

Chapter *13*

Thermodynamics

Introduction

When we discussed the ideal gas, we were able to justify the empirical equation of state $pV = NkT$ from the point of view of Newtonian mechanics. We achieved this by *defining* certain intuitive ideas, such as temperature, in terms of precise mechanical concepts and by making reasonable assumptions concerning the statistical distribution of velocities in the gas. We also showed that our definition of temperature as proportional to the average kinetic energy is consistent with our intuitive notion. Our approach, however, has several weak points. First, our definition of temperature as proportional to the average kinetic energy is appropriate for an ideal gas, for which the potential energy is zero by definition. But we would like to define temperature for all systems, including those (such as solids) whose potential energy is significant or even larger in magnitude than the kinetic energy. It is by no means obvious that our definition of temperature for an ideal gas can be used in other material systems. An even more serious problem with our approach is that we still don't know how to explain the simplest phenomenon that occurs when two bodies are brought into thermal contact: the fact that their temperatures become equal. What is the driving "force" for this phenomenon? Why is it that energy flows from the object with the highest temperature to the object with the lowest temperature? A reversed energy flow would not violate Newton's laws, because energy would still be conserved. However, an spontaneous flow of energy from a cold object to a hot object is never observed. Why?

In principle, the above questions can be answered with Newtonian mechanics. Given the initial positions and velocities of any system, we can use Newton's laws to predict the positions and velocities at any later time, so that we can compute any desired property. (Of course, Newtonian mechanics is superseded by quantum mechanics, but this doesn't change the argument. If we use quantum mechanics, we know that given the initial wave function of our system we can calculate the wave function at all later times by applying Schrödinger's equation. All measurable quantities

can be calculated from a knowledge of the wave function). From a practical point of view, however, our task is completely unrealistic. The number of particles in any macroscopic system is so fantastically high, that there is absolutely no hope of computing the evolution of the system by using Newton's laws. Remember the time it took your spreadsheet to calculate the position as a function of time for two masses connected by springs. How long would it take to do the same for 10^{25} particles? How much computer memory would you need? In one of the end of chapter problems, you are asked to compute the time needed to print the initial positions and velocities for the atoms in a small volume of gas. You will be surprised when you compare this time with the age of the universe. On the other hand, even if we were able to apply Newtonian mechanics to a system of very many particles, this approach appears as overkill when we try to explain such simple phenomena as the equalization of temperatures for objects in thermal contact. This is a very simple phenomenon known by everybody, even those without any instruction in physics. Simple phenomena are often the result of simple underlying laws. There must be some simple principle that allows us to solve these problems without the full machinery of Newton's laws. The branch of physics that deals with this topic is **thermodynamics**.

The suffix "dynamics" to the word "thermodynamics" emphasizes the fact that we are seeking an alternative to the use of Newtonian dynamics. However, it is somewhat misleading in that thermodynamics does not provide the time-dependence of the properties of the system. In other words, thermodynamics, as you will soon learn, can explain why two bodies in thermal contact reach the same final temperature but says nothing about the time needed for this common temperature to be reached. This partial lack of information is one of the prices we will pay for not using Newton's laws to compute the properties of the system. Thermodynamics deals with **equilibrium** states: those states of the system for which the macroscopic properties are constant as a function of time. For example, if we let a gas

expand in a volume, eventually the gas will occupy the entire volume. Thermodynamics will be able to predict the properties of the gas once the entire volume is occupied, but will not be able to make any predictions on the properties of the gas while it is expanding, nor to compute the time needed for this expansion. Typically, the expansion of a gas in a “human-size” volume takes a few seconds. In other cases, the time needed by a system to reach a true “equilibrium” state may be extremely long. A diamond, for example, (which according to the TV ads is “forever”) is unstable relative to graphite: if you wait long enough, all diamonds should become cheap graphite crystals. However, you don’t need to be concerned about the diamonds you may have at home: they will outlast you and whoever you designate as your heir.

The thermodynamic system

We will deal with systems of particles that are characterized by a few **macroscopic** parameters. Examples of such parameters are the pressure in a gas, the volume, the electric and magnetic moments, the temperature, the total number of particles, etc. Another set of useful macroscopic parameters are quantities that are conserved in isolated systems of particles, such as the internal energy U , the total linear momentum \mathbf{p} , and the total angular momentum \mathbf{L} . In our discussions, however, we will only consider systems for which the total linear and angular momenta are zero. If we have gas in a container, this insures that the container is fixed in space and that the gas is not rotating as a whole. These conditions must be relaxed when thermodynamic ideas are applied to the study of the atmosphere or to stellar gases, but we will not deal with these subjects.

The macroscopic parameters are usually the only quantities we are interested in. For example, when you buy a six-pack you only specify the volume, the relative number of particles (alcohol vs. water, etc.) and the temperature. This is very little information for such a complicated system of zillions of particles. The predictions we will make with thermodynamics concern those macroscopic parameters: we will be able to compute their “final” values once equilibrium is

reached.

Extensive and intensive macroscopic parameters

An important distinction can be made between macroscopic parameters. Some of them are called **extensive** because they scale with the size of the system. Other parameters are called **intensive** because they are independent of the size of the system. For example, if we connect two identical samples of a gas, the volume, the number of particles and the energy double, whereas the temperature and the pressure remain the same. Energy, number of particles and volume are extensive parameters; pressure and temperature are intensive parameters.

