

Chapter 2

First Law of Thermodynamics

Thermodynamics developed historically after mechanics, mainly in the XIX century. Development was motivated by two main needs, both outside of pure physics. The first motivation was the search to understand how the living creature “produces” energy; the second was the desire to develop engines capable of transforming heat, generated, for example, by the burning of coal, to produce mechanical work which otherwise had to be done by humans or animals. However, thermodynamics is not important for engineering and biology alone, but represents one of the fundamental chapters in physics.

In the first volume of this course, dealing with mechanics, we saw that, for an isolated system, the total energy, or, more precisely, the total mechanical energy, namely the sum of potential and kinetic energy, is conserved, i.e., remains constant, only if all acting forces are conservative. If dissipative forces are present, the energy appears not to have been conserved. However, this non-conservation is only apparent due to the fact that other forms of energy exist beyond the mechanical energy that we did not include in the balance. Thermodynamics shows us that all physical bodies contain energy, called internal or thermal energy, which does not depend on their velocity (like kinetic energy) or position (like potential energy) but on other variables, like temperature and pressure, which are called thermodynamic coordinates. Thermal energy can be exchanged between systems in two ways: one is work, which we already know, and the other is heat, which we shall learn about in this Chapter. Figure 2.1 shows the life spans of the major contributors to thermodynamics, starting with the theory of gases.

In 1824, the French engineer N.L. Sadi Carnot published the brief but fundamental article “Reflections on the motive force of heat”, in which he made completely clear the limits within which heat can be transformed into work, or, more precisely, the limit on the efficiency of any heat engine. Carnot developed his theory, which became the second law of thermodynamics, when heat was still believed to be a fluid, called “caloric”. Notwithstanding that, his arguments are completely correct. Forty years after his death in 1832 from the plague, his notes

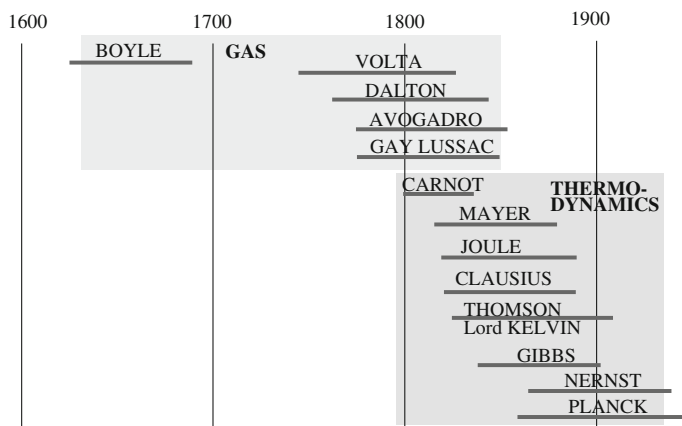


Fig. 2.1 Life spans of the fathers of thermodynamics

were published. Reading these notes, one can understand how the young genius had already understood the equivalence of heat and work.

Twenty-one years after Carnot's article, in 1845, R.J. Mayer published the paper in which he fully established the equivalence between heat and work. This is the first law of thermodynamics, which is the law of energy conservation. In the very same year, J.P. Joule published his simple and ingenious experiment, which we shall discuss in Sect. 2.7.

Thermodynamics is closely linked to mechanics. Indeed, all thermodynamic phenomena can be interpreted through statistical mechanics, as we shall see in Chaps. 5 and 6. All bodies are made of molecules, which are matter particles whose motion follows the laws of mechanics. However, the number of molecules is so huge that it is practically impossible to describe the motion of each of them in detail. But even if it were possible, such a description would be useless. As we have seen in the previous chapter, several of the motions of fluids have already proven incapable of being analytically treated with mechanics equations. Similarly, statistical mechanics considers suitable mean values of the kinematic quantities (velocity, kinetic energy, etc.) Historically, the development of statistical mechanics is mainly due to Maxwell and Boltzmann in the second part of the XIX century.

It is important to realize that thermodynamic and statistical mechanics points of view are different and complementary. The fundamental laws of thermodynamics are established by inference starting from the experiments. They are then assumed to be axioms; their consequences are logically deduced and experimentally controlled. The method is powerful because it allows for obtaining very precise results, while statistical mechanics is sometimes forced to introduce simplifying assumptions in order to be able to proceed. In addition, thermodynamic laws are general. They also hold for systems not composed of molecules, like electromagnetic radiation in a metal box. As a matter of fact, the discovery of quantum mechanics by Planck happened during the study of the thermodynamics of the electromagnetic

field. On the other hand, statistical mechanics unifies thermodynamics and mechanics by showing which elementary mechanical processes are at the basis of heat exchanges and, more generally, of all thermodynamic processes.

In this chapter, we shall start by introducing the concept of the thermodynamic system and the main thermodynamic variables, or coordinates, the pressure, the temperature and the volume. We shall define the thermodynamic state and discuss the different types of processes from one state to another and the equations that govern them. We shall then discuss the experiments and arguments that led to the establishment of the first law of thermodynamics and discuss its consequences.

2.1 The Thermodynamic State

Consider a certain amount of gas contained in a box. The constituent particles, i.e., the molecules, are free to move about inside the box and may have any velocity. There are no constraints, as there are for rigid bodies, limiting the degrees of freedom of the system. If we then want to know the mechanical state of the system, we need to know $6N$ parameters, the three coordinates and the three components of the velocity of each molecule. The number N of molecules being huge, this is impossible in practice.

In thermodynamics, the concept of the state of a system is different from that of the same system in mechanics. The thermodynamic state is defined by a small number of variables, which are different from the mechanical ones. We shall start with a few cases.

Homogeneous fluid of only one chemical species at rest contained in a box.

Think, for example, of a bottle of nitrogen under pressure, of a balloon full of helium, of a pot of water, etc. The quantities that we can easily measure are: the mass of the fluid m , its volume V , its pressure p and its temperature θ . We have considered the volume to be small enough so that the pressure and temperature may be the same at all points of the system. If the system were, for example, the earth's atmosphere, this would not be true. We have already defined the pressure; we shall subsequently define the temperature in the next section. For the moment, just consider what you would measure with a common thermometer.

We might think that the volume would not be enough to characterize the geometrical properties of the system. We might also think that we need to know its shape. The container of the water might be, for example, spherical or cubic, or taller than it is wide, etc. Why did we not include, for example, the area of the surface amongst the variables? Only the experiment can give the answer. As a matter of fact, we have experimentally found that the largest fraction of the thermodynamic properties of a fluid is independent of its shape. However, when the surface to volume ratio is large, as in fog droplets or soap bubbles, the surface must also be considered. We shall do that in Chap. 4.

Homogeneous solid body of only one chemical species.

In this, case we must consider, beyond the variables considered for a fluid, the shear stresses, and the pressures and tensions that can be present in the bulk of the body. Think, for example, of a metal parallelepiped subject to external tension along one axis and pressure on the perpendicular faces. Such situations quickly become complicated, and we shall not discuss them.

Rubber band.

The thermodynamic variables are the length and the temperature of the band.

System composed of one chemical species in different states (or aggregation phases).

Consider, for example, a system composed of liquid water and ice in a container at °C, or an alcohol and its vapor. To specify the thermodynamic state, we now need, beyond the already mentioned variables, the fraction of ice and water, or of alcohol liquid and vapor, etc., for each of the phases. This variable is called concentration.

System composed of more than one chemical species.

The thermodynamic state is defined by the variables: total mass, volume, pressure, temperature and concentrations of the different chemical species.

More complex to describe is the non-homogeneous system, in which some of the variables, for example, the temperature or the pressure, vary from point to point. To study them, one must divide the system into parts that are small enough to be able to be considered homogeneous. We shall not deal with any of these problems.

We shall always assume, as we have already implicitly done, that all of the system's parts are at rest, or moving so slowly that their kinetic energies can be neglected. Notice that the thermodynamic state of a system does not change if it moves all together. For example, the thermodynamic state of a pot of water at a certain temperature is the same whether it is on the ground or on a train moving at 300 km/h.

From what we have established, it is clear that knowledge of the thermodynamic state of a system gives very little to no information on the mechanical state of its molecules. Consider a gas contained in a box. The mass, volume, pressure and temperature are constant; its thermodynamic state does not vary. But its molecules move continuously, and their coordinates and velocities change. The mechanical state varies, while the thermodynamic one is constant.

Particularly important amongst the thermodynamic states are the states of thermodynamic equilibrium. These are the states that remain unaltered as long as the external conditions do not change. A state is of thermodynamic equilibrium when the following conditions are satisfied:

(a) *mechanical equilibrium.*

If, as is usually the case, pressure is one of the thermodynamic variables, it must be equal in all the parts of the system. Otherwise, movements would happen inside the system. Consider, for example, a gas inside a cylinder closed by a piston of surface S , which is movable without friction, as in Fig. 2.2. If p is the pressure of

Fig. 2.2 A gas in a cylinder closed by a movable piston

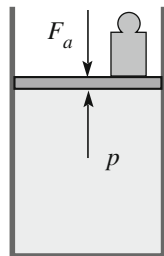
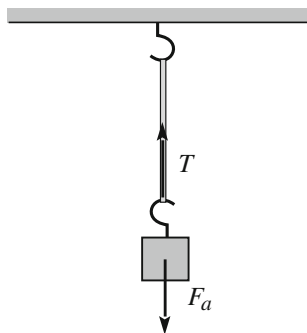


Fig. 2.3 Rubber band in equilibrium



the gas, the force exerted by the gas on the piston is pS , directed vertically up. Let us call the external force on the piston directed down F_a . This is the resultant of the force due to the atmospheric pressure, the weight of the piston and, possibly, of another weight that we laid on the piston. The mechanical equilibrium is reached when the gas pressure force is equal to F_a . If there is no weight on the piston and the weight of the piston itself is negligible, the internal pressure is equal to the external pressure at mechanical equilibrium. If the gas is enclosed in a rigid bottle, its pressure can be completely different from that which is external.

Going back to Fig. 2.2, suppose now that there is friction between the piston and the cylinder, as is always the case in practice. In this case, the mechanical equilibrium can exist, even if the pressure of the gas is larger or smaller than that which is external, as long as the force resulting from the pressure difference is smaller than the maximum static friction force.

As a second example, consider a rubber band fixed at one extreme and hanging vertically down, as in Fig. 2.3. If we apply a force F_a to the other extreme, the rubber band will stretch up to the deformation at which the elastic force T is equal to F_a .

(b) *thermal equilibrium.*

The first necessary condition is that all the parts of the system have the same temperature. Otherwise, temperatures tend to become equal and we do not have equilibrium. The second condition is that temperature should not vary due to the external environment. Suppose that, as is usually the case, the environment has a

definite constant temperature. Clearly, if the temperatures of the system and the environment are equal, the system is in thermal equilibrium. However, this is not a necessary condition. If the walls surrounding the system are thermally insulating, the temperature of the system does not vary even if different from that which is external. Walls having this property are said to be adiabatic, from the Greek words *a* (not), *dia* (through) and *bainein* (to go). Even if perfectly adiabatic conditions cannot be realized in practice, for example polystyrenes boxes or dewars make for good approximations.

(c) *chemical equilibrium*.

If there are more chemical species with thermodynamic equilibrium, the concentrations of the different species must be constant in time. The same is true if there is only one species, in different phases (liquid and solid, liquid and vapor, etc.)

2.2 Temperature

The concept of temperature is linked in the common sense of the world to the feeling of hot or cold. In physics, the concept must be precisely defined. We shall define temperature operationally, namely as the set of operations needed to measure it. We state immediately that we shall proceed by approximations, gradually increasing the precision of the definition. The reason for this is that the most precise definitions of temperature require thermodynamic concepts, which, in turn, require some knowledge of temperature. There is no risk of circular arguments, as we shall always rely on experiments.

Our simpler definition stems from the following considerations. We start from our own perception of “temperature” as a state in which an object is perceived as being either colder or hotter. We take two bodies of different temperature and put them in contact. We feel both temperatures and determine that they vary with time but, after a while, both become stationary. We conclude that the two bodies are in thermal equilibrium. Can we state that they have the same temperature? Not yet. We must pay attention to the fact that equality enjoys the transitive property; if A is equal to B and B is equal to C , then A should be equal to C . We need to check if the property is satisfied through experiment; we cannot state it through logic. Experimentally, we find that, if body A is in thermal equilibrium with body B and, separately, body B is in equilibrium with body C , then, if we put A and C in contact, their temperatures do not vary; they are in thermal equilibrium as well.

