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Kinetic Theory – I

PHYS1013 Energy & Matter looks at the thermal properties of matter from microscopic and macroscopic viewpoints. The microscopic view was second to be developed and was only fully accepted by about 1900, long after the development of macroscopic "classical" thermodynamics. There is no obvious order to take when learning these two topics, because although related, they are largely independent. Kinetic theory predicts a few properties of gases from fundamental principles, but is at best approximate and fails completely to describe liquids and solids. Classical thermodynamics on the other hand is rigorous and exact, but works with bulk properties such as pressure, work and heat, building a theory from elementary observations, without explaining the properties themselves. A third, very powerful approach, statistical thermodynamics, builds up many of the ideas of thermodynamics from a microscopic point of view, but I will touch on this only to illuminate the property of entropy which emerges rather mysteriously in classical thermodynamic.

In this course I will start with kinetic theory as it is closest to the physics that you will have learnt before, building from Newtonian physics with a few assumptions.

1.1 The Assumptions of Kinetic theory

Kinetic theory is a microscopic model of gases which predicts macroscopic quantities such as pressure and heat capacity. It is based on six assumptions:

1. A gas is composed of a large number of molecules.
2. The molecules are small compared to their separation.
3. The molecules are uniformly distributed and move randomly.
4. The molecules obey Newton's laws of motion.
5. The molecules feel no force except during collisions with other molecules or the walls of the container — "hard spheres".
6. Molecules collide elastically, and the walls are smooth.

Assumptions 2 and 5 fail at high densities when the molecules are close together. Thus kinetic theory cannot be expected to describe either liquids or solids. Assumption 4 is wrong: quantum mechanics rules, but the quantum predictions tend to those

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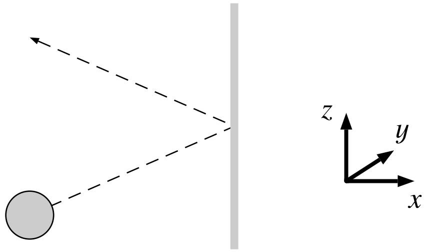

Figure 1.1 The collision of a molecule with a wall, used to derive the relation between pressure and molecular speeds.

of classical physics if the de Broglie wavelength of the molecules, $\lambda = h/mv$, is much less than their mean separation. This is true if the temperature is high so that the speed v is large on average, and at low density when the mean separation is large. These are just the conditions needed for assumptions 2 and 5 to hold as well. Quantum effects can be very important and remarkable (e.g. the amazing properties of liquid helium), but they are for the most part beyond the remit of this course. The important point to realise is that

> kinetic theory is *approximate* and applies best to *gases* at *low density* and *high temperature*.

1.2 Ideal Gases

The concept of an *ideal* gas is an important one in thermal physics. An ideal gas obeys the assumptions of kinetic theory perfectly. Real gases approximate ideal gases in the limit of low density, $\rho \to 0$. Some of the properties of ideal gases also apply in somewhat surprising situations, such as very dilute solutions of salts, and thus one can find equations related to ideal gases cropping up in many places. I will now derive some fundamental relations for ideal gases.

1.2.1 Pressure

Molecules in a gas collide with the walls of their container and transfer momentum to it. Averaged over time, we have what is felt macroscopically as *pressure*. Pressure is a force per unit area, or equivalently the total rate of momentum transfer per unit time per unit area. Referring to Fig. 1.1, a molecule hitting a wall perpendicular to the x-axis will reverse its momentum (elastic collision with a smooth wall) and therefore suffer a change in momentum of $-2mv_x$ where v_x is the x component of its velocity and m is its mass. This momentum is imparted to the wall. In time Δt all atoms within a distance $v_x \Delta t$ of the wall can hit it, but only half are travelling towards the wall (by assumption 3), so the number of collisions per unit area in time Δt is

$$\frac{1}{2} n v_x \Delta t. \tag{1.1}$$

where n is number of molecules per unit volume. The force exerted is the rate of momentum transfer, so the pressure, which is the force per unit area is

$$P = \frac{1}{2} n v_x \Delta t \times \frac{2mv_x}{\Delta t} = nmv_x^2. \tag{1.2}$$

This must be averaged because the molecules have a spread of v_x values. Denoting averages by bars over the top, we have

$$P = nm\overline{v_x^2}, \tag{1.3}$$

The overall speed v, in three dimensions, is given by

$$v^2 = v_x^2 + v_y^2 + v_z^2, \tag{1.4}$$

which carries over to

$$\overline{v^2} = \overline{v_x^2} + \overline{v_y^2} + \overline{v_z^2}. \tag{1.5}$$

The assumption that the molecules move randomly implies that they have no preferred direction, so $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$ which leads to $\overline{v_x^2} = \overline{v^2}/3$. Therefore we have the very important equation

$$\boxed{P = \frac{1}{3}nm\overline{v^2}}. \tag{1.6}$$

For example, for air at *standard temperature and pressure* (STP, 1 atmosphere, 273 K): $P = 101\,000\,\mathrm{N\,m^{-2}}$ and the density $\rho = 1.2\,\mathrm{kg\,m^{-3}}$. Now $\rho = nm$, so

$$v_{\mathrm{rms}} = \sqrt{\overline{v^2}} = \sqrt{\frac{3P}{\rho}} \approx 500\,\mathrm{m\,s^{-1}}. \tag{1.7}$$

This is why air can fill a vacuum so quickly, for example if you break a tungsten filament light bulb. A light bulb 10 cm in diameter will fill up in about 0.1 m/500 m $\mathrm{s^{-1}}$ = 0.2 ms for example.

The SI unit of pressure, $\mathrm{N\,m^{-2}}$ is also known as the pascal or Pa.

1.2.2 Internal energy

The expression for pressure shows that it is related to the kinetic energy of the molecules. If all the energy of a gas is kinetic energy then we can write

$$U = \frac{1}{2}(nV)m\overline{v^2}. \tag{1.8}$$

where U is the total energy of the molecules. Therefore from $P = (1/3)nm\overline{v^2}$ we have

$$U = \frac{3}{2}PV. \tag{1.9}$$

The energy density $U/V = 3P/2$ is therefore directly related to the pressure, a result that you will encounter often in physics. Air for example has energy density $U/V \approx 150\,\mathrm{kJ\,m^{-3}}$. U is known as the *internal energy*; we will encounter it many times in this course.

Now we appeal to the empirical *ideal gas laws*, shown in Table 1.1 on the following page. In particular Boyle's Law tells us that the quantity PV is constant for a fixed temperature, and is therefore a function of temperature alone. Therefore we have that

> the internal energy U of an *ideal gas* depends only upon its temperature, T_{I}, *not* on either P or V.

In other words $U_{\mathrm{I}} = U(T_{\mathrm{I}})$, where the subscript I stands for ideal. Note that this is already one of the gas laws, Joule's law, although the experiments from which he derived this law were not very sensitive.

Avogadro's Law	Equal volumes of all gases, at the same temperature and pressure, have the same number of molecules
Boyle's Law	The volume of an ideal gas at fixed temperature is inversely proportional to its pressure.
Charles' Law	The volume of an ideal gas kept at fixed pressure is proportional to its temperature.
Joule's Law	The internal energy of an ideal gas depends only upon its temperature.

Table 1.1 The ideal gas laws

1.2.3 The Equation of State of an Ideal Gas

Boyle's, Charles' and Avogadro's Laws can be combined into a single simple equation

$$\boxed{PV = NkT_\mathrm{I}}, \tag{1.10}$$

where

N is the number of molecules in volume V,
$k = 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$ is *Boltzmann's constant*,
T_I is the temperature in Kelvin.

In fact this equation *defines* the ideal gas scale of temperature, which I will for now denote T_I. Later on we will see that this particular temperature scale has a special and fundamental significance. The ideal gas scale is an *absolute* scale: it has a zero-point when all motion ceases. As defined by Kelvin, the freezing point of water, which is 0°C on the Celsius scale, is 273.15 K. This seemingly arbitrary number was chosen to make the difference between the freezing and boiling points of water equal to 100 K. We will see more of this in Chapter 7.

Equation 1.10 is an example of an *equation of state*, which is a relation between pressure, volume and temperature. Its existence means that one has only two "degrees of freedom" in fixing the state of a gas. For instance one can fix the temperature and pressure, but not also the volume, or one can set the temperature and volume, but not also the pressure because given the first two, the third is fixed by the equation of state.

There are several other forms of the ideal gas equation of state that you should be familiar with. Defining the number density (number of molecules per unit volume) by $n = N/V$ we have

$$\boxed{P = nkT_\mathrm{I}}. \tag{1.11}$$

Alternatively, it is common to work in terms of "moles". One mole is defined as Avogadro's number, $N_\mathrm{A} = 6.02 \times 10^{23}$, of molecules. More formally, a mole is the number of atoms in 12 g of $^{12}\mathrm{C}$. This means it is very close (but not exactly equal) to the number of atoms in 1 g of $^{1}\mathrm{H}$, or the number of molecules in $(1 + 1 + 16)\,\mathrm{g} = 18\,\mathrm{g}$ of $H_2 0$, etc. In other words the weight in grams of a mole of some substance equals the total relative atomic mass of its constituents. Molar quantities are used extensively in chemistry. For n_m moles, $N = n_m N_\mathrm{A}$ and so

$$PV = n_m N_\mathrm{A} k T_\mathrm{I}, \tag{1.12}$$

and, defining the *gas constant*, $R = N_\mathrm{A} k = 8.314\,\mathrm{J\,K^{-1}\,mole^{-1}}$, we have a very commonly encountered version of the equation of state:

$$\boxed{PV = n_m R T_\mathrm{I}}. \tag{1.13}$$

Finally, defining the *molar volume* $V_m = V/n_m$ (i.e. the volume occupied by one mole), we get

$$PV_m = RT_{\mathrm{I}}. \tag{1.14}$$

Example 1.1 What is the volume of 1 mole of ideal gas at STP?

Answer 1.1 The nice point is that I do not have specify the type of gas: all ideal gases have the same molar volume. The answer is

$$V_m = \frac{RT_{\mathrm{I}}}{P} = \frac{8.314 \times 273}{101,000} = 0.0225\,\mathrm{m}^3 = 22.5\,\mathrm{litre}.$$

Example 1.2 Intel manufactures Pentium chips in chambers where the pressure is equivalent to 1.0×10^{-10} mm of mercury. What fraction is this of atmospheric pressure? How many molecules are there in a chamber 40 cm in diameter and 30 cm tall at 20°C?

Answer 1.2 At atmospheric pressure, P_{atm}, air can support a column of mercury of height 760 mm. Therefore the pressure, P, in the chamber is given by

$$\frac{P}{P_{\mathrm{atm}}} = \frac{10^{-10}\,\mathrm{mm}}{760\,\mathrm{mm}} = 1.32 \times 10^{-13}.$$

Alternatively, if the height of mercury supported is $h = 10^{-10}$ mm and the density of mercury is $\rho = 13\,600\,\mathrm{kg\,m^{-3}}$, the pressure is $P = \rho g h$, and

$$\begin{aligned}\frac{P}{P_{\mathrm{atm}}} = \frac{\rho g h}{P_{\mathrm{atm}}} &= \frac{13\,600\,\mathrm{kg\,m^{-3}} \times 9.81\,\mathrm{m\,s^{-2}} \times 10^{-13}\,\mathrm{m}}{1.01 \times 10^5\,\mathrm{Pa}} \\ &= 1.32 \times 10^{-13}.\end{aligned}$$

To find the number of molecules in the chamber we use

$$\begin{aligned}N &= \frac{PV}{kT_{\mathrm{I}}} \\ &= \frac{13\,600\,\mathrm{kg\,m^{-3}} \times 9.81\,\mathrm{m\,s^{-2}} \times 10^{-13}\,\mathrm{m} \times \pi \times (40/2)^2 \times 30 \times 10^{-6}\,\mathrm{m}^3}{1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 293\,\mathrm{K}} \\ &= 1.24 \times 10^{11}.\end{aligned}$$

This is a large number of molecules, but much much less than N_{A}.

1.2.4 Temperature and Average Kinetic Energy

Combining the ideal gas law in equation 1.10 on the previous page with the kinetic theory expression for the pressure in an ideal gas, equation 1.6 on page 3 we find:

$$\frac{1}{2} m \overline{v^2} = \frac{3}{2} k T_{\mathrm{I}}. \tag{1.15}$$

This tells us that the temperature is a measure of the average molecular kinetic energy for the ideal gas (the factor 3/2 will be explained in section 2.3). Boltzmann's constant k is the conversion factor between units of temperature and energy.

1.3 Summary

The first key point to take from this initial look at kinetic theory (we will return to it later) is that it is an approximate theory which can be expected to apply to low density gases. The other important parts are the relation between pressure and molecular speeds (Eq. 1.6) and the well-known equation of state of the ideal gas, in its various forms (Eqs. 1.10, 1.11 and 1.13).

2

The Boltzmann Factor & Equipartition

In the last chapter I discussed the rms molecular speed and alluded to the fact that not all speeds are the same. What controls how often we find a particular speed? The answer, for a system in thermal equilibrium, is the Boltzmann factor. This factor can be introduced by considering the change of pressure with height in the Earth's atmosphere when the atmosphere is in hydrostatic equilibrium.

2.1 Hydrostatic Equilibrium

Consider the equilibrium of a slab of gas of vertical thickness $\mathrm{d}h$ in a gravitational field g. The pressure at the top of the slab must be less than at the bottom in order to support the weight of the slab. The weight of a slab of area A is

$$\rho A g \, \mathrm{d}h, \tag{2.1}$$

where ρ is the density, while the upwards force is

$$PA - (P + \mathrm{d}P)A = -A \, \mathrm{d}P. \tag{2.2}$$

Therefore, balancing forces we have $\mathrm{d}P = -\rho g \, \mathrm{d}h$, or

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}h} = -\rho g}\,. \tag{2.3}$$

This is the *equation of hydrostatic equilibrium*, which applies to any fluid static under gravity, e.g. the Earth's and other planetary atmospheres and stars. For example,

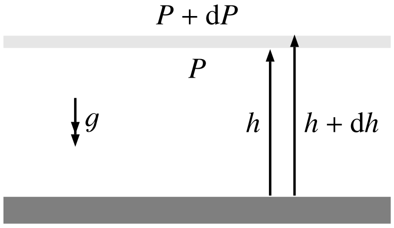

Figure 2.1 Equilibrium of a thin slab of gas in a gravitational field.

if the density ρ is constant, then integrating we get $P = -\rho gh+\text{constant}$. If we switch the sign of h so it is measured downwards, and set $P = 0$ at $h = 0$, this is the usual "$P = \rho gh$" for pressure under the sea.

For an ideal gas we have $P = nkT_\text{I}$ and $\rho = nm$, and so

$$\frac{dn}{dh} = -\frac{mg}{kT_\text{I}}n. \tag{2.4}$$

If the atmosphere is *isothermal* (T_I is constant with h), we can integrate this easily

$$\int_{n_0}^{n} \frac{dn'}{n'} = -\frac{mg}{kT_\text{I}} \int_0^h dh', \tag{2.5}$$

introducing primes to distinguish the integration variable from the limits. This gives

$$\ln \frac{n}{n_0} = -\frac{mgh}{kT_\text{I}}, \tag{2.6}$$

or

$$\frac{n}{n_0} = \frac{P}{P_0} = e^{-mgh/kT_\text{I}}. \tag{2.7}$$

Thus in an isothermal atmosphere under hydrostatic equilibrium, the pressure and number density drop exponentially with height. For example, for air on Earth we have $m = 30u$ and $g = 9.81$ m s^{-2}, and assuming that $T_\text{I} = 300$ K, at a height of $h = 5$ km, one finds $P/P_0 = 0.55$.

