.3),

$$\begin{aligned} \frac{S}{k} &\approx \ln \left(\frac{M^M}{N^N (M-N)^{(M-N)}} \right) \\ &= M \ln M - N \ln N - (M-N) \ln(M-N). \end{aligned} \quad (7.8)$$

Break the first term on the right side into two parts, $M \ln M = N \ln M + (M-N) \ln M$, and incorporate these into the second and third terms in Equation (7.8) to get

$$\frac{S}{k} = -N \ln \left(\frac{N}{M} \right) - (M-N) \ln \left(\frac{M-N}{M} \right). \quad (7.9)$$

Take the derivative of S in Equation (7.8) to get

$$\begin{aligned} \left(\frac{\partial S}{\partial M}\right)_N &= k \left[1 + \ln M - \ln(M-N) - \left(\frac{M-N}{M-N}\right) \right] \\ &= -k \ln \left(1 - \frac{N}{M} \right). \end{aligned} \quad (7.10)$$

Equation (7.10) can be expressed by using the series expansion of the logarithm from Appendix C, $\ln(1-x) \approx -x - x^2/2 + \dots$. If the density of molecules is small, $N/M \ll 1$, you need only the lowest order terms. Substituting Equation (7.10) and Equation (7.7) into the definition of pressure gives

$$\begin{aligned} p &= -kT \left(\frac{M}{V} \right) \ln \left(1 - \frac{N}{M} \right) \\ &\approx \left(-\frac{MkT}{V} \right) \left(-\frac{N}{M} \right) \left(1 + \frac{1}{2} \left(\frac{N}{M} \right) + \dots \right) \approx \frac{NkT}{V}, \end{aligned} \quad (7.11)$$

which is the ideal gas law.

We have derived the ideal gas law from a simple model for the dependence of S on V , using the thermodynamic definition of pressure. We will show in Chapter 24 that keeping the next higher order term in the expansion gives a refinement toward the van der Waals gas law.

1/T, p/T, and μ/T Behave as Forces

Now we'll show that T , p , and μ , mathematically defined by Equation (7.3), coincide with the physically measurable quantities temperature, pressure, and chemical potential. We will do this in two steps. First we will show that T , p , and μ are *intensive* quantities, not dependent on system size. Then we will show that $1/T$, p/T , and μ/T describe forces. $1/T$ describes a tendency for heat flow, p/T represents a tendency for volume change, and μ/T represents a tendency for particle exchange.

T , p , and μ are intensive because $U(S, V, N)$ is a *first-order homogeneous function* (see below). The fundamental energy equation has the form $U = U(x_1, x_2, x_3)$ where the x_i 's are the extensive quantities, S, V, N . If the

system size is scaled up by a factor of λ , then each x_i is replaced by λx_i , and the energy, which is extensive, will increase from U to λU . But since T , p , and μ are partial derivatives ($\partial U/\partial x_i$) (see Equation (7.3)), and since rescaling by λ does not change these partial derivatives, $(\partial(\lambda U)/\partial(\lambda x_i)) = (\partial U/\partial x_i)$, the quantities T , p , and μ are not dependent on the size of the system.

Homogeneous Functions

A first-order homogeneous function increases by a factor λ if the independent variables x_i are all increased by a factor λ :

$$f(\lambda x_1, \lambda x_2, \lambda x_3, \dots, \lambda x_M) = \lambda f(x_1, x_2, x_3, \dots, x_M), \quad (7.12)$$

where λ is a constant.

The volume of a liquid is a first-order homogeneous function of the number of molecules. If you double the number of molecules you double the volume of the liquid. In this case, x = number of molecules, f = volume, and $\lambda = 2$. In contrast, the volume of a sphere is *not* a first-order homogeneous function of the *radius*. If you double the radius, you do not double the volume.

An important property of first-order homogeneous functions is their relation to their partial derivatives. Differentiate both sides of Equation (7.12) with respect to λ and use the chain rule (see page 77) to get

$$\frac{df(\lambda x_1, \lambda x_2, \lambda x_3, \dots, \lambda x_M)}{d\lambda} = f = \sum_{i=1}^M \left(\frac{\partial f}{\partial(\lambda x_i)} \right) \left(\frac{\partial(\lambda x_i)}{\partial \lambda} \right), \quad (7.13)$$

since $(\partial f(x_1, x_2, \dots, x_n)/\partial \lambda) = 0$. The expression on the right side of Equation (7.13) can be simplified because $(\partial(\lambda x_i)/\partial \lambda)$ equals x_i :

$$\sum_{i=1}^M x_i \left(\frac{\partial f}{\partial(\lambda x_i)} \right) = f. \quad (7.14)$$

Since Equation (7.14) must hold for any value of λ , you can express the partial derivatives of the original function $f(x_1, x_2, x_3, \dots, x_M)$ by setting λ equal to one, with the result

$$\sum_{i=1}^M x_i \left(\frac{\partial f}{\partial x_i} \right) = f. \quad (7.15)$$

Equation (7.15) does not apply to functions in general, only to first-order homogeneous functions. For example, for $U(S, V, N)$, Equation (7.15) gives $U = TS - pV + \sum_{i=1}^M \mu_i N_i$.

$dS = 0$ Defines Thermal, Mechanical, and Chemical Equilibria

In the next four examples we show that $1/T$ is a measure of a system's tendency for heat exchange, p/T is a measure of a system's tendency for volume change, and μ/T is a measure of a system's tendency for particle exchange. We follow

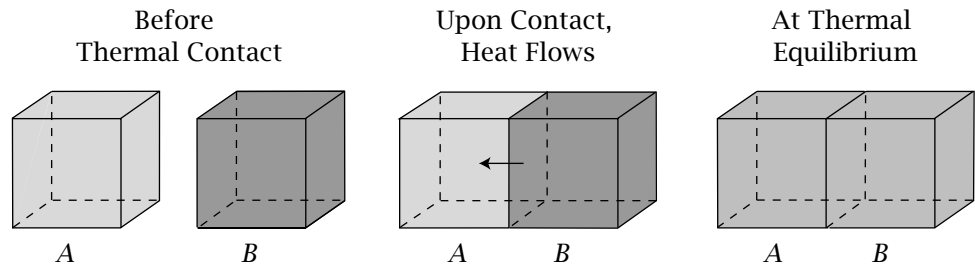


Figure 7.3 When objects A and B are brought into thermal contact, heat q (shown here as shading) can flow from one to the other. If there is no additional exchange with the surroundings, the process will conserve energy (see Equation (7.17)).

the same strategy in each case. We determine the relevant independent variables and apply the fundamental entropy equation, and the constraints. Then the maximum entropy principle ($dS_{\text{total}} = 0$) defines the state of equilibrium.

EXAMPLE 7.2 Temperature describes the tendency for energy exchange. *Temperature* is the quantity that tells you when heat exchange will occur. Objects exchange heat to reach a state of maximum entropy (equilibrium), and in this state their temperatures are equal. Suppose two objects are brought into thermal contact. With *each other*, they can exchange energy but not volume or particles. Both objects are otherwise isolated from their surroundings. So with the *surroundings*, the two objects cannot exchange energy, particles, or volume. Object A has energy U_A , entropy S_A , and temperature T_A , where $1/T_A = (\partial S_A/\partial U_A)$. Object B has energy U_B , entropy S_B , and $1/T_B = (\partial S_B/\partial U_B)$. Although entropy is not experimentally measurable, temperature is, so temperature is a convenient surrogate quantity for determining the closeness to equilibrium. What temperatures will the two objects have at equilibrium? What state maximizes the entropy?

