Chapter 1
Thermodynamic systems and the zeroth law

Ludwig Boltzmann, who spent much of his life studying statistical mechanics, died in 1906, by his own hand. Paul Ehrenfest, carrying on the work, died similarly in 1933. Now it is our turn to study statistical mechanics.

David L. Goodstein, *States of Matter.*

1.1 The goals of thermodynamics

Thermodynamics is the study of macroscopic systems for which thermal effects are important. These systems are normally assumed to be at equilibrium, or at least, close to equilibrium. Systems at equilibrium are easier to study, both experimentally and theoretically, because their physical properties do not change with time. The framework of thermodynamics applies equally well to all such macroscopic systems; it is a powerful and very general framework.

An example of a thermodynamic system is a fluid (a gas or a liquid) confined to a beaker of a certain volume, subjected to a certain pressure at a certain temperature. Another example is a solid subjected to external stresses, at a given temperature. *Any* macroscopic system for which temperature is an important parameter is an example of a thermodynamic system. An example of a macroscopic system which is *not* a thermodynamic system is the solar system, inasmuch as only the planetary motion around the Sun is concerned. Here, temperature plays no role, although it is a very important quantity in solar physics; our Sun is by itself a thermodynamic system.

A typical question of thermodynamics is the following:

> A macroscopic system A, initially at a temperature T_A, is brought in thermal contact with another system B, initially at a temperature T_B. When equilibrium is re-established, what is the final temperature of both A and B?

Another is

> A macroscopic system undergoes a series of transformations which eventually returns it to its initial state. During these transformations, the system absorbs a net quantity Q of heat, and releases a net amount W of energy which can be used for useful work. What is the efficiency of the transformation, that is, the ratio W/Q?

It is an important aspect of thermodynamics that these questions can be formulated quite generally, without any explicit reference to what the thermodynamic

1.6.2 Empirical temperature

The existence of the relation $g(P, V) = \theta$ for isotherms, inferred empirically above, can also be justified by rigourous mathematics. We will now go through this argument. This will serve to illustrate a major theme of thermodynamics: Simple physical ideas (such as the zeroth law) can go very far when combined with powerful mathematics.

We consider two thermodynamic systems, A and B, plus a third C, which will serve as our reference system. For concreteness, although this is not necessary for the discussion, we shall suppose that all three systems consist of fluids, so that P and V can be used as thermodynamic variables. (We could instead have used generic variables, X and Y.) We do not assume that the systems are identical, nor will we say anything about the nature of the fluids (whether they are liquids or gases). We denote by V_A and P_A the volume and pressure of system A, respectively, and we use a similar notation for the thermodynamic variables of B and C. We suppose that V_A and V_B are fixed quantities, so that the volumes do not change during the operations made on the systems. We also suppose that the state of system C is fixed (V_C and P_C do not change during the operations).

We first bring A in thermal contact with C. As a result of the thermal interaction, we see that A's pressure varies with time. When equilibrium is established, we measure the pressure of A to be P_A. This value is determined uniquely by the experimental situation; altering the conditions (for example, changing either one of V_A, V_C or P_C) will produce a different equilibrium pressure. We must conclude that the quantities V_A, P_A, V_C, and P_C are not independent; P_A is *determined* by the other quantities, and a *relation* must exist between them. This can be expressed mathematically by an equation of the form

$$f_{AC}(P_A, V_A, P_C, V_C) = 0, \tag{1.3}$$

where f_{AC} is some function, characteristic of the thermal interaction between systems A and C. We do not need to know the explicit form of this function, only that it exists. (For equal quantities of ideal gases, experiment tells us that the relation is $P_A V_A = P_C V_C$, so that $f_{AC} = P_A V_A - P_C V_C$. For other systems, the function will have a different form.)

Repeating the same procedure with B, we conclude that a relation of the form

$$f_{BC}(P_B, V_B, P_C, V_C) = 0 \tag{1.4}$$

must also exist. Equations (1.3) and (1.4) both express a relation between P_C and the other thermodynamic variables. We may express these relations as

$$P_C = g_{AC}(P_A, V_A, V_C), \qquad P_C = g_{BC}(P_B, V_B, V_C).$$

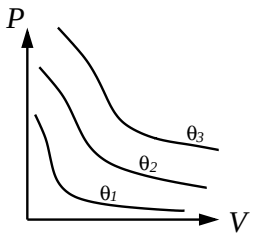
In principle, these equations can be obtained by solving Eqs. (1.4) and (1.5) for P_C, and this determines the form of the new functions g_{AC} and g_{BC}. (For ideal gases, we have $P_C = P_A V_A / V_C$ and $P_C = P_B V_B / V_C$.)