Dependent and independent macroscopic parameters

From our discussion of the ideal gas, it is apparent that not all macroscopic parameters are independent. For example, the pressure, the volume, the temperature and the number of particles in an ideal gas are related by the equation of state $pV = NkT$. The formal development of the theory of thermodynamics requires that a set of independent parameters be identified. The values of the other parameters are found from **equations of state**, such as the one we found for the ideal gas. The choice of a set of independent parameters is not unique and is often dictated by convenience. It is found that the formal theory is easier to develop by considering parameters such as energy and volume as independent, whereas from the point of view of an experimentalist it is easier to control temperature and pressure than energy and volume. In all cases, it is imperative not to include more parameters than needed, for this might lead to errors.

In this course, we will not discuss how to systematically select independent parameters. We are trying to introduce the main ideas of thermodynamics rather than teach its systematic usage. A good rule of thumb to avoid problems is to select as independent macroscopic parameters only those which are extensive. This is because there are “pairs” of extensive-intensive parameters that are related by equations of state. For example, the extensive macroscopic parameters

for an ideal gas are the internal energy U , the volume V and the number of particles N . The intensive parameter that “corresponds” to the volume V is the pressure p . The two are related by the equation of state $pV = NkT$. The intensive parameter that corresponds to the internal energy U is the temperature T . The two are related by $U = \frac{3}{2}NkT$. There is also an intensive parameter that corresponds to the number of particles N . It is called the chemical potential μ , but we will not deal with this quantity here. In most of our problems, the number of particles will remain fixed. However, when two substances are mixed and a chemical reaction takes place, the number of molecules of the different species will change and the chemical potential plays a fundamental role.

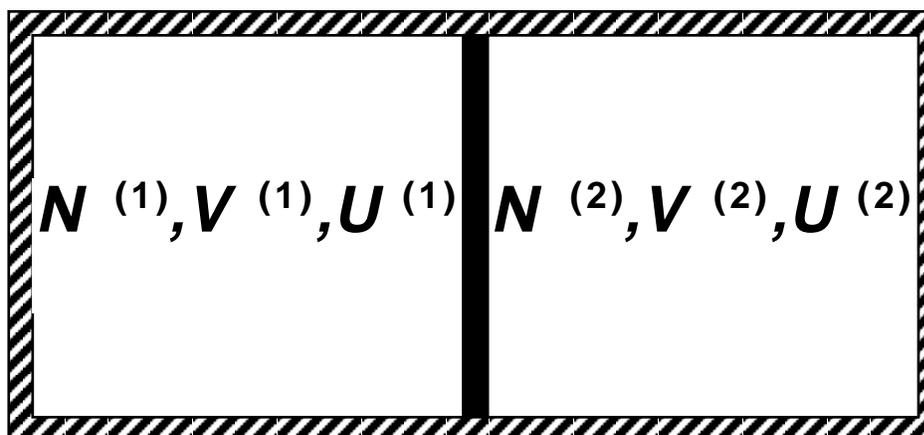


Figure 1 Two gases separated by a wall.

As an example, let us consider the system in Fig. 1, which contains two ideal gases separated by a wall. If we consider the two gases as our system, there are six independent macroscopic parameters: $U^{(1)}$, $V^{(1)}$, $N^{(1)}$, $U^{(2)}$, $V^{(2)}$, and $N^{(2)}$. Suppose that initially all these parameters have fixed, arbitrary values. Next we let the wall slide freely and we also allow for energy exchange (“heat”) through the wall. Walls that let energy flow freely are called **diathermal**, whereas insulating walls are called **adiabatic**. As a result of these interactions, the values of $U^{(1)}$, $V^{(1)}$, $U^{(2)}$, and $V^{(2)}$ (but not those of $N^{(1)}$ and $N^{(2)}$) will change. Thermodynamics will tell us the final values of the parameters that change. The

answer, of course, will be that $U^{(1)}$, $V^{(1)}$, $U^{(2)}$, and $V^{(2)}$ will be such that the pressure and the temperature of the two gases become equal. The pressure condition could have been easily derived from mechanics (by requiring that in equilibrium no net force should act on the wall), but the condition of equal temperatures is the one that is nearly impossible to derive from mechanics, as we discussed above.

External interactions with a macroscopic system

The thermodynamic system will be subject to external forces. In general, these forces change the linear and angular momenta and the energy of the system. We mentioned above that we would discuss systems for which the total linear and angular momenta are zero, so that we only need to be concerned with energy.

The internal energy U is the sum of the kinetic energy (referred to the CM) plus the internal potential energy of the system. As such, it is a function of the positions and velocities of all the particles in the system. In a system of N monatomic particles, the energy is a function of $6N$ variables. (You already know the reason for the “6”!) For example, for an ideal gas enclosed in a box of volume V the potential energy is zero inside the box, and the energy U is given by sum of the kinetic energies of all the particles:

$$U = \sum_{i=1}^N \frac{1}{2} m_i v_i^2 \quad (1)$$

It is very useful for the purpose of thermodynamics to write the energy explicitly as a function of the macroscopic parameters (other than the energy itself, of course) of the system. For an homogenous system such as a liquid or a gas, for example, we would write:

$$U = U(V, N, \text{other microscopic coordinates}) \quad (2)$$

Since the energy cannot be a function of more than $6N$ quantities, the number of positions and velocities that are really independent once we specify macroscopic parameters is reduced by the number of known macroscopic parameters. For example, the positions of the particles are no longer

completely arbitrary once we specify the volume. Similarly, if the total energy is conserved and the number of particles is N , the speed of $N-1$ particles is arbitrary, but the speed of the N th particle must be such that the total energy has the prescribed value.