Entropy is an extensive property, so

$$S_{\text{total}} = S_A + S_B. \quad (7.16)$$

Equation (7.16) does not mean that the total entropy of the system remains fixed during the process. The total entropy can increase as a system approaches equilibrium. Equation (7.16) says only that the total entropy of the system is the sum of the entropies of the subsystems.

When the two subsystems are brought into contact, they can exchange energies U_A and U_B with each other (see Figure 7.3). U_A and U_B are the degrees of freedom and the entropy depends on them, $S_{\text{total}}(U_A, U_B)$. However, the system cannot exchange energy with the surroundings, so the total energy $U_A + U_B$ is constrained:

$$U_A + U_B = U_{\text{total}} = \text{constant}. \quad (7.17)$$

To find the state of thermal equilibrium, determine what variations in U_A and U_B will cause the total entropy of the system to be maximal, $dS = 0$. Write the fundamental entropy equation for the total differential dS_{total} in terms of the degrees of freedom, and set it equal to zero:

$$dS_{\text{total}} = dS_A + dS_B = \left(\frac{\partial S_A}{\partial U_A}\right)_{V,N} dU_A + \left(\frac{\partial S_B}{\partial U_B}\right)_{V,N} dU_B = 0. \quad (7.18)$$

The differential form of the constraint Equation (7.17) is

$$dU_A + dU_B = dU_{\text{total}} = 0 \quad \Rightarrow \quad dU_A = -dU_B. \quad (7.19)$$

Substitute $-dU_A$ for dU_B in Equation (7.18) and rearrange:

$$\begin{aligned} dS_{\text{total}} &= \left[\left(\frac{\partial S_A}{\partial U_A}\right)_{V,N} - \left(\frac{\partial S_B}{\partial U_B}\right)_{V,N} \right] dU_A = 0 \\ \Rightarrow \quad \left(\frac{\partial S_A}{\partial U_A}\right)_{V,N} &= \left(\frac{\partial S_B}{\partial U_B}\right)_{V,N}. \end{aligned} \quad (7.20)$$

Substituting the definition $1/T = (\partial S/\partial U)_{V,N}$ into Equation (7.20) gives the equilibrium condition

$$\frac{1}{T_A} = \frac{1}{T_B} \quad \Rightarrow \quad T_A = T_B. \quad (7.21)$$

When two objects at different temperatures are brought into thermal contact, they exchange heat. They exchange heat because it leads to maximization of the entropy of the combined system ($dS_{\text{total}} = 0$). This results in the equalization of temperatures, $T_A = T_B$. The quantity $1/T$ describes a tendency to transfer energy. When the temperatures are equal, there is no heat exchange. The advantage of describing equilibrium in terms of the equality of temperatures, rather than in terms of the maximization of entropy, is that temperatures are measurable.

In what *direction* does energy exchange between subsystems A and B ? Look at the signs on the differentials. Substituting $1/T = (\partial S/\partial U)_{V,N}$ into Equation (7.20) leads to

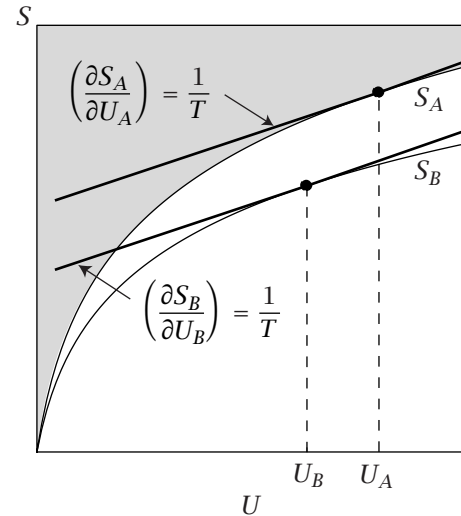
$$dS_{\text{total}} = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A. \quad (7.22)$$

A change *toward* equilibrium *increases* the entropy: $dS_{\text{total}} \geq 0$. For dS_{total} to be positive, the signs on both factors dU_A and $((1/T_A) - (1/T_B))$ must be the same. If dU_A is negative, object A loses energy to object B in the approach to equilibrium. Then, in order that $dS_{\text{total}} > 0$, T_A must be greater than T_B . Thus if object A transfers energy to object B , A must have been the hotter object. The prediction that systems tend toward states of maximum entropy explains why heat flows from hot to cold objects.

What is Temperature? A First Look

Example 7.2 illustrates the relationships among energy, entropy, temperature, and heat. Energy is the capacity of a system to do work. That capacity can flow from one place to another as heat. The entropy describes the tendency of the work capacity (energy) to flow from one object to another. The entropy is a sort of potential to move energy from one place to another and $1/T$ represents the corresponding force. The higher the temperature of an object, the greater the tendency for energy to escape from it.

Figure 7.4 $1/T$ is the slope of S as a function of U for both systems A and B . Two systems at thermal equilibrium have the same temperature, T , not necessarily the same energy or entropy.



Is the flow of heat due to a tendency to equalize energies? No. Heat flows to maximize entropy. Temperatures are equalized, not energies. The First Law describes energy bookkeeping: the sum of heat plus work is constant. It does not tell us why, or when, or how much energy will be exchanged. For that we need a second principle, the principle that systems tend toward their states of maximum entropy, the Second Law of thermodynamics.

Consider money as an analog to energy. Money represents a capacity to produce things, just as energy represents the capacity for work. Money can flow between people, like energy between objects. When person A pays money to person B , the sum of their dollars is unchanged, just as when the two bodies exchange energy in Example 7.2. This conservation of dollars corresponds to the First Law, the conservation of energy.

However, the drive for energy to flow from hot objects to cold objects is not a tendency to equalize the distribution of energy, just as the rich do not pay the poor to equalize their wealth. This is where entropy and temperature come in. Energy flows only if it leads to an increase in the entropy of the whole system.

What is the analog of entropy in the money example? Suppose person A has money and wants widgets and person B has widgets to sell. Person A will benefit in some way by *paying* money to receive a widget. On the other hand, person B will benefit by *receiving* money for a widget. Money will be exchanged because both parties benefit. Economists call this ‘maximizing a utility function’ [1]. Money flows if it leads to an increase in the overall utility function for both parties, just as energy flows to maximize the entropy.

What is temperature in this analogy? Based on its definition, $1/T = (\partial S/\partial U)$, $1/T$ represents the incremental benefit to person A or B of getting a dollar or a widget. When these incremental benefits are equal, there is no further net redistribution of money and widgets. This analogy emphasizes that energy flows if it can increase another quantity, the entropy. When entropy can be increased no further by net changes in a degree of freedom, the system is in equilibrium. However, do not take this analogy too seriously. Money does not always flow to everyone’s maximum benefit. For the limitations of the economics analogy, see reference [2].