We now equate these two results for P_C:

$$g_{AC}(P_A, V_A, V_C) = g_{BC}(P_B, V_B, V_C). \tag{1.5}$$

It is important to understand the meaning of this equation. If the systems A and B are different, which we assume is the case in general, then Eq. (1.5) states that the *value* of function g_{AC}, when evaluated at P_A, V_A, and V_C, is equal to the *value* of the different function g_{BC}, when evaluated at P_B, V_B, and V_C. Equation (1.5) does *not* state that g_{AC} and g_{BC} are equal *as functions*: they are not, unless the systems A and B are identical. [For ideal gases, Eq. (1.5) reduces to $P_A V_A = P_B V_B$. In this

1.7 Equation of state



The all-important relation

$$g(P,V) = \theta$$

is called the *equation of state* of the thermodynamic system. It states that at equilibrium, the system's pressure, volume, and empirical temperature are not all independent, but are related quantities. The relation can be expressed graphically on a P-V diagram. The curves $g(P,V) =$ constant are the system's isotherms.

The exact form of the equation of state depends on the nature of the thermodynamic system. For ideal gases, we have seen that the equation of state takes the form

$$PV = n\theta.$$

This holds quite generally for a gas at low pressure. At higher pressure, the equation of state is more accurately described by

$$PV = n\theta\big[1 + a(\theta)P + b(\theta)P^2 + \cdots\big],$$

where a and b are functions that must be determined empirically. Such an expansion of the equation of state in powers of the pressure is called a *virial expansion*. Another important equation of state is the van der Waals equation,

$$\left(P + \frac{n^2 a}{V^2}\right)\big(V - nb\big) = n\theta,$$

where a and b are constants. This equation describes a simple substance near the vapourisation curve to be described below. In general, however, the equation of state cannot be expressed as a simple mathematical expression; it must then be presented as a tabulated set of values.

The equation of state of a given substance depends on the *phase* occupied by that substance. Fairly generally, three different phases are possible: solid, liquid, and gas. The equation of state adopts a different form in each of these phases. This can be shown graphically in a P-V diagram (Fig. 1). Notice that the isotherms look differently in the three different phases.

What we want to calculate is $(\partial U/\partial V)_T$, and we will do so employing the techniques we have introduced thus far. Let us first go back to the equation

$$đQ = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT,$$

derived above. Using Eq. (2.15), this implies

$$\frac{đQ}{dT} = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}.$$

If we assume that P is treated as a constant in this equation, we obtain

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P.$$

Using Eq. (2.19) and solving for the unknown, we finally arrive at

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{\beta V} - P}. \tag{2.20}$$

This is our answer. Because all quantities on the right-hand side are known, we have complete information about $(\partial U/\partial V)_T$. The result illustrates a very important aspect of what thermodynamics is all about. Quantities that are difficult to measure directly, such as $(\partial U/\partial V)_T$, can be related to easily measurable quantities, such as C_V, C_P and β. It is important to appreciate the complete generality of Eq. (2.20): this equation holds for *any* thermodynamic system.

2.8 More on ideal gases

The ideal gas, with equation of state $PV = nRT$, has been used repeatedly in the preceding sections to illustrate the abstract ideas of thermodynamics. In this section we use the techniques introduced in this chapter to further our understanding of the ideal gas. We shall require additional input from experiment. This will be provided by Joule's experiment, and by measurements of the heat capacities of several ideal gases.

2.8.1 Joule's experiment

The question investigated by Joule in 1843 was the following: What happens to its temperature when an ideal gas undergoes a free expansion in a thermally insulated chamber?

The situation considered here is that of an ideal gas initially confined by a partition to lie in a smaller portion of a chamber. It is assumed that heat is prevented to flow into, or out of, the chamber. When the partition is removed, the gas freely expands into the entire chamber. If the initial temperature was T, what is the final temperature? The answer, as determined by Joule, is that the final temperature is also T. Thus, under adiabatic conditions the temperature of an ideal gas does not change during a free expansion.

