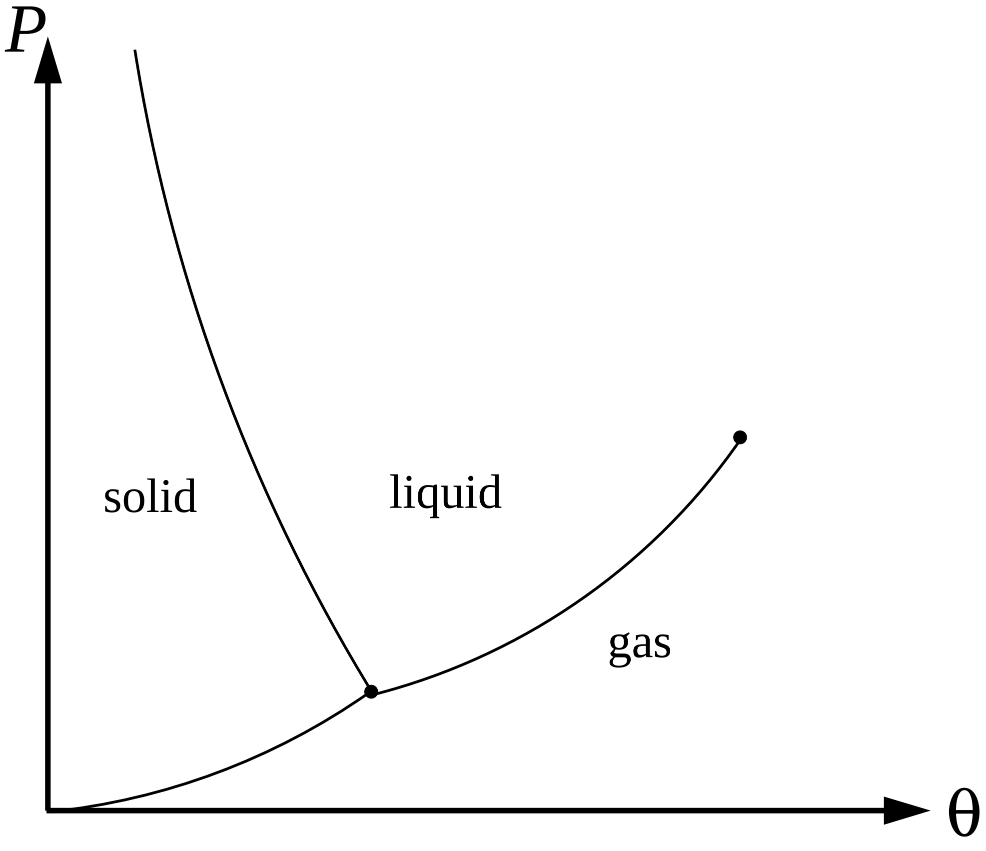
Statistical Physics I
(PHY*3240)

Lecture notes (Fall 2000)



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CONTENTS

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:

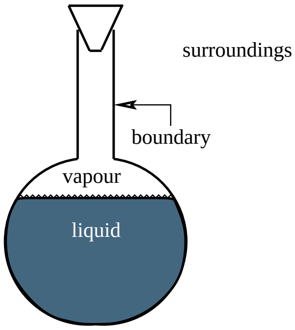
> A macroscopic system A, initially at a temperature T_A, is brought in thermal contact with another system B, initially at a temperature T_B. When equilibrium is re-established, what is the final temperature of both A and B?

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 system actually is. The framework of thermodynamics, because of this generality, is extremely powerful.

It is also important that thermodynamics does not rely on any microscopic model for the system under consideration. For example, it is never stated that a gas consists of a large number of weakly interacting molecules. Though it is very general, the framework of thermodynamics can only hope to give a *partial* description of a macroscopic system.



1.2 The universe and its parts

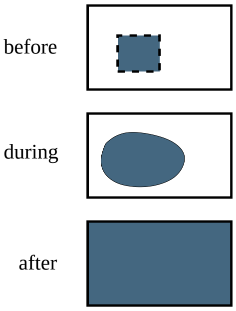
We begin with some definitions:

A thermodynamic system is always confined within some *boundary*. Outside this boundary is the system's *surroundings*. The combination system + boundary + surroundings is called the *universe*. (The Universe is a thermodynamic system without a boundary. Think about this!)

The boundary is usually just as important as the system itself. It is therefore crucial to provide for it a complete description. In particular, it is important to state whether the boundary allows for a *thermal interaction* (an energy exchange in the form of heat) with the surroundings. An *adiabatic* boundary prevents any exchange of energy between the system and the surroundings. On the other hand, a *diathermal* boundary permits such an exchange of energy. A thermodynamic system within an adiabatic boundary is said to be *thermally isolated*. A system within a diathermal boundary is said to be *thermally interacting*.

1.3 Equilibrium

A system is in *equilibrium* if its physical properties do no change with time. For example, in the system depicted above, the proportions of liquid and vapour will not change if the system is in equilibrium. Equilibrium can easily be broken: If the system is heated, for example, the liquid will vapourise, and the proportions will change (the amount of liquid will decrease, while the amount of vapour will increase).

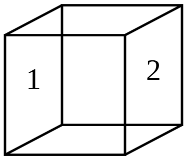


Let us examine how a system reaches equilibrium. Imagine that a certain quantity of gas, initially confined to a small portion of a box, is allowed to slowly fill the entire box by flowing through a porous membrane. (We assume that initially, the rest of the box contains a vacuum.) As long as the gas flows from the small chamber into the larger box, the system is not in equilibrium. Indeed, the very idea of a macroscopic flow of gas within the system is incompatible with the idea of equilibrium. Eventually, of course, the gas will uniformly fill the box, and the macroscopic flow will stop. (The gas molecules continue to flow within the box, but this is a *microscopic* flow.) This is when the system reaches equilibrium.

Imagine that as the gas makes its way from the small chamber into the larger box, we measure its pressure. Initially, we find that the pressure inside the chamber is much larger than everywhere else within the box (where it is almost zero). As the gas flows, we see that the pressure inside the chamber decreases, while the pressure elsewhere within the box increases. Eventually, as equilibrium is established, we find that the pressure is the same *everywhere* within the box. At equilibrium, the pressure is uniform.

Equilibrium is therefore characterized both by the absence of macroscopic flows and by a uniform pressure. There is a relation between these two conditions.

Consider an "element of gas", a small cubical volume containing a small, but still macroscopic, portion of the gas. If the pressure is nonuniform within the box, then $P_1 \neq P_2$, where P_1 is the pressure on face 1 of the element, while P_2 is the pressure on face 2. The force acting on face 1 is P_1A, where A is the face's area. Similarly, the force acting on face 2 is P_2A. If the pressures are unequal, then there is a net force $(P_2 - P_1)A$ acting on the element, forcing it to accelerate. The net effect on all the gas elements is to create a macroscopic flow of the gas. Thus,



$$\text{nonuniform pressure} \Rightarrow \text{macroscopic flow} \Rightarrow \text{absence of equilibrium.}$$

It is also follows that

$$\boxed{\text{equilibrium} \Leftrightarrow \text{uniform pressure}}\,. \tag{1.1}$$

The pressure is therefore *uniform* at equilibrium, and it is only under this condition that we can talk of the pressure of the system *as a whole.* Otherwise, outside of equilibrium, the pressure depends on where, within the box, the pressure is measured. The description of the system is therefore far simpler at equilibrium: Instead of having to provide the changing value of the pressure at every point inside the box, we need only provide one number, the fixed value of the pressure *anywhere* within the box.

1.4 Thermodynamic variables

We need to introduce variables to describe the physical state of a thermodynamic system in equilibrium. These variables will characterize the system as a whole, and the value that these variables take will not depend on where, within the system, they are measured. In fact, our preceding discussion indicates that thermodynamic variables can be defined only when the system is in equilibrium.

Of course, the choice of thermodynamic variables depends on the system being considered. For a fluid (gas or liquid), volume V and pressure P are appropriate thermodynamic variables. To other thermodynamic systems correspond other thermodynamic variables. Here are some examples:

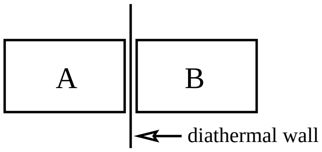
System	First variable	Second variable
fluid	pressure P	volume V
filament	tension f	length ℓ
film	surface tension γ	area A
magnet	applied field H	magnetization M

There are other thermodynamic variables: temperature T, entropy S, and internal energy U. These will be introduced later; they are common to *all* thermodynamic systems.

Thermodynamic variables can be divided into two groups: *extensive* variables and *intensive* variables. Imagine that a thermodynamic system is divided into two equal parts, each of which carrying its own thermodynamic variables. How do the variables of the halved system compare with the variables of the original system? The answer is that some quantities will be unaffected by the division; these are the *intensive* variables. Other quantities will be halved; those are the *extensive* variables. For example, when a fluid is divided into two parts, the pressure is unaffected by the division, but V is smaller by a factor of two. Therefore, P is intensive, while V is extensive. Another way of defining the two groups of variables is to say that extensive variables *scale* with an overall scaling of the system, while intensive variables do *not* scale.

From our previous list of thermodynamic variables, it is easy to see that P, f, γ, and B are intensive variables. On the other hand, V, ℓ, A, and M are extensive variables.

1.5 Zeroth law



Imagine that two systems, A and B, are put on both sides of a diathermal wall, so that energy (in the form of heat) is allowed to be exchanged. These systems are said to be in *thermal contact.*

In general, even when initially A and B are both separately in equilibrium, the thermal interaction between A and B implies that the combined system will be *out* of equilibrium: the physical properties of both A and B will be seen to change. After a time, however, equilibrium is re-established. Systems A and B are then said to be in (mutual) *thermal equilibrium.* Thermal equilibrium is therefore the kind of equilibrium that results when two systems are brought in thermal contact.

A fundamental experimental fact of thermodynamics is summarized by the following statement:

> If two systems are separately in thermal equilibrium with a third, then they must also be in thermal equilibrium with each other.

This statement is so important that it is known as the *zeroth law* of thermodynamics. What this statement really means is that if A is in thermal equilibrium with C, and if B is also in thermal equilibrium with C, then putting A and B in thermal contact produces no change in the state of either A or B; these systems are already in thermal equilibrium.

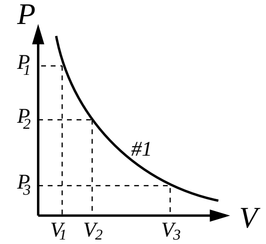
It follows trivially from the zeroth law that if an *arbitrary* number of thermodynamic systems are *all* in thermal equilibrium with a reference system, then they are all in thermal equilibrium with each other. These systems must therefore share a common physical property. As we shall see, they must all have the same temperature.

1.6 Temperature

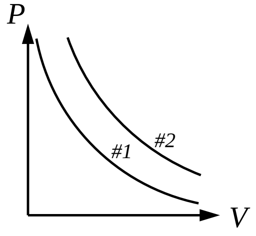
Temperature is a familiar concept from every-day life. It is also the most fundamental concept of thermodynamics. We will show that the notion of temperature emerges naturally as a consequence of the zeroth law.

1.6.1 Isotherms

To bring out the notion of temperature, we consider the following series of experiments.

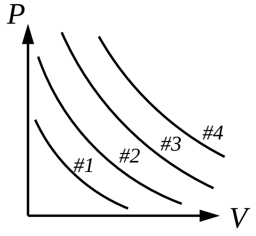


Experiment #1. We put a certain quantity of a fluid (liquid or gas) in a beaker of volume V_{ref}, and we arrange for the fluid to be under a pressure P_{ref}. This is our reference system. We then prepare a test system by putting some quantity of a different fluid in a beaker of volume V_1. We bring the two systems in thermal contact, and we wait for thermal equilibrium; we then measure the pressure of the test system to be P_1. We now transfer the test fluid into a larger beaker of volume V_2, and again we bring it in thermal contact with the reference system. At equilibrium, the pressure of the test fluid is $P_2 < P_1$. Repeating for many different volumes, we are able to trace a curve in the P-V plane. We conclude that when in thermal equilibrium with the reference system, a test system of volume V must have a pressure P such that the point (P, V) lies on the curve.



Experiment #2. We carry out the same steps as in experiment #1, except that now, the reference system is prepared with a volume $V'_{\rm ref} \neq V_{\rm ref}$ and a pressure $P'_{\rm ref} \neq P_{\rm ref}$. As a result, we obtain a *different* curve in the P-V plane.

Experiment #3 and beyond. We repeat the same steps many times, each time varying the volume and pressure of the reference system. We obtain a family of curves in the P-V plane. Furthermore, and this is important, we find that none of these curves intersect each other.



The existence of this family of curves is extremely important, and we must think very carefully about the significance of this result. Consider curve #2. If the test system is prepared with a volume V and a pressure P such that the point (P, V) lies on the curve, then as a result of our experiments, we know that the test system will be in thermal equilibrium with the reference system in its second configuration (with volume $V'_{\rm ref}$ and pressure $P'_{\rm ref}$). If the point (P, V) does not lie on curve #2, then we know that the test system will not be in thermal equilibrium with the reference system.

Consider now another copy of the test system, this time prepared in the state (P', V') also lying on curve #2. This system is also in thermal equilibrium with the reference system (in its second configuration). But by virtue of the zeroth law, we can infer that the first and second test systems must be in thermal equilibrium *with each other.* Pushing these considerations to their logical conclusion, we arrive at the following statements:

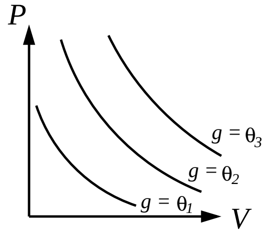
- Every point on curve #2 represents a test system in thermal equilibrium with the reference system in its second configuration. Similar statements hold for the other curves.
- Every point on curve #2 represents a test system in thermal equilibrium with any other test system represented by any other point on the *same* curve. Similar statements hold for the other curves.
- Points on different curves represent test systems which are not in thermal equilibrium with each other.

These curves in the P-V plane are therefore curves of thermal equilibrium. Such curves are called *isotherms.*

The isotherms can be described mathematically by a relation of the form

$$\boxed{g(P, V) = \theta}\,, \tag{1.2}$$

where g is some function, and θ is a constant that serves to label *which* isotherm. This equation states that on each isotherm, P and V are related by $g(P, V) =$ constant. It also states that the value of the constant changes as we go from one isotherm to another: to each isotherm corresponds a unique value of θ. This quantity is called the *empirical temperature.* What we have found is that systems which are in thermal equilibrium necessarily have the *same* empirical temperature. On the other hand, systems which are not in thermal equilibrium have different empirical temperatures.



The form of the function g depends on the nature of the system under consideration. For an *ideal gas*, it is experimentally determined that

$$g(P, V) = \frac{PV}{n},$$

where n is the molar number, given by $n = N/N_A$, where N is the number of molecules in the gas, and $N_A = 6.02 \times 10^{23}$ is Avogadro's number (by definition, the number of molecules in a mole). The isotherms of an ideal gas are therefore given by $PV = n\theta$. This equation describes *hyperbolae* in the P-V plane.

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 special case, g_{AC} has the same form as g_{BC} because we are dealing with identical systems.]

Equation (1.5) can now be solved for P_A, giving a relation of the form

$$P_A = F(P_B, V_A, V_B, V_C). \tag{1.6}$$

[For ideal gases, this reduces to $P_A = P_B V_B / V_A$. Notice that here, the right-hand side does not involve V_C, contrary to what is implied by Eq. (1.6). Stay tuned!]

Imagine now that C is removed from our laboratory table, and that A and B are brought in thermal contact. Since they were both separately in equilibrium with C, the zeroth law guarantees that A and B will be in thermal equilibrium with each other. Therefore P_A and P_B will retain their equilibrium value, and as we have done before, we must conclude that a relation of the form

$$f_{AB}(P_A, V_A, P_B, V_B) = 0 \tag{1.7}$$

exists between these thermodynamic variables. The list does not include P_C and V_C, because C is now absent from our considerations; Eq. (1.7) just states that A and B can be in thermal equilibrium with each other, independently of C. (For ideal gases, it reduces to $P_A V_A - P_B V_B = 0$.)

Equation (1.7) can now be solved for P_A, giving

$$P_A = G(P_B, V_A, V_B). \tag{1.8}$$

This equation has almost the same form as Eq. (1.6), except that here, V_C *does not appear*. The only way both results can be in agreement is if V_C actually drops out of Eq. (1.6). This logically inescapable conclusion is a direct consequence of the zeroth law. The following statement must therefore be true: The function F does not actually depend on V_C, and because F and G now depend on the same set of variables, F and G must be equal as functions. In other words, F and G must be the *same* function of P_B, V_A, and V_B, because the relation between P_A and these variables must be unique.

If F does not depend on V_C, then it must be true that V_C also drops out of Eq. (1.5). [Recall that Eq. (1.6) is obtained by solving (1.5) for P_A.] So we must have

$$g_A(P_A, V_A) = g_B(P_B, V_B). \tag{1.9}$$

(We have dropped the suffix C because C's thermodynamic variables no longer appear in the equation.) This is an important equation. It states that when A is in thermal equilibrium with B, the functions g_A and g_B *share the same value*. (Recall that in general, g_A and g_B are not equal as functions.) We may *define* the shared value of the functions g_A and g_B to be the *empirical temperature*, and denote it by the symbol θ.

To summarize:

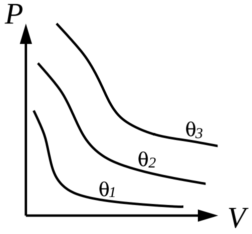
> If thermodynamic systems A and B are in the thermal equilibrium, then
>
> $$g_A(P_A, V_A) = g_B(P_B, V_B) = \theta.$$
>
> Here, g_A is a function characteristic of system A, while g_B is a function characteristic of system B; in general, these functions do not have the same form. The shared value θ of the functions is called the empirical temperature; systems in thermal equilibrium therefore have the same empirical temperature.

In the special case where A and B are identical systems, we recover the relation $g(P, V) = \theta$, with a unique function g describing both systems. This is just Eq. (1.2).

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,

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

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.

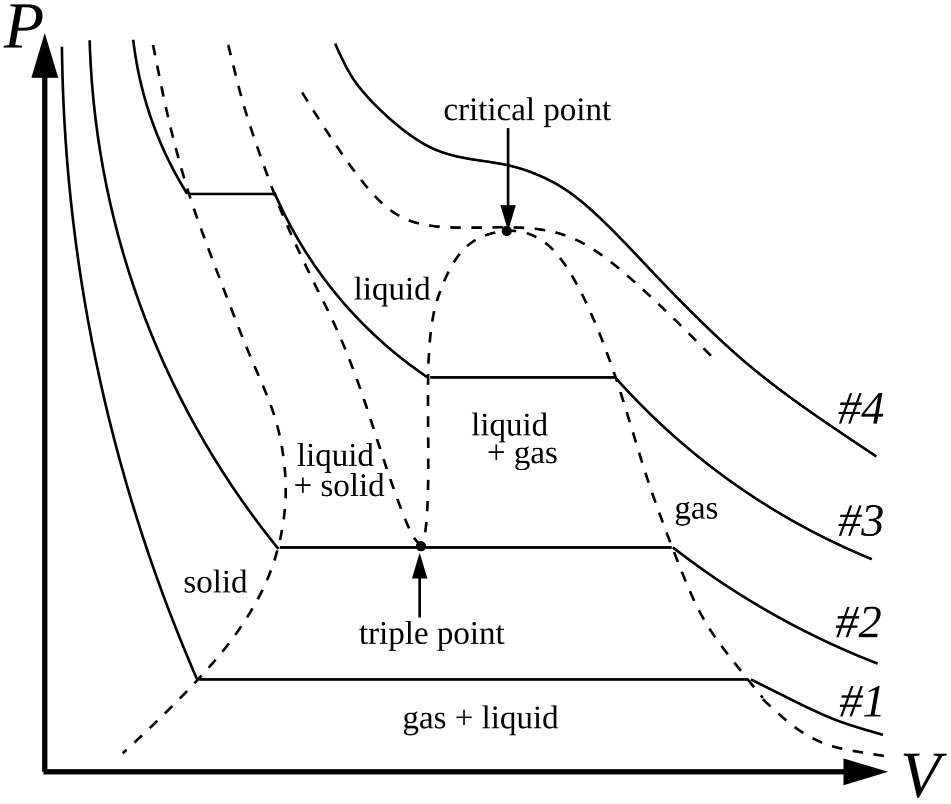


Figure 1.1: **Along isotherm #1:** The system starts in the gas state and undergoes a phase transition (at constant pressure) directly into the solid state. **Along isotherm #2:** The system starts in the gas state and becomes a mixture of gas, liquid, and solid before crossing into the solid state. An equilibrium mixture of solid, liquid, and gas is called the *triple point* of the substance. **Along isotherm #3:** The system starts in the gas state and undergoes a phase transition (at constant pressure) into the liquid state, and then another phase transition into the solid state. **Along isotherm #4:** The system starts in the gas state and then crosses continuously (without a phase transition) into a liquid state. The point at which this first becomes possible is called the *critical point*. An isotherm passing through the critical point has an inflection point there (dashed curve). At this point, both the first and second derivatives of the function $P(V)$ describing the isotherm are zero. To represent this mathematically, we write $(\partial P/\partial V)_\theta = 0$ and $(\partial^2 P/\partial V^2)_\theta = 0$, where the suffix θ indicates that the temperature is kept fixed while V and P are varied.

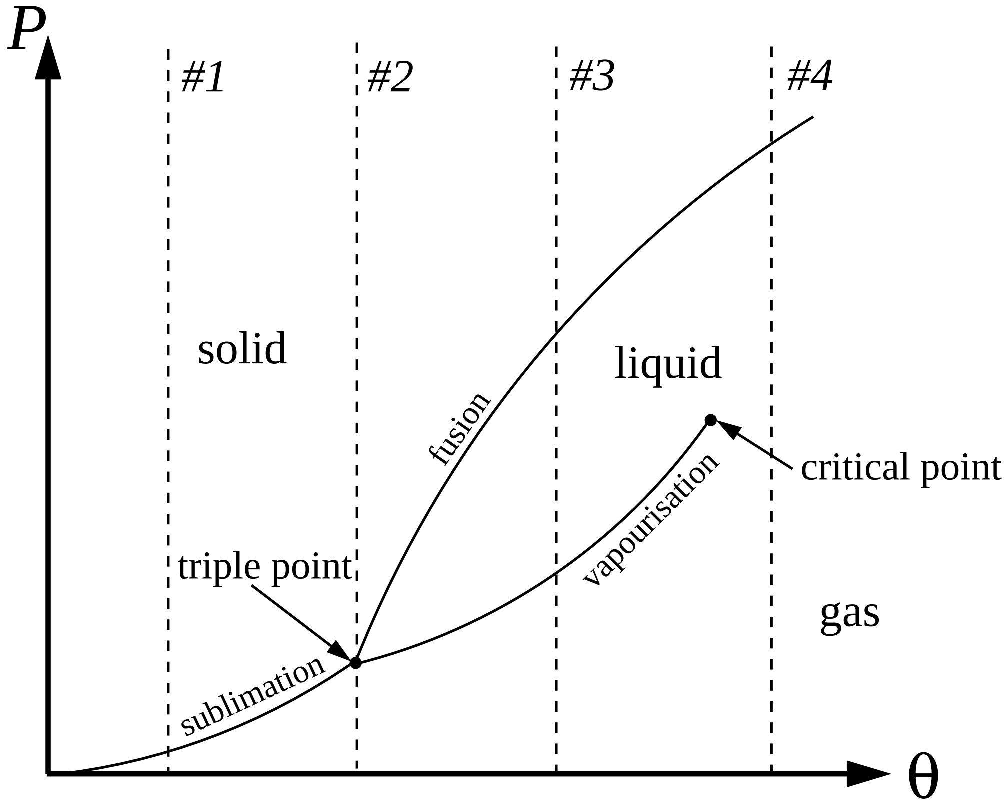
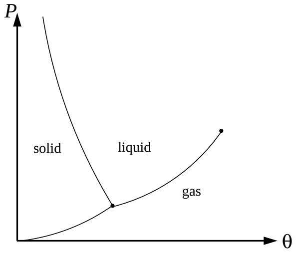


Figure 1.2: **Sublimation curve:** solid and gas states are in equilibrium. **Fusion curve:** solid and liquid states are in equilibrium. **Vapourisation curve:** liquid and gas states are in equilibrium. **Triple point:** solid, liquid, and gas states are in equilibrium. **Critical point:** end point of the vapourisation curve; continuous transition between gas and liquid possible beyond the critical point.



The different phases are neatly represented in a P-θ diagram (Fig. 2).

The preceding diagrams describe most substances, those which (i) solidify under added pressure at constant temperature, and (ii) expand when melting. Water, however, behaves differently: it (ii) melts under added pressure (this is the phenomenon that makes ice skating possible) and (ii) contracts when melting. The P-θ diagram of water is therefore different from the one presented above.

1.8 The ideal-gas temperature scale

We have seen that all thermodynamic systems in thermal equilibrium must have the same empirical temperature θ. This quantity was first introduced as a way of labeling the various isotherms of a system: $g(P,V) = \text{constant} \equiv \theta$. Clearly, this labeling is not unique. We could have written instead $g(P,V) = \theta' \equiv 100\theta$. Or else, $g(P,V) = \theta'' \equiv \theta^2$. To put the concept of temperature on a precise basis, we need to make a specific choice of labeling, unique to all thermodynamic systems. In other words, we need to introduce a unique *temperature scale*.

To do this, we first need to introduce a *standard thermometer*: a thermodynamic system whose physical properties depend in a measurable way on temperature. We choose to use an ideal gas. (Recall that all gases behave ideally at low pressure.) We therefore construct our standard thermometer by putting n moles of an ideal gas inside a bulb of volume V. When we put our thermometer in thermal contact with various other systems, we notice that the gas pressure varies as a function of the state of these systems. We may therefore use the pressure to determine the empirical temperature, via the relation $PV/n = \theta$.

Second, we need to introduce a unit of temperature, generically called a *degree*. We shall call this unit the *Kelvin* (not "degree Kelvin"), and denote it K. We shall demand that this be a new unit of physics, unrelated to other physical units. (Temperature is such an important quantity that it rightly deserves its own unit.)

The empirical temperature, as defined above for an ideal gas, carries the units of pressure × volume, Pa m^3 = Nm = J. Evidently, this is *not* a new unit. Instead of θ, the empirical temperature, we shall work instead in terms of T, the *temperature* (period). These will be related by a linear relation,

$$\boxed{\theta = RT}\,, \tag{1.10}$$

where R is a constant with units J/K. In this way, T will proudly carry the true unit of temperature, the Kelvin. Note that with this definition, the equation of state of an ideal gas becomes $PV = nRT$.