Figure 7.4 shows that at thermal equilibrium, equality of temperatures T_A and T_B is not the same as equality of energies or entropies. We interpret temperature in more detail in Chapter 12.

EXAMPLE 7.3 Pressure is a force for changing volume. How does volume change maximize entropy? Consider a cylinder partitioned into subsystems A and B by a movable piston as shown in Figure 7.5. The volumes of both subsystems change when the piston moves. In this problem, volume is the degree of freedom and there is no energy or matter exchange. You know from Example 7.2 that there will be no energy exchange if the temperatures on both sides are equal, $T_A = T_B$.

The total system is otherwise isolated, so it is not able to exchange energy, volume, or particles with the surroundings. Subsystem A has entropy $S_A(U_A, V_A)$, and subsystem B has entropy $S_B(U_B, V_B)$. Because the system is isolated, the volume of the total system is fixed, $V_A + V_B = V_{\text{total}} = \text{constant}$. Now allow subsystems A and B to exchange volume. For the moment, see what happens if they can also exchange energy. In differential form, the volume constraint is

$$dV_A = -dV_B. \quad (7.23)$$

The state of maximum entropy, $dS = 0$, defines the equilibrium. Write the total differential dS_{total} in terms of the degrees of freedom:

$$dS = \left(\frac{\partial S_A}{\partial V_A}\right) dV_A + \left(\frac{\partial S_B}{\partial V_B}\right) dV_B + \left(\frac{\partial S_A}{\partial U_A}\right) dU_A + \left(\frac{\partial S_B}{\partial U_B}\right) dU_B = 0. \quad (7.24)$$

Because no energy is exchanged with the surroundings, $dU_A = -dU_B$. Substitute dU_A for $-dU_B$ and $1/T$ for (dS/dU) :

$$dS = \left(\frac{\partial S_A}{\partial V_A}\right) dV_A + \left(\frac{\partial S_B}{\partial V_B}\right) dV_B + \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dU_A = 0. \quad (7.25)$$

Since $T_A = T_B$, Equation (7.25) reduces to

$$dS = \left(\frac{\partial S_A}{\partial V_A}\right) dV_A + \left(\frac{\partial S_B}{\partial V_B}\right) dV_B = 0. \quad (7.26)$$

Substituting Equations (7.23) and (7.6) into Equation (7.26), the condition for equilibrium becomes

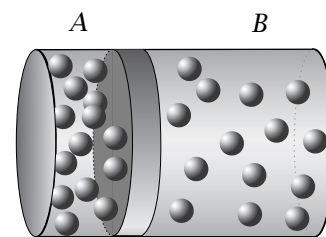
$$dS = \left(\frac{p_A}{T_A} - \frac{p_B}{T_B}\right) dV_A = 0. \quad (7.27)$$

Equation (7.27) is satisfied when

$$\frac{p_A}{T_A} = \frac{p_B}{T_B}. \quad (7.28)$$

Since $T_A = T_B$, *mechanical equilibrium* occurs when the pressures of the two subsystems are equal, $p_A = p_B$. Just as a system with $T_A > T_B$ increases its entropy and moves to equilibrium by transferring heat from subsystem A to subsystem B , a system with $p_A > p_B$ increases its entropy and moves toward equilibrium by increasing volume V_A and decreasing V_B . Volumes change to equalize the pressures.

Before Equilibration



After Equilibration

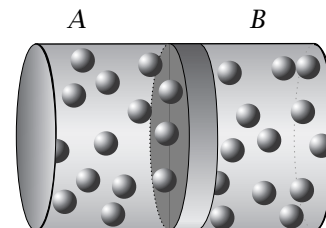


Figure 7.5 Before equilibration, the piston in Example 7.3 is fixed in place and the pressures on the two sides are unequal. After the piston is freed, the volumes will change (subject to the constraint $V_A + V_B = V_{\text{total}} = \text{constant}$) until the pressures equalize.

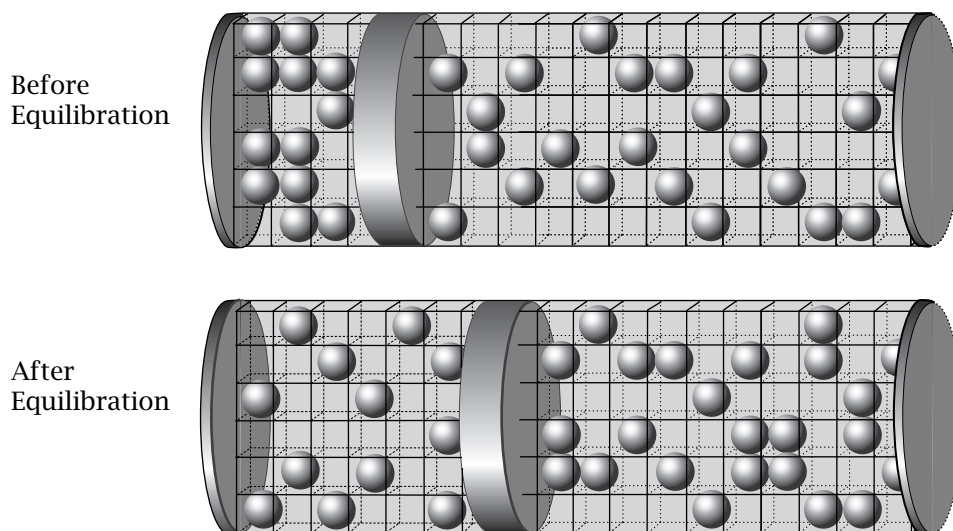


Figure 7.6 Lattice model of volume changes ($T_A = T_B$) for Example 7.4. Particle numbers N_A and N_B are fixed on both sides of a piston. Volumes M_A and M_B change subject to the constraint $M_A + M_B = \text{constant}$. Pressures become equalized, so according to lattice or ideal gas models, densities become equalized.

The pressures of gases are sometimes described as forces per unit area due to gas particles colliding with the walls of containers. Our definition of pressure in Equation (7.3) or Equation (7.6) is much more general. It applies to liquids and solids, and any other circumstance in which the energy changes with volume.

The thermodynamic reasoning in Example 7.3 is quite general, but it gives no insight into the microscopic nature of entropy. Let's return to the lattice model to see how equalizing the pressures maximizes the multiplicity of the arrangements of particles.

EXAMPLE 7.4 How does the equality of pressures maximize the multiplicity of states? Consider a gas contained on two sides of a piston as shown in Figure 7.6. The number N_A of particles on the left and the number N_B on the right are each fixed. The total volume is defined by M lattice sites, and the movable piston partitions the volume into M_A sites on the left and M_B sites on the right, with the constraint $M = M_A + M_B = \text{constant}$.

