Systems of Many Particles

3

It is possible to identify all the external forces acting on a simple system and use Newton's second law ($\mathbf{F} = m\mathbf{a}$) to calculate how the system moves. (Applying this technique in a complicated case such as the femur may require the development of a simplified model, because so many muscles, other bones, and ligaments apply forces at so many different points.) In an atomic-size system consisting of a single atom or molecule, it is possible to use the quantum-mechanical equivalent of $\mathbf{F} = m\mathbf{a}$, the Schrödinger equation, to do the same thing. (The Schrödinger equation takes into account the wave properties that are important in small systems.)

In systems of many particles, such calculations become impossible. Consider, for example, how many particles there are in a cubic millimeter of blood. Table 3.1 shows some of the constituents of such a sample. To calculate the translational motion in three dimensions, it would be necessary to write three equations for each particle[1] using Newton's second law. Suppose that at time t the force on a molecule is $\mathbf{F}$. Between t and $t + \Delta t$, the velocity of the particle changes according to the three equations

$$v_i(t + \Delta t) = v_i(t) + F_i \Delta t/m, \ (i = x, y, z).$$

The three equations for the change of position of the particle are of the form $x(t + \Delta t) = x(t) + v_x(t)\Delta t + F_x(t)(\Delta t)^2/(2m)$. If Δt is small enough the last term can be neglected. Solving these equations requires at least six multiplications and additions for each particle. For 10^{19} particles, this means about 10^{20} arithmetic operations per time interval. If a computer can do 10^{12} operations/s, then the complete calculation for a single time interval will require 10^8 s or 3 years!

Another limitation arises in the physics of the processes. Relatively simple systems can exhibit deterministic chaos: a collection of identical systems differing in their initial conditions by an infinitesimally small amount can become completely different in their subsequent behavior in a surprisingly short period of time. It is impossible to trace the behavior of this many molecules on an individual basis.

Table 3.1 Some constituents of 1 mm^3 of blood

Constituent	Concentration in customary units	Number in 1 mm^3
Water	1 g cm^{-3}	3.3×10^{19}
Sodium	3.2 mg cm^{-3}	8.3×10^{16}
Albumin	4.5 g dl^{-1}	3.9×10^{14}
Cholesterol	200 mg dl^{-1}	3.1×10^{15}
Glucose	100 mg dl^{-1}	3.3×10^{15}
Hemoglobin	15 g dl^{-1}	1.4×10^{15}
Erythrocytes	5×10^6 mm^{-3}	5×10^6

Nor is it necessary. We do not care which water molecule is where. The properties of a system that are of interest are averages over many molecules: pressure, concentration, average speed, and so forth. These average macroscopic properties are studied in *statistical* or *thermal physics* or *statistical mechanics*.

Unfortunately, this chapter relies heavily on your ability to accept delayed gratification. It has only a few biological examples, but the material developed here is necessary for understanding some topics in most of the later chapters, especially Chaps. 4–9 and 14–18. In addition to developing a statistical understanding of pressure, temperature, and concentration, this chapter derives four quantities or concepts that are used later:

1. The *Boltzmann factor*, which tells how concentrations of particles vary with potential energy (Sect. 3.7).
2. The *principle of equipartition of energy*, which underlies the diffusion process that is so important in the body (Sect. 3.10).
3. The *chemical potential*, which describes the condition for equilibrium of two systems for the exchange of particles, and how the particles flow when the systems are not in equilibrium (Sects. 3.12, 3.13, and 3.18).

[1] In computational biology, a mole of differential equations is sometimes called a leibniz (Huang and Wikswo 2006). Solving for the motion of each water molecule in a cubic millimeter of blood requires solving 0.16 millileibniz of equations.

R. K. Hobbie, B. J. Roth, *Intermediate Physics for Medicine and Biology*,
DOI 10.1007/978-3-319-12682-1_3,

4. The *Gibbs free energy*, which tells the direction in which a chemical reaction proceeds and allows us to understand how the cells in the body use energy (Sect. 3.17).

The first six sections form the basis for the rest of the chapter, developing the concepts of microstates, heat flow, temperature, and entropy. Sections 3.7 and 3.8 develop the Boltzmann factor and its corollary, the Nernst equation. Section 3.9 applies the Boltzmann factor to the air molecules in the atmosphere. Section 3.10 discusses the very important equipartition of energy theorem. Section 3.11 discusses heat capacity—the energy required to increase the temperature of a system.

The transport of particles between two systems is described most efficiently using the chemical potential. The chemical potential is introduced in Sect. 3.12, and an example of its use is shown in Sect. 3.13.

Section 3.14 considers systems that can exchange volume. An idealized example is two systems separated by a flexible membrane or a movable piston. The next two sections extend the idea of systems that exchange energy, particles, or volume to the exchange of other variables such as electric charge.

The Gibbs free energy, introduced in Sect. 3.17, is used to describe chemical reactions that take place at constant temperature and pressure. It is closely related to the chemical potential. The chemical potential of an ideal solution is derived in Sect. 3.18 and is used extensively in Chap. 5.[2]

3.1 Gas Molecules in a Box

Statistical physics or *statistical mechanics* deals with average quantities such as pressure, temperature, and particle concentration and with probability distributions of variables such as velocity. Some of the properties of these averages can be illustrated by considering a simple example: the number of particles in each half of a box containing a fixed number of gas molecules. (This is a simple analog for the concentration.) We will not be concerned with the position and velocity of each molecule, since we have already decided not to use Newtonian mechanics. Nor will we ask for the velocity distribution at this time. This simplified example will describe only how many molecules are in the volume of interest. The number will fluctuate with time. We will deal with probabilities:[3] if the number of particles in the volume is measured repeatedly, what values are obtained, and with what relative frequency?

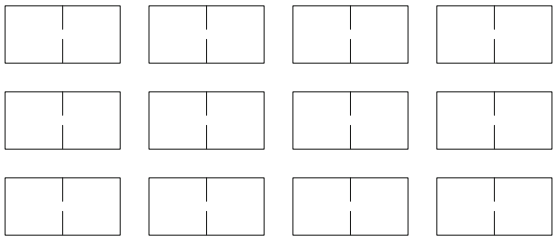


Fig. 3.1 An ensemble of boxes, each divided in half by an imaginary partition

If we were willing to use Newtonian mechanics, we could count periodically how many molecules are in the volume of interest. (This has actually been done for small numbers of particles. See Reif (1964), pp. 8–9.) For larger numbers of particles, it is easier to use statistical arguments to obtain the probabilities. The particles travel back and forth, colliding with the walls of the box and occasionally with one another. After some time has elapsed, all memory of the particles' original positions and velocities has been lost because of collisions with the walls of the box, which have microscopic inhomogeneities. Therefore, the result can be obtained by imagining a whole succession of completely different boxes, in which the particles have been placed at random. We can count the number of molecules in the volume of interest in each box. Such a collection of similar boxes is called an *ensemble*. Ensembles of similar systems will be central to the ideas of this chapter.

Imagine an ensemble of boxes, each divided in half as in Fig. 3.1. We want to know how often a certain number of particles is found in the left half. If one particle is in a box ($N = 1$), two cases can be distinguished, depending on which half the particle is in. Call them L and R. Each case is equally likely to occur, since nothing distinguishes one half of a box from the other. If n is the number of particles in the left half, then case L corresponds to $n = 1$ and case R corresponds to $n = 0$.

The probability of having a particular value of n is defined to be

$$P(n) = \frac{(\text{number of systems in the ensemble in which } n \text{ is found})}{(\text{total number of systems})} \tag{3.1}$$

in the limit as the number of systems becomes very large.

As there are only two possible values of n, 0 or 1, and because each corresponds to one of the equally likely configurations, $P(0) = 0.5$, $P(1) = 0.5$. The sum of the probabilities is 1. A histogram of $P(n)$ for $N = 1$ is given in Fig. 3.2a. To recapitulate: n is the number of molecules in the left half of the box, and N is the total number of molecules in the entire box. Since N will change in the discussion below,

[2] Many excellent introductory textbooks on thermodynamics and statistical mechanics exist, such as those by Reif (1964) and Schroeder (2000). To learn more about how thermodynamics is applied to biological problems, see Haynie (2008).

[3] A good book on probability is Weaver (1963).

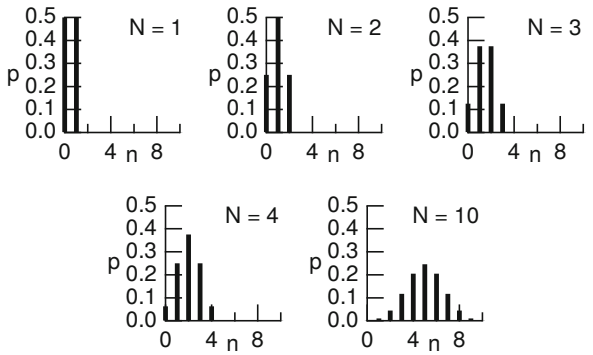


Fig. 3.2 Histograms of $P(n; N)$ for different values of N

we will call the probability $P(n; N)$. (The fixed parameters that determine the probability distribution are located after the semicolon.)

Now let $N = 2$. Each molecule can be on the left or the right with equal probability. The possible outcomes are listed in the following table, along with the corresponding values of n and $P(n; 2)$.

Molecule 1	Molecule 2	n	$P(n; 2)$
R	R	0	$\frac{1}{4}$
R	L	1	$\frac{1}{2}$
L	R	1	
L	L	2	$\frac{1}{4}$

Each of the four outcomes is equally probable. To see this, note that L or R is equally likely for each molecule. In half of the boxes in the ensemble, the first molecule is found on the left. In half of these, the second molecule is also on the left. Therefore LL occurs in one-fourth of the systems in the ensemble. (This is not strictly true, because there can be fluctuations. If we throw a coin six times, we cannot say that heads will always occur three times. If we repeat the experiment many times, the average number of heads will be three.)

If three molecules are placed in each box, there are two possible locations for the first particle, two for the second, and two for the third. If the three particles are all independent, then there are $2^3 = 8$ different ways to locate the particles in a box. If a box is divided in half, each of these ways has a probability of 1/8.

Molecule 1	Molecule 2	Molecule 3	n	$P(n; 3)$
R	R	R	0	$\frac{1}{8}$
R	R	L	1	
R	L	R	1	$\frac{3}{8}$
L	R	R	1	
L	L	R	2	
L	R	L	2	$\frac{3}{8}$
R	L	L	2	
L	L	L	3	$\frac{1}{8}$

The cases of two and three molecules in the box are also plotted in Fig. 3.2.

In each case, $P(n; N)$ has been determined by listing all the ways that the N particles can go into a box. This can become tedious if the number of particles is large. Furthermore, it does not provide a way to calculate P if the two volumes of the box are not equal. We will now introduce a more general technique that can be used for any number of particles and for any fractional volume of the box.

Each box is divided into two volumes, v and v', with total volume $V = v + v'$. Call p the probability that a single particle is in volume v. The probability that the particle is in the remainder of the box, v', is q:

$$p + q = 1. \tag{3.2}$$

As long as there is nothing to distinguish one part of a box from the other, p is the ratio of v to the total volume:

$$p = \frac{v}{V}. \tag{3.3}$$

By the same argument, $q = v'/V$. These values satisfy Eq. 3.2. If N particles are distributed between the two volumes of the box, the number in v is n and the number in v' is $n' = N - n$. The probability that n of the N particles are found in volume v is given by the *binomial probability distribution* (Appendix H):

$$P(n; N) = P(n; N, p) = \frac{N!}{n!\,(N-n)!} p^n (1-p)^{N-n}. \tag{3.4}$$

Table 3.2 shows the calculation of $P(n; 10)$ using this equation. Histograms for $N = 4$ and 10 are also plotted in Fig. 3.2. In each case there is a value of n for which P is a maximum. When N is even, this value is $N/2$; when N is odd, the values on either side of $N/2$ share the maximum value. The probability is significantly different from zero only for a few values of n on either side of the maximum.

A probability distribution, in the form of an expression, a table of values, or a histogram, usually gives all the information that is needed about the number of molecules in v; it is not necessary to ask which molecules are in v. The number of molecules in v is not fixed but fluctuates about the number for which P is a maximum. For example, if $N = 10$, and we measure the number of molecules in the left half many times, we find $n = 5$ only about 25 % of the time. On the other hand, we find that $n = 4$, 5, or 6 about 65 % of the time, while $n = 3$, 4, 5, 6, or 7 about 90 % of the time.

Table 3.2 Calculation of $P(n; 10)$ using the binomial probability distribution. Note that $0! = 1$

$$P(0;10) = \frac{10!}{0!10!}\left(\tfrac{1}{2}\right)^0\left(\tfrac{1}{2}\right)^{10} = \left(\tfrac{1}{2}\right)^{10} = 0.001$$
$$P(1;10) = \frac{10!}{1!9!}\left(\tfrac{1}{2}\right)^1\left(\tfrac{1}{2}\right)^9 = 10\left(\tfrac{1}{2}\right)^{10} = 0.010$$
$$P(2;10) = \frac{10!}{2!8!}\left(\tfrac{1}{2}\right)^2\left(\tfrac{1}{2}\right)^8 = 45\left(\tfrac{1}{2}\right)^{10} = 0.044$$
$$P(3;10) = \frac{10!}{3!7!}\left(\tfrac{1}{2}\right)^3\left(\tfrac{1}{2}\right)^7 = 120\left(\tfrac{1}{2}\right)^{10} = 0.117$$
$$P(4;10) = \frac{10!}{4!6!}\left(\tfrac{1}{2}\right)^4\left(\tfrac{1}{2}\right)^6 = 210\left(\tfrac{1}{2}\right)^{10} = 0.205$$
$$P(5;10) = \frac{10!}{5!5!}\left(\tfrac{1}{2}\right)^5\left(\tfrac{1}{2}\right)^5 = 252\left(\tfrac{1}{2}\right)^{10} = 0.246$$
$$P(6;10) = \frac{10!}{6!4!}\left(\tfrac{1}{2}\right)^6\left(\tfrac{1}{2}\right)^4 = 210\left(\tfrac{1}{2}\right)^{10} = 0.205$$
$$P(7;10) = \frac{10!}{7!3!}\left(\tfrac{1}{2}\right)^7\left(\tfrac{1}{2}\right)^3 = 120\left(\tfrac{1}{2}\right)^{10} = 0.117$$
$$P(8;10) = \frac{10!}{8!2!}\left(\tfrac{1}{2}\right)^8\left(\tfrac{1}{2}\right)^2 = 45\left(\tfrac{1}{2}\right)^{10} = 0.044$$
$$P(9;10) = \frac{10!}{9!1!}\left(\tfrac{1}{2}\right)^9\left(\tfrac{1}{2}\right)^1 = 10\left(\tfrac{1}{2}\right)^{10} = 0.010$$
$$P(10;10) = \frac{10!}{10!0!}\left(\tfrac{1}{2}\right)^{10}\left(\tfrac{1}{2}\right)^0 = \left(\tfrac{1}{2}\right)^{10} = 0.001$$

3.2 Microstates and Macrostates

If we know "enough" about the detailed properties (such as position and momentum) of every particle in a system,[4] then we say that the *microstate* of the system is specified. (The criterion for "enough" will be discussed shortly.) We may know less than this but know the *macrostate* of the system. (In an ideal gas, for example, the macrostate would be defined by knowing the number of molecules and volume, and the pressure, temperature, or total energy.) Usually there are many microstates corresponding to each macrostate. The large-scale average properties (such as pressure and number of particles per unit volume in the ideal gas) fluctuate slightly about well-defined mean values.

In the problem of how many molecules are in half of a box, the macrostate is specified if we know how many molecules there are, while a microstate would specify the position and momentum of every molecule. In other cases, internal motions of the molecule may be important, and it will be necessary to know more than just the position and momentum of each particle.

The relation between microstates and macrostates may be clarified by the following example, which contains the essential features, although it is oversimplified and somewhat artificial. A room is empty except for some toys on the floor. Specifying the location of each of the toys on the floor would

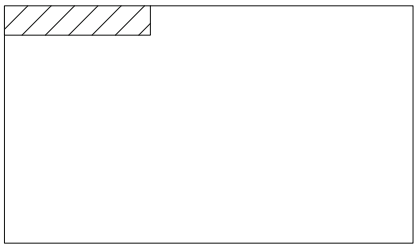


Fig. 3.3 A room with toys. If all the toys are in the shaded area, the macrostate is "picked up." Otherwise, the macrostate is "mess"

specify the microstate of the system. If the toys are in the shaded corner in Fig. 3.3, the macrostate is "picked up." If the toys are in any place else in the room, the macrostate is "mess." There are many more microstates corresponding to the macrostate "mess" than there are corresponding to the macrostate "picked up." We know from experience that children tend to regard any microstate as equally satisfactory; the chances of spontaneously finding the macrostate "picked up" are relatively small.

A situation in which P is small is called *ordered* or *nonrandom*. A situation in which P is large is called *disordered* or *random*. Macrostate "mess" is more probable than macrostate "picked up" and is disordered or random.

The same idea can be applied to a box of gas molecules. Initially, the molecules are all kept in the left half of the box by a partition. If the partition is suddenly removed, a large number of additional microstates are suddenly available to the molecules. The macrostate in which they find themselves—all in the left half of the box, even though the partition has been removed—is very improbable or highly ordered. The molecules soon fill the entire box; it is quite unlikely that they will all be in the left half again if the number of molecules is very large. (Suppose that there are 80 molecules in the box. The probability that all are in the left half is $\left(\frac{1}{2}\right)^{80} = 10^{-24}$. If samples were taken 10^6 times/s, it would take 10^{18} s to sample 10^{24} boxes, one of which, on the average, would have all of the molecules in the left half. This is greater than the age of the universe.)

