

Chapter 5

The Foundations of Thermodynamics

5.1 THERMODYNAMICS VERSUS STAT MECHANICS

The aim of statistical mechanics is to predict the equilibrium properties of a macroscopic system, starting from an adequate model of the microscopic Hamiltonian. However, long before any reliable information about the microscopic structure of matter existed, there was a well-developed science for predicting the equilibrium properties of macroscopic systems; namely, thermodynamics.

Historically, thermodynamics arose out of an attempt to improve the efficiency of heat engines. The mechanical engineering origin of the subject has left a lasting imprint upon it. For example, the most important law of thermodynamics is usually given in the form of a postulate about the impossibility of constructing certain kinds of engines. It is the author's opinion that it would be illogical at this point to make a digression into the study of heat engines, Carnot cycles, etc. We already have a clear idea of the basic mechanism that drives a macroscopic system toward a time-independent equilibrium state. It has little to do with the details of the microscopic dynamics. It is essentially a statistical effect. Almost all of the microstates available to the system have exactly the same macroscopic features, namely, those that define the equilibrium macrostate. Thus, virtually any trajectory in the microstate space of the system will cause the system's macrostate to move to the equilibrium state. This idea, stated in a way that makes no detailed reference to the microscopic structure of the system, should be the central principle of our thermodynamics. Macroscopic systems do not behave as they do in order to frustrate our attempts to build an engine that takes heat from a colder to a hotter body. Therefore, our basic thermodynamic laws should not be formulated in that way. Instead, our basic thermodynamic laws should reflect, simply and accurately, the true mechanism that is driving the system's macroscopic behavior. For example, when one drops a sugar cube into coffee, it dissolves. It is reasonable to ask *why* it dissolves. We would answer that the sugar molecules do not try, preferentially, to dissolve. There are simply so many more *dissolved* states than *undissolved* ones that, in the course of its fairly random motion, the sugar moves from the small set of undissolved states to the vastly larger set of dissolved ones. The traditional theory would answer the same question by showing that, if the sugar did not dissolve, then it would be possible to transfer heat from a colder to a hotter body. As an answer to the question: "Why does the sugar cube dissolve?", that explanation is practically worthless.

With this starting point, our formulation of the laws of thermodynamics will be rather unconventional.* Our objective in this chapter is to construct a thermodynamic theory specifically designed to complement

* Although unconventional, our formulation is not new. A similar treatment of thermodynamics was given in *Thermodynamics* by H. B. Callen (John Wiley & Sons, Publ.). Like much of thermodynamics, it could be traced back to J. W. Gibbs.

statistical mechanics. Therefore, certain decisions, such as choices of variables and units, will be made with this in mind. In the next chapter, the theory will be recast in a form that is both more conventional and more convenient for applications to engineering processes. Before describing the principles of the subject we should discuss in more detail the relationship of thermodynamics to statistical mechanics and the distinction between the two subjects. A very important point is that thermodynamics is a self-contained subject. Its laws should be expressed entirely in terms of the observable macroscopic properties of substances, with no reference to their microscopic structure. The basic question considered by thermodynamics is the following: Given the initial macroscopic state of an isolated system, not necessarily at equilibrium, what will be the system's macroscopic state when it comes to equilibrium? Of course, this does not mean that the laws of thermodynamics cannot be used in answering a large variety of other questions, but only that this is the central question in the subject.

Statistical mechanics is related to thermodynamics in two fundamental ways. First, statistical mechanical arguments can be used to derive the basic axioms of thermodynamics from the laws of quantum or classical mechanics. Second, particular functions needed in thermodynamic calculations, such as the entropy function, can be computed from a model of the microscopic structure of a substance, using statistical mechanical rules. However, since thermodynamics is an independent science, there must be rules within thermodynamics that allow a determination of all the required functions without any recourse to statistical mechanics or any knowledge of the microstructure of the substances studied. Generally, the rules of thermodynamics show how these functions can be determined by experimental measurements, while the rules of statistical mechanics show how they can be computed by mathematical analysis. This may make it appear that statistical mechanics is inherently more powerful than thermodynamics. Why should we bother measuring functions that can be obtained by thought alone? However, when the system under consideration is something like a bucket of tar (which has a very complex microscopic structure) the elegant formulas of statistical mechanics are of no practical value but the simple operational rules of thermodynamics encounter no serious obstacles. In one sense, statistical mechanics *is* more powerful than thermodynamics in that thermodynamics can be derived from statistical mechanics but not vice versa.

The general tone of this chapter will be more formal and axiomatic than that of the previous chapters. This is necessary in order to construct a logically self-contained subject. We will have to be careful that we do not allow information, based on the microscopic models of particular substances, to slip into our fundamental thermodynamic laws. In choosing a system of fundamental axioms for thermodynamics, we will use the following criterion: Anything that follows in a straightforward way from the laws of mechanics, quantum mechanics, or electromagnetic theory, such as the conservation of energy, angular momentum, or electric charge, will be considered as a part of those disciplines and will therefore not be included in the axioms of thermodynamics. Only those universal characteristics of macroscopic systems that do not follow in any simple and direct way from the laws of mechanics, quantum mechanics, or electrodynamics will be taken as postulates of thermodynamics. Generally, they will be properties of macroscopic systems that have no counterpart in systems with only a few degrees of freedom. In other words, the laws of thermodynamics are taken as those new characteristics that appear only in the thermodynamic limit. For example, it will be taken as an axiom that isolated systems approach time-independent equilibrium states, composed of a small number of uniform phases (gas, liquid, solid, etc.). In the traditional formulations of thermodynamics such characteristics are considered to be so obvious that they are unworthy of specific mention. In fact, they are the most exceptional characteristics of the macroscopic world. Nonequilibrium states produce grasshoppers, trees, and snowflakes. No such things are possible at equilibrium. Equilibrium states consist only of dull uniform phases. Certainly this fact is no trivial consequence of the underlying laws of nature, which are the same for equilibrium and nonequilibrium states.

5.2 EQUILIBRIUM STATES

Our first axiom of thermodynamics simply postulates the existence of equilibrium states.

Axiom 1. Any isolated macroscopic system will eventually come to a state in which all of its macroscopic properties remain constant. Such states are called *equilibrium* states.

By the word "isolated" we mean that the system does not exchange energy with anything external to it. The word does not preclude the existence of external force fields, such as gravitational or magnetic fields, as long as they are constant in time and are conservative fields. Such fields would then simply contribute to the definition of the conserved energy of the system.

The next few axioms describe general characteristics of the equilibrium states.

Axiom 2. The values of all other macroscopic observables in the equilibrium state are determined by a finite number of conserved variables.

In all the cases we will consider in this chapter the conserved variables are simply the energy of the system E , the volume of the system V , and the number of particles for each type of conserved particle. A *simple substance* is one that is composed of only one type of particle, such as neon, water, or copper. Initially we will restrict ourselves to simple substances, but the extension of our analysis to complex substances will be very simple. It would only complicate the notation to try to treat the most general case at the start.

Axiom 3. For sufficiently weak external fields, the equilibrium state consists of a finite number of homogeneous *components* or *phases*.

If we formulate this axiom only for zero external fields, then we eliminate any possibility of confirming the theory on the surface of the earth. Actually it is preferable to have a weak gravitational field present for a system composed of two phases, such as liquid and gas, because it pulls the denser phase together at the bottom of the vessel. Strong fields create nonuniform states in which the properties vary continuously with position. An atmosphere of continuously varying density is a good example. A minor problem is that our restriction to weak fields will require that we ignore the easily observed variation of pressure with depth in dense fluids. This restriction to weak fields is only a temporary device to simplify the introduction of thermodynamics. The generalization to continuously varying systems requires no new fundamental physics; it is simply more complicated mathematically. Axioms 2 and 3 are best considered as general descriptions of the sort of systems we will work with in this chapter.

5.3 THE SECOND LAW

The next axiom is the heart of thermodynamics. In the usual formulation of the subject, it appears as the Second Law (in a rather different form). It leads to the calculational scheme for determining the equilibrium state of a system. It is best to motivate and interpret it with some analysis from statistical mechanics. However, this introductory material should not be considered as part of the body of thermodynamics. The axioms of thermodynamics must be powerful enough and clear enough to be usable without external assistance.

To be specific, let us consider a macroscopic quantum mechanical system. We know that the macrostate of the system approaches the equilibrium state because that is the most probable macrostate, where the probability of any macrostate is taken as proportional to the number of quantum states exhibiting that combination of macroscopic features. We also know that, if the system is composed of two spatially separated macroscopic parts, then the number of quantum states corresponding to a given macrostate of the whole system is given by a product of the numbers of quantum states of each part corresponding to the macrostate of that part. [That is, for a system with separated parts, any quantum state of part 1 may be combined with any quantum state of part 2 to give a quantum state of the whole system. If K is the total number of such quantum states, then $K(\text{whole}) = K(\text{part 1}) \times K(\text{part 2})$.] Thus, for a system composed of two parts, the logarithm of the number of microstates of the whole is the sum of the logarithms of the numbers of microstates of the two parts. Also, the equilibrium state is the state that maximizes the number of microstates, which means that it is also the state that maximizes the logarithm of that number, which we call the entropy.

Axiom 4. (The Second Law) There is a function of the macroscopic state of a system, called the *entropy*, with the following characteristics:

- a. If a system is composed of a number of spatially separate parts, then the entropy of the whole is the sum of the entropies of the parts.
- b. The equilibrium state of the system is that state that maximizes the entropy within the constraints of the system and the conservation laws of nature.

Notice that, except for properties (a) and (b), no rules are given about how to calculate the entropy functions of specific systems. Since such rules would depend on the detailed microscopic structure of the systems involved, they lie outside the realm of thermodynamics, which recognizes only the macroscopic features of systems. Somehow, we will have to use the given axioms to devise a scheme for determining the entropy functions needed.

“It is an inference naturally suggested by the general increase of entropy which accompanies the changes occurring in any isolated material system that, when the entropy of the system has reached a maximum, the system will be in a state of equilibrium. Although this principle has, by no means, escaped the attention of physicists, its importance does not appear to have been duly appreciated. Little has been done to develop the principle as a foundation for the general theory of thermodynamic equilibrium.”

“The general criterion for equilibrium can be stated simply and precisely: for the equilibrium of any isolated system, it is necessary and sufficient that, in all possible variations of the state of the system which do not alter its energy, the variation of its entropy shall either vanish or be negative.”

— J. Willard Gibbs

5.4 EXTENSIVITY OF THE ENTROPY

Since, according to Axiom 3, general equilibrium states are composed of a few homogeneous phases, the obvious place to start our analysis is to consider samples composed of a single homogeneous phase. What does the Second Law tell us about the entropy of, let us say, a uniform sample of liquid with particle number N , energy E , and volume V ? Let us call the entropy function that we seek $S(N, E, V)$. (The entropy is a macroscopic observable. By Axiom 2, at equilibrium, all macroscopic observables are functions of N , E , and V . Therefore, S is a function of N , E , and V .) If we conceptually split the sample into K equal parts then, at equilibrium, each part will have a particle number N/K , an energy E/K , and a volume V/K . Thus we can use part (a) of Axiom 4 to state that

$$S(N, E, V) = KS\left(\frac{N}{K}, \frac{E}{K}, \frac{V}{K}\right) \quad (5.1)$$

or

$$S(\lambda N, \lambda E, \lambda V) = \lambda S(N, E, V) \quad (5.2)$$

where $\lambda = 1/K$. It is not difficult to construct a similar argument that will give Eq. (5.2) for any positive rational number L/K , and assuming continuity, we then get Eq. (5.2) for any positive real number. Thus we now know that the entropy function of any single-phase substance is a first-degree homogeneous function of its arguments.* Such a function is called an *extensive* function. The extensive property of the single-phase entropy functions significantly simplifies the task of determining them.