2.2 Boltzmann Factor

The term $mgh = E$, the potential energy of a molecule, and so we can write

$$n \propto e^{-E/kT}. \tag{2.8}$$

We derived an expression for the variation of number density with height, but we can now take an alternative view: for each particle, the *probability* of finding it at height h, where the potential energy is $E = mgh$, is proportional to $e^{-E/kT}$. Although this is a very general result of huge importance: the chance of finding an atom, or any system, with energy E when in thermal equilibrium at temperature T is

$$P(E) \propto e^{-E/kT}. \tag{2.9}$$

This is known as the *Boltzmann factor*. Because it is general, and not dependent upon ideal gases, I have dropped the subscript I on the temperature; the precise meaning of this will only become clear later, but for now just think of it as the absolute temperature in Kelvin. A complicating factor is that there may be many states of the same energy, each of which contributes, and so the Boltzmann factor must be multiplied by a *weight factor* to account for this. The calculation of such factors requires quantum physics. You will encounter the Boltzmann factor many times. For the ideal gas, the energy E is the kinetic energy, and the factor $e^{-mv^2/2kT}$ controls the distribution of molecular speeds (with a weight factor also appearing in this case).

2.2.1 Activation Energies

The Boltzmann factor has important consequences for the rates of chemical and other reactions. Consider a mixture of hydrogen and oxygen. At room temperature it is stable, and can last for years in this state. However a tiny spark can set off an explosive reaction resulting in the formation of water and the liberation of a great deal of heat. Water is therefore a lower energy state, but cannot normally be reached because a certain (positive) amount of energy is required to start the reaction. This is the activation energy, E_A. For a system like hydrogen and oxygen, it is clear that $E_A \gg kT$, or the reaction would start spontaneously. In this case the Boltzmann factor $e^{-E/kT}$ can make rates very sensitive to temperature. This is best seen in an example.

Example 2.1 If $E_A = 100\,kT$ and $T = 300\,\text{K}$ by how much does the Boltzmann factor change if T is raised by 20 K?

Answer 2.1 Initial value is e^{-100}. For $T = 320\,\text{K}$, $E_A/kT = 100(300/320) = 93.75$, so the new value is $e^{-93.75}$. The ratio is

$$\frac{e^{-93.75}}{e^{-100}} = e^{100-93.75} = e^{6.25} = 518. \tag{2.10}$$

A small increase in temperature causes a dramatic increase in the Boltzmann factor. This is the origin of the temperature sensitivity of chemical processes and of fusion processes in stars. Also note that catalysts are substances that can reduce the activation energies and allow reactions to take place at much lower temperatures; they are essential in biology.

2.3 The Equipartition of Energy and Heat Capacities

The Boltzmann factor also leads to an important theorem of classical physics called the equipartition theorem. This theorem gives a simple rule-of-thumb for estimating heat capacities. Unfortunately it is wrong, but for an interesting reason.

2.3.1 The Equipartition Theorem

Consider an atom of a monatomic gas, helium for example. We can write its energy as

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right). \tag{2.11}$$

There are 3 squared terms or *degrees of freedom*. We have met degrees of freedom in another context, that of the number of variables needed to specify the state of a gas. In general the number of degrees of freedom is the number of parameters required to define a system. The *equipartition theorem* states:

> for a classical system in thermal equilibrium, the total energy of the system is shared or *partitioned* equally among all the various degrees of freedom.

The temperature of a classical system in thermal equilibrium can be defined using this average energy per degree of freedom:

$$\frac{1}{2}kT = (\text{average energy in each degree of freedom}). \tag{2.12}$$

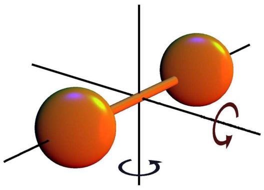

Figure 2.2 Rotation axes for a diatomic molecule.

Our helium atom has kinetic energy only and equipartition says that each squared term has a mean thermal energy of $kT/2$, so that

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT. \tag{2.13}$$

For a mole of identical helium atoms (or the atoms of any ideal gas) the total energy in thermal equilibrium at temperature T becomes $3RT/2$. This means that the internal energy of a monatomic gas is $U = 3RT/2$ per mole, as we have seen before.

Comparing the equation above, Eq. 2.13, with Eq. 1.15 on page 5, we learn that our equipartion-based temperature agrees with the ideal gas temperature. Later, we will define thermodynamic temperature and will discover that this too agrees with the ideal gas (and hence equipartition) temperatures.

Proving the equipartition theorem requires a sophisticated level of classical mechanics. It comes about because of the finite amount of energy a system can have according to the Boltzmann distribution at temperature T. It should be obvious from the form of the distribution, $\exp(-E/kT)$, that the mean energy is of order kT. The factor of $1/2$ needs much more work, and I will take it on trust. The theorem can be applied to more complex systems than monatomic gases, as I now discuss.

2.3.2 Diatomic Gases

Many gases are diatomic, for example H_2, O_2, N_2. They have translational motions (centre of mass motion), but they can also rotate and vibrate (motion relative to the centre of mass). Figure 2.2 shows the rotation axes perpendiclar to the axis of the molecule. In fact there are

3 directions of translation (as before), $mv_x^2/2$ etc.
2 axes of rotation ($I\omega_x^2/2$ etc)
1 vibration ($mv^2/2 + kx^2/2$)

The axis of rotation parallel to the axis of the molecule does not contribute since I assume the atoms are points. I will come back to this later. Each axis of rotation contributes one squared term, a kinetic energy term. The vibration however has *two* squared terms, 1 kinetic and 1 potential, therefore we have a grand total of 7 degrees of freedom, and so $U = 7RT/2$ per mole. Note that the “internal” degrees of freedom contribute more than the translational energy.

2.3.3 Carbon Dioxide

Now let’s look at a more complex case still, that of carbon dioxide, a linear arrangement of three atoms (figure 2.3 on the next page). In this case there are

3 translations
2 rotations
4 vibrations (2 along the bonds, 2 bending in perpendicular planes)

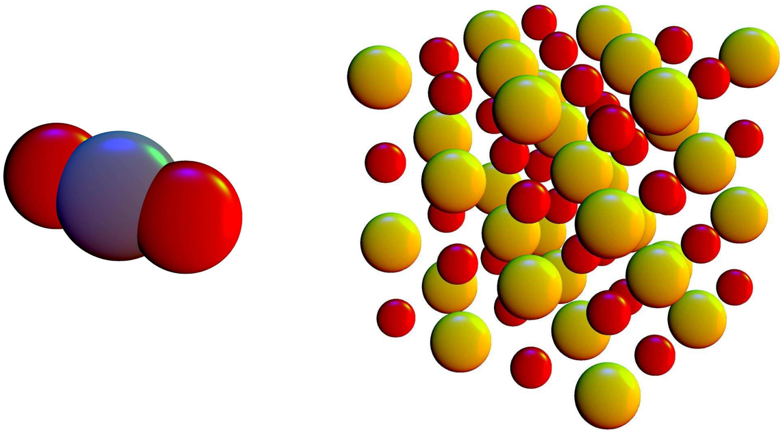

Figure 2.3 Schematic illustrations of a carbon dioxide molecule (left) and a crystal lattice (right).

With two terms per vibration as before, there are a total of $3+2+4\times 2 = 13$ degrees of freedom, and $U = 13RT/2$ per mole.

2.3.4 Solids

Imagine a regular lattice of atoms (figure 2.3). We need three coordinates to specify the position of each atom. Each of these will have an associated kinetic and potential energy term. Therefore we expect 6 degrees of freedom per atom, giving a total internal energy of $U = 3RT$ per mole (this is known as Dulong and Petit's Law). This is the maximum number of degrees of freedom we need since a position and velocity are enough to fully specify atoms. Note that in terms of *atoms* the monatomic and diatomic gases and carbon dioxide amount to $3RT/2$, $7RT/4$ and $13RT/6$, so none of them exceed $3RT$.

2.3.5 Heat Capacities

We can test these predictions experimentally using *heat capacities*. The rate of increase in internal energy of a substance with increasing temperature (or the increase in internal energy per unit rise in temperature) is called its *heat capacity* (I will be more precise about this later: see section 4.7 on page 33). Heat capacities have SI units of $\mathrm{J\,K^{-1}}$. If we measure the heat capacity per mole, per unit mass or per unit volume, it is called the *specific* heat capacity and has units of $\mathrm{J\,K^{-1}\,kg^{-1}}$ or per mole or whatever. In this instance the molar specific heat capacity is of most interest.

For one mole of a monatomic gas, with $U = 3RT/2$, a rise of 1 K causes U to increase by $3R/2$ and so the molar specific heat capacity C is given by

$$C = \frac{\mathrm{d}U}{\mathrm{d}T} = \frac{3}{2}R = 12.5\,\mathrm{J\,K^{-1}\,mole^{-1}}. \tag{2.14}$$

Similarly for a diatomic gas, $C = 7R/2 = 29\,\mathrm{J\,K^{-1}\,mole^{-1}}$. These are values that we can test directly against experiment. Experimentally derived values are listed in Table 2.1. The results are good in parts. Equipartition seems to work very well for the monatomic gases, partly for diatomic gases, fairly poorly for triatomic gases, and is good and bad for solids. Clearly it has elements of the truth about it, but at the same time it is not correct. The question is why does it fail?

Monatomic	He	Ne	Ar	Xe
C (experiment)	12.5	12.5	12.5	12.5
C (predicted)	12.5	12.5	12.5	12.5
Diatomic	H_2	N_2	O_2	I_2
C (experiment)	20.5	20.8	21.1	28.6
C (predicted)	29.1	29.1	29.1	29.1
Triatomic	CO_2	H_2O	O_3	NO_2
C (experiment)	28.8	25.3	29.9	29.6
C (predicted)	54.0	58.2	58.2	58.2
Solids	Cu	Al	Zn	C (diamond)
C (experiment)	24.5	24.3	25.1	6.1
C (predicted)	24.9	24.9	24.9	24.9

Table 2.1 Experimental and theoretical molar specific heat capacities for different substances. Units $\mathrm{J\,K^{-1}\,mole^{-1}}$.

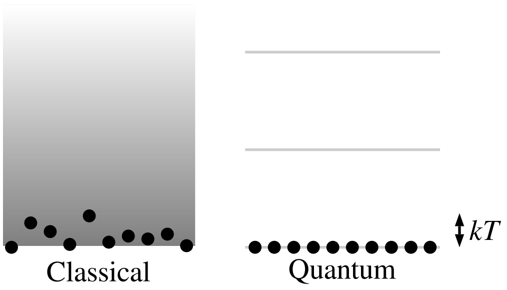

Figure 2.4 A schematic figure of the difference between excitation in a classical systems with a continuum of energy levels and a real system which obeys the laws of quantum physics, with discrete energy levels.

2.3.6 Why Equipartition fails

Fig. 2.4 illustrates why equipartition fails. The reason is that in classical physics, there is a continuum of energy levels. Between any two energies you care to name, there are infinitely many possible states. This means that the total energy of a system can vary continuously and the equipartition theorem assumes this. In the quantum world this is not the case. Energy levels are commonly discrete. In particular there is a finite step between the lowest energy level and the first excited state above it. In a classical system it is always possible for some atoms to be excited above the lowest energy level, and hence contribute towards the $kT/2$. In a real system, if kT is much less than the energy needed to get to the first excited state, ΔE, there can be *no* excitation at all, and *no* contribution to the specific heat. Degrees of freedom therefore “freeze out”, and the lower the temperature, the more this happens.

For typical molecules, it is the case that

$$\Delta E_{\mathrm{trans}} \ll \Delta E_{\mathrm{rot}} \ll \Delta E_{\mathrm{vib}}. \tag{2.15}$$

Starting from a low temperature and gradually increasing it, at first the translational modes come into play, giving $C = 3R/2$. This happens at very low temperatures where typically one must include other factors such as intermolecular forces; I will ignore these for now. As the gas gets hotter, rotations start to contribute. This happens at 50 K or so. In other words, well below this value, the molecules do

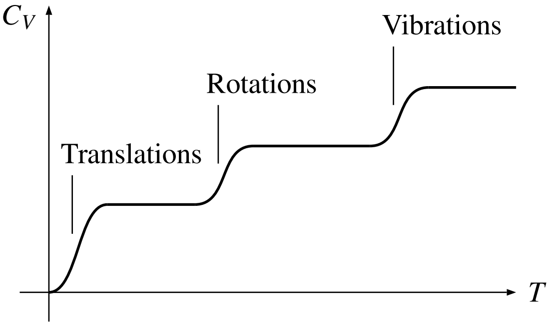

Figure 2.5 A schematic illustration of variation of specific heat with temperature as more and more degrees of freedom become excited.

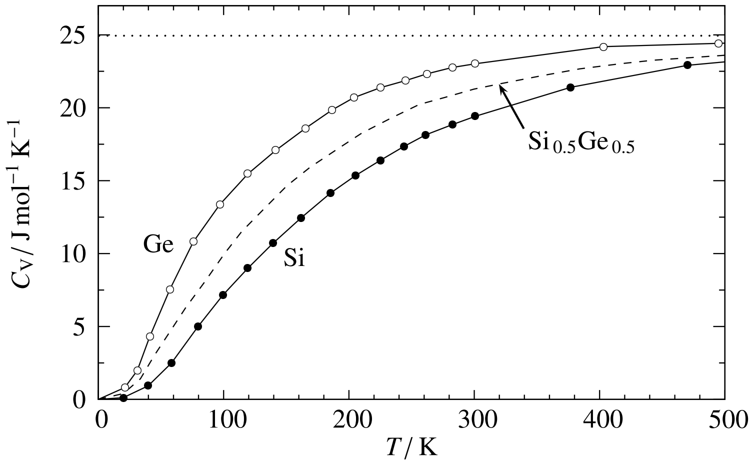

Figure 2.6 Molar specific heats of germanium, silicon and an alloy of the two. Adapted from KL Wang and X Zheng, in E Kasper (ed), *Properties of Strained and Relaxed Silicon Germanium*, EMIS Datareviews, INSPEC, London 1995. The dotted line shows the equipartion prediction, $3R$.

not rotate! Once rotations are fully on, $C = 5R/2 = 20.8\,\mathrm{J\,K^{-1}\,mole^{-1}}$. If you refer to Table 2.1 once more, you will see that this exactly matches the value for nitrogen at room temperature. As the temperature rises more, over 1000 K say, then the vibrational modes start to be excited, and we will eventually reach the original prediction (although once vibrations become fully excited, it also becomes possible for the molecules to break up). The frequency of vibrations is lower for more massive atoms, and so we can expect that a heavier molecule might match the equipartition value better than a light molecule. This can be seen to be the case by comparing hydrogen with iodine in Table 2.1. Fig. 2.5 shows schematically how the specific heat of molecular substances varies with temperature.

I can now come back to my earlier statement that for a diatomic molecule we ignore rotations around the line joining the atoms. Notice that the moment of inertia around this axis will be *much* smaller than those for the two perpendicular axes. But, the kinetic energy of rotation is $L^2/2I$, where L is the angular momentum and I the moment of inertia. Quantum mechanics tells us that the angular momentum takes quantised values, and therefore the rotational energy will be much larger for rotations about the line joining the atoms.

For solids, a nice example is provided by diamond (Table 2.1). This has a very rigid structure with strong bonds and relatively light atoms. Therefore the vibration frequencies are high, and not fully excited at room temperature. Hence its heat capacity is only $1/4$ of the value predicted by equipartition. Figure 2.6 on the previous page shows the molar specific heats for germanium, silicon and an alloy of the two. Again the equipartition value of $3R$ is only approached at temperatures of hundreds of kelvin.

There are much better theories that predict how specific heats vary with temperature; they are all based upon quantum mechanics. I close with two more reasons why we need better theories:

- Many metals contain large numbers of *conduction electrons* which behave essentially freely and so should contribute an extra $3k/2$ per electron to the heat capacity. However, the Dulong-Petit law, which takes into account only the lattice ions, works pretty well for metals at around room temperature.

- Consider a rigid diatomic dumbbell molecule compared to a slightly non-rigid one. Classical equipartition would say that *any* non-rigidity will lead to a fixed contribution to the heat capacity, while the rigid molecule has no such contribution. This would mean a discontinuous change in the heat capacity in the limit of making a molecule infinitely stiff: probably not the behaviour we would expect.