Just after the partition in the box was removed, the situation was very ordered. The system spontaneously approached a much more random situation in which nearly half the molecules were in each half of the box. The actual number n fluctuates about $N/2$, but in such a way that the average $\langle n\rangle$ (taken, say, over several seconds) no longer changes with time. Typical fluctuations with a constant $\langle n\rangle$ are shown in Fig. 3.4a. When the average[5] of the macroscopic parameters is not changing with time, we say that the system is in

[4] A *system* is that part of the universe that we choose to examine. The *surroundings* are the rest of the universe. The system may or may not be isolated from the surroundings.

[5] There is a subtlety about the meaning of average that we are glossing over here. If we take a whole ensemble of identical systems, which were all prepared the same way, and measure n in each one, we have the *ensemble average* $\bar{n}$. This is calculated in the way described in Appendix G. If we watch one system over some long time interval, as in

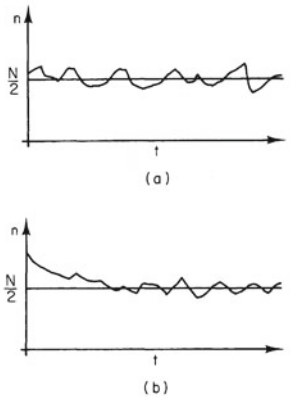


Fig. 3.4 **a** Fluctuations of n about $N/2$. **b** The approach of the system to the equilibrium state after the partition is removed

an *equilibrium state*. Figure 3.4b shows the system moving toward the equilibrium state after the partition is removed.

An equilibrium state is characterized by macroscopic parameters whose average values remain constant with time, although the parameters may fluctuate about the average value. It is also the most random (i.e., most probable) macrostate possible under the prescribed conditions. It is independent of the past history of the system and is specified by a few macroscopic parameters.[6]

The definition of a microstate of a system has so far been rather vague; we have not said precisely what is required to specify it. It is actually easier to specify the microstate of a system when using quantum mechanics than when using classical mechanics. When the energy of an individual particle in a system (such as one of the molecules in the box) is measured with sufficient accuracy, it is found that only certain discrete values of the energy occur. This is because of the wave nature of the particles. The allowed values of the energy are called *energy levels*. You are probably familiar with the idea of energy levels from a previous physics or chemistry course; for example, the spectral lines of atoms are due to the emission of light when an atom changes from one energy level to another. Because the energy levels are well defined, the energy difference, and hence the frequency or color of the light, is also well defined (see Chap. 14).

A particle in a box has a whole set of energy levels at energies determined by the size and shape of the box. Compared to macroscopic measurements of energy, these levels are very close together. The particle can be in any one of these levels; which energy the particle has is specified by a set of *quantum numbers*. If the particle moves in three dimensions, three quantum numbers are needed to specify the energy level. If there are N particles, it will be necessary to specify three quantum numbers for each particle or $3N$ numbers in all. (If there are M molecules, each made up of a atoms, then $N = aM$. The number of quantum numbers is less than $3N$ because the atoms cannot all move independently. If the molecules were thought of as single particles, there would be $3M$ quantum numbers. But the molecules can rotate and vibrate, so that the number of quantum numbers is greater than $3M$ and less than $3N$.)

The total number of quantum numbers required to specify the state of all the particles in the system is called the number of *degrees of freedom* of the system, f.

A microstate of a system is specified if all the quantum numbers for all the particles in the system are specified.

In most of this chapter, it will not be necessary to consider the energy levels in detail. The important fact is that each particle in a system has discrete energy levels, and a microstate is specified if the energy level occupied by each particle is known.

3.3 The Energy of a System: The First Law of Thermodynamics

Figure 3.5 shows some energy levels in a system occupied by a few particles. The total energy of the system U is the sum of the energy of each particle. In making this drawing, we have assumed that all the particles are the same and that they do not interact with one another very much. Then each particle has the same set of energy levels, and the presence of other particles does not change them. In that case, we can say that there is a certain set of energy levels in the system and that each level can be occupied by any number of particles. The energy of the ith level, occupied or not, will be called

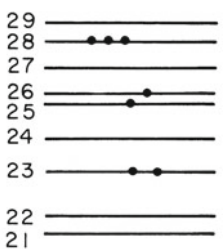


Fig. 3.5 A few of the energy levels in a system. If a particle has a particular energy, a dot is drawn on the level. More than one particle in this system can have the same quantum numbers

Fig. 3.4, we can take the *time average* $\langle n \rangle$. It is taken by recording values of n for a large number of discrete times in some interval. Strictly speaking, an equilibrium state is one in which the ensemble average is not changing with time.

[6] A more detailed discussion of equilibrium states is found in Reif (1964).

u_i. For the example of Fig. 3.5, the total energy is

$$U = 2u_{23} + u_{25} + u_{26} + 3u_{28}.$$

Suppose that the system is isolated so that it does not gain or lose energy. It is still possible for particles within the system to exchange energy and move to different energy levels, as long as the total energy does not change. (Classically, two particles could collide, so that one gains and one loses energy.) Therefore the number of particles occupying each energy level can change, as long as the total energy remains constant. For a system in equilibrium, the average number of particles in each level does not change with time.

There are two ways in which the total energy of a system can change. *Work* can be done on the system by the surroundings, or *heat* can flow from the surroundings to the system. The meaning of work and heat in terms of the energy levels of the system is quite specific and is discussed shortly. First, we define the sign conventions associated with them.

It is customary to define Q to be the heat flow *into* a system. If no work is done, the energy change in the system is

$$\Delta U = Q.$$

It is also customary to call W the work done *by* the system *on* the surroundings. When W is positive, energy flows from the system to the surroundings. If there is no accompanying heat flow, the energy change of the system is

$$\Delta U = -W.$$

The most general way the energy of a system can change is to have both work done by the system and heat flow into the system. The statement of the conservation of energy in that case is called the *first law of thermodynamics*:

$$\Delta U = Q - W. \tag{3.5}$$

The joule is the SI unit for energy, work and heat flow. The calorie (1 cal = 4.184 J) is sometimes used. The dietary Calorie is 1000 cal.

The positions of the energy levels in a system are determined by some macroscopic properties of the system. For a gas of particles in a box, for example, the positions of the levels are determined by the size and shape of the box. For charged particles in an electric field, the positions of the levels are determined by the electric field. If the macroscopic parameters that determine the positions of the energy levels are not changed, the only way to change the total energy of a system is to change the average number of particles occupying each energy level, as in Fig. 3.6. This energy change is called *heat flow*.

Work is associated with the change in the macroscopic parameters (such as volume) that determine the positions of the energy levels. If the energy levels are shifted by doing work without an accompanying heat flow, the change is called *adiabatic*. An adiabatic change is shown in Fig. 3.7. In general, there is also a shift of the populations of the levels in an adiabatic change; the average occupancy of each level can be calculated using the Boltzmann factor, described in Sect. 3.7. There is no heat flow, but work is done on or by the system, and its energy changes.

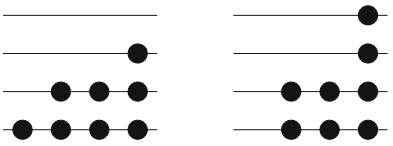


Fig. 3.6 No work is done on the system, but heat is added. The positions of the levels do not change; their average population does change

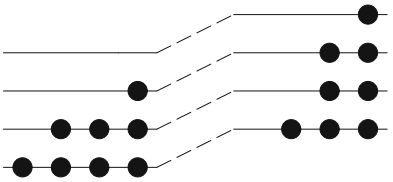


Fig. 3.7 Work is done on the system, but no heat flows. Each level has been shifted to a higher energy

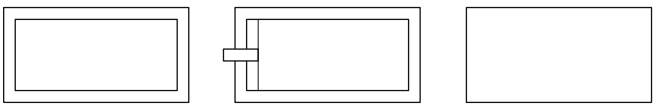


Fig. 3.8 Symbols used to indicate various types of isolation in a system. **a** This system is completely isolated. **b** There is no heat flow through the double wall, but work can be done (symbolized by a piston). **c** No work can be done, but there can be heat flow through the single wall

To summarize: Pure heat flow involves a change in the average number of particles in each level without a change in the positions of the levels. Work involves a change in the macroscopic parameters, which changes the positions of at least some of the energy levels. In general, this means that there is also a shift in the average population of each level. The most general energy change of a system involves both work and heat flow. In that case the total energy change is the sum of the changes due to work and to heat flow.

It is customary in drawing systems to use the symbols in Fig. 3.8 to describe how the system can interact with the surroundings. A double-walled box means that no heat flows, and any processes that occur are adiabatic. This is shown in Fig. 3.8a. If work can be done on the system, a piston is shown as in Fig. 3.8b. If heat can flow to or from the system, a single wall is used as in Fig. 3.8c.

3.4 Ensembles and the Basic Postulates

In the next few sections we will develop some quite remarkable results from statistical mechanics. Making the postulate that when a system is in equilibrium each microstate is equally probable, and arguing that as the energy, volume, or number of particles in the system is increased the number of microstates available to the system increases, we will obtain several well-known results from thermodynamics: heat flows from one system to another in thermal contact until their temperatures are the same; if their volumes can change they adjust themselves until the pressures are the same; and the systems exchange particles until their chemical potentials are the same. We will also obtain the concept of entropy; the Boltzmann factor; the theorem of equipartition of energy; and the Gibbs free energy, which is useful in chemical reactions in living systems where the temperature and pressure are constant.

The initial postulates are deceptively simple. Unfortunately, a fair amount of mathematics is required to get from them to the final results. We start with the basic postulates.

The microstate of a system is determined by specifying the quantum numbers of each particle in the system. The total number of quantum numbers is the number of degrees of freedom. The macrostate of a system is determined by specifying two things:

1. All of the external parameters, such as the volume of a box of gas or any external electric or magnetic field, on which the positions of the energy levels depend. (Classically, all the external parameters that affect the motion of the particles in the system.)
2. The total energy of the system, U.

The external parameters determine a set of energy levels for the particles in the system; the total energy determines which energy levels are accessible to the system.

Statistical physics deals with average quantities and probabilities. We imagine a whole set or ensemble of "identical" systems, as we did in Fig. 3.1. The systems are identical in that they all are in the same macrostate. Different systems within the ensemble will be in different microstates. Imagine that at some instant of time we "freeze" all the systems in the ensemble and examine which microstate each is in. From this we can determine the probability that a system in the ensemble is in microstate i:

$$P(\text{of being in microstate } i) = \frac{\text{number of systems in microstate } i}{\text{total number of systems in the ensemble}}.$$

Imagine that we now "unfreeze" all the systems in the ensemble and let the particles move however they want. At some later time we freeze them again and examine the probability that a system is in each microstate. These probabilities may have changed with time. For example, if the system is a group of particles in a box, and if the initial "freeze" was done just after a partition confining all the particles to the left half of the box had been removed, we would have found many systems in the ensemble in microstates for which most of the particles are on the left-hand side. Later, this would not be true. We would find microstates corresponding to particles in both halves of the box.

We will make two basic *postulates* about the systems in the ensemble.[7]

1. If an isolated system (really, an ensemble of isolated systems) is found with equal probability in each one of its accessible microstates, it is in equilibrium.[8] Conversely, if it is in equilibrium, it is found with equal probability in each one of its accessible microstates.
2. If it is not in equilibrium, it tends to change with time until it is in equilibrium. Therefore the equilibrium state is the most random, most probable state.

For the rest of this chapter, we deal with equilibrium systems. According to our first postulate, each microstate that is accessible to the system (that is, consistent with the total energy that the system has) is equally probable. We will discover that this statement has some far-reaching consequences.

Suppose that we want to consider some variable x, which takes on various values. This variable might be the pressure of a gas, the number of gas molecules in some volume of the box, or the energy that one of the molecules has. For each value of x, there will be some number of microstates in which the system could be that are consistent with that value of x. There will also be some total number of microstates in which the system could be, consistent with its initial preparation. We will use the Greek letter Ω to denote the number of microstates. The total number of accessible microstates (for all possible values of x) is Ω; the number for which x has some particular value is Ω_x. It is consistent with the first assumption to say that the probability that the variable has a value x when the system is in equilibrium is

$$P_x = \frac{\Omega_x}{\Omega}. \tag{3.6}$$

We have been considering ensemble averages. For example, the variable of interest might be the pressure, and we

[7] For a more detailed discussion of these assumptions, see Reif (1964, Chap. 3).

[8] In thermodynamics and statistical mechanics, *equilibrium* and *steady state* do not mean the same thing. Steady state means that some variable is not changing with time. The concentration of sodium in a salt solution flowing through a pipe could be in steady state as the solution flowed through, but the system would not be in equilibrium. Only a few microstates corresponding to bulk motion of the fluid are occupied. In other areas, such as feedback systems, the words equilibrium and steady state are used almost interchangeably.

could find the ensemble average by calculating $\bar{p} = \sum P_p p$, where P_p is the probability of having pressure p. In equilibrium P_p is given by Eq. 3.6, and $\bar{p}$ does not change with time. We could also consider a single system, measure $p(t)$ M times, and compute the time average, $\langle p(t) \rangle = \sum_i p(t_i)/M$. (The equivalence of the time average and the ensemble average for systems in equilibrium is called the *ergodic hypothesis*.)

3.5 Thermal Equilibrium

A system that never interacts with its surroundings is an idealization. The adiabatic walls of Fig. 3.8a can never be completely realized. However, much can be learned by considering two systems that can exchange heat, work, or particles, but that, taken together, are isolated from the rest of the universe. Once we have learned how these two systems interact, the second system can be taken to be the rest of the universe. Eventually, we will allow all three exchanges—heat flow, work, and particles—to take place; for now, it will be convenient to consider only exchanges of energy by heat flow. Figure 3.9 shows the two systems, A and A', isolated from the rest of the universe. The total system will be called A^*. The total number of particles is $N^* = N + N'$. For now N and N' are fixed. The total energy is $U^* = U + U'$. The two systems can exchange energy by heat flow, so that U and U' may change, as long as their sum remains constant.

The number of microstates accessible to the total system is Ω^*. The combined system was originally given a total energy U^* before it was sealed off from the rest of the universe. The barrier between A and A' prevents exchange of particles or work. The total number of microstates depends on how much energy is in each system: when system A has energy U, the total number of microstates is $\Omega^*(U)$.[9]

There are many microstates accessible to the system, with U and U' having different values, subject always to $U^* = U + U'$. Let the total number of microstates, including all possible values of U, be Ω^*_{tot}. Then, according to the postulate, the probability of finding system A with energy U is

$$P(U) = \frac{\Omega^*(U)}{\Omega^*_{\text{tot}}} = C\,\Omega^*(U). \tag{3.7}$$

$C = 1/\Omega^*_{\text{tot}}$ is a constant (independent of U).

If the meaning of Eq. 3.7 is obscure, consider the following example. Systems A and A' each consist of two particles, the energy levels for each particle being at u, $2u$, $3u$, and so forth. The total energy available to the combined system is $U^* = 10u$. The smallest possible energy for system A is $U = 2u$, both particles having energy u. If $U = 3u$, there are two states: in one, the first particle has energy u and the other $2u$; in the second, the particles are reversed. Label these states $(u, 2u)$ and $(2u, u)$. For $U = 4u$, there are three possibilities: $(u, 3u)$, $(2u, 2u)$, and $(3u, u)$. In general, if $U = nu$, there are $n - 1$ states, corresponding to the first particle having energy u, $2u$, $3u$, ..., $(n-1)u$. Table 3.3 shows values for U, U', Ω, and Ω'.

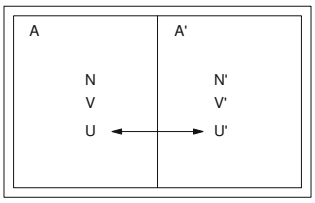


Fig. 3.9 Two systems are in thermal contact with each other but are isolated from the rest of the universe. They can exchange energy only by heat flow

Table 3.3 An example of two systems that can exchange heat energy. The total energy is $U^* = 10u$. Each system contains two particles for which the energy levels are u, $2u$, $3u$, etc

System A		System A'		System A^*
U	Ω	U'	Ω'	Ω^*
$2u$	1	$8u$	7	7
$3u$	2	$7u$	6	12
$4u$	3	$6u$	5	15
$5u$	4	$5u$	4	16
$6u$	5	$4u$	3	15
$7u$	6	$3u$	2	12
$8u$	7	$2u$	1	7
				$\Omega^*_{\text{tot}} = 84$

It is now necessary to consider Ω^* in more detail. If there are two microstates available to system A and 6 available to system A^*, there are $2 \times 6 = 12$ states available to the total system. $\Omega^* = \Omega\Omega'$ is also given in Table 3.3. In a more general case, *the number of microstates for the total system is the product of the number for each subsystem*:

$$\Omega^*(U) = \Omega(U)\,\Omega'(U'). \tag{3.8}$$

For the specific example, there are a total of 84 microstates accessible to the system when $U^* = 10u$. Equation 3.7 says that since each microstate is postulated to be equally probable, the probability that the energy of system A is $3u$ is $12/84 = 0.14$. The most probable state of the combined system is that for which A has energy $5u$ and A' has energy $5u$.

The next question is how Ω and Ω' depend on energy in the general case. In the example, Ω is proportional to U. For three particles, one can show that Ω increases as U^2 (See

[9] If Ω is a continuous function of U, then $\Omega(U)dU$ is actually the number of states wih energy between U and $U + dU$. We ignore this distinction. For a discussion of it, see Chap. 3 of Reif (1964).