There is a technical point that should be clarified here. The number of particles may be measured either in individual particles or in moles (Avagadro’s number of particles). An individual particle is both an impractical and theoretically inappropriate unit for a strictly macroscopic theory. However, in applying our formulas to statistical mechanics, it is an extremely convenient unit. Almost nothing depends on the unit of particle number, and so we will only indicate it when it is a relevant variable. When using an individual particle as our unit, the quantity $S(1, E, V)$ should not be interpreted as the entropy of a one-particle system, which is a meaningless phrase, but as $S(N, NE, NV)/N$ for very large N . For analyzing thermodynamic systems, it is more convenient to measure N in moles and so that is what we will do throughout most of this chapter. However, except where otherwise noted, the formulas are valid when interpreted in individual particles. Writing $s(E, V)$ for $S(1, E, V)$, the extensive property of $S(N, E, V)$ implies that

$$S(N, E, V) = Ns(\varepsilon, v) \quad (5.3)$$

where $\varepsilon = E/N$ and $v = V/N$.

5.5 CONVEXITY OF THE ENTROPY

Part (b) of Axiom 4 also has important implications regarding the properties of the function $s(\varepsilon, v)$. We picture a two-mole sample of liquid, with an energy 2ε , at equilibrium within a cylinder of volume $2v$. We split the sample into two equal parts, of one mole each, by means of a movable, heat-conducting partition (see Fig. 5.1). Since the initial uniform state was an equilibrium state, the entropy must be a maximum when

* A homogeneous function of degree K is a function with the property that $f(\lambda x, \lambda y, \dots) = \lambda^K f(x, y, \dots)$ for any $\lambda > 0$.

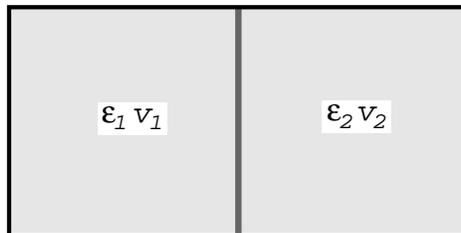


Fig. 5.1 A system composed of two moles of gas, separated by a movable, heat conducting barrier.

the samples on both sides of the partition are in the same state. In that case, each sample has energy ε and volume v . We now picture the system in a different state, but one with the same total energy and volume. Since this new state is not the equilibrium state but is not forbidden by any constraint (the partition only prevents particle transfer between the two halves) or conservation law, then it must have smaller entropy than the equilibrium state. This implies that

$$2s(\varepsilon, v) > s(\varepsilon_1, v_1) + s(\varepsilon_2, v_2) \quad (5.4)$$

whenever $\varepsilon_1 + \varepsilon_2 = 2\varepsilon$ and $v_1 + v_2 = 2v$. It is useful to write Eq. (5.4) in the form

$$s\left(\frac{\varepsilon_1 + \varepsilon_2}{2}, \frac{v_1 + v_2}{2}\right) > \frac{1}{2}(s(\varepsilon_1, v_1) + s(\varepsilon_2, v_2)) \quad (5.5)$$

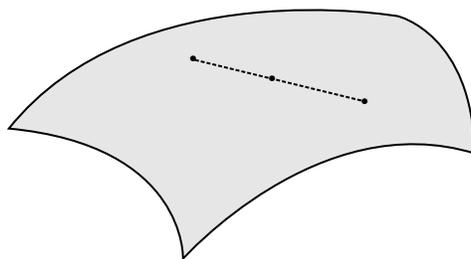


Fig. 5.2 If a convex function of two variables is plotted as a surface, it gives a convex surface. The midpoint of the line between any two points on a convex surface falls below the surface.

If we plot the function $s(\varepsilon, v)$ as a surface over the (ε, v) plane, Eq. (5.5) says that the surface always lies above any chord connecting two points on it. (See Fig. 5.2.) That is, the surface is *convex*. Any function satisfying Eq. (5.5) is also said to be convex. To be more precise, if we have a strict inequality, as in Eq. (5.5), then the function is said to be strictly convex. A function is simply convex if the inequality sign is replaced by \geq . A function whose graph is an upward-pointing cone is just convex (the surface of a cone contains straight lines), while a function whose graph is a paraboloid that opens downward is strictly convex.

5.6 THE THERMODYNAMIC TEMPERATURE

This section will be devoted to a study of the partial derivatives of the entropy function and their identification with measurable properties of the substance. We will first give them names and symbols. The variables α , β , and γ are defined by

$$\alpha = \frac{\partial S}{\partial N}, \quad \beta = \frac{\partial S}{\partial E}, \quad \text{and} \quad \gamma = \frac{\partial S}{\partial V} \quad (5.6)$$

where $S(N, E, V)$ is the entropy function of any simple phase. α is called the *affinity*, β the *inverse temperature* or *coldness*, and γ the *free expansion coefficient*. Their physical meanings will become clear as we proceed.

An *empirical temperature* is any macroscopic parameter with the property that, when two bodies are brought into contact, heat energy will flow spontaneously from the body with the higher value of the

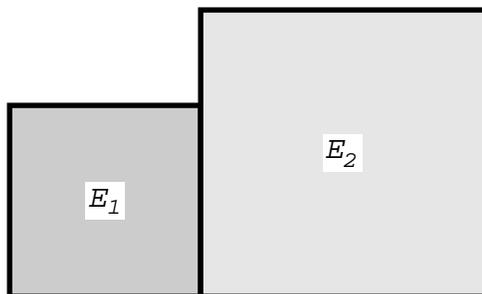


Fig. 5.3 In the equilibrium state, the energies are shared between the two components so as to maximize the total entropy.

temperature to the body with the lower. It is easy to see that there is no unique empirical temperature, since any monotonically increasing function of one empirical temperature is itself an empirical temperature. A common practical empirical temperature is the length of the mercury column on a thermometer in contact with the body, but the length of an uncalibrated ten-penny nail would do just as well, although it might be a bit difficult to read.

Theorem $T = \beta^{-1}$ is an empirical temperature.

Proof Consider the system shown in Fig. 5.3, in which two substances are separated by a thermally conducting partition. The substances have initial energies E_1^o and E_2^o . Their entropy functions are $S_1(E_1)$ and $S_2(E_2)$. Since the constraints of the system prevent particle or volume exchange, we will not bother to indicate those quantities. As a function of E_1 the total entropy of the system is

$$S(E_1) = S_1(E_1) + S_2(E_T - E_1) \quad (5.7)$$

where $E_T = E_1^o + E_2^o$. The condition of equilibrium is that $S(E_1)$ be a maximum.

This implies that the equilibrium value of E_1 satisfies $S'(E_1) = 0$, which gives $S'_1(E_1) = S'_2(E_2)$. Therefore, at equilibrium, $T_1(E_1) = T_2(E_2)$. However, this is not enough to show that T is an empirical temperature. We must show that at no intermediate stage on the movement towards equilibrium is energy flowing from lower T to higher T .

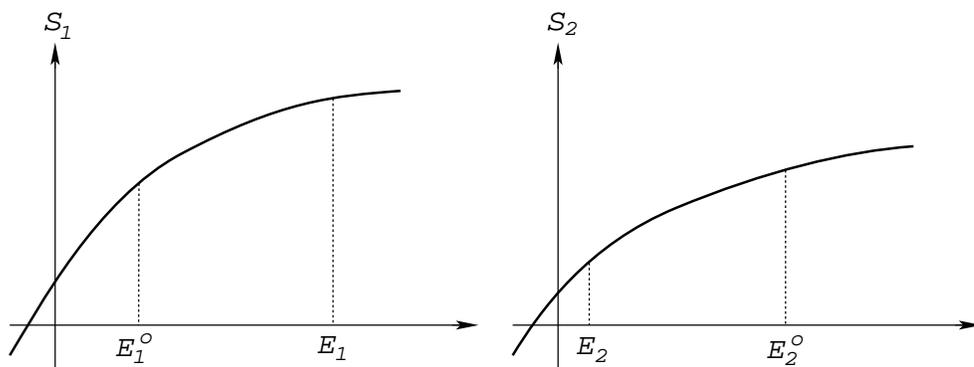


Fig. 5.4 The entropy functions of the two components.

Graphs of the functions S_1 and S_2 are shown in Fig. 5.4. Of course, we do not know the actual form of the entropy functions of these unspecified substances. The values of E_1^o , E_1 , E_2^o , and E_2 are indicated. We have assumed that substance 2 loses energy to substance 1, but the argument we will give would work just as well with the reverse assumption. At the final energies the two entropy graphs must have the same slope. But, by our previous argument, we know that both graphs must be convex, as they have been drawn. Thus at all points on the movement toward equilibrium

$$S'_1(E_1) > S'_2(E_2) \quad \text{or} \quad T_1(E_1) < T_2(E_2) \quad (5.8)$$

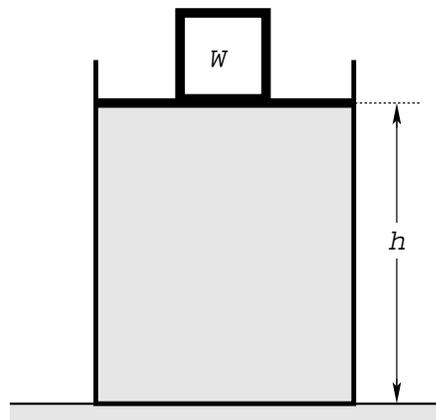


Fig. 5.5 The equilibrium value of h maximizes the system entropy.

Notice that, because of the convexity property of the entropy functions, the slope of each entropy function is a monotonically decreasing function of E . Thus the equation $S'_1(E_1) = S'_2(E_T - E_1)$ cannot have more than one solution. That it *must* have one solution with nonzero values of E_1 and E_2 actually depends on another axiom that will be presented later.

5.7 THE PRESSURE

Theorem $p = \gamma/\beta$ is the mechanical pressure in the substance.

Proof In Fig. 5.5 is shown a sample of fluid in a cylinder under a frictionless movable piston topped by a weight W . The system is surrounded by vacuum. If we let E_o denote the fixed total energy of the system, including the potential energy of the weight, and call the energy of the fluid, not including the gravitational potential energy of the weight, E , then the entropy of the system, as a function of the piston height h is

$$S(h) = S(N, E, V) = S(N, E_o - Wh, Ah) \quad (5.9)$$

where A is the area of the piston. The equilibrium value of h is given by setting $S'(h) = 0$. This gives

$$-W \frac{\partial S}{\partial E} + A \frac{\partial S}{\partial V} = 0 \quad (5.10)$$

or

$$p = \frac{\gamma}{\beta} = \frac{W}{A} \quad (5.11)$$

W/A is clearly the mechanical pressure in the fluid. Since p is the mechanical pressure in this situation and all macroscopic features are unique functions of N , E , and V at equilibrium, then p is the mechanical pressure at equilibrium in all situations.

5.8 THE FREE EXPANSION COEFFICIENT

The parameter γ is therefore related, in a simple way, to the pressure. In order to see the physical meaning of γ directly, consider the system shown in Fig. 5.6. If the plug is pulled, so that the gas can expand into the initially empty volume ΔV , then during the expansion the energy is constant, so that the change in entropy is given by

$$\Delta S = \frac{\partial S}{\partial V} \Delta V = \gamma \Delta V \quad (5.12)$$

Such an expansion into a vacuum is called a *free expansion*, which shows why we have called the parameter γ the *free expansion coefficient*; it is the ratio of the entropy change to the volume change in a free expansion.

5.9 THE AFFINITY

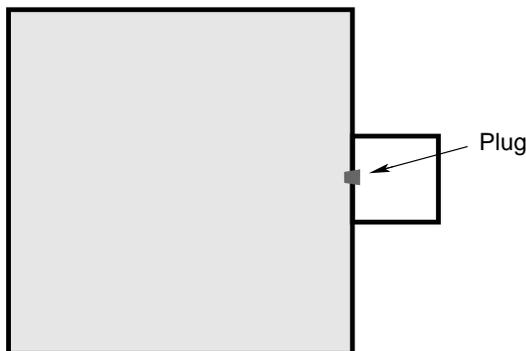


Fig. 5.6 When the plug is pulled, the gas expands into the vacuum, causing an entropy increase of $\gamma\Delta V$.