Third, we need to assign a value to the constant R. This is done by assigning a standard value to the temperature of a standard thermodynamic system in a standard state. Choosing our standard system to be water, there are several possibilities for the standard state: freezing point at atmospheric pressure, boiling point at atmospheric pressure, triple point, critical point, and many others. The adopted standard state, since 1954, is water's triple point, which occurs at a unique pressure and temperature. The temperature of water's triple point is arbitrarily chosen to be 273.16 K. Thus,

$$\boxed{T_{\rm TP} = \frac{P_{\rm TP}V}{nR} = 273.16\ \text{K}}\,. \tag{1.11}$$

This equation expresses the fact that the temperature of the triple point is determined by our standard thermometer, that is, by reading the pressure of an ideal gas when it is in thermal contact with water at the triple point.

To determine the value of R we conduct the following experiment. We construct a standard thermometer by putting $n = 0.1$ moles of an ideal gas in a bulb of volume $V = 10\ \text{cm}^3 = 10^{-3}\ \text{m}^3$. We then place our thermometer in thermal contact with water at the triple point. When thermal equilibrium is established, we measure the gas pressure to be $P_{\rm TP} = 227.13$ kPa = 2.2422 atm. (Recall that one atmosphere corresponds to 101.3 kPa.) Calculation of $R = VP_{\rm TP}/nT_{\rm TP}$ yields

$$\boxed{R = 8.315\ \text{J/K}}\,. \tag{1.12}$$

Knowing the value of R, we can now use our thermometer to measure the temperature of other systems, or of the same system (water) in other states. If we put the thermometer in thermal contact with freezing water (at atmospheric pressure), we find the equilibrium pressure of the gas to be $P_{\rm FP} = 227.12$ kPa. This gives $T_{\rm FP} = 273.15$ K for the temperature of water's freezing point. If instead the water is boiling (also at atmospheric pressure), then $P_{\rm FP} = 310.27$ kPa. This gives $T_{\rm FP} = 373.15$ K for the temperature of water's boiling point.

Clearly, our standard thermometer can be used in the same way to measure the temperature of *any* thermodynamic system in *any* of its states[1]. In practice, it is more convenient to use other types of thermometers to measure temperature. For example, a metallic liquid typically expands when heated, and the height of a liquid

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[1] Actually, the ideal-gas thermometer cannot be used at very low temperatures, because the gas eventually condensates into a liquid or a solid. Other types of thermometers must then be constructed. Adkins' book offers a nice description of various standard thermometers.

column can be used to determine the temperature. It is still true, however, that the temperature scale is *calibrated* with an ideal-gas thermometer: the temperature reading is the *same* that would be inferred from the relation $T = PV/nR$.

1.9 The Celcius temperature scale

We notice that there is a difference of 100 degrees in the temperatures of water's boiling and freezing points: $T_{\mathrm{BP}} - T_{\mathrm{FP}} = 100$ K. This is not an accident: the value of 273.16 K for the triple point was chosen to ensure that 100 degrees would separate the boiling point from the freezing point.

For every-day purposes, it is convenient to reset the zero of temperature so that the freezing point occurs at zero degrees, while the boiling point occurs at 100 degrees. This gives rise to the familiar Celcius scale:

$$t(\text{in degrees Celcius}) = T(\text{in Kelvin}) - 273.15.$$

Notice that the symbol t is used for the Celcius scale, while T is reserved for the ideal-gas (Kelvin) scale.

1.10 A molecular model for the ideal gas

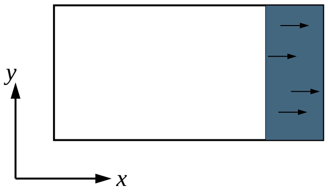
The relation

$$\boxed{PV = nRT}\,, \tag{1.13}$$

is the equation of state of an ideal gas. In the usual context of thermodynamics, this equation must be considered to be empirically determined. It is possible, however, to give a simple *derivation* of this equation by constructing a microscopic model for the ideal gas. This appeal to microscopic ideas is usually poo-pooed by authors of textbooks on thermodynamics, who like to keep their field "pure". We shall not be concerned here with such a snobby attitude. The following discussion will provide us with a better understanding of the physics of the ideal gas, and it will give us some further insight into the notion of temperature.

Our microscopic model for an ideal gas is simply that it consists of N molecules moving about in a container of volume V. For simplicity, we assume that the gas is sufficiently dilute that the molecules almost never collide; the only collisions taking place are between the molecules and the walls of the container. Also for simplicity, we assume that the container has a rectangular shape; we shall attach a coordinate system x, y, z to the three axes of the container.

The gas pressure P is the total force exerted by the molecules on a given wall of the container, divided by its area A; the force is provided by the molecules bouncing off the wall. Let us try to calculate this. The first step is to figure out how many molecules will hit that wall in a time Δt. For concreteness, we will suppose that we are talking about one of the two walls that are perpendicular to the x axis; we choose the right-most wall.



Suppose for simplicity that all the molecules are moving with a unique speed v. Suppose also that the velocities are directed only along the three axes x, y, and z, with no possibility for the molecules to be moving at an angle. (We will examine these seemingly drastic assumptions below.) Of the N molecules in the box, one third of them will be moving in either the positive or negative x direction. Of these, half will be moving in the positive x direction. Thus, the number of molecules moving in the positive x direction is $\frac{1}{6}N$. Of these molecules, the fraction that will hit the wall in a time Δt is given by $A\Delta x/V$, where $\Delta x = v\Delta t$ is the distance traveled by one of these molecules in the time Δt. Thus, the total number of molecules hitting the wall in a time Δt is given by

$$\tfrac{1}{6}N\,\frac{Av\Delta t}{V}.$$

As they bounce off the wall, each of these molecules transfers a momentum $2p = 2mv$ to the wall, where m is the molecule's mass. The total force F exerted by the molecules is the total momentum transfer per unit time:

$$F = \tfrac{1}{6}N\,\frac{Av\Delta t}{V}\,\frac{2mv}{\Delta t} = \tfrac{1}{3}mv^2\,\frac{NA}{V},$$

and the gas pressure is

$$P = \tfrac{1}{3}mv^2\,\frac{N}{V}.$$

We see that we are quite close to the desired result.

We must now introduce the notion of temperature in our microscopic model. The general idea is that microscopically, temperature is *defined* to be a measure of the kinetic energy of our gas molecules. More precisely, temperature is defined by the statement

$$\tfrac{1}{2}mv^2 = \tfrac{3}{2}kT,$$

where $k = 1.38 \times 10^{-23}$ J/K is the *Boltzmann constant.* Using this in our previous expression for P, we obtain

$$PV = NkT,$$

which is essentially the same as Eq. (1.13). To go from here to the usual form $PV = nRT$ we introduce the Avogadro number N_A, and define $n = N/N_A$ and $R = kN_A = 8.31$ J/K.

This concludes our derivation of the equation of state. This discussion is very instructive, because it gives us a direct microscopic picture of what temperature really is, namely, the average kinetic energy of the gas molecules. This makes the relation $P \propto T$ very easy to understand: the larger the temperature, the larger the velocity of the molecules, the larger the amount of momentum transfer to the walls, and finally, the larger the pressure.

Let us finish off with an examination of our two strange assumptions, that the molecules must all move at right angles and with a unique speed v. The right-angle hypothesis is not at all harmful: it is just a way of decomposing the motion into the three fundamental directions, so that we are in fact talking about the x, y, and z *components* of the velocity vector. The assumption of a unique speed is potentially more dangerous. In reality, gas molecules do not move in this way; instead, they have an (almost Gaussian) distribution of speeds around a mean $\bar{v}$. A fancier version of our derivation would reveal that our previous expressions $P = \frac{1}{3}mv^2N/V$ and $\frac{1}{2}mv^2 = \frac{3}{2}kT$ are in fact correct, provided that v be interpreted as the mean speed $\bar{v}$. Thus, the validity of the equation of state $PV = nRT$ is not limited by our assumptions.

1.11 Problems

1. (Zemansky and Dittman, Problem 1.1)

   Systems A, B, and C are gases with coordinates P, V; P', V'; P'', V''. When A and C are in thermal equilibrium, the equation

   $$PV - nbP - P''V'' = 0$$

   is found to be satisfied. When B and C are in thermal equilibrium, the relation

   $$P'V' - P''V'' + \frac{nB'P''V''}{V'} = 0$$

   holds. The symbols n, b, and B' are constants.

   a) What are the three functions which are equal to one another at thermal equilibrium, each of which being equal to θ, the empirical temperature?

   b) What is the relation expressing thermal equilibrium between A and B?

2. (Adkins, Problem 2.3)

   A beaker of volume $V = 1 \times 10^{-3}$ m^3 contains $n = 0.05$ moles of a gas. When using this system as a thermometer, it is assumed that the gas obeys the ideal-gas law, $Pv = RT$, where $v = V/n$ is the molar volume. In fact, its behaviour is better described by the equation

   $$\Big(P + \frac{a}{v^2}\Big)\big(v - b\big) = RT,$$

   where $a = 8 \times 10^{-4}\ \mathrm{N\,m^4}$ and $b = 3 \times 10^{-5}\ \mathrm{m^3}$. By how much will the temperature measurement be in error at the boiling point of water?

3. (Zemansky and Dittman, Problem 1.5)

   It is explained in Sec. 2.7 of Adkins' book how the electric resistance of certain materials can be used to measure temperature. During a series of experiments, it is found that the resistance R of a doped germanium crystal obeys the equation

   $$\log R = 4.697 - 3.917 \log T.$$

   The logarithms are in base 10, R is expressed in ohms, and T in Kelvin.

   a) In a liquid helium cryostat, the resistance is measured to be 218 ohms. What is the temperature?

   b) Make a log-log graph of R as a function of T in the resistance interval between 200 and 30 000 ohms. Try to produce a plot that would be practically useful to convert a resistance measurement into a temperature reading.

4. The van der Waals equation of state,

   $$\Big(P + \frac{n^2 a}{V^2}\Big)\Big(V - nb\Big) = nRT,$$

   describes the gas and liquid phases of a simple substance; a and b are constants specific to each substance, and n is the fixed molar number. This equation of state predicts the existence of a critical point, at which

   $$\bigg(\frac{\partial P}{\partial V}\bigg)_T = 0 = \bigg(\frac{\partial^2 P}{\partial V^2}\bigg)_T.$$

   These conditions specify a unique pressure P_c and a unique volume V_c; to these corresponds a unique temperature T_c.

a) Express a and b in terms of V_c and T_c.

b) Derive the relation

$$\frac{P_c V_c}{nRT_c} = \frac{3}{8}.$$

Test this prediction against the critical constants of carbon monoxide, ethylene, and water. Is the prediction accurate?

c) Rewrite the van der Waals equation in terms of the dimensionless quantities $p = P/P_c$, $v = V/V_c$, and $t = T/T_c$. This form of the equation should not involve the constants a, b, and n.

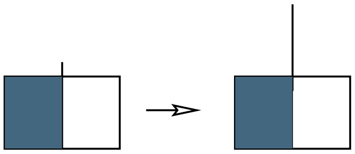
d) Construct a p-v diagram and plot the isotherms of the van der Walls equation of state. Choose several values of t in the interval between 0.8 and 1.2.

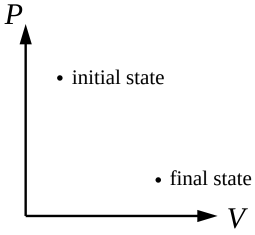
Chapter 2
Transformations and the first law

2.1 Quasi-static transformations

To watch a thermodynamic system in a state of perfect equilibrium offers only so much interest. More interesting is to subject the system to changes, or *transformations*, and study its properties during these changes. Not every transformation, however, can be studied within the framework of thermodynamics.

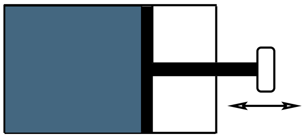
To illustrate this point, consider the free expansion of a gas. We imagine that a certain quantity of gas is maintained on the left-hand side of a box by means of a partition. Initially, before we remove the partition, the gas is in equilibrium; it possesses a well-defined volume and a well-defined pressure. Let us now remove the partition. The gas starts filling the entire box. As it does, the system goes out of equilibrium, and we can no longer speak of the pressure of the system as a whole. (While the system is out of equilibrium, the pressure is larger on the left-hand side of the box.) For this reason, P is no longer a well-defined thermodynamic variable. The transformation, therefore, cannot be described from a thermodynamic point of view, and only the initial and final states can be assigned variables P and V. On a P-V diagram, only the initial and final states can be represented; the transition between these states cannot be represented because P, the pressure of the system as a whole, is not defined during the transformation.

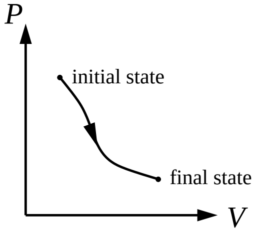




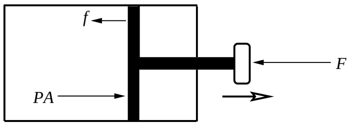
This state of affairs is not satisfying: We would like to be able to describe, within the framework of thermodynamics, the transition of a system from an initial state to a final state. This, however, is possible only if the transformation is carried out very slowly, so as to never disturb the equilibrium. One then speaks of a *quasi-static* transformation.

Consider the expansion of a gas by means of a piston. This offers us a much better control on the rate at which the expansion takes place. If we pull hard on the piston, then the situation is similar to what was considered before: the system goes out of equilibrium and P loses its meaning as a thermodynamic variable. If, however, we pull very gently, then the gas always has time to adjust itself to its new configuration, and departures from equilibrium stay very small. In the limit where the displacement is infinitely slow (the quasi-static limit), the system always stays arbitrarily close to equilibrium.

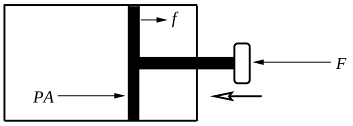




During a quasi-static transformation, the system goes through a succession of equilibrium states, starting from the initial state and ending at the final state. Because the system stays in equilibrium during the entire transformation, P is always well defined, and the transformation can be represented in a P-V diagram. Under these conditions, the system's equation of state remains valid during the transformation. There is therefore no obstacle in studying the transformation within the framework of thermodynamics.



expansion



compression

Let us work out the mechanics of a quasi-static expansion (or compression) of a fluid. To avoid a rapid acceleration of the piston, which would violate the quasi-static condition, we need to ensure that the external force acting on the piston balances exactly the force exerted by the gas. We must also take into account the frictional force acting on the piston. If P is the gas pressure, A the piston's area, and f the frictional force, then the requirement of not net force gives

$$F = PA - f$$

during an expansion, and

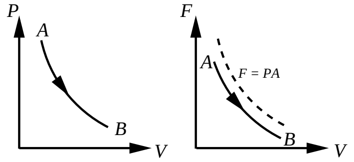
$$F = PA + f$$

during a compression. In situations where f can be neglected, $F = PA$ in both cases (expansion and compression).

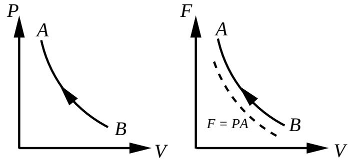
2.2 Reversible and irreversible transformations

A quasi-static transformation from a state A to a state B is said to be *reversible* if the transformation can be carried out in the reverse direction (from B to A) *without introducing any other changes in the system or its surroundings.* A transformation from A to B is said to be *irreversible* if it can only be carried out in that direction, or if the reverse transformation introduces additional changes in the system or its surroundings.

Let us illustrate these concepts with the help of our moving piston. To decide whether a transformation is reversible, we must monitor not only the system itself, but also its surroundings. In our example, the system is a fluid, with thermodynamic variables P and V; the surroundings is the external agent pushing on the piston, and its variables are F and V (because V indicates how far the piston has been pushed).



expansion



compression

Let the forward transformation be a quasi-static expansion from a volume V_A to a larger volume V_B. Such a transformation can easily be represented in a P-V diagram (for the system) and a F-V diagram (for the surroundings). During the expansion, $F = PA - f$. The reverse transformation is then a compression from V_B back to V_A. During the compression, $F = PA + f$, and the curve in the P-V plane retraces itself in the opposite direction. However, because $F_{\text{compression}} \neq F_{\text{expansion}}$, the curve in the F-V diagram does *not* retrace itself during the reverse transformation; there are instead two distinct curves. This shows very clearly that the conditions in the surroundings are not the same during the forward and reverse transformations. Furthermore, the surroundings does not return to its original state at the end of the reverse transformation: $F_{\text{final}} > F_{\text{initial}}$. The transformation from V_A to V_B is therefore irreversible. This conclusion is true even though the reverse transformation (compression from V_B to V_A) exists. The transformation is irreversible because as the system retraces its steps during the reverse transformation, the surroundings does not.

Our conclusion must of course be altered if we eliminate the frictional force f from the system. In the absence of friction, $F = PA$ in both the forward and reverse transformations. Because it is now true that both the system and the surroundings retrace their steps during the reverse transformation, the frictionless, quasi-static expansion from V_A to V_B is reversible.

It is a very general fact that all sources of friction must be eliminated before a transformation can be reversible. The reason is simple: Friction always produces heat, and this heat will be absorbed partially by the system, and partially by the surroundings. (This occurs both during the forward and reverse transformations.) This extra heat prevents the system and the surroundings from both returning to their initial states after the reverse transformation, because the final states contain more heat than the initial states. Friction, therefore, always prevents a transformation from being reversible. If all sources of friction are eliminated, then the transformation can be reversible.

It is useful to note that in the case of a reversible transformation, only a very slight change in the external conditions are necessary to reverse the transformation. In our example, the external force required to compress the gas is the same as the force required to expand the gas: $F = PA$. On the other hand, large changes in the external conditions are required when the transformation is irreversible. In our example, the force goes from $F = PA - f$ during the expansion to $F = PA + f$ during the compression; the change in external conditions is therefore $\Delta F = 2f$. This goes to zero when friction is eliminated, and the transformation becomes reversible.

2.3 Mathematical interlude: Infinitesimals and differentials

2.3.1 Infinitesimals

We begin this interlude by introducing the two-dimensional plane with coordinates x and y. To denote an infinitesimal displacement in the x direction we use dx, and dy denotes an infinitesimal displacement in the y direction. Multiplying an infinitesimal by a finite number returns another infinitesimal. Thus, $2xy^3\,dx$ is an infinitesimal, and so is $3x^2y^2\,dy$. Adding two infinitesimals also returns an infinitesimal. Thus, $2xy^3\,dx + 3x^2y^2\,dy$ is an infinitesimal, and so is $2xy^2\,dx + 3x^2y^3\,dy$.

We need a notation for such combinations of infinitesimals. In general, we will be dealing with quantities of the form $A(x,y)\,dx + B(x,y)\,dy$, where A and B are arbitrary functions of the coordinates. We will denote this by

$$\boxed{đF \equiv A(x,y)\,dx + B(x,y)\,dy}\,. \tag{2.1}$$

The reason for slashing the "d" will become clear below. For the moment, it suffices to say that $đF$ designates an infinitesimal of the general form $A(x,y)\,dx + B(x,y)\,dy$.

2.3.2 Differentials

Forming infinitesimals of the form of Eq. (2.1) is extremely simple. Imagine that we have at our disposal a function of the coordinates, $G(x,y)$. Its *total* derivative $dG \equiv G(x+dx, y+dy) - G(x,y)$ is given by

$$\boxed{dG = \left(\frac{\partial G}{\partial x}\right)_y dx + \left(\frac{\partial G}{\partial y}\right)_x dy}\,, \tag{2.2}$$

where in the first term we differentiate G with respect to x and keep y fixed, while in the second term we differentiate G with respect to y and keep x fixed. (The quantity kept fixed during partial differentiation is indicated by a suffix after the bracket.) If $G(x,y) = x^2y^3$, say, then

$$dG = 2xy^3\,dx + 3x^2y^2\,dy.$$

This clearly is an infinitesimal. Why then are we not using the notation $đG$?

The reason is that dG is more than just an infinitesimal: it is also a *differential*. A differential is an infinitesimal quantity obtained by total differentiation of a function $G(x,y)$. (Differentials are sometimes called *exact differentials*.) Thus, the notation dG will be reserved for differentials, while the notation $đG$ will be used to denote infinitesimals which are not differentials.

2.3.3 Infinitesimals that are not differentials

When is an infinitesimal not a differential? Consider the infinitesimal

$$đF = 2xy^2\,dx + 3x^2y^3\,dy,$$

and let us determine whether there exists a function $F(x,y)$ whose total derivative is equal to $đF$. If such a function exists, then $đF$ would be a differential, and we would be permitted to write dF. If the function F exists, then comparing with Eq. (2.2) gives

$$\left(\frac{\partial F}{\partial x}\right)_y = 2xy^2, \qquad \left(\frac{\partial F}{\partial y}\right)_x = 3x^2y^3.$$

Let us integrate the first equation with respect to x, keeping y fixed:

$$F(x,y) = x^2y^2 + c(y),$$

where we have indicated that the "constant of integration" c can in fact depend on y, because y is treated as a constant during the integration. Let us now integrate the second equation with respect to y, keeping x fixed:

$$F(x,y) = \frac{3}{4}\,x^2y^4 + k(x),$$

where the "constant of integration" k now depends on x. It is clear that these results are not compatible: no conceivable choice of functions $c(y)$ and $k(x)$ will make the two expressions for $F(x,y)$ agree. We must conclude that the function F does *not* exist, and that $đF$ is just an infinitesimal, not a differential.

Notice that when we write dG for a differential, the symbol G possesses a meaning of its own: it denotes the function $G(x,y)$ being differentiated. On the other hand, when we write $đF$ for an infinitesimal, the symbol F does *not* have a meaning of its own: there is no function $F(x,y)$ to be differentiated. The symbol $đF$ therefore comes whole, and the "$đ$" cannot be separated from the "F".

2.3.4 The differential test

It usually is not very practical to integrate Eq. (2.1) to decide whether the right-hand side is a differential. Fortunately, however, there exists a simple way to test whether an expression such as $A(x,y)\,dx + B(x,y)\,dy$ is a differential. Suppose that it is. Then comparing with Eq. (2.2) gives

$$A(x,y) = \left(\frac{\partial G}{\partial x}\right)_y \qquad B(x,y) = \left(\frac{\partial G}{\partial y}\right)_x,$$

where $G(x,y)$ is the function whose total derivative is equal to $A(x,y)\,dx + B(x,y)\,dy$. Now compute the second partial derivatives of $G(x,y)$:

$$\frac{\partial}{\partial y}\left(\frac{\partial G}{\partial x}\right)_y \equiv \frac{\partial^2 G}{\partial y \partial x} = \left(\frac{\partial A}{\partial y}\right)_x,$$

while

$$\frac{\partial}{\partial x}\left(\frac{\partial G}{\partial y}\right)_x \equiv \frac{\partial^2 G}{\partial x \partial y} = \left(\frac{\partial B}{\partial x}\right)_y.$$

These quantities must agree, because for smooth functions $G(x,y)$, the order in which the partial derivatives are taken does not matter. Therefore, if $A(x,y)\,dx + B(x,y)\,dy$ is a differential, then the functions A and B must satisfy the relation

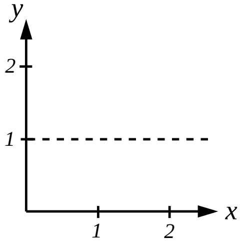
$$\boxed{\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y}\,. \tag{2.3}$$

It is easy to check that Eq. (2.3) is satisfied for $dG = 2xy^3\,dx + 3x^2y^2\,dy$, but that it is violated for $\text{đ}F = 2xy^2\,dx + 3x^2y^3\,dy$.

2.3.5 Integration of infinitesimals

Imagine that we are given the function $A(x,y) = 2xy^2$ and are instructed to integrate it with respect to x, from $x = 0$ to $x = 1$. This presents no difficulty:

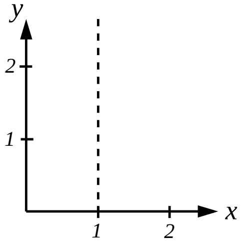
$$\int_0^1 A(x,y)\,dx = x^2y^2\Big|_0^1 = y^2.$$



It is clear that y must be treated as a constant during the integration. In effect, we are integrating the function $A(x,y)$ along a curve $y = \text{constant}$ in the y-x plane. If the value of this constant is chosen to be $y = 1$, then the integral evaluates to 1.

Imagine now that we are told to integrate the function $B(x,y) = 3x^2y^3$ with respect to y, from $y = 1$ to $y = 2$. This also presents no difficulty:

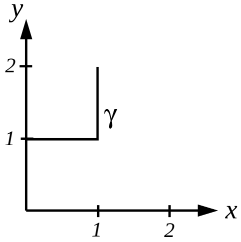
$$\int_1^2 B(x,y)\,dy = \frac{3}{4}\,x^2y^4\Big|_1^2 = \frac{45}{4}\,x^2.$$



Here we are integrating along a curve $x = \text{constant}$ in the y-x plane. If we choose the curve $x = 1$, then the integral evaluates to $45/4$.

Let us combine the two integrals:

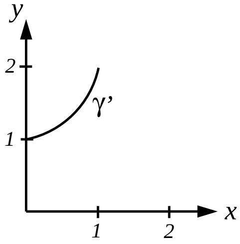
$$\int_0^1 A(x,y)\,dx\Big|_{y=1} + \int_1^2 B(x,y)\,dy\Big|_{x=1}.$$



According to our previous results, this integral is equal to $1 + 45/4 = 49/4$. It corresponds to the integration of $\text{đ}F \equiv A(x,y)\,dx + B(x,y)\,dy$ along a curve γ in the y-x plane; this curve is given by the union of the two segments $(0 < x < 1, y = 1)$ and $(x = 1, 1 < y < 2)$. We may therefore express the result as

$$\int_\gamma \text{đ}F = \frac{49}{4}.$$

Here, $\text{đ}F$ is the infinitesimal quantity being integrated, and γ is the curve along which the integration takes place. Integrals such as this are called *line integrals.*



Line integration can be defined along *any* curve of the y-x plane. As an example, let us integrate $\text{đ}F = 2xy^2\,dx + 3x^2y^3\,dy$ — the same $\text{đ}F$ as in the previous example — along the curve γ' described in parametric form by

$$\gamma' : \big[x(s) = s, y(s) = 1 + s^2\big],$$

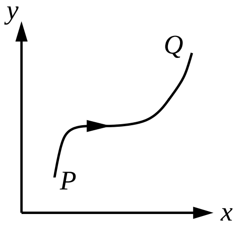
where the parameter s varies from $s = 0$ to $s = 1$. It is easy to check that γ' describes a parabola joining the points $(0,1)$ and $(1,2)$; the curves γ and γ' therefore share the same end points.