2.4 Summary

The Boltzmann factor is of key importance in thermal physics and has an impact in many areas. It also leads to the classical theorem of equipartition, whose failure was one of the first signs that something was seriously amiss with classical physics, at least in hindsight.

3

Kinetic Theory – II

I now continue the development of kinetic theory by looking at some features of the motion of molecules in a gas. The molecules' paths are called *random walks*. We are interested here in how far molecules travel on average over given intervals of time and how far between collisions. The latter in particular sets the scale above which one can expect to see behaviour that is characteristic of large amounts of gas rather than individual molecules. Such average distance is called the mean free path. I will first estimate this and then use it to estimate further properties such as thermal conductivity.

3.1 The Mean Free Path

Molecules collide, travel freely, collide and so on. The mean distance between collisions is the *mean free path*, usually denoted by λ. To estimate λ, consider the situation depicted in Fig. 3.1. Imagine that all molecules are stationary except the molecule on the left, which is travelling from left to right. Let all the molecules be spheres of radius R and diameter $D = 2R$. The moving molecule can potentially hit any molecule located within a distance D from its projected path. In other words the moving molecule sweeps out a cylinder of radius D and any molecule within this cylinder can be hit (after each collision, the direction of the moving molecule changes, so we might also depict the situation as in Fig. 3.2 on the next page). The moving molecule sweeps out a volume

$$\pi D^2 v \tag{3.1}$$

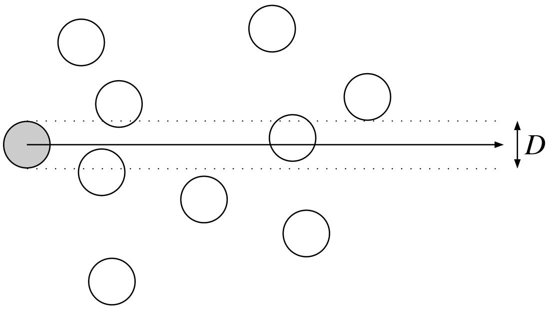

Figure 3.1 Illustration showing which molecules will collide with the one on the left.

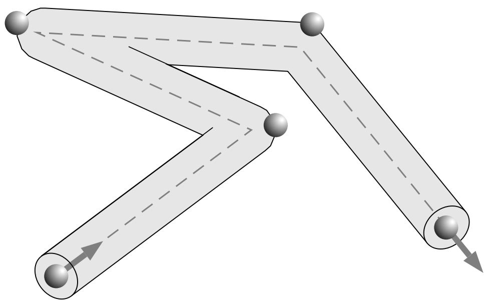

Figure 3.2 Alternative depiction of a moving molecule colliding with other molecules and tracing out a "bent" cylinder.

per unit time giving a collision rate $\pi D^2 nv$. If one accounts for the movement of the other molecules, this is increased by a factor of $\sqrt{2}$, so the collision rate is

$$\sqrt{2}\pi D^2 nv \tag{3.2}$$

For example, for air at STP, $P = nkT_\mathrm{I}$, so

$$n = \frac{P}{kT_\mathrm{I}} = \frac{1.01 \times 10^5\,\mathrm{Pa}}{1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 273\,\mathrm{K}} = 2.7 \times 10^{25}\,\mathrm{m^{-3}}. \tag{3.3}$$

(NB temperature in Kelvin!). Taking $D = 0.3\,\mathrm{nm}$ and $v = 477\,\mathrm{m\,s^{-1}}$, then the collision rate is $\approx 5.1 \times 10^9\,\mathrm{s^{-1}}$.

The mean free path is the speed divided by the collision rate, and so

$$\boxed{\lambda = \frac{1}{\sqrt{2}\pi D^2 n}}, \tag{3.4}$$

where I have included the factor $\sqrt{2}$ mentioned above. For air at STP, we obtain $\lambda \approx 10^{-7}\,\mathrm{m}$.

Example 3.1 Electrons travel 3 km along the SLAC linear collider at Stanford in California. To reduce scattering losses, the electrons need to have a mean free path of at least 50 km. What is the maximum allowed pressure inside the collider's beam pipe at $T_\mathrm{I} = 20°\mathrm{C}$?

Answer 3.1
We have

$$\lambda_\mathrm{electron} = \frac{1}{\sqrt{2}\pi D^2 n}.$$

Now we use the ideal gas relation, $P = nkT_\mathrm{I}$, to find,

$$P = \frac{kT_\mathrm{I}}{\sqrt{2}\pi D^2 \lambda_\mathrm{electron}} = \frac{1 \times 1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}} \times 293\,\mathrm{K}}{\sqrt{2}\;\pi(1 \times 10^{-10}\,\mathrm{m})^2 \times 50 \times 10^3\,\mathrm{m}} = 1.8 \times 10^{-6}\,\mathrm{Pa}.$$

We have taken the gas molecules to have a diameter $D = 0.2\,\mathrm{nm}$, appropriate for diatomic molecules. This pressure is about 2×10^{-11} atm.

3.1.1 What is the distribution of molecular path lengths?

The mean free path tells us how far a molecule travels on average, but sometimes it will go further, and sometimes not so far. What is the distribution of free path distances, or equivalently, what is the chance that a molecule survives a distance r without collision? This can be worked out as follows: the chance of colliding in a small distance dr equals the time taken multiplied by the collision rate,

$$\frac{\mathrm{d}r}{v} \times (\text{collision rate}) = \frac{\mathrm{d}r}{\lambda}. \tag{3.5}$$

Therefore if the probability of traveling distance r is $P(r)$, the probability of travelin $r + \mathrm{d}r$, which by definition is $P(r + \mathrm{d}r)$ can also be written as the chance of getting to r multiplied by the chance of surviving (ie, *not* being hit) within the next short interval dr which gives

$$P(r + \mathrm{d}r) = P(r)\left(1 - \frac{\mathrm{d}r}{\lambda}\right). \tag{3.6}$$

Hence subtracting $P(r)$ from both sides and dividing through by dr we get

$$\frac{P(r + \mathrm{d}r) - P(r)}{\mathrm{d}r} = -\frac{P(r)}{\lambda}. \tag{3.7}$$

The left-hand side is the standard definition of the derivative dP/dr, so

$$\frac{\mathrm{d}P}{\mathrm{d}r} = -\frac{1}{\lambda}P. \tag{3.8}$$

This is another equation of exponential decay, as we saw for the hydrostatic equilibrium of an ideal gas. Integrating it we have

$$P(r) = P(0)e^{-r/\lambda}, \tag{3.9}$$

where $P(0)$ is a constant, the chance of surviving for zero distance, which is clearly unity. Then $P(0) = 1$, and so

$$\boxed{P(r) = e^{-r/\lambda}}. \tag{3.10}$$

This is an exponential probability distribution. The chance of travelling 10λ, for example, is $e^{-10} \approx 5$ in 100,000. The mean free path length is λ and the rms free path length is $\sqrt{2}\lambda$. This distribution is commonly encountered with random events. It is for instance the distribution of times between the arrival of photons from a light source, amongst other things.

3.1.2 Distance travelled

How far will a molecule have travelled after a time t? One answer is vt, where v is its speed, but this would not be the direct distance it has travelled from its point of origin if there are collisions, and we have seen that it cannot get far in this case. Consider where it will be after N steps. Its position vector $\mathbf{r}$ will be

$$\mathbf{r} = \mathbf{s}_1 + \mathbf{s}_2 + \mathbf{s}_3 + \dots, \tag{3.11}$$

where $\mathbf{s}_i$ is the displacement of the i-th step. It might seem hard to progress further: we cannot possibly try to work out $\mathbf{s}$ for more than a few steps at most. However, we can learn something if we focus on the square modulus of $\mathbf{r}$ which is given by

$$r^2 = \mathbf{r} \cdot \mathbf{r} = \mathbf{s}_1^2 + \mathbf{s}_2^2 + \mathbf{s}_3^2 + \dots + \mathbf{s}_1 \cdot \mathbf{s}_2 + \mathbf{s}_1 \cdot \mathbf{s}_3 + \mathbf{s}_2 \cdot \mathbf{s}_1 + \dots \tag{3.12}$$

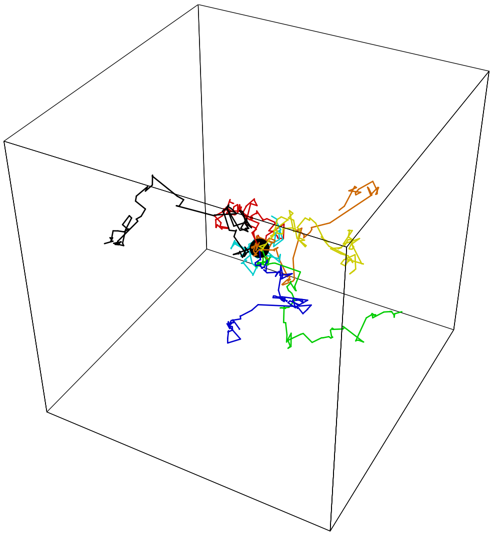

Figure 3.3 Seven random walks of a particle. Each walk comprises 100 steps with step-lengths distributed according to the exponential distribution.

The terms are either of the form $\mathbf{s}_i^2 = s_i^2$ or "cross terms" such as

$$\mathbf{s}_i \cdot \mathbf{s}_j = s_i s_j \cos\theta_{ij}, \tag{3.13}$$

for $i \neq j$, where θ_{ij} is the angle between step i and step j. Assuming that θ_{ij} is random, then the average value $\langle \cos\theta_{ij} \rangle = 0$, and the cross terms disappear. Thus the *mean* squared distance

$$\bar{r^2} = \sum_{i=1}^{N} \bar{s_i^2} \approx N\lambda^2. \tag{3.14}$$

The 'approximately equal to' ($\approx$) appears here because $\bar{s_i^2}$ is the mean squared step-length which we have simply replaced by λ^2 without being too precise. Thus the root-mean-square (rms) distance travelled, measuring in a straight line from the point of origin is

$$\boxed{r \approx \sqrt{N}\lambda}, \tag{3.15}$$

the classic result of a *random walk* of N steps. Fig. 3.3 shows seven such random walks, with the individual step lengths distributed according to the exponential distribution. It is important to realise that the distance travelled (displacement from the starting point) and the path length can be hugely different,

since $\sqrt{N} \ll N$ for large N. A couple of examples will illustrate this.

Example 3.2 How far on average does an air molecule travel in 1 second?

Answer 3.2 From before, $N = 5.1 \times 10^9$ and $\lambda = 0.93 \times 10^{-7}$ m. So $r = \sqrt{N}\lambda = 6.7$ mm. This compares to 477 m of actual flight.

Example 3.3 The mean free path of a photon inside the Sun before it is absorbed and re-emitted in a random direction is about 0.01 m. How many steps will photons take to travel from the centre of the Sun to its surface, a distance of 7 ×

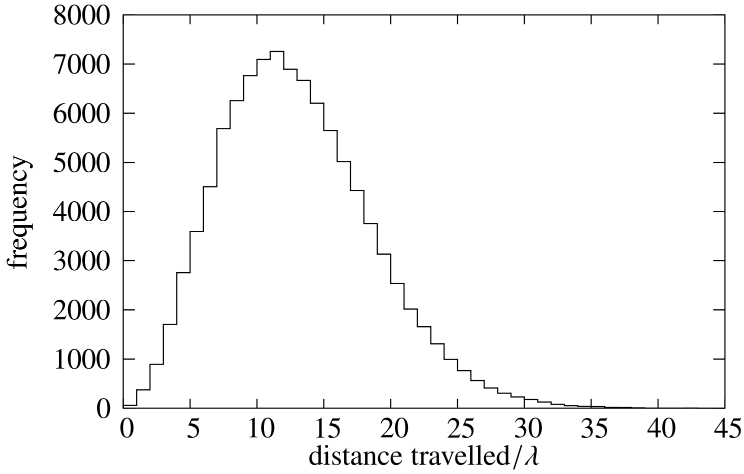

Figure 3.4 Frequency distribution of the distance travelled in 100 000 random walks, each of 100 steps, with the step-lengths themselves distributed according to an exponential distribution with mean λ. The mean distance travelled is 12.99λ, while the rms distance is 14.15λ and the maximum is 44.30λ.

10^8 m? How long will this take if the time between absorption and re-emission can be neglected?

Answer 3.3 Applying $r = \sqrt{N}\lambda$ gives the number of steps as

$$N = (r/\lambda)^2 = (7 \times 10^8\,\mathrm{m}/0.01\,\mathrm{m})^2 = 4.9 \times 10^{21}.$$

Ignoring the delay between absorption and re-emission (bad approximation), each step takes time λ/c, for a total of

$$\frac{N\lambda}{c} = \frac{r^2}{\lambda c} = \frac{(7 \times 10^8\,\mathrm{m})^2}{0.01\,\mathrm{m} \times 3 \times 10^8\,\mathrm{m\,s^{-1}}} = 1.6 \times 10^{11}\,\mathrm{s} = 5200\,\mathrm{years}.$$

It would take the photon 2.3 s to cover this distance directly.

Since the number of collisions scales with time, $N \propto t$, the distance travelled from the origin by a molecule scales with $t^{1/2}$. The distance is in reality best described by a distribution rather than simply a mean. Fig. 3.4 shows such a distribution.

The mean free path is a crucial concept for the next topic, the study of what are called “transport” processes. This forms the final part of my look at kinetic theory.

3.2 Transport

Transport processes apply when there is a departure from equilibrium. For instance, if a temperature gradient is set up, then energy will be transported. If a concentration gradient of one type of molecule is set up, then there will a flow of that type of molecule from high to low concentration (this is called diffusion.) The general situation is illustrated in Fig. 3.5 In this figure, the shaded molecules have some particular property which is transported from regions of high concentration to regions of low concentration simply by the random movement of molecules. I will focus upon the following three possibilities:

- different identity: *diffusion*

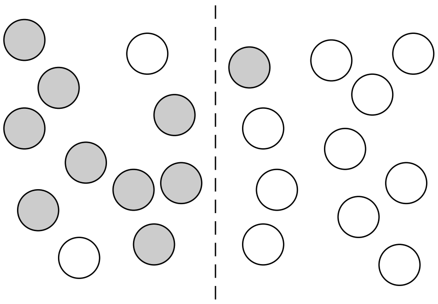

Figure 3.5 The shaded molecules represent those with some type of property such as element type, energy or momentum. As molecules move the shaded molecules will spread themselves out and in doing so "transport" the particular property of interest.

- different energy: *thermal conduction*
- different momentum: *viscosity*.

I will model all transport properties on the following basis:

- $1/6$ of the molecules travel in each of the directions $\pm x$, $\pm y$, $\pm z$ at speed $\bar{v}$.
- Molecules have the average properties of the position of their last collision, λ away from the surface through which the property of interest is being transported.

Although this is very simplified, and fails to account for subtle effects, such as the correlations between the energy, speed and mean free path of molecules, it captures the most important physics, and more sophisticated approaches often still rest on assumptions that mean they are not much better. I begin with the simplest of the transport processes, diffusion and follow this with thermal conductivity and viscosity, which follow through in much the same way.

3.2.1 Diffusion

Diffusion is the movement of a substance driven by a gradient in its concentration. The flow rate across area A in terms of a number of molecules per unit time is governed by an equation known as Fick's Law:

$$\boxed{\frac{dN}{dt} = -DA\frac{\mathrm{d}n}{\mathrm{d}x}}, \tag{3.16}$$

where D is the *diffusion coefficient*. The term $\mathrm{d}n/\mathrm{d}x$ is the gradient in the number density of the substance of interest. This equation *defines* the diffusion coefficient; the minus sign indicates that diffusion causes a flow from high towards low concentrations. The diffusion coefficient has units of $\mathrm{m}^2\,\mathrm{s}^{-1}$. The transported property in the case of diffusion is the type of molecule.

