

Chapter 6

Introduction to thermodynamics

Topics

First law of thermodynamics. Definitions of internal energy and work done, leading to $dU = dq + dw$. Heat capacities, $C_p = C_V + R$. Reversible and irreversible processes. Various types of expansion, isothermal, adiabatic. C_V and C_p according to kinetic theory, monatomic gases, other gases. The meaning of temperature, empirical temperature scale, perfect gas scale, the second law of thermodynamics, thermodynamic temperature scale.

So far, we have concentrated upon developing a *microscopic* model for the behaviour of gases. We now turn our attention to the *macroscopic* description of solids, liquids and gases, which is concerned with the bulk properties of properties of substances. This is the subject of *thermodynamics* and, in contrast to our analysis so far, we deny that the various forms of matter are actually composed of atoms and molecules. Thermodynamics is a large and very powerful branch of physics. In this chapter, we show how thermodynamics can provide crucial clues about the physics of our microscopic model.

6.1 First Law of Thermodynamics

The *first law of thermodynamics* is a statement about the *conservation of energy*.

Energy is conserved when heat is taken into account.

This is a somewhat more subtle statement than might appear at first sight. We have defined the heat capacity in terms of the amount of heat needed to raise the temperature of a substance by one degree, but we have not stated what heat is. The most rigorous approach is to define first of all the *internal energy* U of the system. We have already introduced this concept in our discussion of the internal energy of an ideal gas, but we can now generalise it to any substance or system.

A material can store energy in many different ways besides molecular motions - the molecules may vibrate and rotate, the material may be placed in an electric or magnetic field, the energy density of radiation may be important and so on. Therefore, we need a general way of coping with all these possibilities.

In general, there are two ways in which the system can acquire internal energy

- We can *do work* on the system and so increase its internal energy.
- We can allow heat Q to enter the system.

The first statement is fundamental since it asserts that, by doing work on the system alone, we can raise the internal energy to any given value, quite independent of what we might mean by heat. This is the clue to how we define what heat is. We write down the expression for the change in internal energy due to both causes.

$$dU = dQ + dW, \quad (6.1)$$

where dW is the *work done on the system*. This expression is a formal statement of the *first law of thermodynamics*.

Note how we interpret this statement. The internal energy U is a well-defined physical quantity which we can measure. The amount of work done dW can

<p>The first law of thermodynamics</p> $dU = dQ + dW$
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be measured also. We *define* the heat entering the system dQ to be the quantity

$$dQ = dU - dW. \quad (6.2)$$

This may look like a slightly back-to-front definition of heat, but it is logically self-consistent.

Now consider the case of a gas filling a cylinder with a piston. Figure 6.1 shows the force exerted by the gas on the piston, $F = pA$, where A is the surface area of the piston. Suppose now that the piston moves a tiny distance dx under the influence of F . Then, the *work done by the gas* is

$$\text{Work done} = F dx = pA dx = p dV. \quad (6.3)$$

Since the gas is doing work, this energy must be abstracted from the internal energy of the gas U . Notice the importance of the signs in this calculation. If dV is positive, there is a loss of internal energy from the gas. Therefore, the expression for the change of internal energy of the gas dU is

$$dU = dQ - p dV. \quad (6.4)$$

If dV is negative, the volume decreases and *work is done on the gas*.

Now let us consider the expansion of one mole of the gas under conditions of either *constant volume* or *constant pressure*.

Constant volume In this case, $dV = 0$ and so

$$dU = dQ = \left(\frac{\partial Q}{\partial T} \right)_V dT = C_V dT, \quad (6.5)$$

where C_V is the molar heat capacity at constant volume, which we have already introduced.

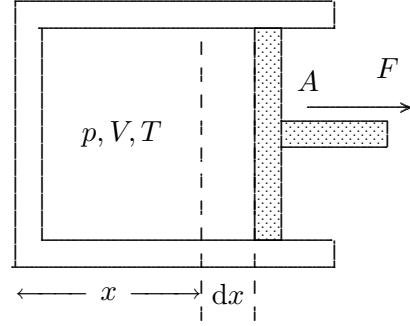
Constant pressure Work is done by the gas as it expands at constant pressure and so more heat dQ has to be supplied to provide the same increase in temperature. From (6.3)

$$dQ = dU + p dV. \quad (6.6)$$

But $dU = C_V dT$ and so

$$dQ = C_V dT + p dV. \quad (6.7)$$

Figure 6.1. The cylinder and piston.



Heat capacity at constant volume

$$dU = \left(\frac{\partial Q}{\partial T} \right)_V dT = C_V dT$$

We can now use the equation of state of the perfect gas to determine the change in volume *at constant pressure*,

$$pV = RT, \quad p \, dV = R \, dT. \quad (6.8)$$

Therefore,

$$dQ = C_V \, dT + R \, dT. \quad (6.9)$$

We can therefore find the *heat capacity at constant pressure*,

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p = C_V + R. \quad (6.10)$$

This is the famous relation between the molar heat capacities at constant pressure and constant volume

$$C_p - C_V = R. \quad (6.11)$$

Relation between C_p and C_V for a perfect gas

$$C_p - C_V = R$$

6.2 Reversible and Irreversible Processes

We need to introduce an important, but subtle, idea here. We are interested in how a thermal system, such as an expansion, evolves from one state to another and hence how much work is done on or by the system and how much heat is exchanged with the surroundings. However, our picture is based upon systems in thermodynamic equilibrium at a particular temperature. We need to be careful about using these concepts when the system evolves from one state to another. This is where the concept of *reversible* processes plays a key role.