Now let us consider the conditions of equilibrium between two phases of the same simple substance (for example, water and water vapor). We will assume that the two phases are liquid and gas and therefore call their entropy functions S_L and S_G . The total entropy is the sum of the entropies of the parts

$$S_T = S_L(N_L, E_L, V_L) + S_G(N_G, E_G, V_G) \quad (5.13)$$

Demanding that S_T be a maximum with respect to changes in N_L , E_L , and V_L , taking into account the constraints that $N_G = N_T - N_L$, $E_G = E_T - E_L$, and $V_G = V_T - V_L$, gives the three equilibrium conditions

$$\alpha_L = \alpha_G, \quad \beta_L = \beta_G, \quad \text{and} \quad p_L = p_G \quad (5.14)$$

Because α is defined as the derivative of S with respect to N , it is clear that, in the system considered, if α_L is greater than α_G , then a transfer of particles from the gas to the liquid would create a net increase in entropy of the system and would therefore occur spontaneously. Thus, we can say that, when possible, particles will spontaneously move from the substance with the smaller affinity to the substance with the larger affinity. The affinity plays the same role with respect to particle transfer as the coldness plays with respect to energy transfer. For a nonsimple substance (one with more than one type of particle) the entropy is a function of the particle numbers of all types, $S(N_A, N_B, \dots, E, V)$. In that case there is a separate affinity for each type of particle. $\alpha_A = \partial S / \partial N_A$, $\alpha_B = \partial S / \partial N_B$, etc.. The physical meaning is unchanged. For example, in a system composed of air over water, water will evaporate into the air if $\alpha_{\text{H}_2\text{O}}(\text{air})$ is greater than $\alpha_{\text{H}_2\text{O}}(\text{liquid})$.

5.10 INTENSIVE VARIABLES

An *intensive* variable is any zero-order homogeneous function of N , E , and V , that is, a function with the property that $f(\lambda N, \lambda E, \lambda V) = f(N, E, V)$ for any $\lambda > 0$.

Theorem α , β , and γ are intensive variables.

Proof We know that

$$S(\lambda N, \lambda E, \lambda V) = \lambda S(N, E, V) \quad (5.15)$$

Differentiating both sides with respect to N , we get

$$\lambda \alpha(\lambda N, \lambda E, \lambda V) = \lambda \alpha(N, E, V) \quad (5.16)$$

which gives the desired result for α . The same could obviously be done for β and γ .

From the equation $\alpha(N, E, V) = \alpha(\lambda N, \lambda E, \lambda V)$, we can, by choosing $\lambda = 1/N$, see that $\alpha(N, E, V) = \alpha(1, \varepsilon, v)$, where ε and v are the energy and volume per mole. The function $\alpha(1, \varepsilon, v)$ will be written simply as $\alpha(\varepsilon, v)$. Clearly, we could also show that β and γ (or p) are also functions of ε and v .

Theorem For any two-phase equilibrium state of a simple substance, α and β are functions of p .

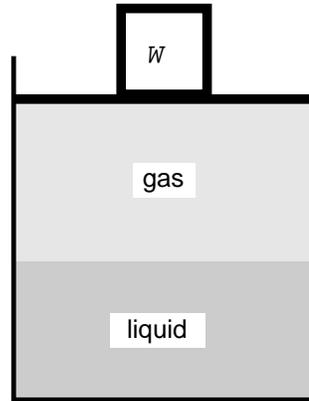


Fig. 5.7 Two phases in equilibrium at pressure p .

Proof Consider two phases in equilibrium at an externally fixed pressure p (see Fig. 5.7). According to Eq. (5.14), the conditions for equilibrium are

$$\begin{aligned}
 p_G(\varepsilon_G, v_G) &= p \\
 p_L(\varepsilon_L, v_L) &= p \\
 \alpha_L(\varepsilon_L, v_L) &= \alpha_G(\varepsilon_G, v_G) \\
 \beta_L(\varepsilon_L, v_L) &= \beta_G(\varepsilon_G, v_G)
 \end{aligned}
 \tag{5.17}$$

These are four equations in the four unknowns ε_L , v_L , ε_G , and v_G . The only free parameter in the equations is p . For a given value of p two things are possible.

1. The equations have no solution, showing that a two-phase equilibrium state is not possible at that pressure. In this case, if the system initially contained two phases, one of them would disappear as the system approached equilibrium. Thus, this case is irrelevant to the situation we are considering.
2. The equations have a solution, $\varepsilon_L(p)$, $v_L(p)$, $\varepsilon_G(p)$, and $v_G(p)$. That the solution must be unique can be shown from the convexity property of the functions $s_L(\varepsilon, v)$ and $s_G(\varepsilon, v)$. Therefore, in this case, $\alpha(p) = \alpha_L(\varepsilon_L(p), v_L(p)) = \alpha_G(\varepsilon_G(p), v_G(p))$ and $\beta(p) = \beta_L(\varepsilon_L(p), v_L(p)) = \beta_G(\varepsilon_G(p), v_G(p))$ are functions of p .

This is important in that it allows us to keep a substance at a constant (although unknown) value of β during its expansion or compression (see Fig. 5.8).

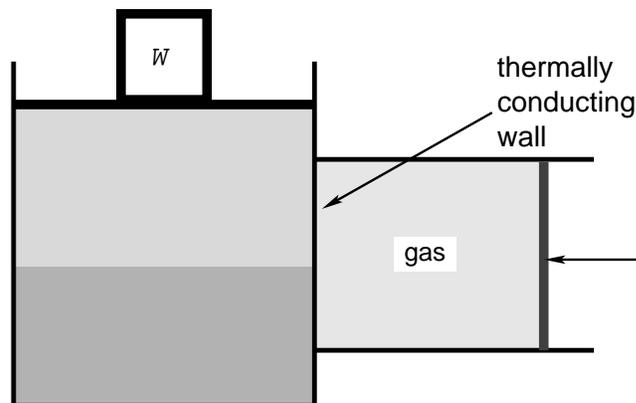


Fig. 5.8 If the piston on the right is moved very slowly, the gas passes through a sequence of states that have the same temperature but different volumes and energies.

5.11 QUASISTATIC PROCESSES

The gradual compression or expansion shown in Fig. 5.8 is our first example of a very important class of processes, called *quasistatic* processes. In a quasistatic process the change in the system brought about by any external agent is assumed to take place so slowly that the system has ample time to maintain internal equilibrium. In Fig. 5.8 the external agent is the force exerted on the piston in the cylinder containing the gas. That force is increased so gradually that only a tiny temperature difference develops between the gas and the two-phase system. It is obvious that some such assumption is necessary if we are to conclude that the gas and the two-phase system are at the same temperature.

Theorem The quasistatic compression or expansion of a substance in an insulating cylinder does not change its entropy.

Proof The force needed to maintain the piston of Fig. 5.9 in a fixed position is $F = pA$. If the piston moves an amount dx the work done on the gas, and therefore its change in energy, will be

$$dE = F dx = -p dV \quad (5.18)$$

But, by the definitions of β and γ and by the relation $\gamma = \beta p$, we get

$$\begin{aligned} dS &= \beta dE + \gamma dV \\ &= \beta(dE + p dV) \\ &= 0 \end{aligned} \quad (5.19)$$

We now have methods of changing the state of a substance that maintain either its temperature or its entropy constant. These processes will be important in devising a technique for measuring the entropy.

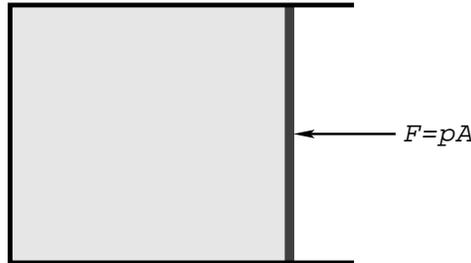


Fig. 5.9 If the piston is slowly moved, the entropy is not changed.

5.12 HEAT TRANSFER

When the volume of a substance enclosed in a cylinder with a movable piston is quasistatically increased an amount dV by moving the piston, then the substance does an amount of work $p dV$ against the piston and its energy changes by an amount $dE = -p dV$. This is an important consideration when heat energy is added to a substance being held at constant pressure. If the amount of heat transferred to the substance is dQ , then the change in the internal energy of the substance will be equal to the heat added minus the work done on the piston as the substance expands due to its increase in temperature.

$$dE = dQ - p dV \quad (5.20)$$

If heat is added to a substance in a closed vessel with a movable piston, then, using the facts that $dN = 0$, $\beta = 1/T$, and $\gamma = p/T$, one can see that the change in entropy is directly proportional to the heat added.

$$dS = \frac{dE + p dV}{T} = \frac{dQ}{T} \quad (5.21)$$

5.13 AMBIGUITY IN THE ENTROPY FUNCTION

In Axiom 4 we postulated the existence of an additive entropy function, but we have not yet shown how to determine the entropy function of any substance. Before we do so, we have to investigate how rigidly these axioms actually define the entropy functions. That is, how many arbitrary parameters are there in the set of entropy functions, one for each phase of a substance, that satisfy Axiom 4. That question is answered by the following theorem. In this analysis it is important that we treat the case of nonsimple substances, and therefore we will consider a substance composed of two different types of particles. The generalization to an arbitrary number of particle types will be completely obvious.

Let $S_K(N_A, N_B, E, V)$ be the entropy function of the K th phase of a substance composed of independently conserved particles of types A and B . We point out the fact that $S_K(N_A, 0, E, V)$ and $S_K(0, N_B, E, V)$ are then the entropy functions of the K th phase of the two related simple substances.

Theorem The set of entropy functions

$$S_K^*(N_A, N_B, E, V) = \lambda S_K(N_A, N_B, E, V) + a_A N_A + a_B N_B \quad (5.22)$$

predict, in all cases, the same equilibrium states as the set of entropy functions $S_K(N_A, N_B, E, V)$, for any $\lambda > 0$ and arbitrary values of a_A and a_B . The functions S_K^* are also extensive if the functions S_K are extensive.

Proof Using the entropy functions S_K^* , the equilibrium state of a system would be determined by maximizing the quantity

$$\begin{aligned} S_{\text{total}}^* &= \sum S_K^* \\ &= \lambda \sum S_K + a_A \sum N_{AK} + a_B \sum N_{BK} \\ &= \lambda S_{\text{total}} + a_A N_A + a_B N_B \end{aligned} \quad (5.23)$$

over all possible distributions of energy, volume, and particle numbers among the various phases in the system, taking into account the constraints of the system and the fundamental conservation laws. Since both types of particles are assumed to be conserved, the term $a_A N_A + a_B N_B$ on the third line is effectively a constant and would have no effect on the maximizing distribution. Since $\lambda > 0$, the maximum of S_{total}^* is given by the same distribution that maximizes S_{total} .

One might be tempted to add another term of the form $bE + cV$ to the definition of S_K^* . This is forbidden by the existence of situations, such as that depicted in Fig. 5.5, in which E and V are not separately conserved (see Problem 5.2).

5.14 MEASUREMENT OF $S(N, E, V)$

We now have all the tools we need to attack the fundamental problem of determining the entropy function of a given substance. We proceed as follows.

1. We first choose some convenient simple substance and call it the *standard thermometric substance*. In practice, the standard substance is pure water. We place one mole of the standard substance in an insulating cylinder with a movable piston. Within the cylinder is a small electrical resistor. Well-controlled amounts of energy can be added to the substance by running a current through the resistor. Therefore, one can easily determine the energy difference between two states of the same volume. (See Fig. 5.10.)