Applying the simple description of transport, the flow rate (number per unit time) from left to right across area A of the dashed line at x is given by

$$\frac{1}{6}n(x-\lambda)A\bar{v}, \tag{3.17}$$

because $1/6$ of molecules within distance $\bar{v}$ of x can reach it (i.e. the same argument as used when deriving $P = nm\overline{v^2}/3$). The important point here is that the number density is evaluated a distance λ from the reference line. This matters because it is the gradient in n that drives diffusion. From right to left the flow rate is

$$\frac{1}{6}n(x+\lambda)A\bar{v}. \tag{3.18}$$

Therefore the total from left to right is the difference

$$\frac{1}{6}[n(x-\lambda)-n(x+\lambda)]A\bar{v}. \tag{3.19}$$

Since λ is small, we now expand each of the terms involving λ to first order as follows:

$$n(x-\lambda)\approx n(x)-\frac{dn}{dx}\lambda \qquad \text{and} \qquad n(x+\lambda)\approx n(x)+\frac{dn}{dx}\lambda, \tag{3.20}$$

so the net flow rate is

$$-\frac{1}{3}\lambda\bar{v}A\frac{dn}{dx}. \tag{3.21}$$

Comparing with Fick's Law, Eq. 3.16, we deduce the kinetic theory estimate for the diffusion coefficient

$$\boxed{D=\frac{1}{3}\lambda\bar{v}}. \tag{3.22}$$

Thus we have a relation between a macroscopic constant, the diffusion coefficient, and the microscopic properties of a gas. I will now illustrate the above with a fairly complex example.

Example 3.4 How fast does water in a test-tube evaporate?

Answer 3.4 The question is very brief, so we have to make some assumptions:

1. The water vapour has its saturated density, n_s, at the water surface.
2. The number density drops to zero at the mouth of test-tube, a height h above the water surface.
3. There are no air currents within the tube.
4. Water vapour can be described as an ideal gas.

In equilibrium, the concentration gradient is constant along the tube, so $\mathrm{d}n/\mathrm{d}x = n_s/h$. Therefore the loss rate/unit area is

$$\frac{\lambda\bar{v}n_s}{3h}=\frac{\lambda\bar{v}P_s}{3hkT_I},$$

using the ideal gas equation, $n_s = P_s/kT_I$. Therefore the rate of reduction in water level is the loss rate in molecules per unit time multiplied by the mass of each molecule m and divided by the density of water ρ:

$$\frac{m\lambda\bar{v}P_s}{3hkT_I\rho}=\frac{m_{\text{mole}}\lambda\bar{v}P_s}{3hRT_I\rho}.$$

In the last step, top and bottom were multiplied by Avogadro's number, N_A, to express the result in terms of the mass of a mole, $m_{\text{mole}} = N_A m$, and $R = N_A k$.

For example, at $T_I = 293$ K, the saturated vapour pressure is $P_s = 1710\,\mathrm{N\,m^{-2}}$ and the density of water is $\rho = 10^3\,\mathrm{kg\,m^{-3}}$. Assuming $h = 0.1$ m and taking $\lambda = 10^{-7}$ m, $\bar{v} = 650\,\mathrm{m\,s^{-1}}$ (water molecules are less massive and move faster than those of air, $m_{\text{mole}} = 0.018$ kg), then the evaporation rate is

$$\begin{aligned}\frac{0.018\,\mathrm{kg}\times 10^{-7}\,\mathrm{m}\times 650\,\mathrm{m\,s^{-1}}\times 1710\,\mathrm{N\,m^{-2}}}{3\times 0.1\,\mathrm{m}\times 8.314\,\mathrm{J\,K^{-1}}\times 293\,\mathrm{K}\times 10^3\,\mathrm{kg\,m^{-3}}} &= 2.7\times 10^{-9}\,\mathrm{m\,s^{-1}}\\ &= 0.24\text{ mm per day.}\end{aligned}$$

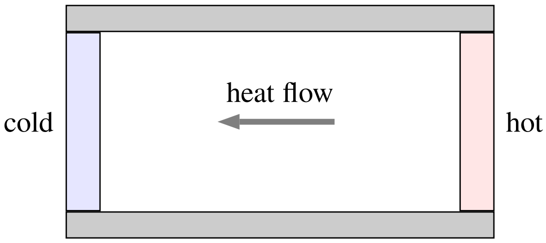

Figure 3.6 A standard setup for studying thermal conduction. Heat is conducted from a hot to a cold reservoir by means of a uniform rod. The rod is insulated (shaded regions) to prevent heat entering or leaving along its sides.

3.2.2 Thermal conduction

Thermal conduction is the transfer of energy as heat that occurs when there is a temperature gradient; see Fig. 3.6 for an illustration of a typical setup for studying it. The fundamental equation of heat conduction is Fourier's Law:

$$\boxed{\frac{\mathrm{d}Q}{\mathrm{d}t} = -KA\frac{\mathrm{d}T}{\mathrm{d}x}}, \tag{3.23}$$

where $\mathrm{d}Q/\mathrm{d}t$ is the energy flow rate across area A down a temperature gradient of $\mathrm{d}T/\mathrm{d}x$. This equation defines the *thermal conductivity* K, which has units of $\mathrm{W\,m^{-1}\,K^{-1}}$. The kinetic theory estimate of K follows as for diffusion, but we are transferring energy. Let the energy/molecule at position x be $E(x)$, then the energy flow rate from left to right is

$$\frac{1}{6}nA\bar{v}E(x-\lambda), \tag{3.24}$$

while from right to left it is

$$\frac{1}{6}nA\bar{v}E(x+\lambda). \tag{3.25}$$

The net flow from left to right is the difference,

$$-\frac{1}{3}nA\bar{v}\lambda\frac{\mathrm{d}E}{\mathrm{d}x}, \tag{3.26}$$

after applying the same expansions as for the diffusion case. Now

$$\frac{\mathrm{d}E}{\mathrm{d}x} = \frac{\mathrm{d}E}{\mathrm{d}T}\frac{\mathrm{d}T}{\mathrm{d}x}, \tag{3.27}$$

while $n\,\mathrm{d}E/\mathrm{d}T$ is the rate of increase of energy/volume with temperature, or *specific heat capacity per unit volume*, c, so

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = -\frac{1}{3}Ac\bar{v}\lambda\frac{\mathrm{d}T}{\mathrm{d}x}. \tag{3.28}$$

Comparing with Fourier's Law, Eq. 3.23, we see that

$$\boxed{K = \frac{1}{3}\lambda\bar{v}c}. \tag{3.29}$$

I emphasize that the heat capacity here is per unit volume and hence density dependent. Observe the similarity of this result to the relation for the diffusion constant with the addition of c.

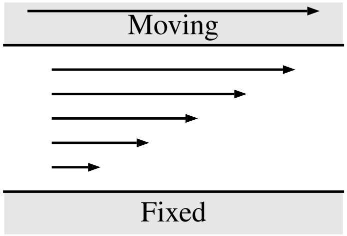

Figure 3.7 A velocity gradient between two parallel surfaces with the top one moving relative to the bottom one.

In the argument above you might legitimately have worried that the temperature gradient causes n and $\bar{v}$ to depend on the position x. However, for the steady-state conditions we are concerned with here, the rates at which molecules cross our small area in either direction must be the same, and these are proportional to the product $n\bar{v}$. Hence we needed only to consider the position dependence of E, the energy per molecule.

3.2.3 Viscosity

The phenomenon of viscosity is seen in its simplest form when considering two parallel flat surfaces, with one moving relative to the other (Fig. 3.7). When molecules hit each surface they stick briefly before leaving (in contradiction to the basic assumptions of kinetic theory). In doing so they acquire the mean velocity of the surface. If one surface moves with respect to the other, there must therefore be a velocity gradient. This produces a drag force on each surface given by

$$\boxed{F_x = -\eta A \frac{\mathrm{d}v_x}{\mathrm{d}y}}, \tag{3.30}$$

where F_x is the force in the x-direction (left to right in the figure), and $\mathrm{d}v_x/\mathrm{d}y$ is the velocity gradient, i.e. the change in v_x with y-position (upwards in the figure); A is the area of the surface. As before, this equation defines the constant, in this case η, which is known as the *viscosity coefficient*, and has units of $\mathrm{N\,m^{-2}\,s^{-1}}$. The minus sign means that the force is a drag force. Viscosity is the transport of momentum, in this case the x-component of momentum transported in the y-direction.

Let the mean x-momentum/molecule at y be $mv_x(y)$. Then as before, the momentum per unit time carried from bottom to top across an imaginary surface in the fluid parallel to the upper and lower surface is

$$\frac{1}{6} nA\bar{v}mv_x(y - \lambda), \tag{3.31}$$

compared with a rate from top to bottom

$$\frac{1}{6} nA\bar{v}mv_x(y + \lambda), \tag{3.32}$$

which leaves a net flow rate of

$$-\frac{1}{3} nA\bar{v}\lambda m \frac{\mathrm{d}v_x}{\mathrm{d}y}. \tag{3.33}$$

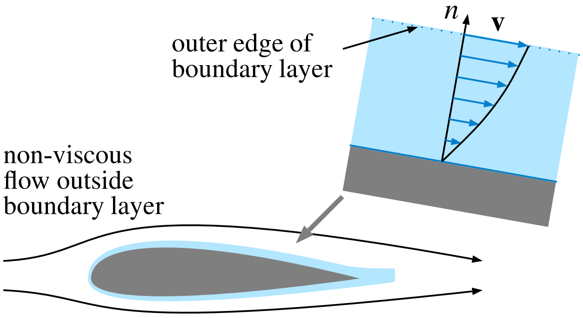

Figure 3.8 Schematic illustration of fluid flow past a wing (adapted from JD Anderson, *Ludwig Prandtl's Boundary Layer*, Physics Today, December 2005).

	transported quantity	macroscopic law	kinetic theory estimate
diffusion	number density or 'identity'	$\frac{dN}{dt} = -DA\frac{\mathrm{d}n}{\mathrm{d}x}$	$D = \frac{1}{3}\lambda\bar{v}$
thermal conduction	thermal energy	$\frac{\mathrm{d}Q}{\mathrm{d}t} = -KA\frac{\mathrm{d}T}{\mathrm{d}x}$	$K = \frac{1}{3}\lambda\bar{v}c$
viscosity	momentum	$\frac{\mathrm{d}p_x}{\mathrm{d}t} = F_x = -\eta A\frac{\mathrm{d}v_x}{\mathrm{d}y}$	$\eta = \frac{1}{3}\lambda\bar{v}\rho$

Table 3.1 Three transport coefficients.

Remembering that nm is the mass/unit volume, i.e. the density ρ, and comparing with Eq. 3.30 we deduce that

$$\boxed{\eta = \frac{1}{3}\lambda\bar{v}\rho}. \tag{3.34}$$

Again this is very similar to the relation for the diffusion coefficient with the addition of the density.

Viscosity is important in the *boundary layer* near the surface of a body moving through a fluid. Outside this layer the flow can be taken as non-viscous. A reasonable description of (non-turbulent) airflow past a wing, say, as illustrated schematically in figure 3.8, can be obtained by considering a thin boundary layer near the wing's surface, where the effects of viscosity are dominant. The figure shows how the flow velocity $\mathbf{v}$ changes, as a function of the normal distance n, from zero at the surface to the full non-viscous flow value at the outer edge of the layer. Calculating the boundary layer flow allows the skin-friction component of the drag on the wing to be determined.

Table 3.1 summarises what we have learned about the three transport coefficients we have studied.

3.2.4 Avogadro's Number

The kinetic theory of transport led to the first reliable estimate of Avogadro's number (Maxwell 1865). This can be obtained as follows. We cannot measure the flow rate of molecules directly, but we can measure it in terms of the mass flow rate, and hence we can measure

$$D_m = mD = \frac{1}{3}\lambda\bar{v}m. \tag{3.35}$$

Temperature K	η $10^{-6}\,\mathrm{N\,m^{-2}\,s}$	K $10^{-3}\,\mathrm{W\,m^{-1}\,K^{-1}}$	K/η $\mathrm{m^2\,s^{-2}\,K^{-1}}$
100	7.400	8.960	1211
150	11.18	13.85	1237
200	14.65	18.35	1253
250	17.80	22.49	1263
300	20.68	26.38	1276
350	23.34	30.10	1289
400	25.83	33.79	1308
500	30.41	41.13	1352
1000	49.05	74.32	1515

Table 3.2 Experimental measurements of the thermal conductivity and viscosity of oxygen as a function of temperature

Then from kinetic theory, the ratio of the viscosity coefficient to the mass diffusion coefficient is expected to be

$$\frac{\eta}{D_m} = \frac{\rho}{m} = n, \tag{3.36}$$

the number of molecules per unit volume. If we now measure the volume of one mole, the molar volume V_m, then $N_A = V_m n$, and therefore

$$N_A = \frac{V_m \eta}{D_m}. \tag{3.37}$$

All the quantities on the right are measurable although Maxwell found that there were no existing measurements of the viscosity of gases and had to devise methods to carry them out.

3.2.5 Temperature dependence of Transport coefficients

All the transport coefficients contain the mean speed $\bar{v} \propto T_{\mathrm{I}}^{1/2}$. On the other hand, the quantities C and ρ are both proportional to n and hence decrease with T_{I} since $n = P/kT_{\mathrm{I}}$, if the pressure remains constant. However, this is compensated by a matching increase of $\lambda \propto 1/n$. Therefore overall all transport coefficients of gases are expected to increase with temperature. This is observed, although not necessarily in good agreement with $T_{\mathrm{I}}^{1/2}$ (or $T_{\mathrm{I}}^{3/2}$ for diffusion) because of the inaccuracy of the “hard sphere” approximation. By contrast, the viscosity of liquids *decreases* with T. This is just another example of the inapplicability of kinetic theory to liquids and solids.

Table 3.2 lists some experimental measurements of the thermal conductivity and viscosity of oxygen as a function of temperature. Figure 3.9 shows the variation of K and η with temperature, while figure 3.10 shows the ratio K/η as a function of temperature, which kinetic theory predicts to be a constant. Remembering the formulae, $K = \lambda \bar{v} n C_m/3$ and $\eta = \lambda \bar{v} n m/3$, where C_m and m are the heat capacity and mass per molecule, then we expect

$$\frac{K}{\eta} = \frac{C_m}{m} = \frac{5k}{2m}, \tag{3.38}$$

with the last line appropriate for a diatomic molecule. We therefore expect from kinetic theory that the ratio of thermal conductivity to viscosity should be independent of temperature. One can see from Table 3.2 that this is approximately correct,

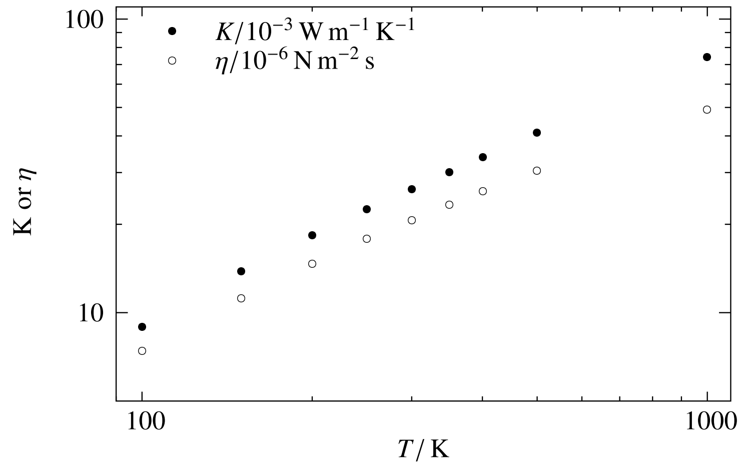

Figure 3.9 Thermal conductivity and viscosity of oxygen as a function of temperature. This is a log-log plot, so both lines should be straight with the same slope if the kinetic theory prediction that K and η are proportional to $T_{\mathrm{I}}^{1/2}$ holds.