The result of the Joule experiment has profound consequences regarding the form of the internal-energy function. Notice first that no work is done on the system during a free expansion, because there is no external agent applying any force. And because the free expansion takes place in a thermally insulated chamber, there is

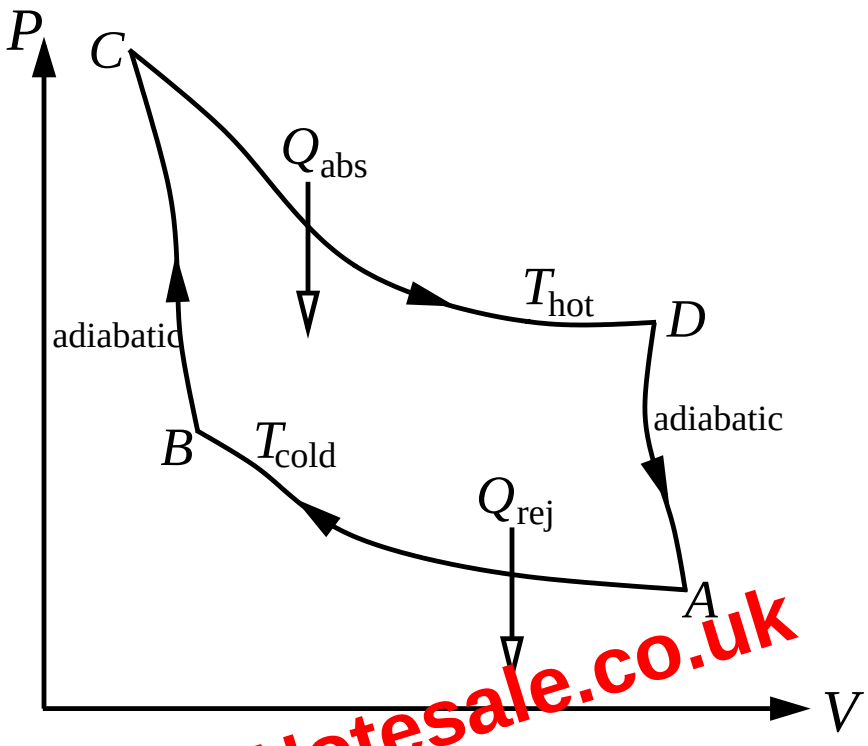


Figure 3.4: The Carnot cycle for an arbitrary fluid.

$A \to B$**:** The fluid is compressed reversibly while maintained in thermal contact with a heat reservoir of temperature $T_{\rm cold}$. A quantity $Q_{\rm rej}$ of heat is rejected to the cold reservoir.

$B \to C$**:** The temperature is increased reversibly from $T_{\rm cold}$ to $T_{\rm hot}$ by performing an adiabatic compression of the fluid.

$C \to D$**:** The fluid is expanded reversibly while maintained in thermal contact with a heat reservoir of temperature $T_{\rm hot}$. A quantity $Q_{\rm abs}$ of heat is absorbed from the hot reservoir.

$D \to A$**:** The temperature is lowered reversibly from $T_{\rm hot}$ back to $T_{\rm cold}$ by performing an adiabatic expansion of the fluid.

The key properties of the Carnot cycle is that (i) it is reversible, and (ii) heat is always transferred at constant temperature, by placing the working substance in thermal contact with a heat reservoir. Any cycle that satisfies these requirements is by definition a Carnot cycle, irrespective of the actual design of the engine, or the choice of working substance. We shall say that a Carnot engine *operates between two reservoirs*, one of temperature $T_{\rm hot}$, the other of temperature $T_{\rm cold}$. Because the operation of a Carnot engine is reversible, the cycle can equally well be operated in the reversed direction, as a refrigerator.

The importance of the Carnot cycle for thermodynamics comes from the following four statements:

1. All Carnot engines, irrespective of size, design, choice of working substance, etc., have the *same* thermal efficiency if they operate between the *same* two reservoirs.

$C \to D$**:** The gas is expanded to a volume V_D, at a constant temperature T_1. The heat absorbed from the hot reservoir is $Q_1 = nRT_1 \ln(V_D/V_C)$.