To integrate $\text{đ}F$ along γ', we simply express $\text{đ}F$ in terms of s and integrate from $s = 0$ to $s = 1$. After some algebra we find $\text{đ}F = 2s(1 + 5s^2 + 10s^4 + 9s^6 + 3s^8)\,ds$, and integration yields

$$\int_{\gamma'} \text{đ}F = \frac{581}{60}.$$

Notice that $\int_\gamma \text{đ}F \neq \int_{\gamma'} \text{đ}F$, even though the curves γ and γ' both connect the same two points, $(0,1)$ and $(1,2)$. This is not surprising: Because the set of values adopted by $\text{đ}F$ on the curve γ is quite different from its values on γ', there is no reason why the two integrations should return the same number. We may conclude that $\int \text{đ}F$ depends not only on the end points of the integration, but also on the choice of curve joining these end points.

2.3.6 Integration of differentials



This conclusion ceases to be true if the quantity being integrated is dG, a differential. In this case, the following theorem holds:

$$\boxed{\int_P^Q dG = G(Q) - G(P), \qquad \text{along } \textit{any} \text{ curve joining } P \text{ and } Q}\;. \tag{2.4}$$

Here, $G(Q)$ is the value of the function $G(x, y)$ at the point Q, while $G(P)$ is its value at P. The theorem states that in the case of differentials, the value of the integral does *not* depend on the curve joining the two end points; it depends *only* on the end points themselves.[1]

We now prove the theorem. We suppose that we are given a curve μ joining P and Q, and that this curves admits a parametric description,

$$\mu : \big[x = x(s), y = y(s)\big],$$

where the parameter varies from $s = s_P$ to $s = s_Q$. Let $g(s)$ be the function that results when the substitution $x = x(s)$, $y = y(s)$ is made in $G(x, y)$:

$$g(s) \equiv G\big(x(s), y(s)\big).$$

In other words, $g(s)$ is the *restriction* of the function $G(x, y)$ to the curve μ; for any point between P and Q on the curve, the values of g and G agree, but unlike G, g is not defined outside the curve. We may differentiate g with respect to s:

$$\frac{dg}{ds} = \left(\frac{\partial G}{\partial x}\right)_y \frac{dx}{ds} + \left(\frac{\partial G}{\partial y}\right)_x \frac{dy}{ds} \equiv \frac{dG}{ds},$$

where dG/ds is to be understood as the ratio of the differential dG to the infinitesimal ds. Using this result, we have

$$\int_P^Q dG = \int_{s_P}^{s_Q} \frac{dg}{ds}\, ds.$$

The second integral is an ordinary integral with respect to the parameter s. By the fundamental theorem of integral calculus, we know that it is equal to $g(s_Q) - g(s_P)$. But because the values of g and G agree at P and Q, we arrive at

$$\int_P^Q dG = G(Q) - G(P).$$

Because this result makes no reference to a particular choice of curve μ, the theorem is established.

2.4 Work

2.4.1 Work equation for fluids

As we saw in Sec. 1, the compression or expansion of a fluid involves an external agent applying a force F to displace a piston over a certain distance. (Recall that $F = PA + f$ during a compression, while $F = PA - f$ during an expansion.) The product (force × displacement) is called *work*, and we say that the compression or

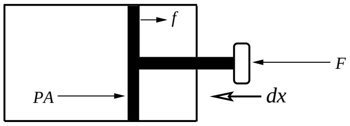
---

[1] You should check that this statement is true for the differential $dG = 2xy^3\, dx + 3x^2y^2\, dy$. Use the curves γ and γ' defined previously. You should find in both cases that the integral from $(0, 1)$ to $(1, 2)$ is equal to 8.

expansion of a fluid involves *doing work* (positive or negative) *on the system.* We will denote work with the symbol W.

The sign of the work done depends on the direction in which the piston is moved. The work done on the system will be *positive* if the displacement is in the same direction as that of the applied force F, and it will be *negative* if the displacement is in the opposite direction. Now, we have seen that the force is always applied in the same direction, independently of the direction in which the piston moves. The reason is that in a quasi-static displacement of the piston, the force F must just barely compensate for the fluid's pressure; because the pressure is always directed outward, the force is always directed inward. During a *compression*, both the external force and the displacement are directed inward: the work done on the system is *positive.* During an *expansion*, the external force is still directed inward, but the displacement is now outward: the work done on the system is *negative.*

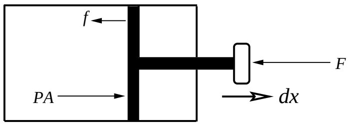
It is easy to calculate the work done by expansion or compression if the displacement is over a very short distance, given by the infinitesimal dx. During a *compression*, the work done is positive, and $đW = +F\,dx = (PA + f)\,dx$. But $A\,dx = -dV$, the change in volume caused by the motion of the piston; this is negative because compression produces a decrease in volume. So



compression

$$đW = -P\,dV + f\,dx \qquad \text{(compression)}.$$

On the other hand, during an expansion the work done is negative, and $đW = -F\,dx = -(PA - f)\,dx$. But $A\,dx = +dV$, because now the volume is increasing. So



expansion

$$đW = -P\,dV + f\,dx \qquad \text{(expansion)}.$$

These expressions are identical: the same work equation can therefore be used for both a compression and an expansion. The work equation implies that $đW \geq -P\,dV$, with the equality sign holding when all sources of friction are eliminated.

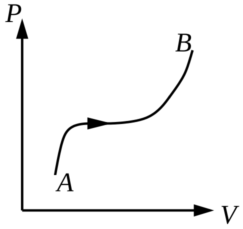
We have obtained the following statement:

> During the quasi-static compression or expansion of a fluid by an amount dV, a quantity of work
>
> $$\boxed{đW \geq -P\,dV} \tag{2.5}$$
>
> is done on the system. The equality sign holds when the transformation is carried out reversibly.

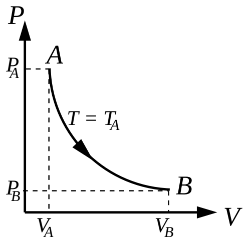
2.4.2 Work depends on path

The work done on a fluid during a compression or expansion by a *finite* amount is obtained by integrating $đW$ over the entire transformation. Denoting the initial state by A and the final state by B, and assuming that the transformation is *reversible*, we have

$$\boxed{W = \int_A^B đW = -\int_A^B P\,dV}\,. \tag{2.6}$$



In order to evaluate the integral, we need to know how P behaves as a function of V during the transformation. In other words, we need to know *which* function $P(V)$ to substitute inside the integral. We must expect that the result for W will depend in a crucial way on this choice of function. In other words, $\int_A^B đW$ will depend on the *path* joining the initial state A to the final state B. (This path can be represented by a curve in the P-V plane.) We were therefore quite justified in using the notation $đW$ to designate the infinitesimal of work: there does not exist a function $W(P, V)$ whose total derivative is equal to $-P\,dV$.



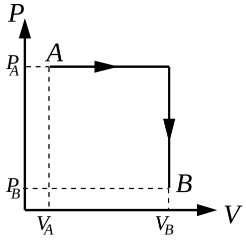
Let us illustrate the dependence on the path by working out two examples.

In the first example we imagine performing an *isothermal expansion* on an ideal gas, taking it from a volume V_A to a larger volume V_B. As the word "isothermal" indicates, the expansion is carried out at constant temperature. We assume that the expansion is also carried out quasi-statically and reversibly. This allows us to use the work equation $đW = -P\,dV$, and the equation of state for an ideal gas: $P(V) = nRT/V$. Because the expansion is isothermal, T is a constant; to indicate this clearly we will write $T = T_A$, where T_A is the temperature of the gas in its initial state. Notice that its pressure is then equal to $P_A = nRT_A/V_A$; in the final state it is equal to $P_B = nRT_A/V_B$. Evaluating the work integral, we have

$$W = -\int_{V_A}^{V_B} P(V)\,dV = -nRT_A \int_{V_A}^{V_B} \frac{dV}{V},$$

or

$$\boxed{W_{\text{isothermal}} = -nRT_A \ln \frac{V_B}{V_A}}\,. \tag{2.7}$$



Because we are dealing with an expansion, the work done on the system is negative.

In the second example we imagine performing an *isobaric expansion* on the same ideal gas, from the same volume V_A to the same volume V_B. As the word "isobaric" indicates, this transformation is carried out at constant pressure, with P maintained at its initial value, $P_A = nRT_A/V_A$. After the isobaric expansion, we decrease the pressure (at constant volume) to the value P_B, so that the system's final state is the same as in the first example. The work done during the isobaric expansion is given by

$$W = -\int_{V_A}^{V_B} P(V)\,dV = -\int_{V_A}^{V_B} P_A\,dV = -\frac{nRT_A}{V_A}\int_{V_A}^{V_B} dV = -nRT_A\biggl(\frac{V_B}{V_A} - 1\biggr).$$

During the second stage of the transformation, when the pressured is lowered at constant volume, the work done is zero (no change in volume, no work). The work done on the system during the entire transformation is therefore given by

$$\boxed{W_{\text{isobaric}} = -nRT_A\biggl(\frac{V_B}{V_A} - 1\biggr)}\,. \tag{2.8}$$

As claimed, this answer is different from the answer obtained in the first example. Even though the transformations connect the same initial state A to the same final state B, the work done depends on the precise nature of the transformation. Thus, work truly depends on path.

2.4.3 Work equation for other systems

The specific form of the work equation depends on the thermodynamic system under consideration. For fluids, we have seen that $đW = -P\,dV$ if the transformation is reversible. Notice that here, $đW$ is proportional to the variation in the quantity affected during the transformation — the volume — and also to the quantity that *opposes* the variation — the pressure, which fights against a change in volume. In other thermodynamic systems, the same rule applies, except that other quantities must be substituted in place of dV and P.

In thin films, work can be done by changing the film's area A. The quantity opposing such a change is the surface tension γ. Here, the sign convention is that stretching a film does positive work on the system (both the applied force and the displacement are directed outward), so that $đW = +\gamma\,dA$. In filaments, work can be done by changing the length ℓ. The quantity opposing such a change is the tension f, and the work equation is $đW = +f\,d\ell$. Finally, work can be done on magnets by changing their magnetization M. This is opposed by the applied magnetic field H, so that the work equation is $đW = +VH\,dM$, where V is the volume of the magnetic sample. We will provide a derivation of this result in Sec. F of the course.

2.4.4 Work done on a solid

Doing work on a solid generally involves applying stresses that distort the shape of the solid. Such a transformation is difficult to describe, because one must specify the directions in which the stresses are being applied, and because the solid's response is more complicated than just an overall change in volume. In this general situation, therefore, the work equation is more complicated than just $đW = -P\,dV$. Nevertheless, in a situation where the stresses are applied uniformly in all directions, they are adequately described by the single number P, and the solid's response under isotropic stresses *is* just an overall change in volume. In such a situation, the equation $đW = -P\,dV$ does accurately describe the work done on a solid.

As an example, let us calculate the work done on a solid when the (isotropic) pressure is increased from P_A to P_B, keeping the temperature constant. (This is therefore an isothermal increase of pressure.) We shall assume that the solid possesses an equation of state of the form $V = V(P,T)$.

Answering this question will obviously involve integrating the work equation. We cannot, however, evaluate $W = -\int_A^B P\,dV$ directly, because this integral describes a change in volume, not a change in pressure. We must therefore relate these changes. For this we differentiate the equation of state:

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT.$$

For an isothermal change of pressure, $dT = 0$ and the second term disappears; we obtain

$$dV = -\kappa V\,dP.$$

We have introduced a new quantity, κ, called the *isothermal compressibility* of the solid. This is defined by

$$\boxed{\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}\,. \tag{2.9}$$

Thus, κ measures the fractional change in volume that results from a change of pressure at constant temperature; because an increase in pressure always produces a decrease in volume, κ is a positive quantity.

Substituting our expression for dV in the work integral gives

$$W = \int_{P_A}^{P_B} \kappa V P\,dP.$$

To evaluate this, we need to know how κV behaves as a function of pressure. Experiment gives us the necessary input: For reasonable changes in pressure, κV remains constant; this quantity can therefore be taken out of the integral. We therefore arrive at

$$\boxed{W = \frac{1}{2}\kappa V\left({P_B}^2 - {P_A}^2\right)}\,. \tag{2.10}$$

This is our final answer. The steps involved in solving this problem are typical of many problems of thermodynamics.

2.5 First law

It is known from mechanics that doing work on an object increases its potential energy. The same is true in thermodynamics: Doing work on a thermodynamic system increases its internal energy. Thus, when a fluid is compressed, its internal energy increases, because the work done on the system is positive. On the other hand, expanding the fluid decreases its internal energy.

Doing work on a thermodynamic system is *one* of the ways by which its internal energy can be altered. The other way is to let the system absorb heat. While doing work can be thought of as increasing the system's potential energy, adding heat can be thought of as increasing its *kinetic* energy. A common way of adding heat to a system consists of putting it in thermal contact with a hotter body: heat naturally flows from hot to cold. (This is in fact a way of defining what is hot and what is cold.)

This statement, that the internal energy of a thermodynamic system can be increased either by doing work or adding heat, is the physical content of the *first law* of thermodynamics.

The precise formulation of the first law consists of two statements. The first is:

> There exists a state function $U(X, Y)$ that represents the internal energy of a thermodynamic system with variables X and Y.

The words "state function" mean that the internal energy is a function of the variables X and Y that characterize the state of the thermodynamic system. For a fluid, the internal energy will depend on P and V: $U = U(P, V)$. Alternatively, because P, V, and T are related by the equation of state, we can equally well express the internal energy as a function of P and T, or as a function of V and T. In most situations, the precise form of the internal-energy function is not known; the first statement of the first law merely guarantees that this functions *exists*. That it does is of course not surprising: The internal energy (the sum of all kinetic and potential energies within the system) is a well-defined quantity that must change if the state of the system is altered.

The second statement is:

> The change in internal energy as a thermodynamic system is taken from an initial state A to a final state B is equal to W, the work done on the system during the transformation, added to Q, the heat absorbed by the system.

In mathematical terms,

$$\boxed{U(B) - U(A) = W(A \rightarrow B) + Q(A \rightarrow B)}\,. \tag{2.11}$$

Note that in this equation, both W and Q can be of either sign; negative heat corresponds to heat *leaving* the system to be absorbed by the surroundings.

The first law can also be expressed in infinitesimal form:

$$\boxed{dU = đW + đQ}\,. \tag{2.12}$$

The notation is important. By writing dU we indicate that an internal-energy function U exists that can be differentiated. On the other hand, by writing $đW$ we indicate that a "work function" W does not exist, and similarly, there is no "heat function" Q. Physically, this corresponds to the fact that while doing work and adding heat surely increases the internal energy, there is no meaningful way in general to decompose a system's internal energy into a "work part" and a "heat part". Thus, an equation such as $U = W + Q$ makes no sense in physics. Equation

(2.12) also implies that while $\int_A^B dU = U(B) - U(A)$ is the same for all transformations taking the system from A to B, the integrals $\int_A^B đW \equiv W(A \to B)$ and $\int_A^B đQ \equiv Q(A \to B)$ depend in a detailed way on the nature of the transformation. Again the notation is important: expressions such as $W(B) - W(A)$ and $Q(B) - Q(A)$ have no meaning.

2.6 Heat capacity

Adding heat to a system is usually done by raising its temperature. Because the integral of $đQ$ depends on the path of integration, it is important to specify *fully* the conditions under which the temperature is raised. For example, is the temperature increased while maintaining the pressure constant, or is it increased while keeping the volume fixed? These two sets of conditions will produce different results: The amounts of heat transferred to the system will be different, even when the change in temperature is the same.

A quantity of interest is the amount of heat absorbed by a thermodynamic system when its temperature is raised by one degree. This quantity is called the *heat capacity* of the thermodynamic system. As was indicated above, the value of the heat capacity depends on what quantity (pressure or volume) is kept constant when the temperature is increased. We must therefore introduce two types of heat capacity: C_V, the heat capacity at constant volume, and C_P, the heat capacity at constant pressure. Mathematically, these are defined by

$$\boxed{C_V = \left(\frac{đQ}{dT}\right)_V, \qquad C_P = \left(\frac{đQ}{dT}\right)_P}. \tag{2.13}$$

The heat capacities are positive quantities: an increase in temperature always corresponds to the system absorbing a positive quantity of heat.

The heat capacities can be used to calculate how much heat is absorbed by a system whose temperature is changed. If the system is kept at constant volume, we use

$$Q(A \to B) = \int_{T_A}^{T_B} C_V \, dT.$$

If instead the system is kept at constant pressure, we use

$$Q(A \to B) = \int_{T_A}^{T_B} C_P \, dT.$$

Of course, these integrals cannot be evaluated until we know the behaviour of the heat capacity as a function of temperature. This depends on the nature of the thermodynamic system, and the determination of the functions $C_V(T)$ and $C_P(T)$ is a major experimental undertaking. It is true fairly generally that the heat capacities vary slowly with temperature. If T_B does not differ greatly from T_A, then the heat capacities can typically be taken out of the integral.

It must be understood that this rule is not always followed. For example, C_P behaves in a very irregular way during phase transitions. When ice goes through the melting point, adding heat does *not* produce a change in temperature. The transition proceeds at constant temperature, and the heat is used instead to unbind the water molecules, thereby allowing the transition to the liquid state. At the melting point, therefore, the heat capacity is formally infinite. The amount of heat required to go through a phase transition is called the *latent heat* of this transition.

The heat capacities of a thermodynamic system are usually proportional to the size of the system: A larger system possesses a larger heat capacity, because a larger quantity of heat is required to raise the temperature by the same amount. It is often useful to scale the heat capacities by the size of system. This can be done by dividing by n, the molar number (equal to N/N_A, where N is the total number of molecules in the system, and N_A is Avogadro's number). The resulting quantities are called specific heat capacities, or more simply, *specific heats.* Mathematically, the specific heats are defined by

$$\boxed{c_V = \frac{1}{n} C_V, \qquad c_P = \frac{1}{n} C_P}\,. \tag{2.14}$$

It is possible also to define specific heats by dividing by the total mass of the system.

Some thermodynamic systems are so large that for all practical purposes, their heat capacities are infinite: extracting heat from these systems does not affect their temperature. Such idealized systems are very useful in thermodynamics; they are called *heat reservoirs.*

2.7 Some formal manipulations

It is possible to derive useful relations between the heat capacities and other thermodynamic quantities by combining the first law with some mathematical trickery. The following discussion will illustrate how pure mathematics is typically used in thermodynamics. In this and the following sections, we will assume that all transformations are quasi-static and reversible, so that we can rely on the existence of a well-defined equation of state and write the work equation as $đW = -P\,dV$.

2.7.1 *Heat capacity at constant volume*

We have seen that the internal energy U can be considered to be a function of two thermodynamic variables among P, V, and T. (These variables are related by the equation of state.) Let us choose V and T to be the fundamental variables. The internal energy can then be written as $U(V,T)$. Let us differentiate this function:

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT.$$

This equation can be combined with the first law, $dU = đQ + đW = đQ - P\,dV$, to give an expression for $đQ$:

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

This equation allows us to calculate the heat absorbed by a system when its volume and temperature are altered in arbitrary ways. Suppose now that during a transformation, the system is kept at constant volume, so that $dV = 0$. The preceding equation then gives

$$\boxed{C_V \equiv \left(\frac{đQ}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V}\,. \tag{2.15}$$

Thus, the heat capacity at constant volume is just the partial derivative of the internal energy with respect to temperature, keeping the volume fixed. This is not a surprising result, because no work is done if $dV = 0$, so that $đQ = dU$.

2.7.2 Heat capacity at constant pressure

A similar statement can be made about C_P, the heat capacity at constant pressure. Suppose that we now express U as a function of P and T, and that we use the equation of state to express V also in terms of P and T. We therefore have the functions $U(P,T)$ and $V(P,T)$. Differentiating them yields

$$dU = \left(\frac{\partial U}{\partial P}\right)_T dP + \left(\frac{\partial U}{\partial T}\right)_P dT$$

and

$$dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT.$$

Substituting these relations into the first law, $đQ = dU + P\,dV$, we obtain

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

This equation allows us to calculate the heat absorbed by a system when its pressure and temperature are altered in arbitrary ways. If P is kept fixed during the transformation, then the first term vanishes, and we have

$$\boxed{C_P \equiv \left(\frac{đQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P}\,. \tag{2.16}$$

This expression for C_P is more complicated than what was obtained previously for C_V.

It is possible to simplify the appearance of Eq. (2.16) by finding a function $H(P,T)$ such that the heat capacity at constant pressure can be expressed as

$$\boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}\,. \tag{2.17}$$

This function is called the *enthalpy*. It is easy to check that the enthalpy function must be given by

$$\boxed{H = U + PV}\,; \tag{2.18}$$

partial differentiation of H with respect to T does indeed reproduce expression (2.16) for C_P. We can also derive the relation $dH = đQ + V\,dP$, so that $dH = đQ$ if the pressure is kept fixed ($dP = 0$). The enthalpy function plays an important physical role in flow processes; see Sec. 3.8 of Adkins' book.

2.7.3 Internal energy as a function of volume

As another exercise, let us now consider the following question. Suppose that the heat capacities, C_V and C_P, of a given substance are known as functions of temperature. Suppose also that β, the *volume expansivity* of that substance, is known. This quantity is defined by

$$\boxed{\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}\,; \tag{2.19}$$

it is the fractional change in volume that results when a substance's temperature is altered at constant pressure. For most substances, increasing the temperature produces a thermal expansion, and $\beta > 0$. What can we then say about the way the substance's internal energy varies with volume if we keep the temperature constant?

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 $(\partial U/\partial V)_T$. This 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 also no heat flow. Therefore, $W = Q = 0$, and the internal energy must stay constant during the transformation.

Suppose that we express the internal energy as a function of volume and temperature: $U = U(V, T)$. Then

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT.$$

If it is found that $dU = dT = 0$ during a transformation, which according to Joule is true for the free expansion of an ideal gas, then we must conclude that

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0 \qquad \text{(ideal gas)}}\,. \tag{2.21}$$

Thus, the internal energy depends only on temperature, and not at all on volume. This statement follows as a direct consequence of Joule's experiment.

2.8.2 Heat capacities

The Joule experiment also has implications regarding the heat capacities. First, the fact that U depends only on T implies immediately that $C_V = (\partial U/\partial T)_V \equiv dU/dT$ also depends only on T. Second, there exists a simple relation between C_P and C_V, which can be derived by putting the left-hand side of Eq. (2.20) to zero. This yields

$$C_P - C_V = \beta PV,$$

where $\beta = V^{-1}(\partial V/\partial T)_P$ is the volume expansivity. It is easy to evaluate β by using the equation of state: $\beta = nR/PV$. We therefore have

$$\boxed{C_P - C_V = nR \qquad \text{(ideal gas)}}\,. \tag{2.22}$$

This relation can also be expressed in terms of the specific heats: $c_P - c_V = R$. Thus, C_P is always larger than C_V: it is more efficient to raise the temperature by transferring heat at constant volume. Finally, Eq. (2.22) implies that C_P is also a function of temperature only.

Equation (2.22) implies that the behaviour of c_P as a function of temperature determines the behaviour of c_V; multiplying by the molar number n gives C_P and C_V. The behaviour of $c_P(T)$ depends on the nature of the ideal gas. For *monoatomic* gases (such as He, Ne, A, and most metallic vapours such as Na, Cd, and Hg), c_P is constant over a wide range of temperatures, being nearly equal to $\frac{5}{2}R$. For *diatomic* gases (such as air, H_2, D_2, O_2, N_2, NO, and CO), c_P is constant at ordinary temperatures, being nearly equal to $\frac{7}{2}R$, but it increases with temperature at high temperatures. For *polyatomic* gases (such as CO_2, NH_3, CH_4, Cl_2, and Br_2), c_P varies with temperature in a way that depends on the gas.

For hydrogen, the behaviour of $c_P(T)$ is quite exceptional: For $T < 50$ K, c_P is roughly constant and equal to $\frac{5}{2}R$, the value appropriate for a monoatomic gas. Between 50 K and 250 K, c_P increases steadily with temperature. Between 250 K and 750 K, c_P is again constant with a value $\frac{7}{2}R$ appropriate for a diatomic gas. Finally, for $T > 750$ K, c_P again increases with temperature.

2.8.3 A molecular model for the heat capacities

The molecular model introduced in Sec. A 10 gives us a simple way of understanding why $C_V = \frac{3}{2}nRT$ for a monoatomic gas, so that $C_P = \frac{5}{2}nRT$ by virtue of Eq. (2.22).

If the gas is monoatomic, the only form of energy that is available to the molecules is kinetic energy, and we know that the avarage kinetic energy per molecule is equal to $\frac{3}{2}kT$. If the total number of molecules is $N = nN_A$, then the internal energy must be given by $U = \frac{3}{2}NkT = \frac{3}{2}nRT$. (Recall that $R = N_A k$.) We therefore see directly that for a monoatomic ideal gas, the internal energy depends only on temperature. Furthermore, Eq. (2.15) implies that $C_V = \frac{3}{2}nR$, the desired expression.

These results hold only for monoatomic gases. The reason is that complicated molecules also possess other forms of energy. For example, a diatomic molecule can have both vibrational and rotational energy, in addition to kinetic energy; the relation $U = \frac{3}{2}NkT$ does not hold is these situations. This explains why the heat capacities of polyatomic gases can have the complicated behaviour described previously.

2.8.4 Adiabatic expansion or compression

To conclude this section, we will calculate how the pressure and temperature vary with volume when an ideal gas undergoes a quasi-static transformation (expansion or compression) under *adiabatic* conditions (so that heat is not allowed to be transferred between the gas and its surroundings). We will employ techniques similar to those used in Sec. 7.