The number of spatially distinguishable configurations on each side of the piston is given by Equation (2.3), $W(N, M) = M!/N!(M - N)!$. The total number of configurations of the system is the product

$$W = \left(\frac{M_A!}{N_A!(M_A - N_A)!} \right) \left(\frac{M_B!}{N_B!(M_B - N_B)!} \right). \quad (7.29)$$

Using Stirling's approximation (page 57) to replace the factorials, and using the constraint $M = M_A + M_B$ to replace M_B by $M - M_A$, you can express W in terms of one degree of freedom, M_A :

$$W \approx \left(\frac{M_A^{M_A}}{N_A^{N_A} (M_A - N_A)^{M_A - N_A}} \right) \left(\frac{(M - M_A)^{M - M_A}}{N_B^{N_B} (M - M_A - N_B)^{M - M_A - N_B}} \right). \quad (7.30)$$

Take the logarithm of both sides of Equation (7.30) to find the entropy S/k :

$$\begin{aligned} S/k = \ln W &= M_A \ln M_A - (M_A - N_A) \ln(M_A - N_A) \\ &\quad + (M - M_A) \ln(M - M_A) - (M - M_A - N_B) \ln(M - M_A - N_B) \\ &\quad - N_A \ln N_A - N_B \ln N_B. \end{aligned} \quad (7.31)$$

Now find the value $M_A = M_A^*$ that maximizes $S/k = \ln W$. The constant terms $-N_A \ln N_A$ and $-N_B \ln N_B$ do not contribute to the derivative with respect to M_A . Taking M , N_A , and N_B as constants, solve

$$\begin{aligned} \frac{d \ln W}{d M_A} &= 0 \\ \Rightarrow 1 + \ln M_A^* - \ln(M_A^* - N_A) - 1 - \ln(M - M_A^*) \\ &\quad - 1 + \ln(M - M_A^* - N_B) + 1 = 0 \\ \Rightarrow \ln \left(\left(\frac{M_A^*}{M_A^* - N_A} \right) \left(\frac{M - M_A^* - N_B}{M - M_A^*} \right) \right) &= 0 \\ \Rightarrow \left(\frac{M_A^*}{M_A^* - N_A} \right) \left(\frac{M - M_A^* - N_B}{M - M_A^*} \right) &= 1. \end{aligned} \quad (7.32)$$

$(M_A^* - N_A)/M_A^*$ is the fraction of A sites that are empty, and the fraction of B sites that are empty is $(M - M_A^* - N_B)/(M - M_A^*)$. Setting these expressions equal according to Equation (7.32) means that the fraction of filled sites must be the same on both sides,

$$\frac{N_B}{M_B^*} = \frac{N_A}{M_A^*}. \quad (7.33)$$

The entropy is maximized and the system is at equilibrium when the density of particles N/M is the same on both sides. Because the pressure of an ideal gas is given by $p/T = Nk/M$, the equality of densities implies that $p_A/T_A = p_B/T_B$ at equilibrium, which is the same as the thermodynamic result in Example 7.3. However, the molecular model gives us information about densities that the thermodynamic model does not.

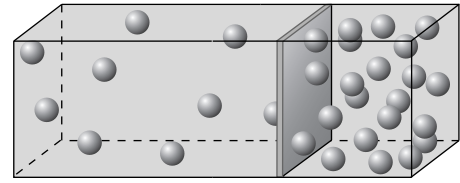
Now we turn our attention from systems that change volumes to systems that change particle numbers.

EXAMPLE 7.5 The chemical potential is a tendency for particle exchange.

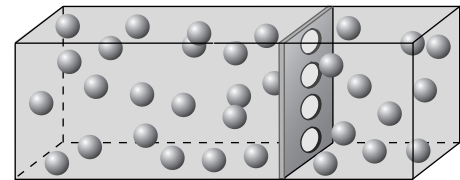
The chemical potential describes a tendency for matter to move from one place to another. Suppose that two compartments (A and B) are separated by a fixed barrier. Consider N identical particles, N_A of which are on side A and N_B of which are on side B (see Figure 7.7). The degrees of freedom are N_A and N_B .

Figure 7.7 Before equilibration a permeation barrier prevents particle flow. After the barrier is removed, the particles exchange until the chemical potential is the same on both sides (see Example 7.5).

Before Equilibration



After Equilibration



When particles are exchanged, they carry energy with them, so energy is also exchanged. However, if the temperatures and pressures of the subsystems are held equal, there will be no net exchange of energy or volume when particles exchange across the barrier.

The subsystems have entropies $S_A(N_A)$ and $S_B(N_B)$. Again write the differential form of the fundamental entropy equation in terms of the degrees of freedom, introduce the constraints, and then find the state that has the maximum entropy. When the permeation barrier is removed, the particle numbers on both sides change, subject to the constraint $N_A + N_B = N = \text{constant}$. In differential form the number constraint is

$$dN_A = -dN_B. \quad (7.34)$$

The condition for equilibrium is

$$dS_{\text{total}} = \left(\frac{\partial S_A}{\partial N_A} \right) dN_A + \left(\frac{\partial S_B}{\partial N_B} \right) dN_B = 0. \quad (7.35)$$

Substitution of $-\mu/T$ for $(\partial S/\partial N)$ (Equation (7.6)) leads to the equilibrium condition

$$dS_{\text{total}} = \left(\frac{\mu_B}{T_B} - \frac{\mu_A}{T_A} \right) dN_A = 0. \quad (7.36)$$

The condition for material balance equilibrium at temperature $T = T_A = T_B$ is

$$\mu_A = \mu_B. \quad (7.37)$$

A change toward equilibrium must increase the entropy,

$$dS_{\text{total}} = \left(\frac{\mu_B}{T} - \frac{\mu_A}{T} \right) dN_A > 0. \quad (7.38)$$

For dS_{total} to be positive, the signs on the factors $((\mu_B/T) - (\mu_A/T))$ and dN_A must be the same. Therefore, if the particle number on side A increases as the system approaches equilibrium, μ_B must be greater than μ_A . The chemical

potential μ is sometimes called the *escaping tendency* because particles tend to escape from regions of high chemical potential to regions of low chemical potential. The chemical potential pertains not just to particles in different spatial locations, say on different sides of a membrane. It also pertains to molecules in different phases or in different chemical states, as we will see in Chapters 13 and 16. Chemical potentials are found by measuring concentrations.

So far, we have used thermodynamics in two ways. First, in Example 7.1 we combined the thermodynamic definition of pressure with a molecular model to derive an equation of state, the ideal gas law. Second, in Examples 7.2, 7.3, and 7.5, we found that the condition for various equilibria ($dS = 0$) could be restated in terms of the experimentally accessible quantities, T , p , and μ .

$1/T$ is a tendency for exchanging energy, p/T is a tendency to change volume, and μ/T is a tendency for particles to exchange. For thermal, mechanical, and chemical equilibrium between subsystems A and B , $T_A = T_B$, $p_A = p_B$, and $\mu_A = \mu_B$.

Thermodynamic Logic Gives Unmeasurable Predictors of Equilibria from Measurable Properties

Thermodynamic logic often seems to be complex. This apparent complexity arises because the fundamental equilibrium functions cannot be measured directly. Equilibria are governed by energy and entropy through the First and Second Laws, but unfortunately there are no energy or entropy ‘meters’ to measure these quantities. Instead, inferences about equilibria are indirect and drawn from observations of quantities that can be measured, such as temperature, pressure, work, heat capacities, concentrations, or electrical potentials. Thermodynamics is a business of making clever inferences about unmeasurable quantities from observable ones, by various means.