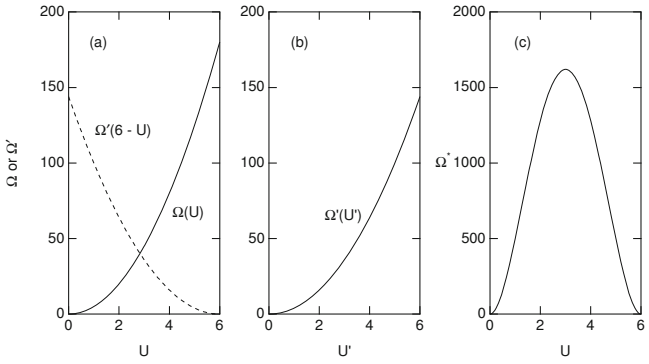


Fig. 3.10 Example of the behavior of Ω, Ω', and Ω^*. In this case, the values used are $\Omega(U) = 5U^2$ and $\Omega'(U') = 4(U')^2$. (These functions give $\Omega = 0$ when $U = 0$, which is not correct. But they are simple and behave properly at higher energies.) The total energy is 6, so only values of U between 0 and 6 are allowed. **a** Plot of $\Omega(U)$. The dashed line is $\Omega'(6 - U)$. **b** Plot of $\Omega'(U')$. **c** Plot of $\Omega^* = \Omega\Omega'$

Problem 19). In general, the more particles there are in a system, the more rapidly Ω increases with U. For a system with a large number of particles, *increasing the energy drastically increases the number of microstates accessible to the system*.

As more energy is given to system A and $\Omega(U)$ increases, there is less energy available for system A' and $\Omega'(U')$ decreases. The product $\Omega^* = \Omega\Omega'$ goes through a maximum at some value of U, and that value of U is therefore the most probable. These features are shown in Fig. 3.10, which assumes that U and Ω are continuous variables. The continuous approximation becomes excellent when we deal with a large number of particles and very closely spaced energy levels. The solid line in Fig. 3.10a represents $\Omega(U)$; $\Omega'(U')$ is the solid line in Fig. 3.10b. The function Ω' is also plotted against U, rather than U', as the dashed line in Fig. 3.10a. As more energy is given to A, Ω increases but Ω' decreases. The product, $\Omega^* = \Omega\Omega'$, shown in Fig. 3.10c, reaches a maximum at $U = 3$.

The most probable value of U is that for which $P(U)$ is a maximum. Since P is proportional to Ω^*, $\Omega^*(U)$ is also a maximum. Therefore,

$$\frac{d}{dU}\left[\Omega^*(U)\right] = 0 \tag{3.9}$$

at the most probable value of U. This derivative can be evaluated using Eq. 3.8. Since $U + U' = U^*$, Eq. 3.8 can be rewritten as

$$\Omega^*(U) = \Omega(U)\,\Omega'(U^* - U). \tag{3.10}$$

The derivative is

$$\frac{d\Omega^*}{dU} = \frac{d\Omega}{dU}\,\Omega' + \Omega\,\frac{d\Omega'}{dU}.$$

By the chain rule for taking derivatives,

$$\frac{d\Omega'}{dU} = \left(\frac{d\Omega'}{dU'}\right)\left(\frac{dU'}{dU}\right).$$

Since $U' = U^* - U$, $dU'/dU = -1$. Therefore

$$\frac{d\Omega^*}{dU} = \Omega'\,\frac{d\Omega}{dU} - \Omega\,\frac{d\Omega'}{dU'}. \tag{3.11}$$

Factoring out $\Omega\,\Omega'$ gives

$$\frac{d\Omega^*}{dU} = \Omega\,\Omega'\left(\frac{1}{\Omega}\,\frac{d\Omega}{dU} - \frac{1}{\Omega'}\,\frac{d\Omega'}{dU'}\right). \tag{3.12}$$

In equilibrium, this must be zero by Eq. 3.9. Since $\Omega^* = \Omega\Omega'$ cannot be zero, the most probable state or the equilibrium state exists when

$$\frac{1}{\Omega}\,\frac{d\Omega}{dU} = \frac{1}{\Omega'}\,\frac{d\Omega'}{dU'}. \tag{3.13}$$

It is convenient to define the quantity τ as

$$\frac{1}{\tau} \equiv \frac{1}{\Omega}\,\frac{d\Omega}{dU}$$

for any system. We must remember that this derivative was taken when the number of particles and the parameters that determine the energy levels were held fixed. These parameters are such things as volume and electric and magnetic fields. To remind ourselves that everything *but* U is being held fixed, it is customary to use the notation for a *partial derivative*: ∂ instead of d (Appendix N). Therefore, we write

$$\frac{1}{\tau} \equiv \frac{1}{\Omega}\left(\frac{\partial\Omega}{\partial U}\right)_{N,V,\text{etc.}}. \tag{3.14}$$

Often we will be careless and just write $\partial\Omega/\partial U$.

The quantity τ defined by Eq. 3.14 depends only on the variables of one system, system A. It is therefore a property of that system. Thermal equilibrium occurs when $\tau = \tau'$. Since Ω is just a number, Eq. 3.14 shows that τ has the dimensions of energy.

Systems A and A', which are in thermal contact, will be in equilibrium (the state of greatest probability) when $\tau = \tau'$. This is reminiscent of something that is familiar to all of us: if a hot system is placed in contact with a cold one, the hotter one cools off and the cooler one gets warmer. The systems come to equilibrium when they are both at the same temperature. This suggests that τ is in some way related to temperature, even though it has the dimensions of energy. We will not prove it, but many things work out right if the absolute temperature T is defined by the relationship

$$\tau = k_B T. \tag{3.15}$$

The proportionality constant is called *Boltzmann's constant*. If T is measured in kelvin (K), k_B has the value

$$k_B = 1.380\,651 \times 10^{-23}\,\mathrm{J\,K^{-1}} = 0.861\,734 \times 10^{-4}\,\mathrm{eV\,K^{-1}}. \quad (3.16)$$

(The *electron volt* (eV) is a unit of energy commonly used when considering atoms or molecules. $1\,\mathrm{eV} = 1.602\,18 \times 10^{-19}\,\mathrm{J}$.) The most convincing evidence in this book that Eq. 3.15 is reasonable is the derivation of the thermodynamic identity in Sect. 3.16.

The *absolute temperature* T is related to the temperature in degrees centigrade or Celsius by

$$T = (\text{temperature in } ^\circ\mathrm{C}) + 273.15. \quad (3.17)$$

3.6 Entropy

The preceding section used the idea that the number of microstates accessible to a system increases as the energy of the system increases, to develop a condition for thermal equilibrium. There are two features of those arguments that suggest that there are advantages to working with the natural logarithm of the number of microstates. First, the total number of microstates is the product of the number in each subsystem: $\Omega^* = \Omega\Omega'$. Taking natural logarithms of this gives

$$\ln \Omega^* = \ln \Omega + \ln \Omega'. \quad (3.18)$$

The other feature is the appearance of $(1/\Omega)\,(\partial\Omega/\partial U)$ in the equilibrium condition. For any non-negative, differentiable function $y(x)$,

$$\frac{d}{dx}(\ln y) = \frac{1}{y}\frac{dy}{dx}.$$

Therefore, Eq. 3.14 can be written as

$$\frac{1}{\tau} = \frac{\partial}{\partial U}(\ln \Omega). \quad (3.19)$$

The *entropy* S is defined by

$$S = k_B \ln \Omega, \qquad \Omega = e^{S/k_B}. \quad (3.20)$$

If both sides of Eq. 3.19 are multiplied by k_B, it is seen that

$$\left(\frac{\partial S}{\partial U}\right)_{N,V,\text{etc.}} = \frac{k_B}{\tau} = \frac{1}{T}. \quad (3.21)$$

This is a fundamental property of entropy that may be familiar to you from other thermodynamics textbooks; if so, it forms a justification for defining temperature as we did.

Another important property of the entropy is that the entropy of system A^* is the sum of the entropy of A and the entropy of A':

$$S^* = S + S'. \quad (3.22)$$

This can be proved by multiplying Eq. 3.18 by k_B.

A third property of the entropy is that S^* is a maximum when systems A and A' are in thermal equilibrium. This result follows from the fact that Ω^* is a maximum at equilibrium, since $S^* = k_B \ln \Omega^*$ and the logarithm is a monotonic function.

Finally, the entropy change in the system can be related to the heat flow into it. Equation 3.21 shows that if there is an energy change in the system *when N and the parameters that govern the spacing of the energy levels are fixed*, then

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V,\text{etc.}} dU = \left(\frac{dU}{T}\right)_{N,V,\text{etc.}}.$$

But the energy change when N, V, and any other parameters are fixed is the heat flow dQ:

$$dS = \frac{dQ}{T}. \quad (3.23)$$

3.7 The Boltzmann Factor

Section 3.5 considered the equilibrium state of two systems that were in thermal contact. It is often useful to consider systems in thermal contact when one of the systems is a single particle. This leads to an expression for the total number of microstates as a function of the energy in the single-particle system, known as the *Boltzmann factor*. The Boltzmann factor is used in many situations, as is its alternate form, the *Nernst equation* (Sect. 3.8).

Let system A be a single particle in thermal contact with a large system or *reservoir* A'. Transferring energy from A' to A decreases the number of microstates in A'. The number of microstates in A may change by some factor G or remain the same. We will discuss G at the end of this section.

To make this argument quantitative, consider system A when it has two different energies, U_r and U_s. Reservoir A' is very large so that its temperature T' remains constant, and it has many energy levels almost continuously distributed. Let $\Omega'(U')$ be the number of microstates in A' when it has energy U'. The relative probability that A has energy U_s compared to having energy U_r is given by the ratio of the total number of microstates accessible to the combined system:

$$\frac{P(U_s)}{P(U_r)} = \frac{\Omega^*(U = U_s)}{\Omega^*(U = U_r)} = \frac{\Omega(U_s)\,\Omega'(U^* - U_s)}{\Omega(U_r)\,\Omega'(U^* - U_r)}. \quad (3.24)$$

This probability is the product of two functions, one depending on system A and one on reservoir A':

$$G = \frac{\Omega(U_s)}{\Omega(U_r)},$$
$$R = \frac{\Omega'(U^* - U_s)}{\Omega'(U^* - U_r)}. \tag{3.25}$$

Ratio R is calculated most easily by using Eq. 3.14, remembering the definition $\tau = k_B T$. Since neither the volume nor number of particles is changed, we use an ordinary derivative. We write it in terms of the temperature of the reservoir:

$$\frac{1}{\Omega'}\left(\frac{d\Omega'}{dU'}\right) = \frac{1}{k_B T'},$$
$$\frac{d\Omega'}{dU'} = \left(\frac{1}{k_B T'}\right)\Omega'. \tag{3.26}$$

Since T' is constant, this is easily integrated:

$$\Omega'(U') = \text{const} \times e^{U'/k_B T'}.$$

Therefore the ratio is

$$R = \frac{\text{const} \times e^{(U^* - U_s)/k_B T'}}{\text{const} \times e^{(U^* - U_r)/k_B T'}}$$
$$= e^{-(U_s - U_r)/k_B T}. \tag{3.27}$$

Although the temperature T' is a property of the reservoir, we drop the prime. This ratio is called the *Boltzmann factor*. It gives the factor by which the number of microstates in the reservoir decreases when the reservoir gives up energy $U_s - U_r$ to the system A.

The relative probability of finding system A with energy U_r or U_s is then given by

$$\frac{P(U_s)}{P(U_r)} = G\, e^{-(U_s - U_r)/k_B T} = \left[\frac{\Omega(U_s)}{\Omega(U_r)}\right] e^{-(U_s - U_r)/k_B T}. \tag{3.28}$$

The exponential Boltzmann factor is a property of the reservoir. The factor G is called the *density of states factor*. It is a property of the system. If system A is a single atom with discrete energy levels and we want to know the relative probability that the atom has a particular value of its allowed energy, G may be unity. In other cases, there may be two or more sets of quantum numbers corresponding to the same energy, a situation called *degeneracy*. In that case G may be a small integer. We would have to know the details to calculate it.

3.8 The Nernst Equation

The Nernst equation is widely used in physiology to relate the concentration of ions on either side of a membrane to the electrical potential difference across the membrane. It is an example of the Boltzmann factor.

Suppose that certain ions can pass easily through a membrane. If the membrane has an electrical potential difference across it, the ions will have different energy on each side of the membrane. As a result, when equilibrium exists they will be at different concentrations. The ratio of the probability of finding an ion on either side of the membrane is the ratio of the concentrations on the two sides:

$$\frac{C_2}{C_1} = \frac{P(2)}{P(1)}.$$

The total energy of an ion is its kinetic energy plus its potential energy: $U = E_k + E_p$. Chapter 6 will show that when the electrical potential is v, the potential energy is $E_p = zev$. In this equation z is the valence of the ion ($+1, -1, +2$, etc.) and e is the *elementary charge* (1.6×10^{-19} C).

The concentration ratio is given by a Boltzmann factor, Eq. 3.28:

$$\frac{C_2}{C_1} = \left[\frac{\Omega(2)}{\Omega(1)}\right] e^{-(U_2 - U_1)/k_B T}. \tag{3.29}$$

We must now evaluate the quantity in square brackets. It is the ratio of the number of microstates available to the ion on each side of the membrane. The concentration is the number of ions per unit volume and is proportional to the probability that an ion is in volume $\Delta x \Delta y \Delta z$. We will state without proof that for a particle that can undergo translational motion in three dimensions, $\Omega(U)$ is $\alpha\, \Delta x \Delta y \Delta z$, where α is a proportionality constant. Therefore

$$\frac{\Omega(2)}{\Omega(1)} = \frac{\alpha\, \Delta x \Delta y \Delta z}{\alpha\, \Delta x \Delta y \Delta z} = 1.$$

The energy difference is

$$U_2 - U_1 = E_k(2) - E_k(1) + ze(v_2 - v_1).$$

It will be shown in Sect. 3.10 that the average kinetic energy on both sides of the membrane is the same if the temperature is the same. Therefore,

$$\frac{C_2}{C_1} = e^{-ze(v_2 - v_1)/k_B T}. \tag{3.30}$$

If the potential difference is $v_2 - v_1$, then the ions will be in equilibrium if the concentration ratio is as given by Eq. 3.30. If the ratio is not as given, then the ions, since they are free to move through the membrane, will do so until equilibrium is attained or the potential changes.

If the ions are positively charged and $v_2 > v_1$, then the exponent is negative and $C_2 < C_1$. If the ions are negatively charged, then $C_2 > C_1$.

The concentration difference is explained qualitatively by the electrical force within the membrane that causes the potential difference. If $v_2 > v_1$, the force within the membrane

on a positive ion acts from region 2 toward region 1. It slows positive ions moving from 1 to 2 and accelerates those moving from 2 to 1. Thus it tends to increase C_1.

The Nernst equation is obtained by taking logarithms of both sides of Eq. 3.30:

$$\ln\left(\frac{C_2}{C_1}\right) = -\frac{ze}{k_B T}(v_2 - v_1).$$

From this,

$$v_2 - v_1 = \frac{k_B T}{ze}\ln\left(\frac{C_1}{C_2}\right).$$

Multiplying both numerator and denominator of $k_B T/ze$ by *Avogadro's number* $N_A = 6.022\,141 \times 10^{23}$ molecule mol^{-1} gives the quantities $N_A k_B$ and $N_A e$. The former is the *gas constant*:

$$N_A k_B = R = 8.314\,46\,\text{J mol}^{-1}\,\text{K}^{-1}. \tag{3.31}$$

The latter is the Faraday constant:

$$N_A e = F = 96\,485.34\,\text{C mol}^{-1}. \tag{3.32}$$

The coefficient is therefore

$$\frac{k_B T}{ze} = \frac{RT}{zF}. \tag{3.33}$$

At body temperature, $T = 37\,^\circ\text{C} = 310\,\text{K}$, the value of RT/F is $0.0267\,\text{J C}^{-1} = 26.7\,\text{mV}$.

In the form

$$v_2 - v_1 = \frac{RT}{zF}\ln\left(\frac{C_1}{C_2}\right), \tag{3.34}$$

the Boltzmann factor is called the *Nernst equation*.

3.9 The Pressure Variation in the Atmosphere

It is well known that the atmospheric pressure decreases with altitude. This truth has medical significance because of the effects of lower oxygen at high altitudes. We will derive an approximate, constant-temperature model for the decrease using the Boltzmann factor, and then we will do it again using hydrostatic equilibrium.

The gravitational potential energy of an air molecule at height y is mgy, where m is the mass of the molecule and g is the gravitational acceleration. If the atmosphere has a constant temperature, there will be no change of kinetic energy with altitude. For a molecule to increase its potential energy, and therefore its total energy, by mgy, the energy of all the other molecules (the reservoir) must decrease, with a corresponding decrease in the number of accessible microstates. The number of particles per unit volume is given by a Boltzmann factor:

$$C(y) = C(0)e^{-mgy/k_B T}. \tag{3.35}$$

Since for an ideal gas $p = Nk_B T/V = Ck_B T$, the pressure also decreases exponentially with height.