Recall the statement of the first law of thermodynamics, in the form $đQ = dU + P\,dV$, or in the form $đQ = dH - V\,dP$, where $H \equiv U + PV$ is the enthalpy function. Recall also that U, and therefore H, are functions of T only, so that we can write $C_V = dU/dT$ and $C_P = dH/dT$. We therefore have

$$đQ = C_V\,dT + P\,dV, \qquad đQ = C_P\,dT - V\,dP.$$

For an adiabatic transformation, $đQ = 0$, and we have

$$P\,dV = -C_V\,dT, \qquad V\,dP = C_P\,dT.$$

Dividing the second equation by the first, we obtain

$$\frac{V}{P}\frac{dP}{dV} = -\gamma,$$

where γ is the ratio of the heat capacities:

$$\boxed{\gamma \equiv \frac{C_P}{C_V} = \frac{c_P}{c_V}}\,. \tag{2.23}$$

This quantity is approximately constant for moderate changes in temperature; for monoatomic gases, $\gamma = 5/3 \simeq 1.6666$, while for diatomic gases, $\gamma = 7/5 = 1.4$. We may therefore treat γ as a constant when integrating the equation for dP/dV. Integration is elementary, and we obtain

$$\boxed{PV^\gamma = \text{constant} \qquad \text{(ideal gas, adiabatic transformation)}}\,. \tag{2.24}$$

This is the desired relation between pressure and volume. To obtain T as a function of V, we simply use the equation of state: $T = \text{constant} \times PV$. This yields $TV^{\gamma-1} =$ constant.

2.9 Problems

1. In this problem we will consider the infinitesimal quantities

$$đF = -\frac{1}{y}\,dx + \frac{1}{x}\,dy, \qquad đG = \left(1 - \frac{y}{x^2}\right)dx + \frac{1}{x}\,dy.$$

a) Is $đF$ a differential? Is $đG$?

b) Integrate $đF$ and $đG$ along the following curve in the y-x plane: a complete circle of unit radius centered at the origin. Choose any point on the circle as the starting (and ending) point of the integral.

2. (Zemansky and Dittman, Problem 3.3)

   During a quasi-static, reversible, and adiabatic expansion of an ideal gas, the pressure at any moment is given by $PV^\gamma = c$, where γ and c are constants.

   a) Show that the work done on the gas by expanding from a volume V_A to a volume V_B is

$$W(A \to B) = -\frac{P_A V_A - P_B V_B}{\gamma - 1}.$$

   b) If the initial pressure and volume are 10^6 Pa and 10^{-3} m^3, respectively, and the final volume is 3.16×10^{-3} m^3, how many joules of work is done on the gas if $\gamma = 1.4$? What is the final pressure?

   c) What is the work done if instead the expansion is carried out isothermally? What is the final pressure?

3. (Zemansky and Dittman, Problem 3.6)

   The pressure on 0.1 kg of metal is increased quasi-statically, reversibly, and isothermally from 0 to 10^8 Pa. Assuming the density and the isothermal compressibility to remain constant at the values 10^4 kg/m^3 and 6.75×10^{-12} Pa^{-1}, respectively, calculate the work done on the metal.

4. Two quantities of importance in thermodynamics are the isothermal compressibility κ and the volume expansivity β. They are defined by

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P.$$

   Both quantities can be calculated if the system's equation of state is known.

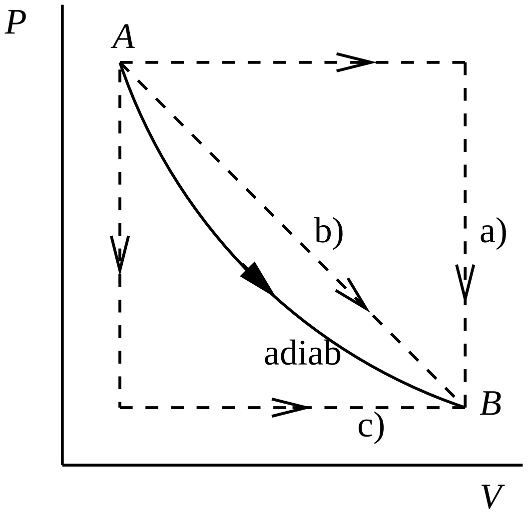
   Calculate κ and β for the van der Waals gas, for which the equation of state is

$$(P + a/v^2)(v - b) = RT.$$

   Here, a and b are constants and $v = V/n$ is the molar volume. Check that in the ideal-gas limit ($v \to \infty$), $\kappa \to 1/P$ and $\beta \to 1/T$.

5. In a quasi-static, reversible transformation $A \to B$ during which no heat is exchanged with the environment (see diagram), the pressure of a certain amount of gas is found to change with volume according to the relation $P =$

$\alpha V^{-5/3}$, where α is a constant.



Find the work done on the system, and the net amount of heat absorbed by the gas, in each of the following three transformations which take the system from state A to state B. You may assume that the transformations are quasi-static and reversible. Express your results in terms of P_A, P_B, V_A, and V_B (the constant α should not appear in your results).

a) The system is expanded from its original volume to its final volume, heat being added to maintain the pressure constant. The volume is then kept constant, and heat is extracted to reduce the pressure to its final value.

b) The volume is increased and heat is supplied to cause the pressure to decrease linearly with the volume.

c) The steps of process a) are carried out in the opposite order.

6. The (molar) specific heat of copper for temperatures lower than 1 K is given by
$$c_V = aT,$$
where $a = 0.665$ mJ/K^2. Calculate the heat required to raise the temperature of 100 grams of copper from 0.05 K to 0.5 K. The atomic weight of copper is 63.5, in units of the proton mass.

7. Assuming that the internal energy of a fluid is expressed as a function of P and T, derive the relations
$$\left(\frac{\partial U}{\partial T}\right)_P = C_P - \beta PV$$
and
$$\left(\frac{\partial U}{\partial P}\right)_T = \kappa PV - \frac{C_P - C_V}{(\partial P/\partial T)_V},$$
where β is the volume expansivity and κ the isothermal compressibility.

8. In a calorimetric experiment designed to determine the specific heat capacity of copper, 0.1 kg of the metal at 100 °C is added to 2×10^{-4} m^3 of water at 15 °C. The water is contained in a thermally insulated vessel of negligible thermal capacity. After the mixture has reached equilibrium, the temperature

is found to be 18.8 °C. If the heat capacities of copper and water are essentially constant over the range of temperatures concerned, what is the specific heat of copper? (The specific heat of water is approximately 4.2 kJ/kgK.)

Does this experiment measure c_P or c_V? Would there be much of a difference between these quantities for copper under the conditions of the experiment?

9. (Adkins, Problem 3.8)

   Below 100 K the specific heat capacity of diamond varies as the cube of temperature: $c_P = aT^3$. A small diamond, of mass 100 mg, is cooled to 77 K by immersion in liquid nitrogen. It is then dropped into a bath of liquid helium at 4.2 K, which is the boiling point of helium at atmospheric pressure. When cooling the diamond to 4.2 K, some of the helium is boiled off. The gas is collected and found to occupy a volume of 2.48×10^{-5} m^3 when measured at a temperature of 0 °C and a pressure of 1 atmosphere. What is the value of a in the formula for the specific heat? (The latent heat of vapourization of helium at 4.2 K is 21 kJ/kg.)

10. In this problem we consider a *photon gas* in thermal equilibrium at a temperature T. Such a thermodynamic system is usually called *black-body radiation.* It is known that the internal energy U of a photon gas is related to its volume V and temperature T by

$$\frac{U}{V} = cT^4,$$

where c is a constant. It is also known that the equation of state is given by

$$P = \frac{1}{3}\frac{U}{V} = \frac{c}{3}T^4,$$

so that the pressure depends only on temperature.

a) Calculate how the temperature of a photon gas varies with volume during a quasi-static, reversible, and adiabatic compression of the gas. [Hint: You should find a result of the form $T^\alpha V$ = constant, with a specific value for the constant α.]

b) What is C_V for a photon gas?

c) What is C_P for a photon gas?

CHAPTER 3

HEAT ENGINES AND THE SECOND LAW

3.1 Conversion of heat into work

The field of thermodynamics emerged in the nineteenth century as an effort to perfect the design of machines that could convert the heat generated by a burning fuel (such as coal) to useful forms of mechanical work. Such machines, an example of which is the steam engine, are called *heat engines.* Today's internal-combustion engine is another example of a heat engine: The heat liberated by the combustion of a mixture of air and gazoline is used, after having been converted to work by means of a rotating shaft, to power an automobile.

A heat engine is useful only if it can be run continuously. The process by which heat is converted to mechanical work must therefore be repeatable; and after each repetition, the engine must be able to return to its original state. A useful engine will therefore go through a succession of *cycles*, during each of which heat is converted to work, and after each of which the engine returns to its original state. Any series of transformations by which a thermodynamic system starts and ends in the same state is called a cycle, or a *cyclic transformation.* A heat engine is therefore a thermodynamic system undergoing a cyclic transformation during which a certain quantity of heat is absorbed by the system, and a certain quantity of work is done *by* the system. (Work done *by* a system is the negative of the work done *on* the system.) The thermodynamic system is often called the *working substance* of the heat engine.

A quantity of central interest in the design of heat engines is η, the engine's *thermal efficiency.* This is defined by

$$\boxed{\eta = \frac{W_{\text{ext}}}{Q_{\text{abs}}}}, \tag{3.1}$$

where W_{ext} is the work extracted from the engine during one of its cycles, while Q_{abs} is the heat absorbed during one cycle. A thermal efficiency of unity implies the complete conversion of heat into work. As we shall see, η can never attain this value, however perfect the design of the heat engine. The reason is that in the course of its cycle, the engine will always reject a certain quantity of heat without converting it to work. We will denote Q_{rej} the heat rejected by the system during one cycle. From the fact that the change in internal energy is zero at the end of a cycle, because the system returns to its original state, it is easy to see that $W_{\text{ext}} = Q_{\text{abs}} - Q_{\text{rej}}$. We therefore have an alternative expression for the thermal

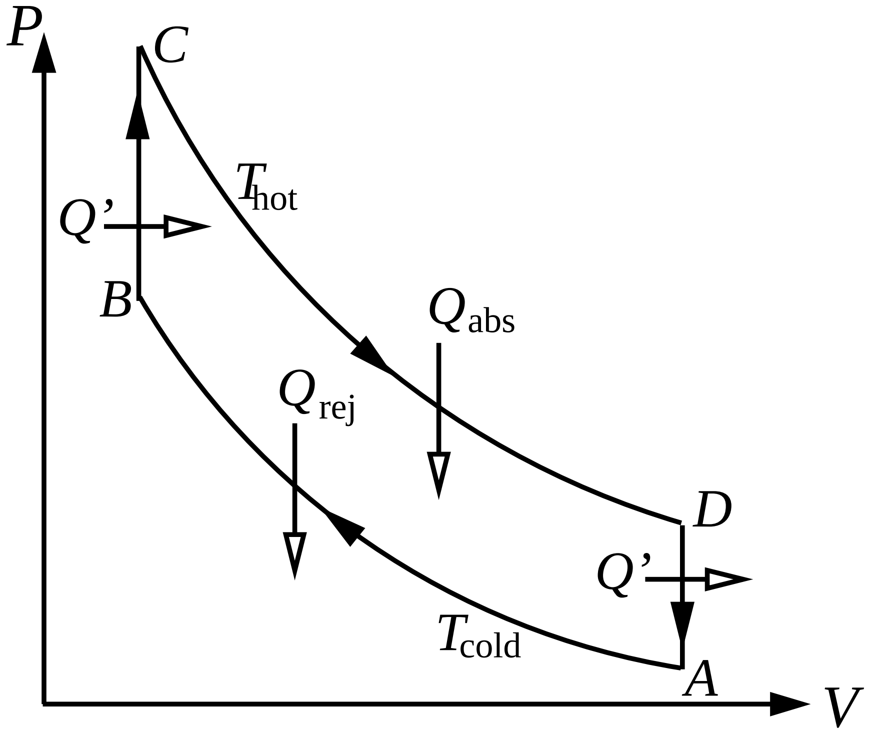


Figure 3.1: The Stirling cycle.

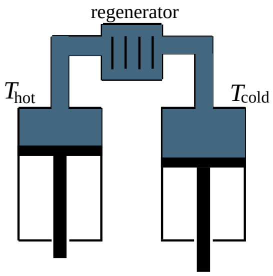
efficiency:

$$\boxed{\eta = 1 - \frac{Q_{\text{rej}}}{Q_{\text{abs}}}}\,. \tag{3.2}$$

The fact that Q_{rej} is never zero prevents any engine from having a thermal efficiency of 100%. This is the physical content of the second law of thermodynamics, whose precise formulation will be given in Sec. 5.

3.2 The Stirling engine

Among the very first heat engines was the one devised by Robert Stirling in 1816. While it was eventually out-classed by the steam and internal-combustion engines, the Stirling engine is still a useful machine by virtue of its low exhaust emissions and its high thermal efficiency. It is also simple to analyze within the framework of thermodynamics.



The Stirling engine involves two pistons, one situated to the left of the engine, the other to the right. The space between the pistons is filled with a gas, assumed to be ideal. The left-hand side of the engine is kept in thermal contact with a heat reservoir at a high temperature T_{hot}, while the right-hand side is put in contact with another reservoir at a low temperature T_{cold}. The two sides are separated by a *regenerator*, a device which supports the temperature difference in the engine, and through which the gas can flow from one side to the other. (The regenerator typically consists of a series of metal baffles with low thermal conductivity.) The gas flow is provoked by the motion of the pistons, which are attached to a shaft, allowing for the extraction of the work done by the engine.

The Stirling cycle consists of four transformations (Fig. 3). These are:

$A \rightarrow B$: While the left piston remains in the top position, the right piston moves up, compressing the cold gas at a constant temperature T_{cold}. During this transformation, (positive) work $W(A \rightarrow B)$ is done *on* the system. But because the temperature is kept constant, the transformation produces no change in the internal energy of the ideal gas. The gas therefore rejects a positive quantity of heat to the cold reservoir. This is given by $Q_{\text{rej}} = W(A \rightarrow B)$.

$B \rightarrow C$: The right piston continues to rise, but the left piston now starts to move down. As a result, the volume of the space between the two pistons stays constant. The movement of the pistons forces the gas to enter the hot side of the engine. The gas temperature therefore increases to T_{hot}. No work is done during this transformation, but the regenerator supplies a quantity Q' of heat to the gas.

$C \rightarrow D$: While the right piston stays in the top position, the left piston continues to move down, expanding the hot gas at a constant temperature T_{hot}. During this transformation, (negative) work $W(C \rightarrow D)$ is done *on* the system, but there is no change in internal energy. The gas must therefore absorb a positive quantity of heat from the hot reservoir. This is given by $Q_{\text{abs}} = -W(C \rightarrow D)$.

$D \rightarrow A$: The left piston now moves up, and the right piston starts moving down to keep the volume constant. The gas is now transferred to the cold side of the engine, and its temperature drops to T_{cold}. No work is done during this transformation, but the regenerator absorbs a quantity Q' of heat from the gas.

The net result of the complete cycle is the absorbtion by the system of a quantity Q_{abs} of heat from the hot reservoir, the rejection by the system of a quantity Q_{rej} of heat to the cold reservoir, and the performance *by* the system of a quantity W_{ext} of work. This is given by $W_{\text{ext}} = -W(A \rightarrow B) - W(C \rightarrow D) = Q_{\text{abs}} - Q_{\text{rej}}$. The heat Q' supplied and re-absorbed by the regenerator does not enter in the final analysis.

It is easy to calculate the thermal efficiency of the Stirling cycle. The (negative) work done on the gas during the expansion $C \rightarrow D$ is obtained by integrating $đW = -P\,dV$ from V_C to V_D, substituting $P(V) = nRT_{\text{hot}}/V$ inside the integral. This yields

$$Q_{\text{abs}} = -W(C \rightarrow D) = nRT_{\text{hot}} \ln(r),$$

where $r \equiv V_D/V_C$ is the *expansion ratio*. On the other hand, calculating the (positive) work done on the gas during the compression $A \rightarrow B$ gives

$$Q_{\text{rej}} = W(A \rightarrow B) = nRT_{\text{cold}} \ln(r).$$

Because $T_{\text{cold}} < T_{\text{hot}}$, the engine rejects less heat than it absorbs. The work extracted is therefore positive, and is given by

$$W_{\text{ext}} = Q_{\text{abs}} - Q_{\text{rej}} = nR(T_{\text{hot}} - T_{\text{cold}}) \ln(r).$$

Finally, the thermal efficiency is

$$\boxed{\eta = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}} \qquad \text{(Stirling engine)}}\,. \tag{3.3}$$

We see that the efficiency is necessarily smaller than 1, unless the cold reservoir is at the absolute zero of the Kelvin scale. For $T_{\text{cold}} = 20°\text{C}$ and $T_{\text{hot}} = 200°\text{C}$, the efficiency is 38%.

It should be noted that the preceding analysis applies to a somewhat idealized version of the Stirling engine. We have assumed that the gas is ideal, that the transformations are all reversible, and that the heat absorbed and rejected during the steps $B \to C$ and $D \to A$ cancel out exactly. In reality, none of these assumptions are exact, and the thermal efficiency of a real Stirling engine is somewhat *lower* than what is predicted here.

3.3 The internal-combustion engine

The operation of a gasoline engine involves a cycle consisting of six transformations. Four of these require the motion of a piston inside a cylinder; they are called *strokes*. The six transformations are:

Intake stroke: A mixture of air and gasoline vapour is drawn (at atmospheric pressure) into the cylinder by the suction of the piston.

Compression stroke: The mixture is compressed by the piston so that the pressure and temperature increase to high values.

Ignition: An electric spark causes the combustion of the hot mixture. The pressure and temperature of the combustion products increase further. The piston does not move during the ignition stage, so that the volume does not change.

Power stroke: The combustion products push the piston outward. The volume increases, while the pressure and temperature drop.

Valve exhaust: The exhaust valve opens, allowing for the evacuation of some of the combustion products. The pressure drops to one atmosphere. The piston does not move during the valve-exhaust stage.

Exhaust stroke: The piston pushes the remaining combustion products out of the cylinder. This is the end of the cycle.

In a real internal-combustion engine, the transformations described here are not quasi-static: They take the system out of equilibrium, and they cannot be given a proper thermodynamic description.

To make progress, we will consider an idealized version of the cycle, in which all the transformations are quasi-static and reversible. This is the *Otto cycle*. We will assume that the working substance in the engine's cylinder is an ideal gas. The Otto cycle consists of the following six transformations (Fig. 4):

$E \to A$**:** The gas is drawn into the cylinder, at constant atmospheric pressure P_0 and constant exterior temperature T_A. The volume varies from zero to V_A as the number of moles increases from zero to n according to the relation $P_0 V = nRT_A$. This step corresponds to the intake stroke.

$A \to B$**:** The gas is compressed adiabatically from volume V_A to volume V_B. During the compression, the pressure and temperature increase according to $PV^\gamma =$ constant and $TV^{\gamma-1} =$ constant, where $\gamma > 1$ is a constant. The relation $T_A {V_A}^{\gamma-1} = T_B {V_B}^{\gamma-1}$ determines the temperature at B. This step corresponds to the compression stroke.

$B \to C$**:** The pressure and temperature are raised at constant volume. The final temperature is T_C, and a quantity Q_{abs} of heat is absorbed by the gas. This step corresponds to the ignition stage.

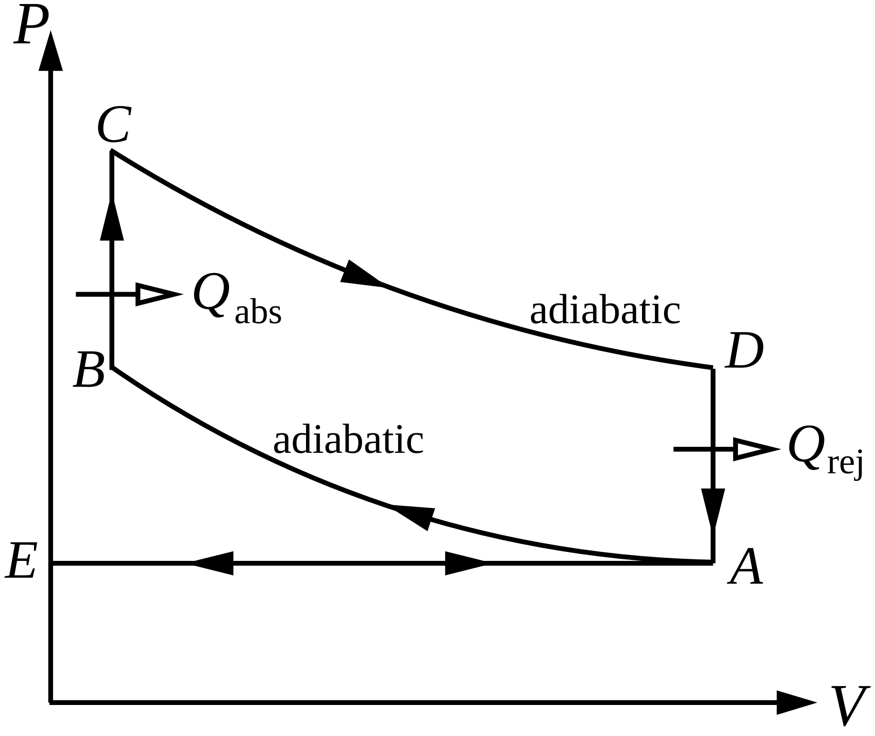


Figure 3.2: The Otto cycle.

$C \to D$**:** The gas is expanded adiabatically from volume V_B back to volume V_A. The final temperature is T_D, determined by the equation $T_C {V_B}^{\gamma-1} = T_D {V_A}^{\gamma-1}$. This step corresponds to the power stroke.

$D \to A$**:** The pressure and temperature are lowered at constant volume. The final temperature is T_A, and a quantity Q_{rej} of heat is rejected by the gas. This step corresponds to the valve-exhaust stage.

$A \to E$**:** The gas is expelled from the cylinder, at constant atmospheric pressure and constant exterior temperature. The volume varies from V_A to zero while the number of moles decreases from n to zero. This step corresponds to the exhaust stroke.

We now use this information to calculate the thermal efficiency of the Otto cycle. The transformations $E \to A$ and $A \to E$ cancel each other out, so there is no need to consider them in detail. We calculate Q_{abs} and Q_{rej} under the assumption that C_V, the heat capacity of the ideal gas, does not vary with temperature. This yields

$$Q_{\text{abs}} = C_V(T_C - T_B), \qquad Q_{\text{rej}} = C_V(T_D - T_A),$$

and the thermal efficiency is given by

$$\eta = 1 - \frac{Q_{\text{rej}}}{Q_{\text{abs}}} = 1 - \frac{T_D - T_A}{T_C - T_B}.$$

This ratio of temperature differences can be related to $r \equiv V_A/V_B$, the expansion ratio. For this we use the adiabatic relations

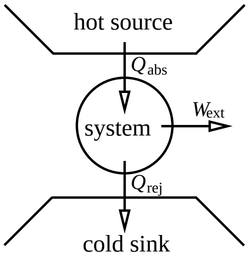
$$T_A {V_A}^{\gamma-1} = T_B {V_B}^{\gamma-1}, \qquad T_D {V_A}^{\gamma-1} = T_C {V_B}^{\gamma-1}.$$

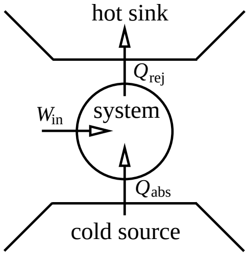
Subtracting the first equation from the second gives $(T_D - T_A){V_A}^{\gamma-1} = (T_C - T_B){V_B}^{\gamma-1}$, and we arrive at $\eta = 1 - (V_B/V_A)^{\gamma-1}$, or

$$\boxed{\eta = 1 - \frac{1}{r^{\gamma-1}} \qquad \text{(internal-combustion engine)}}\,. \tag{3.4}$$

We see that the efficiency is necessarily smaller than 1, unless the expansion ratio is infinite. For a typical value of $r = 9$ and with $\gamma = 1.5$, we have $\eta = 67\%$. This is somewhat higher than what can be achieved with real internal-combustion engines (from 25% to 40%).

3.4 The refrigerator





We have seen that a heat engine is a device by which a thermodynamic system — the working substance — is taken through a cycle in such a direction that (i) a quantity of heat is absorbed from a hot source, (ii) a smaller quantity of heat is rejected to a cold sink, and (iii) a positive quantity of work is done by the system. A *refrigerator* is a device that runs the cycle in the opposite direction, such that (i) a quantity of heat is extracted from a cold source, (ii) a larger quantity of heat is rejected to a hot sink, (iii) and a positive quantity of work is done on the thermodynamic system. In this case the system is called the *refrigerant*.

We will denote Q_{abs} the heat absorbed by the refrigerant during one cycle, Q_{rej} the heat rejected during one cycle, and W_{in} the work done on (injected in) the system during one cycle. A measure of the performance of the refrigerator is the ratio of heat absorbed to work injected. This ratio will be called the *coefficient of performance*, and will be denoted by ω. We therefore have

$$\boxed{\omega = \frac{Q_{\text{abs}}}{W_{\text{in}}}}\,. \tag{3.5}$$

The first law gives the following relation among the heats absorbed and rejected, and the work injected: $Q_{\text{rej}} = Q_{\text{abs}} + W_{\text{in}}$. This means that the coefficient of performance can also be expressed as

$$\boxed{\omega = \frac{Q_{\text{abs}}}{Q_{\text{rej}} - Q_{\text{abs}}}}\,. \tag{3.6}$$

This coefficient is always finite, because Q_{rej} is always larger than Q_{abs}, implying that positive work is done on the system. The coefficient of performance is larger than unity when $2Q_{\text{abs}} > Q_{\text{rej}}$.

As an example, let us calculate ω for the Stirling refrigerator, which works by running the Stirling cycle in the reversed direction. We assume that the refrigerent consists of an ideal gas. As in Sec. 2, there are four transformations to consider (Fig. 5):

$A \to B$**:** The gas is compressed at a constant temperature T_{hot}. Because the internal energy of an ideal gas does not change during an isothermal expansion, $Q_{\text{rej}} = W(A \to B) = nRT_{\text{hot}} \ln(r)$, where $r \equiv V_A/V_B$ is the expansion ratio.

$B \to C$**:** The gas temperature is lowered at constant volume. The gas loses a quantity Q' of heat.

$C \to D$**:** The gas is expanded at a constant temperature T_{cold}. The amount of heat absorbed is $Q_{\text{abs}} = -W(C \to D) = nRT_{\text{cold}} \ln(r)$.