In this and the next two chapters, we show six of the main methods of thermodynamics for drawing such inferences: (1) obtaining energies by measuring work, (2) obtaining entropies by measuring heat, (3) obtaining energies and entropies by measuring heat capacities, (4) using thermodynamic cycles to obtain some quantities from others, (5) obtaining partial derivative quantities from others by using Maxwell’s relations, and (6) linking some partial derivative quantities to others by using the mathematics of homogeneous functions. Key concepts are *processes* and *cycles*, real or fictitious, as described below.

Cycles and Fictitious Processes

At the root of the classical thermodynamics of engines is the fact that work is an important and measurable quantity. However, work, while measurable, is rarely predictable. The work performed by a gas expanding in an engine piston can depend on pressure, volume, temperature, speed of the piston motion, frictional forces, and other factors in complex ways that are not fully understood.

Nevertheless, under some limited circumstances, predictions are possible. To describe those circumstances, we distinguish *state variables*, like p , V , T , N , U , and S that characterize the stable states of a system, from *process*

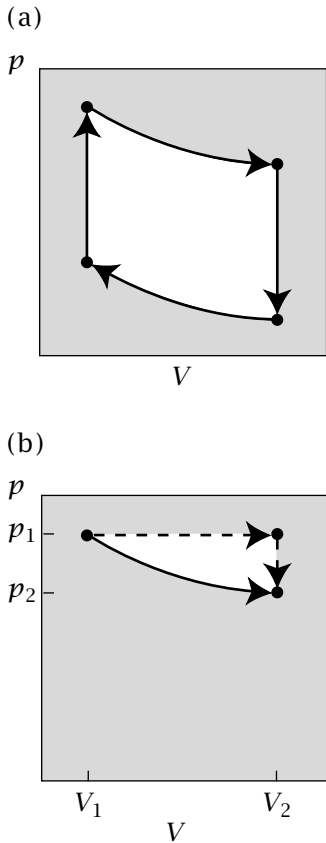


Figure 7.8 (a) Thermodynamic cycle for pressure-volume changes. (b) Modelling one step of the cycle (continuous line) by using a fictitious constant pressure process followed by a fictitious constant volume process (dashed lines).

variables, like piston velocity, thermal gradients, friction, diffusion, and other time-dependent quantities that characterize how the system gets from one state to another. Functions like energy $U(S, V, N)$ and entropy $S(U, V, N)$ have a special simplicity—they depend only on state variables such as U, S, V, N , and not on process variables. In contrast, work w and heat q are more complex, because they depend on both state and process variables. If gas expansion is fast, it can generate much heat and little work. Slower expansion can generate more work and less heat. Just knowing state quantities like (p_1, V_1, T_1) and (p_2, V_2, T_2) without knowing the quantities that describe the intervening *process*, you cannot in general predict the work performed by a gas in a cylinder.

However, even if processes are performed infinitely slowly, so that time-dependent quantities are negligible, heat and work still depend on the process (or pathway) in ways that state functions do not. Recall from Chapter 5 (page 73) that for some functions $f(x, y)$, a change Δf , computed by integration, depends on the pathway of integration, while for others, called *state functions*, the integral Δf does not depend on the pathway of integration. Heat and work are path-dependent functions, while U and S are state functions. The work as a gas expands from (p_1, V_1) to (p_2, V_2) will be different if the system passes through an intervening state, say (p_x, V_x) , than if it passes through a state (p_y, V_y) . To compute the work, you need to know the sequence of intervening states in the physical process. However, to compute the difference in a state function, such as ΔU , you do not need to know the intervening states. That is, you get the same value of $\Delta U = U(p_2, V_2) - U(p_1, V_1)$ whether you assume that the system passed through state x : $U_2 - U_1 = (U_2 - U_x) + (U_x - U_1)$ or through state y : $U_2 - U_1 = (U_2 - U_y) + (U_y - U_1)$. The intervening term cancels in each of these expressions.

Two key principles follow from this logic. First, a thermodynamic change from state 1 to state 2 can be expressed as a sum of component steps, say from 1 to x followed by x to 2. Second, this logic is the basis for inventing *fictitious* processes and *imaginary* intervening states. Suppose that the pressure and volume of a gas change from initial state (p_1, V_1) to final state (p_2, V_2) . To compute the difference in a state function, say ΔU , you are free to imagine that the real system passes through any state you wish to invent if it helps to make your calculation easier. You could model the overall change as a sum of two processes: a volume change at constant pressure $(p_1, V_1) \rightarrow (p_1, V_2)$ followed by a pressure change at constant volume $(p_1, V_2) \rightarrow (p_2, V_2)$, even if the real physical process never passes through such a state (p_1, V_2) (see Figure 7.8(b)). To compute differences in state functions such as ΔU , you can invent imaginary intervening states, even nonphysical ones, in whatever ways make it simpler to calculate. One important class of fictitious process is the *quasi-static process*.

Quasi-Static Processes

Quasi-static describes processes that are performed sufficiently slowly that properties are independent of time and independent of the speed of the process. To be quasi-static, a process must be significantly slower than a relaxation time of a system. Only quasi-static processes can be represented on state diagrams, because non-quasi-static processes involve more variables than just those that define state points. Non-quasi-static processes also depend on gra-

dients or time-dependent quantities such as velocities and friction coefficients. The power of the idea of quasi-static processes is that it provides a relationship between the work w and the state variables, pressure and volume. For a gas in a piston expanding by a volume dV against an applied external pressure p_{ext} , the increment of work in a *quasi-static* process is defined to be

$$\delta w = -p_{\text{ext}}dV. \quad (7.39)$$

If a process is not quasi-static, Equation (7.39) is not valid.

Here are examples of different quasi-static processes or thermodynamic paths that could be taken when a gas expands in a piston at constant volume, constant pressure, or constant temperature.

EXAMPLE 7.6 Constant-volume work. Whenever there is no volume change in a quasi-static process in a simple system, no work is performed because $p dV = 0$.

EXAMPLE 7.7 Constant-pressure work. When the externally applied pressure p_{ext} is constant, the total work in a quasi-static process of expansion from volume V_A to V_B is

$$w = - \int_{V_A}^{V_B} p_{\text{ext}} dV = -p_{\text{ext}}(V_B - V_A). \quad (7.40)$$

According to our sign convention, δw is positive when the volume inside a piston decreases ($dV < 0$). That is, work is positive when it is done *on the system* to compress the gas, and negative when it is done *by the system* to expand.

EXAMPLE 7.8 Constant-temperature work. A gas does work when it expands quasi-statically in a piston at constant temperature. Now both the pressure and volume can change during the expansion, so you need to know the functional form of $p(V)$ for this process. A quasi-static process is slow enough for the gas pressure inside to equilibrate with the external pressure, $p_{\text{int}} = p_{\text{ext}}$. To compute the work of an ideal gas at constant T , integrate:

$$\begin{aligned} w &= - \int_{V_A}^{V_B} p_{\text{ext}} dV = - \int_{V_A}^{V_B} p_{\text{int}} dV \\ &= - \int_{V_A}^{V_B} \frac{NkT}{V} dV = -NkT \ln \left(\frac{V_B}{V_A} \right). \end{aligned} \quad (7.41)$$

At the core of thermodynamics are *thermodynamic cycles*. A cycle is a series of steps that begin in one state, pass through other states, then return to the initial state to begin again. Engines take in fuel, which is combusted to form a vapor. The gas expands and performs work. The spent vapor exits. New fuel enters to begin another cycle. In refrigerators, a working fluid flows through cooling coils to cool a compartment, flows through other coils to dump heat outside the refrigerator, then flows around again to repeat the cycle. Muscle proteins convert energy to motion in repetitive cycles. Cycles are described by *state diagrams*, which show how certain state variables change throughout the

cycle. Figure 7.8(a) illustrates a pressure–volume state diagram, a common way in which to describe the states of a gas in an engine. Figure 7.8(b) shows two fictitious processes that model a pV change in one step of the cycle.