We can now define temperature as follows. We take two bodies, one, say A , is the thermometer, the other, B , is the body the temperature of which we want to measure. We put them in contact and wait for thermal equilibrium. If we now have a third body, C , which is in thermal equilibrium with B , the transitory property we have found insures that the thermometer A will measure the same temperature when put in contact with C as it did with B .

The traditional thermometers consist of a glass bulb containing a liquid connected to a capillary tube several centimeters long. When in contact with a warmer body, the liquid expands; the higher the temperature, the higher it rises in the capillary. Mercury was in standard use as thermometer liquid until the 1990s, when it was judged to be too risky to handle, being poisonous and thus potentially dangerous in cases of the glass accidentally breaking. Mercury was subsequently replaced as a thermometric liquid by colored alcohols. These thermometers, in turn, were soon replaced by so-called electronic thermometers. We shall come back to their working principles at the end of the section, and base our discussion on liquid-in-glass thermometers, which are conceptually simpler.

For quantitative measurement, we need a scale. To have a scale, we must fix two values, the zero and the step or degree of the scale, namely the unit. For that, we need two systems having a well-defined temperature. We observe that a mixture of pure water and ice always has the same temperature provided it is at the same pressure. We can check with our thermometer, even if we still lack a scale, by observing that it always sets at the same level when in contact with the mixture. The same is true for a mixture of water and its vapor in equilibrium at the same pressure. On the Celsius scale, zero ($0\text{ }^{\circ}\text{C}$) is defined as the water-ice equilibrium temperature at the standard atmospheric pressure. It is named after Anders Celsius (Sweden, 1701–1744). The standard atmospheric pressure is defined as $p = 1.013 \times 10^5\text{ Pa}$. A temperature of one hundred degrees ($100\text{ }^{\circ}\text{C}$) is defined as the water-vapor equilibrium temperature at the standard atmospheric pressure.

We can proceed as follows. We immerse our thermometer in the ice-water mixture at atmospheric pressure and mark a line on the capillary at the level of the thermometer liquid, writing a 0 on the tube. We do the same with the water-vapor mixture, and mark 100. We still need the degree. The best we can do is to divide the length between the two marks into one hundred equal parts. We can continue with the same step above 100 and below 0.

Pay attention, however. In dividing the length into equal parts, we have implicitly assumed that the length of the liquid in the capillary does vary linearly with temperature. Is that true? One way to check is to build, following the above procedure, a number of thermometers, say several made of different glasses, with different diameters, containing different liquids, etc. Then, we measure the temperature, which should be different from 0 and 100, of a reference body with all of them. We find that the readings of the thermometers are equal only upon first approximation. We can find differences of a few tenths of a degree between thermometers with the same liquid and up to a few degrees if the liquid is different. As a matter of fact, the thermal dilatation of the bodies is not exactly a linear function of temperature. In addition, the temperature reading depends on the glass as well and, even if only weakly, on the age of the glass.

In conclusion, the liquid-based thermometers are very simple, cheap and easy to use. They are particularly useful for somewhat imprecise measurements. However, in physics, temperature is a very important quantity, and must be defined as accurately as possible (as usual, infinite accuracy does not exist). The method is the ideal gas thermometer.

We preliminarily observe that the gas thermometer measures the *absolute temperature*. As a matter of fact, the Celsius scale (and the Fahrenheit scale as well) is arbitrary; it is not based on a physical law. However, a temperature exists that must necessarily be considered to be zero on a physical basis. This is called *absolute zero*. The most direct experimental evidence comes from the laws experimentally established by Alessandro Volta (Italy, 1745–1827), Joseph Louis Gay-Lussac (France, 1778–1850) and others. These heuristic laws were later included in the gas law that we shall discuss in the next section. We anticipate here that these authors found both the pressure of a gas at constant volume and its volume at constant pressure to be linear functions of the temperature, which was measured on the Celsius scale. An important observation was that both the pressure and the volume tend towards zero when the temperature tends towards the same well-defined value, which is $-273.15\text{ }^{\circ}\text{C}$. The same laws predict both pressure and volume to be negative below that temperature. This fact being meaningless, the temperature of $-273.15\text{ }^{\circ}\text{C}$ is the absolute zero. It is physically impossible to reach temperatures lower than that. The zero of the absolute temperature scale is the absolute zero.

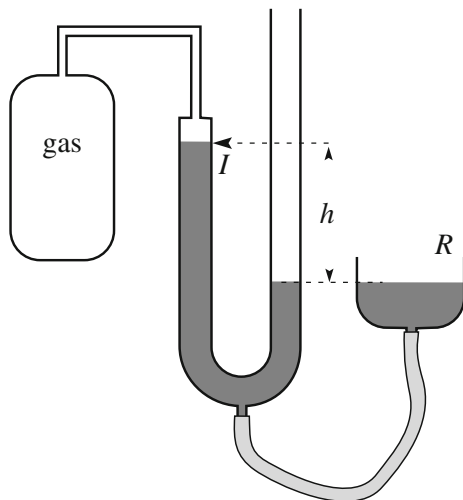
We now need the unit of temperature, which is called the kelvin¹ (K), after Lord William Thomson, Baron of Kelvin (UK, 1824–1907). The definition of kelvin is, as for the other units, the responsibility of the Bureau International des Poids et Mesures (BIPM, for short). The BIPM has changed the definition over time to make it as precise as possible, taking advantage of technological progress. The kelvin is defined by establishing the temperature of a fixed point. A mixture of the three phases of a substance, water in particular, is in equilibrium at a certain temperature and a certain pressure only. This is called the triple point. The water triple point temperature (water, ice and vapor in equilibrium) is by definition 273.16 K . The number has been chosen to have one kelvin be almost equal to the pre-existing one degree Celsius.

As we have already stated, the gas thermometer is a precision instrument. As such, it is not of simple use. Accurate procedures are required to reduce systematic errors as much as possible. We shall not enter into such issues, being interested here in the operation principles.

The thermometer, schematically shown in Fig. 2.4, consists of a bulb (made of quartz or metal) containing a gas, which is connected through thin tubing to a mercury manometer, so as to measure the gas pressure. All the pressure measurements are done *at constant volume*. We have also prepared the water, ice, and vapor mixture in equilibrium at the triple point. We are going to measure the temperature of a reference system, say a mixture of water and vapor in equilibrium at atmospheric pressure.

We put into the bulb a certain quantity, say m_1 , of a gas, say nitrogen. We then put the bulb in contact with the triple point bath. The auxiliary container R , which is connected to the manometer by a flexible rubber tube, is used, lifting or lowering it according to need, to ensure that the level of the mercury in the branch of the

¹Notice that the name is “kelvin”, not “degree kelvin” and that the symbol is K, not $^{\circ}\text{K}$.

Fig. 2.4 The gas thermometer

manometer on the side of the gas is always at the same level, for every measurement. The position is marked by the index I . In such a way, we guarantee that the volume of the gas will always be the same. The measurement of the height h gives the difference between atmospheric and gas pressures, and the latter when the atmospheric pressure is known. Let us call it p_{tr} . It is convenient to choose a mass m_1 small enough to have a rather low p_{tr} compared to the atmospheric pressure.

We now put the bulb in contact with the water vapor mixture. We measure the pressure as before and we call it p . We now preliminarily define the temperature of the mixture, assuming it to be proportional to the pressure, namely as

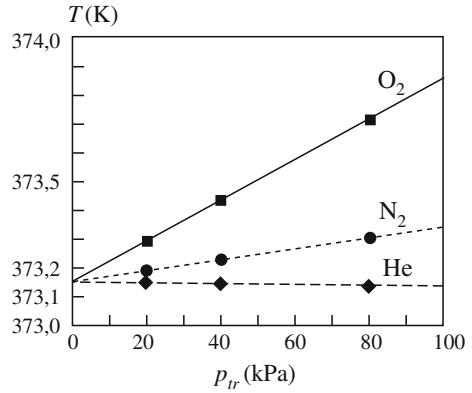
$$T(p) = \frac{p}{p_{tr}} 273.16 \text{ K} \quad (2.1)$$

where we anticipated in the notation that the so-defined temperature might depend on the pressure p .

The definition can be accepted only if we find the same result using another gas. In practice, this is not so. We perform three measurements with bulbs full of, respectively, nitrogen, oxygen and helium. We regulate the quantities of the different gases to obtain the same pressure at the triple point. It is equal to 80 kPa in this case. We find that the three pressures measured with the bulb in contact with the water-vapor mixture are a bit different. Consequently, the temperatures given by Eq. (2.1) are also a bit different. They are shown in Fig. 2.5 at the abscissa of 80 kPa. The differences are of a few tenths of a degree. They are small, but nonetheless tell us that the definition Eq. (2.1) is not sufficiently accurate.

We proceed, introducing into the bulb smaller quantities of the gases. The pressure measured at the triple point is now $p_{tr} = 40 \text{ kPa}$ for all the gases. We repeat the operations and find the three temperatures in Fig. 2.5 at the abscissa of 40 kPa. The values are now closer to one another. We perform a third set of

Fig. 2.5 Temperature, as defined by Eq. (2.1) measured with different gases and different pressures



measurements, again halving the pressures to $p_{tr} = 20$ kPa. We find that the measured temperatures get still closer. But Fig. 2.4 shows us more. If we linearly extrapolate the measurement made with each gas to zero p_{tr} , all of them lead to the same value! The extrapolated value does not depend on the gas we use. The behavior of the gases tends to be the same at zero pressure. The gas having this limit behavior is called an *ideal gas*.

In conclusion, we define ideal gas temperature, which is also the absolute temperature, as

$$T(p) = \left(\lim_{p_{tr} \rightarrow 0} \frac{p}{p_{tr}} \right) 273.16 \text{ K}. \quad (2.2)$$

In practice, the procedure just discussed is very delicate and requires weeks of work. The measurements are done in metrological laboratories. The temperatures of the triple points and, at a definite pressure, the fusion and boiling points of a number of pure substances are accurately measured. These points are then employed to calibrate secondary thermometers that are simpler to use.

The gas thermometer does not allow for measuring very low temperatures, because all gasses liquefy at low enough temperatures. The lowest liquefaction temperature is for He, at 4 K at atmospheric pressure. In practice, the lowest measurable temperature with the gas thermometer is about 1 K. Below that, the ideal gas temperature is not defined. We shall see in Sect. 3.5 how a temperature scale based on thermodynamic arguments can be defined. This is called thermodynamic temperature and is meaningful at all temperatures. In the interval of definition of both, the two scales coincide.

Many types of thermometers are commercially available. They are based on a number of temperature-dependent physical processes, work in a certain temperature range, and have different accuracies, depending on the use for which they are meant (medical, room, laboratory, etc.). Here, we recall only the already mentioned and very common electronic thermometers, also called digital because they display the

temperature on a digital screen. The majority of them are based on the thermoelectric effect; the electric resistance of some metal varies almost linearly with temperature. The resistance of the metal sensor is measured by means of an electronic circuit and displayed. The thermometers are calibrated by the production company. The accuracy is typically a few tenths of a degree ($\pm 0.1^\circ$ – 0.2° for medical models). Better accuracy can be obtained with thermistors, which employ the temperature dependence of the electric resistance of semiconductors.

We add a final consideration. In any temperature measurement, whatever the thermometer may be, the temperature of the thermometer is what is measured. Consequently, we must always ascertain that the thermometer is in thermal equilibrium with the object whose temperature we are measuring. In practice, the thermal contact between the two must be good, and one must wait for the equilibrium to be reached. In this process, there is always some heat transfer from body to thermometer, or vice versa. As a consequence, both temperatures vary. However, if the mass (or, even better, the heat capacity, which we shall define) of the thermometer is much smaller than that of the body, the temperature change of the latter is negligible.

Lastly, we notice that the water-ice equilibrium temperature at normal atmospheric pressure, namely 0°C , is equal to 273.15 K .