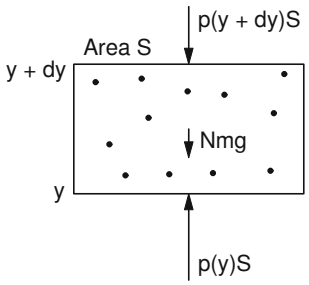


Fig. 3.11 Forces on a small volume element of the atmosphere

The same result can be obtained without using statistical physics, by considering a small volume of the atmosphere that is in static equilibrium. Let the volume have thickness dy and horizontal cross-sectional area S, as shown in Fig. 3.11. The force exerted upward across the bottom face of the element is $p(y)S$. The force down on the top face is $p(y+dy)S$. The N molecules in the volume each experience the downward force of gravity. The total gravitational force is Nmg. In terms of the concentration, $N = CSdy$. Therefore, the condition for equilibrium is $p(y)S - p(y+dy)S - CSmg\,dy = 0$. Since $p(y) - p(y+dy) = -(dp/dy)\,dy$, this can be written as

$$\left[-\left(\frac{dp}{dy}\right) - Cgm\right] S\,dy = 0.$$

The next step is to use the ideal gas law to write $p = Ck_B T$:

$$-k_B T\frac{dC}{dy} - Cmg = 0.$$

If this is written in the form

$$\frac{dC}{dy} = -\frac{mg}{k_B T}C \tag{3.36}$$

it will be recognized as the equation for exponential decay. The solution is Eq. 3.35.

3.10 Equipartition of Energy and Brownian Motion

A very important application of the Boltzmann factor is the proof that the average translational kinetic energy per degree of freedom of a particle in thermal contact with a reservoir at

temperature T is $k_B T/2$. This result holds for any term in the total energy that depends on the square of one of the variables (such as a component of the position or the momentum).

The proof is done for the kinetic energy resulting from the x component of momentum. The same procedure can be used for the other components. When the x component of the momentum of a particle is between p_x and $p_x + dp_x$, the kinetic energy is $p_x^2/2m$. The relative probability that the particle has this energy is given by the Boltzmann factor, $e^{-p_x^2/2mk_BT}$. We assert that the probability that the particle has momentum in this interval is also proportional to dp_x.[10] The average kinetic energy associated with p_x is obtained by multiplying the energy by the Boltzmann factor and integrating over all values of p_x. We normalize the probability by dividing by the integral of the Boltzmann factor.

$$\overline{\left(\frac{p_x^2}{2m}\right)} = \frac{\int_{-\infty}^{\infty} (p_x^2/2m) e^{-p_x^2/2mk_BT}\, dp_x}{\int_{-\infty}^{\infty} e^{-p_x^2/2mk_BT}\, dp_x}. \tag{3.37}$$

The integral in the denominator is evaluated in Appendix K and is $(2\pi mk_BT)^{1/2}$. The integral in the numerator of Eq. 3.37 is

$$\left(\frac{1}{m}\right)\left(\frac{1}{4}\right)(2mk_BT)(2\pi mk_BT)^{1/2}.$$

Combining these gives

$$\overline{\left(\frac{p_x^2}{2m}\right)} = \frac{k_BT}{2}. \tag{3.38}$$

The average value of the kinetic energy corresponding to motion in the x direction is $k_BT/2$, independent of the mass of the particle. The only condition that went into this derivation was that the energy depended on the square of the variable. Any term in the total energy that is a *quadratic function of some variable* will carry through the same way, so that the average energy will be $k_BT/2$ for that variable. This result is called the *equipartition of energy*.

The total translational kinetic energy is the sum of three terms $(p_x^2 + p_y^2 + p_z^2)/2m$, so the total translational kinetic energy has average value $\frac{3}{2}k_BT$.

This result is true for particles of *any* mass: atoms, molecules, pollen grains, and so forth. Heavier particles will have a smaller velocity but the same average kinetic energy. Even heavy particles are continually moving with this average kinetic energy. The random motion of pollen particles in water was first seen by a botanist, Robert Brown, in 1827. This *Brownian motion* is an important topic in the next chapter.

[10] A more detailed justification of this is found in earlier editions of this book, in texts on statistical mechanics, or on the web site associated with this book.

3.11 Heat Capacity

Consider a system into which a small amount of heat Q flows. In many cases the temperature of the system rises. (An exception is when there is a change of state such as the melting of ice.) The *heat capacity* C of the system is defined as

$$C = \frac{Q}{\Delta T}. \tag{3.39}$$

Heat capacity has units of J K^{-1}. It depends on the size of the object and the substance it is made of. The *specific heat capacity*, c, is the heat capacity per unit mass (J K^{-1} kg^{-1}) or the heat capacity per mole (J K^{-1} mol^{-1}).

The heat capacity also depends on any changes in the macroscopic parameters that take place during the heat flow. Recall the first law of thermodynamics, Eq. 3.5: $\Delta U = Q - W$. Only part of the energy transferred to the system by the heat flow increases the internal energy. Some also goes to work done by the system. For example, if the volume changes, there will be pressure-volume work done by the system (Sect. 1.18).

One special case is the heat capacity at constant volume, C_V. In that case, no pdV work is done by the system and $\Delta U = Q$, so

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V. \tag{3.40}$$

Many processes in the body occur at constant pressure. The heat capacity at constant pressure, C_p, is not equal to C_V. If both the pressure and volume change during the process, the heat capacity depends on the details of the pressure and volume changes.

The simplest example is the heat capacity at constant volume of a monatomic ideal gas. The average kinetic energy of a gas molecule at temperature T moving in three dimensions is $\frac{3}{2}k_BT$, and the total energy of N molecules is $U = \frac{3}{2}Nk_BT$. Therefore at constant volume $C_V = \frac{3}{2}Nk_B$. For one mole of monatomic ideal gas the heat capacity is $\frac{3}{2}N_Ak_B = \frac{3}{2}R$. Molecules with two or more atoms can also have rotational and vibrational energy, and the heat capacity is larger. The heat capacity can also depend on the temperature.

As a biological example, consider the energy loss from breathing (Denny 1993). In each breath we inhale about $V = 0.5$ l of air. Our body warms this air from the surrounding temperature to body temperature. (The body has a much higher heat capacity and does not significantly cool. See Problem 49.) The specific heat of air under these conditions is $c \approx 1000$ J K^{-1} kg^{-1}, and the density of air is $\rho = 1.3$ kg m^{-3}. Therefore the heat flow required to raise the air temperature in each breath is

$$Q = c\rho V \left(T_{\text{body}} - T_{\text{surroundings}}\right). \tag{3.41}$$

For a body temperature of 37 °C and surroundings at 20 °C, the temperature difference is 17 °C = 17 K. From Eq. 3.41, $Q = 11$ J. We breathe about once every 5 s, so the average power lost to the air we breathe is 2.2 W. A typical basal metabolic rate is about 100 W, so this represents 2 % of our energy consumption.

3.12 Equilibrium When Particles Can Be Exchanged: the Chemical Potential

Section 3.5 considered two systems that could exchange heat. The most probable or equilibrium state was that in which energy had been exchanged so that the total number of microstates or total entropy was a maximum. This occurred when (Eq. 3.13)

$$\frac{1}{\Omega}\left(\frac{\partial\Omega}{\partial U}\right)_{N,V} = \frac{1}{\Omega'}\left(\frac{\partial\Omega'}{\partial U'}\right)_{N',V'},$$

which is equivalent to $T = T'$. Since $S = k_B \ln\Omega$ this is also equivalent to

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \left(\frac{\partial S'}{\partial U'}\right)_{N',V'}.$$

This section considers the case in which the systems can exchange both energy by heat flow and particles; they are in thermal and diffusive contact (Fig. 3.12). The number of particles in each system is not fixed, but their sum is constant:

$$N + N' = N^*. \tag{3.42}$$

Equilibrium will exist for the most probable state, which means that there is heat flow until the two temperatures are the same and Eq. 3.13 is satisfied. The most probable state also requires a maximum in Ω^* or S^* vs N. The arguments used in the earlier section for heat exchange can be applied to obtain the equilibrium condition

$$\frac{1}{\Omega}\left(\frac{\partial\Omega}{\partial N}\right)_{U,V} = \frac{1}{\Omega'}\left(\frac{\partial\Omega'}{\partial N'}\right)_{U',V'}. \tag{3.43}$$

The condition in terms of entropy is

$$\left(\frac{\partial S}{\partial N}\right)_{U,V} = \left(\frac{\partial S'}{\partial N'}\right)_{U',V'}. \tag{3.44}$$

For thermal contact, the temperature was defined in terms of the derivative of S with respect to U, so that equilibrium occurred when $T = T'$. An analogous quantity, the *chemical potential*, is defined by

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U,V}. \tag{3.45}$$

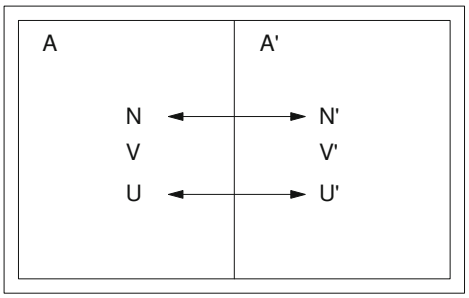


Fig. 3.12 Two systems can exchange energy by heat flow and paticles. The volume of each system remains fixed

(The reason T is included in the definition will become clear later.) Both thermal and diffusive equilibrium exist when

$$T = T', \qquad \mu = \mu'. \tag{3.46}$$

Two systems are in thermal and diffusive equilibrium when they have the same temperature and the same chemical potential.

Since the units of S are J K^{-1} and the units of N are dimensionless,[11] Eq. 3.45 shows that the units of chemical potential are J.

Consider next what happens to the entropy of the total system if particles are exchanged when the system is not in equilibrium. Let the number of particles in the unprimed system increase by ΔN and the number in the primed system change by $\Delta N' = -\Delta N$. The change of total entropy is

$$\Delta S^* = \left(\frac{\partial S^*}{\partial N}\right)\Delta N = \left(\frac{\partial S}{\partial N}\right)\Delta N + \left(\frac{\partial S'}{\partial N'}\right)\Delta N'.$$

Using the definition of the chemical potential we can rewrite this as

$$\Delta S^* = \left(-\frac{\mu}{T}\right)\Delta N - \left(-\frac{\mu'}{T'}\right)\Delta N.$$

If the two temperatures are the same, this is

$$\Delta S^* = \left(\frac{\mu' - \mu}{T}\right)\Delta N. \tag{3.47}$$

We see again that the entropy change will be zero for a small transfer of particles from one system to the other if $\mu = \mu'$. Suppose now that particles flow from A' to A, so that ΔN is positive. If $\mu' > \mu$, that is, the chemical potential of A' is greater than that of A, this will cause an increase in entropy of the combined system. *If particles move from a system of higher chemical potential to one of lower chemical potential, the entropy of the total system increases.*

[11] In this book, N represents the number of particles, and the chemical potential has units of energy per particle. In other books it may have units of energy per mole.

3.13 Concentration Dependence of the Chemical Potential

The change in chemical potential of an ideal gas (or a solute in an ideal solution)[12] when the concentration changes from C_0 to C and there is also a change in its potential energy has the form

$$\Delta\mu = k_B T \ln\left(\frac{C}{C_0}\right) + \Delta(\text{potential energy per particle}). \tag{3.48}$$

We will derive this in Sect. 3.18; for now we show that it is plausible and consistent with the Boltzmann factor.

We know from experience that particles tend to move from a region of higher to lower potential energy, thus increasing their kinetic energy, which can then be transferred as heat to other particles by collision. We also know that particles will move from a region of high concentration to a region of lower concentration. This process, called diffusion, is discussed in Chap. 4. Both processes cause a decrease in the chemical potential and therefore an increase in the entropy.

It is the combination of these two factors that causes the Boltzmann distribution of particles in the atmosphere. When the atmosphere is in equilibrium, the potential energy term increases with height and the concentration term decreases with height so that the chemical potential is the same at all heights.

To see the equivalence between Eq. 3.48 and the Boltzmann factor, suppose that particles can move freely from region 1 to region 2 and that the potential energy difference between the two regions is ΔE_p. The particles will be in equilibrium when $\mu_1 = \mu_2$. From Eq. 3.48 this means that

$$k_B T \ln C_1 + E_{p1} = k_B T \ln C_2 + E_{p2}.$$

This equation can be rearranged to give

$$\ln C_2 - \ln C_1 = -\frac{E_{p2} - E_{p1}}{k_B T}.$$

If exponentials are taken of each side, the result is

$$\frac{C_2}{C_1} = e^{-\Delta E_p / k_B T}.$$

If the temperature of each region is the same, the average kinetic energy will be the same in each system, and $\Delta E_p = \Delta U$. This is then the same as the Boltzmann factor, Eq. 3.29.

There is still another way to look at the concentration dependence. In an ideal gas, the pressure, volume, temperature, and number of particles are related by the equation of state $pV = Nk_B T$. In terms of the particle concentration $C = N/V$, this is $p = Ck_B T$. The work necessary to concentrate the gas from volume V_1 and concentration C_1 to V_2 and C_2 is (see Eq. 1.57)

$$W_{\text{on gas}} = -\int_{V_1}^{V_2} p(V)\, dV. \tag{3.49}$$

The concentration work at a constant temperature is

$$W = -Nk_B T \int_{V_1}^{V_2} \frac{dV}{V} = -Nk_B T \ln\frac{V_2}{V_1}.$$

If the final volume is smaller than the initial volume, the logarithm is negative and the concentration work is positive. In terms of the particle concentration $C = N/V$ or the molar concentration $c = n/V$, the concentration work is

$$W_{\text{conc}} = Nk_B T \ln\frac{C_2}{C_1} = nRT \ln\frac{c_2}{c_1}. \tag{3.50}$$

The last form was written by observing that $Nk_B = nR$ where R is the gas constant per mole.

Comparing Eq. 3.50 with Eq. 3.48, we see that the concentration work at constant temperature is proportional to the change in chemical potential with concentration. It is, in fact, just the number of molecules N times the change in μ: $W_{\text{conc}} = N\Delta\mu$.

The concentration work or change of chemical potential can be related to the Boltzmann factor in still another way. Particles are free to move between two regions of different potential energy at the same temperature. The work required to change the concentration is, by Eq. 3.50,

$$W_{\text{conc}} = N\Delta\mu = Nk_B T \ln\frac{C_2}{C_1}.$$

The concentration ratio is given by a Boltzmann factor:

$$C_2/C_1 = e^{-(E_{p2}-E_{p1})/k_B T},$$

so that $\ln(C_2/C_1) = -(E_{p2} - E_{p1})/k_B T$. Therefore, the concentration work is $W_{\text{conc}} = -N(E_{p2} - E_{p1})$.

If $C_2 < C_1$, W is negative and is equal in magnitude to the increase in potential energy of the molecules. The concentration energy lost by the molecules is precisely that required for them to move to the region of higher potential energy. If $C_2 > C_1$, the loss of potential energy going from region 1 to region 2 provides the energy necessary to concentrate the gas. Alternatively, one may say that the sum of the concentration energy and the potential energy is the same in the two regions. This was, in fact, the statement about the chemical potential at equilibrium: $\mu_2 = \mu_1$.

The same form for the chemical potential is obtained for a dilute solute. (We will present one way of understanding why in Sect. 3.18.) Therefore, the concentration work calculated for an ideal gas is the same as for an ideal solute. The

[12] An ideal solution is defined in Sect. 3.18.

work required to concentrate 1 mol of substance by a factor of 10 at 310 K is (1 mol)(8.31 J mol^{-1} K^{-1})(310 K) ln(10) or 5.93×10^3 J. The H^+ ion in gastric juice has a pH of 1. Since it was concentrated from plasma with a pH of about 7, the concentration ratio is 10^6. The work necessary to concentrate 1 mol is therefore $RT\ \ln(10^6) = (8.31)(310)(13.82) = 3.56 \times 10^4$ J.

3.14 Systems That Can Exchange Volume

We have considered two systems that can exchange energy or particles. Now consider the systems shown in Fig. 3.13. They are isolated from the rest of the universe. The vertical line that separates them is a piston that can move and conduct heat, so that energy and volume can be exchanged between the two systems. The piston prevents particles from being exchanged. The constraints are $V^* = V + V'$ and $U^* = U + U'$ from which $dV = -dV'$, $dU = -dU'$. As before, equilibrium exists when the total number of microstates or the total entropy is a maximum. The conditions for maximum entropy are

$$\left(\frac{\partial S^*}{\partial U}\right)_{N,V} = 0, \qquad \left(\frac{\partial S^*}{\partial V}\right)_{N,U} = 0.$$

The derivation proceeds as before. For example,

$$\left(\frac{\partial S^*}{\partial V}\right)_{N,U} = \left(\frac{\partial S}{\partial V}\right)_{N,U} + \left(\frac{\partial S'}{\partial V}\right)_{N,U} = \left(\frac{\partial S}{\partial V}\right)_{N,U} - \left(\frac{\partial S'}{\partial V'}\right)_{N',U'}.$$

Equilibrium requires that $T = T'$ so that there is no heat flow. The piston will stop moving and there will be no change of volume when

$$\left(\frac{\partial S}{\partial V}\right)_{N,U} = \left(\frac{\partial S'}{\partial V'}\right)_{N',U'}. \tag{3.51}$$

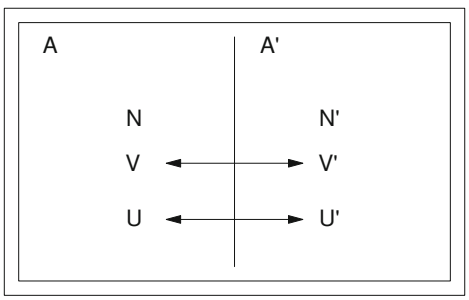


Fig. 3.13 Two systems that can exchange volume are separated by a movable piston. Heat can also flow through the piston

These derivatives can be evaluated in several ways. The method used here involves some manipulation of derivatives; a more detailed description, consistent with the microscopic picture of energy levels, is found in Reif (1964, pp. 267–273).