We now aim to relate the two path-dependent quantities, q and w , to state functions like U and S , for two reasons. First, such relationships give ways of getting fundamental but unmeasurable quantities U and S from measurable quantities q and w . Second, there is an increase in predictive power whenever q and w depend only on state variables and not on process variables. The First Law of thermodynamics gives such a relationship.

The First Law Interrelates Heat, Work, and Energy

The **First Law of thermodynamics** relates a change in energy, dU , to increments of heat δq and work δw :

$$dU = \delta q + \delta w. \quad (7.42)$$

The use of δ as a differential element indicates that heat and work are path-dependent quantities, while the use of d indicates that their sum, the internal energy dU , is a state function (see pages 73–77). The signs of the quantities in the First Law are defined so that the internal energy increases when heat flows *into* a system, $\delta q > 0$, and when work is done *on* a system, $\delta w > 0$. Energy is a property of a *system* while heat and work are properties of a process of energy *transfer across a boundary*.

This difference is illustrated by an analogy: the level of water in a lake is like the amount of internal energy in a system, and the different modes of water exchange between the lake and its surroundings are like heat and work [3]. Say that rainfall corresponds to the process of heat going into the system ($q > 0$), evaporation corresponds to the process of heat going out of the system ($q < 0$), streams flowing into the lake correspond to work done on the system ($w > 0$), and streams flowing out of the lake correspond to work done *by* the system ($w < 0$). The change in internal energy $\Delta U = q_{\text{in}} - q_{\text{out}} + w_{\text{in}} - w_{\text{out}}$ is the sum of the heat and work *into* the system minus the heat and work *out of* the system, just as the change in the water level of the lake is the sum of rainfall plus river flows in, minus evaporation and river flows out. Once the water is in the lake, you cannot tell whether it came from rainfall or from streams. Similarly, you cannot tell whether the amount of internal energy in a system was acquired as heat or work. In this analogy, the internal energy corresponds to a property of the lake, while heat and work correspond to processes of the transfer across the boundaries of the lake.

Method (1)

Using Adiabatic Boundaries to Relate U and w

The First Law gives a way of relating w , a path-dependent quantity, to U , a state function. If you surround a working device with an insulating (adiabatic) boundary ($\delta q = 0$) it follows from the First Law that $dU = \delta w$. The point is to determine a change ΔU from an experimentally measurable quantity, the work done on the system. In the lake analogy, you could cover the lake with a tarp

and measure the flow of streams to determine the change in water level. With an adiabatic boundary, work becomes a function of state properties only.

Heat, which is path-dependent, is related to the entropy, a state function, for quasi-static processes, as shown below.

Method (2)

Combine the First Law and the Fundamental Energy Equation to Find the Entropy

What experiment can determine entropy changes? Combining the First Law with the fundamental energy equation (Equation (7.4)) for a closed system (no loss or gain of particles), $dU = TdS - pdV$, gives

$$dU = TdS - pdV = \delta q + \delta w. \quad (7.43)$$

In a quasi-static process, the work is

$$\delta w = -pdV. \quad (7.44)$$

Substituting Equation (7.44) into (7.43) gives $\delta q = TdS$, or

$$dS = \frac{\delta q}{T} \quad \text{for quasi-static processes in closed systems.} \quad (7.45)$$

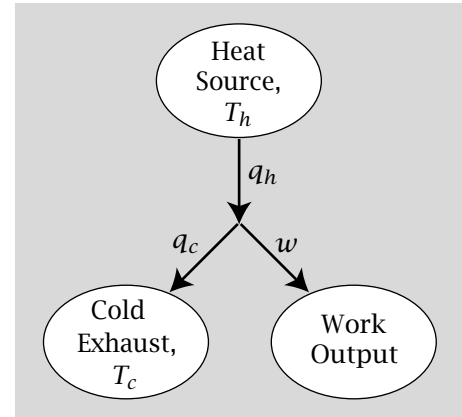
Equation (7.45) is sometimes called the **thermodynamic definition of entropy**. It shows how to obtain the entropy change (which you cannot otherwise measure directly) from experimentally observable quantities (heat transfer and temperature) by using a quasi-static process.

A central problem of the industrial revolution, understanding what makes steam engines efficient, was solved in the 1800s, establishing the importance of thermodynamics. Steam engines convert heat to work by the expansion of a hot gas in a piston. James Watt's original steam engine converted only 7% of the energy (heat) input to work. The remaining 93% was exhausted to the surroundings. The design of efficient engines had overwhelming economic importance for the industrial revolution. It was necessary to understand the nature of heat in order to convert heat to work efficiently. Is efficiency determined by the type of gas, its temperature, or the volume or shape of the piston? The concepts of thermodynamics emerged from the effort to solve this problem. To understand why an engine wastes heat, you need to know how the engine balances its energy books at the same time as it tends toward equilibrium. We need another idealization, called *reversibility*. We need three ideas: a reversible process, a reversible work source, and a reversible heat source.

Reversible Processes

Reversibility is an idealization that defines the maximum work that can be achieved. To achieve the maximum work requires more than just extreme slowness. Reversible processes are a subset of quasi-static processes. (Any process that is fast enough is irreversible.) Processes are reversible if they are both very slow and also if they can be undone by equilibrium physical changes that involve no entropy change, $\Delta S = 0$. (In Chapter 8 we will discuss processes

Figure 7.9 Schematic diagram of heat and work sources in which the hot gas in an engine partly converts to work, and partly converts to colder exhaust gas. The ellipses indicate reversible heat and work sources. The arrows indicate processes. A physical realization is shown in Figure 7.10.



at constant temperature; then reversibility will be defined as an unchanging *free energy*.) You can stretch clay very slowly, but it cannot be ‘reversed’ to its unstretched state by equilibrium steps. You can turn a paddle wheel clockwise in water to dissipate heat through frictional forces, but the process cannot be reversed: heat from the liquid cannot make the paddle wheel move counterclockwise. You can put a droplet of dye in water and watch it spread, but the reverse does not happen. Dinosaurs decompose into hydrocarbons over the eons, but you cannot turn hydrocarbons back into dinosaurs. All these are examples of processes that can happen slowly, but are not reversible.

Reversible Heat and Work Sources

To compute the maximum work, we need two other idealizations. A *reversible work source* can change volume or perform work of any other kind quasi-statically, and is enclosed in an impermeable adiabatic wall, so $\delta q = TdS = 0$ and $dU = \delta w$. A *reversible heat source* can exchange heat quasi-statically, and is enclosed in a rigid wall that is impermeable to matter but not to heat flow, so $\delta w = -pdV = 0$ and $dU = \delta q = TdS$. A reversible *process* is different from a reversible heat or work *source*. A reversible heat source need not have $\Delta S = 0$. A reversible *process* refers to changes in a whole system, in which a collection of reversible heat plus work sources has $\Delta S = 0$. The frictionless weights on pulleys and inclined planes of Newtonian mechanics are reversible work sources, for example. The maximum possible work is achieved when reversible processes are performed with reversible heat and work sources.