2.3 State Equation

Consider a homogeneous fluid made of a single substance. As we said, the thermodynamic coordinates of the system are the occupied volume V , the pressure p and the absolute temperature T , which we take in the kelvin scale. In order for the coordinates to have definite values, the system must be in thermodynamic equilibrium.

In our study, we shall consider only closed systems. Consequently, in its processes, the mass of the fluid does not vary. The state variables are then three: p , V and T . A system described by these variables is called a hydrostatic system. It is experimentally found that the three variables are not independent; only two of them are as such. For example, if a gas is enclosed in a given volume and we exert a certain pressure, then it assumes a well-defined temperature. Similarly, if we take a defined volume of a gas at a certain temperature, its pressure assumes a definite value. The relationship amongst the three values is called a *state equation* and can be expressed as

$$f(p, V, T) = 0. \quad (2.3)$$

Every hydrostatic system is characterized by its own state equation. No real system has a state equation that can be expressed analytically. It is, however, always possible, and extremely useful, to determine the equation experimentally. To do that, we put the system in a sufficiently large number of different states and measure

the thermodynamic coordinates in each of them. We have limited our considerations to hydrostatic systems for simplicity. Notice, however, that all the thermodynamic systems are ruled by a state equation that connects its state variables. We shall see an example at the end of the section.

As a consequence, two thermodynamic variables are sufficient to define any equilibrium state of a hydrostatic system of given mass. The most often used pair is volume and pressure. The equilibrium states are represented as points on the p , V Cartesian plane, with V as abscissa and p as ordinate. Clearly, only the positive part of the V axis is meaningful. The pressure is almost always positive too, but it may exceptionally be negative.

Several scientists in the XVII and XVIII centuries were responsible for developing the physics of gases and, in particular, their thermodynamics. We have graphically represented the life spans of the main contributors in Fig. 2.1. They are: Edme Mariotte (France, 1620–1684), Robert Boyle (UK, 1627–1691), Alessandro Volta (Italy, 1745–1827), John Dalton (UK, 1766–1844), Amedeo Avogadro (Italy, 1776–1856) and Joseph Louis Gay-Lussac (France, 1778–1850).

The results of their work can be summarized as follows. If we change the volume of a gas, keeping its temperature fixed, the pressure varies in almost inverse proportion to the volume. In other words, the product of pressure and volume remains nearly constant at constant temperature. If the temperature varies, the product of pressure and volume vary proportionally to it, provided it is the absolute temperature. The proportionality constant is, in turn, proportional to the mass of the gas. The state equation of the gas we are considering is thus

$$pV = rmT$$

where r is the proportionality constant, which is different for different gases. The equation is very simple and, as we shall now see, contains a lot of information. But there is more to it.

A quantity of a well-defined substance can be measured in two units: the kilogram, which measures its mass, and the *mole*, which measures its number of molecules, which are of one species only because the substance is defined. The symbol of the mole is mol. A mole of a substance is an Avogadro number of molecules of that substance. When the mole was defined, and originally called a gram molecule, the unit of mass was the gram. The molecular masses were defined in grams as well. A mole is the number of grams of the considered substance that contains an Avogadro number of molecules. For example, a mole of hydrogen has a mass of one gram. The Avogadro number is one of the fundamental constants of physics. Its first digits should be remembered by heart. It is very large, namely

$$N_A = (6.02214129 \pm 0.00000027) \times 10^{23} \text{ mol}^{-1}. \quad (2.4)$$

Coming back to the gas equation, let us express the quantity of gas in number of moles, $n = m \times 10^{-3}/M$, where M is the molar mass of the substance and the 10^{-3} factor is due to the fact that m is in kilograms. The state equation becomes

$$PV = nRT \quad (2.5)$$

where R is a new constant ($R = rm/n$). Up to now, we have simply re-defined the proportionality constant. However, what matters is that experiments show that R is a universal constant, namely that it is the same for all gases. This is called the *gas constant*. Its value is

$$R = 8.3144598 \pm 0.0000048 \text{ J mol}^{-1} \text{ K}^{-1}. \quad (2.6)$$

Rigorously spiking, no gas follows Eq. (2.5) exactly. However, the most common gases, such as the gases in the atmosphere, behave approximately according to that equation in a large interval of pressures and temperatures. The approximation is better the higher the temperature and the lower the pressure. The *ideal gas* is defined as a gas that rigorously obeys Eq. (2.5). This is called the *ideal gas equation*, but also the *Boyle law* and *Boyle-Mariotte law*. We can see now that the definition of absolute temperature given in the preceding section was based on this law.

A fundamental implication of the gas law was established in 1811 by Amedeo Avogadro. The Avogadro law states that *equal volumes of different (ideal) gases with the same conditions of temperature and pressure contain the same number of molecules*. Today, we see that this is an immediate consequence of the universality of the R constant. A useful quantity is the *molar volume*, which is the volume occupied by a mole of (ideal) gas at, as it is called, STP, meaning standard temperature and pressure. These are defined as $T = 273 \text{ K}$ (about 0°C) and $p = 10^5 \text{ Pa}$ (about one atmosphere). The molar volume of ideal gases is

$$V_m = 0.0224 \text{ m}^3 = 22.4 \text{ L}. \quad (2.7)$$

The gas equation Eq. (2.5) contains several heuristic laws that were discovered by different researchers, as mentioned in the previous section. Very importantly, it contains the law discovered in 1801 by John Dalton, called the *Dalton law* after him, and also the *law of partial pressures*. The law states that: “*In a mixture of different gases the partial pressure of each of them is the pressure it would exert if it occupied all the volume alone.*” It is as if each gas was kept unto itself without any interaction with the other ones. The Dalton law is rigorously valid for the ideal gases.

We close this section considering an example of a non-hydrostatic thermodynamical system; the rubber band represented in Fig. 2.3. The thermodynamical variables are the length l and the tension τ , which depends at equilibrium on the applied force F_a , and the temperature T . The elastic constant of rubber depends on the temperature, increasing as the temperature increases. The rubber becomes “harder” if heated. In other words, for a fixed length, the tension depends on temperature. We can also find that stretching the band causes its temperature to increase, while relaxing the band causes it to diminish. Even in this case, there is a state equation, linking the three thermodynamical variables. Only two of them are independent. However, this equation of state cannot be expressed analytically.

2.4 Processes

A thermodynamic process, or thermodynamic transformation (the two terms are synonyms), happens when a thermodynamic system changes from an initial to a final state. Generally speaking, each of them can be an equilibrium state or not. However, we shall only consider the former case. The states of the system during transformation can never be rigorously of equilibrium, because an equilibrium state is stationary. We shall now define different types of processes.

Quasi-static processes. A process is said to be quasi-static if the states taken by the system differ from stationary states by infinitesimal quantities. In practice, the coordinates of the system should vary very slowly, allowing it the time to adjust to the changed conditions before the coordinates change again. The initial and final states of a quasi-static process are necessarily equilibrium states.

Consider, for example, a gas in a cylinder closed by a piston. If we want to increase its pressure in a quasi-static manner, we must move the piston slowly. At each small displacement of the piston, the pressure of the gas increases in a layer immediately under the piston. The other parts of the gas still have the initial pressure. Soon, the pressure increase propagates gradually throughout the volume. The piston must move slowly enough to allow the pressure throughout the gas volume to reach (close to) the same value. If we lay a heavy weight on the piston and abandon it, the piston will move down quickly and the process will not be quasi static. Contrastingly, if we gradually pour some sand on the piston, the process will be quasi-static.

Reversible processes. A process is reversible if it is quasi-static and if dissipative forces are negligible. Consider a generic state P in a certain instant of a quasi-static process. P is almost an equilibrium state. Immediately before that instant, an infinitesimal variation of the external conditions, the system was in a state infinitely near to P . If the process is reversible, when we invert the infinitesimal variation of the external conditions with the system in P , the system goes back to the state it was in immediately before P .

Let us again consider the gas contained in a cylinder, as in Fig. 2.6. Suppose friction to be present between the piston and the cylinder. The force F_a is applied externally to the piston, normally downward. To have a quasi-static expansion process, we slowly decrease the applied force. Assume a friction force F_r to be present. Its direction is opposite to that of the motion. The gas exerts a force pS on the piston directed vertically upward. To have the piston moving up, it should be $F_a < pS - F_r$, as in Fig. 2.6a. If we want the motion to be slow, the inequality should be just satisfied.

The process is quasi-static but not reversible. Indeed, if we want to invert the process, namely to compress the gas and have the piston moving down, we must increase F_a , but not only by an infinitesimal quantity. This is because the friction force, which always opposes the motion, changes signs and is finite, not infinitesimal. The condition becomes $F_a > pS + F_r$, as in Fig. 2.6b.

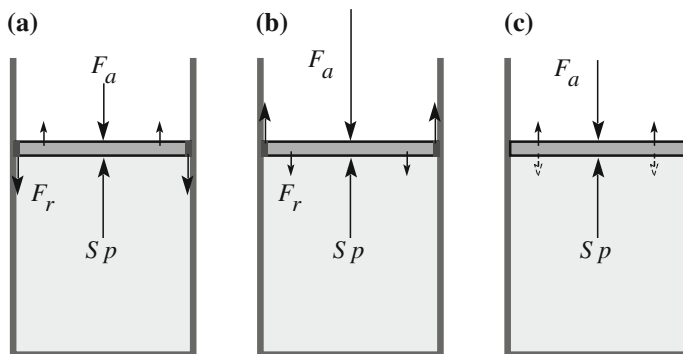


Fig. 2.6 Forces on the piston. **a** Expansion, with friction, **b** compression, with friction, **c** reversible, no friction

We see that, in order to pass from expansion to compression, changing the external conditions by an infinitesimal quantity (the force F_a in the example), the friction must be zero, as in Fig. 2.6c.

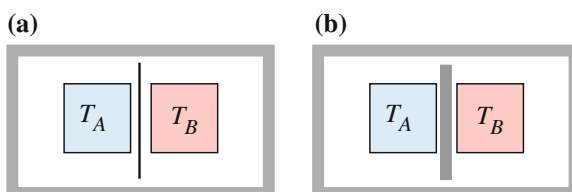
Rigorously speaking, quasi-static processes do not exist, and even less so the reversible ones. However, we can often operate in conditions that are close enough.

Irreversible processes. All the processes that are not reversible (all the natural ones), namely when dissipative effects are present, or the system goes through states that do not only differ by infinitesimals from equilibrium states (or both), are irreversible.

Cyclic processes. A process is cyclic if initial and final states coincide. Clearly, a reversible process can be quasi-static, reversible or irreversible.

We now define the *adiabatic wall*. Consider two systems A and B at different temperatures, T_A and T_B , respectively. If we put them in contact, both temperatures vary until they become equal. We make a series of experiments with plates of different materials introduced between the two systems, as shown in Fig. 2.7. We find that the time necessary to reach thermal equilibrium, starting from the same temperatures, are different for different materials. If the plate is metallic and thin, the time is very short; if it is foamed polystyrene and thick, the time is very long. Other materials give intermediate results. The materials of the first type are called *good thermal conductors*, those of the second, *good thermal insulators*.

Fig. 2.7 Thermodynamic systems at different temperatures separated by (a) diathermic wall, (b) adiabatic wall



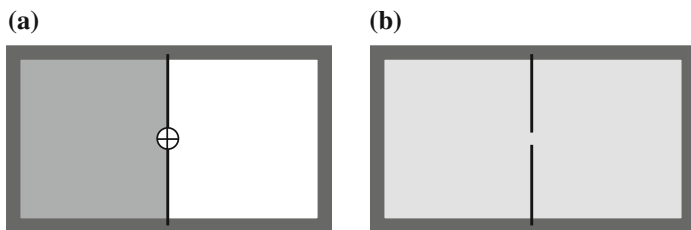


Fig. 2.8 A gas in an adiabatic and rigid box. **a** All the gas on the *left-hand side*, tap closed, **b** gas in all the box, tap open

Two idealized cases are considered. We call walls perfectly permeable to heat *diathermic walls* and walls that completely block the heat transfer *adiabatic walls*. When two systems are separated by a diathermic wall, the temperature equilibrium is reached exactly as if the wall was not present; if the wall is adiabatic, each system keeps its temperature indefinitely.