$D \to A$**:** The gas is expanded adiabatically to the larger volume V_A. During this transformation, the temperature decreases from T_1 to T_2 according to the relation $TV^{\gamma-1} = \text{constant}$, which implies $T_1/T_2 = (V_A/V_D)^{\gamma-1}$.

Our two expressions for T_1/T_2 allow us to deduce that $V_B/V_C = V_A/V_D$, or $V_D/V_C = V_A/V_B$, and we find that the ratio of heat absorbed to heat rejected is equal to

$$\frac{Q_1}{Q_2} = \frac{nRT_1 \ln(V_D/V_C)}{nRT_2 \ln(V_A/V_B)} = \frac{T_1}{T_2}.$$

Comparing with Eq. (3.7), we see that the thermodynamic temperature Θ must be related to the ideal-gas temperature T by a relation of the form $\Theta = cT$, where c is a constant. This constant plays no role in relations such as (3.7), and we may as well choose $c = 1$. We conclude that the thermodynamic temperature is *equal* to the ideal-gas temperature:

$$\boxed{\Theta(T) = T} \tag{3.8}$$

This is remarkable in fact, because while the definition of T is intimitely tied to the thermal behaviour of a *particular* thermodynamic system (the ideal gas), the definition of Θ is tied to a *universal* property of the Carnot engines.

To summarize, we have found that the thermal efficiency of *any* Carnot engine operating between a hot reservoir at T_1 and a cold reservoir at T_2 is given by

$$\boxed{\eta = 1 - \frac{T_2}{T_1} \qquad \text{(any Carnot engine)}}\,, \tag{3.9}$$

irrespective of the specific design of the engine. This is statement #2. Notice that this is equal to the thermal efficiency of the Stirling engine, which was calculated in Sec. 2. Is the Stirling engine a Carnot engine?

We do not yet have the tools to prove that $1 - T_2/T_1$ is the maximum efficiency that can be achieved by a generic engine working between these two extremes of temperature. We will therefore defer the proof of statement #4 to the next chapter.

3.8 Problems

1. The operation of a Diesel engine is based on the cycle depicted below. It is assumed that the working substance is an ideal gas. Calculate the thermal efficiency of the Diesel engine, and show that it can be expressed as

$$\eta = 1 - \frac{1}{\gamma} \frac{(V_C/V_A)^\gamma - (V_B/V_A)^\gamma}{(V_C/V_A) - (V_B/V_A)},$$

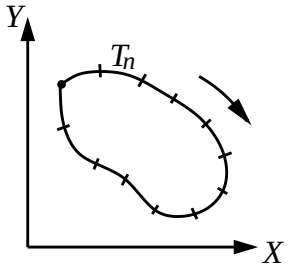
Chapter 4
Entropy and the third law

4.1 Clausius' theorem

Entropy is a quantity of fundamental importance in thermodynamics. Its existence as a *state function*, on the same footing as the internal energy, comes as a consequence of Clausius' theorem, our first topic in this chapter. In turn, the Clausius theorem comes as a consequence of the second law of thermodynamics. Thus, the entropy owes its existence to the second law.

We will consider a cyclic transformation involving a generic thermodynamic system with variables X and Y. The transformation is completely arbitrary apart from the requirements that it eventually returns the system to its original state, and that it be quasi-static. In particular, we do not assume that the transformation is reversible.

During the cyclic transformation, the system exchanges heat with its surroundings, and its temperature changes in some way. We imagine breaking up the complete transformation into a large number of steps, N of them, during each of which the system's temperature is constant to a high degree of accuracy. If T_n denotes the system's temperature during the nth step, and if Q_n denotes the (positive or negative) heat aborbed *by* the system during this step, then we will show that in the course of the complete cycle,



$$\sum_{n=1}^{N} \frac{Q_n}{T_n} < 0$$

if the transformation is irreversible, while

$$\sum_{n=1}^{N} \frac{Q_n}{T_n} = 0$$

if the transformation is reversible. Notice that this last equation is satisfied by the Carnot cycle, for which $Q_1/T_1 = |Q_2|/T_2$, with Q_1 denoting the heat entering the system, while $|Q_2| = -Q_2$ is the heat leaving the system.