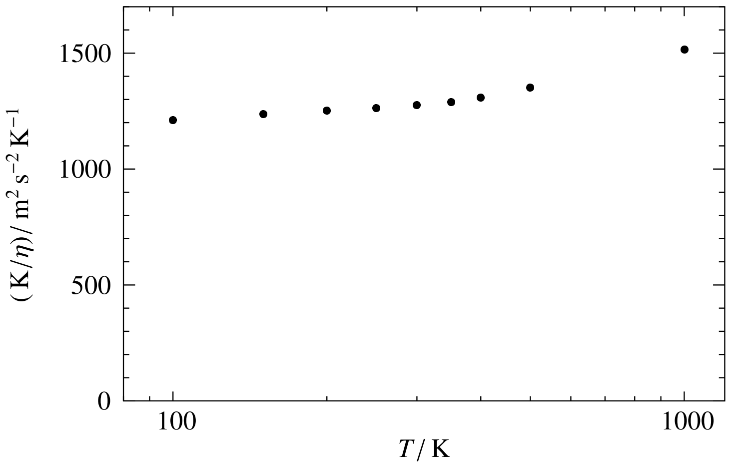

Figure 3.10 Ratio of thermal conductivity and viscosity of oxygen as a function of temperature. This should be a constant if the kinetic theory prediction that K and η are both proportional to $T_{\mathrm{I}}^{1/2}$ holds.

although it does rise, partly as a result of the excitation of vibrations in the oxygen molecule. For molecular oxygen, $m = 32\,u$, and the ratio is expected to be 650. This is too low, but is at least the correct order of magnitude, which is all one can expect given the simple assumptions made.

3.2.6 Pressure dependence of transport coefficients

Recall once more the viscosity and thermal conductivity coefficients:

$$\begin{aligned}\eta &= \frac{1}{3}\lambda\bar{v}\rho,\\ K &= \frac{1}{3}\lambda\bar{v}C.\end{aligned}$$

As I mentioned above, both ρ and C scale with n, while $\lambda \propto n^{-1}$, and therefore

$$\boxed{\text{kinetic theory predicts that } K \text{ and } \eta \text{ are } \textit{independent of pressure}!}$$

Pressure atm	K $10^{-3}\,\mathrm{W\,m^{-1}\,K^{-1}}$
1	26.2
5	26.6
10	27.0
20	27.8
40	29.4
60	31.0
100	34.3

Table 3.3 Thermal conductivity of oxygen as a function of pressure at 300 K

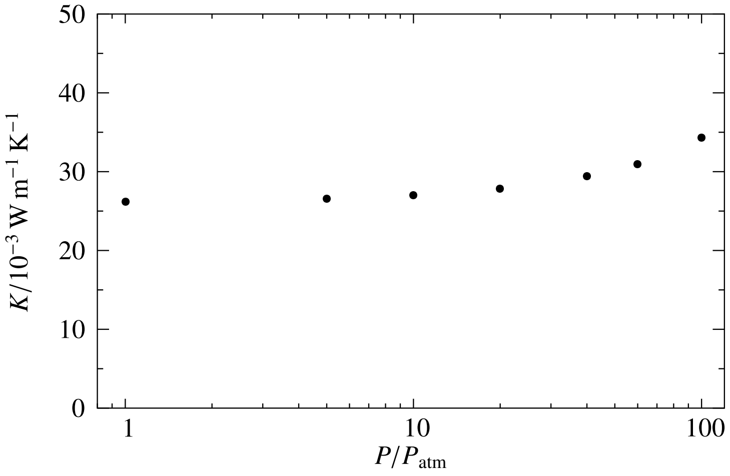

Figure 3.11 Thermal conductivity of oxygen as a function of pressure at 300 K. This should be a constant if the kinetic theory prediction holds.

Table 3.3 and figure 3.11 show that this rather unexpected result is indeed approximately correct in the case of oxygen, for which the thermal conductivity increases by only 30% while the pressure increases by a factor of 100. At first one might have guessed that the conductivity would also increase by a factor of 100, because the density has increased by this factor, but of course the mean free path simultaneously drops by the same factor, leading to the relatively small dependence.

However, there is still something wrong about this result. For instance, it implies that removing air from between two pieces of glass in a double glazing unit makes no difference to the rate of heat loss! However, surely if there was no air there could be no conduction of heat by air molecules. In fact both statements are correct: over a wide range of pressures these two coefficients are fairly constant, but they do tend to zero in the limit of zero pressure. The key point is in the transition between the two cases. The mean free path does get larger as the pressure drops, but eventually it will become similar in size to the dimensions of the apparatus. It then ceases to increase and the transport coefficients start to drop. This is known as the “Knudsen regime” of pressures, and is difficult to treat accurately since results start to depend upon details of the apparatus. However the formula for λ can be used as a useful guide to when such effects start to matter. At high densities, other problems set in as interatomic forces becomes significant.

The following example shows very roughly how one can take account of low pressures.

Example 3.5 Estimate the power per unit area carried by conduction between two plates differing in temperature by 10 K and separated by a 1 mm thick air gap at pressures of $10^5\,\mathrm{N\,m^{-2}}$ and $0.1\,\mathrm{N\,m^{-2}}$ at $T = 298\,\mathrm{K}$.

Answer 3.5 For $P = 10^5\,\mathrm{N\,m^{-2}}$ (1 bar), $\lambda = 10^{-7}\,\mathrm{m} \ll d$, so we use

$$K = \frac{1}{3}\lambda\bar{v}c. \tag{3.39}$$

with $\bar{v} = 500\,\mathrm{m\,s^{-1}}$. Estimate c, the heat capacity *per unit volume*, using the equipartition theorem for a diatomic gas with no vibrations:

$$c = \frac{5}{2}kn = \frac{5}{2}\frac{P}{T_\mathrm{I}}, \tag{3.40}$$

Hence,

$$K = \frac{10^{-7} \times 500 \times 5 \times 10^5}{3 \times 2 \times 298} = 0.014\,\mathrm{W\,m^{-1}\,K^{-1}}. \tag{3.41}$$

For $\Delta T = 10\,\mathrm{K}$, $\Delta x = 0.001\,\mathrm{m}$, $\mathrm{d}T/\mathrm{d}x = 10^4\,\mathrm{K\,m^{-1}}$ and so the conduction rate is $140\,\mathrm{W\,m^{-2}}$.

For $P = 0.1\,\mathrm{N\,m^{-2}}$, $\lambda = 0.1\,\mathrm{m} \gg d$, where d is the thickness of the air gap, so we expect the rate to be $d/\lambda = 150$ times smaller, very roughly.

3.2.7 Variation with nature of gas

The kinetic theory model gives an intuitive feel for how different gases should compare in thermal conductivity etc. Large mean free paths will lead to good conduction, which means that small molecules will conduct better. Small molecules are often low mass molecules, which means they move faster at a given temperature, which increases the conductivity still further. Therefore we expect hydrogen and helium to be better heat conductors than carbon dioxide for instance. (Remember: for fixed P and T_I, n is the same for all ideal gases.)

3.3 Limitations of kinetic theory

Kinetic theory gives an intuitive feel for several phenomena, most importantly the pressure exerted by a gas. However, it is far from being a generally useful model, and fails to explain such basic phenomena as

- phase changes (boiling, melting),
- the existence of liquids and solids,
- deviations from the ideal gas law.

It is the neglect of interatomic forces which is most important (without them there could be no liquids). Although we can do much better than the simple theory I have outlined, we are still far from being able to predict the properties of a substance composed of a given molecule. Although this is an important aim, it is an undeniably difficult one. Can we go no further then? Neither easily nor accurately with a microscopic approach. Instead I will start in the next chapter upon a more utilitarian approach in which we take some measured properties for granted and try to extrapolate from these. This is the subject of classical thermodynamics.

4

An Introduction to Thermodynamics

Thermodynamics is a subject of great generality, rigour and power, but one which you may well find quite different in flavour from any physics you have done before. Thermodynamics deals with quantities such as work, heat and temperature, and provides a firm basis for these concepts. It is concerned with macroscopic, not microscopic physics (by "thermodynamics" I mean what is often called "classical thermodynamics" as opposed to "statistical thermodynamics"). This is unusual in that in physics one normally tries to reduce phenomena to their most fundamental level. However, this is difficult with thermodynamics. What after all is the "temperature" of a single particle? Indeed, some of the fundamental aspects of thermodynamics can almost seem like mirages that disappear on a microscopic scale. Therefore from this point we will see relatively little in the way of microscopic models.

Thermodynamics is of huge practical importance, and has applications to

engines, jets, rockets,
power generation,
chemistry and biology,
astrophysics and cosmology,
refrigerators and heat pumps,
weather forecasting,

and many more. It is built from four fundamental laws deduced from experiment:

- *Zeroth law*: defines *temperature*.
- *First law*: defines *internal energy* and expresses the conservation of energy.
- *Second Law*: defines *entropy* and how efficiently once can convert heat to work.
- *Third Law*: establishes the unattainability of absolute zero.

These laws form the bedrock of thermodynamics. When you encounter them you will see it is hard to imagine thermodynamics being overturned, in the same way that Newtonian physics was when relativity was developed.

4.1 Thermodynamic Definitions

It is important in thermodynamics to be precise with one's use of language. In Table 4.1 I show three important terms that will be used often. In thermodynamics we are often concerned with changes of a *system* but very often these must be considered

System	the piece of Universe under study. Its precise extent must be clearly defined.
Surroundings	anything that is not part of the system.
Boundary	whatever separates the system from its surroundings.

Table 4.1 Three basic terms defined.

Closed	lets no matter in or out.
Open or permeable	can let matter pass.
Rigid	does not allow any change in the system by external forces, such as pressure.
Adiabatic	does not allow any heat to flow in or out.
Diathermal	opposite of adiabatic — does allow heat transfer.
Isolating	allows nothing in or out: closed, rigid and adiabatic.

Table 4.2 The different possible types of boundary.

in conjunction with changes in the *surroundings*. The two are linked by a *boundary* (sometimes called a "wall") which can come in several different varieties. These are listed in Table 4.2. To start with, all boundaries that I consider will be closed, i.e. no matter will enter or leave the system. I will often switch between adiabatic and diathermal boundaries. I prefer the term "boundary" to "wall" as the dividing line need not be a physical object.

I now start on the laws underlying thermodynamics. I will proceed in historical order, starting with the First Law.

4.2 The First Law of Thermodynamics

In the 1840's Joule carried out careful experiments which led him to conclude:

> "If the state of an otherwise isolated system is changed by the performance of work, the amount of work needed depends solely upon the change effected and not on the means by which the work is performed, nor on the intermediate stages through which the system passes between its initial and final states."

This is the formal statement of the First Law of thermodynamics in the case with no heat flow. Two terms need explaining:

1. *performance of work*: any process which, in principle, can be carried out by lowering a weight ($W = mgh$).
2. *otherwise isolated*: we can do work, but no heat can flow in or out.

The definition of work may seem restricted, but in fact it encompasses anything that one would consider to be work. For instance, consider electrical work. Electricity can be generated via hydro-electric power, in which water drops in height. Therefore electricity is included within the definition.

4.2.1 What did Joule do?

Joule deduced the first law by trying different ways of carrying out work on a system, measuring the amount of work and determining the change in the system via its

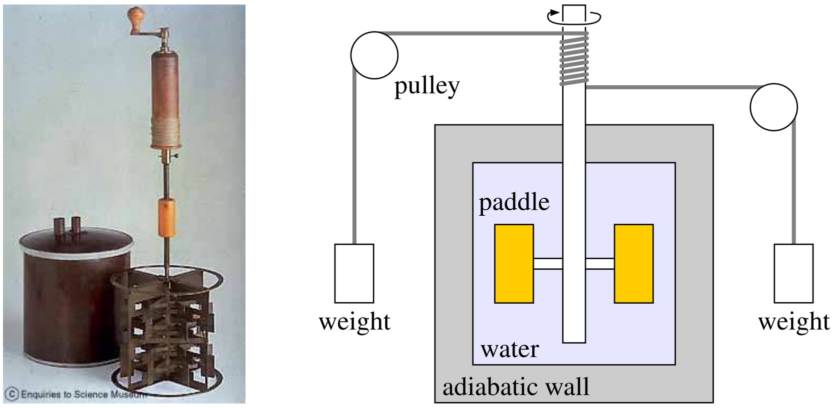

Figure 4.1 Joule's paddle-wheel experiment. Photograph: Science Museum.

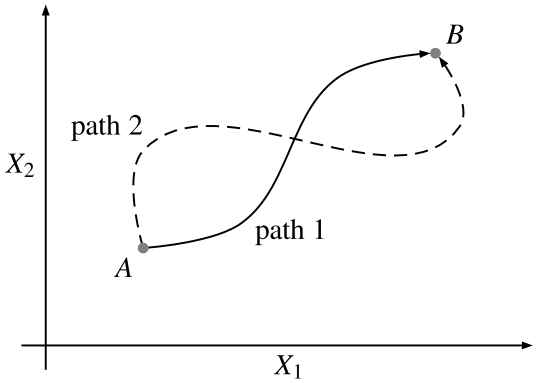

Figure 4.2 An illustration of different paths between two states, A and B. X_1 and X_2 define the state of the system, and could be, for instance, pressure and volume.

change in temperature. The famous example is his use of a paddle wheel driven by weights to stir water (Fig. 4.1): it is worth noting that Joule was a brewer when contemplating this apparatus. The important point is that Joule could calculate the amount of mechanical work; it is not for nothing that our unit of energy, representing the work done by a force of 1 N moving 1 m, is named after him. He took great care over this. For instance in the paddle wheel experiments, he took account of the kinetic energy of the weights at the end of their travel. He also performed electrical work, in which a current is passed through a system, requiring a work rate of I^2R, known as Joule heating.

What Joule found was that the amount of work required to change a system, when no heat is allowed to enter or escape, depends only upon the initial and final states of the system. The First Law is nothing more than the conservation of energy. The energy represented by the performance of the same amount of work causes the same change in a system. This leads to the recognition of something we have encountered already, the *internal energy*.

4.3 Internal Energy

Joule's experiments show that the work done depends only upon the initial and final states of a system. In other words, when a system changes from state A to B, as illustrated in Fig. 4.2, the work done can be written as $W = f(B) - f(A)$, where f is a *function of the state of the system* and not the path taken. Such a function is known simply as a "function of state". Such functions play an important role in thermodynamics. Examples are pressure and volume: the same state of a system must have the same volume by definition. Not everything is a function of state. For instance, the distance travelled by a system is not a function of state. More interestingly, we will see that work and heat are not functions of state.

Returning to the first law, the function of state has a particular name, the *internal energy*, U. This is defined by

$$W = U_{\text{final}} - U_{\text{initial}} = \Delta U. \tag{4.1}$$

The work done on the system W changes its internal energy by W. Note the *sign convention:* work done *on* the system is *positive*. Work done *by* the system is negative. Not all texts agree on this; older books and engineering books, where work done by a system is often of most interest, tend to use the reverse definition: watch out!

4.4 Heat

We can equally change a system by bringing it into contact with a hot or cold reservoir.

> *Heat* is the transfer of energy between a system and its environment due to a temperature difference between them.

Having calibrated the internal energy with Joule's experiments, we can define the heat entering a system, Q, in the case of no work as

$$Q = \Delta U. \tag{4.2}$$

Heat *added to* a system is *positive*. Heat *given up by* a system is *negative*.

Joule showed that heat and work are two forms of the same thing, which we call *energy*. Before Joule, heat was measured in calories, defined as the amount of heat needed to raise the temperature of 1 g of water by 1°C. Work was measured in terms of force times distance. Joule calibrated calories in terms of mechanical work, sometimes known as the "mechanical equivalent of heat". The conversion is

$$1\,\text{calorie} = 4.2\,\text{J}. \tag{4.3}$$

Food energy values are often quoted in terms of "Calories" which are the amount of heat needed to raise 1 kg of water by 1°C:

$$1\,\text{Calorie} = 4200\,\text{J}. \tag{4.4}$$

The persistence of these units is rather remarkable given that Joule performed his experiments more than 150 years ago!

4.5 Mathematical expression of the First Law

If heat is added and work is performed on a system, then the first law becomes

$$\boxed{\Delta U = Q + W}\,. \tag{4.5}$$

This is an important equation *which you should remember*. This is the mathematical form of the first law, and has the following significance:

- energy is conserved,
- generalises conservation of kinetic + potential energy,
- defines heat as a form of energy.