Figure 2.8 represents two thermodynamic systems closed in a single container. The walls of the container are adiabatic; the two systems can interact with one another, but not with the environment.

A system is *closed* if it does not exchange matter with the surrounding environment. A pot of water boiling on the fire is not a closed system (even with a cover), because vapor exits; water in a pressure cooker, before it whistles, is a closed system.

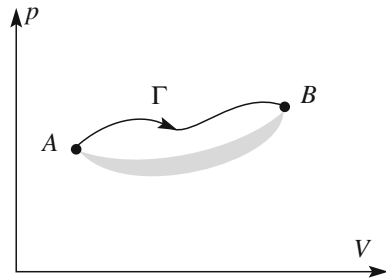
A thermodynamic system is *isolated* if it can exchange neither mass nor energy with the environment. A necessary condition is for it to be completely enclosed in adiabatic walls. The condition forbids energy exchanges as heat (see discussion in the following section), but not as work. Consequently, the condition is not sufficient.

An isolated system in an equilibrium state remains indefinitely in that state. To move it out of that state, it is necessary to add energy to it or subtract energy from it, which is not possible by definition. If, contrastingly, the system is initially in a non-equilibrium state, it spontaneously performs a process that brings it to an equilibrium state. The processes of this type are called *spontaneous processes*. Consider, for example, the two parts of a system, isolated from the external environment, in thermal contact at different temperatures in Fig. 2.7a. They are not in an equilibrium state. The system spontaneously evolves towards the equilibrium state in which the temperatures are equal.

Consider a container with adiabatic and rigid walls. A diaphragm with a tap divides the container into two halves. The half on the left-hand side contains a gas; the half on the right-hand side is empty. This is an equilibrium state, but ceases to be one when we open the tap. The system then spontaneously evolves until the point when the gas occupies the entire volume with uniform pressure. The system is now in equilibrium and its state no longer changes.

Obviously, all spontaneous processes are irreversible.

Fig. 2.9 A and B are equilibrium states of a hydrostatic system. Of the two processes, Γ is reversible, the grey area is not



As we already mentioned in the previous section, we can represent any equilibrium state of a hydrostatic system with a point on a Vp plane. In Fig. 2.9, points A and B represent equilibrium states. The non-equilibrium states cannot be represented by points, because at least some of their thermodynamic coordinates are not defined. In this case, only V is defined, because the system is in a rigid container, while the pressure and the temperature are not defined. A quasi-static process is represented on the Vp plane by a curve; the points of the curve are the equilibrium states crossed by the system. The curve Γ in the figure is an example of a quasi-static process from A to B . If the process is not quasi-static, even if it joins two equilibrium states, it cannot be represented by a curve. In Fig. 2.9, we have schematically drafted such a process with a grey area, to indicate the lack of definition of the intermediate states.

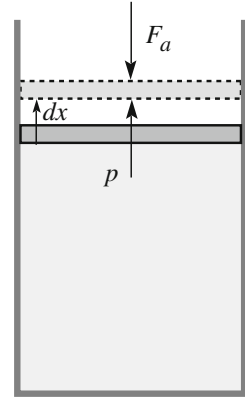
2.5 Work

Any hydrostatic system has a definite volume bounded by surfaces that may be the surrounding walls of a container, the free surface of a liquid, etc. The system can interact with the surrounding environment by exchanging energy through its surfaces. External forces may be present and exert work, as defined in mechanics, on the system. The following convention is adopted in thermodynamics: work is positive if exerted on the system, negative if exerted by the system. The underlying reason for this is the fact that thermodynamics began historically as the science of engines.

The forces with which the system exchanges work with the surroundings act on its surfaces. They can do work only if their application points move, meaning that at least part of the surface must move. Movement of the surface is, however, not sufficient. To have work, the volume of the system must also change, as we shall now see.

Consider the simple system of Fig. 2.10, which is a gas contained in a cylinder with mobile piston of area S . Let p be the pressure and F_a the external force, perpendicular to the piston. Suppose that the friction between piston and cylinder is negligible. Consider a reversible expansion. The piston moves very slowly. The

Fig. 2.10 Forces acting on the piston, in absence of friction



forces on the piston are F_a and the pressure of the gas Sp . The latter is larger than the former by a mere infinitesimal quantity. The work done by the pressure forces of the gas for an elementary displacement dx of the piston is

$$\delta W_g = pSdx = pdV \quad (2.8)$$

where, at the last member, we have taken into account that $S dx$ is the volume variation dV . The work of the external force F_a is

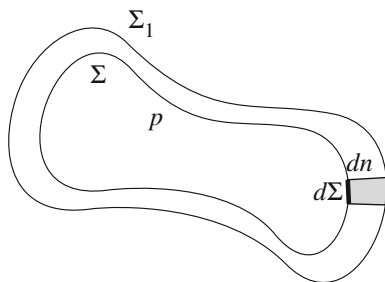
$$\delta W_e = F_a dx. \quad (2.9)$$

Notice that in both expressions, we have used the symbol δW rather than dW , because these are infinitesimal quantities but are not, in general, the differentials of any function, namely they are not exact differentials.

The two works we have expressed are equal in magnitude, because the two forces are equal. Notice, however, that if the friction is not negligible, and the process is quasi-static but not reversible, the two works are different. In this case, the work of the pressure force is larger, because it acts against the sum of F_a and the friction force (see Fig. 2.6). If the process is not even quasi-static, the gas goes through non-equilibrium states, in which the pressure is not even defined. Equation (2.8) loses its meaning. However, we can calculate the external work made by the gas on the surroundings even if the process is irreversible. Indeed, the motion of the piston very often takes place to produce a useful work (raising a weight, rotating the axis of an engine, etc.). In all these cases, an external force, F_a , acts against the motion and we can use Eq. (2.9) to calculate the work done. If friction is present, the work against the friction force must be added.

Within the mentioned limitations, the expression of the elementary work of the pressure force for a variation of the volume can be generalized to surfaces of any shape. Consider a hydrostatic system with pressure p enclosed in a surface Σ of arbitrary shape (see Fig. 2.11). Consider an infinitesimal quasi-static process in which the surface changes to Σ_1 . The process being quasi-static, the pressure

Fig. 2.11 Infinitesimal expansion of a hydrostatic system



remains definite and independent of the position. Let $d\Sigma$ be an infinitesimal surface element and dn the magnitude of its displacement, measured normally to the surface. The pressure force of the gas on the surface element is $p d\Sigma$. Its work is $p d\Sigma dn$. We obtain the total work by integration on the surface. p being constant, we have $\delta W = p \int_{\Sigma} dn d\Sigma$. As we see in the figure, the quantity $\int_{\Sigma} dn d\Sigma$ is the volume variation dV , and we thus get

$$\delta W_g = p dV. \quad (2.10)$$

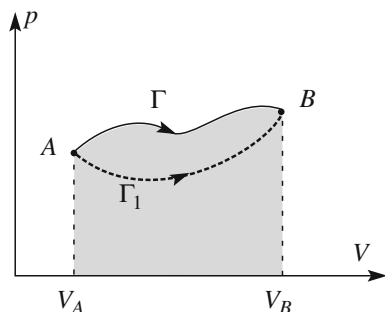
The work done by the gas in a quasi-static process Γ , from state A to B , is obtained by integration

$$W_{AB;\Gamma} = \int_{A;\Gamma}^B p dV. \quad (2.11)$$

In general, the work depends not only on the initial and final states, but also on the particular process joining them.

Consider the quasi-static process Γ of a hydrostatic system from the initial state A to the final state B . In the plane Vp , the process is represented by an oriented curve, which we also call Γ , as in Fig. 2.12. In the process, the system goes through states having definite values of pressure and volume. We can then consider the pressure to be a certain function $p(V)$ of the corresponding volume. The curve in the Vp plane represents this function. The work in the process is

Fig. 2.12 Two quasi-static processes between the same initial and final states



$$W_{AB;\Gamma} = \int_{V_A;\Gamma}^{V_B} p(V) dV \quad (2.12)$$

where V_A and V_B are the volumes of the initial and final states. Graphically, the work is the area under the curve, which is grey in the figure. The work is positive if the final volume is larger than the initial one, and negative in the opposite case. We easily understand how, if the process between the same states is changed, the work changes too, in general. The work for a different process, as with Γ_1 in the figure, is the area under this curve, which is different from the area under Γ .

Up to now, we have implicitly assumed the process to be such that the system has a certain state only once. Only in this case, the function $p(V)$ is single-valued. If this is not the case, it is always possible to divide the process into parts, for which p is the single valued function of V . Let us look at an important example.

In a cyclic process, the system starts from a state, goes through the process and then returns to its initial state. A cyclic quasi-static process of a hydrostatic system is represented by a closed curve in the pV plane. Figure 2.13 shows such a process starting from the initial state I and eventually coming back to it.

The work generated by the system in the cycle is, geometrically, the area enclosed within the cycle taken with the positive sign if the direction is clockwise, and negative if it is anti-clockwise. Let A and B be the states of minimum and maximum volume reached through the process, respectively. Let Γ_1 be the section of the process from A to B and Γ_2 the section from B to A . The work done in section Γ_1 is the area under this curve and is positive. The work done in section Γ_2 is the area under it and is negative. The total work is the difference between the two areas, corresponding to what we have stated. It is immediately understood that the work would have been negative if the sense was anti-clockwise. Notice that work is a definite quantity when the cycle is given; it does not depend on the initial and final state I .

Isochoric process. A process is said to be isochoric if the corresponding external work is zero. When the work can be expressed by Eq. (2.10), we must have $dV = 0$ for all the elements of the process, namely the isochoric processes must take place at constant volume. As a matter of fact, that is the meaning of the name (in Greek, *iso* means equal, and *choros* means space). However, the definition is more general. A process may also be isochoric when Eq. (2.10) does not hold.

Isobaric process. This is a process at a constant pressure.

Fig. 2.13 Cyclic quasi-static process of a hydrostatic system

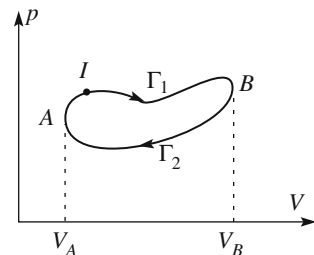
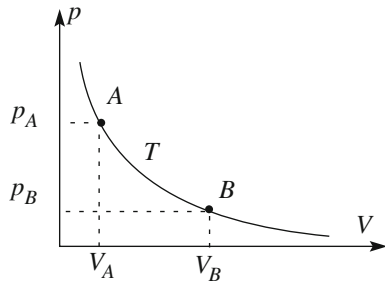


Fig. 2.14 Isothermal process in a gas



Let us calculate the work of a hydrostatic system in an isobaric process. This is immediate. The pressure being constant, we can take it out of the integral and write

$$W_{AB} = \int_A^B p dV = p(V_B - V_A). \quad (2.13)$$

Isothermal process. This is a process at a constant temperature.

The isothermal curves for a gas in the Vp plane are hyperbolas having asymptotes on the axes. Let us calculate the work of n moles of an ideal gas in an isothermal process from $A = (p_A, V_A, T)$ to $B = (p_B, V_B, T)$, represented in Fig. 2.14. Using the gas state equation Eq. (2.5), we have

$$W_{AB} = \int_A^B p dV = \int_A^B \frac{nRT}{V} dV = nRT \int_A^B \frac{dV}{V} = nRT(\ln V_B - \ln V_A).$$

The last member looks strange, because the arguments of the mathematical functions should always be dimensionless. But it is just a matter of writing it. Indeed, the difference between two logarithms is the logarithm of the ratio of their arguments. It is better for us to write the expression in the form

$$W_{AB} = nRT \frac{V_B}{V_A}. \quad (2.14)$$

2.6 Heat

We have mentioned several times that if two systems at different temperatures are brought into thermal contact, their temperatures will vary until they become equal. In this type of process, the two systems exchange energy. The form of exchange is not work, because nothing is moved mechanically; rather, the form of exchange is heat. Heat is an energy exchange between two systems at different temperatures, as we shall now discuss.