These equations are the content of the Clausius theorem, which is usually formulated in the continuum limit, $N \to \infty$. In this limit, the heat exchanged during each step is infinitesimal, so that $Q_n \to đQ$. Similarly, T_n becomes T, the continuously changing temperature of the system. Finally, the discrete sum becomes an integral, and we obtain the continuous version of *Clausius' theorem*:

In any quasi-static, cyclic transformation,

$$\boxed{\oint \frac{đQ}{T} \leq 0}\,, \tag{4.1}$$

4.2 Entropy

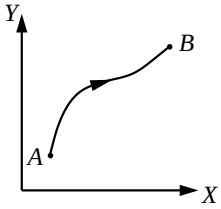
4.2.1 Definition

The entropy function S is defined by the infinitesimal relation

$$\boxed{dS = \frac{đQ_{\text{rev}}}{T}}\,, \tag{4.2}$$

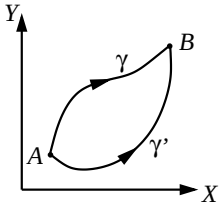
where dS is the differential of entropy, $đQ_{\text{rev}}$ is the infinitesimal of heat when it is delivered *reversibly* to the system, and T is the temperature; this equation is defined for *reversible* transformations only. The integral form of this equation is

$$\boxed{S(B) - S(A) = \int_A^B \frac{đQ_{\text{rev}}}{T}}\,, \tag{4.3}$$



where it is assumed that the path linking the final state B to the initial state A represents a reversible transformation. Apart from this assumption, however, we will see that the relation is true for *any* path of integration. The entropy is therefore truly a state function, because the integral of $đQ_{\text{rev}}/T$ depends only on the endpoints, and not on the path of integration. It should be noted that the unit of entropy is the J/K.

The statement that S is a state function follows from a simple application of Clausius' theorem. Suppose that the curve γ in the P–V plane represents a reversible transformation from an initial state A to a final state B. Suppose also that γ' is another such transformation. We may form a cyclic transformation by going from A to B along the curve γ, and returning to A by going along the curve $-\gamma'$, that is, by going along γ' in the opposite direction. Because the cycle is reversible, we have



$$0 = \oint \frac{đQ_{\text{rev}}}{T} = \int_{\gamma} \frac{đQ_{\text{rev}}}{T} + \int_{-\gamma'} \frac{đQ_{\text{rev}}}{T}.$$

Reversing the direction of $-\gamma'$ yields

$$\int_{\gamma} \frac{đQ_{\text{rev}}}{T} = \int_{\gamma'} \frac{đQ_{\text{rev}}}{T},$$

where both integrals are from A to B, but along different paths. This implies that the integral depends only on the endpoints, and not on the path of integration. This means that $dS = đQ_{\text{rev}}/T$ is a *differential*, and that S is truly a state function, as claimed.

Equation (4.3) provides a way of calculating the entropy *difference* between two states A and B: One selects a reversible transformation between these states, and evaluates the integral of $đQ_{\text{rev}}/T$ along this transformation. Equation (4.3), however, does not provide a way of assigning a specific *value* to the entropy of a particular state A. For this purpose it is necessary to choose, as a reference, a state O and assign to it an arbitrary entropy $S(O)$. Then the entropy of any other state A can then be calculated from the relation

$$S(A) = S(O) + \int_O^A \frac{đQ_{\text{rev}}}{T},$$

where the integral is evaluated along any reversible transformation from O to A.

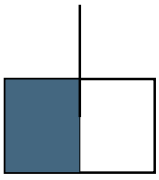
a detailed description of which cannot be attempted here. We will nevertheless illustrate some key points, and see how the notion of entropy emerges in the microscopic point of view.

Thermodynamics provides a purely macroscopic description of a system. For example, the thermodynamic description of a gas involves the specification of a very small number of quantities, such as pressure, volume, and temperature, which characterize the system as a whole. By adopting this macroscopic description, we choose to discard a great deal of information that is in principle available about the system. For example, we could want to keep track of the motion of the individual gas molecules, and thus retain the complete information about the microscopic state of the system. For a number of molecules of the order of 10^{23}, this is a *lot* of extra information. Of course, to discard this information is not a bad idea: The macroscopic description is much more economical, and it is not clear a priori that much is to be gained by adopting the microscopic description.