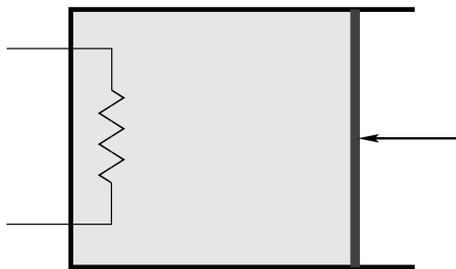


Fig. 5.10 The system whose entropy is to be measured.

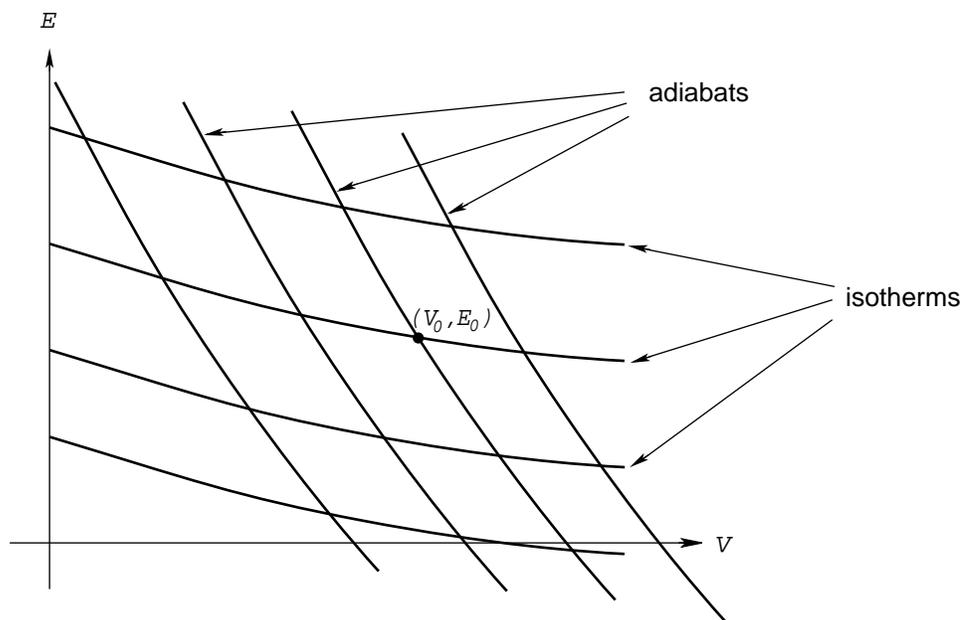


Fig. 5.11 Adiabats and isotherms in the E - V plane.

By quasistatically moving the piston and carefully keeping track of the work done in the process, we can determine the energy difference between two arbitrary states. The energy, being partly potential energy, always has some arbitrary constant associated with it. Therefore, we can choose some *standard state*, let us say a single-phase state of volume V_o and pressure p_o , and declare it to have energy E_o . Having done that, we can locate any physical state on the E - V plane by purely mechanical measurements.

2. Starting from any state, we can, by quasistatic expansion or compression of the standard substance within the insulated cylinder, determine a sequence of states that have equal (but unknown) entropy. A sequence of states with the same value of S is called an *adiabatic curve*. Thus, we can construct the set of adiabatic curves shown in Fig. 5.11.

3. We now return the system to the standard state (E_o, V_o) . Making use of the arbitrary constant λ in the entropy functions, we are free to declare that the inverse temperature of the standard state of the standard substance is some arbitrarily chosen positive number β_o . Making use of the arbitrary constant a_A in the entropy functions, where A is the standard substance, we are free to declare that the entropy of the standard state of the standard substance is some arbitrarily chosen number S_o .

4. Starting from the standard state, and using a device like that shown in Fig. 5.8, we can determine a sequence of states (an *isothermal curve*) that all have the inverse temperature β_o (see Fig. 5.11). Since, during isothermal compression, the standard substance gives up energy to the two-phase system, the energy rises less rapidly with decreasing volume on an isothermal curve than on an adiabatic one.

5. Starting from the standard state, we can determine the entropy of any state (E_1, V_1) that lies on the isothermal curve by using the relation $dS = \beta_o(dE + p dV)$. (Remember that the pressure is directly measurable by mechanical means.)

$$S(E_1, V_1) = S_o + \beta_o \int_{(E_o, V_o)}^{(E_1, V_1)} (dE + p dV) \quad (5.24)$$

6. Using the fact that all the states on any adiabatic curve have the same entropy, we can then determine the entropy of one mole of the standard substance at any point in the (E, V) plane.

Since we have been dealing with one mole of the standard substance, the function we have actually determined is the entropy per mole and should more properly have been written as $s(\varepsilon, v)$. The entropy of an arbitrary amount of the standard substance would then be given by

$$S(N, E, V) = Ns(E/N, V/N) \quad (5.25)$$

“In the present state of physical science, therefore, a question of extreme interest arises: *Is there any principle on which an absolute thermometric scale can be founded?* It appears to me that Carnot’s theory of the motive power of heat enables us to give an affirmative answer.”

— William Thompson (Lord Kelvin)

(Lord Kelvin was the first person to give, by an analysis equivalent to that given in this chapter, the definition of the absolute scale of temperature.)

Having determined the entropy function of the standard substance, one can differentiate it to obtain the numerical value of the inverse temperature $\beta(\varepsilon, v) = \partial s / \partial \varepsilon$ for any state of the standard substance. By putting it in thermal contact with other substances, one can use the standard substance as a thermometer to determine the temperature of anything else.

Suppose we have one mole of another simple substance, which we will call B (A is the standard substance). We can easily determine $\beta(\varepsilon_B, v_B)$ by using the standard substance as a thermometer. Note that we cannot arbitrarily define β for some standard state of substance B . The single free multiplicative parameter λ has been used up in defining β for the standard state of the standard substance. But we do still have one free parameter, namely a_B . This is an additive parameter. We are therefore free to assign an arbitrary value to $s_B(\varepsilon_o, v_o)$, where (ε_o, v_o) is some chosen standard state of substance B . Since we know $\beta(\varepsilon_B, v_B)$ and we can measure $p(\varepsilon_B, v_B)$ mechanically, we can now integrate the differential $dS = \beta(dE + p dV)$ along any curve we like from the standard state to any other state in order to determine the entropy function of substance B .

All this has been done without any mention of a perfect gas. An essentially unique definition of thermodynamic temperature, namely $1/T = \partial S / \partial E$, emerges from the fundamental principles of thermodynamics. The value of T does not depend upon the specific properties of any particular substance. If we use substance B as our standard substance, the only change that it can make in the entropy functions we obtain is a different set of arbitrary constants, λ , a_A , and a_B . The new temperature scale would be exactly proportional to the old. Thus, the change would simply constitute choosing a different unit of temperature.

5.15 UNITS, RATIONAL AND PRACTICAL

As we mentioned before, the entropy is proportional to $\log K$, where K is the number of quantum states associated with a given macrostate. In a *rational* system of units, S is set exactly equal to $\log K$. However, this choice can only be made after a fully developed quantum theory exists that allows one to determine the number K for some substance. In reality, the development of thermodynamics preceded the development of quantum theory by about a century. Therefore, the early thermodynamicists were obliged to construct a somewhat arbitrary system of thermodynamic units that we will call the *practical* system. (These names should not be construed to imply that the practical system is irrational nor that the rational system is impractical. The word *practical* simply means “what is used in practice”. The term *rational* is commonly used to describe any system of units in which the number of physical constants is reduced by using fundamental theoretical relationships.)

The two systems of units differ only by the values of the multiplicative constant λ . The modern version of the practical system is defined by choosing water as the standard substance. The standard state is chosen as that unique value of pressure and temperature at which the three phases, solid, liquid, and gas, are simultaneously in equilibrium (the *triple point*), and it is declared that, at the triple point, $T = (\partial S / \partial E)^{-1} = 273.16$ exactly. In this system, the unit of temperature is the *Kelvin*, written K. The relationship between the entropy in the practical system and the number of quantum states is

$$S = k \log K \tag{5.26}$$

where k is a physical constant, called *Boltzmann’s constant*, with the value and units of

$$k = 1.3807 \times 10^{-23} \text{ J/K} \tag{5.27}$$

Equations 5.26 and 5.27 may be interpreted in two different ways. In the first way, one declares that the Kelvin is a dimensionless quantity. The entropy then has the physically bizarre units of joules. They are

called bizarre because the entropy has no natural interpretation as an energy of any kind. In the second way, the Kelvin is taken to be another unit of energy. Boltzmann's constant is then merely a conversion factor between the two independently defined energy units. In this interpretation S is dimensionless. Interpreting the Kelvin as an energy unit is in accord with the common practice in low-temperature physics of specifying all energy values, such as quantum mechanical energy levels, in Kelvins. It is the second interpretation that will be used in this book.

In order to avoid confusion, whenever rational units are being specifically used, the entropy will be written as S° and the temperature as τ . In rational units, the temperature τ is measured in Joules. The affinity, being the derivative of S with respect to N , depends on the units used for both S and N . There are four possibilities, but we will carefully restrict ourselves to two of them. When using rational units, we will always express N in particles and, when using practical units, in moles. The conversion from practical to rational units is given by

$$S^\circ = S/k, \quad \tau = kT, \quad \text{and} \quad \alpha(\text{rat.}) = \alpha(\text{prac.})/R \quad (5.28)$$

Another point regarding notation is that in this chapter we have been using the symbol β to mean the inverse of the temperature in whatever system of units is being used. The well-established custom is to use β to mean only $1/\tau$. After this chapter we will strictly abide by that custom.

5.16 THERMODYNAMIC STATE SPACE

We will now consider a nonsimple substance with two types of conserved particles, A and B . According to Axiom 2, the set of independent thermodynamic variables for this system is the set (N_A, N_B, E, V) . We view this as a point in a four-dimensional *thermodynamic state space* \mathcal{S}_T .

$$(N_A, N_B, E, V) \in \mathcal{S}_T \quad (5.29)$$

All properties of the equilibrium states of this system are unique functions of position in \mathcal{S}_T . For examples, the pressure on the containing walls and the volume occupied by the liquid phase (which might very well be zero) are functions $p(N_A, N_B, E, V)$ and $V_L(N_A, N_B, E, V)$ defined throughout \mathcal{S}_T . For a different system the thermodynamic state space would be different, but the general results given in this section would still hold with obvious adjustments.

The first question we want to consider is: "What are the boundaries of \mathcal{S}_T ?" If one or both of the particles have absolutely incompressible hard cores, then there will be an inequality relating N_A , N_B , and V that defines the maximum packing density. It will be of the form $V_{\min}(N_A, N_B) < V$, where V_{\min} is an extensive function of N_A and N_B . Even if the particles do not have absolutely hard cores, because the interaction potential becomes larger and larger as the particles are pushed closer and closer together, for any fixed value of E , there is a certain volume, V_{\min} , at which the quantum mechanical ground state energy becomes equal to E . For V less than V_{\min} , there are no physical states with the specified energy. This gives a more general inequality of the form

$$V_{\min}(N_A, N_B, E) < V < \infty \quad (5.30)$$

For given N_A , N_B , and V , the energy must be larger than some minimum energy that is just the ground-state energy of a system composed of N_A particles of type A and N_B particles of type B in a volume V . There is no natural upper bound on the energy for a system of particles. Thus

$$E_{\min}(N_A, N_B, V) < E < \infty \quad (5.31)$$

Actually, this is just the inequality given in Eq. (5.30), solved for E as a function of V .

There are two axioms of thermodynamics remaining to be presented. They concern the behavior of the entropy at the boundaries of \mathcal{S}_T .

A state is called *thermodynamically inaccessible* if it can never be brought about by bringing the system into contact with other systems. For example, a state with zero volume but nonzero particle number is thermodynamically inaccessible, because it would require infinite pressure to achieve it.