We warn the reader that the common linguistic use of the word “heat” might generate confusion in this case. Indeed, the common language often uses the words “heat” and “temperature” interchangeably. In physics, however, they have very different meanings. We have already discussed temperature; we shall now discuss heat.

The physical dimensions of heat are the same as those of energy. However, heat is NOT energy. Similar to work, heat is an ENERGY EXCHANGE. Heat, as work, cannot be “owned” by a system. If one moves a book that is on the floor up onto a shelf, one does work on the book. Nobody would think that the book now “has” that work. It has potential energy, relative to the floor, which is equal to that work. In the common language, we say that friction “produces” heat. For example, brakes become hot when they act. But no heat has been produced. Even more to the point, no heat has been exchanged. Instead, the friction forces have done work, the kinetic energy of the car has decreased and the temperature of the brakes has increased. As we shall see, the temperature increase corresponds to an increase in the internal energy of the brakes.

Another example of confusion is sentences like: “I have been in Texas and the heat was unbearable”. What was unbearable was the temperature, not the heat. The very word “hot” tends to induce confusion, as it comes from heat. However, a body is hot not when it “has” a lot of heat, but when its temperature is high. In physics, we repeat, heat is always an exchange. To talk of heat, at least two systems must be present, not only one.

Let us now precisely define heat. We will give an operational definition, namely we define the set of operations needed to measure heat. The instruments used to measure heat are calorimeters. By definition, heat is the physical quantity measured with a calorimeter. We must thus define the calorimeter.

In thermodynamics, by convention, heat is positive if absorbed, negative if released by the system. The reader will note that the conventions on the sign for heat and work are opposite. This is a consequence of the fact that thermodynamics was developed to build engines able to absorb heat and produce work.

The calorimeter is itself a thermodynamic system. It is made of a substance, called the calorimetric substance, sealed inside a container. The substance is often pure water or ice or a mixture of the two. The masses of the substance are known, having been measured. To measure a heat exchange, we need a second system, a body that gives out or absorbs the heat to be measured. The exchange must take place with the calorimeter alone. Consequently, the calorimeter and the body must be enclosed in an adiabatic container, to forbid, as much as possible, any heat exchange with the surroundings.

We know that heat exchanges produce temperature changes. The simplest, preliminary choice is assuming the temperature change to be proportional to the heat exchange, at least for variations of the former that are not too large. We must then guarantee that no other thermodynamic variable actually varies but temperature. First, we shall work at constant volume. Consequently, we shall use a liquid or a solid as the calorimetric substance, whose volume does not vary much with temperature, and we shall avoid gases. Second, we shall work at constant pressure. Third, we shall avoid chemical reactions, by using pure substances.

Let us now build our calorimeter. As an adiabatic container, we shall use a vacuum flask, technically known as a Dewar flask. This type of vessel, called a thermos, greatly lengthens the time over which its contents remain hotter or cooler than its surroundings. The technique was invented by James Dewar (UK, 1842–1923) in 1892. It consists of two flasks, one inside the other, joined at the neck. The walls of the flasks are made of thin glass and are aluminized like mirrors. The gap between the flasks is evacuated. In this way, the different modes of heat transmission, convection, conduction and radiation (which we shall study in Chap. 6) are strongly reduced. The flask has an opening that can be closed with an insulating plug.

We introduce a certain quantity of pure water into the flask, of which we have measured the mass, m , and the temperature, T_i . The system that exchanges heat with the calorimeter can be, for example, a piece of metal that we heat at a temperature higher than T_i . We introduce the body into the calorimeter and close the plug. In the calorimeter, we also have a thermometer. We see the measured temperature increasing and finally becoming constant at a certain value T_f . The heat given out by the body and the heat absorbed by the water are equal because the system is isolated. We can say that this heat Q absorbed by the water is proportional to $T_f - T_i$.

As one can imagine, the temperature rise $T_f - T_i$ depends, for the same absorbed heat, on the mass of water. We find experimentally that the product of the water mass and the temperature difference $m(T_f - T_i)$ is proportional to the absorbed heat. We finally state that

$$Q = cm(T_f - T_i). \quad (2.15)$$

The proportionality constant c depends on the substance. If we had used, for example, an oil or an alcohol in place of water, we would have found different values. The constant is called the *specific heat* of the substance. The measurement unit for heat, which is the *kilocalorie*, is defined by fixing the specific heat of the water, to be exact, at a certain temperature.

The definition is as follows: *The kilocalorie is the heat quantity that must be given to a kilogram of water in order to increase its temperature from 14.5 to 15.5 °C, at the constant pressure of one atmosphere.*

The temperature of the exchange must be specified because the specific heat varies, even if not by much, with the temperature.

We note here that the calorimetric measurements are always very delicate. For example, the thermal insulation, even if good, is never perfect, and corrections must be applied to the measurements to take into account heat leaks. What is interesting here is the principle of operation of the calorimeter.

We finally note that, heat being the physical dimension of energy, its unit in the SI is the joule. We need the provisional calorimetric unit of the kilocalorie, for the following discussion.

2.7 Equivalence of Heat and Work

The equivalence between heat and work was established for the first time by Julius Robert von Mayer (Germany, 1814–1878) in a paper published in 1845. We shall specify here what “equivalence” means.

We have seen that both work and heat are forms of energy exchange. The two quantities are measured in completely different manners and a priori look very different. However, they are strongly connected. Indeed, engines absorb heat and produce work. Let us look at two examples.

In the first example (Fig. 2.15a), which is a system we have already considered, the gas is contained in a cylinder closed by a piston, on which there is a weight, producing the force F_a . Suppose now that we give heat to the system using a flame through the bottom of the cylinder, which is diathermic. We observe that the gas expands and the piston rises, elevating the weight with it. Work is produced. The process is the constant pressure expansion we considered in Chap. 5.

In the second example, which we have also already considered, we have a weight hanging on a rubber band (Fig. 2.15b). If we gently heat the band with a flame, it contracts, because the elastic constant increases with the temperature. The weight rises. Again, the system absorbs heat and produces work, which is the product of the tension (that is constant) and the displacement.

We cannot conclude from these examples that the work produced by a system is equal to the heat it absorbs. As a matter of fact, both exchanges also vary the energy of the system. Here, we mean energy related to the internal, thermodynamic state of the system, which is different from the mechanical kinetic and potential energies. It is the *internal energy* of the system that we shall define in the next section. Before

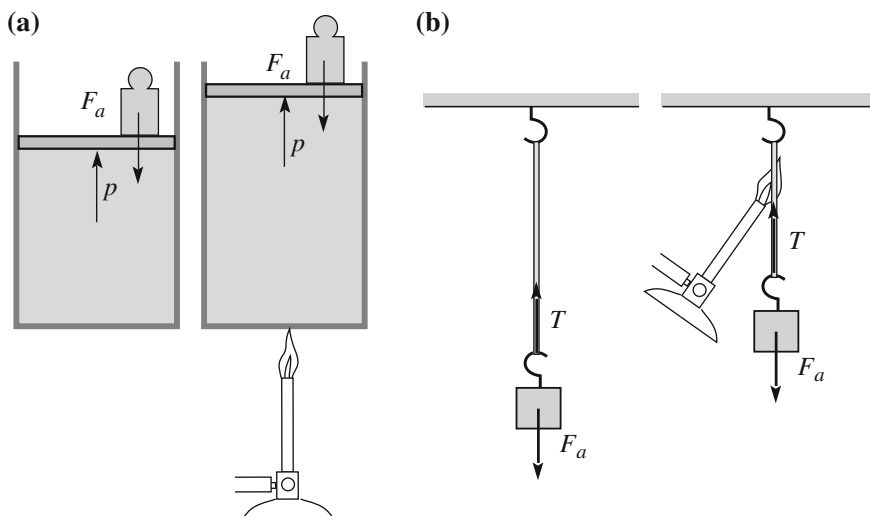


Fig. 2.15 **a** A gas in a cylinder, **b** a rubber band

doing that, we shall prove its fundamental property: that the variation of the internal energy of a system is always equal to the algebraic sum of the heat received and the work done. This is the first law of thermodynamics.

Indeed, the first law of thermodynamics is the energy conservation law. In mechanics, the energy of an isolated system is conserved only if all the acting forces are conservative. The decrease of *mechanical* energy observed in the presence of dissipative forces does not really mean that energy is not conserved. The point is that the mechanical energy is not the only form of energy in the game. As a matter of fact, the energy that seems to be lost actually did transform into internal energy.

Clearly, what we have just stated needs to be experimentally proven. We shall now describe the elegant and fundamental experiment conducted by James Prescott Joule (UK, 1818–1889) in 1845. The experiment establishes what is known as equivalence between heat and work. More importantly, it establishes the existence of internal energy.

Figure 2.16 shows a schematic of the experiment, which is performed in two phases, (a) and (b) in the figure. A thermally-insulated vessel contains water (or another liquid). A vertical axis with a number of horizontal vanes is placed inside of the vessel with enough room so that it can rotate under the action of two external weights linked to a system of pulleys. Other vanes soldered onto the walls are interleaved with the mobile ones to hinder the common mode motion of the water. The water is forced to move slowly between the vanes, to maximize the mechanical energy dissipation in the liquid.

We determine the initial state of the system by measuring its mass M and its temperature T_i . The mass of each weight is m .

In the first process, we perform the mechanical work W_1 on the system with no heat exchange ($Q_1 = 0$). We take the weights in their higher position and let them descend. They move very slowly and we can neglect their kinetic energy. We measure the drop h . The work done on the system (remember the sign convention) is $W_1 = -2mgh$.

In the second process, we bring the system back into its initial state. We do that extracting heat without any work being done ($W_2 = 0$). We take the thermal

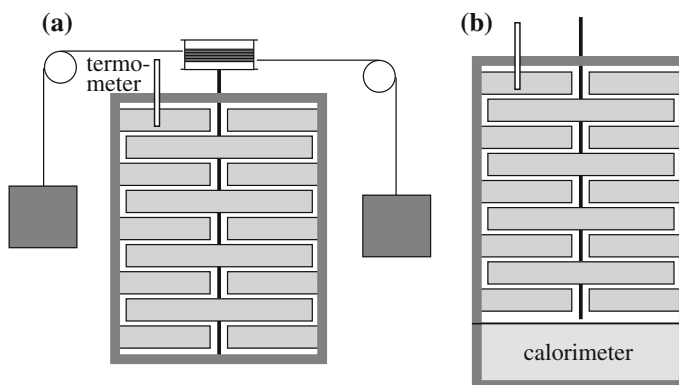


Fig. 2.16 The Joule experiment; (a) the first process; (b) the second process

insulation off of the bottom of the vessel and we lay it on a calorimeter, as shown schematically in Fig. 2.16b. While the system gives away heat to the calorimeter, we measure its temperature, and we stop the process when it is back to the initial value T_i . Let Q_2 be the heat measured by the calorimeter, which is also the heat given away by the system. Overall, the process is a cycle.

The total work in the cyclic process is $W = W_1 + W_2 = W_1 + 0 = W_1$ and the heat exchanged is $Q = Q_1 + Q_2 = 0 + Q_2 = Q_2$. We take the ratio between the two quantities we measured and we find

$$\frac{W}{Q} = 4186 \text{ J/kcal.} \quad (2.16)$$

Up to now, we have not proven anything. Indeed, the ratio of two quantities must have a value. However, if we repeat the experiment with different quantities of water, different liquids, different quantities of work, etc., provided that the process is cyclic, we find that the ratio of total work and total heat *always* has the value of Eq. (2.17), within the experimental uncertainties. The symbol for the ratio is J and we write that, for *every cyclic process*,

$$J \equiv \frac{W}{Q} = 4186 \text{ J/kcal.} \quad (2.17)$$

J is called the *mechanical equivalent of heat*. We can also state, in an equivalent manner, that experiments show that. In any thermodynamic cyclic process, the equation

$$JQ - W = 0 \quad (2.18)$$

holds, where W is the sum of all the works taken as positive if done by the system, negative if done on the system, and Q is the sum of all the heat exchanges, taken as positive if absorbed by the system, negative if released by it. Notice that we established the equation using irreversible processes. The equations we found, Eq. (2.19) in particular, hold for any cyclic process.