Supposing that we nevertheless choose to adopt the microscopic point of view, how would we go about specifying the microscopic state of our gas? A complete description would involve specifying, at a given moment of time, the positions $\boldsymbol{x}_n$ and velocities $\boldsymbol{v}_n$ of every single gas molecule; here, the index n runs from 1 to N, where N the total number of molecules. The system's *microstate* is therefore specified by providing values for all these positions and velocities; it is the complete set $\{\boldsymbol{x}_1, \boldsymbol{x}_2, \cdots, \boldsymbol{x}_N; \boldsymbol{v}_1, \boldsymbol{v}_2, \cdots, \boldsymbol{v}_N\}$. (To simplify the notation, we will write this as $\{\boldsymbol{x}_n; \boldsymbol{v}_n\}$.) With 3 coordinates and 3 velocities per molecule, specifying the microstate involves providing $6N$ pieces of information. As was remarked before, this is a lot more information than what is provided by the macroscopic description, which involves the specification of just three quantities.

It should be clear that many different microstates $\{\boldsymbol{x}_n; \boldsymbol{v}_n\}$ will give rise to a gas with the same macroscopic properties. In other words, there are many ways to choose all the positions and velocities such that the gas will have the same pressure, volume, and temperature. For example, changing the sign of all the velocities will not alter the macroscopic aspects of the gas. A quantity of central interest in statistical mechanics is Ω, the number of distinct microstates which give rise to the same macroscopic description. In other words, Ω is the number of distinct choices $\{\boldsymbol{x}_n; \boldsymbol{v}_n\}$ such that for all these choices, the gas has the same pressure P, the same volume V, and the same temperature T. This number is called the *statistical weight* of the thermodynamic system. As we shall see, the statistical weight is intimately related to the entropy function.

To see that such a relation must exist, we imagine the following situation: A gas is initially confined to the left-hand side of a box by means of a removable partition. We assume that the gas is perfectly isolated from its surroundings, and we consider the transformation that results when the partition is removed. (This is of course not a quasi-static transformation.) We take the initial state of the gas to be what it is immediately after the partition is removed, with all the molecules still in the left-hand side of the box. We take the final state of the gas to be what it is when equilibrium is established, with the molecules now uniformly occupying both sides of the box.



Our first observation is that at the initial moment, when all the molecules are in the left-hand side of the box, the number of possible microstates $\{\boldsymbol{x}_n; \boldsymbol{v}_n\}$ is *smaller* than what it is at the final moment. The reason is clear: At the final moment, the only constraint on the positions $\boldsymbol{x}_n$ is that the molecules must all be somewhere within the box; at the initial moment, however, there is the additional constraint that the molecules must all be in the left-hand side. Thus, the number of possible choices for the positions $\boldsymbol{x}_n$ must be smaller initially, and must grow as the molecules redistribute themselves within the box. It follows that Ω *increases* as the system evolves toward equilibrium; at equilibrium, Ω has achieved its maximum

Knowledge of the existence of a relation $U(S,V)$ for thermodynamic systems, even if its explicit form is not known, is a useful piece of information: It shows that the variables U, S, and V are not all independent. This relation can be expressed in a number of ways. For example, we may choose instead to express S as a function of U and V. That such a function $S(U,V)$ must exist follows directly from this alternative expression for the first law:

$$dS = \frac{1}{T}\,dU + \frac{P}{T}\,dV.$$

This implies that T and P can also be defined by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V, \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_U.$$

5.2 Enthalpy and the free energies

5.2.1 Enthalpy revisited

The observation that we can define certain thermodynamic quantities (such as temperature and pressure) in terms of partial derivatives of a state function (such as internal energy or entropy) is the key idea behind the notion *thermodynamic potentials*. The goal is to introduce as many state functions as we can and see how many quantities can be defined by partial differentiation. The internal energy was our first example of a thermodynamic potential.

We have already encountered another thermodynamic potential in Sec. B7: the enthalpy. This is defined as

$$\boxed{H = U + PV}, \tag{5.3}$$

from which follows the differential relation $dH = dU + P\,dV + V\,dP$. Using Eq. (5.1), this can be written as

$$\boxed{dH = T\,dS + V\,dP}\,. \tag{5.4}$$

This equation reveals that the enthalpy must be viewed as a function of entropy and pressure: $H = H(S,P)$. It also gives us formal definitions for temperature and volume:

$$\boxed{T = \left(\frac{\partial H}{\partial S}\right)_P, \qquad V = -\left(\frac{\partial H}{\partial P}\right)_S}\,. \tag{5.5}$$

Notice that Eq. (5.4) comes with the following physical interpretation for the enthalpy: During an isentropic transformation in which the pressure is kept constant, the enthalpy of a thermodynamic system does not change.