Axiom 5. The boundary of \mathcal{S}_T consists of limit states that are thermodynamically inaccessible because, at all finite boundaries, the normal derivative of S approaches minus infinity. That is, $\partial S/\partial \mathbf{n} \rightarrow -\infty$. This implies that

$$\begin{aligned} \alpha_i &\rightarrow \infty & \text{as } N_i &\rightarrow 0, & i &= A, B \\ \beta &\rightarrow \infty & \text{as } E &\rightarrow E_{\min}(N_A, N_B, V) \\ \gamma &\rightarrow \infty & \text{as } V &\rightarrow V_{\min}(N_A, N_B) \end{aligned} \quad (5.32)$$

To see how these limiting properties make the border states thermodynamically inaccessible, consider what would happen if we put the system we are considering in thermal contact with another system. Since the other system is also a thermodynamic system, it would naturally also satisfy Axiom 5. Thus, for each system, the entropy, as a function of the energy, is given by a strictly convex curve that is vertical at its left end. The equilibrium condition is that the slopes of the two curves be equal ($\beta_1 = \beta_2$). Regardless of the initial total energy, this would obviously occur at some interior point on both curves. (See Fig. 5.12.)

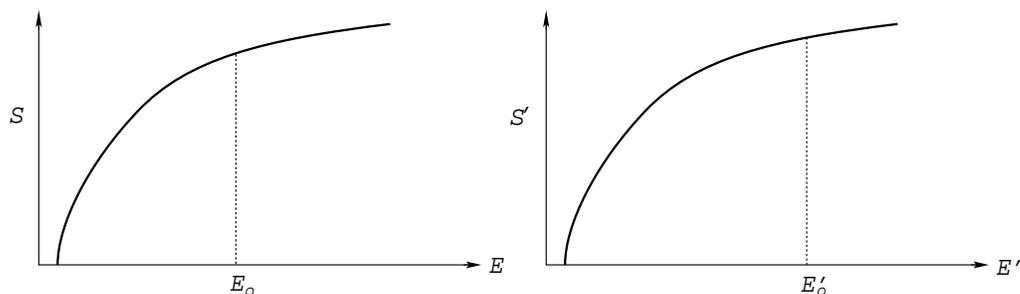


Fig. 5.12 Both curves have infinite slope at their left ends.

Let us try to communicate, in a casual way, the physical content of the three conditions. The first says, for example, that as air gets drier and drier, it will eventually steal water from anything with which it comes into contact; the second says that the temperature approaches zero at the lowest possible energy. Since $\gamma = p/T$, the third line says that as the system is brought to its minimum volume, either the temperature goes to zero or the pressure goes to infinity. For quantum mechanical systems, it is the first possibility that always occurs. For classical systems, the first possibility occurs for interaction potentials that go smoothly to infinity; the second occurs for an interaction potential with a discontinuous hard core or for a perfectly ideal gas.

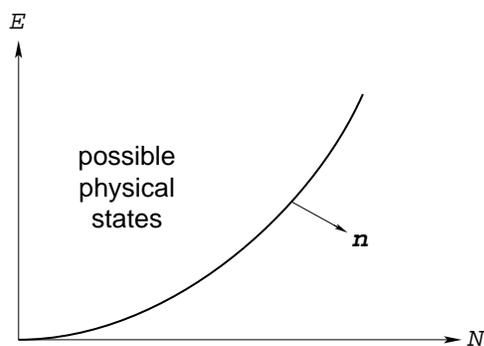


Fig. 5.13 For a fixed value of V , the lower boundary of the state space in the N - E plane is given by a curve that can be described either by the function $E_{\min}(N, V)$ or, equivalently, by the function $N_{\max}(E, V)$. $\partial S/\partial \mathbf{n} \rightarrow -\infty$ (where \mathbf{n} is always the outward-pointing normal) as one approaches the boundary.

5.17 NEGATIVE TEMPERATURE

Axiom 5 has interesting consequences for any system in which either N or E is restricted to a finite range. For example, a system composed of hard-core particles (that is, impenetrable particles, like billiard balls) has

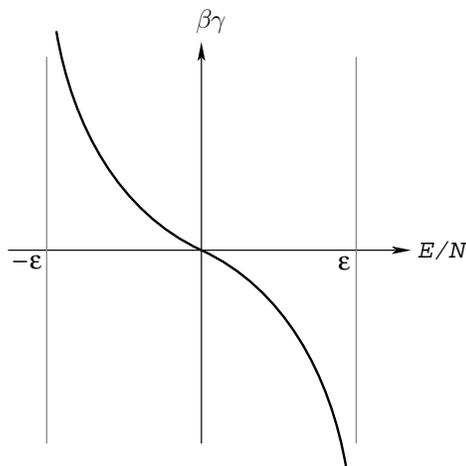


Fig. 5.14 The inverse temperature, as a function of $E/N\varepsilon$, for the system of spins in a magnetic field. At positive energies, β is negative.

an upper bound on the number of particles that can be fit within a given volume. Thus $0 \leq N \leq N_{\max}(V)$. For particles without absolutely hard cores, the potential energy rises to very high values as more and more particles are added at fixed volume. Thus at fixed energy and volume there is a maximum packing density. $0 \leq N \leq N_{\max}(E, V)$ (see Fig. 5.13). This is just another way of saying that the ground-state energy of the system increases with increasing density. That $\partial S/\partial \mathbf{n} \rightarrow -\infty$ at the boundary shown in Fig. 5.13 implies the two conditions that $T \rightarrow 0$ as $E \rightarrow E_{\min}(N, V)$ and that $\alpha \rightarrow -\infty$ as $N \rightarrow N_{\max}(E, V)$. The ideal Fermi–Dirac gas, to be considered in Chapter 7, is an excellent example of this phenomenon.

A more interesting case is that of a system whose range of possible energies is finite. The simplest example is a collection of N noninteracting half-integer magnetic moments in an external magnetic field. There are a number of real physical systems that are fairly well approximated by this simplified model. If the magnetic field strength is B and the projection of the magnetic moment in the field direction is $\pm m$, then a single magnetic moment has two possible energy states $\pm\varepsilon$, where $\varepsilon = mB$. The entropy function for such a system has been worked out in Exercise 3.14. It gives the following relationship between energy and inverse temperature (in rational units).

$$\beta = \frac{1}{2\varepsilon} \log \left(\frac{1 - E/N\varepsilon}{1 + E/N\varepsilon} \right) \quad (5.33)$$

The range of possible energies for the system is obviously $-N\varepsilon \leq E \leq N\varepsilon$. The plot of β in that range is shown in Fig. 5.14. In the positive half of the energy range ($0 < E < N\varepsilon$) $\beta = \partial S^o/\partial E$ is negative and goes to $-\infty$ as E approaches its maximum, in agreement with Axiom 5. Naturally, a state with negative coldness is less cold (that is, hotter) than a state with positive coldness. If a system in such a state is put into contact with any system at positive β , energy will spontaneously flow from the hotter (negative coldness) system to the colder (positive coldness) one. This has the physically reasonable implication that, if two identical systems of magnetic moments, one in a positive energy state and one in a negative energy state, are put into thermal contact, then heat energy will flow from the higher-energy system to the lower-energy one, finally bringing the two systems to the same intermediate energy (which might be a negative or a positive coldness state).

The temperature, related to the coldness by $\tau = 1/\beta$, is an inconvenient variable to use in describing these systems. As the energy passes smoothly through zero, from left to right, τ goes to $+\infty$, then jumps to $-\infty$ and moves toward zero from the left. One must keep in mind that the negative temperature states are hotter than the positive temperature states. They are even hotter than the state at $\tau = \infty$.

“The present discoveries in science are such as lie immediately beneath the surface of common notions. It is necessary, however, to penetrate the more secret and remote parts of nature, in order to abstract both notions and axioms from things, by a more certain and guarded method”

— Francis Bacon (*Novum Organum*)

Most systems contain kinetic energy terms in their Hamiltonian functions. Since the kinetic energy alone can range up to $+\infty$, such systems cannot have any upper bound to their energy. Also, we know that $T \rightarrow \infty$ (that is, $\beta \rightarrow 0$) as $E \rightarrow \infty$. Thus these *normal* systems always have positive temperatures. Any system in a negative temperature state is always unstable with respect to thermal contact with any normal system. No matter what the relative sizes of the two systems are, energy will continue to flow from the negative temperature (hotter) system to the normal system until both systems are left in a common *positive* temperature state. In this sense, the negative temperature states are somewhat exotic. However, it is not difficult to find systems of nuclear magnetic moments that are so well isolated from energy exchange with the other normal degrees of freedom of the substance that they can be maintained in negative temperature states for appreciable lengths of time. The trick used to move a system into such a negative temperature state is to first put it into a low positive temperature (large positive β) state in which a majority of the magnetic moments are parallel to the magnetic field. In such a state the system has a negative energy. The field direction is then reversed. Because the system of nuclear spins is isolated, it has no way of shedding its excess energy by flipping its magnetic moment to point in the new field direction. The system of nuclear spins is therefore left in a positive energy, negative β state.

5.18 NERNST'S LAW

Our sixth and last axiom is usually called Nernst's Law or the Third Law of Thermodynamics. We seem to have been somewhat profligate in our axiom creation.*

Axiom 6. (Nernst's Law) All minimum energy states have zero entropy. That is,

$$\lim_{E \rightarrow E_{\min}} S(N_A, N_B, E, V) = 0 \quad (5.34)$$

regardless of the values of N_A , N_B , and V .

Before we discuss the consequences of Nernst's law, we should give some idea of the quantum mechanical origin of the law, for the explanation of Nernst's law must be given in quantum mechanical terms. As we will see, systems described by purely classical models do not satisfy Nernst's law. For classical systems, as T approaches zero, the entropy goes to minus infinity.

Using the fact that $S^o = \log K$, one can give a facile, but erroneous, explanation of the law by noting that, at the ground state energy, the system must be in its ground-state (which we will assume to be nondegenerate) and therefore K , the number of quantum states available to the system, must become unity. $\log K$ would then become zero. Such an effect would come into play when the probability of finding the system in its ground state was close to one. That happens when the total energy of the system is less than the energy separation between the ground state and the first excited state. For a truly macroscopic system, an energy of that magnitude would give a temperature on the order of 10^{-19} K, a temperature that is quite unattainable. In reality, the approach of the entropy to its limiting value becomes definitely noticeable at temperatures below 10 K. This is a temperature at which the average energy *per particle* becomes comparable to the distance between the ground- and excited-state energy levels. The two criteria differ by a factor of 10^{20} . The true origin of Nernst's law is the Bose–Einstein or Fermi–Dirac symmetry requirements on allowed wave functions and not merely the discreteness of the energy levels. At small values of the energy per particle, the density of energy eigenstates (that is, the number of different eigenstates of the system per unit of energy) is much less than it would be if there were no symmetry requirements imposed upon allowed quantum states. (For more details, see Problem 5.19.)

One great benefit of Nernst's law is that it provides a natural way of choosing all of the arbitrary *additive* constants, a_A , a_B , etc., in the entropy functions. The requirement that the entropy of every simple

* But much less so than was David Hilbert who, in reformulating Euclidean geometry, increased the number of axioms from five to twenty three.

substance approach zero as T goes to zero fixes all of the additive constants. No new arbitrary constants appear in the entropy functions of nonsimple substances. Thus, the laws of thermodynamics leave only a single multiplicative arbitrary constant in the set of all the entropy functions for all substances.

Nernst's law has some unexpected and surprising consequences. Two examples are given in the following. *The Pressure Paradox:* If a sample of any real substance is kept in a sufficiently small volume, then its pressure will remain finite as E approaches E_{\min} . But

$$\frac{\partial S}{\partial V} = \beta p \quad \text{and} \quad \beta \rightarrow \infty \quad \text{as} \quad E \rightarrow E_{\min} \quad (5.35)$$

Therefore

$$\lim_{E \rightarrow E_{\min}} \left(\frac{\partial S}{\partial V} \right) = \infty \quad (5.36)$$

However, according to Nernst's law

$$\frac{\partial}{\partial V} \left(\lim_{E \rightarrow E_{\min}} S \right) = 0 \quad (5.37)$$

which suggests that this is a rather nasty limit. The simplest system for which one can check that both of the above equations are true is the ideal Fermi gas, and therefore, the verification of this odd result will have to be postponed until we treat that system in detail.