For a small exchange of heat and work, the first law can be written as $dU = dQ - dW$. In the present case the only form of work is that related to the change of volume, so $dU = dQ - pdV$. It was shown in Eq. 3.23 that $dQ = TdS$. Therefore $dU = TdS - pdV$. This equation can be solved for dS:

$$dS = \left(\frac{1}{T}\right) dU + \left(\frac{p}{T}\right) dV. \tag{3.52}$$

The entropy depends on U,V and N: $S = S(U, V, N)$. If N is not allowed to change, then

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV. \tag{3.53}$$

Comparison of this with Eq. 3.52 shows that

$$\left(\frac{\partial S}{\partial U}\right)_{N,V} = \frac{1}{T},$$

$$\left(\frac{\partial S}{\partial V}\right)_{N,U} = \frac{p}{T}. \tag{3.54}$$

The first of these equations was already seen as Eq. 3.21. The second gives the condition for equilibrium under volume change. Referring to Eq. 3.51 we see that at equilibrium

$$\frac{p}{T} = \frac{p'}{T'}.$$

Therefore, equilibrium requires both $T = T'$ and

$$p = p'. \tag{3.55}$$

This agrees with common experience. The piston does not move when the pressure on each side is the same.

3.15 Extensive Variables and Generalized Forces

The number of microstates and the entropy of a system depend on the number of particles, the total energy, and the positions of the energy levels of the system. The positions of the energy levels depend on the volume and may also depend on other macroscopic parameters. For example, they may depend on the length of a stretched muscle fiber or a protein molecule. For charged particles in an electric field, they depend on the charge. For a thin film such as the fluid lining the alveoli of the lungs, the entropy depends on the surface area

Table 3.4 Examples of extensive variables and the generalized force associated with each of them

x	X	$dU = -dW$
Volume V	$-$pressure $-p$	$-p\,dV$
Length L	Force F	$F\,dL$
Area a	Surface tension σ	$\sigma\,da$
Charge q	Potential v	$v\,dq$

of the film. The number of particles, energy, volume, electric charge, surface area, and length are all *extensive variables*: if a homogeneous system is divided into two parts, the value of the variable for the total system (volume, charge, etc.) is the sum of the values for each part. A general extensive variable will be called x.

An adiabatic energy change is one in which no heat flows to or from the system. The energy change is due to work done on or by the system as a macroscopic parameter changes, shifting at least some of the energy levels. For each extensive variable x we can define a *generalized force* X such that the energy change in an adiabatic process is

$$dU = -dW = X dx. \tag{3.56}$$

(Remember that dU is the increase in energy of the system and dW is the work done by the system on the surroundings.) Examples of extensive variables and their associated forces are given in Table 3.4.

3.16 The General Thermodynamic Relationship

Suppose that a system has N particles, total energy U, volume V, and another macroscopic parameter x on which the positions of the energy levels may depend. The number of microstates, and therefore the entropy, will depend on these four variables: $S = S(U, N, V, x)$. If each variable is changed by a small amount, there is a change of entropy

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V,x} dU + \left(\frac{\partial S}{\partial N}\right)_{U,V,x} dN + \left(\frac{\partial S}{\partial V}\right)_{U,N,x} dV + \left(\frac{\partial S}{\partial x}\right)_{U,N,V} dx. \tag{3.57}$$

Now consider the change of energy of the system. If only heat flow takes place, there is an increase of energy $dQ = TdS$. If an adiabatic process with a constant number of particles takes place, the energy change is $-dW = Xdx - pdV$. If particles flow into the system without an accompanying flow of heat or work, the energy change is dU_N. It seems reasonable that this energy change, due solely to the movement of the particles, is proportional to dN: $dU_N = a\,dN$. (It will turn out that the proportionality constant is the chemical potential.) For the total change of energy resulting from all these processes, we can write a statement of the conservation of energy: $dU = TdS + Xdx - pdV + adN$. This is an extension of Eq. 3.5 to the additional variables on which the energy can depend. It can be rearranged as

$$dS = \left(\frac{1}{T}\right) dU - \left(\frac{a}{T}\right) dN + \left(\frac{p}{T}\right) dV - \left(\frac{X}{T}\right) dx. \tag{3.58}$$

Comparison of Eqs. 3.57 and 3.58 shows that

$$\left(\frac{\partial S}{\partial U}\right)_{N,V,x} = \frac{1}{T}, \tag{3.59a}$$

$$\left(\frac{\partial S}{\partial N}\right)_{U,V,x} = -\frac{a}{T}, \tag{3.59b}$$

$$\left(\frac{\partial S}{\partial V}\right)_{U,N,x} = \frac{p}{T}, \tag{3.59c}$$

$$\left(\frac{\partial S}{\partial x}\right)_{U,N,V} = -\frac{X}{T}. \tag{3.59d}$$

Comparison of Eq. 3.59b with Eq. 3.45 shows that $a = \mu$. This is why the factor of T was introduced in Eq. 3.45.

Equation 3.58, with the correct value inserted for a, is

$$TdS = dU - \mu\,dN + p\,dV - X\,dx. \tag{3.60}$$

This is known as the *thermodynamic identity* or the *fundamental equation of thermodynamics*. It is a combination of the conservation of energy with the relationship between entropy change and heat flow in a reversible process. (A reversible process is one that takes place so slowly that all parts of the system have the same temperature, pressure, etc.) This equation and derivative relations such as Eqs. 3.59 form the basis for the usual approach to thermodynamics.

Finally, let us consider the addition of a particle to a system when the volume is fixed. If we do this without changing the energy, it increases the number of ways the existing energy can be shared and hence the number of microstates. Therefore the entropy increases. If we want to restore the entropy to its original value, we must remove some energy. Exactly the same argument can be made mathematically. We have seen in Eqs. 3.45 and 3.59b that

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

Since adding the particle at constant energy increases the entropy, $(\partial S/\partial N)_{U,V}$ is positive and the chemical potential is negative. Next, we rearrange Eq. 3.60 as $dU = TdS + \mu\,dN - p\,dV$ and by inspection see that

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

Therefore adding a particle at constant volume while keeping the entropy constant requires that energy be removed from the system.

3.17 The Gibbs Free Energy

A conventional course in thermodynamics develops several functions of the entropy, energy, and macroscopic parameters that are useful in certain special cases. One of these is the *Gibbs free energy*, which is particularly useful in describing changes that occur in a system while the temperature and pressure remain constant. Most changes in a biological system occur under such conditions.

3.17.1 Gibbs Free Energy

Imagine a system A in contact with a much larger reservoir as in Fig. 3.14. The reservoir has temperature T' and pressure p'. A movable piston separates A and A'. (At equilibrium, $T = T'$ and $p = p'$.) The reservoir is large enough so that a change of energy or volume of system A does not change T' or p'.

Consider the change of entropy of the total system that accompanies an exchange of energy or volume between A and A'. Above, this entropy change was set equal to zero to obtain the condition for equilibrium. In this case, however, we will express the total entropy change of system plus reservoir in terms of the changes in system A alone. The total entropy is $S^* = S + S'$, so the total entropy change is $dS^* = dS + dS'$.

If reservoir A' exchanges energy with system A, the energy change is

$$dU' = T'\,dS' - dW' = T'\,dS' - p'\,dV'.$$

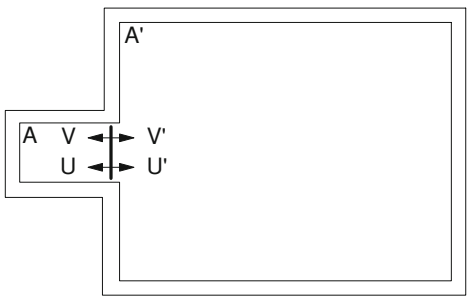


Fig. 3.14 System A is in contact with reservoir A'. Heat can flow through the piston, which is also free to move. The reservoir is large enough to ensure that anything that happens to system A takes place at constant temperature and pressure

This can be solved for dS', and the result can be put in the expression for the total entropy change:

$$dS^* = dS + \frac{dU'}{T'} + \frac{p'\,dV'}{T'}.$$

We are trying to get dS^* in terms of changes in system A alone. Since A and A' together constitute an isolated system, $dU = -dU'$ and $dV = -dV'$. Therefore,

$$dS^* = -\frac{-T'\,dS + dU + p'\,dV}{T'}. \tag{3.61}$$

(Note that a minus sign was introduced in front of this equation.) This expresses the total entropy change in terms of changes of S, U, and V in system A and the pressure and temperature of the reservoir.

The Gibbs free energy is *defined* to be

$$G \equiv U - T'S + p'V. \tag{3.62}$$

If the reservoir is large enough so that interaction of the system and reservoir does not change T' and p', then the change of G as system A changes is

$$dG = dU - T'dS + p'dV. \tag{3.63}$$

Comparison of Eqs. 3.61 and 3.63 shows that

$$dS^* = -\frac{dG}{T'}. \tag{3.64}$$

The change in entropy of system plus reservoir is related to the change of G, which is a property of the system alone, as long as the pressure and temperature are maintained constant by the reservoir.

To see why G is called a free energy, consider the conservation of energy in the following form:

$$\begin{aligned}\text{(work done by the system)} = \text{(energy lost by the system)} \\ + \text{(heat added to the system)},\end{aligned}$$

$$dW = -dU + T\,dS.$$

Subtracting pdV from both sides of this equation gives

$$dW - p\,dV = -dU + T\,dS - p\,dV = -dG.$$

The right-hand side is the decrease of Gibbs free energy of the system. The work done in any isothermal, isobaric (constant pressure) reversible process, *exclusive of pdV work*, is equal to the decrease of Gibbs free energy of the system. This non–$p\,dV$ work is sometimes called *useful work*. It may represent contraction of a muscle fiber, the transfer of particles from one region to another, the movement of charged particles in an electric field, or a change of concentration of particles. It differs from the change in energy of the system,

dU, for two reasons. The volume of the system can change, resulting in $p\,dV$ work, and there can be heat flow during the process. For example, let the system be a battery at constant temperature and pressure which decreases its internal (chemical) energy and supplies electrical energy. From a chemical energy change dU we subtract $T\,dS$, the heat flow to the surroundings, and $-p\,dV$, the work done on the atmosphere as the liquid in the battery changes volume. What is left is the energy available for electrical work.

3.17.2 An Example: Chemical Reactions

As an example of how the Gibbs free energy is used, consider a chemical reaction that takes place in the body at constant temperature and pressure. System A, the region in the body where the reaction takes place, is in contact with a reservoir A' that is large enough to maintain constant temperature and pressure. Suppose that there are four species of particles that interact. Capital letters represent the species and small letters represent the number of atoms or molecules of each that enter in the reaction:

$$aA + bB \longleftrightarrow cC + dD.$$

An example is 1 glucose$+6O_2 \longleftrightarrow 6CO_2+6H_2O$, where $a = 1, b = 6, c = 6, d = 6$. The state of the system depends on U, V, N_A, N_B, N_C, and N_D.

We begin with the definition of G, Eq. 3.62, and we call the pressure and temperature of the system and reservoir p and T:

$$G = U - TS + pV.$$

Differentiating, we obtain

$$dG = dU - T\,dS - S\,dT + p\,dV + V\,dp.$$

Generalize Eq. 3.60 for the case of four chemical species:

$$T\,dS = dU - \mu_A\,dN_A - \mu_B\,dN_B - \mu_C\,dN_C - \mu_D\,dN_D + p\,dV.$$

Insert this in the equation for dG and remember that since the process takes place at constant temperature and pressure, dT and dp are both zero. The result is

$$dG = \mu_A\,dN_A + \mu_B\,dN_B + \mu_C\,dN_C + \mu_D\,dN_D.$$

In Sect. 3.13 we saw that the concentration dependence of the chemical potential is given by a logarithmic term. Equation 3.48 can be used to write

$$\mu_A = \mu_{A0} + k_B T\,\ln(C_A/C_0),$$

where μ_{A0} is the chemical potential at a standard concentration (usually 1 molar, that is, 1 mol l^{-1}) and depends on temperature, pH, etc. Note that C_0 is the same reference concentration for all species. As the reaction takes place to the right, we can write the number of molecules gained or lost as $dN_A = -a\,dN$, $dN_B = -b\,dN$, $dN_C = c\,dN$, $dN_D = d\,dN$, so that we have

$$\begin{aligned} dG = &\left[\mu_{A0} + k_B T\,\ln(C_A/C_0)\right](-a\,dN) \\ &+ \left[\mu_{B0} + k_B T\,\ln(C_B/C_0)\right](-b\,dN) \\ &+ \left[\mu_{C0} + k_B T\,\ln(C_C/C_0)\right](c\,dN) \\ &+ \left[\mu_{D0} + k_B T\,\ln(C_D/C_0)\right](d\,dN). \end{aligned}$$

This can be rearranged as (letting $C_A = [A]$, etc.)

$$\begin{aligned} dG = &[c\mu_{C0} + d\mu_{D0} - a\mu_{A0} - b\mu_{B0} \\ &+ k_B T\,\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right) - k_B T\,\ln\left(\frac{[C_0]^a[C_0]^b}{[C_0]^c[C_0]^d}\right)\Bigg]\,dN. \end{aligned}$$

The two logarithm terms together represent logs of concentration ratios. Therefore concentrations $[A]$, $[B]$, $[C]$, $[D]$, and C_0 must all be measured in the same units. The last term can be made to vanish if the units are such that C_0 is unity (for example 1 mol per liter). Then

$$\begin{aligned} dG = &[c\mu_{C0} + d\mu_{D0} - a\mu_{A0} - b\mu_{B0} \\ &+ k_B T\,\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)\Bigg]\,dN. \end{aligned}$$

Multiplying the expression in square brackets by Avogadro's number converts the chemical potential per molecule to the standard Gibbs free energy per mole, and $k_B T$ to RT. To compensate, the change in number of molecules dN is changed to moles dn or Δn:

$$\begin{aligned} \Delta G = &[(cG_{C0} + dG_{D0} - aG_{A0} - bG_{B0}) \\ &+ RT\,\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right)\Bigg]\,\Delta n. \end{aligned} \tag{3.65}$$

The term in small parentheses is the standard free energy change for this reaction, ΔG^0, which can be found in tables. At equilibrium $\Delta G = 0$, so

$$0 = \Delta G^0 + RT\,\ln\left(\frac{[C]^c[D]^d}{[A]^a[B]^b}\right) = \Delta G^0 + RT\,\ln K_{\text{eq}}.$$

The *equilibrium constant* K_{eq} is related to the standard (1 molar) free-energy change by

$$\Delta G^0 = -RT\,\ln K_{\text{eq}},$$

$$K_{\text{eq}} = \frac{[C]^c[D]^d}{[A]^a[B]^b}.$$

Many biochemical processes in the body receive free energy from the change of adenosine triphosphate (ATP) to

adenosine diphosphate (ADP) plus inorganic phosphate (P_i). This reaction involves a decrease of free energy. The energy is provided initially by forcing the reaction to go in the other direction to make an excess of ATP. One way this is done is through a very complicated series of chemical reactions known as the *respiration of glucose*. The net effect of these reactions is[13]

$$\text{glucose} + 6O_2 \rightarrow 6CO_2 + 6H_2O, \quad \Delta G^0 = -680\,\text{kcal},$$

$$36\text{ADP} + 36P_i \rightarrow 36\text{ATP} + 36H_2O, \quad \Delta G^0 = +263\,\text{kcal}\,.$$

The decrease in free energy of the glucose more than compensates for the increase in free energy of the ATP. The creation of glucose or other sugars is the reverse of the respiration process and is called *photosynthesis*. The free energy required to run the reaction the other direction is supplied by light energy.

3.18 The Chemical Potential of a Solution

We now consider a binary solution of *solute* and *solvent* and how the chemical potential changes as these two substances are intermixed.[14] This is a very fundamental process that will lead us to the logarithmic dependence of the chemical potential on solute concentration that we saw in Sect. 3.13, as well as to an expression for the chemical potential of the solvent that we will need in Chap. 5.

To avoid having the subscript s stand for both solute and solvent, we call the solvent water. The distinction between solute and water is artificial; the distinction is usually that the concentration of solute is quite small. We need the entropy change in a solution when N_s solute molecules, which initially were segregated, are mixed with N_w water molecules. We make the calculation for an ideal solution—one in which the total volume of water molecules does not change on mixing and in which there is no heat evolved or absorbed on mixing. This is equivalent to saying that the solute and water molecules are the same size and shape, and that the force between a water molecule and its neighbors is the same as the force between a solute molecule and its neighbors.[15] The resulting entropy change is called the *entropy of mixing*.

To calculate the entropy of mixing, imagine a system with N sites, all occupied by particles. The number of microstates is the number of different ways that particles can be placed in the sites. The first particle can go in any site. The second can go in any of $N-1$ sites, and so forth. The total number of different ways to arrange the particles is $N!$ But if the particles are identical, these states cannot be distinguished, and there is actually only one microstate. The number of microstates is $N!/N!$, where the $N!$ in the numerator gives the number of arrangements and the $N!$ in the denominator divides by the number of indistinguishable states.[16]

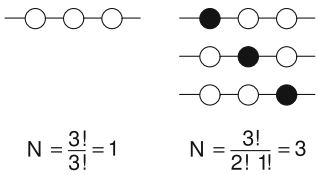


Fig. 3.15 The system on the *left* contains three water molecules. Because they are indistinguishable there is only one way they can be arranged. The system on the *right* contains two water molecules and one solute molecule. Three different arrangements are possible. In each case the number of arrangements in given by $(N_w + N_s)!/(N_w!N_s!)$

Suppose now that we have two different kinds of particles. The total number is $N = N_w + N_s$, and the total number of ways to arrange them is $(N_w+N_s)!$. The N_w water molecules are indistinguishable, so this number must be divided by $N_w!$. Similarly it must be divided by $N_s!$. Therefore, purely because of the ways of arranging the particles, the number of microstates Ω in the mixture is $(N_w + N_s)!/\,(N_w!\,N_s!)$. An example of counting microstates is shown in Fig. 3.15.