The mathematical form makes clear the equivalence of heat and work in terms of their effect upon a system. Given a change in internal energy ΔU it is *impossible* to say how much of it was work or how much was heat, without more information. An infinity of different combinations of Q, W values can give the same ΔU. This means that:

> Heat and work are *not* functions of state. They depend upon the path taken.

We cannot therefore talk about the "heat" or "work" of a system in the same way as we say "the pressure of a system".

For infinitesimal changes, we write the first law as

$$\boxed{\mathrm{d}U = \text{đ}Q + \text{đ}W}\,. \tag{4.6}$$

The lines through the "d"s in front of Q and W are a reminder that they are not functions of state. The distinction turns out to be significant.

4.6 Perpetual Motion Machines of the First Kind

A loose way of expressing the first law goes as follows: "you can't get something for nothing, you can only ever break even". That is, you cannot create energy from nothing. Unfortunately, there have been many instances of inventors who have failed to appreciate this, and have tried to promote devices that apparently run for ever without the need for fuel. These are known as "perpetual motion machines of the first kind" (I will discuss the more subtle second type later). Imagine that the first law was not true. Then moving from state A to B via path 1 in figure 4.2, would require us to put in work W_1, while we could extract work W_2 when moving back from B to A via path 2, and, crucially, $W_2 \neq W_1$. We could then extract a total amount of work $W = W_2 - W_1$, and, if we went round the cycle in the right direction, we could ensure that $W > 0$. This would be a perpetual motion machine; the first law implies instead that $W = 0$, we can only "break even". The Patent Office rejects all applications for perpetual motion machines — if they recognise them as such, which they don't always. No one has proved them wrong as yet.

4.7 Heat Capacities

The first law of thermodynamics allows us to define the concept of heat capacity more carefully. From the differential form of the first law

$$\text{đ}Q = \mathrm{d}U - \text{đ}W. \tag{4.7}$$

The change $\mathrm{d}U$ is seen through an associated temperature change, $\mathrm{d}T$. The "heat capacity" is then defined by the heat input divided by the change in temperature:

$$C = \frac{\text{đ}Q}{\mathrm{d}T} = \frac{\mathrm{d}U}{\mathrm{d}T} - \frac{\text{đ}W}{\mathrm{d}T}. \tag{4.8}$$

This depends upon the work $đW$, and so in defining heat capacities we must define the work done as well. Note that the term “heat capacity” is inaccourate: once heat enters a system it loses its identity and should be thought of as energy. As we will see, in many cases, part of the heat “stored” in a system is in fact used up as work.

The heat capacity one normally thinks of is the heat capacity *at constant volume*. If we don’t allow a system to change its volume (rigid boundary) then it performs no work against external pressure. The specific heat capacity at constant volume is usually denoted by C_V; the equipartition heat capacities were of this form, although I did not say so explicitly. Since $W = 0$ we can write

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V . \tag{4.9}$$

This expression says that C_V is the partial derivative of the internal energy with respect to temperature. It is a *partial* derivative because only the temperature is varied. However, an additional complication in thermodynamics is caused by the equation of state: we can hold the volume fixed, or the pressure, but not both when we are varying the temperature. Therefore in thermodynamics whenever we write a partial derivative, we must indicate precisely *which* parameter is being held fixed; in this case it is the volume, and hence the subscript V.

It is usually easier to measure the specific heat capacity at constant pressure, C_P. In this case the system expands and does work on the surroundings, so the work *done on the system*, $W < 0$. Thus

$$C_P > C_V. \tag{4.10}$$

This is important for gases as we will see.

4.8 Calorimetry

The measurement of heats of reaction and specific heats is an important part of chemistry. It is called calorimetry, and provides a simple application of the first law. The basic idea is to use an isolating container, i.e. $Q = W = 0$. In practice, this is not easy when high accuracies are desired, and calorimetry experiments require much care. However, stripped down to its basics, one measures the specific heat capacity as follows:

1. put a mass m_w of water in a container,
2. measure its temperature, T_w,
3. take a mass m_s of the substance and measure its temperature T_s,
4. allow the substance and water to come to thermal equilibrium,
5. measure the final temperature, T_f.

Then since $Q = W = 0$, we have $\Delta U = Q + W = 0$, and so

$$U(\text{initial}) = U(\text{final}), \tag{4.11}$$

or, since the internal energy of mass m of specific heat capacity C at temperature T is given by $U = mCT$ (if C does not vary with temperature),

$$m_w C_w T_w + m_s C_s T_s = m_w C_w T_f + m_s C_s T_f. \tag{4.12}$$

We know m_w, m_s, C_w (Joule), T_w and T_s, and therefore we can deduce C_s:

$$C_s = \frac{m_w C_w (T_f - T_w)}{m_s (T_s - T_f)}. \tag{4.13}$$

Note that this defines C_s as a multiple of C_w, which is why calories were useful. This formula is as one would deduce more intuitively from the idea that the heat lost by the substance equals the heat gained by the water. This case gives the impression of a conserved property that flows from the substance to the water. It was this idea that lead to the old "caloric" model of heat. Caloric was an indestructible fluid that flowed into an object when it was heated. This idea founders when work is considered, as was famously realised by Count Rumford when supervising the boring of cannons, during which work expended is converted to heat.

4.9 Expansion & Compression of Gases

The second application of the first law that I consider is to the expansion of gases. There are three distinctly different ways to expand or compress a gas (although one can also perform intermediate versions of these as well). The three methods are:

1. *Isothermally:* temperature remains constant.
2. *Adiabatically:* no heat in or out.
3. *Joule expansion:* adiabatic. Gas in one part of a container, vacuum in the other. The separating wall is removed. The container is rigid.

4.9.1 Isothermal compression & expansion

If the gas is ideal, then U is a function of T_{I} only, i.e. $U(T_{\mathrm{I}})$. Therefore since T_{I} is constant, $\Delta U = 0$. Hence

$$Q + W = 0. \tag{4.14}$$

As the gas expands it does work, so $W < 0$, therefore $Q > 0$. In words, during an isothermal expansion, the gas absorbs heat but does an exactly equivalent amount of work; its internal energy is unchanged (ideal gases only). During compression, *you* do work, which is given out as heat.

4.9.2 Adiabatic compression & expansion

In the adiabatic case, $Q = 0$, so $\Delta U = W$. All work done during compression is stored as internal energy in the gas.

4.9.3 Joule expansion

Note first that there is no such thing as a Joule "compression". We will see why later. A Joule expansion is adiabatic and the container is rigid, so no work is done. Therefore, $Q = W = 0$, and so $\Delta U = 0$. This is true whether or not an ideal gas is involved (c.f. isothermal expansion). If U is a function of T *and* V, i.e. $U(T,V)$ then we have the mathematical identity

$$\mathrm{d}U = \left(\frac{\partial U}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial U}{\partial V}\right)_T \mathrm{d}V. \tag{4.15}$$

Since $\mathrm{d}U = 0$, then

$$\mathrm{d}T = -\frac{(\partial U/\partial V)_T}{(\partial U/\partial T)_V}\,\mathrm{d}V. \tag{4.16}$$

Joule measured $\mathrm{d}T = 0$ for gases and so deduced that

$$\left(\frac{\partial U}{\partial V}\right)_T = 0. \tag{4.17}$$

If this is the case, then U is indeed a function of T only, $U = U(T)$. In this case, we no longer need to qualify the derivative as being at constant volume, and we can write

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\mathrm{d}U}{\mathrm{d}T}. \tag{4.18}$$

This means that $\mathrm{d}U = C_V\,\mathrm{d}T$. This is a useful relation, but one should remember that it only applies when $U = U(T)$. It is not easy to detect a change in temperature because the heat capacities of gases per unit volume are small.

4.10 Summary

In this chapter I have made a start on thermodynamics, which is based upon four experimentally derived laws. I have looked at the First Law of Thermodynamics which generalises energy conservation to include heat, and proves the existence of a function of state, the internal energy. We see that heat and work are two forms of energy. Objects have internal energy, they do not contain "heat" or "work". The latter are not functions of state. They are entirely equivalent in terms of their effect upon a system. You should remember the First Law. It is important throughout physics and I will be using it many times in the course. We will return to the expansion of gases.

5

Reversibility and the Calculation of Work

Reversible and irreversible processes are important in thermodynamics. Reversible processes are an idealisation but are important because they can be quantified. The results of computations can have general applicability because for some quantities, such as internal energy, the change depends only upon the initial and final states and not on how the change was made. In such cases we imagine that the process was reversible, allowing us to calculate numbers which then apply in general.

Irreversibility is interesting from another perspective. On a microscopic scale our physical laws are reversible, so how can they lead to processes which are irreversible on a macroscopic scale?

5.1 Reversible Changes

A process is reversible if the system and surroundings return to their original state when the process is reversed. Consider a very rapid compression of a gas. Shock waves develop during the compression, but they dissipate as the system settles back to equilibrium. Imagine filming this and running the film backwards (this idea is often useful in deciding whether a process is reversible). You would see shock waves develop in the middle of the gas for no apparent reason. This never happens; this process is not reversible.

A reversible change must occur through intermediate states which are themselves in *thermal equilibrium* (the initial and final states must therefore also be in equilibrium). A reversible change can be carried out by making a tiny change, allowing the system to settle to equilibrium, making another tiny change, etc. This is called a *quasi-static* change. However, this is still not enough, because there must also be no friction. It is possible to compress a gas quasi-statically but if the piston used has friction, then work is converted to heat and the surroundings will not return to their initial state when the process is reversed. Before coming up with a more general definition, let's consider heat transfer.

5.1.1 Reversible heat transfer

Imagine placing a pan of cold water onto a hotplate. At first there is a temperature gradient which gradually disappears as the water warms up. Again imagine a film of this run backwards. One would see a spontaneous development of a temperature gradient, something that never happens. The process is irreversible. For heat transfer to be reversible, no temperature gradients must occur. This can be done by making a tiny increase in surrounding temperature, allowing the system to warm up, making another tiny increase, etc. This leads to a general criterion for reversible changes.

5.1.2 General Criterion for Reversibility

The following statement provides a general criterion for reversibility:

> A reversible change is one which can be reversed in direction by an infinitesimally small change in the surroundings.

This is best explained with a few examples.

1. A piston of area A holds a gas at pressure P in equilibrium with an external force, $F = PA$. The applied force is suddenly doubled, $F' = 2PA$, causing compression.

   This is *irreversible*, because a small change in F', $\delta F' = 0.1PA$ say, would not reverse the compression.

2. A stone is heated to $T = 500\,^\circ\mathrm{C}$ and thrown into water.

   This is *irreversible*, because a small change in temperature, $\delta T = 20\,^\circ\mathrm{C}$ say, would still heat the water.

3. A sealed container of water and vapour is cooled, condensing some of the vapour.

   This is *reversible* if done slowly, because a tiny change in temperature can reverse the effect.

In reality all changes are irreversible, but it is possible to come close to reversibility, and as we will see, this is closely connected with issues such as engine efficiency.

5.2 Calculating Reversible work

Reversible work is calculable. Irreversible work can be too, but can be nearly impossible to quantify when shock waves and the like develop. The essential definition of work is force F times distance x, so

$$W = Fx. \tag{5.1}$$

This is fine unless F varies with x. Then it is better to consider infinitesimal changes in x so

$$đW = F(x)\,\mathrm{d}x, \tag{5.2}$$

and

$$W = \int_{x_1}^{x_2} F(x)\,\mathrm{d}x. \tag{5.3}$$

Example 5.1 How much work is needed to extend a spring, force constant k from x_1 to x_2?

Answer 5.1

$$W = \int_{x_1}^{x_2} F(x)\,\mathrm{d}x = \int_{x_1}^{x_2} kx\,\mathrm{d}x = \left[\frac{1}{2}kx^2\right]_{x_1}^{x_2} = \frac{1}{2}k(x_2^2 - x_1^2).$$

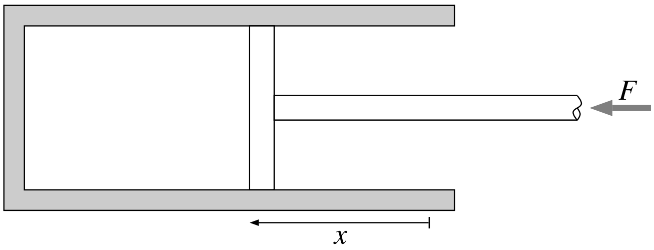

Figure 5.1 A piston compressing a gas

5.2.1 Compressing a Gas

Now let's consider the work done when compressing a gas. Fig. 5.1 shows a cross-section of a piston compressing a gas. The face of the piston is flat, has area A, and moves perpendicular to its surface. If the gas pressure is P, then the force needed to move the (frictionless) piston is $F = PA$. This requires one to move the piston slowly so that pressure gradients do not build up. Therefore to move the piston in by an amount dx requires an amount of work

$$đW_R = F\,\mathrm{d}x = PA\,\mathrm{d}x. \tag{5.4}$$

The subscript R indicates that the change is reversible. The change in volume of the gas is $\mathrm{d}V = -A\,\mathrm{d}x$ (V decreases as x increases), and so we find

$$\boxed{đW_R = -P\,\mathrm{d}V}. \tag{5.5}$$

Although calculated for a simple setup, this is a general result; *remember it.* The sign is correct because this is the work done by the piston, which is the work done on the gas. For a finite change

$$\boxed{W_R = \int_{V_1}^{V_2} -P\,\mathrm{d}V}. \tag{5.6}$$

5.3 Heat Capacities of Gases

In section 4.7 I discussed heat capacities and the need to define the work done. We can now obtain an explicit formula because for a reversible change

$$đQ_R = \mathrm{d}U - đW_R = \mathrm{d}U + P\,\mathrm{d}V. \tag{5.7}$$

Since the right-hand side is a function of state, this is a general relation for $đQ$, whether reversible or not. Now consider 1 mole of ideal gas, for which $PV = RT_\mathrm{I}$, and $\mathrm{d}U = C_V\,\mathrm{d}T_\mathrm{I}$. For a change at *constant pressure*, we must have

$$\mathrm{d}(PV) = P\,\mathrm{d}V = R\mathrm{d}T_\mathrm{I}. \tag{5.8}$$

Therefore the molar specific heat capacity at constant pressure C_P is given by

$$C_P = \frac{đQ}{\mathrm{d}T_\mathrm{I}} = \frac{C_V\,\mathrm{d}T_\mathrm{I} + R\,\mathrm{d}T_\mathrm{I}}{\mathrm{d}T_\mathrm{I}}, \tag{5.9}$$

hence, the molar specific heats of an ideal gas at constant pressure and volume are related by

$$\boxed{C_P = C_V + R}. \tag{5.10}$$

The work against the surroundings, which occurs in the constant pressure case, appears as the gas constant R. This is another very well-known relation, and is important for adiabatic changes in gases.

5.3.1 Reversible Isothermal Compression of a Gas

For an ideal gas $P = n_m RT_\mathrm{I}/V$ so

$$W_R = -\int_{V_1}^{V_2} P\,\mathrm{d}V = -\int_{V_1}^{V_2} \frac{n_m RT_\mathrm{I}}{V}\,\mathrm{d}V. \tag{5.11}$$

If we restrict ourselves to isothermal changes, then T_I is constant and so can be taken outside the integral to give

$$W_R = -n_m RT_\mathrm{I} \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = -n_m RT_\mathrm{I}\,[\ln V]_{V_1}^{V_2} = n_m RT_\mathrm{I} \ln\left(\frac{V_1}{V_2}\right). \tag{5.12}$$

Sanity check on the sign: if $V_1 > V_2$, I will have compressed the gas, and so have done work on it. I would therefore expect $W_R > 0$, which is OK since then $\ln(V_1/V_2) > 0$. This is the minimum amount of work one would require to effect the compression; any departure from reversibility such as friction, would increase this value.