The Mixing Paradox: Consider a container of volume $2V$, filled with a mixed ideal gas composed of one mole each of two types of particles. At very low temperatures the entropy of this system is essentially zero. Now consider two containers, each of volume V and containing one mole of the two gases separated. Again, at low temperature the entropy is negligible. Thus it should be possible reversibly to go from one system to the other. There is no "entropy of mixing" at very low temperature. (See Exercise 5.11 for a discussion of the entropy of mixing.) We will again have to postpone the verification of this until we treat low-temperature quantum gases.

5.19 THE GIBBS–DUHEM EQUATION

For a simple substance, the extensivity of the entropy is expressed by the equation

$$\lambda S(N, E, V) = S(\lambda N, \lambda E, \lambda V) \quad (5.38)$$

If we differentiate this equation with respect to λ and then set λ equal to one, we get

$$S = \alpha N + \beta E + \gamma V \quad (5.39)$$

This fundamental relation will be very useful in the future. Taking a differential of this relation gives

$$dS = \alpha dN + \beta dE + \gamma dV + N d\alpha + E d\beta + V d\gamma \quad (5.40)$$

But by the definitions of α , β , and γ we know that

$$dS = \alpha dN + \beta dE + \gamma dV \quad (5.41)$$

Subtracting this equation from the previous one gives the Gibbs–Duhem equation

$$N d\alpha + E d\beta + V d\gamma = 0 \quad (5.42)$$

It is useful to eliminate γ in favor of p to obtain

$$N d\alpha + (E + pV) d\beta + \beta V dp = 0 \quad (5.43)$$

This relates the changes in the intensive variables α , β , and p as the system goes from one equilibrium state to a neighboring one. The major use of the Gibbs–Duhem relation is to calculate α , the affinity of a substance, in terms of the more easily measured variables, p and T .

An *isobar* or isobaric curve is a sequence of equilibrium states of the same pressure. Along an isobar, $dp = 0$, and hence

$$N d\alpha + (E + pV) d\beta = 0 \quad (5.44)$$

or

$$\left(\frac{\partial\alpha}{\partial\beta}\right)_p = -(\varepsilon + pv) \quad (5.45)$$

Along an isotherm $d\beta = 0$. This gives

$$\left(\frac{\partial\alpha}{\partial p}\right)_\beta = -\beta v \quad (5.46)$$

The fact that $\partial^2\alpha/\partial p\partial\beta = \partial^2\alpha/\partial\beta\partial p$ leads to the following consistency equation, which will be useful in the next section.

$$\left(\frac{\partial\varepsilon}{\partial p}\right)_\beta = -p\left(\frac{\partial v}{\partial p}\right)_\beta + \beta\left(\frac{\partial v}{\partial\beta}\right)_p \quad (5.47)$$

5.20 THE ENTROPY OF AN IDEAL GAS

Although we have avoided the use of the ideal gas in formulating the fundamental laws of thermodynamics, there is no question about the fact that it occupies a uniquely important place in thermodynamic theory and practice. In this section the phrase *ideal gas* will be used in the restricted sense of a substance that satisfies the classical ideal gas equation of state. This excludes quantum ideal gases, which are systems of noninteracting particles, but do not satisfy that equation. In rational units the ideal gas equation takes the form $pV = N\tau$, or, in terms of the volume per particle,

$$v = \tau/p = 1/\beta p \quad (5.48)$$

Equation (5.47) then gives

$$\left(\frac{\partial\varepsilon}{\partial p}\right)_\beta = -p\left(\frac{-1}{\beta p^2}\right) + \beta\left(\frac{-1}{\beta^2 p}\right) = 0 \quad (5.49)$$

which shows that ε is not a function of pressure. Thus ε is a function of β alone. $\varepsilon = f(\beta)$. This function can be inverted to give $\beta(\varepsilon)$. Integrating the relation $(\partial s^o/\partial\varepsilon)_v = \beta$ gives

$$s^o(\varepsilon, v) = \int^\varepsilon \beta(\varepsilon) d\varepsilon + F(v) \quad (5.50)$$

where F is an unknown function of v . Equation (5.48), combined with the relation $\gamma = \partial s^o/\partial v$, implies that

$$\left(\frac{\partial s^o}{\partial v}\right)_\varepsilon = \beta p = \frac{1}{v} \quad (5.51)$$

which, upon integration, gives

$$s^o(\varepsilon, v) = \log v + G(\varepsilon) \quad (5.52)$$

with G an unknown function of ε . These two formulas for $s^o(\varepsilon, v)$ give the entropy per particle within an arbitrary constant.

$$\begin{aligned} s^o(\varepsilon, v) &= \log v + \int^\varepsilon \beta d\varepsilon + C \\ &\equiv \log v + g(\varepsilon) + C \end{aligned} \quad (5.53)$$

From the extensivity relation for $S^o(N, E, V)$ we get

$$S^o(N, E, V) = N[\log(V/N) + g(E/N) + C] \quad (5.54)$$

The detailed form of the energy–temperature relationship, which defines $g(\varepsilon)$, depends on the internal structure of the particles and cannot be derived from the pressure equation of state. For point particles

(a good approximation to the noble gases, He, Ne, etc.), we have the energy equation $\varepsilon = \frac{3}{2}\tau$, giving $\beta = 3/2\varepsilon$ and

$$S^o = N(\log(V/N) + \frac{3}{2} \log(E/N) + C) \quad (5.55)$$

Clearly, for this system, the minimum energy is zero ($E_{\min}(N, V) = 0$). A simple calculation will verify that all three parts of Axiom 5 are satisfied, which guarantees that the boundary states of \mathcal{S}_T are thermodynamically inaccessible. However, it is also easy to see that

$$\lim_{E \rightarrow E_{\min}} S^o(N, E, V) = -\infty \quad (5.56)$$

which is a clear violation of Nernst's law. This violation of Nernst's law is not surprising, since the ideal gas equation of state is valid only when quantum mechanical effects can be neglected, and, therefore, it is not valid close to zero temperature.

5.21 THERMODYNAMIC POTENTIALS

As was noted in Section 4.7, most experiments are actually carried out at fixed temperature, not at fixed energy. Usually it is also much easier to maintain a fixed pressure on an experimental sample than to keep the sample's volume fixed. It would therefore be helpful if the conditions for thermodynamic equilibrium could be expressed in terms of T and p , rather than E and V . The convexity of S guarantees that such transformations of independent variables are possible. For example, at fixed N and V ,

$$\frac{\partial \beta}{\partial E} = \frac{\partial^2 S}{\partial E^2} < 0 \quad (5.57)$$

Therefore, the transformation from E to β is one-to-one, which is what is needed in order to replace E by β as an independent variable (see Fig. 5.15).

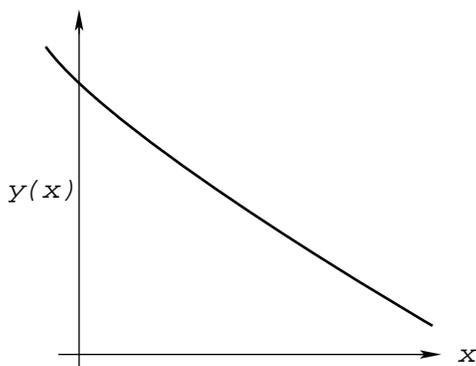


Fig. 5.15 If the slope of the curve $y(x)$ is always negative, then there is only one value of x that gives a particular value of y so that the function $y(x)$ can be inverted to give the function $x(y)$.

The transformation from E to β is most easily carried out by a method due to Legendre. We define a new thermodynamic function, which will be immediately recognized as the canonical potential, by

$$\phi = S - \beta E \quad (5.58)$$

The difference in ϕ between two neighboring thermodynamic states is

$$\begin{aligned} d\phi &= \alpha dN + \beta dE + \gamma dV - \beta dE - E d\beta \\ &= \alpha dN - E d\beta + \gamma dV \end{aligned} \quad (5.59)$$

It is clear from Eq. (5.59) that, if ϕ is expressed in terms of the variables N , β , and V , then

$$\begin{aligned} \left(\frac{\partial\phi}{\partial N}\right)_{\beta V} &= \alpha \\ \left(\frac{\partial\phi}{\partial\beta}\right)_{NV} &= -E \\ \text{and} \quad \left(\frac{\partial\phi}{\partial V}\right)_{N\beta} &= \gamma = \beta p \end{aligned} \quad (5.60)$$

The first and last of these equations give the affinity and the free expansion coefficient (or pressure) in terms of N , β , and V . The second gives the old variable E in terms of the new variable β . These formulas are identical with Eqs. (4.46) and (4.47), confirming the identification of ϕ as the canonical potential.

In Chapter 7, another ensemble will be defined that describes a system that can exchange both particles and energy with a large reservoir. It is called the *grand canonical ensemble*. The independent variables defining a grand canonical ensemble are α , β , and V . The logarithm of its normalization constant will be another thermodynamic potential, namely, the grand potential. From a thermodynamic viewpoint, the grand potential is the potential obtained in a Legendre transformation to the variables α , β , and V .

5.22 THE GRAND POTENTIAL

If ψ is defined everywhere in the thermodynamic state space \mathcal{S}_T by

$$\psi = S - \alpha N - \beta E \quad (5.61)$$

then the change in ψ , in going from one point in \mathcal{S}_T to a neighboring point, is

$$d\psi = -N d\alpha - E d\beta + \gamma dV \quad (5.62)$$

which shows that, if ψ is written in terms of the variables α , β , and V , then

$$\begin{aligned} \left(\frac{\partial\psi}{\partial\alpha}\right)_{\beta V} &= -N \\ \left(\frac{\partial\psi}{\partial\beta}\right)_{\alpha V} &= -E \\ \text{and} \quad \left(\frac{\partial\psi}{\partial V}\right)_{\alpha\beta} &= \gamma = \beta p \end{aligned} \quad (5.63)$$

A particular choice of independent variables is called a *representation*. We have considered the (N, E, V) , the (N, β, V) , and the (α, β, V) representations. It is clear that a Legendre transformation could be used to eliminate any one or two of the extensive variables, N , E , and V , in favor of their thermodynamically *conjugate* variables, α , β , and γ . However, it is not possible to eliminate all extensive variables. There are two ways of seeing this. First, because of the Gibbs–Duhem relation, it is not possible to make arbitrary changes in the three variables, α , β , and γ . Thus, they cannot form a set of three independent variables. Second, if one attempted to make such a triple transformation by means of a Legendre transformation, the appropriate thermodynamic potential would be

$$\omega = S - \alpha N - \beta E - \gamma V \quad (5.64)$$

But, because of the fundamental relation, Eq. (5.39), the function ω would be identically zero in \mathcal{S}_T and thus could not fill the role of a thermodynamic potential at all.

5.23 THERMODYNAMIC VARIATIONAL PRINCIPLES

In Fig. 5.16 is shown a system, containing three phases, in contact with a large thermal reservoir. Certainly, the condition that the system be in equilibrium with respect to energy transfer between the phases and

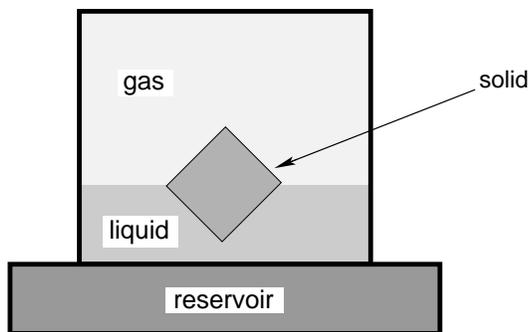


Fig. 5.16 A system containing three phases in contact with a thermal reservoir.

between the system and the reservoir is that the temperature of every phase be equal to that of the reservoir. We now want to show that, in determining the equilibrium conditions with respect to all other variables (volumes and particle numbers of all phases), the total canonical potential of the system, not including the reservoir, plays the same role as the total entropy for an isolated system. We number the phases, in any order, 1, 2, and 3. We assume that each phase contains two types of particles, such as sugar and water. The numbers of particles of the two types in phase i we call N_i' and N_i'' . The total canonical potential is $\phi_T = \sum_i \phi_i(N_i', N_i'', \beta, V_i)$.