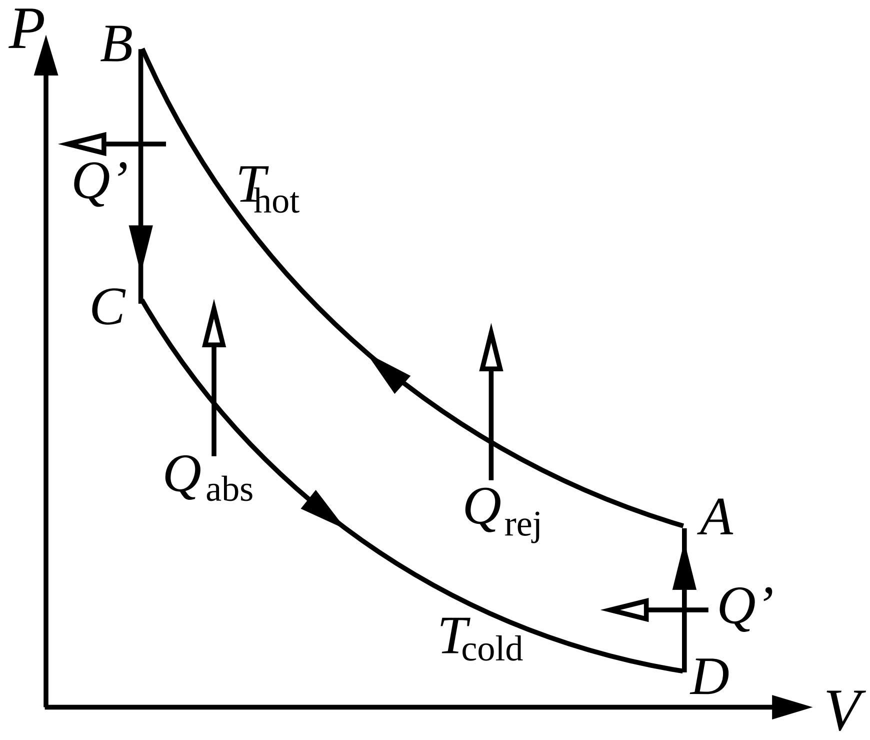


Figure 3.3: The reversed Stirling cycle.

$D \to A$**:** The gas temperature is raised at constant volume. The gas regains the quantity Q' of heat that was lost in the transformation $B \to C$.

Gathering the results, the coefficient of performance of the Stirling refrigerator is given by

$$\omega = \frac{1}{Q_{\text{rej}}/Q_{\text{abs}} - 1} = \frac{1}{T_{\text{hot}}/T_{\text{cold}} - 1} = \frac{T_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}}.$$

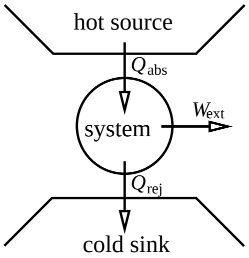
For $T_{\text{cold}} = 5°\text{C}$ and $T_{\text{hot}} = 20°\text{C}$, $\omega = 18.5$. The work required to run the refrigerator during one cycle is given by

$$W_{\text{in}} = Q_{\text{rej}} - Q_{\text{abs}} = nR(T_{\text{hot}} - T_{\text{cold}})\ln(r).$$

This is always larger than zero, so long as a temperature difference is maintained between the two reservoirs.

3.5 The second law

3.5.1 The Kelvin statement

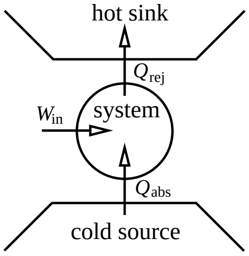


At the simplest level, all heat engines can be described as follows: The working substance undergoes a cycle during which (i) a quantity Q_{abs} of heat is extracted from a hot source, (ii) a quantity Q_{rej} of heat is delivered to a cold sink, and (iii) a quantity W_{ext} of work is done on the surroundings. We have learned from the previous examples that W_{ext} is always *smaller* than Q_{abs}, so that the thermal efficiency is always smaller than unity. This statement is true quite generally: No conceivable heat engine, however perfect, operates with a thermal efficiency of unity. This fundamental experimental fact is the physical content of the *Kelvin statement* of the second law of thermodynamics, whose precise formulation is:

> No transformation is possible whose *sole* result is the absorbtion of heat from a source and the complete conversion of this heat into work.

In this statement, the word “sole” is crucial: Transformations do exist which convert heat completely into work. An example is the isothermal expansion of an ideal gas. This does not violate the second law, because conversion of heat into work is not the *sole* result of the transformation: the volume of the gas is also affected.

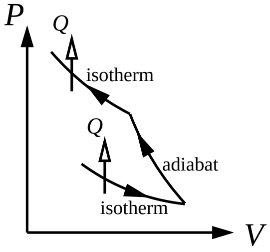
3.5.2 The Clausius statement



At the simplest level, all refrigerators can be described as follows: The refrigerant undergoes a cycle during which (i) a quantity Q_{abs} of heat is extracted from a cold source, (ii) a quantity Q_{rej} of heat is delivered to a hot sink, and (iii) a quantity W_{in} of work is done on the system. We have found in the previous example that Q_{rej} is always *larger* than Q_{abs}, so that (positive) work is required to run the cycle. This statement is true quite generally: No conceivable refrigerator, however perfect, operates with an infinite coefficient of performance. This fundamental experimental fact is the physical content of the *Clausius statement* of the second law of thermodynamics, whose precise formulation is:

> No transformation is possible whose *sole* result is the transfer of heat from a cooler to a hotter body.

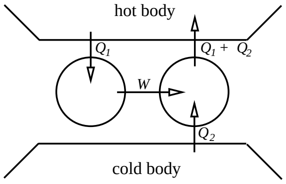
In this statement, the word “sole” is also crucial: Transformations do exist which transfer heat from a cold body to a hot body. Such transformations, however, invariably involve additional changes in the system. As an example, consider the following series of transformations on an ideal gas. First, the gas is expanded at a constant temperature T_{cold}, thereby extracting a quantity Q of heat from a cold source. Second, the gas is transferred to a thermally insulated chamber, and compressed so that its temperature increases to the value T_{hot}. Third, the gas is transferred out of the thermally insulated chamber, and compressed some more at a constant temperature T_{hot}, until the same quantity Q of heat is delivered to the hot sink. This series of transformations does not violate the second law, because in the end, the ideal gas does not return to its initial state.



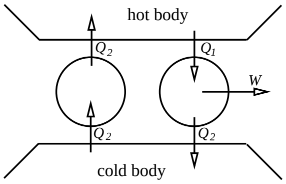
3.5.3 *Equivalence of the two statements*

Although they appear to be quite disconnected, the Kelvin and Clausius statements are in fact entirely equivalent: there is only *one* second law of thermodynamics. To prove this we will show that if either one of the statements is false, then the other one must also be false.

We begin by showing that a violation of the Kelvin statement implies a violation of the Clausius statement. We consider a heat engine that rejects no heat to the cold body, thereby violating the Kelvin statement. Suppose that this engine extracts a quantity Q_1 of heat from the hot body. Because there is no heat rejected, the work delivered by the engine is $W = Q_1$. Suppose now that this work is used to drive a refrigerator that operates between the same two bodies. The refrigerator extracts a quantity Q_2 of heat from the cold body, and it rejects a quantity $Q_2 + W = Q_2 + Q_1$ of heat to the hot body. This refrigerator does not violate the second law, but the composite system, heat engine plus refrigerator, does. The reason is that the net result of operating the composite system is to extract a quantity Q_2 of heat from the cold body and to deliver it to the hot body. The composite system therefore violates the Clausius statement of the second law. This proves our assertion, that violating the Kelvin statement produces a violation of the Clausius statement.



We now prove that a violation of the Clausius statement implies a violation of the Kelvin statement. We consider a refrigerator that requires no work to transfer a quantity Q_2 of heat from a cold body to a hot body, thereby violating the Clausius statement. Suppose that a heat engine is operating between the same two bodies. We arrange for this engine to reject a quantity Q_2 of heat to the cold body. In order to do so, the engine must absorb a larger quantity Q_1 of heat from the hot body, and it will do a quantity $W = Q_1 - Q_2$ of work on the surroundings. This heat engine does not violate the second law, but the composite system, refrigerator plus heat engine, does. The reason is that the net result of operating the composite system is to extract a quantity $Q_1 - Q_2$ of heat from the hot body and to convert it entirely into work. The composite system therefore violates the Kelvin statement of the second law. This proves our assertion, that violating the Clausius statement produces a violation of the Kelvin statement.



We may therefore conclude that indeed, the Kelvin and Clausius statements of the second law are equivalent. Which statement is used in a particular application is a matter of convenience.

3.6 Carnot cycle

The *Carnot cycle* is particularly important for the logical development of thermodynamics. When operated as a heat engine, the Carnot cycle consists of a sequence of four transformations. For the purpose of the following discussion, we will assume that the working substance is a fluid (not necessarily an ideal gas) with thermodynamic variables P and V. (This assumption is not necessary: Carnot engines can be operated with all sorts of working substances.)

The transformations are (Fig. 6):

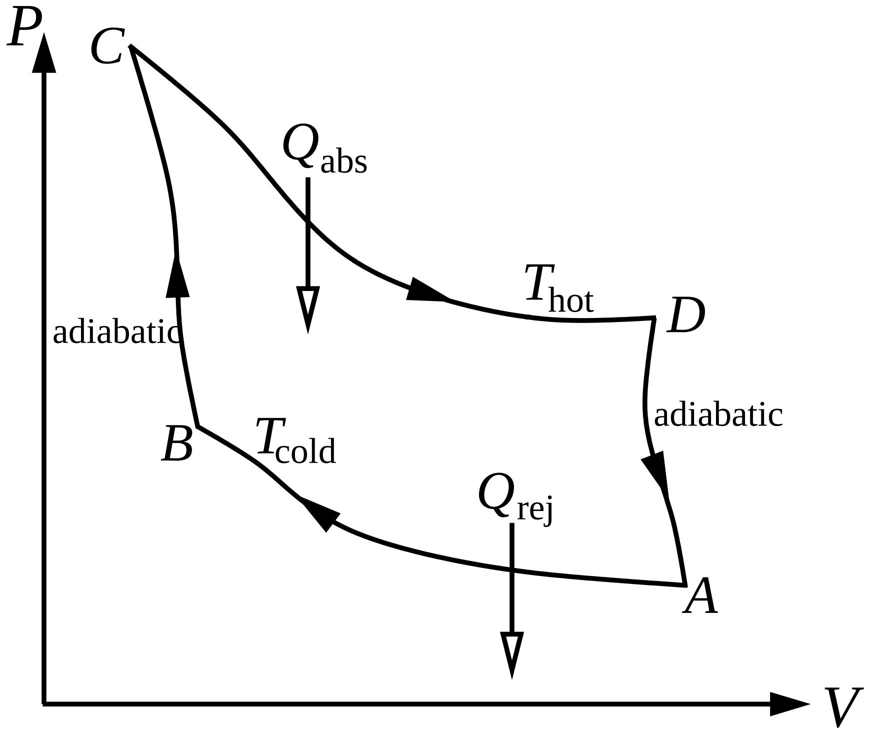


Figure 3.4: The Carnot cycle for an arbitrary fluid.

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

$B \to C$**:** The temperature is increased reversibly from T_{cold} to T_{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_{hot}. A quantity Q_{abs} of heat is absorbed from the hot reservoir.

$D \to A$**:** The temperature is lowered reversibly from T_{hot} back to T_{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_{hot}, the other of temperature T_{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.

2. The thermal efficiency of all Carnot engines operating between a hot reservoir of temperature T_{hot} and a cold reservoir of temperature T_{cold} is given by

   $$\eta_{\text{Carnot}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}.$$

   It depends *only* on the temperatures of the two heat reservoirs.

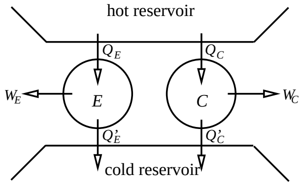
3. If a generic heat engine is operating between two reservoirs of temperatures T_{hot} and T_{cold}, respectively, but is not reversible, then its thermal efficiency will be less than $1 - T_{\text{cold}}/T_{\text{hot}}$, the Carnot limit.

4. If, in the course of its operation, a generic heat engine reaches a maximum temperature of T_{max} and a minumum temperature of T_{min}, then its thermal efficiency can be no higher than $1 - T_{\text{min}}/T_{\text{max}}$, the Carnot limit.

The first two statements are remarkable: they tell us that no matter how different two Carnot engines might be in terms of their design, their thermal efficiencies are guaranteed to be the same, so long as the engines operate between the same two temperatures. And this thermal efficiency can be expressed as a simple function of the two temperatures involved. (Since η_{Carnot} cannot depend on the details of the engine, it can only be a function of the two temperatures.) The last two statements are also remarkable: they tell us that given two extremes of temperature, a Carnot engine operating between these two temperatures is guaranteed to yield the highest thermal efficiency.

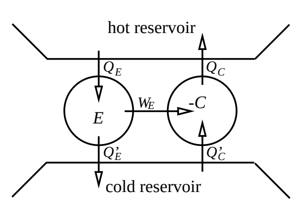
These statements are truly powerful, and they make the Carnot cycle one of the most useful tools of thermodynamics. We will prove statements #1 and #3 presently. The proof of statement #2 will be given in the next section. The proof of statement #4, however, will only be presented in the next chapter.

We will begin by showing that if a generic heat engine E operates between a hot reservoir of temperature T_{hot} and a cold reservoir of temperature T_{cold}, then its thermal efficiency η_E can be no higher than η_C, the efficiency of a Carnot engine C operating between the same two reservoirs. Next, we will see that if E is not reversible, then $\eta_E < \eta_C$, which is just statement #3. If, however, E is reversible, then we will see that $\eta_E = \eta_C$. In this case E is by definition also a Carnot engine, and we have obtained statement #1. We will prove all this by showing that if a generic engine E exists such that $\eta_E > \eta_C$, then a violation of the second law must occur.



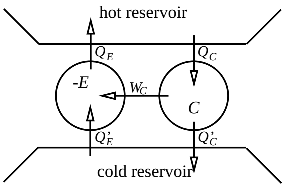
Let E absorb a quantity Q_E of heat from the hot reservoir and reject a quantity Q'_E of heat to the cold reservoir. The work done by E is then $W_E = Q_E - Q'_E$. On the other hand, let C absorb a quantity Q_C of heat from the hot reservoir and reject a quantity Q'_C of heat to the cold reservoir. The work done by C is then $W_C = Q_C - Q'_C$. If E's thermal efficiency is larger than C's, then

$$\frac{W_E}{Q_E} > \frac{W_C}{Q_C}.$$



Suppose now that the direction of the Carnot cycle is reversed, so that $-C$ absorbs a quantity Q'_C of heat from the cold reservoir, rejects a quantity Q_C of heat to the hot reservoir, and receives a quantity W_C of work. The equation $Q_C = Q'_C + W_C$ still holds. Suppose also that we design the Carnot engine so that $W_C = W_E$: $-C$ receives just as much work as E produces. By combining E and $-C$ we form a composite refrigerator that requires no work but extracts a quantity $Q'_C - Q'_E$ of heat from a cold source and delivers a quantity $Q_C - Q_E$ of heat to a hot sink. Equality between $W_E = Q_E - Q'_E$ and $W_C = Q_C - Q'_C$ ensures that the quantities of heat absorbed and delivered are equal.

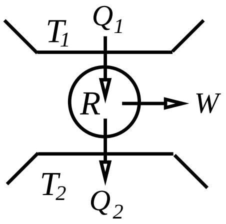
If $Q_C - Q_E$ is positive, then we have a violation of the Clausius statement of the second law. That we do, in fact, have a positive quantity of heat transferred from a cold source to a hot sink, follows from the assumption that $\eta_E > \eta_C$. Indeed, with $W_C = W_E$ this inequality gives $Q_C > Q_E$, and $Q_C - Q_E > 0$. The assumption that $\eta_E > \eta_C$ is therefore incompatible with the second law of thermodynamics. We must conclude that $\eta_E \leq \eta_C$. Thus, E cannot be more efficient than the Carnot engine. What remains to be shown is that $\eta_E < \eta_C$ if E is irreversible, while $\eta_E = \eta_C$ if E is reversible.



Let us assume that E is reversible (so that it is also a Carnot engine), and let us consider a new composite system formed by operating C in the forward direction and E in the reversed direction. If we arrange for $W_E = W_C \equiv W$, then we again have a refrigerator that requires no work, but extracts a quantity $Q'_E - Q'_C = Q_E - Q_C$ from a cold source and delivers it to a hot sink. To avoid a violation of the second law, we must insist that $Q_E - Q_C \leq 0$, which implies $W/Q_E \geq W/Q_C$, or $\eta_E \geq \eta_C$. But this result must be compatible with our previous conclusion, that $\eta_E \leq \eta_C$. The only way out is equality: Under the assumption that E is a reversible engine, it must be true that $\eta_E = \eta_C$. In other words: All Carnot engines operating between the same two reservoirs have the same thermal efficiency. This is statement #1.

We have seen that equality between η_E and η_C occurs if and only if E is reversible. Otherwise, if E is not reversible, we must have $\eta_E < \eta_C$. An irreversible engine operating between two heat reservoirs must therefore be less efficient than a Carnot engine operating between the same reservoirs. This is statement #3.

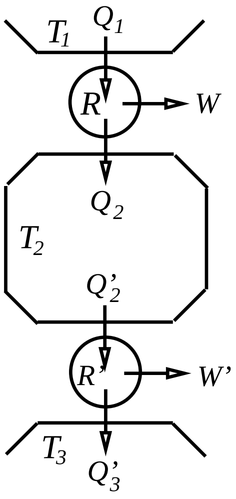
3.7 Thermodynamic temperature



We have just found that the thermal efficiency of all Carnot engines operating between the same two heat revervoirs is *universal*: η is the same for *all* such heat engines. Thus, η does not depend on the specific design of the engine. Instead, it can only depend on the properties of the reservoirs. Because the only relevant property is temperature, it must be that η is a function of just two variables, the temperatures of both reservoirs. It follows that if Q_1 denotes the heat absorbed from a hot reservoir of temperature T_1, and Q_2 is the heat rejected to a cold reservoir of temperature T_2, then

$$\frac{Q_1}{Q_2} = f(T_1, T_2),$$

where f is a universal function, the same for all Carnot engines.



We can obtain some information about the form of f by forming a composite engine out of two Carnot engines, one (R) operating between reservoirs at temperatures T_1 and T_2, the other (R') operating between reservoirs at temperatures T_2 and T_3. We assume $T_1 > T_2 > T_3$. The first engine absorbs a quantity Q_1 of heat from the reservoir at T_1, and rejects a quantity Q_2 of heat to the revervoir at T_2; for this engine, we have $Q_1/Q_2 = f(T_1, T_2)$. The second engine absorbs a quantity Q'_2 of heat from the reservoir at T_2, and rejects a quantity Q'_3 of heat to the revervoir at T_3; for this engine, we have $Q'_2/Q'_3 = f(T_2, T_3)$. If we design our engines so that R' absorbs the same quantity of heat as R rejects, then $Q'_2 = Q_2$, and we have $Q_1/Q'_3 = f(T_1, T_2)f(T_2, T_3)$. We now consider the composite engine, operating between the reservoirs at T_1 and T_3, absorbing a quantity Q_1 of heat from the hot reservoir, and rejecting a quantity Q'_3 of heat to the cold reservoir. Because the composite engine is also a Carnot engine (it is reversible and it operates between the reservoirs at T_1 and T_3), we have $Q_1/Q'_3 = f(T_1, T_3)$. This means that f must satisfy the functional relation

$$f(T_1, T_3) = f(T_1, T_2)f(T_2, T_3).$$

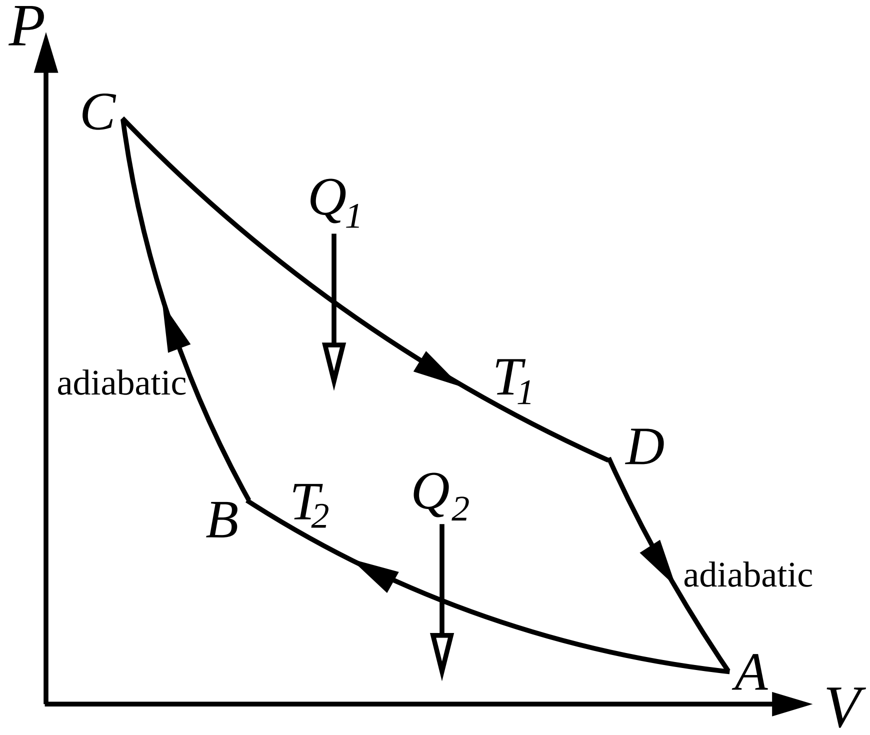


Figure 3.5: The Carnot cycle for an ideal gas.

The only possible solution is $f(T_1, T_2) = \Theta(T_1)/\Theta(T_2)$, where $\Theta(T)$ is a *universal* function of temperature. This function is called the *thermodynamic temperature.*

To summarize, the ratio of heat absorbed to heat rejected by any Carnot engine operating between the same two reservoirs is given by

$$\boxed{\frac{Q_1}{Q_2} = \frac{\Theta_1}{\Theta_2}}\,, \tag{3.7}$$

where $\Theta_1 \equiv \Theta(T_1)$ and $\Theta_2 \equiv \Theta(T_2)$ are the thermodynamic temperatures of the hot and cold reservoirs, respectively. The great generality of this result is most remarkable.

We still have to determine the relation between Θ and T. Because this relation is universal, it is the same for all Carnot engines operating between the same two reservoirs. It therefore suffices to consider one *particular* type of Carnot engine. We shall choose a Carnot engine whose working substance is an ideal gas. Calculating the thermal efficiency for this engine will allow us to deduce the form of the relation $\Theta(T)$.

The four stages of the Carnot cycle are (Fig. 7):

$A \to B$**:** The ideal gas is compressed from a volume V_A to a volume V_B, at a constant temperature T_2. The work done on the gas is $W(A \to B) = nRT_2 \ln(V_A/V_B)$. This is equal to Q_2, the heat rejected to the cold reservoir.

$B \to C$**:** The gas is compressed adiabatically to a smaller volume V_C. During this transformation, the temperature increases from T_2 to T_1 according to the relation $TV^{\gamma-1} = \text{constant}$, which implies $T_1/T_2 = (V_B/V_C)^{\gamma-1}$.

$C \to D$: 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 relation, 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?

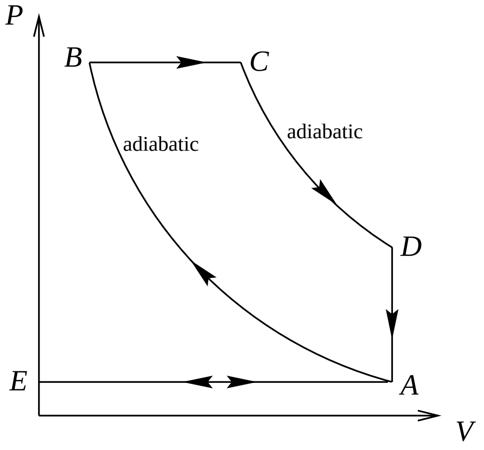
We do not yet have the tools to prove that $1 - T_2/T_1$ is the maximum efficiency that can be achieved by a generic engine working between these two extremes of temperature. We will therefore defer the proof of statement #4 to the next chapter.

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

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

where $\gamma = C_P/C_V$. What is the thermal efficiency for $V_A/V_C = 5$, $V_A/V_B = 15$, and $\gamma = 1.5$? How does this compare with the Carnot limit if $T_A = 300$ K?



2. (Zemansky and Dittman, Problem 6.5)

A vessel contains 10^{-3} m^3 of helium gas at 3 K and 10^3 Pa. Take the zero of internal energy of helium to be at this point. We assume that helium behaves as an ideal, monoatomic gas.

a) The temperature is raised at constant volume to 300 K. How much heat is absorbed by the gas during this transformation? What is the internal energy of helium in this state?

b) The gas is now expanded adiabatically to a temperature of 3 K. How much work is done on the gas during this transformation? What is the new value for the internal energy? Is the second law of thermodynamics violated in these two transformations? (Explain.)

c) The gas is now compressed isothermally to its original volume. What is the work done on, and heat absorbed by, the gas during this transformation?

d) Plot the cycle on a P-V diagram, and calculate its thermal efficiency.

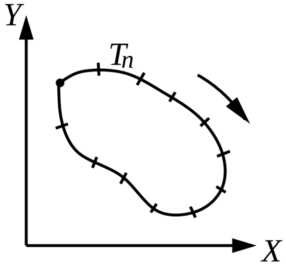
Chapter 4
Entropy and the third law

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

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

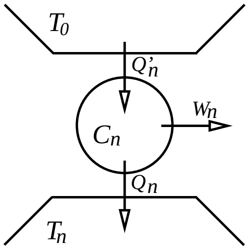
if the transformation is reversible. Notice that this last equation is satisfied by the Carnot cycle, for which $Q_1/T_1 = |Q_2|/T_2$, with Q_1 denoting the heat entering the system, while $|Q_2| = -Q_2$ is the heat leaving the system.

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,

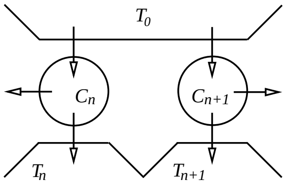
$$\boxed{\oint \frac{đQ}{T} \leq 0}\,, \tag{4.1}$$

with the equality sign holding for a reversible cycle only.