We assume that, in passing from one state to another, *the system passes through a continuous set of equilibrium states*. There is no loss of energy due to friction, turbulence, sound waves, and so on. In order to achieve this, the passage from one state to another must take place very slowly indeed so that there are no unbalanced forces at any stage. The important idea is that, if we perform the change in this idealised way, we could *reverse the process exactly* and get back to where we started *without any change in the whole Universe as compared with the*

initial state. This is what we mean by a *reversible* process.

This is a very highly idealised picture and should be contrasted with the real world in which we cannot eliminate entirely heat losses due to, say, friction or turbulence. A number of systems can approach reversible behaviour, but it is impossible to eliminate unwanted losses of internal energy entirely.

Nonetheless, the importance of these idealised reversible processes is that they set the standard against which we can compare real systems. They also provide us, as a matter of principle, with the means of setting up the whole foundations of classical thermodynamics.

6.3 Isothermal and Adiabatic Expansions

Let us show how these idealisations enable us to understand the thermodynamic behaviour of thermal systems. We can contrast two limiting cases.

6.3.1 Isothermal Expansion

Let us allow the gas in the cylinder to expand reversibly at constant temperature. The gas does work on the piston in expanding and so the gas would lose internal energy and cool, unless heat is allowed to flow into the gas from the surroundings to compensate for the work done. Now, for a perfect gas, the internal energy U is a function of T alone, $U = U(T)$, and since T is constant so is U :

$$dU = dQ - p dV = 0, \quad dQ = p dV \quad (6.12)$$

in an isothermal expansion. There must therefore be a (reversible) heat flow $dQ = p dV$ into the volume of the gas to maintain the temperature at T .

Isothermal

Isothermal means at constant temperature.

6.3.2 Adiabatic Expansion

The opposite extreme is that the gas is allowed to expand reversibly, completely isolated from its surroundings so that no energy flows into or out of the

system. In this case $dQ = 0$, and hence the first law of thermodynamics becomes

$$dU = -p dV. \quad (6.13)$$

We can now reorganise this expression to find a relation between the pressure and volume of the gas in such an expansion. We recall that

$$dU = C_V dT \quad (6.14)$$

and we can also find an expression for $p dV$ from the perfect gas law by differentiation.

$$\begin{aligned} pV &= RT \\ dpV + p dV &= R dT \end{aligned} \quad (6.15)$$

We can eliminate dT from (6.14) and (6.15) so that

$$dU = \frac{C_V}{R} (dpV + p dV) \quad (6.16)$$

and then substitute for dU in (6.13). This results in an expression involving only p and V .

$$\frac{C_V}{R} (dpV + p dV) = -p dV. \quad (6.17)$$

This can be reorganised as follows

$$\begin{aligned} \frac{C_V V}{R} dp &= -p \left(1 + \frac{C_V}{R} \right) dV, \\ &= -p \left(\frac{R + C_V}{R} \right) dV, \\ C_V V dp &= -p C_p dV, \end{aligned} \quad (6.18)$$

where we have used the relation $C_p - C_V = R$. If we now write the ratio of heat capacities as $\gamma = C_p/C_V$, we obtain a simple integral

$$\begin{aligned} \frac{dp}{p} &= -\gamma \frac{dV}{V}, \\ \ln p &= -\gamma \ln V + \text{constant}, \\ \ln(pV^\gamma) &= \text{constant}, \\ pV^\gamma &= \text{constant}. \end{aligned} \quad (6.19)$$

This is the famous expression for the relation between pressure and volume in a reversible adiabatic expansion. The gas must cool in such an expansion

Adiabatic

Adiabatic means without the transference of heat.

since the piston has done work and the only source of work is the internal energy of the gas. Therefore, using $pV = RT$ to substitute for p , we find

$$TV^{\gamma-1} = \text{constant}. \quad (6.20)$$

Alternatively, eliminating V , we find

$$\begin{aligned} p \left(\frac{RT}{p} \right)^{\gamma} &= \text{constant}, \\ p^{(1-\gamma)/\gamma} T &= \text{constant}. \end{aligned} \quad (6.21)$$

This is the principle used in adiabatic refrigerators for cooling gases.

Notice that we have carried out a calculation in classical thermodynamics. There was no mention of the microscopic structure of the gas. The next step is to compare the predictions of the kinetic theory of gases with the measured values of γ .