Work and heat

As discussed in the previous chapter, the external work done on the system can be such that one or several of the macroscopic parameters that appear explicitly in Eq. (2) are changed, or it can be such that those macroscopic parameters remain unchanged. In the latter case, the changes would occur in the positions and velocities of the particles (the remaining microscopic coordinates once we specify the macroscopic parameters) needed to determine the energy. The distinction between the two forms of work is very important because the work can be easily computed in the case where a macroscopic parameter is changed. For example, if the external work is such that the volume of a gas is changed, this external work is given by $dW_{\text{ext}} = -pdV$. (We need a minus sign in front of this expression because the external work is positive when the gas is compressed, but dV is negative.). On the other hand, if the change in energy occurs without a change of macroscopic parameters, it is usually impossible to write a simple expression for this work, since we don't know the individual positions and velocities of the particles. We introduced the concept of work W to indicate that part of the external work that involves a change in macroscopic parameters. The part of the external work that does not involve a change in macroscopic parameters was referred to as **heat** Q . We can thus write

$$W_{\text{ext}} = W + Q \quad (3)$$

or, in terms of infinitesimal changes

$$dW_{\text{ext}} = dW + dQ \quad (4)$$

Multiplicity and the second law of thermodynamics

Macrostates and microstates

The state of a system is characterized by the values of all the variables needed to compute the properties of the system at a later time. If we use Newtonian mechanics, the state of the system is characterized by the positions and velocities of all the particles in the system. In thermodynamics, we use the expression **microstate** to refer to such a state. The prefix **micro** stresses the fact that we know the positions and velocities of all the microscopic components of the system. By contrast, we use the expression **macrostate** when we only specify the values of the macroscopic parameters of the system. Of course, this does not characterize the system completely. There may be many possible microstates that are consistent with a given macrostate. The number of microstates in a macrostate is called the **multiplicity** of the macrostate. The following analogy will clarify these concepts. Suppose we have a set of four colored balls: red (R), blue (B), yellow (Y) and green (G). Suppose also that we have two boxes: box 1 and box 2, where we place the balls. A microstate of the system is defined by specifying exactly which ball goes to which box. For a macrostate, we only provide partial information. For example, a macrostate could be specified by determining how many balls are in each box, without regard of its color. Let us construct a table with the possible combinations.

MACROSTATES		MICROSTATES		MULTIPLICITY
Balls in box 1	Balls in box 2	Detail of box 1	Detail of box 2	Number of detailed arrangements
4	0	BGRY		1
3	1	BGR	Y	4
		BGY	R	
		BRY	G	
		GRY	B	
2	2	BG	RY	6
		BR	GY	
		BY	GR	
		GR	BY	
		GY	BR	
		RY	BG	
1	3	B	GRY	4
		G	BRY	
		R	BGY	
		Y	BGR	
0	4		BGRY	1

Notice that the multiplicity is highest (6) for the macrostate that specifies an equal amount of balls in the two boxes. This trend is very strongly reinforced if the number of particles in the system is high. Suppose for example we have 20 equal balls. There is only one microstate with 20 balls in box 1 and no balls in box 2. Hence the macrostate (20,0) has a multiplicity of 1. On the other hand, the multiplicity of the

macrostate (10,10) is the number of possible ways you can put 10 balls in box 1 and 10 balls in box 2. This number is given by $\frac{20!}{10!10!} = 184,756$.

The second law of thermodynamics

A thermodynamic system has very many particles, certainly many more than 20. This means that some macrostate of the system will have a multiplicity that is overwhelmingly higher than the multiplicity of the other macrostates. Suppose now that we ask the following question: in what macrostate are we going to find a system when we do a measurement? This question can be answered if we make a very reasonable assumption. This assumption is the **second law of thermodynamics**:

the probability of finding an isolated system in one of the microstates compatible with the known macroscopic parameters is the same for all such microstates. Thus this probability is simply 1 divided by the total number of possible microstates.

In the example of the four colored balls and two boxes, this probability is 1/16. Since all microstates are equally likely, the most likely macrostate is the one with the highest number of microstates, that is, with the highest multiplicity. In our example, the probability of the macrostate (2,2) is $6/16 = 0.38$. This number is the highest for any macrostate of the system but not particularly high. In a thermodynamic system, however, we have a very high number of particles. This means that the multiplicity of one of the macrostates is so much higher than the multiplicity of the other macrostates that the probability of finding the system in this particular macrostate approaches 1. Hence an alternative formulation of the second law of thermodynamics is

An isolated system of many particles will evolve toward the macrostate of largest multiplicity and will remain in that macrostate.

Notice that our very innocent assumption -equal probabili-

ties for all microstates - is reasonable but has not been derived from Newton's laws. It is certainly consistent with them, but this is a far cry from being a consequence of the laws of mechanics. Attempts to “derive” the second law of thermodynamics are discussed in advanced courses on statistical mechanics. We will consider this law to be an independent principle. While it is always distressing for a physicist to add new principles to the physical theory, the very simple second law of thermodynamics allows us to solve a multitude of physical problems. Its enormous success justifies the expansion of our basic “axioms” beyond Newton's laws.

Multiplicity of macrostates in material systems

The ideal gas

In order to apply the second law of thermodynamics to real systems, we need to calculate the multiplicity of the macrostates of the system. The simplest material system we can think of is the ideal gas. It is reasonable to attempt a calculation for this system first.

A microstate of an ideal gas is specified by stating the positions and velocities of all of its particles. A macrostate is specified by stating the total energy U , the volume V , and the total number of particles N . The multiplicity, which we shall denote by the symbol Ω , is the number of microstates in the ideal gas for given values of V , N , and U . A serious problem arises here when we attempt to *count* microstates. Position and velocities are given by *real* numbers. A set of real numbers that fully occupies a certain interval cannot be counted (real numbers can have infinite decimal places). A possible solution to this problem is to divide the space into little cubes of side δx . Hence the number of possible ways to put a single particle inside a volume V becomes $V/(\delta x)^3$. Similarly, the “velocity space” can be divided into little cubes of side δv . The problem with this approach is that the multiplicity is not entirely a property of the system but depends on the arbitrary values δx and δv . Fortunately, in order to apply the second law of thermodynamics we don't need to know the *value* of the multiplicity of a given

macrostate. It is sufficient to find the macrostate with the highest multiplicity. Thus if the multiplicity is known but for an arbitrary multiplicative constant, we can proceed with the application of the second law.