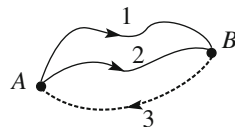
Having shown that heat and work are homogenous physical quantities, we can measure both of them in the same measurement unit. From now on, we shall measure the heat in joules. Equation (2.18) becomes

$$Q - W = 0. \quad (2.19)$$

2.8 First Law of Thermodynamics

In the previous section, we experimentally established an extremely important law of physics, the law of energy conservation.

Fig. 2.17 Processes from A to B and from B to A



Let us demonstrate that. Consider two different equilibrium states A and B of any thermodynamic system and two arbitrary processes 1 and 2 from A to B , as well as a third one 3, from B to A , as shown Fig. 2.17. The processes 1 + 3 and 2 + 3 are cyclic. We then apply Eq. (2.19) to both of them, obtaining $(Q - W)_1 + (Q - W)_3 = 0$ and $(Q - W)_2 + (Q - W)_3 = 0$. Subtracting the two relations, we have $(Q - W)_1 - (Q - W)_2 = 0$, or

$$(Q - W)_1 = (Q - W)_2.$$

Given the arbitrary nature of processes 1 and 2, we can conclude that the quantity $Q - W$ depends only on the origin and the end of the process and not on the particular transformation. This quantity can be written as the difference between the values in the final and initial states of a state function which we call U :

$$\Delta U = U(B) - U(A) = Q - W. \quad (2.20)$$

State function means that U is a function of the thermodynamic coordinates (temperature, pressure, volume, chemical species concentration, tension for a rubber band, etc.). With $U(A)$, we mean the value of the function for the coordinates of the state A . U is the *internal energy* of the system. Equation (2.20) defines the internal energy a part of an additive constant, as is the case with energies.

Internal energy is a thermodynamic quantity. As such, it regards the macroscopic state of the system. Indeed, thermodynamics does not deal with the underlying microscopic physics. We shall come to that in Chap. 5 when we address statistical mechanics. We anticipate a few hints here. Consider a system made of only one chemical species. It is composed of a very large number of identical molecules, on the order of the Avogadro number. The molecules move at different speeds, which increase, on average, with increasing temperature. As a matter of fact, their mean kinetic energy is proportional to the absolute temperature. In addition, the molecules have interactions between them. The internal energy of the system is the sum of the kinetic energy and potential energies of its molecules (namely their mechanical energies). If the system is an ideal gas, the molecules are considered non-interacting and their energy is only kinetic. The molecules of a monoatomic gas can be considered point-like and their kinetic energies are those of their center of mass. If the gas is polyatomic, the kinetic energy about the centers of mass must be considered too. If more chemical species are present, the internal energy can vary when chemical reactions take place.

We now come back to thermodynamics. Equation (2.20) is the mathematical expression of the *first law of thermodynamics*. In particular, if the system is

isolated, both work and heat exchanges are zero and the internal energy is constant for any process.

Equation (2.20) has a completely general validity, for whatever process, provided the initial and final states are equilibrium states. Otherwise, we cannot define any function of the thermodynamic coordinates, because these coordinates are not defined.

Consider now the particular case of *quasi-static*, in which all the intermediate states, not only those that are extreme, are equilibrium states. Consequently, the internal energy is defined in the intermediate states as well, and Eq. (2.20) also holds for any elementary part of the processes, in the form

$$dU = \delta Q - \delta W. \quad (2.21)$$

Pay attention to the fact that, from the mathematical point of view, dU is the differential of a function (U), namely an exact differential, while δW and δQ are not. They are infinitesimal quantities, but there is no function for which they would be differentials. For this reason, we use the symbol δ rather than d .

We now consider the changes in internal energy for some relevant processes.

Isochoric processes. The work is zero by definition. The variation in internal energy is equal to the absorbed heat:

$$\Delta U = Q. \quad (2.22)$$

This was the case for the second process of the Joule experiment of the previous section. In general, we can state that the internal energy of a system increases through heating (namely giving it heat) at constant volume, and decreases through cooling at constant volume.

Adiabatic processes. The exchanged heat is zero. The variation in internal energy is the opposite of the work done by the system:

$$\Delta U = -W. \quad (2.23)$$

This was the case for the first process of the Joule experiment. In general, when the system does work on the surroundings $W > 0$, without heat exchange, as in an adiabatic expansion, its internal energy diminishes. Contrastingly, the internal energy increases in any adiabatic compression.

Example E 2.1 A body of mass m falls on the floor from a height h_1 and, after the collision, bounces back to the height h_2 . Assuming that the body absorbs all the dissipated mechanical energy, how much does its internal energy vary?

The dissipated mechanical energy is $mg(h_2 - h_1)$. This energy is lost in the collision and corresponds to a mechanical work done on the body. Under the thermodynamic conventions, it is negative. Indeed, the heat exchanges during the brief instant of the collision can be neglected. Hence, for the first law, the variation of internal energy is $\Delta U = mg(h_1 - h_2)$.

As we shall see, the internal energy is an increasing function of temperature. Consequently, the final temperature of the body is higher than the initial one. If we wish, we can bring back the body to its initial state by extracting a quantity of heat equal to ΔU , that is, to the lost mechanical energy. One can find written instances stating that the process is a transformation of work into heat. This statement is wrong. The work has transformed into internal energy. \square

Example E 2.2 We heat a room having volume V from temperature T_1 to temperature T_2 . Knowing that the internal energy of a gas is $U = nc_V T$ (see Sect. 2.12), where c_V is a constant, how much does the internal energy vary? We must pay attention, because the quantity of air at the end of the process is different from that at the beginning. Indeed, even if the room is closed, some leakage under the windows and the doors will always be present. When the temperature of the air increases, the air expands and becomes less dense, the pressure remaining constant. We are dealing with a constant pressure process in an open system. Let n_1 and n_2 be the numbers of moles in the initial and final states, respectively. We write the gas equation as $pV = nRT$ and notice that p and V are constant during the process. Consequently, $n_1 T_1 = n_2 T_2$ and also $U_2 = U_1$. \square

2.9 Specific Heats

If a body absorbs the heat δQ , its temperature increases by dT . The ratio of the two quantities is called the *heat capacity* of the body.

$$C = \frac{\delta Q}{dT}. \quad (2.24)$$

As already mentioned in Sect. 2.6, it has been experimentally found that the heat capacity of a given substance, under the same thermodynamic conditions, is proportional to its mass. We thus define it as *specific heat*, namely the heat capacity per unit mass. Thus, if the temperature of a body of mass m of that substance increases by dT when it absorbs the heat δQ , the specific heat of the substance is

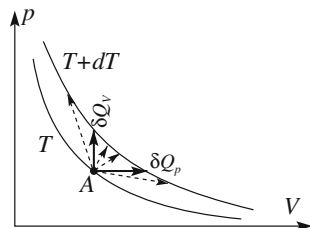
$$c = \frac{C}{m} = \frac{1}{m} \frac{\delta Q}{dT}. \quad (2.25)$$

Note that heat capacity is a characteristic of a body, while specific heat is a characteristic of a substance.

The definitions we just gave are not sufficiently precise, because the heat absorbed by a body for a certain increase in its temperature depends on the process in which the absorption takes place. Consequently, a substance does not have just one, but indeed many, or even infinite, specific heats.

Consider the case of the hydrostatic system. Figure 2.18 represents two isothermal transformations of such a system, one at temperature T , and the other at

Fig. 2.18 Elementary heat exchanges at constant volume and at constant pressure



$T + dT$. Starting from a state at temperature T , namely a point on that isothermal curve, we can pass on the second curve, namely increase temperature by dT , in an infinite number of different ways (see Fig. 2.18). For each of them, the heat exchange δQ is different. The system has infinite specific heats.

Particularly important are the specific heats at constant volume and constant pressure. In the particular case of a hydrostatic system, whose states are represented by points along the pV plane, all the other specific heats are linear combinations of those two (see Fig. 2.18). If the temperature of a mass m of a substance increases by dT when it absorbs the heat δQ_p or δQ_v , respectively, at constant pressure and constant volume, the specific heats of the substance are

$$c_p = \frac{1}{m} \frac{\delta Q_p}{dT}, \quad c_v = \frac{1}{m} \frac{\delta Q_v}{dT}. \quad (2.26)$$

Other useful quantities are the *molar heats*, which are the heat capacities of a mole of the substance. Namely, if the temperature of n moles of a substance increases by dT when it absorbs the heat δQ_p or δQ_v , the molar heats of the substance are

$$C_p = \frac{1}{n} \frac{\delta Q_p}{dT}, \quad C_v = \frac{1}{n} \frac{\delta Q_v}{dT}. \quad (2.27)$$

Consider now a hydrostatic system and suppose that the entire heat exchange takes place in quasi-static processes. The first law tells us that

$$dU = \delta Q - \delta W = \delta Q - p dV. \quad (2.28)$$

If the process is at a constant volume, $dV = 0$, and consequently $\delta Q_v = dU$. All the absorbed heat goes towards increasing the internal energy, and we can write for both the specific and the molar heat

$$c_v = \frac{1}{m} \left(\frac{dU}{dT} \right)_v, \quad C_v = \frac{1}{n} \left(\frac{dU}{dT} \right)_v \quad (2.29)$$

where the subscripts indicate that the derivatives are taken at constant volume V . This notation, often used in thermodynamics, is necessary because the internal

energy (and other state functions) does not depend solely on the volume, but also on the other thermodynamic coordinates.

We now heat (i.e., give heat to) the system at constant pressure. The heat now goes in part towards increasing the internal energy and in part towards producing work, because the volume of the system varies. The first law is now

$$\delta Q_p = dU + pdV = d(U + pV) \quad (2.30)$$

where we could write the last member because the pressure is constant. We see that the heat is now equal to the differential of the function

$$H = U + pV. \quad (2.31)$$

This is another state function of the system, because U , p and V are such. This is called the *enthalpy* of the system. We can write Eq. (2.30) as

$$dH = \delta Q_p. \quad (2.32)$$

The expression tells us that the heat transferred to the system at constant pressure determines an equal variation of the enthalpy.

In practice, we often operate at atmospheric pressure and, consequently, the heat exchanges are at constant pressure. Some examples are the chemical reactions, which usually take place in open containers. In these cases, the reaction heat is the enthalpy variation from the initial to the final state.

In conclusion, the specific and molar heats at constant pressure can be expressed as derivatives of enthalpy:

$$c_p = \frac{1}{m} \left(\frac{dH}{dT} \right)_p, \quad C_p = \frac{1}{n} \left(\frac{dH}{dT} \right)_p. \quad (2.33)$$

We observe that the specific and molar heats at constant pressure are always larger than those, of the same substance, at constant volume:

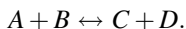
$$C_p > C_v. \quad (2.34)$$

One might believe this difference to be due simply to the fact that, in the exchange at constant volume, all the heat goes towards increasing the internal energy, while at constant pressure, part of it goes towards external work, because the system expands. However, this is not so. Indeed, we also see that $C_p > C_v$ in the (very few) cases in which the substance contracts, rather than expands, through heating. This is the case for water between 0 and 4 °C. The property is a consequence of a general law of thermodynamics, the *Le Châtelier principle*, which we shall discuss in the next section.

2.10 Le Châtelier's Principle

The *Le Châtelier principle*, or law of mobile equilibrium, was established by Henry Louis Le Châtelier (France, 1850–1936) in 1885. It allows us to foresee, in several cases and without any calculation, the direction in which a thermodynamic system will change in response to a change in the external conditions. The law states that, if the conditions external to a thermodynamic system in equilibrium change, the equilibrium of the system will change in the direction to oppose to the variation.

The law is useful in thermodynamics and chemistry. Suppose we have a container with different chemical species (A , B , C , D) that react with the reaction



The reaction can proceed in both directions. The chemical equilibrium is reached when the concentrations of the four substances remain constant. Suppose the reaction from left to right to be endothermic. In this case, if the temperature is increased, the equilibrium moves to the right side to increase the concentration of the species C and D . Indeed, this implies the absorption of heat, opposing the external change in this way (the temperature increase). The opposite happens for exothermic reactions.