5.2.2 Legendre transformations

From a mathematical point of view, it is interesting to see that shifting the internal energy by the quantity PV turns a function of the variables S and V into a function — the enthalpy — of the variables S and P. This phenomenon has nothing to do with thermodynamics as such; it is a general property of what are known as *Legendre transformations*.

Consider the differential relation

$$df = a\,dx + b\,dy.$$

It tells us that f is a function of x and y, and that a and b can be defined by partial differentiation: $a = (\partial f/\partial x)_y$ and $b = (\partial f/\partial y)_x$. Consider now the following transformation from f to a new function g:

$$f \to g = f - by.$$

Because the order in which the derivatives of U are taken does not matter, we find that the quantities appearing on the left-hand side must be equal. We have therefore established our first Maxwell relation:

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}. \tag{5.12}$$

This relation is very useful, because it equates $(\partial P/\partial S)_V$, a quantity which is difficult to measure or calculate, to $(\partial T/\partial V)_S$, a quantity which is much easier to measure or calculate. For example, if the system is an ideal gas, then keeping S constant means that the transformation must be adiabatic, so that $T = cV^{-(\gamma-1)}$, where c is a constant. This relation is easy to differentiate, and the result can immediately be equated to $-(\partial P/\partial S)_V$. The great utility of the formal definitions for T and P is now apparent: They give rise to the Maxwell relation (5.12).

Additional Maxwell relations can be generated by using the other thermodynamic potentials. Starting with the enthalpy and following the same steps as above, we arrive at the relation

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}. \tag{5.13}$$

Starting with the Helmholtz free energy, we obtain

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}. \tag{5.14}$$

Finally, using the Gibbs free energy yields

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}. \tag{5.15}$$

These remarkable relations provide a further illustration of a recurring theme in this course: Limited experimental input (such as the equation of state) and a few key physical ideas (such as the first and second laws of thermodynamics) can go a very long way when combined with powerful mathematical reasoning. As an exercise, you may check the validity of the last two Maxwell relations for the specific case of an ideal gas, by using the expressions derived in Sec. D4 for the entropy function. Of course, the great power of these relations resides in the fact that they are completely general: They hold for *all* thermodynamic systems.

As an illustration of the usefulness of the Maxwell relations, we now give a *proof* of Joule's law, which states that the internal energy of an ideal gas depends on temperature *only*. Thus, we want to show that $(\partial U/\partial V)_T = 0$ for an ideal gas. We begin with the first law written in the form

$$\frac{dU}{dV} = T\frac{dS}{dV} - P.$$

For the special case of an isothermal transformation, this equation becomes

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

Using Eq. (5.14), we obtain

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P}. \tag{5.16}$$

This equation holds for all thermodynamic systems. If we now specialize to an ideal gas, we may use the equation of state to calculate $(\partial P/\partial T)_V = nR/V = P/T$. We then find that the right-hand side evaluates to zero, and we have proven Joule's law.

Chapter 6
Thermodynamics of magnetic systems

6.1 Thermodynamic variables and equation of state

In this last section of the course we will turn our attention to the thermal properties of magnetic systems, and show how the general framework of thermodynamics can readily be applied to such systems. This discussion will provide us with a concrete illustration of the fact that the methods of thermodynamics are not limited to the study of gases, but are quite general.

We wish to study how temperature affects the magnetic response of some material. For simplicity, we will be dealing only with *paramagnetic* materials. Paramagnetism is a rather weak form of magnetism, characterized by the fact that the material has a magnetization only when it is subjected to an applied magnetic field; turning the field off removes all traces of magnetic activity. The stronger form of magnetism associated with permanent magnets is called ferromagnetism. (This form of magnetism is difficult to incorporate within the framework of thermodynamics because the phenomenon of hysteresis prevents the system from having a well-defined equation of state.)