The above problem with the size of the little boxes does not appear in a rigorous quantum mechanical description of the system. The possible microstates of a quantum system confined to a certain volume are quantized and can be counted. This is to be expected because quantum mechanics provides a natural definition for the size of the little cubes in real and velocity spaces. According to Heisenberg's uncertainty principle, the position and velocity of a particle cannot be known simultaneously with arbitrary accuracy. The product of the position and velocity uncertainty is $\delta x \delta v \geq h/m$, where m is the mass of the particle and h is Planck's constant.

Let us start by computing the volume-dependent part of the multiplicity of the ideal gas. Consider a single particle. The number of ways this particle can be accommodated in a volume V is proportional to V . The proportionality constant will depend on our choice for the size of the little cubes into which we divide the volume, but we are not interested in absolute values. Knowing what the multiplicity is proportional to will be enough for our purposes.

If we have two particles, the number of ways we can accommodate them in a volume V is equal to the number of ways we can position one particle *times* the number of ways we can accommodate the other particle. This is clearly proportional to $V \times V = V^2$. Here we neglect the vanishingly small probability that the particles may occupy *exactly* the same position. This probability is strictly zero for an ideal gas of point particles; moreover, its neglect is justified in all cases in view of the very small size of atoms and molecules compared with typical human-size volumes. It is now easy to extrapolate our results for the case of N particles: the multiplicity of such a system is proportional to V^N .

Once we specify the positions, we are still free to assign velocities to our particles. For an ideal gas, the average kinetic energy is U/N . This means that the average absolute value of the velocity in a given direction is $\left(\frac{2U}{3mN}\right)^{1/2}$, that is, proportional to $(U/N)^{1/2}$. In other words, the value of one of the components (say the x -component) of the velocity of any particle is very likely to be found between

$$-\text{few} \times \left(\frac{2U}{3mN}\right)^{1/2} \leq v_x \leq +\text{few} \times \left(\frac{2U}{3mN}\right)^{1/2} \quad (6)$$

where “few” means a small number, say 2 or 3. The “size” of a cube with sides of this size is proportional to $(U/N)^{3/2}$. Hence the velocity part of the multiplicity for a single particle is proportional to $(U/N)^{3/2}$. For N particles, we can reason in a form analogous to the volume part of the multiplicity. The conclusion is that the multiplicity must be proportional to $(U/N)^{3N/2}$. The total multiplicity is the number of possible arrangements for the position *times* the number of possible arrangements for the velocity. Hence we can finally write

$$\Omega(U, V, N) = B V^N U^{3N/2} N^{-3N/2} \quad (7)$$

where B is a proportionality constant.

Application of the second law to an ideal gas. Entropy

We are now ready to solve the problem illustrated in Fig. 1. The total multiplicity Ω of the system is clearly the product of the multiplicities of the two individual gases, since we can match every single microstate of one of the gases with all the possible microstates of the other gas. Hence we have

$$\begin{aligned} \Omega(U^{(1)}, V^{(1)}, N^{(1)}, U^{(2)}, V^{(2)}, N^{(2)}) &= \\ &= \Omega^{(1)}(U^{(1)}, V^{(1)}, N^{(1)}) \Omega^{(2)}(U^{(2)}, V^{(2)}, N^{(2)}) \end{aligned} \quad (8)$$

When we let the wall slide and allow for exchange of energy between the two gases, the energies and volumes of the individual gases, $U^{(1)}$, $V^{(1)}$, $U^{(2)}$, and $V^{(2)}$, are no longer fixed. The second law of thermodynamics predicts that these variables will adjust their values to make the multiplicity Ω in Eq. (8) a maximum. To maximize Ω , we clearly need to compute its derivative relative to the volume and energy.

Our task can be simplified if we note that if a function has a maximum, its logarithm also has a maximum. This is because $\ln x$ is a monotonically increasing function of x . We thus define a new quantity, called **entropy**, as

$$S = k \ln \Omega \quad (9)$$

where k is Boltzmann's constant. This constant k is introduced here for convenience. Since Ω is a number, the units of entropy coincide with the units of k , *i.e.*, $[S] = \text{J/K}$. Using the definition of entropy, Eq. (8) becomes

$$S = k \ln \Omega = k \ln (\Omega^{(1)} \Omega^{(2)}) = k \ln \Omega^{(1)} + k \ln \Omega^{(2)} = S^{(1)} + S^{(2)} \quad (10)$$

This means that entropy is an extensive property. This is another reason why it is much easier to work with entropy than with multiplicities. The maximization of the multiplicity Ω is now reduced to the maximization of the entropy $S^{(1)} + S^{(2)}$ subject to the conditions $U^{(1)} + U^{(2)} = \text{constant}$ and $V^{(1)} + V^{(2)} = \text{constant}$, since the total energy and the total volume of the entire system do not change. From Eq. (9), the entropy of an ideal gas is given by

$$S = k \ln B + kN \ln V + \frac{3}{2} kN \ln U - \frac{3}{2} k \ln N \quad (11)$$

Notice that the multiplicative constant B , related to the size of the small cubes in real-and velocity space, becomes part of an additive constant in the expression for the entropy. Thus if we are interested in *changes* of entropy, we never have to deal with B .