Let us show that a hypothetical system that does not obey the Le Châtelier principle cannot have equilibrium states. Consider, for example, an exothermic reaction favored by an increase in the external temperature. In the presence of an increase in the temperature, even if very small, the reaction of the system would be an increase in released heat. This would cause, in turn, a further increase in the temperature and a further increase in the reaction process. The process would not stop until all the substances that were able to react have completely disappeared. Such behavior does not contradict any thermodynamic principle, but it does stand in contrast with the existence of equilibrium states. This argument should make clear the nature of the Le Châtelier principle. It is not a consequence of the laws of thermodynamics and, additionally, does not have the same importance. It is, however, useful, because it characterizes the states of stable equilibrium.

We now use the Le Châtelier principle to show that the specific heat at constant pressure is always larger than that at constant volume. Let us transfer a certain quantity of heat to the system at constant volume. Let dT_V be the corresponding temperature increase. As a consequence, the pressure of the system varies too, thus altering the equilibrium conditions. Notice that the pressure has increased if the system expands upon heating and has decreased if it contracts. The Le Châtelier principle tells us that the equilibrium of the system moves in opposition to the change in conditions. Namely, it has to return to the initial pressure. Its pressure must decrease in the former case, and increase in the latter. The process must imply a certain release of heat (it must oppose). This means that the change in temperature at constant pressure dT_p is less than that at constant volume dT_V , for the same heat

quantity δQ . It follows that the specific heat at constant pressure is larger than that at constant volume.

We shall make further use of the principle in Sect. 4.3.

2.11 Solid Body

In this section, we consider a thermodynamic system consisting of a solid body. Its shape and volume are practically invariable. Approximately, we can neglect thermal dilatation. Thus, the only thermodynamic variable is the temperature. The internal energy is consequently a function of the temperature alone, $U(T)$. Consider a state A with temperature T_A and a generic state P with temperature T . For whatever process leading from A to P , the first law states that

$$Q - W = U(T) - U(T_A). \quad (2.35)$$

The work of $p \, dV$ type is zero because the volume does not vary. In principle, other types of work might be done on the body, for example, by hammering or wiping. But we do not have any work of this type in the process we are considering. Then, the absorbed heat is equal to the variation in internal energy, and we have

$$Q = U(T) - U(T_A). \quad (2.36)$$

If the process is quasi-static, we can write the same for all its infinitesimal elements:

$$\delta Q = dU. \quad (2.37)$$

If m is the mass and c the specific heat of the body, we have

$$\delta Q = mc \, dT. \quad (2.38)$$

Note that, as we have assumed the volume to be invariable, the body has only one specific heat, namely at constant pressure.

We can then write for the derivative of the energy with respect to the temperature

$$\frac{dU}{dT} = mc(T) \quad (2.39)$$

where we have explicitly written that the specific heat might be a function of temperature. We now obtain the internal energy by integration:

$$U(T) - U(T_A) = m \int_{T_A}^T c(T) dT. \quad (2.40)$$

In practice, the temperature dependence of the specific heat of several substances is modest, provided one considers temperature intervals of several degrees. Under these conditions, considering the specific heat *constant*, we have

$$U(T) - U(T_A) = mc(T - T_A). \quad (2.41)$$

We shall come back to the specific heats of solids in Sect. 5.3.

Let us now go back to the calorimeter we have considered in Sect. 2.6. It can be used to measure the specific heat of solid substances. Suppose, for example, we want to measure the specific heat c of copper. We proceed as follows. We heat a small block of pure copper of mass M at the temperature T_C , higher than that of the water in the calorimeter. We measure the water temperature T_i . We introduce the block into the water and close the plug. We read the temperature of the water and wait for it to stabilize at, say, T_f . Block and water now have the same temperature. Let us write down that the heat released by the block is equal to that absorbed by the water, namely

$$Q = m(T_f - T_i) = cM(T_C - T_f) \quad (2.42)$$

where we have remembered that the specific heat of water is equal to 1. From this equation, we have c . In practice, a number of measures that we did not mention are

Table 2.1 Specific heats of several materials at 25 °C in J kg⁻¹ K⁻¹

Substance	Spec. heat (kJ kg ⁻¹ K ⁻¹)	Substance	Spec. heat (kJ kg ⁻¹ K ⁻¹)
Acrylic	1.4–1.5	Hydrogen	14.27
Aluminum	0.90	Ice (0 °C)	2.05
Argon	0.52	Iron	0.44
Beryllium	1.83	Lead	0.13
Bricks	0.85	Mercury	0.14
Calcium	0.65	Neon	1.03
Cesium	0.24	Nitrogen	1.04
Copper	0.39	Oxygen	0.92
Diamond	0.52	Platinum	0.13
Germanium	0.32	Silicon	0.70
Glass (crown)	0.67	Silver	0.24
Glass (flint)	0.50	Sulfur (yellow)	0.73
Gold	0.13	Tungsten	0.13
Graphite	0.71	Zinc	0.39
Helium	5.19	Wood	1.67

necessary. The most important is taking into account the heat absorbed by the walls of the calorimeter, by the thermometer and by any other auxiliary equipment that might be present in the calorimeter, referred to as the calorimeter water equivalent.

Table 2.1 reports the specific heats of several substances at 25 °C temperatures for several substances in $\text{J kg}^{-1} \text{K}^{-1}$.

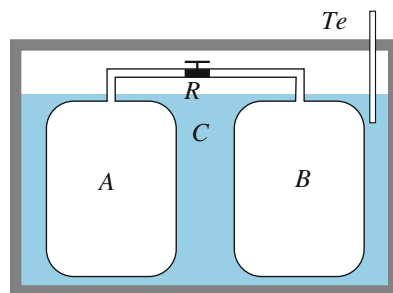
2.12 Internal Energy of the Ideal Gas

Consider a hydrostatic system. As we know, for a given mass, only two of the three thermodynamic variables, p , V and T , are independent. Consequently, its internal energy is, in general, a function of two variables. Even if their choice is arbitrary, it is usually convenient to choose volume and temperature. Indeed, at the microscopic level, the kinetic energy of the molecules is proportional to the temperature, as we have already mentioned. In addition, the potential energy of their interactions depends on the distances between molecules, whose mean value obviously depends on the volume. In conclusion, we shall write the internal energy as $U(V, T)$.

J. Joule conducted an experiment that gave important information on the internal energy of gases, known as the *free expansion experiment*. Figure 2.19 shows the scheme of the experiment. The two vessels A and B have metallic walls. Consequently, we can consider their volumes to be invariable. The vessels are connected by a tube that can be closed or opened with the tap R . Joule introduced a gas at high pressure into vessel A (up to 200 kPa) and pumped the air out of vessel B (R being closed, obviously). Opening R , the gas expands to fill both vessels. Notice that no external work is done in the expansion, as the gas expands in a space that was prepared to accept it. The expansion does not push anything. The external work is zero, because the total volume in the rigid surrounding walls does not vary. This process is called free expansion or expansion without external work.

The two vessels, whose walls, being metallic, were diathermic, had been lodged in a calorimeter. Joule did not measure any temperature change during the expansion. The following two conclusions can be extracted from the result: (1) the global heat exchange during the free expansion is zero; (2) the temperatures of the

Fig. 2.19 The Joule free expansion experiment



gas before and after the expansion are the same, considering that the gas is in thermal equilibrium with the calorimeter before and after the process.

We note here that the sensitivity of the experiment is rather limited, because the heat capacity of the gas is small. Joule worked with high initial pressures to partially reduce this limitation. However, in doing so, he moved away from the ideal gas behavior. The above conclusions should be regarded as valid only in a first approximation. We shall see in Sect. 4.4 that they are valid only for the ideal gas, as later established by Joule himself in more sensitive experiments performed in collaboration with W. Thomson.

Let us now go back to the consequences of the above observations. We can talk of internal energy in the initial and in the final states because they are equilibrium states (the intermediate states are not so, but this does not matter). In the process leading from the former to the latter, both work and heat exchanges were zero. Consequently, $U(V_f, T) - U(V_i, T) = Q - W = 0$. Here V_i is the initial volume of the gas (one vessel), V_f is its final volume (two vessels) and T is the temperature that does not vary. The internal energy is the same in the two states, while their volumes are different. Consequently, the internal energy does not depend on the volume. It can depend only on temperature. For an ideal gas, we can write

$$U = U(T). \quad (2.43)$$

We can reach the same conclusion with a different argument. We start from the expression of the specific heat at constant volume Eq. (2.29)

$$C_V = \frac{1}{n} \left(\frac{dU}{dT} \right)_V \quad (2.44)$$

and integrate it between a reference state A and the generic state P , obtaining

$$U(T) - U(T_A) = n \int_A^P C_V dT. \quad (2.45)$$

Here, we need experimental input to know how the molar heat depends on temperature. Experiments tell us that it is almost constant (exactly constant for ideal gases) and we have

$$U(T) - U(T_A) = nC_V(T - T_A) = mC_V(T - T_A) \quad (2.46)$$

where, to be complete, we have also included the expression in terms of the specific heat.

Let us now consider the other state function we have met, enthalpy. For the ideal gas, it also depends on temperature alone. It is

$$H = U + pV = U + nRT. \quad (2.47)$$

Taking the derivative with respect to temperature and dividing it by the number of moles n , we have

$$\frac{1}{n} \frac{dH}{dT} = \frac{1}{n} \frac{dU}{dT} + R. \quad (2.48)$$

There has not been any need to specify whether the derivatives are made at constant pressure or at constant volume, because neither enthalpy nor internal energy depends on these variables. We then recognize that the left-hand side is the molar heat at constant pressure and the first term in the right-hand side is the molar heat at constant volume, and can write

$$C_p - C_V = R \quad (2.49)$$

This equation is called the Mayer's relation for ideal gases. It states that the difference between the molar heats at constant pressure and at constant volume has a universal value for all the gases, the gas constant, within the limits they can be considered as ideal.

We notice that in the case we are considering, the difference between the two heats is due to the fact that when the gas is heated at constant pressure, it performs an external work. Contrastingly, no external work is done in the heating at constant volume. In the latter case, all the heat goes towards increasing the internal energy, while in the former, part of it goes towards external work. As we know, however, this is not the reason why $C_p > C_V$.

A further experimental result is the dependence of the molar heats of the gases on the type of their molecules. All the monoatomic gases have the same molar heat at constant volume. It is (almost) independent of temperature down to rather low temperatures. Its value is

$$C_V = \frac{3}{2}R = 12.5 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{monoatomic gas.} \quad (2.50)$$

The situation of the diatomic gases is more complicated. However, the larger fraction of these gases (especially those with less massive molecules), at ambient temperature and in a rather wide interval of temperatures, have molar heats around the value

$$C_V = \frac{5}{2}R = 20.8 \text{ J mol}^{-1} \text{ K}^{-1} \quad \text{diatomic gas.} \quad (2.51)$$

The simplicity of the relations just determined cannot be casual. As a matter of fact, they are deeply rooted in statistical mechanics, as we shall see in Sect. 5.2.

Let us use them together with the Mayer's relation. We obtain for the molar heats at constant pressure

Table 2.2 Molar heats of some gases at 25 °C in J mol⁻¹ K⁻¹

		C_p	C_v	$C_p - C_v$	C_p/C_v
Monoatomic	Ar	20.8	12.5	8.3	1.67
	He	20.9	12.5	8.3	1.67
Diatomic	Air	29.1	20.8	8.3	1.40
	N ₂	29.1	20.8	8.3	1.40
	O ₂	29.4	21.1	8.3	1.40
	H ₂	28.8	20.4	8.3	1.41
Polyatomic	CO ₂	37.0	28.5	8.5	1.30
	NH ₃	36.8	27.8	9.0	1.32
	CH ₄	35.6	27.2	8.4	1.31

$$C_p = \frac{5}{2}R \text{ monoatomic gas; } C_p = \frac{7}{2}R \text{ diatomic gas.} \quad (2.52)$$

In addition, defining the dimensionless parameter

$$\gamma = \frac{C_p}{C_v} \quad (2.53)$$

we have

$$\gamma = \frac{5}{3} = 1.67 \text{ monoatomic gas; } \gamma = \frac{7}{5} = 1.40 \text{ diatomic gas.} \quad (2.54)$$

The above conclusions would be rigorously valid for the ideal gases and approximately so for many real gases, within large intervals of the thermodynamic variables. We shall study the real gases in Chap. 4. Here, we report the molar heats of some gases at room temperature in Table 2.2.