6.4 C_p and C_V according to kinetic theory

6.4.1 Monatomic gases

In the case of monatomic gases, such as helium, argon and so on, the internal energy is entirely associated with the kinetic energy of the atoms and so we already know that the internal energy U for one mole is

$$U = N_A \frac{3}{2} kT. \quad (6.22)$$

The molar heat capacity at constant volume is therefore

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = \frac{3}{2} N_A k = \frac{3}{2} R, \quad (6.23)$$

and the heat capacity at constant pressure is

$$C_p = C_V + R = \frac{5}{2} R. \quad (6.24)$$

The ratio of heat capacities γ therefore has the value

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3}. \quad (6.25)$$

This value is in excellent agreement with the measured values of γ for monatomic gases.

6.4.2 Other Gases

This calculation works very well for monatomic gases, but it gives the wrong answer for molecular gases such as oxygen and nitrogen. At room temperature, their ratios of heat capacities are about 1.4. This means that the internal energy density must be greater than $U = N_A \frac{3}{2} kT$. In other words, there must be more ways of storing energy in the gas than simply in the translational motion of the molecules.

One solution would be to store the energy in the rotational energy of the molecules about their three independent rotational axes. The additional terms in the internal energy would then be

$$\frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2, \quad (6.26)$$

where I_x, I_y, I_z are the moments of inertia about the x, y and z axes and $\omega_x, \omega_y, \omega_z$ their angular frequencies of rotation about these axes. We could have performed exactly the same sort of simulation which we carried out for the translation motion of the particles and we would have found again that in statistical equilibrium, each of these terms would have an energy $\frac{1}{2} kT$. Therefore, the total internal energy of the gas would be $3N_0 kT$, $C_V = 3R$, $C_p = 4R$ and so the ratio of heat capacities would be

$$\gamma = \frac{C_p}{C_V} = 1.333. \quad (6.27)$$

This flew in the face of the experimental evidence which clearly demonstrated that $\gamma = 1.4$ for diatomic gases. This was a major problem for the kinetic theory of gases and it was only resolved once the concept of quantisation was introduced by Einstein in 1905. This is a story which we will take up in the Easter term.

6.5 The Meaning of Temperature

Let us reflect on a problem lurking behind our treatment of thermal physics so far. We have unambiguous definitions of pressure and volume, but we lack a satisfactory definition of temperature in terms of fundamental physics.

6.5.1 Thermometers and empirical scales of temperature

We have a physiological sense of *hotness*, and it has long been realised that certain physical systems, such as the length of the mercury column in a glass thermometer, vary systematically with our physiological appreciation of temperature. Defining temperature using such an approach leads to what is called an *empirical temperature scale*.

We have already seen how the concept of temperature enters directly into our definition of an ideal gas from Boyle's and Charles law. In setting up Charles law,

$$V/V_0 = T/T_0,$$

we define a scale of temperature which has a zero point fixed on physical grounds, in this case the temperature of an ideal gas as its volume tends to zero; the linear scaling with volume defines how temperature relates to a physically measurable quantity. This is the basis of the *constant volume gas thermometer* which uses $p/p_0 = T/T_0$ to estimate T (Figure 6.2). The reference volumes, pressures and temperatures are arbitrary, but their choice only leads to an overall linear scaling. Defining temperature in this way leads to the *ideal gas scale for temperature*; this is a better temperature scale than one arbitrarily associated with a mercury-in-glass thermometer. However, it breaks down at high pressures and close to values of p and V at which the gas condenses. In fact, the Joule-Kelvin effect shows that gases in fact depart from ideal behaviour if sufficiently accurate measurements are made. Therefore, the ideal gas temperature scale still does not provide us with a truly fundamental definition of the temperature scale.

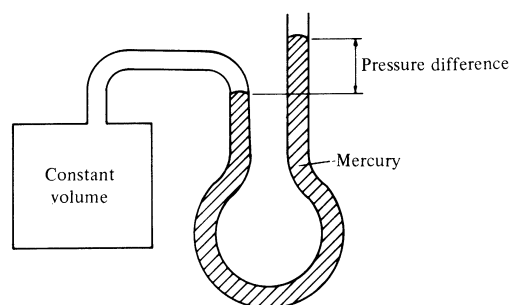


Figure 6.2. The constant volume gas thermometer.

6.5.2 Hotness and the second law of thermodynamics

What does it mean to say that A is hotter than B? Although we each have a sense of this we need a proper definition. An objective definition of hotness concerns *the direction of heat flow*. If A is

hotter than B then we mean that, if the two systems are brought into thermal contact, heat flows of its own accord from A to B and not in the other direction. This certainly agrees with our physiological definition – we get hot or burnt in contact with a hot object.

The idea that heat flows only from hot to cold is so important that we encapsulate it in the *Second Law of Thermodynamics*. The statement of the law by Clausius is:

No process exists whose sole effect is the transfer of heat from a colder to a hotter body.

This is a very deep and profound statement and turns out to be the basis of a rigorous definition of temperature which is known as the *thermodynamic temperature scale*. In addition, we need to relate this definition of temperature to the appropriate measure of temperature according to the concepts of statistical physics. We will look a little more deeply into these issues in the quantum physics half of the course.

The Second Law of Thermodynamics

No process exists whose sole effect is the transfer of heat from a colder to a hotter body.