Only the second and third term in Eq. (11) will change in our example, since the number of particles in each of our gases remains fixed. (But we could have a *permeable* wall that allows for the exchange of molecules, in which case the last term would also change.). Differentiating Eq. (10) with respect to $U^{(1)}$, $U^{(2)}$, $V^{(1)}$, and $V^{(2)}$, we obtain, if S is a maximum,

$$\begin{aligned}
0 &= dS = dS^{(1)} + dS^{(2)} = \\
&= kN^{(1)} \frac{dV^{(1)}}{V^{(1)}} + \frac{3}{2} kN^{(1)} \frac{dU^{(1)}}{U^{(1)}} + kN^{(2)} \frac{dV^{(2)}}{V^{(2)}} + \frac{3}{2} kN^{(2)} \frac{dU^{(2)}}{U^{(2)}} \quad (12)
\end{aligned}$$

Since the total volume and the total energy remain constant, we must have $dV^{(1)} = -dV^{(2)}$ and $dU^{(1)} = -dU^{(2)}$. Substituting into Eq. (12), we obtain

$$\left(\frac{kN^{(1)}}{V^{(1)}} - \frac{kN^{(2)}}{V^{(2)}} \right) dV^{(1)} + \frac{3}{2} \left(\frac{kN^{(1)}}{U^{(1)}} - \frac{kN^{(2)}}{U^{(2)}} \right) dU^{(1)} = 0 \quad (13)$$

The expressions within the parenthesis can be rewritten in terms of the equations of state $U = \frac{3}{2}NkT$ and $pV = NkT$. We obtain

$$\left(\frac{p^{(1)}}{T^{(1)}} - \frac{p^{(2)}}{T^{(2)}} \right) dV^{(1)} + \left(\frac{1}{T^{(1)}} - \frac{1}{T^{(2)}} \right) dU^{(1)} = 0 \quad (14)$$

These condition can only be fulfilled for arbitrary infinitesimal changes $dV^{(1)}$ and $dU^{(1)}$ if

$$\begin{aligned}
p^{(1)} &= p^{(2)} \\
T^{(1)} &= T^{(2)} \quad (15)
\end{aligned}$$

Hence we have finally shown that in equilibrium conditions the pressure and the temperature on both sides of the wall must be equal. The equal pressures conditions is quite obvious from simple mechanical considerations (no net force on the wall), but the equal temperatures conditions is nearly impossible to derive by a simple application of Newton's laws. Our derivation is so simple because we made the assumption of equal probabilities of all accessible microstates, which constitutes the second law of thermodynamics.

A rigorous definition of temperature

From Eq. (14) we observe that, for the ideal gas,

$$\frac{\partial S}{\partial U} = \frac{1}{T} \quad (16)$$

where T is the temperature we defined as proportional to the average kinetic energy of the gas. We still do not have a rigorous definition of temperature for systems other than

the ideal gas. However, we note that in all cases the application of the second law of thermodynamics leads to the conclusion that for two systems in thermal contact, the derivatives $\partial S/\partial U$ must be equal on both sides when equilibrium is reached. Because this is precisely the property we expect from temperature, we can *define* temperature from Eq. (16). This is consistent with our previous definition for the ideal gas. More importantly, it can be applied to any material system, so that now we have a definition of this fundamental thermodynamic concept that is not based on arbitrary scales or idealized materials.

Entropy and information

The internal energy U is a function of the macroscopic parameters of the system (N and V in the case of a gas) and of all other microscopic parameters needed to completely identify the microstate of the system. Suppose we have a gas for which N remains constant, V changes and the microscopic parameters also change. For such a gas,

$$dU = -pdV + dQ, \quad (17)$$

where dQ represents the change in energy produced by the change in the microscopic parameters.

Unlike the internal energy, the entropy S has been defined in terms of macroscopic parameters, $S = S(U, V, N)$. For the ideal gas, for example, this function is given by Eq. (11). We can formally invert this expression and write the internal energy solely in terms of macroscopic parameters: $U = U(V, N, S)$. Hence $dU = \frac{\partial U}{\partial V} dV + \frac{\partial U}{\partial N} dN + \frac{\partial U}{\partial S} dS$. This expression is consistent with Eq. (16) and Eq. (17) if we identify $\partial U/\partial V = -p$ and $\frac{\partial U}{\partial S} dS = TdS = dQ$. We thus arrive to the following conclusions: instead of writing the energy as a function of N , V and $6N$ -(a few) microscopic coordinates, we can write it as a function of U , V , and S . The effect on the energy of the $6N$ -(a few) microscopic parameters is consolidated in a single macroscopic function, which we call entropy. Thus the entropy is the amount of information we have about those parameters, whose values we don't know in detail. The

mathematical theory of information has been developed by Shannon. This theory shows that a satisfactory definition of information is indeed formally identical to the concept of entropy.

Entropy and heat

In the above paragraph, we found a connection between entropy and heat: $TdS = dQ$. This connection is very important because up to now we have a very rigorous definition of entropy, but it is not clear how we can measure this quantity experimentally. Since we can measure heat transfers, the connection between S and Q gives us a chance to measure changes in entropy. Let us examine this relationship in detail. Consider the ideal gas enclosed in the container of Fig. 2.