There could also be dependence on volume and energy; in fact, the dependence on volume and energy may also contain factors of N_w and N_s. However, our assumption that the molecules of water and solute have the same size, shape, and forces of interaction ensures that these dependencies will not change as solute molecules are mixed with water molecules. The only entropy change will be the entropy of mixing.

The entropy change of the mixture relative to the entropy of N_w molecules of pure water and N_s molecules of pure solute is

$$S_{\text{solution}} - S_{\substack{\text{pure water,}\\ \text{pure solute}}} = k_B \ln\left(\frac{\Omega_{\text{solution}}}{\Omega_{\substack{\text{pure water,}\\ \text{pure solute}}}}\right). \tag{3.66}$$

Since with our assumptions Ω is unity for the pure solute and the pure water, the entropy difference is

$$\begin{aligned} &S_{\text{solution}} - S_{\substack{\text{pure water,}\\ \text{pure solute}}} \\ &= k_B \ln\left(\frac{(N_w + N_s)!}{N_w!\,N_s!}\right) \\ &= k_B \left\{\ln\left[(N_w + N_s)!\right] - \ln(N_w!) - \ln(N_s!)\right\}. \end{aligned} \tag{3.67}$$

This is symmetric in water and solute, and it is valid for any number of molecules.

[13] There are multiple pathways in glucose respiration. The 36 is approximate.

[14] See also Hildebrand and Scott (1964), p. 17 and Chap. 6.

[15] Extensive work has been done on solutions for which these assumptions are not true. See Hildebrand and Scott (1964); Hildebrand et al. (1970).

[16] The fact that there is only one microstate because of the indistinguishability of the particles is called the *Gibbs paradox* (Reif 1965).

Since we usually deal with large numbers of molecules and factorials are difficult to work with, let us use Stirling's approximation (Appendix I) to write

$$S_{\text{solution}} - S_{\substack{\text{pure water,}\\ \text{pure solute}}} = k_B \left[(N_w + N_s) \ln(N_w + N_s) - N_w \ln N_w - N_s \ln N_s \right]. \tag{3.68}$$

The next step is to relate the entropy of mixing to the chemical potential. This is done by recalling the definition of the Gibbs free energy, (Eq. 3.62): $G = U + p\,V - T\,S$. The sum of the first two terms, $H = U + p\,V$, is called the *enthalpy*. Any change of the enthalpy is the heat of mixing; in our case it is zero. (The present case is actually more restrictive: p, V, and U are all constant.) Therefore, since T is also constant, the change in Gibbs free energy is due only to the entropy change:

$$\Delta G = -T\,\Delta S = k_B T \left[N_w \ln\left(\frac{N_w}{N_w + N_s}\right) + N_s \ln\left(\frac{N_s}{N_w + N_s}\right) \right].$$

This is still symmetric with water and solute, but it diverges if either N_w or N_s is zero, because of our use of Stirling's approximation.

We now need an expression that relates the change in G to the chemical potential. This can be derived for the general case using the following thermodynamic arguments. We use Eq. 3.62 to write the most general change in G:

$$dG = dU + p\,dV + V\,dp - T\,dS - S\,dT.$$

The fundamental equation of thermodynamics, Eq. 3.60, generalized to two molecular species, is

$$T\,dS = dU - \mu_w\,dN_w - \mu_s\,dN_s + p\,dV,$$

so

$$dG = \mu_w\,dN_w + \mu_s\,dN_s + V\,dp - S\,dT. \tag{3.69}$$

This can be used to write down some partial derivatives by inspection that are valid in general:

$$\mu_w = \left(\frac{\partial G}{\partial N_w}\right)_{N_s,p,T}, \tag{3.70a}$$

$$\mu_s = \left(\frac{\partial G}{\partial N_s}\right)_{N_w,p,T}, \tag{3.70b}$$

$$V = \left(\frac{\partial G}{\partial p}\right)_{N_s,N_w,T}, \tag{3.70c}$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{N_s,N_w,p}. \tag{3.70d}$$

To find the chemical potential, we differentiate our expression for G, Eq. 3.69, with respect to N_w and N_s to obtain

$$\mu_w = k_B T\,\ln x_w, \qquad \mu_s = k_B T\,\ln x_s. \tag{3.71}$$

These have been written in terms of the *mole fractions* or *molecular fractions*

$$x_w = \frac{N_w}{N_w + N_s}, \qquad x_s = \frac{N_s}{N_w + N_s}. \tag{3.72}$$

Each chemical potential is zero when the mole fraction for that species is one (i.e., the pure substance). The expressions for μ diverge for x_w or x_s close to zero because of the failure of Stirling's approximation for small values of x.

The last step is to write the chemical potential in terms of the more familiar concentrations instead of mole fractions. We can write the change in chemical potential of the *solute* as the concentration changes from a value C_1 to C_2 as

$$\Delta\mu_s = \mu_s(2) - \mu_s(1) = k_B T\,\ln(x_2/x_1).$$

As long as the solute is dilute, $N_w + N_s \approx N_w$, so $x_2/x_1 = C_2/C_1$ and

$$\Delta\mu_s = k_B T\,\ln(C_2/C_1),$$

which agrees with Eq. 3.48.

The change in chemical potential of the *water* can be written in terms of the *solute* concentration. Since $x_w + x_s = 1$, $\mu_w = k_B T \ln(1 - x_s)$. For small values of x_s the logarithm can be expanded in a Taylor's series (Appendix D):

$$\ln(1 - x_s) = -x_s - \frac{1}{2}x_s^2 - \cdots.$$

The final result is

$$\mu_w = -k_B T\,x_s = -k_B T\,N_s/(N_s + N_w) \approx -k_B T\,(N_s/V)/(N_w/V),$$

or

$$\mu_w \approx -k_B T\,\frac{C_s}{C_w}. \tag{3.73a}$$

To reiterate: this is the chemical potential of the water for small solute concentrations. The zero of chemical potential is pure water. The term is negative because the addition of solute decreases the chemical potential of the water, due to the entropy of mixing term. For a change of solute concentration, the chemical potential of the water changes by

$$\Delta\mu_w = -\frac{k_B T \Delta C_s}{C_w}. \tag{3.73b}$$

We now know the concentration dependence of the chemical potential. In Chap. 5 we will be concerned with the movement of solute and water, and we will also need to know

the dependence of the chemical potentials on pressure. To find this, we write

$$\Delta\mu_w = \left(\frac{\partial\mu_w}{\partial p}\right)_{T,N_w,C_s} \Delta p + \left(\frac{\partial\mu_w}{\partial C_s}\right)_{T,p,N_w} \Delta C_s.$$

The second term is just Eq. 3.73b. To obtain the derivative in the first term, we use the fact that when the partial derivative of a function is taken with respect to two variables, the result is independent of the order of differentiation (Appendix N):

$$\left[\frac{\partial}{\partial p}\left(\frac{\partial G}{\partial N_w}\right)_{T,p,N_s}\right]_{T,N_w} = \left[\frac{\partial}{\partial N_w}\left(\frac{\partial G}{\partial p}\right)_{T,N_w,N_s}\right]_{T,p}$$

From Eqs. 3.70a and 3.70c, we get

$$\left(\frac{\partial\mu_w}{\partial p}\right)_{T,N_w} = \left(\frac{\partial V}{\partial N_w}\right)_{T,p}. \tag{3.74}$$

For a process at constant temperature, the rate of change of μ_w with p for constant solute concentration is the same as the rate of change of V with N_w when p is fixed.

The quantity $(\partial V/\partial N_w)_{T,p}$ is the rate at which the volume changes when more molecules are added at constant temperature and pressure. For an ideal incompressible liquid it is the molecular volume, $\overline{V}_w$. We can repeat this argument for the solute to obtain

$$\left(\frac{\partial\mu_w}{\partial p}\right)_{T,N_w} = \overline{V}_w, \qquad \left(\frac{\partial\mu_s}{\partial p}\right)_{T,N_s} = \overline{V}_s. \tag{3.75}$$

In a solution, the total volume is $V = N_w\overline{V}_w + N_s\overline{V}_s$ where $\overline{V}_w$ and $\overline{V}_s$ are the average volumes occupied by one molecule of water and solute. Dividing by V gives $1 = C_w\overline{V}_w + C_s\overline{V}_s$. If the solution is dilute,

$$\overline{V}_w \approx \frac{1}{C_w}. \tag{3.76}$$

In an ideal solution $\overline{V}_w = \overline{V}_s$. For an ideal dilute solution, we then have

$$\Delta\mu_w = \overline{V}_w(\Delta p - k_BT\ \Delta C_s) \approx \frac{\Delta p - k_BT\ \Delta C_s}{C_w}. \tag{3.77}$$

$$\begin{aligned}\Delta\mu_s &= k_BT\ \ln(C_{s2}/C_{s1}) + \overline{V}_s\ \Delta p \\ &\approx k_BT\ \ln(C_{s2}/C_{s1}) + \overline{V}_w\ \Delta p.\end{aligned} \tag{3.78}$$

We saw this concentration dependence earlier, in Sect. 3.13. If the concentration difference is small, we can write $C_{s2} = C_{s1} + \Delta C_s$ and use the expansion $\ln(1+x) \approx x$ to obtain

$$\Delta\mu_s \approx \frac{k_BT\ \Delta C_s}{C_s} + \frac{\Delta p}{C_w}. \tag{3.79}$$

3.19 Transformation of Randomness to Order

When two systems are in equilibrium, the total entropy is a maximum. Yet a living creature is a low-entropy, highly ordered system. Are these two observations in conflict? The answer is no; the living system is not in equilibrium, and it is this lack of equilibrium that allows the entropy to be low. The conditions under which order can be brought to a system—its entropy can be reduced—are discussed briefly in this section.

A car travels with velocity $\mathbf{v}$ and has kinetic energy $\frac{1}{2}mv^2$. In addition to the random thermal motions of the atoms making up the car, all the atoms have velocity $\mathbf{v}$ in the same direction (except for those in rotating parts, which have an ordered velocity that is more complicated to describe). If the brake shoes are brought into contact with the brake drums, the car loses kinetic energy, and the shoes and drums become hot. Ordered energy has been converted into disordered, thermal energy; the entropy has increased. Is it possible to heat the drums and shoes with a torch, apply the brakes, and have the car move as the drums and shoes cool off? Energetically, this is possible, but there are only a few microstates in which all the molecules are moving in a manner that constitutes movement of the car. Their number is vanishingly small compared to the number of microstates in which the brake drums are hot. The probability that the car will begin to move is vanishingly small.

An animal is placed in an insulated, isolated container. The animal soon dies and decomposes. Energetically, the animal could form again, but the number of microstates corresponding to a live animal is extremely small compared to all microstates corresponding to the same total energy for all the atoms in the animal.

In some cases, thermal energy can be converted into work. When gas in a cylinder is heated, it expands against a piston that does work. Energy can be supplied to an organism and it lives. To what extent can these processes, which apparently contradict the normal increase of entropy, be made to take place? These questions can be stated in a more basic form.

1. To what extent is it possible to convert internal energy distributed randomly over many molecules into energy that involves a change of a macroscopic parameter of the system? (How much work can be captured from the gas as it expands the piston?)
2. To what extent is it possible to convert a random mixture of simple molecules into complex and highly organized macromolecules?

Both these questions can be reformulated: under what conditions can the entropy of a system be made to decrease?

The answer is that the entropy of a system can be made to decrease if, and only if, it is in contact with one or more auxiliary systems that experience at least a compensating increase in entropy. Then the total entropy remains the same or

increases. This is one form of the *second law of thermodynamics*. For a fascinating discussion of the second law, see Atkins (1994).

One device that can accomplish this process is a *heat engine*. It operates between two thermal reservoirs at different temperatures, removing heat from the hotter one and injecting heat into the cooler one. Even though less heat goes into the cooler reservoir than was removed from the hotter one (the difference being the mechanical work done by the engine), the overall entropy of the two reservoirs increases. The entropy change of the hot reservoir is a decrease, $-\Delta Q/T$, while the entropy change of the cooler reservoir is an increase, $+\Delta Q'/T'$. Since $T' < T$, the entropy increase more than balances the decrease, even though $\Delta Q' < \Delta Q$. The increase in the number of accessible microstates of the cooler reservoir is greater than the decrease in the number of accessible microstates of the hotter reservoir. The coupled chemical reactions that we saw in Sect. 3.17 are analogous.

Symbols Used in Chap. 3

Symbol	Use	Units	First used page
$\mathbf{a}$	Acceleration	m s^{-2}	53
a	Number of atoms in a molecule		57
a, b, c, d	Number of atoms of species A, B, C, and D		71
a	Area	m^2	69
c_j	Concentration (molar)	mol m^{-3}, mol l^{-1}	67
c	Specific heat capacity	J K^{-1} kg^{-1}	65
e	Elementary charge	C	63
f	Number of degrees of freedom		57
g	Gravitational acceleration	m s^{-2}	64
k_B	Boltzmann's constant	J K^{-1}	61
m	Mass	kg	53
n	Number of particles in a volume		54
p	Probability of "success"		55
p	Pressure	Pa	60
p_x, p_y, p_z	Momentum	kg m s^{-1}	65
q	Probability of "failure"		55
q	Electric charge	C	69
t	Time	s	53
u_i	Energy of the ith energy level	J	58
v, v'	Volume	m^3	55
v	Electrical potential	V	63
v, v_x, v_y, v_z	Velocity	m s^{-1}	53
x, y, z	Position coordinate	m	53
x	General variable		59
x	Extensive variable		69
x_s, x_w	Mole fractions of solute and water		73
y	General variable		62
y	Height	m	64
z	Valence		63
A, A', A^*	Thermodynamic systems		60
A, B, C, D	Chemically reacting species		71
C_i, C	Concentration (particles per volume)	m^{-3}, l^{-1}	63
C	Heat capacity	J K^{-1}	65
E_k	Kinetic energy	J	63
E_p	Potential energy	J	63
$\mathbf{F}, F$	Force	N	53
F	Faraday constant	C mol^{-1}	64
G	Ratio of accessible microstates in a small system		62
G	Gibbs free energy	J	70
H	Enthalpy	J	73
K_{eq}	Equilibrium constant in a chemical reaction		71
M	Number of molecules in a system		57
M	Number of repeated measurements		60
N, N', N^*	Number of particles		54
N_w, N_s	Number of solvent (water) or solute molecules		72
N_A	Avogadro's number	mol^{-1}	64
N_A, N_B, N_C, N_D	Number of molecues of species A, B, C, and D consumed or produced in a chemical reaction		71
P	Probability		54
Q	Flow of heat to a system	J	58
R	Ratio of accessible states in a reservoir (Boltzmann factor)		63
R	Gas constant	J mol^{-1} K^{-1}	64
S	Area	m^2	64
S, S', S^*	Entropy	J K^{-1}	62
T	Absolute temperature	K	61
U, U', U^*	Total energy of a system	J	58
V	Volume	m^3	55
$\overline{V}_w, \overline{V}_s$	Volume of water or solute molecule	m^3	74
W	Work done by a system on the surroundings	J	58
W_{conc}	Work done on a system to increase the concentration	J	67
X	Generalized force		69
α	General variable		63
ρ	Density	kg m^{-3}	65
σ	Surface tension	N m^{-1}	69
τ	$k_B T$	J	61
μ	Chemical potential	J molecule^{-1}	66
μ_w, μ_s	Chemical potential of water or solute	J molecule^{-1}	73
$\Omega, \Omega', \Omega^*$	Number of accessible microstates		59
–	An overscript bar means an average over an ensemble		56
$\langle\rangle$	Angular brackets mean an average over time		56

Problems

Section 3.1

Problem 1. Some systems are so small that only a few molecules of a particular type are present, and statistical arguments begin to break down. Estimate the number of hydrogen ions inside an *E. coli* bacterium with $pH = 7$. (When $pH = 7$ the concentration of hydrogen ions is 10^{-7} mol l^{-1}.)

Problem 2. Use the last column of Table 3.2 to calculate the average value of n, which is defined by $\overline{n} = \sum n P(n)$. Verify that $\overline{n} = Np$ in this case.

Problem 3. A loose statement is made that "if we throw a coin 1 million times, the number of heads will be very close to half a million." What is the mean number of occurrences of heads in 1 million tries? What is the standard deviation? What does "very close" mean? (You may need to consult Appendices G and H.)

Problem 4. Evaluate $P(n; 4, 0.5)$ using Eq. 3.4. Check your results against the histogram of Fig. 3.2 and by listing all the possible arrangements of four particles in the left or right sides of the box.

Problem 5. Write a computer program to simulate measurements of which half of a box a gas molecule is in. Make several measurements with different sets of random numbers, and plot a histogram of the number of times n molecules are found in the left half. Try this for $N = 1$, 10, and 100. Many computer languages have a built-in routiine to generate random numbers. For a discussion of how to construct and use random number generators, see Press et al. (1992).