Now consider the problem of mechanical efficiency that motivated the development of thermodynamics.

EXAMPLE 7.9 Why do engines waste heat? Why can’t you design an engine that converts 100% of the heat input to work output? This question was finally resolved by Sadi Carnot in the 1820s, when he determined the maximum efficiency of an idealized engine by the following logic. Treat the energy and entropy of the gas as though there were three compartments, two reversible heat sources and a reversible work source (see Figure 7.9). Heat and work can exchange among these imaginary compartments. The heat source loses energy,

$\Delta U_h = -q_h$ and the cold exhaust 'heat source' gains energy, $\Delta U_c = q_c$. The heat q_h from the hot gas parcels into two components: some of the heat converts to work w and the remaining heat q_c exits as cooler gas that leaves the engine: $q_h = q_c + w$. Rearranging gives

$$w = q_h - q_c. \quad (7.46)$$

Define the *efficiency* η of the system as the work output divided by the heat input:

$$\eta = \frac{w}{q_h} = 1 - \frac{q_c}{q_h}. \quad (7.47)$$

Figure 7.10 shows an alternative way of thinking about the compartments. Imagine a gas sealed in a cylinder with a piston. Bring a heat source at temperature T_h into contact, so that heat q_h flows into the cylinder. The heated gas in the cylinder expands and performs work w . Then bring the cylinder into thermal contact with another object at a lower temperature T_c , so that heat q_c flows out of the cylinder. No gas need ever enter or leave the cylinder, in this case.

The Second Law gives the entropy change toward equilibrium of the whole system, ΔS_{total} , as the sum of the three components, ΔS_h from the hot gas, ΔS_c from the cooled gas, and ΔS_w from the work source. $\Delta S_{\text{total}} = \Delta S_h + \Delta S_c + \Delta S_w \geq 0$. Because a reversible work source is adiabatic, $\Delta S_w = q_w/T = 0$, so

$$\Delta S_{\text{total}} = \Delta S_h + \Delta S_c \geq 0. \quad (7.48)$$

For reversible heat sources operating at high temperature T_h and low temperature T_c , the entropy changes are:

$$\Delta S_h = \frac{-q_h}{T_h}, \quad \text{and} \quad \Delta S_c = \frac{q_c}{T_c}. \quad (7.49)$$

Substitute Equations (7.49) into (7.48) and rearrange to get

$$\frac{q_c}{q_h} \geq \frac{T_c}{T_h}. \quad (7.50)$$

The maximum possible efficiency defines the reversible process, $\Delta S_{\text{total}} = 0$. All other processes cause larger changes in the entropy $\Delta S_{\text{total}} > 0$. The largest possible value of η is achieved by the smallest possible value of q_c/q_h in Equation (7.47), which is T_c/T_h (see Equation (7.50)), so

$$\eta \leq 1 - \frac{T_c}{T_h}. \quad (7.51)$$

Equation (7.51) implies that heat is most efficiently converted to work by engines that bring in heat at the highest possible temperature and exhaust it at the lowest possible temperature. The calculation of the efficiency of an idealized reversible engine answered two historically important questions. First, it said that the efficiency of an engine depends only on the temperatures of the heat intake and exhaust, and not on the type of gas or the volume of the piston. Second, the only way to reach 100% efficiency is to exhaust the waste heat at $T_c = 0\text{ K}$.

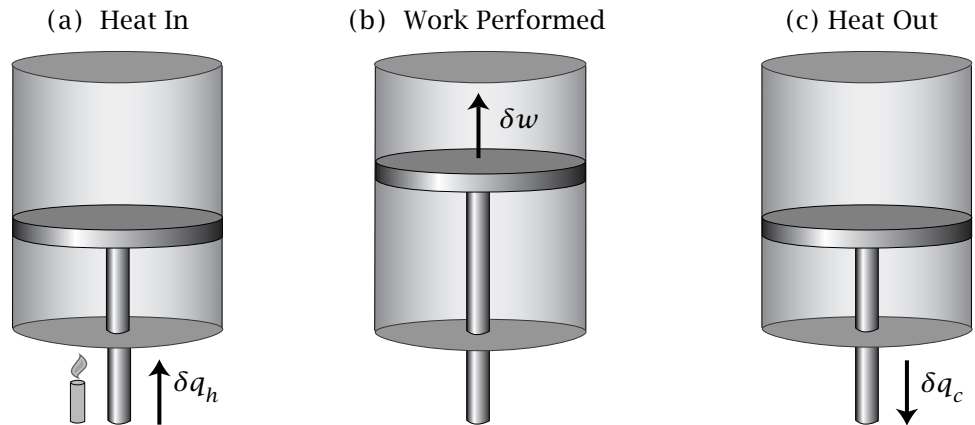


Figure 7.10 (a) In this idealized heat engine, a piston containing cooled gas starts at rest. When heat q_h enters from the reversible heat source, the energies of the gas molecules increase. (b) Work is performed by the expansion of the heated gas (the reversible work source), extracting energies from the molecules. (c) Heat q_c flows out from the reversible heat source and the volume in the piston decreases.

The inability to achieve 100% efficiency in engines is *not* a consequence of friction or turbulence. We are assuming quasi-static processes here. Since T_c/T_h is usually greater than zero, a heat engine has an inherent inefficiency. For a typical automobile engine, the high-temperature source (radiator water temperature) is about $T_h \approx 380\text{ K}$, the exhaust temperature is $T_c \approx 300\text{ K}$, and so the efficiency is $w/q_h = 0.21$. A considerable fraction (79%) of the heat input is lost to the environment as heat and is not converted to work. The problem is that perfect efficiency would require extracting all the motion and all the internal energy from the gas molecules, $T_c = 0$.

Engines can be reversed to make heat pumps. A heat pump creates a hot exhaust from a cold input when work is put in.

Why Is There an *Absolute* Temperature Scale?

How should we define a practical measure of temperature? Three scales are popular: Kelvin, Celsius, and Fahrenheit. The Kelvin scale is the most fundamental because it defines *absolute* temperature T . The idea of an absolute temperature scale derives from Equation (7.51), which relates the efficiency of converting heat to work to a ratio of temperatures, T_c/T_h . An absolute zero of the temperature scale, $T_c = 0$, is the point at which heat is converted to work with 100% efficiency, $\eta = 1$. This defines the zero of the Kelvin scale.