5.3.2 Reversible Adiabatic Compression

Now I consider reversible adiabatic compression (or expansion). We have the same general expression for the work as Eq. 5.11 but cannot now assume that the temperature is constant. Instead we need first to work out just how the temperature varies in a reversible adiabatic change. For an adiabatic change, $đQ = 0$, and if the change is reversible then $đW = -P\,\mathrm{d}V$. Therefore $\mathrm{d}U = đW + đQ$, becomes $\mathrm{d}U = đW$ and so

$$\mathrm{d}U + P\,\mathrm{d}V = 0. \tag{5.13}$$

But for an ideal gas $\mathrm{d}U = C_V\,\mathrm{d}T_\mathrm{I}$, so

$$C_V\,\mathrm{d}T_\mathrm{I} + P\,\mathrm{d}V = 0. \tag{5.14}$$

Restricting ourselves to one mole, we can write $PV = RT_\mathrm{I}$, so

$$C_V\,\mathrm{d}T_\mathrm{I} + RT_\mathrm{I}\frac{\mathrm{d}V}{V} = 0, \tag{5.15}$$

for one mole. Dividing by T_I

$$C_V\frac{\mathrm{d}T_\mathrm{I}}{T_\mathrm{I}} + R\frac{\mathrm{d}V}{V} = 0, \tag{5.16}$$

and integrating gives

$$C_V \ln T_\mathrm{I} + R \ln V = \text{constant}. \tag{5.17}$$

Dividing by C_V and taking the exponential of this expression gives

$$T_\mathrm{I} V^{R/C_V} = \text{constant}, \tag{5.18}$$

where the constant is different from the line before, but is still a constant. This relation between T_I and V is enough to evaluate the expression of Eq. 5.11 but there is a rather nicer path to the same end result. Remember that the ideal gas equation of state for one mole is $PV = RT_\mathrm{I}$, and so

$$PVV^{R/C_V} = PV^{(C_V+R)/C_V} = \text{constant}. \tag{5.19}$$

From before we had $C_P = C_V + R$, and defining the "ratio of specific heats" γ by

$$\boxed{\gamma = \frac{C_P}{C_V} = \frac{C_V + R}{C_V}}, \tag{5.20}$$

we have the important relation for reversible adiabatic compression and expansion of gases:

$$\boxed{PV^\gamma = \text{constant}}. \tag{5.21}$$

Note that although I derived this for one mole, in this form, since the heat capacities are in the form of a ratio, this expression is general. The ratio of specific heats, γ, is clearly greater than unity, and so since $P \propto 1/V^\gamma$, this leads to a steeper dependence of pressure on volume than the isothermal case, $P \propto 1/V$. This is as one might guess because as you compress a gas adiabatically its temperature rises which increases the pressure compared to the isothermal case. In fact all the work applied is stored as internal energy during an adiabatic compression.

It is the adiabatic pressure–volume relation which applies to sound waves, because there is not enough time for heat to be conducted from the peaks to the troughs of pressure and temperature, and one can show that the speed of sound is given by $C_S = \sqrt{\gamma R T_I/m}$, where m is the mass of one mole of gas. If one assumes isothermal compression, then the result is $C_S = \sqrt{R T_I/m}$, an underestimate of the true speed, a mistake that Newton made. As a result, measurements of sound speed, which can be done very accurately, can give estimates of γ.

We saw how to estimate heat capacities from the equipartition theorem. For a monatomic gas we had $C_V = 3R/2$, therefore $C_P = 3R/2 + R = 5R/2$, and so $\gamma = C_P/C_V = 5/3 = 1.666$. For diatomic gases such as nitrogen, we found that without excitation of vibrations, $C_V = 5R/2$, and therefore $\gamma = 7/5 = 1.4$. This is the value that applies to air.

Let's now return to the computation of work. We can write

$$PV^\gamma = P_1 V_1^\gamma, \tag{5.22}$$

where a gas starts at P_1, V_1. Then the work is

$$\begin{aligned} W_R &= -\int_{V_1}^{V_2} P\,\mathrm{d}V = -P_1 V_1^\gamma \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V^\gamma} \\ &= -P_1 V_1^\gamma \left[\frac{V^{1-\gamma}}{1-\gamma}\right]_{V_1}^{V_2} = \frac{P_1 V_1}{\gamma - 1}\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right]. \end{aligned} \tag{5.23}$$

I leave you to fill in the details of this calculation. Again, it is worth doing a sanity check on the sign. For a compression we expect $W_R > 0$, but this is OK because then $V_1 > V_2$ (and $\gamma > 1$).

What about Joule expansion? We already saw that no work is performed. It is also irreversible, which is why you will never hear about "Joule compression".

5.4 Indicator Diagrams

Changes of gases and other substances can usefully be represented by plotting pressure versus volume on P–V or *indicator* diagrams. These diagrams are especially useful in representing the cycles of engines as I will show later. Fig. 5.2 shows an example of an indicator diagram. One reason they are useful is that the work changing

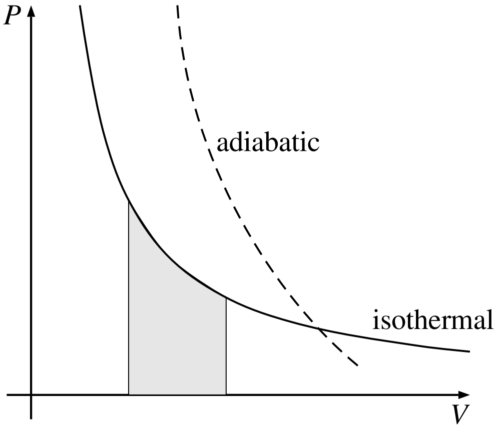

Figure 5.2 An example of an indicator diagram. The shaded area under part of the solid curve represents the work done during a change from one end of the curve at the top of the shaded area to the other end. The dashed line represents a reversible adiabatic change while the solid line represents a reversible isothermal change.

Form of Work	Expression	Comment
Gas compression	$-P\,dV$	most common form in this course
Magnetic work	$\mathbf{B}\cdot d\mathbf{m}$	**m** is the magnetic dipole moment of a specimen
Electrical work	$\mathbf{E}\cdot d\mathbf{p}$	**p** is the electric dipole moment of a specimen
Battery	$\mathcal{E}\,dq$	q is the charge that flows, $\mathcal{E}$ is the voltage
Spring, rubber band	$F\,dL$	L is the length

Table 5.1 Forms of work and expressions for them when they are carried out reversibly.

a volume is given by $-\int P\,dV$. In an indicator diagram this equals the area under the curve, and so areas in indicator diagrams are directly related to work. Fig. 5.2 shows schematic tracks of reversible isothermal and adiabatic changes. The key point is that the adiabatic change is steeper than the isothermal one. Mathematically this is a consequence of PV = const for isothermal changes versus PV^γ = const for adiabatic ones, with $\gamma > 1$. Physically it is because in an adiabatic compression, the work applied goes into the gas and heats it up giving it a higher pressure for a given volume than in an isothermal compression.

5.5 Other Forms of Work

You should not get the impression that “PDV” ($P\,dV'$) work is the only form ever encountered, although it is the one that we will use most in this course. A more complete list of expressions for work is shown in Table 5.1. Some of these should be obvious, while the expressions for electrical and magnetic work are beyond the scope of this course, although magnetic work in particular is of great importance in low temperature physics. The main reason for listing these expressions is to show that they are all of the same form “$Y\,dX$”, where X is some coordinate defining a system and Y is an associated “force” in a very generalised sense. The X variable in each case is “extensive”, which is to say that it scales in proportion to the size of system, whereas the Y force does not scale with the size of the system, and is called "intensive". In general the expression for the reversible work that one needs for the first law is of the form

$$W_R = -P\,\mathrm{d}V + F\,\mathrm{d}L + \mathbf{B}\cdot\mathrm{d}\mathbf{m} + \cdots, \tag{5.24}$$

i.e. the sum of all possible forms of work. Each extra term implies another variable needed to define a system of course, that is another degree of freedom. Thus for a system involving magnetic and $-P\,\mathrm{d}V$ work we would need to define the system with T, V and $\mathbf{m}$ or P, V and $\mathbf{m}$, etc.

5.6 Summary

In this chapter I have discussed the idea of reversible and irreversible processes. These are key concepts. Reversible processes, although an idealisation, are at the heart of equilibrium thermodynamics, and lead to tractable answers for quantities of interest such as work. I applied these ideas to gases, and derived the relation $W_R = -P\,\mathrm{d}V$. Applied to ideal gases, this also lead to the relation for adiabatic changes of $PV^{\gamma} =$ constant, where γ is the ratio of the specific heat capacity at constant pressure to the specific heat capacity at constant volume.

6

The Second Law of Thermodynamics

The first law of thermodynamics is not enough to describe all thermal phenomena. In particular there are many energetically allowed transitions that never happen. I have already mentioned the stability of hydrogen and oxygen mixtures which do not convert to water without some trigger such as a spark. This is because a certain activation energy is needed to start the reaction. There are other phenomena however, which do not need any apparent activation energy and are possible, but which do not happen. For instance, it is possible under the first law that a quantity of water could suddenly split into a small part which boils, while the remainder cools. Similarly, energetically, a mixture of gases could separate into its components, but this never happens either. These ideas are connected to reversibility and irreversibility and were developed in the 19th century to find the simplest, most self-evident expression from which quantitative progress could be made. This led to the Second Law of Thermodynamics.

6.1 Statements of the Second Law

There are two statements of the second law. The first is the Clausius statement:

> It is impossible to construct a device that, operating in a cycle, produces no effect other than the transfer of heat from a colder to a hotter body.

You might also see this in the form "heat cannot of itself flow from a colder to a hotter body". The longer statement makes the meaning of "of itself" explicit. The Clausius statement of the second law is something that we know from experience. It is never the case when you pour hot water into a cup, that the water gets hotter while the cup gets colder; instead the water always cools while the cup warms up. The second version of the second law is the Kelvin-Planck statement:

> It is impossible to construct a device that, operating in a cycle, produces no effect other than the extraction of heat from a single body at uniform temperature and the performance of an equivalent amount of work.

Again this is somewhat wordy, and more succinct, although less explicit, versions exist such as: "a process whose only effect is the complete conversion of heat into work is impossible", or "heat cannot be completely converted into work without other effect".

The Kelvin-Planck statement rules out perpetual motion machines of the *second kind*, which are those that live off stored thermal energy in the environment, converting it into work. Such machines do not violate the first law (conservation of energy), but would nevertheless provide an endless supply of power; these are ruled out by the second law. The Clausius statement of the second law seems perhaps more obvious, but in fact the two are equivalent as I will demonstrate. To do so I need to introduce the concept of *heat engines* which played an important role in the development of thermodynamics. These will also make clear what kind of "devices" are referred to in the two statements above and why they refer to operation in a cycle.

6.1.1 Conversion of work to heat

There is no problem converting work to heat: an electric kettle is an example of a device in which work is 100% converted into heat. Similarly, in Joule's paddle wheel setup, the work of the paddle wheel is dissipated as heat, and this is true regardless of how hot the water is. Therefore we can always assume that work can be dumped into a reservoir in a way entirely equivalent to heating it. This is called *irreversible work*, in contrast, for example to storing the work by winding up a spring. This will be used in showing the equivalence of the two statements of the second law.

6.2 Heat Engines

Much of the development of engines has been about making them more efficient. The advantages are obvious: just think of the effect of raising the typical efficiency of car engines from 30% to 100% upon pollution, energy consumption and global warming. Most of this development occurred through trial-and-error. It has been remarked that "thermodynamics owes more to steam engines than steam engines owe to thermodynamics". Nevertheless, it is interesting to establish just how efficient an engine can be. Unfortunately real engines come in many designs and are complex. It would seem hard to derive any general conclusions about them. Remarkably this is not the case, as was first realised by a French engineer, Sadi Carnot. It was he who in 1824 clarified the idea of efficiency, and identified the simplest form of engine, that we know as a *heat engine*.

A heat engine operates between two heat *reservoirs*, one hotter than the other (Fig. 6.1). You should think of the reservoirs as having such a large capacity that they don't change temperature as heat is taken from or added to them. The reservoirs themselves are in equilibrium and therefore of uniform temperature. The heat engine illustrated has the following key features:

1. It takes an amount of heat Q_1 from the hot reservoir.
2. It dumps an amount of heat Q_2 to the cold reservoir.
3. It performs an amount of work W
4. In doing the above, it completes one cycle, at the end of which it is in exactly the same state as it was at the start.

The last point is crucial, because it means that we do not have to worry about any change of internal energy of the engine, and can therefore write down by conserva-

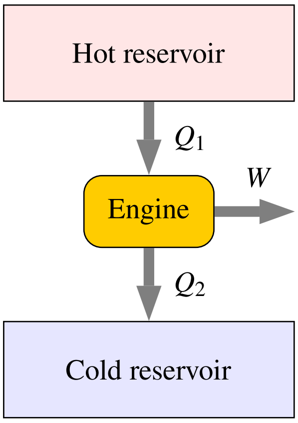

Figure 6.1 A heat engine.

tion of energy (the First Law) that:

$$W = Q_1 - Q_2. \tag{6.1}$$

The heat engine is the simplest form of engine we can envisage. For instance, a single reservoir is no good because then one would extract Q_1 from it, dump Q_2 back to it, and extract work W, but this is in violation of the Kelvin-Planck statement of the second law.

We are used to thinking of the need for a *hot reservoir*, such as the boiler in a steam engine, but the need for a cold reservoir seems less clear. However, a crucial part of a steam engine is the condenser, or just letting the steam escape to the atmosphere. Cooling towers, or large masses of water go hand-in-hand with power stations. Carnot's brilliance was to abstract the heat engine as a simplest form of engine, making it very clear why one must have two reservoirs.

When you sketch a heat engine, and you always should in any question involving them, *always* indicate the direction of the heat and work because it defines the signs. This is *very* important. If you get the sign wrong, you can end up with a completely incorrect answer.

6.2.1 Efficiency of a Heat Engine

To rate an engine, we are interested in how much work can be obtained for a given amount of fuel, the number of "miles per gallon" in other words. The fuel heats the hot reservoir and is represented by Q_1. So the efficiency of the heat engine depicted in Fig. 6.1 is given by

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}. \tag{6.2}$$

Clearly, the smaller the amount of heat dumped to the cold reservoir, the more efficient the engine. A major result of thermodynamics is that we will be able to place an upper limit on this efficiency, and this upper limit is a function only of the temperatures of the reservoirs.

6.2.2 Equivalence of the Clausius and Kelvin-Planck Statements

I will now use heat engines to demonstrate that the two forms of the Second Law are equivalent. I will do so by considering a potential engine that violates the Kelvin-Planck statement but show that it is ruled out by the Clausius version. Consider a

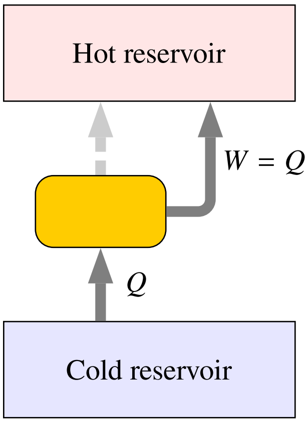

Figure 6.2 An (impossible) engine which violates the Kelvin-Planck statement of the Second Law of Thermodynamics.

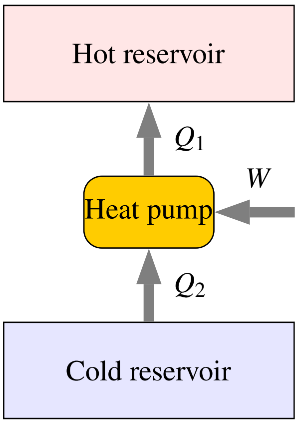

Figure 6.3 A heat engine run backwards as a heat pump or refrigerator.

hypothetical device that *can* convert heat completely into work. This is illustrated in Fig. 6.2 which depicts heat Q being extracted from a cold reservoir and converted into work so that $W = Q$. The dashed line is an indication that in this hypothetical engine, no other heat is transferred. The figure also shows the work being directed into a hot reservoir. As I discussed above, we can always convert work completely into heat, and so this is equivalent to transferring heat Q to the hot reservoir. The whole process, however, violates the Clausius statement, because we have transferred heat Q from the cold reservoir to the hot reservoir with no other effect (because the engine works in a cycle). We conclude that the hypothetical engine cannot exist, and therefore it is not possible to make an engine which fully converts heat into work without other effect. In other words the Clausius statement implies the Kelvin-Planck statement of the second law. We are free to use either in the knowledge that they are equivalent.