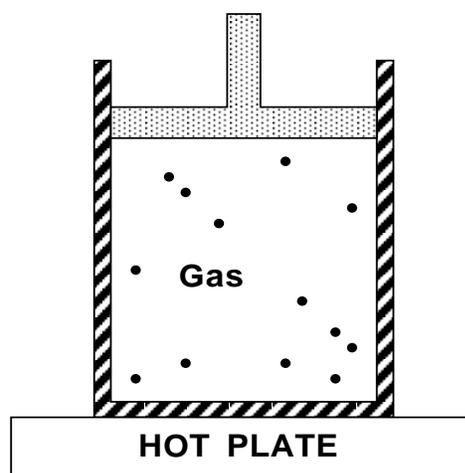


Figure 2 A gas in contact with a hot plate is let expand in such a way that its energy remains constant

The gas is kept at constant temperature, so that its energy remains constant (of course, this is true only for an ideal gas, whose internal energy depends only on the temperature). Hence the amount of heat absorbed must equal the expansion work. In other words, $dU = 0 = -pdV + dQ$. On the other hand, from Eq. (11) we obtain for this gas (N and U are constant)

$$dS = \frac{kN dV}{V} = \frac{kNp dV}{pV} = \frac{kN dQ}{NkT} = \frac{dQ}{T} \quad (18)$$

where we have used the equation of state of the ideal gas. This expression confirms that the change in entropy is given by the heat absorbed divided by the temperature. Hence it is easy to determine the change in entropy in a given process. Because changes in entropy are far more important for our thermodynamic considerations than the absolute value of the entropy, this expression will be extremely useful for the solution of thermodynamic problems.

Notice that when we write $dS = dQ/T$, we obtain different results depending on the units we use for temperature. This expression assumes that we are using the Kelvin scale of temperatures and cannot be used with any other scale. You must be very careful when you apply these equations to homework problems, where the temperature is frequently quoted in degrees Celsius or Fahrenheit.

Equation 18 was derived under the assumption that the temperature of the gas remains constant. This requires that the expansion of the gas be very slow, because heat takes time to be transferred from the hot plate to the gas. Strictly speaking, for the temperature to be exactly constant at all times the process should be infinitesimally slow. Such a process is called **quasistatic**. Let us study the opposite limit. Suppose that we remove the hot plate and suddenly displace the piston to its final position. Since we are moving the piston very fast, (we can't do this experiment in the lab, but no law of physics would in principle prevent a Superman from moving the piston fast enough that no molecules can hit it.) no pressure is exerted on the piston. Hence no external work is done on the gas and its energy remains constant. Because the final state of the gas is identical to the final state we reached by expanding the gas very slowly and keeping it in contact with a hot plate, the change in entropy is the same in the two processes. However, no heat has been absorbed in the sudden-expansion example, so that $dS = dQ/T$ cannot be valid. We can therefore write

$$dS \geq \frac{dQ}{T}, \quad (19)$$

where the equal sign applies only if the process is quasistatic. If the temperature remains constant during the process, integration of this expression gives

$$S_{final} - S_{initial} = \Delta S \geq \frac{Q}{T} \quad (20)$$

The efficiency of thermal engines

The science of thermodynamics was developed in the XIXth century to study the behavior of thermal engines. These engines played a key role in the enormous increase in economic productivity that accompanied the industrial revolution. The fundamental question to be asked is the following: can we design a machine such that it absorbs heat Q from a certain thermal source and converts it into work W ? Such a machine would have 100% efficiency if we define the efficiency ε as

$$\varepsilon = \frac{\text{work delivered}}{\text{heat absorbed}} = \frac{-W}{Q} \quad (21)$$

(Notice the minus sign in front of W . This is because W is positive when we do work on the system, and negative when the system delivers work). It is clear, however, that such a machine would violate the second law of thermodynamics. In a typical engine, the machine undergoes a cycle, after which it returns to its initial state to initiate a new cycle. Let us consider one such cycle. The change in entropy of the system engine + heat source is equal to the sum of the changes of their individual entropies. But the change in entropy of the engine itself is zero, since it returns to its original state. On the other hand, the heat source *delivers* heat to the engine, so that the heat absorbed by the source is negative. This means that its entropy will be reduced. Hence the total entropy will be reduced, and this contradicts the second law of thermodynamics. In terms of multiplicities, it is clear that the multiplicity associated with the random motion of atoms in the heat source is much higher than the multiplicity

associated with the coordinated motion of atoms in the engine, so that a process in which all the *disordered* energy in the heat source is converted into *ordered* energy in the engine is in clear violation of the second law of thermodynamics.

A solution to the above problem is to “sacrifice” some work in order to increase the entropy of some other object and comply with the second law of thermodynamics. A possible scheme is illustrated in Fig. 3

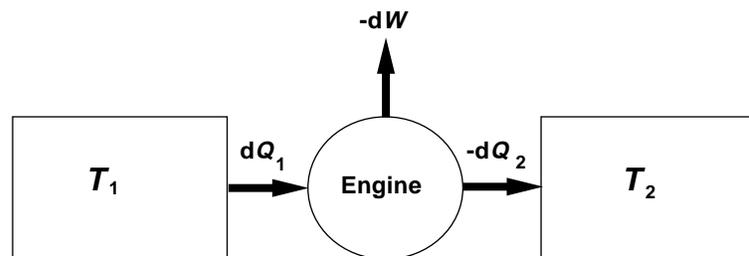


Figure 3 A possible way to extract useful work from heat sources and comply with the second law of thermodynamics.