We will prove the theorem in its discrete formulation. We begin by focusing our attention on the nth step of the transformation, during which the system is at a temperature T_n and absorbs a quantity Q_n of heat. We may imagine that this heat is provided by a Carnot engine C_n operating between the temperatures T_0 and T_n, where $T_0 > T_n$. This Carnot engine absorbs a quantity Q'_n of heat from the reservoir at T_0, and performs a quantity $W_n = Q'_n - Q_n$ of work on its surroundings. We know that $Q'_n/Q_n = T_0/T_n$. We repeat this construction for each step of the transformation, thereby introducing a Carnot engine for all N steps. We assume that all these Carnot engines draw heat from the same revervoir at T_0, which we assume is the largest temperature at hand ($T_0 > T_n$ for all n). The total amount of heat absorbed by all the Carnot engines is

$$Q' \equiv \sum_{n=1}^{N} Q'_n = T_0 \sum_{n=1}^{N} \frac{Q_n}{T_n}.$$



We now form a composite heat engine by combining our original thermodynamic system — the one undergoing the cycle — with all these Carnot engines. We want to calculate the total amount of work done by the composite engine. This will be equal to the sum of the works extracted from the Carnot engines, added to the work done by the system itself during the cycle. The total work done by all the Carnot engines is given by

$$W_C \equiv \sum_{n=1}^{N} W_n = \sum_{n=1}^{N} (Q'_n - Q_n) = Q' - Q,$$

where Q' was calculated above, and where $Q = \sum_{n=1}^{N} Q_n$ is the net heat absorbed by the system during its cycle. Because $\Delta U = 0$ at the end of the cyclic transformation, $Q = W$, where W is the work done *by* the system during the cycle. The net work done by the composite engine is therefore

$$W_{\mathrm{net}} = W_C + W = (Q' - Q) + Q = Q'.$$

In other words, the composite engine absorbs a quantity Q' of heat from the reservoir at T_0 and converts it entirely into work. Unless $Q' \leq 0$, we have a violation of the second law. We must therefore conclude that

$$\frac{Q'}{T_0} = \sum_{n=1}^{N} \frac{Q_n}{T_n} \leq 0$$

for any cyclic transformation. This establishes the first part of Clausius' theorem.

We still have to prove that the equality sign holds for reversible transformations only. This is easy. If the transformation is reversible, then the cycle can be operated in the opposite direction, and the relation $\sum_{n=1}^{N} Q_n/T_n \leq 0$ would apply to the reversed cycle. However, reversing the cycle amounts to changing the sign of Q_n, $Q_n \to -Q_n$, in the *forward* cycle. Going through the same steps as before would then reveal the relation $\sum_{n=1}^{N} Q_n/T_n \geq 0$. Because both relations must be true, it follows that

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

for a reversible cycle. This concludes the proof of Clausius' theorem.

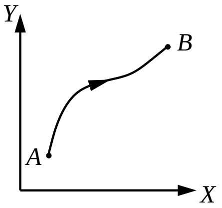
4.2 Entropy

4.2.1 Definition

The entropy function S is defined by the infinitesimal relation

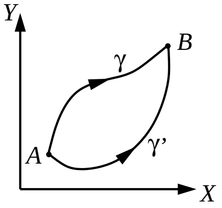
$$\boxed{dS = \frac{\text{đ}Q_{\text{rev}}}{T}}\ , \tag{4.2}$$

where dS is the differential of entropy, $\text{đ}Q_{\text{rev}}$ 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



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

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 $\text{đ}Q_{\text{rev}}/T$ 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 Y-X 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

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

Reversing the direction of $-\gamma'$ yields

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

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 $dS = \text{đ}Q_{\text{rev}}/T$ 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 $\text{đ}Q_{\text{rev}}/T$ 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

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

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

4.2.2 Example: System in thermal contact with a reservoir

Let us imagine that heat is added reversibly to a system with constant heat capacity C, so that its temperature increases from T_A to T_B. Using the relation $đQ = C\,dT$, we find that the change in the system's entropy is given by

$$\Delta S_{\text{system}} = C\int_{T_A}^{T_B}\frac{dT}{T} = C\ln\biggl(\frac{T_B}{T_A}\biggr).$$

We see that the system's entropy *increases* during this transformation.

Let us now suppose that the heat is extracted from a revervoir, whose temperature T_B is not affected by the transformation. (Recall that a reservoir is a thermodynamic system so large that its heat capacity is essentially infinite.) Using $dS = đQ/T_B$, we find that the entropy change in the reservoir is given by

$$\Delta S_{\text{reservoir}} = \frac{Q_{\text{reservoir}}}{T_B},$$

where $Q_{\text{reservoir}}$ is the heat absorbed *by* the reservoir during the transformation. This is minus the heat transferred to the system, so that $Q_{\text{reservoir}} = -C(T_B - T_A)$. Thus,

$$\Delta S_{\text{reservoir}} = -C\biggl(1 - \frac{T_A}{T_B}\biggr),$$

and we see that the reservoir's entropy *decreases* during this transformation.

The *overall* change in entropy is the sum of the individual changes:

$$\begin{aligned}\Delta S &= \Delta S_{\text{system}} + \Delta S_{\text{reservoir}}\\ &= C\biggl[\ln\biggl(\frac{T_B}{T_A}\biggr) - 1 + \frac{T_A}{T_B}\biggr];\end{aligned}$$

just like the internal energy, the entropy is an additive quantity. Thus, the overall change in entropy caused by the thermal interaction of a system of constant heat capacity C with a heat reservoir is given by

$$\boxed{\Delta S = C(x - 1 - \ln x), \qquad x = \frac{T_A}{T_B}}\,, \tag{4.4}$$

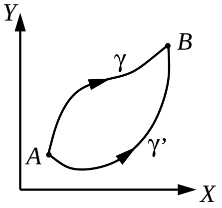
where T_A is the system's original temperature, and T_B its final temperature, equal to that of the reservoir. This result is valid both for $x < 1$ and $x > 1$; both increases and decreases of temperature are allowed.

We may prove that $\Delta S \geq 0$, so that the overall change in entropy is always an *increase*, for all possible values of x in the interval between 0 and ∞. (The case $x = 1$ corresponds to no thermal interaction at all, and only in this case is ΔS equal to zero.) Consider the function $f(x) = x - 1 - \ln x$, to which ΔS is proportional. We may show that this function has a single minimum at $x = 1$, so that $f(x) \geq f(1) = 0$, thereby proving the statement. The steps are simple: The function possesses an extremum when $f'(x) = 0$, where a prime denotes differentiation; the only solution is $x = 1$, and this extremum is in fact a minimum because $f''(1) = 1 > 0$.

4.2.3 Principle of entropy increase

The result that the entropy of an isolated system can never decrease is a very general one; it is not limited to the example considered above, in which the isolated system was the combination system + reservoir.

To prove this, we must first generalize Eq. (4.3) to allow for irreversible transformations between A and B. Suppose that two transformations link the same two



states A and B. The first, γ, is reversible, while the second, γ', is irreversible. For the (irreversible) cyclic transformation $\gamma' + (-\gamma)$, the Clausius theorem implies

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

with the equality sign holding if and only if γ' is, after all, reversible. The second integral is equal to $S(A) - S(B)$, and we obtain

$$\boxed{S(B) - S(A) \geq \int_A^B \frac{đQ}{T}}\,, \tag{4.5}$$

where the strict inequality ($>$) holds if the transformation from A to B is irreversible, while the equality ($=$) holds if the transformation is reversible.

Equation (4.5) means that if the transformation between A and B is irreversible, then the change in entropy is *not* equal to the integral of $đQ/T$ along the transformation, but is *larger* than this. It is therefore necessary to find a *reversible* transformation between A and B to calculate the entropy change; otherwise the integral of $đQ/T$ gives only a *lower bound* on the change in entropy. The differential form of Eq. (4.5) is

$$dS \geq \frac{đQ}{T},$$

with the "$>$" sign applying to irreversible transformations, and the "$=$" sign applying to reversible transformations; in this case it is better to write $dS = đQ_{\text{rev}}/T$, as we have done previously.

The principle of entropy increase follows at once from Eq. (4.5). If the system is thermally isolated, then it cannot exchange heat with its surroundings, and $đQ = 0$. It follows that $S(B) \geq S(A)$: the entropy of the final state must be larger than the entropy of the initial state, unless the transformation is reversible, in which case the entropy does not change. Thus:

> The entropy of a thermally isolated system can never decrease: It always increases during an irreversible transformation, and it always stays constant during a reversible transformation.

It is very important to understand that the system must be *isolated* for these statements to be true. The entropy of a thermally interacting system can decrease if the system is losing heat to its surroundings.

4.3 Reversible changes of temperature

The principle of entropy increase gives us a useful tool to determine whether or not a specified transformation on a isolated system is reversible. If the transformation alters the value of the entropy, then it must be irreversible.

As an example, an isothermal exchange of heat between the two parts of a composite system (assumed isolated) is reversible, because the entropy Q/T lost by one part of the system is gained by the other part, and the overall change in entropy is zero. A concrete realization of this example is the isothermal compression of an ideal gas in thermal contact with a heat reservoir at a temperature T: During the compression, the gas loses a quantity Q of heat to the reservoir, and therefore loses a quantity Q/T of entropy which is gained by the reservoir; there is no overall change in the entropy of the composite system gas + reservoir.

On the other hand, when a transfer of heat is accompanied by a change in temperature, the transformation is usually irreversible. For example, imagine that a system A, initially at a temperature T_A, is put in thermal contact with another system B, initially at a temperature $T_B < T_A$. As a result of the thermal interaction, heat flows from A to B and the systems achieves thermal equilibrium at a new temperature T_C. It is clear that this transformation is irreversible, because once the temperatures have equalized, the systems cannot be returned to their original temperatures (unless additional changes are involved). This is confirmed by the fact that the entropy increases during the transformation. To verify this statement, we will assume for simplicity that A and B have the same heat capacity C. The heat leaving A is given by $Q = C(T_A - T_C) > 0$, and the heat entering B is $Q = C(T_C - T_B) > 0$. Since both results must agree, we have $T_C = \frac{1}{2}(T_A + T_B)$: the final temperature is just the average of the original temperatures. The entropy change in A is given by

$$\Delta S_A = \int_{T_A}^{T_C} \frac{đQ}{T} = C \int_{T_A}^{T_C} \frac{dT}{T} = C \ln\biggl(\frac{T_C}{T_A}\biggr) < 0,$$

while the entropy change in B is

$$\Delta S_B = \int_{T_B}^{T_C} \frac{đQ}{T} = C \int_{T_B}^{T_C} \frac{dT}{T} = C \ln\biggl(\frac{T_C}{T_B}\biggr) > 0.$$

The overall change in entropy is then

$$\Delta S = \Delta S_A + \Delta S_B = C \ln\biggl(\frac{{T_C}^2}{T_A T_B}\biggr).$$

It is easy to show that this is always greater than zero: The entropy increases during the transformation, and we conclude that it is indeed irreversible.

A similar example was considered in Sec. 2b, where we calculated the overall change in entropy resulting from the thermal interaction of a system with a heat reservoir. If the reservoir is at a temperature T_B and the system's initial temperature is T_A, then

$$\Delta S = C(x - 1 - \ln x),$$

where C is the system's heat capacity, and $x \equiv T_A/T_B$. As we have seen, this equation implies that $\Delta S > 0$ unless $x = 1$, and we are again dealing with an irreversible transformation. This confirms the general observation made earlier, that when a transfer of heat is accompanied by a change of temperature, the transformation is usually irreversible.

This raises a question. If bringing two systems in thermal contact usually results in an irreversible transfer of heat, how can the temperature of a thermodynamic system be altered *reversibly*? After all, we have assumed that such a reversible increase of temperature was possible when we calculated ΔS in Sec. 2b. We must now identify how this can be done.

We will show that the temperature of a thermodynamic system can be changed reversibly from an initial value T_A to a final value T_B by bringing the system in thermal contact with a *succession* of heat reservoirs, each with a temperature only slightly different from the previous one. For concreteness, we will assume that $T_B > T_A$. We must therefore imagine a large collection of reservoirs, the first of which being at a temperature $T_A + \delta T$, the second at a temperature $T_A + 2\delta T$, the nth one at a temperature $T_A + n\delta T$, and the last one at a temperature T_B. Here, $\delta T = (T_B - T_A)/N$, with N denoting the total number of reservoirs, is the (small) increment in temperature from one reservoir to the next. We will show that in the limit $N \to \infty$, $\delta T \to 0$, the total change in entropy in bringing the system gradually from T_A to T_B is zero, hence proving that this transformation is *reversible*.

We first calculate $\Delta S_n \equiv S_n - S_{n-1}$, the change in entropy incurred during the nth stage of the transformation, as the temperature of the system is increased from $T_{n-1} = T_A + (n-1)\delta T$ to $T_n = T_A + n\delta T$. This is given by the same formula as before,

$$\Delta S_n = C(x - 1 - \ln x),$$

where $x = T_{n-1}/T_n = 1 - \delta T/T_n$. Because x is very close to unity, we may use the approximation $\ln(1+\epsilon) = \epsilon - \frac{1}{2}\epsilon^2 + \cdots$, where $\epsilon \equiv -\delta T/T_n$. This gives $\Delta S_n = C(\epsilon - \epsilon + \frac{1}{2}\epsilon^2 + \cdots) \simeq \frac{1}{2}C\epsilon^2$, or

$$\Delta S_n \simeq \frac{C\delta T}{2}\frac{\delta T}{{T_n}^2}.$$

To obtain the *total* change in entropy, we must add up these contributions:

$$\Delta S = \sum_{n=1}^{N} \Delta S_n = \frac{C\delta T}{2}\sum_{n=1}^{N}\frac{\delta T}{{T_n}^2}.$$

In the limit $N \to \infty$, $\delta T \to 0$, the sum becomes the integral

$$\int_{T_A}^{T_B}\frac{dT}{T^2} = \frac{1}{T_A} - \frac{1}{T_B},$$

and the total change in entropy becomes

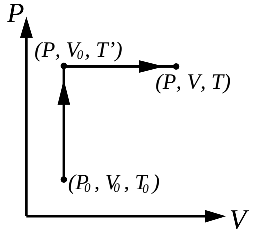
$$\Delta S = \frac{C\delta T}{2}\left(\frac{1}{T_A} - \frac{1}{T_B}\right) \to 0.$$

As claimed, the gradual increase in the system's temperature, as it is brought in thermal contact with an infinite succession of heat reservoirs, is a reversible transformation: $\Delta S \to 0$ in the limit $\delta T \to 0$.

It is important to understand that while the existence of a reversible transformation between a state A and a state B is crucial to the calculation of $S(B) - S(A)$, it is not actually all that important to be able to perform this transformation *in practice*, in a laboratory. The reason is that this reversible transformation is used in a *calculation*, and that it does not matter for the purpose of doing a calculation whether or not the transformation can be carried out in practice. All that is required is that the reversible transformation exists *in principle*. For example, it would be very difficult in practice to arrange for an infinite succession of heat reservoirs, but there is no difficulty in imagining that such a collection of reservoirs is available in principle.

4.4 Entropy of an ideal gas

To help make the concept of entropy more concrete, let us calculate the entropy function for an ideal gas. For this purpose, we consider a reversible transformation from a reference state (P_0, V_0), to which we assign a value S_0 for the entropy, to a state (P, V), for which we want to know the entropy S. We may choose the transformation to be a reversible increase in pressure from P_0 to P keeping the volume contant, followed by a reversible expansion from V_0 to V keeping the pressure constant. For concreteness we assume $P > P_0$ and $V > V_0$, although this is not necessary for the calculation. We will rely on the equation of state $PV = nRT$, and treat both C_V and C_P as constants.



During the first stage of the transformation, the pressure is increased at constant volume. We may therefore write $đQ_{\text{rev}} = C_V\, dT$, and $dS = đQ_{\text{rev}}/T = C_V\, dT/T$. Integration yields

$$S' - S_0 = C_V \ln\left(\frac{T'}{T_0}\right),$$

where S' is the entropy of the state (P, V_0), whose temperature is given by $PV_0 = nRT'$. During the second stage of the transformation, the volume is increased at contant pressure. We write $đQ_{\text{rev}} = C_P\,dT$, $dS = đQ_{\text{rev}}/T = C_P\,dT/T$, and integration yields

$$S - S' = C_P \ln\biggl(\frac{T}{T'}\biggr).$$

Combining the results yields

$$S = S_0 + C_V \ln\biggl(\frac{T'}{T_0}\biggr) + C_P \ln\biggl(\frac{T}{T'}\biggr).$$

This can be expressed in a variety of ways, using the relations $T'/T_0 = P/P_0$, $T/T' = V/V_0$, and $C_P = C_V + nR$. For example, expressing S in terms of C_V gives

$$\boxed{S = S_0 + C_V \ln\biggl(\frac{T}{T_0}\biggr) + nR \ln\biggl(\frac{V}{V_0}\biggr)}\,. \tag{4.6}$$

Alternatively, expressing S in terms of C_P gives

$$\boxed{S = S_0 + C_P \ln\biggl(\frac{T}{T_0}\biggr) - nR \ln\biggl(\frac{P}{P_0}\biggr)}\,. \tag{4.7}$$

Both Eqs. (4.6) and (4.7) give the entropy function of an ideal gas, in terms of a reference state (P_0, V_0, T_0) to which we arbitrarily assign the entropy S_0.

These results can be made more precise if we recall that the heat capacity (at constant volume) of an ideal gas is given by $C_V = \alpha n R$, where $\alpha = \frac{3}{2}$ for monoatomic gases, while $\alpha = \frac{5}{2}$ for diatomic gases. Substituting this in Eq. (4.6), we obtain

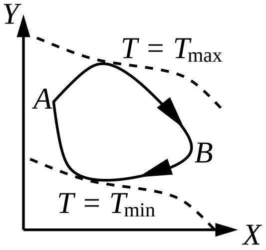
$$\boxed{S = S_0 + nR \ln\biggl[\biggl(\frac{T}{T_0}\biggr)^{\alpha} \frac{V}{V_0}\biggr]}\,. \tag{4.8}$$

We may use this expression to check that a reversible, adiabatic transformation on an ideal gas does not affect its entropy. From Eq. (4.8) we see that a transformation will be *isentropic* if during the transformation, T and V are related by $T^{\alpha}V =$ constant, or $TV^{1/\alpha} =$ constant. Using the equation of state, $T = (\text{constant})PV$, we have that $PV^{1+1/\alpha} =$ constant during the isentropic transformation. This is the same equation as $PV^{\gamma} =$ constant, which describes an adiabatic transformation. Indeed, $\gamma \equiv C_P/C_V = 1 + nR/C_V = 1 + 1/\alpha$, and this shows that an isentropic transformation is also adiabatic. This conclusion is quite general, because if a transformation is reversible, then $dS = 0$ when $đQ = 0$.

4.5 The Carnot limit

In Sec. 3 we saw that the entropy is a useful tool to determine whether or not a transformation on an isolated system is reversible. Here we will use this tool to prove that a generic heat engine working between two extremes of temperature cannot be more efficient than a Carnot engine operating between the same two temperatures. This is statement #4 of Sec. C6. Recall that the thermal efficiency of a Carnot engine is given by $\eta_{\text{Carnot}} = 1 - T_{\min}/T_{\max}$, where $T_{\min}$ is the lowest temperature, while $T_{\max}$ is the highest temperature.

We consider a generic heat engine running an arbitrary cycle, which may be reversible or irreversible. During the portion $A \to B$ of the cycle, the engine's working substance absorbs a quantity Q_{abs} of heat from a hot source. At some



point during this part of the cycle, the system achieves its maximum temperature, $T = T_{\max}$. During the portion $B \to A$ of the cycle, the working substance rejects a quantity Q_{rej} of heat to a cold sink. At some point during this part of the cycle, the system achieves its minimum temperature, $T = T_{\min}$.

Because the entropy is a state function, the system's overall change in entropy after a complete cycle is zero, because the system has returned to its initial state. Using Eq. (4.5), we have

$$0 = \Delta S \geq \oint \frac{đQ}{T} = \int_A^B \frac{đQ}{T} + \int_B^A \frac{đQ}{T},$$

or

$$\int_A^B \frac{đQ}{T} \leq \int_B^A \frac{(-đQ)}{T}.$$

In the first integral, $đQ$ is the infinitesimal of heat entering the system during the portion $A \to B$ of the cycle. In the second integral, $-đQ$ is the infinitesimal of heat leaving the system during the portion $B \to A$ of the cycle — the quantity $(-đQ)$ is positive. The equality sign holds if and only if the cycle is reversible.

Now, during the portion $A \to B$ of the cycle, the system's temperature T is always lower than $T_{\max}$, and

$$\int_A^B \frac{đQ}{T} \geq \frac{Q_{\text{abs}}}{T_{\max}},$$

where $Q_{\text{abs}} = \int_A^B đQ$ is the total heat absorbed by the system. Here the equality sign holds if and only if $A \to B$ is an isothermal transformation, with T always equal to $T_{\max}$. On the other hand, during the portion $B \to A$ of the cycle, the system's temperature T is always higher than $T_{\min}$, and

$$\int_B^A \frac{(-đQ)}{T} \leq \frac{Q_{\text{rej}}}{T_{\min}},$$

where $Q_{\text{rej}} = \int_B^A (-đQ)$ is the total heat rejected by the system. Here the equality sign holds if and only if $B \to A$ is an isothermal transformation, with T always equal to $T_{\min}$.

Combining the inequalities, we have

$$\frac{Q_{\text{abs}}}{T_{\max}} \leq \int_A^B \frac{đQ}{T} \leq \int_B^A \frac{(-đQ)}{T} \leq \frac{Q_{\text{rej}}}{T_{\min}},$$

or

$$\frac{Q_{\text{abs}}}{T_{\max}} \leq \frac{Q_{\text{rej}}}{T_{\min}}.$$

The engine's thermal efficiency is $\eta = 1 - Q_{\text{rej}}/Q_{\text{abs}}$. Since $Q_{\text{rej}}/Q_{\text{abs}} \geq T_{\min}/T_{\max}$, we have that

$$\boxed{\eta \leq 1 - \frac{T_{\min}}{T_{\max}} \equiv \eta_{\text{Carnot}}}\,. \tag{4.9}$$

Our engine can therefore not be more efficient than a Carnot engine operating between the temperatures $T_{\max}$ and $T_{\min}$. According to the preceding results, the situation $\eta = \eta_{\text{Carnot}}$ occurs only when (i) the cycle is reversible, (ii) the system absorbs heat at a constant temperature $T_{\max}$, and (iii) it rejects heat at a constant temperature $T_{\min}$. In other words, the Carnot limit is reached if and only if the engine is a Carnot engine!

4.6 Entropy and the degradation of energy

Now that are better acquainted with the entropy, we are ready to face the big question: What is the physical meaning of the entropy function? We will present some clues toward an answer in this and the following sections. We will begin by showing that an increase in entropy is generally associated with a *degradation* of energy.

Consider a quantity Q of heat delivered to a heat engine from a heat reservoir at a temperature T_1. If T_0 is the temperature of the coolest reservoir at hand, then the Carnot limit guarantees that

$$W_1 = Q\biggl(1 - \frac{T_0}{T_1}\biggr)$$

is the maximum amount of work that can be extracted from the engine. Now, suppose that instead of being immediately converted to work, the heat Q is transferred — say by means of a metallic bar — to a cooler reservoir at a temperature T_2. If this heat is now passed on to the engine, the maximum amount that can be extracted is

$$W_2 = Q\biggl(1 - \frac{T_0}{T_2}\biggr).$$

This is *smaller* than W_1: After the heat is transferred to the cool reservoir, it is less capable of doing work. This is what we mean by the *degradation* of energy: Although energy is conserved during the transfer to the cool reservoir, its *capacity to do work* has decreased. The amount by which the energy has been degraded is given by

$$E_{\text{degraded}} \equiv W_1 - W_2 = QT_0\biggl(\frac{1}{T_2} - \frac{1}{T_1}\biggr).$$

Let us now calculate the overall change in entropy incurred during the heat transfer. Because the reservoir at T_1 loses heat, its entropy decreases by the amount $\Delta S_1 = -Q/T_1$. On the other hand, the reservoir at T_2 gains heat, so its entropy increases by the amount $\Delta S_2 = Q/T_2$. The overall change in entropy is

$$\Delta S = \Delta S_1 + \Delta S_2 = Q\biggl(\frac{1}{T_2} - \frac{1}{T_1}\biggr).$$

This is positive, indicating that the heat transfer is an irreversible transformation. We see that there is a direct relation between the entropy increase and the degration of energy:

$$\boxed{E_{\text{degraded}} = T_0\,\Delta S}\,. \tag{4.10}$$

Thus, an overall increase of entropy signifies that energy — while conserved — becomes less capable of doing work. This statement is known as Kelvin's principle of energy degradation.

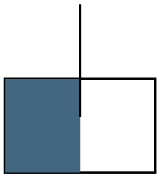
4.7 Statistical interpretation of the entropy

The fundamental meaning of the entropy function can only be revealed by microscopic considerations. These, however, take us outside the scope of thermodynamics, which is not concerned with the microphysics of the systems it studies. As long as such a purely macroscopic point of view is maintained, the true physical meaning of the entropy must remain obscure. To go beyond the macroscopic description and make contact with the system's microphysics is the purpose of *statistical mechanics*, 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.

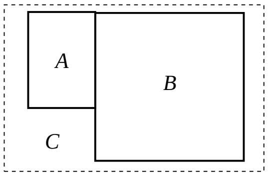
Supposing that we nevertheless choose to adopt the microscopic point of view, how would we go about specifying the microscopic state of our gas? A complete description would involve specifying, at a given moment of time, the positions $\boldsymbol{x}_n$ and velocities $\boldsymbol{v}_n$ of every single 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 value, and it then stays constant. Now, because the free expansion of a gas is an irreversible transformation, we know that the system's entropy *also increases* as the gas evolves toward equilibrium, and that it also stays constant when equilibrium is established. This suggests that the entropy should be a monotomic function of the statistical weight.



To determine what this function might be, we consider a composite system C consisting of two subsystems, A and B. For concreteness, we assume that both A and B are gases. Subsystem A contains N_A molecules, and its microstates are the sets $\{\boldsymbol{x}_n; \boldsymbol{v}_n\}$, where $n = 1, 2, \ldots, N_A$; there is a number Ω_A of such microstates. On the other hand, subsystem B contains N_B molecules, and its microstates are the sets $\{\boldsymbol{x}'_m; \boldsymbol{v}'_m\}$, where $m = 1, 2, \ldots, N_B$; there is a number Ω_B of such microstates. Finally, the composite system C contains $N_C = N_A + N_B$ molecules, and clearly, its microstates are specified by the sets $\{\boldsymbol{x}_n, \boldsymbol{x}'_m; \boldsymbol{v}_n, \boldsymbol{v}'_m\}$. How many such microstates are there? Because for every choice of microstate $\{\boldsymbol{x}_n; \boldsymbol{v}_n\}$ there is a number Ω_B of microstates $\{\boldsymbol{x}'_m, \boldsymbol{v}'_m\}$ to choose from, the answer is clearly

$$\Omega_C = \Omega_A \Omega_B.$$

Thus, the statistical weights *multiply.* On the other hand, we know that the entropy is an *additive* quantity:

$$S_C = S_A + S_B.$$

There is only one function $S(\Omega)$ which satisfies these properties: the logarithm. We conclude that the entropy of a thermodynamic system is related to its statistical weight by the equation

$$\boxed{S = k \ln \Omega}\,, \tag{4.11}$$

where k is a constant of proportionality, whose value will be determined below.