We will need a device capable of supplying the external magnetic field, which we denote $\boldsymbol{H}$. It is simplest to deal with a field that is very uniform, and this can be provided by a very long solenoid. The magnetic field inside the solenoid can easily be calculated from the Maxwell equation

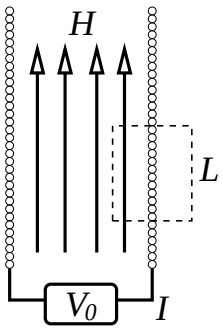
$$\oint \boldsymbol{H} \cdot d\boldsymbol{\ell} = \mu_0(\text{current enclosed}),$$

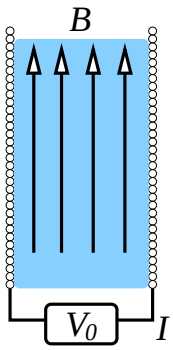
where the integral is calculated along the closed contour depicted in the figure; the constant μ_0 is the permeability of vacuum. If the length of the circuit is L and p is the number of windings per unit length, then the current enclosed within the contour is pLI, where I is the current running through the solenoid. The previous equation then gives $HL = \mu_0 pLI$, or

$$\boxed{H = \mu_0\, p\, I}\,, \tag{6.1}$$

where H is the magnitude of the magnetic field $\boldsymbol{H}$.

We now insert a magnetic sample inside the solenoid. For simplicity, we assume that the sample is prepared in a long, cylindrical shape that fits perfectly within the solenoid. The fact that the sample has magnetic properties implies that the magnetic field measured inside the solenoid (and inside the sample) is now different





a) T as a function of V along this line.

b) The value of V at which T is maximum.

c) The values of T_0, $T_{\max}$, and T_1.

d) Q, the heat transferred to the gas when it goes from the volume V_0 to any other volume V along the line.

e) The value of P and V at which Q is a maximum.

10. (Zemansky and Dittman, Problem 7.10)

A Carnot engine operates with a non-ideal gas whose equation of state is $P(v-b) = RT$, where v is the molar volume and b is a constant, and whose molar internal energy u is a function of T only. Prove that the thermal efficiency of this particular Carnot engine is given by

$$\eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$

This result provides another illustration of the fact that the thermal efficiency of a Carnot engine does not depend on the specifics of the engine.

11. A thermodynamic system A is n times as massive as another system B, so that their heat capacities (at constant pressure) are related by $C_A = nC_B$. Initially, both systems are isolated from each other, and are at temperatures T_A and T_B ($T_A > T_B$), respectively. The systems are then brought in thermal contact; their respective pressures do not change during the interaction. After equilibrium is re-established, the systems are separated again, and are found to be at a common temperature T_F.

a) Calculate T_F.

b) Calculate ΔS, the amount by which the total entropy has increased during the interaction.

c) Consider the case $n \gg 1$. Show that in this case, your expressions for T_F and ΔS reduce to

$$\begin{aligned} T_F &\simeq T_A\Big[1 - \frac{1}{n}(1-x)\Big], \\ \Delta S &\simeq C_B(x - 1 - \ln x), \end{aligned}$$

where $x = T_B/T_A$. [Hint: Use the approximation $\ln(1+\epsilon) \simeq \epsilon$, valid for $\epsilon \ll 1$.]

12. (Zemansky and Dittman, Problem 8.16)

The entropy function of an ideal gas can be expressed as

$$S = S_0 + C_V \ln\left(\frac{T}{T_0}\right) + nR\ln\left(\frac{V}{V_0}\right).$$

Imagine a box divided by a partition into two equal compartments of volume V, each containing 1 mol of the same gas at the same temperature and pressure.

a) Calculate the entropy of the two portions of gas while the partition is in place.

b) Calculate the entropy of the entire system after the partition has been removed.

c) Has any transformation taken place? If so, was it reversible or irreversible?

d) Has any entropy change taken place? If not, why not?

13. (Zemansky and Dittman, Problem 9.3)
From the fact that dV/V is an exact differential, derive the relation

$$\left(\frac{\partial \beta}{\partial P}\right)_T = -\left(\frac{\partial \kappa}{\partial T}\right)_P.$$

14. (Zemansky and Dittman, Problem 9.5)
Derive the third "$T\,dS$" equation,

$$T\,dS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV.$$