Problem 6. Color blindness is a sex-linked defect. The defective gene is located in the X chromosome. Females carry an XX chromosome pair, while males have an XY pair. The trait is recessive, which means that the patient exhibits color blindness only if there is no normal X gene present. Let X_d be a defective gene. Then for a female, the possible gene combinations are

$$XX, XX_d, X_dX_d.$$

For a male, they are

$$XY, X_dY.$$

In a large population about 8 % of the males are color-blind. What percentage of the females would you expect to be color-blind?

Problem 7. A patient with heart disease will sometimes go into *ventricular fibrillation*, in which different parts of the heart do not beat together, and the heart cannot pump. This is cardiac arrest. The following data show the fraction of patients failing to regain normal heart rhythm after attempts at ventricular defibrillation by electric shock (Weaver 1982).

Number of attempts	Fraction persisting in fibrillation
0	1.00
1	0.37
2	0.15
3	0.07
4	0.02

Assume that the probability p of defibrillation on one attempt is independent of other attempts. Obtain an equation for the probability that the patient remains in fibrillation after N attempts. Compare it to the data and estimate p.

Problem 8. There are N people in a class ($N = 25$). What is the probability that no one in the class has a birthday on a particular day? Ignore seasonal variations in birth rate and ignore leap years.

Problem 9. The death rate for 75-year-old people is 0.089 per year (Commissioners 1941 Standard Ordinary Mortality Table).

(a) What is the probability that an individual aged 75 will die during a 12-h period? Neglect the fact that some are sick, some are terminally ill, and so on, and assume that the probability is the same for everyone.

(b) Suppose that 10 000 people, all aged 75, are given the flu vaccine at $t = 0$. What is the probability that none will die during the next 12 h? (This underestimates the probability, since sick people would not be given the vaccine, but they are included in the death rate.)

Problem 10. This problem is intended to help you understand some of the nuances of the binomial probability distribution.

(a) In a macabre "game" of "roulette" the victim places one bullet in the cylinder of a revolver. (A less hazardous game could be done with dice.) There is room for six bullets in the cylinder. The victim spins the cylinder, so there is a probability of 1/6 that the bullet is in firing position. The victim then places the gun to the head and fires. If the victim survives, the cylinder is spun again and the process is repeated. We can look either at the cumulative probability of "success" (being killed), or the cumulative probability of "failure" (surviving). Make a table for 1000 victims who keep playing the game over and over. Plot the number surviving, the number killed on each try, and the cumulative number killed.

(b) Show that the number surviving can be expressed as $1000e^{-bN}$, where N is the number of tries, and find b.

(c) The data in the following table are from Schwartz and Mayaux (1982). They show the cumulative success rates in different age groups for patients being treated for infertility by artificial insemination from a donor. That is, each month at the time of ovulation each patient who has not yet become pregnant is inseminated artificially.

The table shows the fraction of patients who have become pregnant at the end of each cycle. Plot these data. What do they suggest? Make whatever plots can confirm or rule out what you suspect.

Cycle	Age ≤ 25	Age $\geqslant 35$
0	0	0
1	0.11	0.03
2	0.23	0.14
3	0.30	0.20
4	0.39	0.27
5	0.44	0.35
6	0.51	0.35
7	0.55	0.36
8	0.63	0.39
9	0.65	0.43
10	0.67	0.43
11	0.70	0.46
12	0.74	0.54

Problem 11. Use Eq. 3.4 to verify that the probability of all 80 particles being in the left half of the box is approximately 10^{-24}.

Problem 12. Appendix H describes how to calculate the magnitude of fluctuations for N particles in a box (the standard deviation). Calculate $\langle n \rangle$ and its standard deviation for $N = 80$ and $p = q = 0.5$. Estimate the value of N in Fig. 3.4.

Section 3.3

Problem 13. A thermally insulated ideal gas of particles is confined within a container of volume V. The gas is initially at absolute temperature T. The volume of the container is very slowly reduced by moving a piston that constitutes one wall of the container. Give qualitative answers to the following questions.

(a) What happens to the energy levels of each particle?
(b) Is the work done on the gas as its volume decreases positive or negative?
(c) What happens to the energy of the gas?

Section 3.5

Problem 14. Suppose you have a system with 10 particles and three energy levels. The particles are distributed among the levels as follows: 5 particles are in the level with energy 0, three particles are in the level with energy $2E$, and two in the level with energy $4E$. An interaction with the surroundings occurs in which work is done on the system and heat flows out of the system in such a way that $\Delta U = 0$. The work causes the energy of each level to rise by an amount E.

(a) Draw a picture like Fig. 3.7 showing the new levels and the distribution of particles among the levels before and after the interaction.
(b) Calculate the average energy of the particles before and after the interaction.
(c) Draw a picture like that in Fig. 3.8 appropriate for this system.

Problem 15. System A has 10^{20} microstates, and system A' has 10^{19} microstates. How many microstates does the combined system have?

Problem 16. Calculate the Celsius and absolute temperatures corresponding to a room temperature of 68 °F, a normal body temperature of 98.6 °F, and a febrile body temperature of 104 °F.

Problem 17. Calculate and plot Ω, Ω', and Ω^* for Fig. 3.10, thus reproducing the figure. Write down an analytic expression for Ω^* and differentiate to find the value of U for which Ω^* is a maximum.

Problem 18. Let $\Omega(U) = 5U^2 + 1$, $\Omega'(U') = U' + 1$, and $U + U' = 100$. Make plots like those in Fig. 3.10 for this system and determine the most probable value of U.

Problem 19. Systems A and A' each consist of 3 particles, whose energy levels are u, $2u$, $3u$, etc. The total energy available to the combined system is $U^* = 12u$.

(a) Make a table similar to Table 3.3. (If you have difficulty, see part (d) of this problem.)
(b) Find the most probable state. To what values of U and U' does it correspond?
(c) Plot Ω^* vs U. What is the probability that all three particles in system A have energy u?
(d) Consider system A. If it has energy U, the maximum energy the first particle can have is $U - 2u$. How many microstates are there for which the first particle has energy $U - 2u$? $U - 3u$? Show that the total number of microstates for system A is given by

$$\sum_{i=1}^{U/u-2} \left(\frac{U}{u} - i - 1 \right) = \frac{1}{2} \left[\left(\frac{U}{u} \right)^2 - 3 \left(\frac{U}{u} \right) + 2 \right].$$

This proves the assertion in the text that for 3 particles, Ω increases as U^2.

Problem 20. We have seen that in general with volume, number of particles, and other parameters that determine the positions of the energy levels held fixed,

$$\frac{1}{\Omega} \frac{d\Omega}{dU} = \frac{1}{k_B T}.$$

Suppose that $U = CT$, where C is the heat capacity of the system. Find $\Omega(U)$.

Problem 21. Systems A and A' are in thermal contact. Show that if $T < T'$, energy flows from A' to A to increase Ω^*, while if $T > T'$, energy flows from A to A'.

Problem 22. A simple system has *only two* energy levels for each single entity in the system. (The system could, for example, be a collection of "gates" in a cell membrane, each

with two states, open and closed.) One level has energy u_1, the other has energy u_2. There are N entities in the system. You can answer the following questions without doing any calculations.

(a) What is the minimum energy of the system? How many microstates are there for the minimum energy?
(b) What is the maximum energy of the system? How many microstates are there for which the system has maximum energy?
(c) Sketch what $\Omega(U)$ must look like.
(d) Recall the definition of T, Eqs. 3.14 and 3.15. Are there any values of U for which the temperature is negative? Where?

Section 3.6

Problem 23. Calculate the temperature (in K) and entropy (in eV K^{-1}) of system A' in Fig. 3.10 at equilibrium. Assume U and U' are given in electron volts. Your values may seem odd because this example is not biologically realistic.

Problem 24. Consider the following arrangements of the 26 capital letters of the English alphabet: (a) TWO, (b) any three letters, in any order, that are all different, and (c) any three letters, in any order, which may repeat themselves. For (b) and (c), consider the same letters in a different order to be a different arrangement. If each arrangement is a "microstate," find Ω and S in each case.

Problem 25. Ice and water coexist at 273 K. To melt 1 mol of ice at this temperature, 6 000 J are needed. Calculate the entropy difference and the ratio of the number of microstates for 1 mol of ice and 1 mol of water at this temperature. Do not worry about any volume changes of the ice and water.

Problem 26. If a system is maintained at constant volume, no work is done on it as the energy changes. In that case $dU = C(T)\,dT$, where U is the internal energy, C is the heat capacity, and T is the temperature. The heat capacity in general depends on the temperature. Suppose that in some temperature region the heat capacity varies linearly with temperature: $C(T) = C_0 + DT$.

(a) What is the entropy change of the system when it is heated from temperature T_1 to temperature T_2, both of which are in the region where $C(T) = C_0 + DT$?
(b) What is the ratio of the number of microstates at T_2 to the number at T_1?

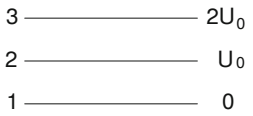
Problem 27. A substance melts at constant temperature. There are 7 times as many microstates accessible to each molecule of the liquid as there were to each molecule of the solid. Ignore volume changes.

(a) What is the change in entropy of each molecule?
(b) How much heat is required to melt a mole of the substance if the melting temperature is 50 °C?

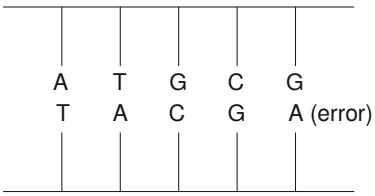
Problem 28. The entropy of a monatomic ideal gas at constant energy depends on the volume as $S = Nk_B \ln V + \text{const.}$ A gas of N molecules undergoes a process known as a free expansion. Initially it is confined to a volume V by a partition. The partition is ruptured and the gas expands to occupy a volume $2V$. No work is done and no heat flows, so the total energy is unchanged. Calculate the change of entropy and the ratio of the number of microstates after the volume change to the number before.

Section 3.7

Problem 29. A pore has three configurations with the energy levels shown. The pore is in thermal equilibrium with the surroundings at temperature T. Find the probabilities p_1, p_2, and p_3 of being in each level. Each level has only one microstate associated with it.



Problem 30. The DNA molecule consists of two intertwined linear chains. Sticking out from each monomer (link in the chain) is one of four bases: adenine (A), guanine (G), thymine (T), or cytosine (C). In the double helix, each base from one strand bonds to a base in the other strand. The correct matches, A–T and G–C, are more tightly bound than are the improper matches. The chain looks something like this, where the last bond shown is an "error."



The probability of an error at 300 K is about 10^{-9} per base pair. Assume that this probability is determined by a Boltzmann factor e^{-U/k_BT}, where U is the additional energy required for a mismatch.

(a) Estimate this excess energy.
(b) If such mismatches are the sole cause of mutations in an organism, what would the mutation rate be if the temperature were raised 20 °C?

Problem 31. In Chap. 18 we will study how the "spin" magnetic moment of an atomic nucleus interacts with a magnetic field **B**, leading to magnetic resonance imaging. Assume a nucleus has a *magnetic dipole moment* μ, which can point in only one of two directions: parallel to B ("spin up") or antiparallel ("spin down"). The energy of a nucleus with spin up is $-\mu B$; with spin down it is $+\mu B$. Use the Boltzmann factor to determine an expression for the ratio of the number of particles with spin up to the number with spin down.

Evaluate this ratio for $\mu = 1.4 \times 10^{-26}\,\mathrm{J\,T^{-1}}$, $B = 2\,\mathrm{T}$, and $T = 300\,\mathrm{K}$.

Problem 32. The data of Problem 2.10 were used to obtain an empirical relationship between the charge integration time τ and the temperature T. It might be that τ is determined by a chemical reaction whose rate is given by a Boltzmann factor. Make a new plot based on that assumption and determine the appropriate constants.

Problem 33. Oxygen and carbon monoxide compete for binding to hemoglobin. If enough CO binds to hemoglobin, the ability of the blood to deliver oxygen is impaired, and carbon monoxide poisoning ensues. Consider the hemoglobin molecule to be a two-state system: the heme group is bound either to O_2 or to CO. Calculate the probability of binding to CO. Let the G factor of Eq. 3.25 be equal to the ratio of the concentrations of CO and O_2. Assume CO is 100 times less abundant than O_2. CO is more tightly bound than O_2 to the heme group by about 0.15 eV. Let $T = 300$ K.

Problem 34. The function of many enzymes is to act as a *catalyst*: they increase the speed of a chemical reaction. To get an idea of how a catalyst works, consider the reaction

$$\text{enzyme} + \text{substrate} \rightarrow \text{enzyme} + \text{product}.$$

In order for the reaction to proceed, some energy barrier ΔE must be overcome. The probability of the substrate having an energy ΔE or greater depends primarily on a Boltzmann factor, $e^{-\Delta E/k_B T}$. Determine by what factor this probability increases if the enzyme decreases the activation energy by (a) 0.1 eV, (b) 1 eV. Assume $T = 310\,\mathrm{K}$.

Problem 35. Chemists use Q_{10} to characterize a chemical reaction. It is defined by

$$Q_{10} = \frac{(\text{reaction rate at } T + 10)}{(\text{reaction rate at } T)},$$

where T is the absolute temperature. If the reaction rate is proportional to the fraction of reacting atoms that have an energy exceeding some threshold ΔU, then to a first approximation

$$R \propto \int_{\Delta U}^{\infty} e^{-U/k_B T}\, dU.$$

(This neglects more slowly varying factors such as a $U^{1/2}$ which are introduced in more accurate analyses.)

(a) Show that $R \propto k_B T e^{-\Delta U/k_B T}$.

(b) Show that

$$\frac{Q_{10} T}{T + 10} = \exp\left[\frac{\Delta U}{k_B}\frac{10}{T(T + 10)}\right].$$

(c) Estimate ΔU if $Q_{10} = 2$ at $T = 300$ K.

Problem 36. The vapor pressure of a substance can be calculated using the following model. All molecules in the vapor that strike the surface of the liquid stick. (This number is proportional to the pressure.) Those molecules in the liquid that reach the surface and have enough energy escape. Equilibrium is established when the number sticking per unit area per unit time is equal to the number escaping.

(a) The number of molecules with energy U is proportional to $e^{-U/k_B T}$. What will be the number with energy greater than the escape energy, U_0?

(b) Use the result of part (a) and look up values for the vapor pressure of water as a function of temperature, to make a plot on semilog paper. From this plot, estimate the escape energy U_0.

(c) The "heat of vaporization" of water is 540 cal per g. Convert the energy per molecule you found in part (b) to calories per gram and compare it with this figure.

Problem 37. A macromolecule of density ρ and mass m is immersed in an incompressible fluid of density ρ_w at temperature T. The volume v occupied by one macromolecule is known. A dilute solution of the macromolecules is placed in an ultracentrifuge rotating with high angular velocity ω. In the frame of reference rotating with the centrifuge, a particle at rest is acted on by an outward force $m\omega^2 r$, where r is the distance of the particle from the axis.

(a) What is the net force acting on the particle in this frame? Include the effect of buoyancy of the surrounding fluid, of density ρ_w.

(b) Suppose that equilibrium has been reached. Use the Boltzmann factor to find the number of particles per unit volume at distance r.

Problem 38. Suppose that particles in water are subjected to an external force $F(y)$ that acts in the y direction. The force is related to the potential energy $E_p(y)$ by $F = -dE_p/dy$. Neglect gravity and buoyancy effects.

(a) Apply Newton's first law to a slice of the fluid in equilibrium to obtain an expression for $p(y)$.

(b) If the particles have a Boltzmann distribution, show that $p(y) - p(0) = k_B T\,\big[C(y) - C(0)\big]$.

Section 3.8

Problem 39. The concentrations of various ions are measured on the inside and outside of a nerve cell. The following values are obtained when the potential inside the cell is −70 mV with respect to the outside.

Ion	Inside (mmol $\mathrm{l^{-1}}$)	Outside (mmol $\mathrm{l^{-1}}$)
Na^+	15	145
K^+	150	5
Cl^-	9	125

Comment on which species have concentrations that are consistent with being able to pass freely through the cell wall. Assume $T = 300$ K.

Problem 40. Calculate the volume of 1 mole of water in liters. Pour yourself a mole of water and drink it. Calculate the concentration of water in moles per liter.

Section 3.9

Problem 41. A virus has a mass of 1.7×10^{-14} g. If the virus particles are in thermal equilibrium in the atmosphere, their concentration will vary with height as $C(y) = C(0)e^{-y/\lambda}$. Evaluate λ. Do you think this answer is reasonable?

Problem 42. Calculate the length constant λ for the exponential decay ($e^{-y/\lambda}$) of atmospheric pressure. Assume the atmosphere is made up entirely of nitrogen, N_2. Nitrogen has an atomic weight of 14. Use your result to compare air pressure at sea level to air pressure at the top of Mt. Everest (8.8 km). Assume the atmosphere is all at the same temperature; it is not.

Section 3.10

Problem 43. Use Appendix K to verify the expressions given for the integrals in the numerator and denominator of Eq. 3.37.

Problem 44. Calculate the average kinetic energy (in J and eV) of a particle moving in three dimensions at body temperature, 37 °C .

Problem 45. This is our first model for the important problem of detecting a "signal" in the presence of "noise." We will discuss this in detail in Chapters 9 and 11. A sensitive balance consists of a weak spring hanging vertically in the earth's gravitational field. The equilibrium position of the end of the spring is $x = 0$. When a mass m is added to the spring, it elongates to an average position x_0, around which it vibrates because of thermal energy. In terms of $\Delta x = x - x_0$, the momentum of the mass p_x and the spring constant K, the force which the spring exerts on the mass is Kx_0, and the total energy is $U = p_x^2/2m + \frac{1}{2}K(\Delta x)^2$.