The relation $S = k \ln \Omega$ means that fundamentally, the entropy is a measure of the number of ways that a thermodynamic system can be prepared at the microscopic level so that its *macroscopic* aspects will be the same. Indeed, the statistical weight is the number of possible choices for the microstates $\{\boldsymbol{x}_n; \boldsymbol{v}_n\}$ given the system's macroscopic description, and the entropy is just the natural logarithm of this number. The physical picture that emerges is that fundamentally, the entropy is a measure of the *microscopic disorder* in a thermodynamic system. By this we mean that if in some system the degree of microscopic disorder is high, then Ω will be large, and S will correspondingly be large; if, on the other hand, the degree of microscopic disorder is low, then Ω will be small, and S will also be small. For example, a gas whose molecules are all confined to the left-hand potion of a box is much more ordered than a gas whose molecules are free to be anywhere within the box; the entropy of the first gas is therefore lower.

To calculate the statistical weight of a given thermodynamic system is typically a difficult task which will not be attempted here. We will simply mention that for an ideal gas,

$$\Omega \propto \left(V T^{\alpha}\right)^N,$$

where N is the number of molecules, and α is the same numerical factor that appears in Eq. (4.7): α is defined by the relation $C_V = \alpha n R$. This relation implies that Ω grows rapidly with increasing V or T. This is easy to understand: By increasing the volume, the number of possible choices for the positions $\boldsymbol{x}_n$ increases, thereby increasing the value of Ω. On the other hand, raising the temperature increases the average kinetic energy of the molecules, which means that the number of possible choices for the velocities $\boldsymbol{v}_n$ also increases, thereby making Ω larger.

We may use the preceding expression for Ω to calculate the entropy of an ideal gas. This gives

$$S = Nk \ln V + \alpha N k \ln T + \text{constant}.$$

This agrees with Eq. (4.7), provided that we make the identification $Nk = nR$, giving us a way of determining the constant k. Because $n \equiv N/N_A$, where N_A is Avogadro's number, we have

$$\boxed{k = R/N_A = 1.38 \times 10^{-23}\ \text{J/K}}\,. \tag{4.12}$$

This is *Boltzmann's constant.*

4.8 The third law

4.8.1 Statement and justification

The third law of thermodynamics comes as a consequence of the relation $S = k \ln \Omega$. It states:

> At the absolute zero of temperature, the entropy of any thermodynamic system is zero.

This follows from the fact that at $T = 0$, the system can be in one microstate only, the *ground state*; consequently, $\Omega = 1$ and $S = 0$.

To understand how this result comes about, let us consider a solid, the most common form of matter at very low temperatures. What distinguishes a solid from other forms of matter is that the molecules are arranged in a regular pattern called a *lattice*. This lattice has a periodic structure in which a basic molecular arrangement, called the *unit cell*, is repeated throughout the solid. There are many possibilities for the geometry of the unit cell, and the properties of the solid depend on this geometry. We will denote the position of the nth molecule in the solid by $\boldsymbol{x}_n$, and its velocity by $\boldsymbol{v}_n$. The solid's microstate is the complete listing of all positions and velocities, $\{\boldsymbol{x}_n, \boldsymbol{v}_n\}$.

At nonzero temperatures, the thermal activity within the solid produces a motion of the molecules about their preferred position in the lattice. They behave essentially as simple harmonic oscillators, each of them vibrating about its equilibrium position $\boldsymbol{X}_n$, and each of them possessing an average kinetic energy given by $\frac{1}{2}m{\boldsymbol{v}_n}^2 \sim kT$, where m is the molecule's mass. As T decreases toward the absolute zero, the average kinetic energy decreases also, and the oscillations decrease in amplitude. In the limit $T \to 0$, the molecules have no kinetic energy left, and the oscillations cease. As a result, the molecules sit quietly in their preferred positions $\boldsymbol{X}_n$, and their velocities are $\boldsymbol{v}_n = \boldsymbol{0}$. The solid must therefore be in the microstate $\{\boldsymbol{X}_n, \boldsymbol{0}\}$ at the absolute zero; this is the solid's ground state. Because the equilibrium positions of the molecules are uniquely determined by the intermolecular forces acting within the solid, this ground state is *unique.* Therefore, $\Omega = 1$, and $S = 0$ when $T = 0$.

4.8.2 Behaviour of heat capacities near $T = 0$

The fact that the entropy must vanish at the absolute zero of temperature has an interesting consequence regarding the behaviour of heat capacities near $T = 0$. Suppose that the temperature of a thermodynamic system is varied while keeping some other quantity, denoted X, fixed. As a result of this change in temperature, the entropy varies according to $dS = đQ/T = C_X dT/T$, where C_X is the heat capacity at constant X. Integration, starting at $T = 0$, yields

$$S(T) = \int_0^T \frac{C_X(T)}{T}\, dT,$$

where we have used the fact that $S(0) = 0$. Suppose now that near $T = 0$, the heat capacity varies with temperature according to

$$C_X(T) \sim aT^\beta,$$

where a and β are constants. Because heat capacities are always positive, a must be greater than zero. The sign of β, however, is not (yet) constrained. If $\beta > 0$, then $C_X \to 0$ when $T \to 0$; if $\beta = 0$, then $C_X \to$ constant when $T \to 0$; finally, if $\beta < 0$, then $C_X \to \infty$ when $T \to 0$. Thus, the simple relation $C_X \sim aT^\beta$ qualitatively captures all the possible behaviours of the heat capacity near $T = 0$. Let us now substitute this relation in the preceding equation for the entropy. After integration, we obtain

$$S(T) \sim \frac{a}{\beta} T^\beta,$$

showing that β must be positive, because otherwise this result would not be compatible with the third law: $S(T)$ would not go to zero at $T = 0$. This allows us to conclude that the heat capacity C_X must go to zero at $T = 0$.

Thus, a consequence of the third law of thermodynamics is that

> all heat capacities of all thermodynamic systems must go to zero at the absolute zero of temperature.

This prediction is in full agreement with experimental results. Typically, the heat capacity of solids behaves as $C \propto T^3$ near $T = 0$.

4.8.3 Unattainability of the absolute zero

A further consequence of the third law is that it is in fact impossible to cool a thermodynamic system down to the absolute zero of temperature. Thus, the situation $T = 0$ can be approached as a limiting procedure, but the limit itself is unattainable. The precise formulation of this unattainability principle is:

> It is impossible to bring a thermodynamic system to the absolute zero of temperature with a finite number of operations.

It is easy to see why this statement must be true. Suppose that it is desired to cool some thermodynamic system to the lowest possible temperature, well below $T_{\rm amb}$, the ambiant temperature. To achieve this cooling it is clearly necessary to insulate the system from its surroundings, because otherwise, heat would naturally flow from the surroundings to the system, thereby spoiling the effect. It is therefore necessary to perform an *adiabatic* transformation on the system. But adiabatic transformations are also *isentropic*, and the entropy must therefore stay constant during the transformation. Because $S \neq 0$ initially, the entropy cannot be zero at the end of the transformation, showing that the absolute zero cannot be attained.

4.9 Problems

1. (Zemansky and Dittman, Problem 8.7)

   a) A kilogram of water at 273 K is brought in thermal contact with a heat reservoir at 373 K. When the water has reached 373 K, what is the entropy change of the water? Of the heat reservoir? What is the overal change in entropy?

   b) If the water had been heated from 273 K by first bringing it in contact with a reservoir at 323 K and then with the reservoir at 373 K, what would have been the overall change in entropy?

c) Explain how the water might be heated from 273 to 373 K with almost no overall change in entropy.

2. (Adkins, Problem 5.5)

   Calculate the change in the entropy of 1 kg of water when it is heated from 15 to 100 °C and then completely vapourized. [Take the specific heat of water to be constant at 4.2 kJ/kg K. The latent heat of vapourization of water at a pressure of 1 atm is 2.3×10^6 J/kg.] Does the change in entropy imply any irreversibility in the transformation?

3. (Zemansky and Dittman, Problem 8.9)

   According to Debye's law, the molar heat capacity at constant volume of diamond varies with temperature according to

$$c_V = \frac{12\pi^4}{5} R \left(\frac{T}{T_D} \right)^3 ,$$

   where T_D is the Debye temperature. What is the entropy change in a diamond of mass 1.2 g when it is heated at constant volume from 10 to 350 K? [The atomic weight of carbon is 12, and the Debye temperature of diamond is 2230 K.]

Chapter 5
Thermodynamic potentials

5.1 Internal energy

In Sec. B4 we saw that the work equation for a fluid is

$$đW \geq -P\,dV,$$

with the equality sign holding if the transformation is reversible. On the other hand, we saw in Sec. D2 that the infinitesimal of heat is related to the differential of entropy by the equation

$$đQ \leq T\,dS,$$

where again the equality sign holds for a reversible transformation. These results imply that for reversible transformations, the first law of thermodynamics can be expressed as

$$dU = đQ + đW = T\,dS - P\,dV.$$

The relation $dU = T\,dS - P\,dV$ is interesting, because it involves only quantities which are state variables, and all infinitesimals are differentials: It is a *differential relation* among state functions. This means that this relation must hold for *arbitrary* transformations, whether they are reversible or irreversible. Thus, the relation

$$\boxed{dU = T\,dS - P\,dV}\,, \tag{5.1}$$

puts the first law of thermodynamics in a form that is universally valid. Note that this is also true of the original form $dU = đQ + đW$ which, however, does not convey quite as much information. Note also that Eq. (5.1) comes with the usual physical interpretation of the first law: During an isentropic transformation in which the volume is kept constant, the internal energy of a thermodynamic system does not change.

When examined from a purely mathematical point of view, Eq. (5.1) implies that the internal energy must be considered to be a function of entropy and volume. Indeed, if such a function $U(S,V)$ exists, then taking its total derivative gives

$$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV,$$

which has the same form as Eq. (5.1). This means that we can make the associations

$$\boxed{T = \left(\frac{\partial U}{\partial S}\right)_V, \qquad P = -\left(\frac{\partial U}{\partial V}\right)_S}\,, \tag{5.2}$$

and view these relations as formal *definitions* for temperature and pressure. Although it may appear that these relations are of no particular interest, we will see that they have far-reaching consequences.

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 by

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

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:

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

This is an example of a Legendre transformation, by which the original function is shifted by a quantity that mixes the fundamental variables (x and y) with the derived quantities (a and b). On what variables does the new function depend? The answer comes by differentiation, which gives

$$dg = a\,dx - y\,db.$$

This shows that g is a function of x and b, and that y is now a derived quantity: $y = -(\partial g/\partial b)_x$.

Other Legendre transformations are possible. For example, the transformation

$$f \to h = f - ax \quad \Rightarrow \quad dh = -x\,da + b\,dy$$

produces a function of a and y, and x has become a derived quantity. The only other possibility is the transformation

$$f \to j = f - ax - by \quad \Rightarrow \quad dj = -x\,da - y\,db,$$

which takes the function $f(x,y)$ to the new function $j(a,b)$.

As we shall see, the idea of introducing Legendre transformations in thermodynamics is a powerful one. You may recall that Legendre transformations are also extremely important in advanced mechanics: The transformation $L \to H = p\dot{q} - L$ takes the Lagrangian L — a function of the generalized coordinate q and velocity $\dot{q}$ —- to the Hamiltonian H — a function of q and momentum $p = \partial L/\partial \dot{q}$.

5.2.3 *Helmholtz free energy*

It is easy to generate new thermodynamic potentials by applying Legendre transformations to the internal energy. For example, the *Helmholtz free energy* is defined by

$$\boxed{F = U - TS}\,, \tag{5.6}$$

from which follows the differential relation $dF = dU - T\,dS - S\,dT$. Using Eq. (5.1), this can be written as

$$\boxed{dF = -S\,dT - P\,dV}\,. \tag{5.7}$$

This equation reveals that the Helmholtz free energy must be viewed as a function of temperature and volume: $F = F(T,V)$. It also gives us formal definitions for entropy and pressure:

$$\boxed{S = -\left(\frac{\partial F}{\partial T}\right)_V, \qquad P = -\left(\frac{\partial F}{\partial V}\right)_T}\,. \tag{5.8}$$

We note that Eq. (5.7) gives us the following physical interpretation for the Helmholtz free energy: During an isothermal transformation in which the volume is kept constant, the Helmholtz free energy of a thermodynamic system does not change.

5.2.4 *Gibbs free energy*

The only remaining thermodynamic potential is the *Gibbs free energy*, defined by

$$\boxed{G = U - TS + PV}\,. \tag{5.9}$$

Its differential relation is

$$\boxed{dG = -S\,dT + V\,dP}\,, \tag{5.10}$$

implying that the Gibbs free energy must be viewed as a function of temperature and pressure: $G = G(T, P)$. Equation (5.10) also gives us formal definitions for entropy and volume:

$$\boxed{S = -\left(\frac{\partial G}{\partial T}\right)_P, \qquad V = \left(\frac{\partial G}{\partial P}\right)_T}. \tag{5.11}$$

Equation (5.10) provides us with the following physical interpretation for the Gibbs free energy: During an isothermal transformation in which the pressure is kept constant, the Gibbs free energy of a thermodynamic system does not change.

5.2.5 Summary

We have seen that Legendre transformations can be used to generate a number of thermodynamic potentials which, in turn, can be used to generate formal definitions for thermodynamic quantities. The following table gives a summary of the various definitions:

Potential	Differential relation	Functional relation
U	$dU = T\,dS - P\,dV$	$U(S, V)$
$H = U + PV$	$dH = T\,dS + V\,dP$	$H(S, P)$
$F = U - TS$	$dF = -S\,dT - P\,dV$	$F(T, V)$
$G = U - TS + PV$	$dG = -S\,dT + V\,dP$	$G(T, P)$

The formal definitions, in terms of partial derivatives, can easily be read off the differential relations for the four thermodynamic potentials.

5.3 Maxwell relations

The formal definitions of thermodynamic quantities in terms of partial derivatives of thermodynamic potentials become useful when they are incorporated into statements about the *second* partial derivatives of these potentials. In this section, we will use the commutativity property of second partial derivatives to generate a number of useful identities among thermodynamic quantities. These identities hold for *all* thermodynamic systems, and they are known as the *Maxwell relations*.

Let us begin with the formal definitions of temperature and pressure in terms of partial derivatives of the internal energy:

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

Because U is viewed as a function of S and V, we must also view T and P as functions of these variables. Let us calculate *their* partial derivatives:

$$\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial U}{\partial S}\right)_V \equiv \frac{\partial^2 U}{\partial V \partial S}$$

and

$$-\left(\frac{\partial P}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial U}{\partial V}\right)_S \equiv \frac{\partial^2 U}{\partial S \partial V}.$$

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.

5.4 Mathematical interlude: Reciprocal and reciprocity relations

Suppose that three variables, x, y, and z, are related by an equation of the form

$$f(x, y, z) = 0.$$

This means that the variables are not all independent, and that x (say) can be viewed as a function of y and z. Under changes in y and z, x changes according to

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz.$$

Alternatively, y can be viewed as a function of x and z, and

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz.$$

Substituting the second equation into the first, we obtain

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz.$$

Now, we know that of the three variables x, y, and z, only two are independent, and we may choose x and z to be the independent variables. If we consider a displacement purely in the x direction, then $dz = 0$ and the previous equation gives

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z = 1.$$

In other words,

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = \left[\left(\frac{\partial y}{\partial x}\right)_z\right]^{-1}}\,, \tag{5.17}$$

which established that $(\partial x/\partial y)_z$ is the reciprocal of $(\partial y/\partial x)_z$. Equation (5.17) is known as the *reciprocal relation*. It is crucial to note that the partial derivatives are calculated with the *same variable* kept fixed.

We now consider a displacement purely in the z direction. Then $dx = 0$, and

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0.$$

In other words,

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -\left(\frac{\partial x}{\partial z}\right)_y}\,. \tag{5.18}$$

This is the *reciprocity* relation. To help remember it, it is useful to notice that the ∂y's cancel each other out on the left-hand side, and that y is the quantity kept fixed on the right-hand side. Using the reciprocal relation, Eq. (5.18) can also be expressed as

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}\,. \tag{5.19}$$

Notice that the left-hand side involves three factors in which the basic ordering x-y-z is permuted in a cyclic fashion.

5.5 The heat-capacity equation

We know that the heat capacities of an ideal gas are related by the equation $C_P = C_V + nR$, indicating that the heat capacity at constant pressure is larger than the heat capacity at constant volume. As we shall now prove, the relation $C_P \geq C_V$ is quite general: It is valid for *all* thermodynamic systems.

Recall that in Sec. B6 we derived the relation

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{\beta V} - P,$$

where

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

is the volume expansivity. Equation (5.16) above gives us another expression for the same quantity:

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

Equating these results gives

$$C_P - C_V = \beta V T\left(\frac{\partial P}{\partial T}\right)_V.$$

Now, the reciprocity relation (5.18) allows us to write

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P = -\beta V\left(\frac{\partial P}{\partial V}\right)_T,$$

and the reciprocal relation (5.17) implies

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{\kappa V},$$

where

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

is the isothermal compressibility, a *positive* quantity for all known substances. Gathering the results, we obtain

$$\boxed{C_P - C_V = \frac{\beta^2 V T}{\kappa}}. \tag{5.20}$$

This equation is valid for all thermodynamic systems, and it shows that for all known substances, $C_P \geq C_V$. Its generality makes Eq. (5.20) one of the most important results of thermodynamics. Among the consequences of this equation is the fact that the heat capacities must become equal at the absolute zero of temperature. The heat capacities must also be equal when β, the volume expansivity, vanishes; this happens, for example, to water at 4 °C, at which its density is a maximum. (Why does β vanish when the density is maximum?)

It is instructive to derive the heat-capacity equation (5.20) from scratch, without relying on old results. We will proceed via the derivation of the "$T\,dS$" equations.

We have seen in Sec. 1 that the entropy can be viewed as a function of U and V. On the other hand, the internal energy is a function of T and V. We may therefore choose to view S as a function of T and V, and this gives rise to the differential relation

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV,$$

or

$$T\,dS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV.$$

From the fact that $T\,dS = \text{đ}Q_{\text{rev}}$, we have

$$T\left(\frac{\partial S}{\partial T}\right)_V = C_V.$$

On the other hand, the Maxwell relation (5.14) gives

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

Combining the results, we arrive at

$$\boxed{T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV}\,, \tag{5.21}$$

our first "$T\,dS$" equation.

The second "$T\,dS$" equation is obtained by taking S to be a function of T and P instead of T and V. This gives

$$T\,dS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP.$$

The coefficient of dT is just C_P, and the Maxwell relation (5.15) changes the coefficient of dP to $-T(\partial V/\partial T)_P$. We therefore obtain

$$\boxed{T\,dS = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP}\,, \tag{5.22}$$

our second "$T\,dS$" equation.

We now equate Eqs. (5.21) and (5.22) and get

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

Solving for dT yields

$$dT = \frac{T(\partial P/\partial T)_V}{C_P - C_V}\,dV + \frac{T(\partial V/\partial T)_P}{C_P - C_V}\,dP.$$

This equation confirms that T is a function of V and P, with partial derivatives

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{T(\partial P/\partial T)_V}{C_P - C_V}$$

and

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{T(\partial V/\partial T)_P}{C_P - C_V}.$$

Using the reciprocal relation (5.17), both equations imply

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V.$$

We may now use the reciprocity relation

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

and express our final result as

$$\boxed{C_P - C_V = T\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2\left[-\left(\frac{\partial P}{\partial V}\right)_T\right]}\,. \tag{5.23}$$

With the definitions $\beta = V^{-1}(\partial V/\partial T)_P$ and $\kappa = -V^{-1}(\partial V/\partial P)_T$, this reduces to Eq. (5.20).

5.6 Problems

1. (Zemansky and Dittman, Problem 9.4)

   Derive the following equations:

   a)
   $$U = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\left(\frac{\partial F/T}{\partial T}\right)_V.$$

   b)
   $$C_V = -T\left(\frac{\partial^2 F}{\partial T^2}\right)_V.$$

   c)
   $$H = G - T\left(\frac{\partial G}{\partial T}\right)_P = -T^2\left(\frac{\partial G/T}{\partial T}\right)_P.$$

   d)
   $$C_P = -T\left(\frac{\partial^2 G}{\partial T^2}\right)_P.$$

2. (Zemansky and Dittman, Problem 9.9)

   A gas obeys the equation $P(v-b) = RT$, where $v = V/n$ is the molar volume and b is a constant. It is also known that c_V, the molar specific heat, is a constant. Prove that:

   a) The specific internal energy $u = U/n$ is a function of T only.

   b) The quantity $\gamma = c_P/c_V$ is constant.

   c) During an adiabatic transformation, the relation $P(v-b)^\gamma =$ constant, holds.

3. (Zemansky and Dittman, Problem 9.13)

   a) Derive the equation
   $$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V.$$

   b) Use the preceding result to prove that for an ideal gas, C_V is a function of T only.

   c) In the case of a gas obeying the equation of state
   $$\frac{Pv}{RT} = 1 + \frac{B}{v},$$
   where $v = V/n$ and B is a function of T only, prove that
   $$c_V = -\frac{RT}{v}\frac{d^2}{dT^2}(BT) + (c_V)_0,$$
   where $(c_V)_0$ is the value at very large volumes.

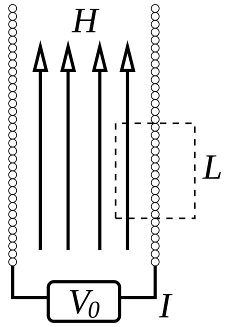
Chapter 6

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.)



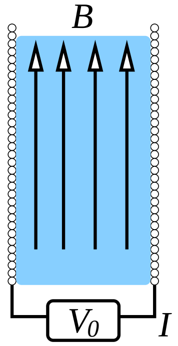
We will need a device capable of supplying the external magnetic field, which we denote $\boldsymbol{H}$. It is simplest to deal with a field that is very uniform, and this can be provided by a very long solenoid. The magnetic field inside the solenoid can easily be calculated from the Maxwell equation

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

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 from $\boldsymbol{H}$. We denote this magnetic field $\boldsymbol{B}$, and we shall keep $\boldsymbol{H}$ to designate the field measured in the *absence* of the magnetic sample. Thus, $\boldsymbol{H}$ is the field created *solely* by the current I running through the solenoid, and the magnitude of $\boldsymbol{H}$ shall always be given by Eq. (6.1). The difference between the actual magnetic field $\boldsymbol{B}$ and the field $\boldsymbol{H}$ defines $\boldsymbol{M}$, the *magnetization* of the material. More precisely,

$$\boxed{\boldsymbol{B} = \boldsymbol{H} + \mu_0 \boldsymbol{M}} \,. \tag{6.2}$$

The fields $\boldsymbol{B}$ and $\boldsymbol{H}$ are measured in Tesla (T), and the unit of magnetization is $\mathrm{J/m^3T}$.

As was mentioned above, the magnetization of a paramagnetic material is nonzero only when an applied field is present. Thus, $\boldsymbol{M} = 0$ when $\boldsymbol{H} = 0$. When $\boldsymbol{H} \neq 0$, $\boldsymbol{M}$ is also nonzero, and points in the same direction as the applied field; the actual magnetic field $\boldsymbol{B}$ is therefore larger than $\boldsymbol{H}$. To understand this behaviour, we must picture the molecules within the magnetic material as tiny loops of current, the current being generated by moving electrons. These tiny current loops generate tiny magnetic fields within the sample, and under the right conditions, these microscopic fields add up and produce the observed macroscopic magnetization. What are these conditions?

Consider one of these molecules pictured as a tiny current loop. The product (current)(loop area) defines the vector $\boldsymbol{\mu}$, the *magnetic moment* of the molecules. This vector points in the direction perpendicular to the plane of the loop, in accordance with the right-hand rule. It is the quantity $\boldsymbol{\mu}$ that dictates the strength and direction of the molecule's contribution to the magnetic field inside the sample. In the absence of an applied field $\boldsymbol{H}$, there is no preferred axis within the sample, and the magnetic moments point in random directions. As a result, the molecular fields add incoherently, and there is no macroscopic buildup of the magnetic field inside the sample. When a field $\boldsymbol{H}$ is turned on, however, there is a net tendency for the magnetic moments to align themselves with the applied field, and the molecular fields now add *coherently*, producing a macroscopic reinforcement of the applied field. As a result, $B > H$.

The vectorial sum of all the molecular magnetic moments defines the *total magnetic moment* of the sample, whose magnitude is denoted $\mathcal{M}$. The sample's *magnetization* is then the total magnetic moment per unit volume. Thus,

$$\boxed{\mathcal{M} = MV} \,. \tag{6.3}$$

The total magnetic moment depends on H, the magnitude of the applied magnetic field: A larger applied field produces a better alignment of the magnetic moments, and thus, a larger magnetization; when $H = 0$, $M = 0$. The total magnetic moment depends also on temperature T: A larger temperature produces more thermal agitation within the sample, and this tends to spoil the alignment of the magnetic moments. The *equation of state* of a paramagnetic system is

$$\boxed{\mathcal{M} = \alpha\, n\, R' \frac{H}{T} \qquad \text{(paramagnetic material)}} \,, \tag{6.4}$$

where n is the number of moles (the number of molecules within the sample divided by Avogadro's number), and $R' = 10.4\ \mathrm{J^2/T^2}$. The dimensionless quantity α is a constant whose value depends on the paramagnetic material. A few such materials are listed in the following table, together with the corresponding value of α:

Paramagnetic salt	α
Chromium potassium alum	15
Iron ammonium alum	35
Gadolinium sulphate	63

It should be noted that Eq. (6.4), known as *Curie's law*, does not stay valid at very cold temperatures: Instead of approaching infinity as $T \to 0$, $\mathcal{M}$ saturates at some maximum value.