Theorem At equilibrium, the total canonical potential is a maximum with respect to all possible changes in particle numbers and volumes.

Proof The conditions for ϕ_T to be stationary with respect to a transfer of particles between phases i and j is that $\partial\phi_i/\partial N_i' = \partial\phi_j/\partial N_j'$ and $\partial\phi_i/\partial N_i'' = \partial\phi_j/\partial N_j''$. But these are just the already known equilibrium conditions that $\alpha_i' = \alpha_j'$ and $\alpha_i'' = \alpha_j''$. Similarly, the condition that ϕ_T be stationary with respect to changes in the volumes occupied by the three phases leads to another known equilibrium condition, namely, that $p_1 = p_2 = p_3$. That the stationary point is a maximum relies on the facts that, for any substance,

$$\frac{\partial^2 \phi}{\partial N^2} = \left(\frac{\partial \alpha}{\partial N} \right)_{\beta V} < 0 \quad (5.65)$$

and

$$\frac{\partial^2 \phi}{\partial V^2} = \beta \left(\frac{\partial p}{\partial V} \right)_{N\beta} < 0 \quad (5.66)$$

The first of these conditions says that adding particles at constant temperature and volume reduces the affinity for particles. The second says that compressing the system at constant temperature increases the pressure. Both conditions seem intuitively obvious, but they turn out to be surprisingly tricky to actually prove from the fundamental principles of thermodynamics (see Problem 5.6).

The statistical mechanism underlying this variational principle is that the number of quantum states of the system plus the reservoir, as a function of the system parameters, is equal to $\exp(\phi_T + \text{const.})$. Therefore, the statement that ϕ_T goes to a maximum is equivalent to the statement that the combined system goes to its most probable macrostate. It can also be shown that, for a system that can exchange energy and particles with a reservoir, the total grand potential of the system is a maximum at equilibrium.

5.24 THERMODYNAMIC FLUCTUATIONS

Thermodynamics has been defined as the collection of those universal properties of macroscopic systems that emerge only in the thermodynamic limit. From that point of view, it can be seen that a major item of thermodynamic theory has been omitted. All our thermodynamic laws describe properties of the equilibrium state. In statistical mechanics, that state can be identified with the most probable macrostate. That most probable macrostate is the state that is actually observed at equilibrium because, in the thermodynamic limit, the fluctuations in macroscopic observables about their most probable values approach zero. The reason for this is that a macroscopic observable has been defined as an average of some type of “local” observable over a large region, and the values of the local observable in different portions of the large region

are statistically independent. The statistical independence brings the Law of Large Numbers into play, suppressing the fluctuations.

However, for averages of large numbers of statistically independent variables, the Law of Large Numbers and the Central Limit Theorem give much more detailed information about the fluctuation probability than the simple fact that the fluctuations approach zero. The Law of Large Numbers gives a detailed estimate of the statistical uncertainty, while the Central Limit Theorem gives an explicit formula for the probability distribution of the small fluctuations that remain at any finite stage in the limiting procedure. Corresponding formulas can be given for the fluctuations in large but finite thermodynamic systems. They do not require a knowledge of the Hamiltonian function of the system, but rather are written in terms of thermodynamic potentials, which can be obtained by purely macroscopic measurements. Therefore, these formulas logically form part of the body of thermodynamic theory. Two special cases of the thermodynamic fluctuation formulas will be given, which should make the general principle clear.

We first consider energy fluctuations. If a thermodynamic system is in contact with a reservoir at temperature T , then its energy is not perfectly predictable because only the total energy of the system plus reservoir is exactly constant. We saw in this chapter, using thermodynamic methods, and in Chapter 4, using the canonical ensemble, that the average energy is given in terms of the canonical potential by

$$\bar{E} = -\frac{\partial\phi}{\partial\beta} \quad (5.67)$$

where $\beta = 1/kT$. We also saw in Chapter 4 that the mean-square fluctuation in the energy, $(\Delta E)^2$, could be written in terms of the canonical potential by a similar formula.

$$(\Delta E)^2 = \langle (E - \bar{E})^2 \rangle = \frac{\partial^2\phi}{\partial\beta^2} \quad (5.68)$$

In thermodynamic fluctuation theory, this formula must be taken as a fundamental postulate. It is the equivalent, for a system containing a large number of particles, of the Law of Large Numbers for the fluctuations in the average value of a large number of independent random variables. In fact, for an ideal gas, it is exactly the same as the Law of Large Numbers (see Problem 5.17), but, for systems of interacting particles, this formula includes effects due to statistical correlations between the particles. Such effects fall outside the range of the Law of Large Numbers. Actually these formulas for \bar{E} and $(\Delta E)^2$ can both be derived from a more general postulate that gives the detailed probability, $P(E)$, that the system will be found with energy E . This formula is the thermodynamic equivalent of the Central Limit Theorem in probability theory. In Problem 4.11, the reader was asked to show, using the canonical ensemble, that

$$P(E) = e^{S^o(E) - \beta E} / Z(\beta) \quad (5.69)$$

where $Z(\beta)$ is the partition function.

For a system that can exchange both energy and particles with a reservoir at affinity α and inverse temperature β , the average values of particle number and energy are given, in terms of the grand potential, $\psi(\alpha, \beta, V)$ by Eq. (5.63).

$$\bar{N} = -\frac{\partial\psi}{\partial\alpha} \quad \text{and} \quad \bar{E} = -\frac{\partial\psi}{\partial\beta} \quad (5.70)$$

The fluctuations in those quantities are given by formulas that will be derived in Chapter 7.

$$(\Delta N)^2 = \langle (N - \bar{N})^2 \rangle = \frac{\partial^2\psi}{\partial\alpha^2} \quad (5.71)$$

$$(\Delta E)^2 = \langle (E - \bar{E})^2 \rangle = \frac{\partial^2\psi}{\partial\beta^2} \quad (5.72)$$

The pattern should now be obvious; when certain variables can fluctuate, the first derivatives of the appropriate thermodynamic potential, *which must be written in rational units*, give the average values of the variables while the second derivatives give the mean-square fluctuations. The probability of finding the



Fig. 5.17 The “sample” is a small subvolume within a larger solution of glucose in water.

system with exactly N particles and energy E is given by a formula that will also be derived in Chapter 7 and is obviously analogous with Eq. (5.69).

$$P(N, E) = e^{S^o(N, E) - \alpha N - \beta E} / \Lambda(\alpha, \beta) \quad (5.73)$$

The normalization constant, Λ , for the probability distribution, called the grand partition function, is related to the thermodynamic potential, ψ , in the same way that the cononical partition function is related to the canonical potential. That is, $\psi = \log \Lambda$.

5.25 THE AFFINITY OF A DILUTE SOLUTION

From Eq. (5.71), a formula for the affinity of a dilute solution can be derived that has a wide range of useful applications. In order to focus on a specific problem, we consider a large vessel containing a dilute solution of glucose in water (Fig. 5.17). The “sample” is taken as a small subvolume ΔV within the vessel. The rest of the system acts as a reservoir. Since the sample can exchange both particles and energy with the reservoir, the appropriate thermodynamic potential is $\psi(\alpha_g, \alpha_w, \beta, \Delta V)$, where α_g and α_w are the affinities for glucose and water, respectively. The fluctuation in the number of glucose molecules in the sample is given by

$$(\Delta N_g)^2 = \frac{\partial^2 \psi}{\partial \alpha_g^2} = -\frac{\partial N_g}{\partial \alpha_g} \quad (5.74)$$

But, if the solution is very dilute, then the glucose molecules drift in and out of the volume independently and the Poisson distribution is valid [see Eq. (1.29)]. This gives

$$(\Delta N_g)^2 = N_g \quad (5.75)$$

Therefore

$$\frac{\partial \alpha_g}{\partial N_g} = -\frac{1}{N_g} \quad (5.76)$$

This can be integrated to give

$$\alpha_g = -\log N_g + \text{const.} \quad (5.77)$$

The constant may depend on any variables other than N_g . Because α_g is an intensive quantity, it should be possible to express this relation in terms of the density of glucose molecules, $n_g = N_g / \Delta V$. The way to do so is to write the arbitrary constant as $\log \Delta V + f_g^o$, where f_g^o is another arbitrary constant. Then Eq. (5.77) becomes

$$\alpha_g = -\log n_g + f_g^o \quad (5.78)$$

We have been using rational units and, therefore, the affinity given here is defined as $\partial S^o / \partial N_g$ where N_g is the number of glucose molecules. In practical units α_g is defined as $\partial S / \partial N_g$ where $S = kS^o$ and N_g is the number of moles of glucose. The conversion from one system of units to the other adds a factor of the gas constant to the equation. Therefore, in practical units, the equivalent relation is

$$\alpha_g(\text{prac.}) = -R \log n_g + f_g \quad (5.79)$$

where $f_g = Rf_g^o$ and n_g is the molar density.

5.26 CONDITIONAL THERMODYNAMIC POTENTIALS

All the entropy functions that have been used so far have been equilibrium entropy functions. As such, they are functions only of the independently conserved variables N , E , and V . Such equilibrium entropy functions are adequate for doing minimal, bare, thermodynamics. That is, they allow the prediction of the equilibrium distributions of those same conserved quantities under conditions in which transfer of the quantities is allowed between subsystems in a larger isolated system. However, by extending the definition of an entropy function to include functions of other macroscopic variables, a much richer set of physical problems can be attacked with thermodynamic methods. The same extension can also be made for other thermodynamic potentials, such as the canonical and grand potentials.

The equilibrium entropy, $S^o(N, E, V)$ is defined as the logarithm of the number of quantum states of the system for fixed values of N , E , and V . Consider some macroscopic observable, $A(x, p)$, that is not a conserved quantity, such as the electric polarization or the kinetic energy. We could then define a *conditional entropy function* by selecting, from a microcanonical ensemble, only those states that have a specific value, say a , of the observable, $A(x, p)$. The logarithm of the normalization constant for that restricted ensemble would be an entropy that was a function of N , E , V , and a .

$$e^{S(N, E, V, a)} = \frac{1}{N! h^{3N}} \int \delta(E - H) \delta(a - A) d^{3N} x d^{3N} p \quad (5.80)$$

The conditional entropy function, $S(N, E, V, a)$, is equal to the logarithm of the number of quantum states available to the system, conditioned on the facts that the number of particles is N , the energy is E , the volume is V , and the value of the observable A is a . It might be compared with the conditional probability, $P(y|x)$, which is the probability of y , conditioned on the value of x .

Our first application of these conditional thermodynamic potentials will be to generalize the thermodynamic fluctuation formulas presented before. It is clear from Eq. (1.51) that, if we are using a microcanonical ensemble, then the probability of finding a system in the ensemble with the value a for the observable $A(x, p)$ is equal to

$$\begin{aligned} P_A(a) &= \int \delta(E - H) \delta(a - A) d^{3N} x d^{3N} p \bigg/ \int \delta(E - H) d^{3N} x d^{3N} p \\ &= e^{S(a)} / \Omega'(E) \end{aligned} \quad (5.81)$$

For other ensembles, $S(a)$ would be replaced by the conditional thermodynamic potential appropriate to the ensemble. Expanding $S(a)$ to second order about \bar{a} , one obtains a Gaussian approximation to $P_A(a)$, which can be used to calculate the mean-square fluctuation in A .

$$(\Delta A)^2 = \left| \frac{\partial^2 S(a)}{\partial a^2} \right|_{\bar{a}}^{-1} \quad (5.82)$$

where \bar{a} is the value of a for which $\partial S(a)/\partial a = 0$.