(a) What is x_0 in terms of m, g, and K?
(b) Find $\overline{\Delta x^2} = \overline{(x - x_0)^2}$.
(c) What is the smallest mass that can be measured taking a single "snapshot" of the system to find the position of the mass?

Section 3.11

Problem 46. The specific heat capacity of water is $4\,184\,\mathrm{J\,K^{-1}\,kg^{-1}}$ (Denny 1993). Convert this to cal $\mathrm{g^{-1}\,°C^{-1}}$. Historically, the calorie was defined in terms of the specific heat capacity of water.

Problem 47. The "Calorie" we see listed on food labels is actually 1 000 cal or 1 kcal. How many kcal do you expend each day if your average metabolic rate is 100 W?

Problem 48. Your body must dissipate energy from metabolism at a rate of about 100 W by various mechanisms to keep the body from overheating. Suppose these mechanisms stopped working (perhaps you are wrapped in a very good thermal blanket, so no heat can flow from or to your body). At what rate will your body temperature increase? How long will it take for your body temperature to increase by 5 °C? Assume you have a mass of 70 kg, and the specific heat of your body tissue is the same as of water, $4\,200\,\mathrm{J\,K^{-1}\,kg^{-1}}$.

Problem 49. A person of mass 70 kg and body temperature 37 °C breathes in 0.5 l of air at a temperature of 20 °C. Assume that there are no other sources of heat (turn off metabolism for a moment), and the body as a whole is insulated so no heat is lost to the environment. Find the equilibrium temperature that the air and body will ultimately attain. Useful data: $\rho_{\mathrm{air}} = 1.3\ \mathrm{kg\,m^{-3}}$, $\rho_{\mathrm{water}} = 1000\ \mathrm{kg\,m^{-3}}$, $c_{\mathrm{air}} = 1000\ \mathrm{J\ K^{-1}\ kg^{-1}}$, $c_{\mathrm{water}} = 4200\ \mathrm{J\,K^{-1}\ kg^{-1}}$. Assume that the person's body tissue has the same heat capacity and density as water.

Problem 50. Fish are cold blooded, and "breathe" water (in other words, they extract dissolved oxygen from the water around them using gills). Could a fish be warm blooded and still breathe water? Assume a warm-blooded fish maintains a body temperature that is 20 °C higher than the surrounding water. Furthermore, assume that the blood in the gills is cooled to the temperature of the surrounding water as the fish breathes water. Calculate the energy required to reheat 1 l of blood to the fish's body temperature. One liter of blood carries sufficient oxygen to produce about 4000 J of metabolic energy. Is the energy needed to reheat 1 l of blood to body temperature greater than or less than the metabolic energy produced by 1 l of blood? What does this imply about warm-blooded fish? Why must a warm-blooded aquatic mammal such as a dolphin breathe air, not water? Use $c = 4\,200\,\mathrm{J\ K^{-1}\,kg^{-1}}$ and $\rho = 10^3\,\mathrm{kg\ m^{-3}}$ for both the body and the surrounding water. For more on this topic, see Denny (1993).

Problem 51. Forensic scientists sometimes use *Newton's law of cooling* to determine how long ago a victim died. Assume that at the time of death (t_{death}) the body had a temperature T_{body}, and after death it cools to the temperature of the surroundings, T_{surr}. Assume that the rate of heat loss by the body is proportional to the surface area of the body, S, and the temperature difference $T - T_{\mathrm{surr}}$. The constant of proportionality is called the *convection coefficient*. As the corpse cools, the decrease in temperature is determined by the heat capacity.

(a) Relate the rate of heat loss to the rate of temperature change, and derive a differential equation for the body temperature T.

(b) Solve this differential equation (if you are having trouble, see Sect. 2.8). The solution is Newton's law of cooling.
(c) Write an expression for the time constant of cooling in terms of the specific heat capacity, density, volume, area, and the convection coefficient.
(d) For two bodies with the same shape but different sizes, which will cool faster: the large body or the small one?

Problem 52. Determine whether the specific heat capacity of air, 1000 J K^{-1} kg^{-1} is the same as the molar specific heat capacity of a monatomic ideal gas, $3R/2$. If not, why not? Assume air is all nitrogen, N_2.

Section 3.12

Problem 53. Modify the system shown in Fig. 3.10 so that $\Omega(U, N) = 5U^2N^3$, $\Omega'(U') = 4(U')^2(N')^3$, $U + U' = 6$, and $N + N' = 10$.
(a) Show that this change does not affect the calculation of the temperature.
(b) Plot $\Omega(N)$, $\Omega'(N')$ and $\Omega^*(N)$ over $0 < N, N' < 10$ using the equilibrium value $U = 3\,\text{eV}$.
(c) Find the average value $\langle N \rangle$.
(d) Calculate the chemical potential (in eV) in equilibrium.

Problem 54. A small system A is in contact with a reservoir A' and can exchange both heat and particles with the reservoir. The number of microstates available to system A does not change. Show that the difference in total entropy when A is in two distinct states is

$$\Delta S^* = -(N_1 - N_2)\left(\frac{\partial S}{\partial N}\right)_U - (U_1 - U_2)\left(\frac{\partial S}{\partial U}\right)_N,$$

so that

$$\frac{P(N_1, U_1)}{P(N_2, U_2)} = \frac{e^{(N_1\mu - U_1)/k_BT}}{e^{(N_2\mu - U_2)/k_BT}}.$$

where T and μ are the temperature and chemical potential of the reservoir. This is called the *Gibbs factor*, and it reduces to the Boltzmann factor if $N_1 = N_2$. Chemists use the notation $\lambda = e^{\mu/k_BT}$, where λ is the absolute activity. Then

$$\frac{P(N_1, U_1)}{P(N_2, U_2)} = \frac{\lambda^{N_1}}{\lambda^{N_2}} \frac{e^{-U_1/k_BT}}{e^{-U_2/k_BT}}.$$

Problem 55. Specialize the results of the previous problem to a series of binding sites on a surface, such as a myoglobin molecule. The two states are

No particle bound at the site	$N_1 = 0$,	$U_1 = 0$
One particle bound at the site	$N_2 = 1$,	$U_2 = U_0$

(a) Show that the fraction of sites occupied is

$$f = \frac{\lambda e^{-U_0/k_BT}}{1 + \lambda e^{-U_0/k_BT}}.$$

(b) If the sites are in equilibrium with a gas, then $\mu_{\text{gas}} = \mu_{\text{sites}}$ or $\lambda_{\text{gas}} = \lambda_{\text{sites}}$. From the definition $\mu = -T(\partial S/\partial N)_{U,V}$ and the expression for the entropy of a monatomic ideal gas,

$$S(U, V, N) = Nk_B\left(\ln V + \frac{3}{2}\ln U - \frac{5}{2}\ln N + \frac{5}{2} + c\right),$$

where $c = \frac{3}{2}\ln(m/3\pi\hbar^2)$, show that $f = p/(p_0 + p)$, where p is the gas pressure and

$$p_0 = \frac{(k_BT)^{5/2}\, m^{3/2}\, e^{U_0/k_BT}}{(2\pi\hbar^2)^{3/2}}.$$

This expression fits the data very well. See Rossi-Fanelli and Antonini (1958).

Section 3.13

Problem 56. The entropy of a monatomic ideal gas is

$$S(U, V, N) = Nk_B\left(\ln V + \frac{3}{2}\ln U - \frac{5}{2}\ln N + \frac{5}{2} + c\right),$$

where $c = \frac{3}{2}\ln(m/3\pi\hbar^2)$ depends only on the mass of the molecule. Consider two containers of gas at the same temperature and pressure that can exchange particles. Expand the total entropy in a Taylor's series, keep terms to second order, and use the result to find the variance in the fluctuating number of particles in one system. Assume $N \ll N'$. You should obtain the same result obtained from the binomial distribution ($\sigma^2 = N$) if you take into account that it is the *temperature* of the gas in the container, and not its energy, that should be held fixed. (For a monatomic ideal gas $U = 3Nk_BT/2$. Use this result to rewrite the entropy in terms of T, V, and N.)

Problem 57. Show that the chemical potential of an ideal gas is proportional to the logarithm of the concentration, a result that we have now seen several times for dilute ideal systems. To do so, use the expression for the entropy of a monatomic ideal gas given in the previous problems. Rewrite the thermodynamic identity as $dU = TdS + \mu\, dN - p\, dV$, from which we can identify the partial derivative

$$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}.$$

The chemical potential is the increase in energy of the system if one particle is added while keeping the entropy and volume fixed. Use the expression for the entropy of the monatomic ideal gas, for the case of N particles with total energy U and $N + 1$ particles with total energy $U + \mu$, to show that the chemical potential of the ideal gas is

$$\mu = k_BT\left[\ln\left(\frac{N}{V}\right) - \frac{3}{2}\ln(3k_BT/2) - \text{const}\right]$$

or

$$\mu = -k_B T \ln\left[\frac{V}{N}\left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}\right].$$

A more extensive discussion for other simple systems is given by Cook and Dickerson (1995).

Problem 58. Derive the Nernst equation (Eq. 3.34) by making the chemical potential the same on each side of a charged membrane. Use Eq. 3.48, with the potential energy per particle given as zev.

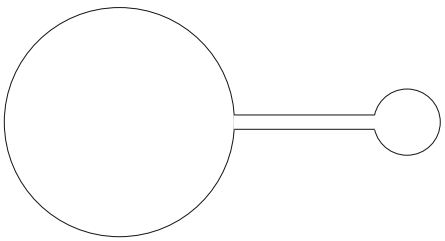
Section 3.15

Problem 59. Consider two systems that can exchange energy U and surface area a, but not volume V or number of particles N. The total energy is $U^* = U + U'$ and the total surface area is $a^* = a + a'$. Repeat the analysis of Sect. 3.5 and show that in equilibrium $T = T'$ and $\sigma = \sigma'$, where the surface tension is defined as

$$\sigma = -T\left(\frac{\partial S}{\partial a}\right)_{U,V,N}.$$

Problem 60. Consider a spherical air bubble in water.

(a) Equate the pressure-volume work to the surface work, and find a relationship between the pressure and the radius. This relationship is analogous to the Law of Laplace (Problem 1.19).



(b) Consider a small bubble attached to a large one. Use the relationship derived in (a) to determine which bubble has the larger internal pressure. Which bubble tends to shrink and which tends to expand?

(c) The bubbles in (b) are a model for two alveoli connected by a bronchiole in our lungs. Explain why a special fluid called a surfactant is needed to reduce the surface tension in the water on the surface of the alveolus. For more on the biological implications of surface tension, see Denny (1993).

Section 3.16

Problem 61. Use the analysis presented in Sect. 3.16 to show that the surface tension is

$$\sigma = \left(\frac{\partial U}{\partial a}\right)_{S,V,N}.$$

Therefore, increasing the surface area when the entropy, volume and number of particles are fixed requires energy. For water, the surface tension is approximately $0.07\,\mathrm{J\ m^{-2}}$, which is a large value Denny (1993).

Section 3.17

Problem 62. The reaction $1\ \mathrm{glucose} + 6O_2 \leftrightarrow 6CO_2 + 6H_2O$ must conserve the number of each type of atom. Determine the chemical formula of glucose.

Section 3.18

Problem 63. System A consists of N particles that move from a region where the concentration is C_1 to another where the concentration is C_2, each experiencing a change in chemical potential $\Delta\mu = k_B T\ \ln(C_2/C_1)$. The process occurs at constant temperature and pressure. What is the ratio of the total number of microstates of system and surroundings after the move to the number before the move? Assume the concentrations do not change.

Problem 64. In pure water, some of the molecules dissociate into $H_2O \rightarrow H^+ + OH^-$. The standard Gibbs free energies are $G^0_{\mathrm{H2O}} = -237.2\,\mathrm{kJ\ mol^{-1}}$, $G^0_{\mathrm{OH}} = -157.3\,\mathrm{kJ\ mol^{-1}}$ and $G^0_{\mathrm{H}} = 0$.

(a) Determine ΔG^0 for this reaction.

(b) Calculate K_{eq} assuming $T = 25\,^\circ\mathrm{C}$.

(c) Derive an expression that relates K_{eq}, $[H^+]$ and $[OH^-]$. Note: By convention the reference concentration for water is taken to be the concentration of pure water instead of 1 mole per liter. The small amount of dissociation does not change $[H_2O]$ significantly, so the logarithmic term for water is zero: $K_{eq} = [H^+][OH^-]$.

(d) H^+ and OH^- are produced as a pair, so their concentrations are equal. Calculate $[H^+]$.

(e) The pH of water is defined as $-\log_{10}([H^+])$. What is the pH of pure water?

Problem 65. If one increases the volume of a liquid at constant p and T, a portion of the liquid evaporates. The amount of liquid decreases as V increases until all the liquid is vaporized. The pressure at which the two phases coexist is called the *vapor pressure*. The vapor pressure depends on the temperature, as shown. When two phases are in equilibrium, they are in mechanical, thermal, and diffusive equilibrium:

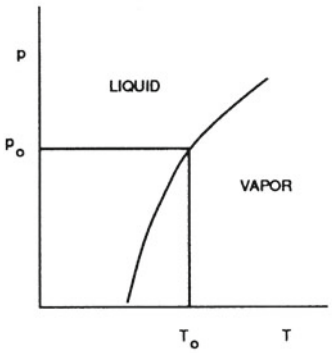
$T_l = T_g$, $p_l = p_g$, $\mu_l = \mu_g$. Thus, at any arbitrary point on the vapor-pressure curve, $\mu_g(T_0, p_0) = \mu_l(T_0, p_0)$. Consider some nearby point in the vapor-pressure curve, and expand both chemical potentials in a Taylor's series to show that

$$\frac{dp}{dT} = \frac{(\partial\mu_g/\partial T)_p - (\partial\mu_l/\partial T)_p}{(\partial\mu_l/\partial p)_T - (\partial\mu_g/\partial p)_T},$$

where dp/dT is the slope of the vapor-pressure curve. Use the fact that $G = N\mu(p, T)$, that $(\partial G/\partial T)_{N,p} = -S$, and that $(\partial G/\partial p)_{N,T} = V$, to show that

$$\frac{dp}{dT} = \frac{L}{T\Delta V},$$

where L is the latent heat of vaporization and ΔV is the volume change on vaporization. (Since L and V are both extensive parameters, they can be expressed per mole or per molecule.) This is called the *Clausius–Clapeyron* equation.



Problem 66. Use the Clausius–Clapeyron equation for the vapor pressure as a function of temperature (see Problem 65), $dp/dT = L/T\Delta V$, and assume an ideal gas so that $\Delta V \approx V_g = Nk_BT/p$ to find the vapor pressure p as a function of temperature.

Problem 67. Use the definition of Gibbs free energy $G = U - TS + pV$ and the thermodynamic identity $T\,dS = dU - \mu\,dN + p\,dV$ to find the partial derivatives of G when N, T, and p are the independent variables. Note that U, S, and V are all extensive variables so that G is proportional to N: $G = N\Phi$. Thereby relate Φ to the chemical potential.

Problem 68. (a) Find the change in Gibbs free energy $G = U - TS + pV$ for an ideal gas which changes pressure reversibly from p_1 to p_2 at a constant temperature.

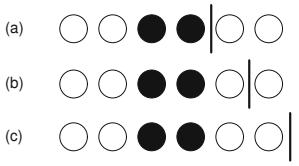
(b) Since $\Delta G = N\Delta\mu$, find $\Delta\mu$.

Problem 69. The argument leading to the change in G in a chemical reaction can be applied to a single particle moving from a region where the chemical potential is μ_A to a region where the chemical potential is μ_B by letting $dN = -dN_A = dN_B$, in which case $dG = (\mu_B - \mu_A)\,dN$. We saw in Sect. 3.13 that the chemical potential of a solute in an ideal solution had the form $\Delta\mu = k_BT\,\ln(C/C_0) + \Delta$(potential energy per particle). Sodium ions of charge $+e$ ($e = 1.6 \times 10^{-19}$ C) are found on one side of a membrane at concentration 145 mmol l^{-1}. The electrical potential is zero. On the other side of the membrane the concentration is 15 mmol l^{-1} and the potential is -90 mV. The change in electrical potential energy is $e\Delta v$. What is the change in Gibbs free energy if a single sodium ion goes from one side to the other? The temperature is 310 K and the pressure is atmospheric.

Section 3.18

Problem 70. Suppose that a potential energy term as well as a pressure must be added to the chemical potential, as was argued in Sect. 3.13. Consider a column of pure water. What is the difference in chemical potential between the top of the column and the bottom?

Problem 71. The open circles in the drawing represent water molecules. The solid circles are solute molecules. The vertical line represents a membrane that is permeable to water but not solute. In case (a) there are two water molecules to the right of the membrane. In (b) there is one, and in (c) none. What is the total number of microstates of the combined system in each case?



Problem 72. If we want to apply Eq. 3.79 when there is an appreciable difference in concentration, we can define an average concentration by

$$\Delta\mu_s = k_BT\,\ln(C_{s2}/C_{s1}) \equiv k_BT\,(\Delta C_s/\overline{C}_s),$$

$$\overline{C}_s \equiv \frac{\Delta C_s}{\ln(C_{s2}/C_{s1})} = \frac{\Delta C_s}{\ln(1 + \Delta C_s/C_{s1})}.$$

Use the Taylor's-series expansion $y = x/ln(1 + x) \approx 1 + x/2 - x^2/12 + \cdots$ to find an approximate expression for $\overline{C}_s$.

Problem 73. Verify that differentiation of Eq. 3.69 with respect to N_w and N_s gives Eq. 3.71.

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