A heat source at temperature T_1 delivers heat to the engine. The engine delivers heat to a second source at temperature T_2 . Obviously, we would like the amount of heat delivered to the second source to be less than the amount of heat absorbed from the second source. Otherwise, there is no energy left to produce useful work. However, since the overall entropy cannot decrease, Eq. (20) implies that if $|dQ_1| > |dQ_2|$ then $T_1 > T_2$. In other words the source that delivers heat to the engine must be “hot” and the source that absorbs heat from the engine must be “colder”. Let us now examine how much work can be extracted from such a combination of heat sources and engine. Since the engine returns to its initial state after completion of a cycle, the first law of thermodynamics requires that

$$-dW = dQ_1 + dQ_2 \quad (22)$$

Note that dQ_2 is negative, so that the amount of work available is reduced due to the transfer of heat to the second

source. According to the second law, the overall entropy cannot decrease. This implies

$$dS_{total} = \frac{-dQ_1}{T_1} + \frac{-dQ_2}{T_2} \geq 0 \quad (23)$$

since the hot source “absorbs” an amount of heat $-dQ_1$, the cold source absorbs $-dQ_2$ and the entropy of the engine itself doesn’t change. If we still define the efficiency as work delivered over heat absorbed, we obtain by using Eqs. (22) and (23)

$$\varepsilon = \frac{-dW}{dQ_1} = 1 + \frac{dQ_2}{dQ_1} \leq 1 - \frac{T_2}{T_1} \quad (24)$$

This means that the maximum efficiency of a thermal engine is limited by the temperatures of the hot and cold sources. This is a very severe limitation. Let us consider for example a nuclear power plant. The nuclear fission is used to heat up the refrigerant water in the reactor. This water heats up water in a secondary circuit. The temperature of the overpressurized steam in the secondary circuit is typically of the order of 300 °C, or 570 K. This is the temperature T_1 of the “hot” source. On the other hand, the steam is typically condensed by water of a nearby river after passing through the turbines. Hence T_2 is of the order of 20 °C or 290 K. Using Eq. (24) we conclude that the efficiency of such a power plant cannot be higher than $1 - 290/570 = 49\%$. In real life, the efficiency is much less. This is because the equal sign in Eq. (24) is only applicable if the process is infinitely slow. From the point of view of a power plant, however, this is unacceptable. We need the energy within our lifetime! A power plant should optimize the power it delivers, not the energy. This means running the cycle fast, which implies that the efficiency is less than the maximum allowed by thermodynamics. Under conditions of maximum power, the efficiency can often be approximated by $\varepsilon = 1 - \left(\frac{T_2}{T_1}\right)^{1/2}$, which in our example becomes $\varepsilon = 29\%$. This number is much closer to the efficiencies measured in real power plants.

The Carnot cycle

A possible process that achieves maximum efficiency is the Carnot cycle. We start with the working substance of our engine, typically a gas, in thermal contact with the hot source. (Point A in Fig. 4). Next we allow the system to expand isothermally. This will increase its entropy, since the spatial part of the multiplicity increases. The system reaches point B in Fig. 4. Now the gas is isolated from the heat sources and allowed to expand. This process is called an **adiabatic** expansion. Since no heat is transferred to the gas, its entropy doesn't change. However, since negative work is done on the system during an expansion, the energy will decrease. This leads to a decrease in temperature. The expansion is continued until the system reaches the temperature T_2 of the cold source (point C in the figure). Next the system, in contact with the cold source, is compressed at constant temperature. Hence its entropy is reduced. The compression is continued until the system recovers its initial temperature (point D). Finally, the system is returned to its initial state (point A) by an adiabatic compression.

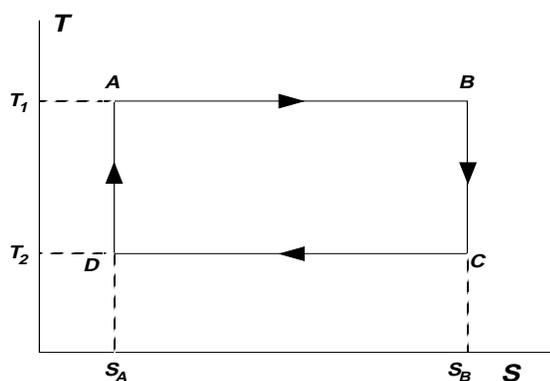


Figure 4 Diagram of a Carnot cycle in a T - S plot.

For an ideal gas, the Carnot cycle can be easily plotted in a p - V diagram, which illustrates the process more clearly, as we did in the previous chapter. This is shown in Figure 5, where we have used $p = NkT/V$ for the isothermal parts of the process.

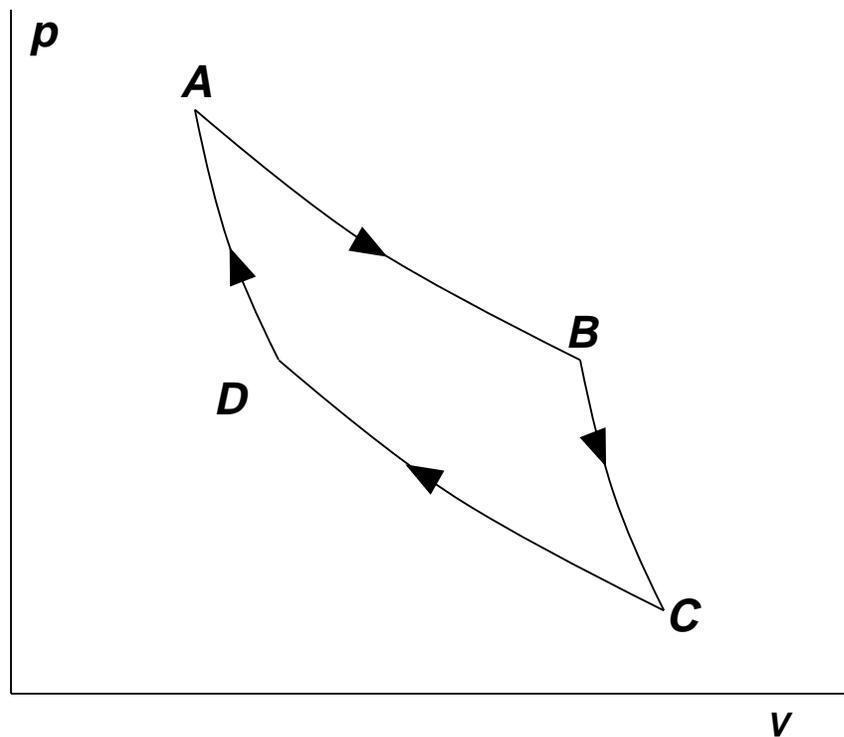


Figure 5 Diagram of a Carnot cycle in a p - V graph.