Other scales of temperature T' are 'shifted' so that their zero points coincide, for example, with the freezing point of water (Celsius scale) or with a point of coexistence of salt, water, and ice (Fahrenheit),

$$T' = aT - b,$$

where a and b are constants. For example, for the Celsius scale, $a = 1$ and $b = 273.15$. On these scales, the efficiency of a Carnot engine approaches some value other than one as the cold temperature approaches zero, $T'_c \rightarrow 0$:

$$\eta = 1 - \frac{T_c}{T_h} = 1 - \frac{(T'_c + b)/a}{(T'_h + b)/a} = 1 - \left(\frac{T'_c + b}{T'_h + b} \right)$$

so $\eta \rightarrow [1 - b/(T'_h + b)]$ as $T'_c \rightarrow 0$. For example, if the temperature of the hot reservoir is $T'_h = 100^\circ\text{Celsius}$ and the cold reservoir is $T'_c = 0^\circ\text{Celsius}$, then $\eta = 1 - 273.15/373.15 = 0.268$. So the zero-point of the Celsius scale has no special meaning for thermodynamic efficiency.

Other Statements of the Second Law of Thermodynamics

Our statement of the Second Law is that isolated systems tend toward their states of maximum entropy. For example, heat does not spontaneously flow from cold to hot objects because that would *decrease* the entropy. The earliest statements of the Second Law of thermodynamics were based on such examples. One such statement was that heat will not flow from a colder body to a hotter one without the action of some external agent. We can express this quantitatively by modifying the system that we examined in Example 7.2. For a system in which two objects are brought into thermal contact, and are also allowed to exchange some other extensive quantity Y , in place of Equation (7.18), the direction toward equilibrium is given by

$$\begin{aligned} dS &= \left(\frac{\partial S_A}{\partial U_A} \right) dU_A + \left(\frac{\partial S_B}{\partial U_B} \right) dU_B + \left(\frac{\partial S_A}{\partial Y_A} \right) dY_A + \left(\frac{\partial S_B}{\partial Y_B} \right) dY_B \geq 0 \\ &= \left(\frac{1}{T_A} - \frac{1}{T_B} \right) dU_A + \left(\frac{\partial S_A}{\partial Y_A} \right) dY_A + \left(\frac{\partial S_B}{\partial Y_B} \right) dY_B, \end{aligned}$$

where $(\partial S/\partial Y)dY$ accounts for the entropy change due to changes in Y . The difference in $(1/T_A) - (1/T_B)$ can be less than or equal to zero if the additional work compensates. This implies that heat *can be* moved from cold objects to hot ones by the input of some kind of work or chemical change. This is what refrigerators do. Spontaneous processes lead to an entropy increase in isolated systems, but when heat or work can cross a boundary, the entropy of a system can be caused to decrease.

Summary

The First Law of thermodynamics is a bookkeeping tool that defines a conserved quantity, the internal energy, as a sum of heat plus work. The Second Law describes the tendencies of systems toward their states of maximum entropy. The fundamental equation $S(U, V, \mathbf{N})$ is $dS = (1/T)dU + (p/T)dV - \sum_{j=1}^M (\mu_j/T)dN_j$. The importance of this equation is twofold. It gives definitions of temperature, pressure, and chemical potential, and it is the basis for the maximum-entropy extremum principle. Set $dS = 0$ subject to the appropriate constraints for the problem at hand to find the condition for equilibrium in terms of experimental quantities. In the next chapter, we will introduce enthalpies and free energies, and move from heat engines and historical engineering problems to laboratory experiments in chemistry and biology.

Problems

1. The work of compression. One mole of a van der Waals gas is compressed quasi-statically and isothermally from volume V_1 to V_2 . For a van der Waals gas, the pressure is

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

where a and b are material constants, V is the volume and RT is the gas constant \times temperature.

- Write the expression for the work done.
- Is more or less work required than for an ideal gas in the low-density limit? What about the high-density limit? Why?

2. Deriving the ideal gas law in two dimensions. Molecules at low density on a surface, such as surfactants at an interface of air and water, often obey a two-dimensional equivalent of the ideal gas law. The two-dimensional equivalent of p is π , where π is a lateral two-dimensional pressure. A is area. Using

$$\pi = T \left(\frac{\partial S}{\partial A} \right)_N \quad (7.52)$$

and assuming no energetic interactions, derive the two-dimensional equivalent of the ideal gas law by using a lattice model in the low-density limit.

3. The work of expansion in freezing an ice cube. At 1 atm, freeze an amount of liquid water that is $2 \text{ cm} \times 2 \text{ cm} \times 2 \text{ cm}$ in volume. The density (mass per unit volume) of liquid water at 0°C is 1.000 g cm^{-3} and the density of ice at 0°C is 0.915 g cm^{-3} .

- What is the work of expansion upon freezing?
- Is work done *on* the system or *by* the system?

4. Compute $S(V)$ for an ideal gas.

- How does the entropy $S(V)$ depend on volume for an ideal gas, where $pV = NkT$?
- What is the entropy change if you double the volume from V to $2V$?

5. The work of expanding a gas. Compute the total work performed when expanding an ideal gas, at constant temperature, from volume V to $2V$.

6. Pulling out the partition between two chambers of a gas. A partition separates equal volumes containing equal numbers N of ideal gas molecules of the same species at the same temperature. Using a simple lattice model for ideal gases, evaluate the relevant multiplicity terms to show that the entropy of the composite system does not change when the partition is removed (hint: use Stirling's approximation from page 57).

7. The work in a thermodynamic cycle. A thermodynamic cycle is a series of steps that ultimately returns to its beginning point. Compute the total work performed around the thermodynamic cycle of quasi-static processes in Figure 7.11.

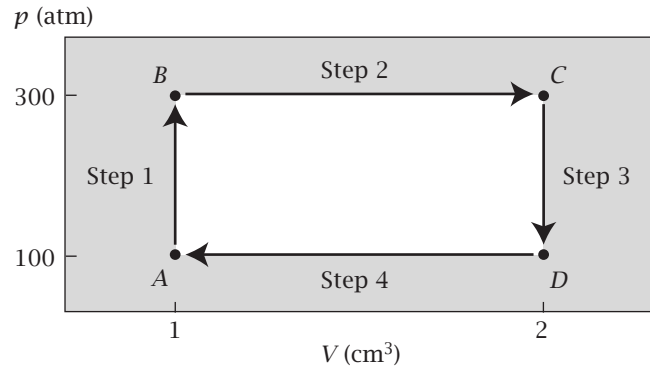


Figure 7.11

8. Engine efficiencies. Consider a Carnot engine that runs at $T_h = 380 \text{ K}$.

- Compute the efficiency if $T_c = 0^\circ\text{C} = 273 \text{ K}$.
- Compute the efficiency if $T_c = 50^\circ\text{C} = 323 \text{ K}$.

References

- PA Samuelson. *Economics*, 10th edition. McGraw-Hill, New York, 1976.
- P Mirowski. *More Heat than Light: Economics as Social Physics, Physics as Nature's Economics*. Cambridge University Press, Cambridge, 1989.
- HB Callen. *Thermodynamics and an Introduction to Thermostatistics*, 2nd edition. Wiley, New York, 1985.

Suggested Reading

- CJ Adkins, *Equilibrium Thermodynamics*, 3rd edition, Cambridge University Press, Cambridge, 1983. Excellent introduction to thermodynamics and reversibility.
- SG Brush, *The Kind of Motion We Call Heat*, North-Holland, New York, 1976. An excellent history of thermodynamics and statistical mechanics.
- HB Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd edition, Wiley, New York, 1985. The classic text on the axiomatic approach to thermodynamics. The logic of thermodynamics is explained with great clarity.