The thermodynamic variables of our paramagnetic system are therefore the total magnetic moment $\mathcal{M}$, the applied field H, and the temperature T. These are related by the equation of state (6.4), which plays the same role as the equation $PV = nRT$ for ideal gases.

6.2 Work equation

The next order of business is to derive a work equation for magnetic systems. This will be the analogue of $đW = -P\,dV$ for fluids. Our discussion here will be quite general: We will not assume that the sample is necessarily a paramagnetic material, and we will not rely on the equation of state (6.4).

We want to calculate the work done on a magnetic sample when its magnetization M is changed. (Because we assume throughout that the volume of the sample is kept fixed, a change in M is simply proportional to a change in $\mathcal{M}$.) The calculation will involve keeping track of the potential difference at the current source, and it will rely on Faraday's law of induction, which states that a change in magnetic flux across a closed circuit creates an electromotive force (a potential difference) in the circuit.

Suppose that the magnetization of the sample is increased: $\Delta M > 0$. (This may be achieved by reducing the temperature.) We assume that the current I running through the solenoid is kept contant, so that the applied magnetic field H does not change during the transformation. An increase in M corresponds to an increase in B and a corresponding increase in $\Phi = BA$, the magnetic flux across the sample; A is the cylinder's cross-sectional area. Faraday's law implies that this change in magnetic flux induces a potential difference across the solenoid. For a single loop of the solenoid, there is a voltage *drop* of $\Delta\Phi/\Delta t$, where $\Delta\Phi = A\Delta B = \mu_0 A \Delta M$ and Δt is the time over which the transformation takes place. If we look at a portion of length L of the sample, then the number of loops is pL, and the total drop in voltage is

$$\Delta V_0 = \mu_0\, p\, LA\, \frac{\Delta M}{\Delta t} = \mu_0 p V \frac{\Delta M}{\Delta t},$$

where $V = LA$ is the volume of that portion of the sample. Because we wish the keep the current constant, the source must compensate for this induced drop in voltage. The source must therefore deliver additional power, given by $I\Delta V_0$. The extra work done by the source during the transformation is then

$$I\,\Delta V_0\,\Delta t = \mu_0\, p\, I\, V\,\Delta M = HV\Delta M,$$

where we have used Eq. (6.1). The extra work done by the current source is done on the magnetic sample, and we conclude that $W = HV\Delta M = H\Delta\mathcal{M}$ describes the work done on a magnetic system during a change in magnetization.

The work equation is therefore

$$\boxed{đW = H\,d\mathcal{M}}\ . \tag{6.5}$$

We see that for magnetic systems, H is the quantity analogous to $-P$, and $\mathcal{M}$ is the quantity analogous to V. These analogies will allow us to quickly arrive at all the thermodynamic relations relevant to magnetic systems: They can be obtained directly from their fluid counterparts just by relacing P by $-H$, and V by $\mathcal{M}$. The following three sections contain the most important results, without much discussion.

6.3 First law and heat capacities

The form of the work equation (6.5) allows us to write the first law of thermodynamics as

$$\boxed{dU = T\,dS + H\,d\mathcal{M}}\ , \tag{6.6}$$

where U is the internal energy of the magnetic sample, and S its entropy. This differential relation holds for arbitrary transformations.

The heat capacities of magnetic systems are defined by

$$\boxed{C_{\mathcal{M}} = \left(\frac{đQ}{dT}\right)_{\mathcal{M}}, \qquad C_H = \left(\frac{đQ}{dT}\right)_H}\ . \tag{6.7}$$

Experiments have shown that for paramagnetic samples,

$$\boxed{C_{\mathcal{M}} = \frac{\beta\,n\,R}{T^2} \qquad \text{(paramagnetic material)}}\ , \tag{6.8}$$

where R is the usual gas constant. The constant β has units of K^2, and its value depends on the material. A few values are listed in the following table:

Paramagnetic salt	β (K^2)
Chromium potassium alum	0.018
Iron ammonium alum	0.013
Gadolinium sulphate	0.35

Equation (6.8) breaks down at very cold temperatures: As a consequence of the third law, $C_{\mathcal{M}}$ must approch zero at the absolute zero of temperature. A relation between C_H and $C_{\mathcal{M}}$ will be given below.

6.4 Thermodynamic potentials and Maxwell relations

The following thermodynamic potentials can be defined for magnetic systems: internal energy U, enthalpy H', Helmholtz free energy F, and Gibbs free energy G. Their definitions and differential relations are given in the following table:

Potential	Differential relation	Functional relation
U	$dU = T\,dS + H\,d\mathcal{M}$	$U(S,\mathcal{M})$
$H' = U - H\mathcal{M}$	$dH' = T\,dS - \mathcal{M}\,dH$	$H'(S,H)$
$F = U - TS$	$dF = -S\,dT + H\,d\mathcal{M}$	$F(T,\mathcal{M})$
$G = U - TS - H\mathcal{M}$	$dG = -S\,dT - \mathcal{M}\,dH$	$G(T,H)$

It is easy to read off the various partial-derivative definitions from the differential relations listed in the table; for example, $S = -(\partial F/\partial T)_{\mathcal{M}}$. These give rise to the following Maxwell relations:

$$\boxed{\left(\frac{\partial T}{\partial \mathcal{M}}\right)_S = \left(\frac{\partial H}{\partial S}\right)_{\mathcal{M}}}\,, \tag{6.9}$$

$$\boxed{\left(\frac{\partial T}{\partial H}\right)_S = -\left(\frac{\partial \mathcal{M}}{\partial S}\right)_H}\,, \tag{6.10}$$

$$\boxed{\left(\frac{\partial S}{\partial \mathcal{M}}\right)_T = -\left(\frac{\partial H}{\partial T}\right)_{\mathcal{M}}}\,, \tag{6.11}$$

and

$$\boxed{\left(\frac{\partial S}{\partial H}\right)_T = \left(\frac{\partial \mathcal{M}}{\partial T}\right)_H}\,. \tag{6.12}$$

6.5 "$T\,dS$" and heat-capacity equations

If we view the entropy as a function of T and $\mathcal{M}$, then $T\,dS$ can be expressed as

$$T\,dS = T\left(\frac{\partial S}{\partial T}\right)_{\mathcal{M}} dT + T\left(\frac{\partial S}{\partial \mathcal{M}}\right)_T d\mathcal{M}.$$

The coefficient in front of dT is $C_{\mathcal{M}}$, and using Eq. (6.11), we arrive at our first "$T\,dS$" equation:

$$\boxed{T\,dS = C_{\mathcal{M}}\,dT - T\left(\frac{\partial H}{\partial T}\right)_{\mathcal{M}} d\mathcal{M}}\,. \tag{6.13}$$

Taking now S to be a function of T and H, the second "$T\,dS$" equation reads:

$$\boxed{T\,dS = C_H\,dT + T\left(\frac{\partial \mathcal{M}}{\partial T}\right)_H dH}\,. \tag{6.14}$$

These equations can now be used to derive an important relation between the heat capacities. Equating (6.13) to (6.14) and solving for dT yields

$$dT = \frac{T(\partial\mathcal{M}/\partial T)_H}{C_{\mathcal{M}} - C_H}\,dH + \frac{T(\partial H/\partial T)_{\mathcal{M}}}{C_{\mathcal{M}} - C_H}\,d\mathcal{M},$$

which implies

$$\left(\frac{\partial T}{\partial H}\right)_{\mathcal{M}} = \frac{T(\partial\mathcal{M}/\partial T)_H}{C_{\mathcal{M}} - C_H}$$

and

$$\left(\frac{\partial T}{\partial \mathcal{M}}\right)_H = \frac{T(\partial H/\partial T)_{\mathcal{M}}}{C_{\mathcal{M}} - C_H}.$$

Using the reciprocal relation on any one of these two equations gives

$$C_H - C_{\mathcal{M}} = -T\left(\frac{\partial \mathcal{M}}{\partial T}\right)_H \left(\frac{\partial H}{\partial T}\right)_{\mathcal{M}}.$$

Using now the reciprocity relation, the last factor can be expressed as

$$\left(\frac{\partial H}{\partial T}\right)_{\mathcal{M}} = -\left(\frac{\partial H}{\partial \mathcal{M}}\right)_T \left(\frac{\partial \mathcal{M}}{\partial T}\right)_H,$$

and we finally obtain

$$\boxed{C_H - C_{\mathcal{M}} = T\left[\left(\frac{\partial \mathcal{M}}{\partial T}\right)_H\right]^2 \left(\frac{\partial H}{\partial \mathcal{M}}\right)_T}. \tag{6.15}$$

It should be noted that depending on the magnetic material, the magnetization can either increase or decrease as a result of an increase in H. Consequently, the quantity $(\partial\mathcal{M}/\partial H)_T$, called the *magnetic susceptibility*, can be of either sign, and Eq.(6.15) predicts that the sign of $C_H - C_{\mathcal{M}}$ goes with the sign of the susceptibility.

For paramagnetic materials, we can use the equation of state (6.4) to evaluate the partial derivatives appearing in Eq. (6.15). We have $(\partial\mathcal{M}/\partial T)_H = -\mathcal{M}/T$ and $(\partial\mathcal{M}/\partial H)_T = \mathcal{M}/H$, and we arrive at

$$\boxed{C_H - C_{\mathcal{M}} = \frac{\mathcal{M}H}{T} \qquad \text{(paramagnetic material)}}. \tag{6.16}$$

Because the susceptibility of a paramagnetic sample is always positive, $C_H > C_{\mathcal{M}}$.

6.6 Adiabatic demagnetization

One of the most practically important aspects of the thermodynamics of magnetic systems is the *magneto-caloric effect*: the property that an adiabatic change in magnetization causes a change in temperature. The experimental technique of *adiabatic demagnetization* is now used widely to cool samples to very low temperatures, well below 1 K.

This phenomenon comes as a consequence of the relation (6.13),

$$T\,dS = C_{\mathcal{M}}\,dT - T\left(\frac{\partial H}{\partial T}\right)_{\mathcal{M}} d\mathcal{M}.$$

If the transformation is reversible and adiabatic, then $dS = 0$ and this equation becomes

$$\boxed{C_{\mathcal{M}}\left(\frac{\partial T}{\partial \mathcal{M}}\right)_S = T\left(\frac{\partial H}{\partial T}\right)_{\mathcal{M}}}. \tag{6.17}$$

For a paramagnetic sample, $(\partial H/\partial T)_{\mathcal{M}} = \mathcal{M}/(\alpha n R') > 0$, and therefore,

$$\left(\frac{\partial T}{\partial \mathcal{M}}\right)_S > 0.$$

This means that an adiabatic reduction of magnetization (caused by a reduction of the applied field H) will result in a drop of temperature. This is the magneto-caloric effect.

We shall now put this on a more quantitative basis. Imagine that a paramagnetic sample undergoes adiabatic demagnetization, during which its total magnetic moment $\mathcal{M}$ goes from $\mathcal{M}_A$ to zero. We want to calculate the final temperature T_B, assuming that the sample begins at a temperature T_A. Using Eqs. (6.4), (6.8), and (6.17), we obtain the differential equation

$$\frac{\beta n R}{T^2}\frac{dT}{d\mathcal{M}} = \frac{\mathcal{M}T}{\alpha n R'}.$$

Integrating (from T_A to T_B and from $\mathcal{M}_A$ to zero, we obtain

$$\frac{1}{{T_A}^2} - \frac{1}{{T_B}^2} = -\frac{{\mathcal{M}_A}^2}{\alpha\beta n^2 R R'}.$$

After a little algebra, using the equation of state to express $\mathcal{M}_A$ in terms of H_A, the initial value of the applied field, we obtain

$$\boxed{\left(\frac{T_A}{T_B}\right)^2 = 1 + \frac{\alpha R'}{\beta R}\,{H_A}^2}\,. \tag{6.18}$$

For chromium potassium alum, adiabatic demagnetization from an initial temperature of 1 K and an initial applied field of 1 T produces a final temperature of 0.03 K.

6.7 Statistical mechanics of paramagnetism

We have already observed, in Sec. D.6, that the framework of thermodynamics is severely limited by its insistence on keeping a purely macroscopic point of view. The methods of statistical mechanics, which make contact with the microphysics of the system under study, typically offer many insights into the thermodynamics of that system, insights that cannot be obtained from purely macroscopic considerations. We will conclude this chapter by offering a concrete illustration of this statement: We will apply the methods of statistical mechanics to our study of paramagnetic systems. We will rely mostly on the relation $S = k \ln \Omega$, where k is the Boltzmann constant and Ω the number of distinct microstates giving rise to the same macroscopic description.

6.7.1 Microscopic model

We picture our paramagnetic sample as a collection of N molecules in a volume V. Because the sample is a solid, we may assume that the molecules are located on specific sites on a regular lattice. We again picture each molecule as a tiny loop of current, with a magnetic moment $\boldsymbol{\mu}$ which tends to align itself in the direction of the applied magnetic field $\boldsymbol{H}$. Thermal agitation, however, prevents a perfect alignment of all the moments. For simplicity, we assume that two orientations are possible: either a perfect alignment of $\boldsymbol{\mu}$ in the direction of $\boldsymbol{H}$, or else a perfect alignment in the *opposite* direction. We denote the two possible values of the magnetic moment by $\pm\mu$, with the upper sign indicating alignment, and the lower sign indicating anti-alignment. Of the N molecules, we will suppose that a number n_+ have a magnetic moment $+\mu$, while a number n_- have a magnetic moment $-\mu$; evidently, $n_+ + n_- = N$. As a result of its interaction with the applied field $\boldsymbol{H}$, each molecule acquires a magnetic energy $-\boldsymbol{\mu}\cdot\boldsymbol{H}$, which is minimum (and negative) if $\boldsymbol{\mu}$ points in the same direction as $\boldsymbol{H}$. With two possible orientations for $\boldsymbol{\mu}$, the magnetic energy becomes $\mp\mu H$, with the same sign convention as above. The total magnetic moment

$\mathcal{M}$ is the vectorial sum of the individual moments. Thus, $\mathcal{M} = n_+(\mu) + n_-(-\mu)$, or

$$\boxed{\mathcal{M} = (2n_+ - N)\mu}\,. \tag{6.19}$$

Similarly, the total magnetic energy is given by $U_{\text{mag}} = n_+(-\mu H) + n_-(\mu H)$, or

$$\boxed{U_{\text{mag}} = -H\,\mathcal{M}}\,. \tag{6.20}$$

We use the label "mag" to indicate that U_{mag} is just the magnetic contribution to the sample's internal energy. There may be other contributions, for example, from the vibrational motion of the molecules within the paramagnetic solid.

6.7.2 Statistical weight and entropy

The macroscopic state of the paramagnetic sample is specified by selecting a value for its total magnetic moment $\mathcal{M}$. Equation (6.19) then indicates that the macroscopic state is characterized just as well by the value of n_+, the number of moments $\boldsymbol{\mu}$ aligned with the applied field $\boldsymbol{H}$. We must now calculate Ω, the number of distinct ways that the n_+ positive moments and the $n_- = N - n_+$ negative moments can be placed on the lattice. This is a classic problem of combinations and permutations.

Let us start with the first lattice site. We have N molecules to choose from to occupy this site, and there are therefore N distinct choices. When we move on to the second site, we see that there are $N-1$ molecules left, and that there are $N-1$ ways to choose among them. Thus far, the total number of choices is $N(N-1)$. By the time we get to the last site, the total number of choices has climbed to $N(N-1)(N-2)\cdots(2)(1) = N!$. Thus, the number of distinct ways of placing the N molecules on the lattice is $N!$. This number, however, is not equal to Ω. The reason is that we still have the freedom to permute the n_+ positive moments among themselves, and the n_- negative moments among themselves, without altering the macroscopic state of the paramagnetic system. The number of distinct permutations of the positive moments among themselves is equal to $n_+!$, and similarly, the number of distinct permutations of the negative moments among themselves is $n_-!$. This means that the statistical weight of the paramagnetic system must be given by

$$\Omega = \frac{N!}{n_+!\,n_-!} = \frac{N!}{n_+!(N-n_+)!}.$$

Because $n_+ = \frac{1}{2}(N + \mathcal{M}/\mu)$, we see that Ω is a function of the total magnetic moment $\mathcal{M}$.

The fundamental relation of statistical mechanics, $S = k\ln\Omega$, allows us now to calculate the function $S_{\text{mag}}(\mathcal{M})$, which represents the magnetic contribution to the sample's entropy. Along the way, we will need to calculate such quantities as $\ln(N!)$, where N is an extremely large number (of the order of N_A, the Avogadro number). We will rely on *Stirling's approximation*,

$$\ln(N!) \simeq N\ln(N) - N.$$

It is then a simple matter to derive the relation

$$\boxed{S_{\text{mag}} = k\Big[N\ln(N) - n_+\ln(n_+) - (N-n_+)\ln(N-n_+)\Big]}\,. \tag{6.21}$$

We may check that this expression complies fully with the third law of thermodynamics: When the temperature is very close to the absolute zero, there is very little thermal agitation in the sample, and nearly all the magnetic moments align themselves with the applied magnetic field. Thus, $n_+ \to N$ and $n_- \to 0$ when $T \to 0$. This means that $\mathcal{M} \to N\mu$ and Eq. (6.21) implies that $S \to 0$, as predicted by the third law.

6.7.3 Thermodynamics

How do we now obtain information about the thermodynamics of our paramagnetic system? The answer is that we use the information already available to derive how $\mathcal{M}$ must behave as a function of temperature. Equations (6.19) and (6.21) tell us that $S_{\rm mag}$ is a function of $\mathcal{M}$ only, since N and μ are constant parameters. On the other hand, Eq. (6.20) informs us that $U_{\rm mag}$ is a function of both $\mathcal{M}$ and H. Differentiation of the relation $U_{\rm mag} = -H\mathcal{M}$ yields

$$dU_{\rm mag} = -H\frac{d\mathcal{M}}{dS_{\rm mag}}\, dS_{\rm mag} - \mathcal{M}\, dH,$$

and we notice that this has the form of the first law, with the coefficient in front of $dS_{\rm mag}$ to be identified with temperature. Thus,

$$\boxed{dU_{\rm mag} = T\, dS_{\rm mag} - \mathcal{M}\, dH}\,, \tag{6.22}$$

with

$$T \equiv -H\frac{d\mathcal{M}}{dS_{\rm mag}}.$$

It is a simple matter to use Eqs. (6.21) and (6.19) to calculate $dS_{\rm mag}/d\mathcal{M}$, and we obtain

$$\frac{1}{T} = -\frac{k}{2\mu H}\,\ln\!\left(\frac{N-n_+}{n_+}\right),$$

or

$$\frac{n_+}{N} = \frac{1}{1+e^{-2\mu H/kT}}.$$

Finally, substituting this into Eq. (6.19) yields

$$\boxed{\mathcal{M} = N\mu\tanh\!\left(\frac{\mu H}{kT}\right)}\,. \tag{6.23}$$

This is the *equation of state* of the paramagnetic sample. We see that the methods of statistical mechanics allow us to *derive*, from first principles, the equation of state of the thermodynamic system under consideration. This constitutes substantial progress: In the framework of pure thermodynamics, the equation of state cannot be derived but must be provided as experimental input.

Equation (6.23) confirms that $\mathcal{M} \to N\mu$ when $T \to 0$. Indeed, in this limit the argument of the hyperbolic tangent is very large, and $\tanh(x \gg 1) \simeq 1$. On the other hand, $\tanh(x \ll 1) \simeq x$, and we see that at high temperatures,

$$\mathcal{M} \simeq \frac{N\mu^2 H}{kT} = n\,\frac{(N_A\mu)^2}{R}\,\frac{H}{T},$$

where $n = N/N_A$ is the number of moles and $R \equiv N_A k$ is the gas constant. This result is identical to Eq. (6.4), provided that we make the identification $\alpha R' \equiv (N_A\mu)^2/R$. Thus, Curie's law is recovered as the high-temperature limit of the general relation (6.23).

6.7.4 Different forms of the first law

We still have to explain why Eq. (6.22) does not agree with Eq. (6.6), the first law of thermodynamics for magnetic systems. The reason resides partly with the fact that Eq. (6.22) accounts for the system's magnetic degrees of freedom *only.* Writing the total internal energy as

$$U_{\rm tot} = U_{\rm mag} + U_{\rm other}$$

and the total entropy as

$$S_{\text{tot}} = S_{\text{mag}} + S_{\text{other}},$$

we may write the first law of thermodynamics as

$$\begin{aligned} dU_{\text{tot}} &= dU_{\text{mag}} + dU_{\text{other}} \\ &= T\,dS_{\text{mag}} - \mathcal{M}\,dH + T\,dS_{\text{other}} + đW_{\text{other}} \\ &= T\,dS_{\text{tot}} - \mathcal{M}\,dH + đW_{\text{other}}. \end{aligned}$$

Here, $đW_{\text{other}}$ represents the non-magnetic work done on the system. The last relation, which accounts for *all* the degrees of freedom, still does not agree with Eq. (6.6). Why? The reason is that these equations actually make statements about *different measures of internal energy.* Suppose that according to some different energy convention, we made the choice of excluding $U_{\text{mag}} = -\mathcal{M}H$ from U_{tot}, thereby defining the new quantity

$$U_{\text{int}} = U_{\text{tot}} - U_{\text{mag}} = U_{\text{tot}} + \mathcal{M}H.$$

The first law for this new internal energy reads

$$\begin{aligned} dU_{\text{int}} &= dU_{\text{tot}} + \mathcal{M}\,dH + H\,d\mathcal{M} \\ &= T\,dS_{\text{tot}} + \mathcal{M}\,dH + đW_{\text{other}}. \end{aligned}$$

In the absence of non-magnetic sources of work, this relations reduces to

$$dU_{\text{int}} = T\,dS_{\text{tot}} + \mathcal{M}\,dH,$$

in agreement with Eq. (6.6). There are therefore many different ways of expressing the first law of thermodynamics, and one must be clear as to what measure of internal energy the quantity U refers.

CHAPTER 7
PROBLEMS FOR REVIEW

1. (Zemansky and Dittman, Problem 2.4)

   A metal whith volume expansivity $\beta = 5.0 \times 10^{-5}$ K^{-1} and isothermal compressibility $\kappa = 1.2 \times 10^{-11}$ Pa is at a pressure of 1×10^{5} Pa and a temperature of 20 °C. A thick surrounding cover of negligible expansivity and compressibility maintains the metal at constant volume.

   a) What will be the final pressure if the temperature is raised to 32 °C?

   b) If the surrounding cover can withstand a maximum pressure of 1.2×10^{8} Pa, what is the highest temperature to which the the system may be raised?

2. (Zemansky and Dittman, Problem 2.9)

   At the critical point of a phase diagram, $(\partial P/\partial V)_T = 0$. Show that at the critical point, both the volume expansivity and the isothermal compressibility are infinite.

3. (Zemansky and Dittman, Problem 3.2)

   Calculate the work done on 1 mol of gas during a quasi-static, isothermal expansion from an initial volume V_A to a final volume V_B when the equation of state is:

   a) $P(v - b) = RT$, where $v = V/n$ is the molar volume and b is a constant;

   b) $Pv = RT(1 - B/v)$, where B is a function of T only.

4. (Zemansky and Dittman, Problem 4.5)

   A vessel with rigid walls and covered with asbestos is divided into two parts by a partition. One part contains a gas, and the other is evacuated. If the partition is suddenly removed, show that the initial and final internal energies of the gas are equal.

5. (Zemansky and Dittman, Problem 4.17)

   One mole of gas obeys the equation of state

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT,$$

   where v is the molar volume and a and b are constants. The molar internal energy of this gas is given by $u = cT - a/v$, where c is another constant. Calculate the molar heat capacities, c_V and c_P.

6. (Zemansky and Dittman, Problem 5.11)

   Show that the heat transferred to an ideal gas during an infinitesimal quasi-static transformation can be written as

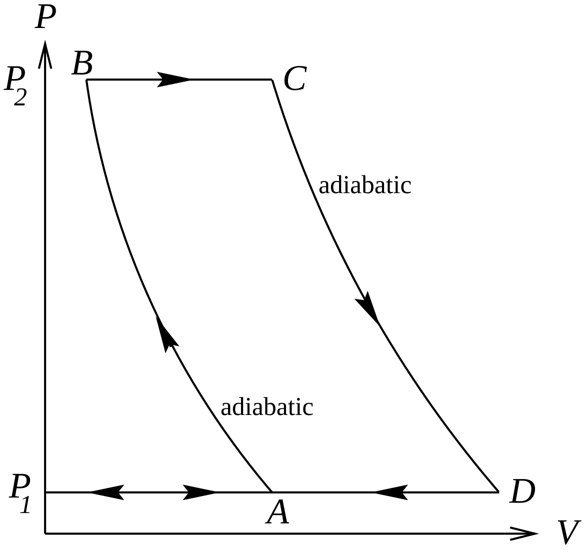
$$đQ = \frac{C_V}{nR}\, V\, dP + \frac{C_P}{nR}\, P\, dV.$$

   Applying this equation to an adiabatic transformation, prove that $PV^\gamma =$ constant, where $\gamma = C_P/C_V$.

7. (Zemansky and Dittman, Problem 6.1)

   The figure represents a simplified P-V diagram of the Joule ideal-gas cycle. All transformations are quasi-static and reversible, and C_P is constant. Prove that the thermal efficiency of an engine performing this cycle is given by

$$\eta = 1 - \left(\frac{P_1}{P_2}\right)^{(\gamma-1)/\gamma}$$



8. (Zemansky and Dittman, Problem 6.4)

   An ideal-gas engine operates in a cycle which, when represented on a P-V diagram, is a rectangle. Call P_1 and P_2 the lower and higher pressures, respectively, and call V_1 and V_2 the smaller and larger volumes, respectively.

   a) Calculate the net work done on the gas during one cycle.

   b) Calculate the net amount of heat transferred to the gas during one cycle. (You may assume that the heat capacities are constant.)

   c) Prove that the thermal efficiency of this engine is given by

$$\eta = \frac{\gamma - 1}{\dfrac{\gamma P_2}{P_2 - P_1} + \dfrac{V_1}{V_2 - V_1}}.$$

9. (Zemansky and Dittman, Problem 6.11)

   The initial state of 0.1 mol of an ideal, monoatomic gas is $P_0 = 32$ Pa and $V_0 = 8$ m^3. The final state is $P_1 = 1$ Pa and $V_1 = 64$ m^3. Suppose that the gas undergoes a transformation along the *straight line* joining these two points, with equation $P = aV + b$, where $a = -31/56$ and $b = 255/7$. Plot this line to scale on a P-V diagram. Calculate:

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,

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