PROBLEMS

5.1 Suppose $S(N, E, V)$ is an entropy function that gives the correct equilibrium states of a particular substance. Let $S^* = S + AE + BV$, where A and B are constants. Show that S^* will not give the correct equilibrium states for the situation shown in Fig. 5.5.

5.2 One mole of a substance satisfies the equations of state

$$T = \lambda \varepsilon^{2/3} v^{-1/2} \quad \text{and} \quad pv = \frac{3}{2} \varepsilon \quad (5.83)$$

where λ is a constant. Determine $s(\varepsilon, v)$ within an arbitrary constant.

5.3 Consider a substance containing K different types of particles. For example, $K = 3$ for a water, sugar, and salt solution. Let the spatial densities of the particles be called n_1, \dots, n_K . For a single phase of the substance, we can independently vary the K densities and the temperature, but all other physical quantities are then determined by those $K + 1$ parameters. Thus, for a single phase, we have $K + 1$ *free variables*. For an equilibrium state of the substance containing two phases in contact (a two-phase state), one has the $2K + 1$ variables $n'_1, \dots, n'_K, n''_1, \dots, n''_K$, and β , but these are restricted by $K + 1$ equilibrium conditions, $\alpha'_1 = \alpha''_1, \dots, \alpha'_K = \alpha''_K$, and $p' = p''$. This leaves only K free variables. Show that, for a state containing P phases in equilibrium, the number of free variables is $F = K - P + 2$. This is the *Gibbs phase rule*. Notice that it says that the triple point of a simple substance has no free variables—there is a unique temperature and pressure at which three phases of a simple substance can be in equilibrium.

5.4 The entropy per unit volume of a system composed of particles of types A and B is

$$s = \frac{3}{2} (n_A + n_B) \log \left(\frac{u}{n_A + n_B} \right) - n_A \log(n_A/C_A) - n_B \log(n_B/C_B) \quad (5.84)$$

where n_A and n_B are the particle densities, u is the energy density, and C_A and C_B are constants. What is the entropy function $S(N_A, N_B, E, V)$?

5.5 Let $s(\varepsilon, v)$ be the molar entropy of a simple substance. In Exercise 5.6 it is shown that, due to the convexity properties of s , the 2×2 matrix

$$M = \begin{bmatrix} \partial^2 s / \partial \varepsilon^2 & \partial^2 s / \partial \varepsilon \partial v \\ \partial^2 s / \partial \varepsilon \partial v & \partial^2 s / \partial v^2 \end{bmatrix} \quad (5.85)$$

has only negative eigenvalues. For an ideal monatomic gas, compute the eigenvalues explicitly and verify that they are negative.

5.6 Let $s(n, \varepsilon)$ be the entropy per unit volume (the entropy density), expressed as a function of the particle density and the energy density. Consider 2 moles of a simple substance, with an energy $2E$, in a cylinder of volume $2V$. The cylinder is divided into two equal volumes by an immovable partition that has a small hole in it. (a) Assuming that the uniform state is the equilibrium state, derive a convexity condition on the entropy function $s(n, \varepsilon)$ by an argument similar to that used in Section 5.5. (b) Following the method used in Exercises 5.6 and 5.7, show that $\partial \alpha(n, \beta) / \partial n < 0$.

5.7 Show that the entropy function given in Eq. (5.55) satisfies Axiom 5 but does not satisfy Nernst's Law.

5.8 Consider a monatomic ideal gas that can exchange energy and particles with a reservoir. (a) Using Eq. (5.73), show that the energy and particle number fluctuations are not statistically independent by showing that $\langle (N - \bar{N})(E - \bar{E}) \rangle \neq 0$. (b) Show that, if we define another energy variable, Q , by $Q(E, N) = E - N\bar{E}/\bar{N}$, then the fluctuations in N and Q are statistically independent. Give a physical explanation of this result.

5.9 Many ideal gases satisfy equations of state of the form $pV = NkT$ and $E = KNkT$. (For monatomic gases, $K = \frac{3}{2}$, for diatomic gases with only rotational kinetic energy, $K = \frac{5}{2}$, and, for diatomic gases in which rotational and vibrational degrees of freedom can be treated classically, $K = \frac{7}{2}$.) (a) For such an ideal gas, show that, along an adiabatic curve,

$$pV^{(K+1)/K} = \text{const.} \quad \text{and} \quad VE^K = \text{const.} \quad (5.86)$$

(b) Also show that, in the E - V plane, the adiabatic curves are steeper than the isotherms.

5.10 The interaction potential between most molecules has the following characteristics. (1) It is negligible at very large distances; therefore, very dilute gases satisfy the ideal gas equation, in which the interaction potential energy is neglected completely. (2) It is attractive (negative) at moderate distances, typically in the range of a few Ångströms to a few tens of Ångströms. Thus, as the density of the gas is increased, the deviations from the ideal gas law are initially in the direction of lower pressure (the particles are pulled toward one another). The attractive part of the interaction is also responsible for the eventual condensation of the gas into a liquid. (3) At small distances, the potential becomes strongly repulsive (large and positive). This is why most liquids are relatively incompressible. Taking these properties into account, van der Waals proposed the following approximate pressure equation of state:

$$p = \frac{RT}{v - v_o} - \frac{a}{v^2} \quad (5.87)$$

where v is the volume per mole and v_o and a are positive constants, different for each substance. A monatomic van der Waals gas is one that satisfies the additional condition that the molar energy ε approaches $\frac{3}{2}RT$ as $v \rightarrow \infty$. (a) Determine the molar entropy function $s(\varepsilon, v)$ of a monatomic van der Waals gas. (b) Show that $\varepsilon = \frac{3}{2}RT - a/v$ for a monatomic van der Waals gas. (c) Show that, in terms of the dimensionless variables $\tilde{p} = pv_o^2/a$, $t = RTv_o/a$, $\tilde{v} = v/v_o$, and $\tilde{\varepsilon} = \varepsilon v_o/a$, all monatomic van der Waals gases have the same equation of state, $\tilde{p} = t/(\tilde{v} - 1) - 1/\tilde{v}^2$ and $\tilde{\varepsilon} = \frac{3}{2}t - 1/\tilde{v}$. (d) Plot the isotherms for the pressure equation of state in the \tilde{p} - \tilde{v} plane over the range $1.3 < \tilde{v} < 10$ for $t = 7/27$, $8/27$, and $9/27$, and show that the first curve has unphysical characteristics. (To understand where the peculiar constant $8/27$ came from, see Exercise 5.20.)

5.11 A highly relativistic classical ideal gas of point particles satisfies the equations of state

$$pV = NkT = \frac{1}{3}E \quad (5.88)$$

For such a system, derive the entropy function $S(N, E, V)$.

5.12 In the nineteenth century, using Maxwell's equations, it was possible to show that the pressure exerted on the walls of an evacuated container by the electromagnetic radiation inside was related to the energy density of the radiation by the formula $p = \frac{1}{3}E/V$. The entropy function of that "system" of electromagnetic radiation would be a function $S(E, V)$. Assuming that the energy density is related to the temperature by an equation of the form $E/V = AT^\lambda$, where A and λ are constants, show that λ must be equal to 4. This result was first derived by Ludwig Boltzmann after being guessed at, from an analysis of experimental data, by Josef Stefan.

5.13 In Section 4.12 the canonical potential for a gas of dipolar molecules in an electric field was given as

$$\phi(N, \beta, V) = N \left[\log\left(\frac{V}{N}\right) - \frac{5}{2} \log \beta + \log\left(\frac{\sinh(\beta\mu\mathcal{E})}{\beta\mu\mathcal{E}}\right) + \text{const.} \right] \quad (5.89)$$

Use this result to calculate the molar entropy of that system as a function of density and temperature.

5.14 For an ideal gas of diatomic molecules with the energy equation $E = \frac{5}{2}NkT$, calculate the grand potential, $\psi(\alpha, \beta, V)$, and verify Eq. (5.63).

5.15 For a system of N quantum mechanical harmonic oscillators, the entropy function $S^o(N, E)$ was shown to be

$$S^o = \left(N + \frac{E}{\hbar\omega}\right) \log\left(N + \frac{E}{\hbar\omega}\right) - N \log N - \frac{E}{\hbar\omega} \log\left(\frac{E}{\hbar\omega}\right) \quad (5.90)$$

Show that this entropy function satisfies Axiom 5 and Nernst's law. (Note: there is no relevant "volume" for this system.)

5.16 Calculate the canonical potential $\phi(N, \beta, V)$ for the system of Problem 5.14 and verify the inequalities given in Eqs. (5.65) and (5.66).

5.17 For a monatomic ideal gas in the canonical ensemble the total energy of the system is the sum of the kinetic energies of all the particles, which are N statistically independent variables. Thus the Law of Large Numbers can be applied. Show that the Law of Large Numbers predicts the same value for $(\Delta E)^2$ as the thermodynamic fluctuation formula, $(\Delta E)^2 = \partial^2 \phi / \partial \beta^2$.

5.18 For one mole of an ideal monatomic gas in equilibrium with a reservoir at STP , use Eq. (5.68) to calculate the ratio of ΔE to E .

5.19 In Section 5.18, it was stated that the source of Nernst's law is the Bose–Einstein or Fermi–Dirac statistics of the particles and not simply the discreteness of quantum mechanical energy levels. To show that this is so, let us consider an imaginary system of noninteracting *boltzons*. They are quantum mechanical point particles that have the usual Hamiltonian operator for an ideal gas, but they differ from real particles in that their quantum states do not have to satisfy any symmetry or antisymmetry conditions. Show that, in the thermodynamic limit, the system will satisfy the equations of state of a classical monatomic ideal gas at any temperature and pressure. From this one can conclude that the entropy function of the system satisfies Axiom 5 but not Nernst's law. (Hint: Look carefully at the section entitled The Classical Limit in the Mathematical Appendix.)

5.20 Most diatomic gases satisfy the equations of state, $pV = N\tau$ and $E = \frac{5}{2}N\tau$, over some appreciable temperature interval. (a) For such a gas, use Equations 5.45 and 5.46 to calculate the affinity, α , (within an arbitrary constant) as a function of p and τ . (b) Now combine the result in (a) with Eq. (5.39) to calculate the entropy function, $S^\circ(N, E, V)$.

5.21 Consider a container separated into two parts by means of a rigid partition that can pass water molecules but not glucose molecules. On one side is pure water but on the other is a dilute solution of glucose. Using the Gibbs–Duhem equation and Eq. (5.78) for α_g , show that, at equilibrium, the pressure in the solution will exceed that in the pure water by an amount (called the *osmotic pressure*) $\Delta p = n_g kT$. Notice that this is exactly what would be obtained by treating the glucose molecules as an ideal gas, although a derivation of the result using that picture would be very questionable.

5.22 In the canonical ensemble, the probability of finding a system in a state described by the phase-space point (x, p) is

$$P(x, p) = e^{-\beta H(x, p)} / h^K N! Z(N, \beta, V) \quad (5.91)$$

The uncertainty in the energy is defined by

$$(\Delta E)^2 = \int [H(x, p) - \bar{E}]^2 P(x, p) d^K x d^K p \quad (5.92)$$

Show that $(\Delta E)^2 = \partial^2 \phi / \partial \beta^2$, where ϕ is the canonical potential.

5.23 In Eq. (5.81), assume that the function $S(a)$ can be expanded about its maximum value, $S(\bar{a})$, as a Taylor series through second order and derive Eq. (5.82). Hint: Use the fact that $\Omega'(E) = \int \exp S(a) da$ and make the same expansion of S in both numerator and denominator.

5.24 A wire is held under tension by a force F . Assume that the entropy of the wire is a function $S(E, L)$ of its energy and length. Show that the tension force is related to the entropy function of the wire by $F = -T \partial S / \partial L$.