Using the concept of entropy we can rederive the dependence of p on V during an adiabatic process; we note that in this case $dS = 0$. From Eq. (11) this implies

$$dS = 0 = \frac{kN}{V} dV + \frac{3}{2} \frac{Nk}{U} dU \quad (25)$$

By using the two equations of state, we can write the energy as $U = \frac{3}{2}pV$. This means $dU = \frac{3}{2}(p dV + V dp)$. Substituting into Eq. (25) and rearranging, we obtain

$$\frac{5}{2} \frac{dV}{V} = -\frac{3}{2} \frac{dp}{p} \quad (26)$$

Integrating this expression, we finally obtain for an adiabatic process

$$pV^\gamma = \text{constant}, \quad (27)$$

where $\gamma = \frac{5}{3}$. For non-ideal gases, the coefficient γ may take different values. Since $\gamma > 1$, the curve p versus V is steeper

for an adiabatic process. This explains the general shape of Figure 5.

The efficiency of the Carnot cycle is easily calculated from the T - S diagram of the cycle. For a complete cycle, the first law of thermodynamics requires

$$Q_1 + Q_2 + W = 0 \quad (28)$$

On the other hand, the change in entropy of the gas undergoing the Carnot cycle is also zero after completion of a cycle. The entropy only changes during the steps $A \rightarrow B$ and $C \rightarrow D$, during which the temperature is constant. We thus have

$$\Delta S_{gas} = \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0 \quad (29)$$

Combining these equations we obtain for the efficiency of the cycle

$$\varepsilon = \frac{-W}{Q_1} = 1 - \frac{T_2}{T_1}, \quad (30)$$

which is the maximum efficiency allowed by the second law of thermodynamics.

Problems

1. Suppose you have 1 liter of a gas at room temperature and pressure and a new laser printer that prints 12 pages per minute. You would like to print the positions and velocities of all particles in the gas at a given time, using a reasonable font size. Estimate the time it would take to print that information and weight of the paper you will need. Compare the time with the age of the Universe and the weight of the needed paper with the weight of the Earth.

2. In the main text we discuss a system of two boxes and a set colored balls. Suppose that the total number of different balls is N . For several values of N , construct a bar graph showing the probability of each macrostate. Interpret these graphs in terms of the second law of thermodynamics.

3. When a 1 kg ice cube melts, it absorbs an amount of energy given by 3.35×10^5 J. This energy is called *latent heat of fusion*. While the ice melts, its temperature remains constant.

a) Calculate the change in entropy of the ice as it melts.

b) Calculate the ratio of the multiplicity of liquid water and the multiplicity of ice.

4. Show that the entropy of an ideal gas can be written as $S = Nk \ln V + \frac{3}{2} Nk \ln T + \text{constant}$.

5. During a slow adiabatic expansion, the entropy of a gas does not change. Since the volume increases, however, one would expect the multiplicity to increase. Explain this apparent contradiction.

6. (Callen) If a monatomic ideal gas is permitted to expand into an evacuated region, thereby increasing its volume from V to λV , and if the walls are rigid and adiabatic, what is the ratio of the initial and final pressures? What is the ratio of the initial and final temperatures? What is the difference of the initial and final entropies?

7. (Callen) A tank has a volume of 0.1 m^3 and is

filled with He gas at a pressure of 5×10^6 Pa. A second tank has a volume of 0.15 m^3 and is filled with He gas at a pressure of 6×10^6 Pa. A valve connecting the two tanks is opened. Assuming He to be a monatomic ideal gas and the walls of the tanks to be adiabatic and rigid, find the final pressure of the system. *Hint:* Note that the internal energy is constant.

Answer: $p_f = 5.6 \times 10^6$ Pa.

8. The entropy of the electromagnetic radiation (photon gas) is proportional to $U^{3/4}V^{1/4}$. Consider the universe as an expanding electromagnetic cavity which is now at a temperature of 2.7 K. What will be the temperature of the radiation when the volume of the universe becomes twice its present value?

9. An ideal gas undergoes a Carnot cycle. The gas is initially in contact with the hot heat source, and in the first stage of the cycle it is expanded from volume V_A to volume V_B . Calculate the work and heat transfers in each of the four steps of the cycle in terms of the temperatures of the heat sources, the number of particles N , V_A , and V_B . Directly corroborate that the efficiency of the cycle is the Carnot efficiency.

10. A rough approximation to a gasoline engine is provided by the so-called Otto cycle, depicted below. Initially, the mixture of air and gasoline vapor is compressed adiabatically ($A \rightarrow B$). Next the mixture is heated at constant volume ($B \rightarrow C$). This step represents the gasoline combustion. In the third step the working fluid is expanded adiabatically in the "power stroke" ($C \rightarrow D$). Finally the fluid is cooled at constant volume to its initial state A .

a) Sketch Otto's cycle in a p - V diagram.

b) Show that if the fluid is an ideal gas, the efficiency

of an Otto engine is given by $\epsilon = 1 - \left(\frac{V_B}{V_A} \right)^{1-\gamma}$. The ratio V_B/V_A is called the compression ratio.