2.13 Adiabatic Processes in Gases

We shall now discuss the quasi-static adiabatic processes of an ideal gas.

For example, we can expand or compress a gas adiabatically and quasi-statically by enclosing it in a cylinder with a piston. All the surrounding surfaces should be adiabatic. We shall move the piston very slowly in one or the other direction. In expanding, the gas delivers external work. In the absence of a heat exchange, all the work done corresponds to a decrease in internal energy. Internal energy being a function of temperature, the gas cools down. Contrastingly, temperature increases in adiabatic compression. You can feel that when you inflate the tire of a bike. We now seek the quantitative relation between temperature and volume.

Consider, for simplicity, a mole of gas. We apply the first law to an infinitesimal section of the process, in which, clearly, $\delta Q = 0$. We have

$$dU + pdV = 0.$$

Using Eq. (2.44) and eliminating p with the state equation, we have

$$C_V dT + \frac{RT}{V} dV = 0$$

namely

$$\frac{dT}{T} + \frac{R}{C_V} \frac{dV}{V} = 0.$$

Integrating, within the limits in which we can consider C_V to be constant, we get

$$\ln T + \frac{R}{C_V} \ln V = 0.$$

We take the exponential of this expression and obtain

$$TV^{R/C_V} = \text{constant}.$$

We want this expression in terms of the ratio γ of the specific heats, Eq. (2.53), which we write as

$$\gamma = \frac{C_p}{C_V} = \frac{C_V + R}{C_V} = 1 + \frac{R}{C_V}.$$

Hence, the expression we have found is just

$$TV^{\gamma-1} = \text{constant}. \quad (2.55)$$

This expression tells us how much a gas cools down in an adiabatic expansion. Consider, for example, a quantity of air, whose volume doubles adiabatically. The air is mainly N_2 and O_2 , two diatomic gases. Hence, $\gamma = 1.4$. The temperature decreases by the factor $(1/2)^{0.4} = 0.76$.

Equation (2.55) can be written in two other equivalent forms, which are sometimes useful, using the state equation $pV = RT$. As immediately found, they are

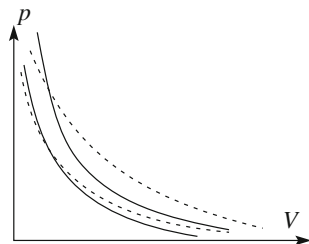
$$pV^\gamma = \text{constant} \quad (2.56)$$

and

$$Tp^{1/\gamma-1} = \text{constant}. \quad (2.57)$$

Equation (2.56) is the equation of the adiabatic transformations in the pV plane. Let us compare it with the equation of the isothermal processes, namely

Fig. 2.20 Figure shows two isothermal (*dotted*) and two adiabatic (*continuous*) curves



$pV = \text{constant}$. The adiabatic curves are similar to the isothermal curves, but are steeper because, in any case, $\gamma > 1$.

Figure 2.20 shows two isothermal (dotted) and two adiabatic (continuous) curves.

2.14 Compressibility and Thermal Expansion

Gases are easy to compress and to expand. A small pressure increase is sufficient to change their volume considerably. The same is not true for condensed bodies, namely solids and liquids. However, even those are compressible, if subject to large enough pressures. As the volume changes if the temperature also varies, compressibility must be defined at constant temperature.

The isothermal compressibility is defined as

$$\kappa = -\frac{1}{V} \left(\frac{dV}{dp} \right)_T. \quad (2.58)$$

Note that the derivative is negative, because the volume diminishes when the pressure increases. The minus sign in the definition is used to have κ be positive. The dimensions of κ are the reciprocal of a pressure, as immediately seen in Eq. (2.58).

Let us consider some orders of magnitude. The isothermal compressibilities of liquids are in the range of 10^{-11} – 10^{-10} Pa^{-1} . Suppose we want to have a relative variation of volume of one per cent, namely $dV/V = 10^{-2}$. If $\kappa = 10^{-10} \text{ Pa}^{-1}$, the change of pressure must be 1 MPa, which is about ten times the atmospheric pressure. For example, for water, $\kappa = 5 \times 10^{-10} \text{ Pa}^{-1}$, and for mercury, $\kappa = 0.4 \times 10^{-10} \text{ Pa}^{-1}$.

The isothermal compressibility of the large majority of solids is even smaller. For example, it is $\kappa = 0.6 \times 10^{-11} \text{ Pa}^{-1}$ for iron, and $\kappa = 1.4 \times 10^{-11} \text{ Pa}^{-1}$ for aluminum.

Let us now consider the gases. The state equation can be written as $V = nRT/p$. By derivation, we obtain

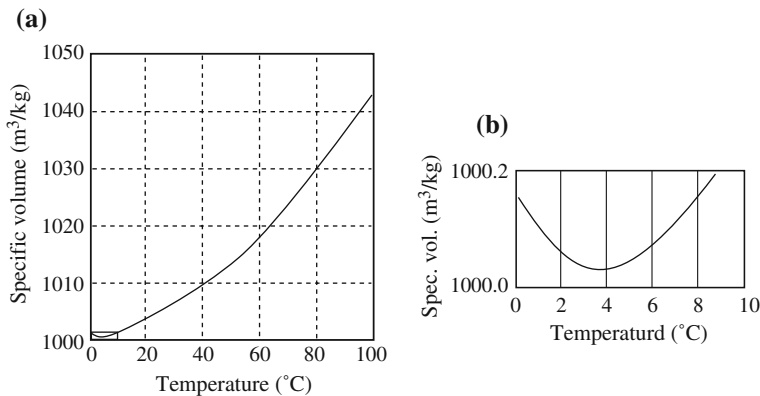


Fig. 2.21 Specific volume of water

$$\kappa = 1/p. \quad (2.59)$$

At atmospheric pressure, the compressibility of a gas is $\kappa = 10^{-5} \text{ Pa}^{-1}$, about one million times more compressible than a condensed body at the same pressure.

Another quantity employed to characterize the thermal properties of the bodies is the *volumetric thermal expansion coefficient at constant pressure*, defined by the relation

$$\alpha = -\frac{1}{V} \left(\frac{dV}{dT} \right)_p. \quad (2.60)$$

The physical dimensions of the coefficient are the reciprocal of temperature, and are measured in K^{-1} . The large majority of substances expand when heated, hence α is positive. However, there are exceptions, that is, substances that expand when cooled. Their α is negative. The most common of these is water between 0 and 4 °C, while others include graphene, some complex compounds, some iron alloys, etc. Cubic zirconium tungstenate (ZrW_2O_8) has a negative expansion coefficient in the largest temperature range, namely all of them up to its fusion.

Figure 2.21 shows the specific volume (which is the inverse of the density) of water as a function of temperature in °C. The part in the small box near 0 °C in part (a) of the figure is enlarged in part (b).

We again fix the orders of magnitude. The thermal expansion coefficients of liquids are on the order of 10^{-4} – 10^{-3} K^{-1} ; for example, at ambient temperature, it is $\alpha = 2.1 \times 10^{-4} \text{ K}^{-1}$ for water and $\alpha = 1.1 \times 10^{-3} \text{ K}^{-1}$ for alcohol. The coefficients of solids are smaller, typically by one order of magnitude. For example, iron has $\alpha = 3.5 \times 10^{-5} \text{ K}^{-1}$. In some cases, one needs to build structures whose dimensions vary as little as possible in regard to temperature. Special alloys have been

developed for this very purpose. For example, invar, an iron-nickel alloy, has $\alpha = 3.6 \times 10^{-6} \text{ K}^{-1}$.

Let us now compare these with gases. We write the state equation as $V = nRT/p$, and take the derivative with respect to temperature, obtaining

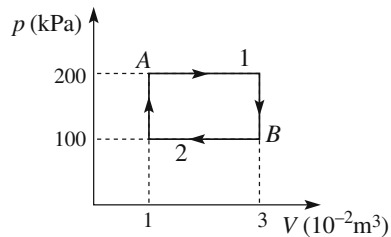
$$\alpha = 1/T. \quad (2.61)$$

Hence, under normal conditions, $T = 293 \text{ K}$, and a gas has $\alpha = 3.4 \times 10^{-3} \text{ K}^{-1}$, which is not much larger than for some liquids.

Problems

- 2.1 Let us introduce into a calorimeter, which is at a temperature of 80°C , 300 g of water at a temperature of 20°C (and nothing else). We observe that equilibrium is reached when the water temperature is 60°C . Can we find the heat capacity of the calorimeter from these data?
- 2.2 The air in two rooms of equal volume has the same pressure. If the temperatures are different, which room contains more air?
- 2.3 If we know the pressure, temperature and volume of a gas, which of the following quantities can be known: the type of gas; its number of molecules; its number of atoms?
- 2.4 Find the number n_p of molecules per unit volume of air at standard temperature and pressure.
- 2.5. Find the mass of a cubic meter of air at STP.
- 2.6 The air composition on the earth's surface is the following: N_2 78.08 %, O_2 20.95 %, Ar 0.93 % and other gases 0.04 %. Find the molar mass of air.
- 2.7 Consider the following processes of an ideal gas: (a) volume increases and pressure increases proportionally; (b) volume increases and pressure is constant; (c) the gas expands isothermally; (d) the gas expands adiabatically; (e) volume increases and pressure decreases more rapidly than in an adiabatic process. Qualitatively draw the representative curves in the Vp plane and state the behavior of internal energy in each case.
- 2.8 A mixture of hydrogen and oxygen gases is enclosed in a container with rigid and adiabatic walls. We fire a spark (its heat release is negligible) and the gases violently react, resulting in an increase in pressure and temperature. How much does the internal energy vary?
- 2.9 Suppose we want to perform the Joule experiment on the equivalence between heat and work with a calorimeter containing one liter of water ($m = 1 \text{ kg}$). Each of the two weights has a mass $M = 10 \text{ kg}$ and the drop is $h = 2.5 \text{ m}$. What is the temperature increase to be measured?
- 2.10 The heat capacity of a body, in the considered temperature interval, depends on temperature according to the expression $C = 10 + 0.002T + 3 \times 10^{-5}T^2 \text{ J K}^{-1}$. How much heat is released when the temperature varies from $T_1 = 400 \text{ K}$ to $T_2 = 300 \text{ K}$?

Fig. 2.22 The two processes of problem 2.11



- 2.11 A system transforms from state A to state C once by process 1, once by process 2, as shown Fig. 2.22. Find the difference $Q_1 - Q_2$ between the exchanged heats (necessary data are in the figure).
- 2.12 A certain quantity of a gas passes from state 1 with internal energy $U_1 = 500$ kJ to state 2 with $U_2 = 100$ kJ, doing the work $W = 200$ kJ. How much is the absorbed heat Q if (a) the process is reversible, or (b) the process is irreversible?
- 2.13 A certain quantity of an ideal monoatomic gas is compressed adiabatically, reversibly changing its pressure from p_1 to $p_2 = 10 p_1$. After that, the gas is compressed back to its initial volume, in an isothermal, reversible process, to the pressure p_3 . Find p_3/p_1 .
- 2.14 A certain quantity of an ideal monoatomic gas expands in a reversible process at constant pressure p from the volume V_1 to V_2 . Find the expressions for: (a) the internal energy variation ΔU , (b) the work done by the gas W and (c) the absorbed heat Q .
- 2.15 One mole of an ideal gas heats from $T_1 = 273$ K to $T_2 = 373$ K in a reversible constant pressure process, absorbing the heat $Q = 6.65$ kJ. Determine: (a) the specific heat ratio γ , (b) the internal energy increase ΔU and (c) the work done W . (See problem 2.14).
- 2.16 A certain quantity of an ideal gas expands at constant temperature from the volume $V_1 = 1$ m³ to $V_2 = 2$ m³. The final pressure is $p_2 = 100$ kPa. Find: (a) the internal energy increase ΔU , (b) the work done W and (c) the absorbed heat Q .

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