6.3 Heat Pumps and Refrigerators

If we run a heat engine backwards we have device known as a *heat pump*. This situation is depicted in Fig. 6.3 which shows a device which when work W is performed on it, extracts Q_2 from a cold reservoir and dumps Q_1 to the hot reservoir. As before, we restrict ourselves to complete cycles and can therefore say

$$Q_1 = Q_2 + W. \tag{6.3}$$

One can think of the hot reservoir as a house to be heated, while the cold reservoir is a nearby stream, for example. Then for every W of work done to run the heat pump (usually electrical), one obtains $W + Q_2$ of heating. Compare this with an electric fire, where one simply converts W directly to heat. Therefore a heat pump is potentially more efficient than normal heating. The efficiency of a heat pump is defined as

$$\eta_{\mathrm{HP}} = \frac{Q_1}{W}. \tag{6.4}$$

The higher this is, the better; it is greater than one in general. In section 7.3 I will obtain a simple expression for the maximum value this ratio can have.

If the cold reservoir is an insulated box, while the hot reservoir is the room the box is in, then we have a refrigerator or freezer. In this case one is interested in the amount of cooling per unit work, so the refrigerator efficiency is

$$\eta_{\mathrm{R}} = \frac{Q_2}{W}. \tag{6.5}$$

Again, I will obtain an upper limit on this value in section 7.3.

6.4 Carnot's Theorem

Carnot focussed upon the idea of a *reversible* engine. A reversible engine is one in which every part of its cycle is thermodynamically reversible in the sense I discussed earlier. Note that this more than simply saying that one can apply a torque to the drive shaft of the engine and make it run backwards: it has to be completely reversible so that to draw the engine in reverse I need only reverse the directions of the arrows in Fig. 6.1, but the numerical values of Q_1, Q_2 and W are *unchanged.* I have already discussed running an engine backwards as a heat pump, but there was no need there for it to be reversible.

Carnot's implementation of a reversible engine is called a "Carnot cycle". I will discuss this below. First I want to establish Carnot's theorem, which shows the importance of reversible engines. Carnot's theorem says that reversible engines are the most efficient of all. This can be proved by considering two engines, A and B. Engine B is reversible and is run as a heat pump using the power generated by engine A, which may or may not be reversible (Fig. 6.4). Carnot's theorem can be expressed as $\eta_B \geq \eta_A$. Since B is reversible, then we can say

$$\eta_B = \frac{W}{Q'_1}. \tag{6.6}$$

We could not say this if B was not reversible because then the magnitudes of Q'_1 and Q'_2 would not remain the same through the switch from engine to heat pump. The efficiency of engine A, which is running as an engine, is given as usual by

$$\eta_A = \frac{W}{Q_1}. \tag{6.7}$$

All the work produced by A is used to run B, thus the two engines form a complete system (indicated by the dashed box) which produces no work but just transfers heat

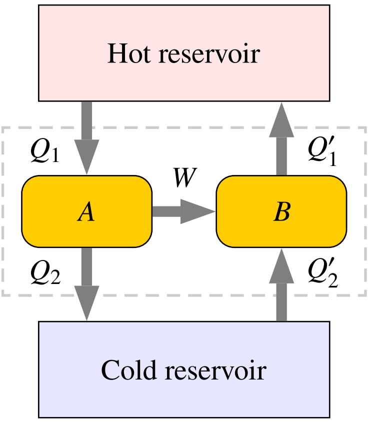

Figure 6.4 The setup used to prove Carnot's theorem. Engine A, which may or may not be reversible, is used to run the reversible engine B as a heat pump.

from one reservoir to another. By the Clausius statement of the 2nd law, the heat must flow from the hot to the cold reservoir. Therefore we must have that

$$Q_1 - Q'_1 \geq 0. \tag{6.8}$$

Therefore $Q_1 \geq Q'_1$, which implies that

$$\frac{W}{Q_1} \leq \frac{W}{Q'_1}, \tag{6.9}$$

which, from the relations above, shows that

$$\boxed{\eta_A \leq \eta_B}. \tag{6.10}$$

This is Carnot's theorem.

Had A been reversible, we could have reversed the argument to show that $\eta_B \leq \eta_A$. For both to be correct, we must have $\eta_A = \eta_B$. Therefore we now know that reversible engines are the most efficient of all engines, and that all reversible engines operating between the same reservoirs have the same efficiency. This means that one only needs to conceive of one reversible engine to know the efficiency of them all.

6.5 The Carnot Cycle

The discussion of heat engines has been a little abstract. We need to convince ourselves that we can at least contemplate a real example of a reversible heat engine. Carnot provided such an example. This is an engine that operates in a cycle of four reversible steps, which together are known as the *Carnot Cycle*. The Carnot cycle is based upon the expansion and compression of an ideal gas. Remember that we are free to choose as simple a system as possible, because Carnot's theorem shows that all reversible heat engines operating between the same reservoirs have the same efficiency.

Starting with the gas in thermal contact with the hot reservoir, at a point labelled A (see Fig. 6.5), the steps of the Carnot cycle are as follows:

- A → B
  While in contact with the hot reservoir, the gas is expanded isothermally, doing work W_1 while absorbing heat Q_1. As it is ideal, $U = U(T)$, so $\Delta U = 0$. Therefore $W_1 = Q_1$ (NB: W_1 here defined as work done *by* the gas, not on it).

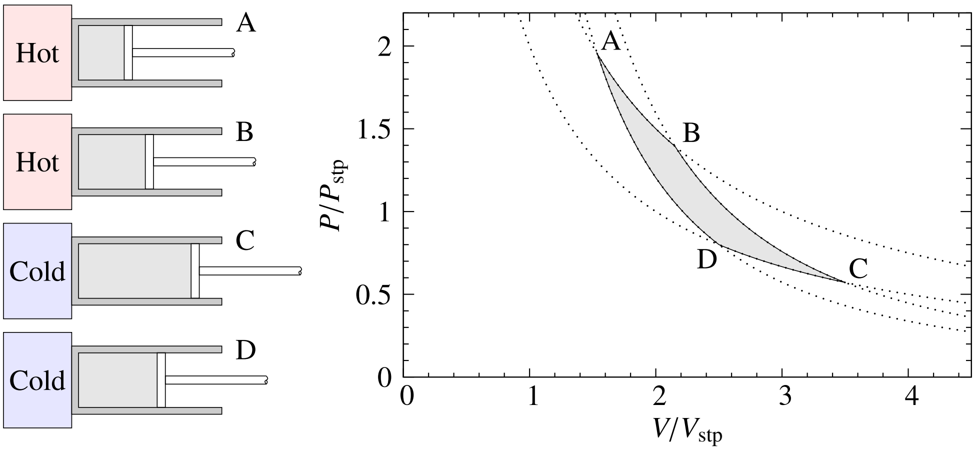

Figure 6.5 The left-hand part of the figure shows the configurations of piston and reservoirs at the ends of each of the steps of the Carnot cycle. The equivalent pressure–volume plot is shown on the right. Between points B and C and points D and A the piston is not in contact with either reservoir. The plot is drawn for one mole of an ideal gas with $\gamma = 1.83$ running in a Carnot cycle between temperatures $3T_{\text{stp}}$ and $2T_{\text{stp}}$.

- B → C
  The gas is removed from contact with the hot reservoir and expanded adiabatically until it is in thermal equilibrium with the cold reservoir (its temperature drops during adiabatic expansion). During the expansion it performs work W_2, while $Q = 0$. Therefore $\Delta U_2 = -W_2$.

- C → D
  The gas is placed into thermal contact with the cold reservoir and isothermally compressed. Work W_3 is done on the gas during the compression, and it gives up heat Q_2 to the cold reservoir. As in step 1, $\Delta U = 0$, so $Q_2 = W_3$.

- D → A
  Finally the gas is removed from thermal contact with the cold reservoir and adiabatically compressed until it is once more in thermal equilibrium with the hot reservoir, and it has the volume that it started with. Work W_4 is done on the gas during this stage, while $Q = 0$, so $\Delta U_4 = W_4$.

The end result is that the gas has completed a cycle, ending in the same state as it started. Q_1 has been extracted from the hot reservoir, while Q_2 has been dumped to the cold reservoir, and the net work extracted is:

$$W = W_1 + W_2 - W_3 - W_4 = Q_1 - Q_2 \tag{6.11}$$

Fig. 6.5 shows the configurations of the piston and reservoirs at each end of the steps of the Carnot cycle. The right-hand side shows the indicator diagram of the cycle. Since areas in indicator diagrams represent work, the shaded area in Fig. 6.5 is the work extracted from one cycle of the Carnot cycle. Note that when drawing indicator diagrams, the two lines representing the adiabatic changes, PV^{γ} = constant rise more steeply than those representing the isothermal changes, PV = constant, and that the isotherms cross the adiabatics, but isotherms do not cross each other, nor do adiabatics. This should be obvious for isotherms (the same state cannot have two different temperatures); it will only become “obvious” for adiabatic changes later.

6.6 Summary

We need more than just the First Law of thermodynamics to describe the thermal behaviour of matter. There are some processes possible under the First Law which nevertheless never happen. The Second Law (in the form proposed by Clausius) is a statement of one such impossible process, the spontaneous transfer of heat from a cold to a hot body. This also leads to an equivalent statement to the effect that heat cannot be turned completely into work. The equivalence was established through the idea of a "heat engine". Further the second law applied to such engines was used to establish that thermodynamically reversible engines are the most efficient, and also that all reversible engines running between the same reservoirs have the same efficiency.

7

Temperature and Entropy

Boltzmann's tomb with his definition of entropy engraved on it.

The second law of thermodynamics can be used to prove the existence of a new function of state known as *entropy* which allows us to determine quantitatively whether a process is reversible and whether it can occur naturally or not. Entropy is of fundamental significance in thermal physics and it is recognition of entropy rather than any effect upon the design of engines that is the truly important legacy of the development of thermodynamics. We shall see that entropy is inextricably linked to temperature, about which I have said little so far. I was careful when presenting the second law, to talk in terms of hot and cold, rather than high or low temperature. In fact, from what I have said so far, it is not necessarily the case that temperature is linked uniquely to "hot" or "cold", although this is the case of course. It was realised rather late in the development of thermodynamics that temperature was not clearly defined. In an effort to address this, a simple way of defining temperature was devised. As this was felt to be the most basic of all the laws of thermodynamics, and since numbers one, two and three had already been used, it was called the *zeroth law*; this name has stuck. I start this chapter therefore by looking at the meaning of temperature.

7.1 The Zeroth Law and Empirical Temperature

The Zeroth Law states that

> "if a system A is in thermal equilibrium with two other systems, B and C, then the systems B and C are in equilibrium with each other."

Two systems are in *thermal equilibrium* if neither of them changes (no heat is transferred between them) when they are placed in thermal contact. A moment's thought will show that if this was not the case, we could not talk about the temperature of an object. A thermometer is calibrated by allowing it to come into thermal equilibrium with some system or systems of fixed temperature, for example a water/ice mixture. If the thermometer is used to measure the temperature of another system which gives the same value as the water/ice mixture did, then the new system would be in thermal equilibrium with water/ice if we chose to bring them into thermal contact. This empirical fact is raised to the status of a law.

The Zeroth Law means that we can assign a label to any system, the label being the value shown on a thermometer when it is thermal equilibrium with the system. We call the label *temperature*. Temperature is a function of state which determines whether one system will be in thermal equilibrium with another.

7.1.1 Empirical Temperature Scales

To put this into practice we need a thermometer, a device with some easily measured property, X, that varies with temperature, such as the length of the mercury column in a mercury-in-glass thermometer, or the pressure of a constant volume gas thermometer. The temperature θ is some function of X, $\theta(X)$. We *choose*

$$\theta(X) = aX + b,$$

where a and b are constants, fixed using two easily reproduced calibration temperatures. Such temperatures are called *empirical*, denoted by the symbol θ.

For instance, the *Centigrade* temperature scale assigns values of 0 °C for the temperature of ice in equilibrium with water (known as the ice point) and 100 °C for the temperature of boiling water (the steam point). Letting the values of X at these two points be X_0 and X_{100}, the Centigrade temperature is defined as

$$\theta = 100\left(\frac{X - X_0}{X_{100} - X_0}\right). \tag{7.1}$$

The Centigrade scale is not very good for two reasons. First, the ice and steam points are not well defined as both depend upon pressure, and dissolved air makes a difference to the ice point in particular. Second, any errors made during the calibration are amplified when extrapolating to very low temperatures ($\approx -270°\mathrm{C}$).

Temperatures are now defined by setting $\theta(X{=}0) = 0$ (so that $b = 0$) and choosing one other calibration point. A good choice is the *triple point*, the unique temperature (and pressure) at which ice, water and water vapour are in equilibrium. Temperatures are given by:

$$\theta = 273.16\left(\frac{X}{X_{\mathrm{TP}}}\right), \tag{7.2}$$

where X_{TP} is the value of X at the triple point.

The trouble with empirical temperatures is that, except at the calibration points, the temperature depends upon the thermometer. For instance, the rate at which the length of a mercury-in-glass thermometer changes will slow dramatically once the mercury shrinks to be inside the bulb. The temperature can thus depend upon the substance (mercury versus alcohol for instance), and the exact dimensions of the thermometer. When quoting a temperature, we would have to detail the exact design of the thermometer used, a very unsatisfactory situation.

7.1.2 The Ideal Gas Scale

In constant volume gas thermometers, as the name implies, the volume of a quantity of gas is kept constant, while the pressure is measured. Fig. 7.1 shows a schematic

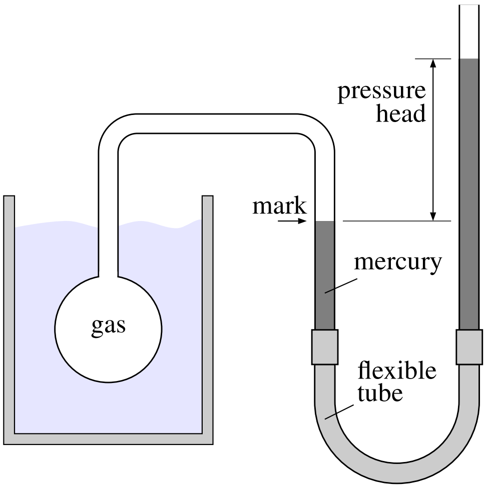

Figure 7.1 Schematic figure of a constant volume gas thermometer. The height of the right-most tube is adjusted to hold the mercury at the level of the mark, keeping the gas volume constant. The pressure is read from the difference in the heights of the mercury in different tubes.

picture of a constant volume gas thermometer. For an ideal gas, $PV = n_m R T_\mathrm{I}$, and so if V is constant, $T \propto P$, so the pressure is used for "X" above:

$$T_\mathrm{I} = 273.16 \left(\frac{P}{P_\mathrm{TP}} \right)_{\rho \to 0} . \tag{7.3}$$

The units of this scale are Kelvin, symbol K. The measurement is carried out in the limit of zero density since that is when gases tend to the ideal. Unlike other thermometers, all gases give the same value of temperature, and so seem in some sense more "fundamental" than the others. We will see that this is indeed the case. Constant volume gas thermometers are not very convenient, but they can be used to calibrate more convenient thermometers.

The Celsius temperature scale is directly related to the ideal gas scale, and is defined by

$$t = T_\mathrm{I} - 273.15, \tag{7.4}$$

with symbol C (there is no degree, °, here). The triple point has temperature 0.01 C by definition, so using 273.15 in the relation above ensures that the temperature of the ice point is 0 C = 0 °C. The number 273.16 in equation 7.3 was chosen to get a 100 K = 100 C temperature difference between the ice and steam points to coincide with the Centigrade scale. In fact a slight mistake was made in doing this and the steam point is actually 99.97 C = 100.00 °C. I have loosely referred to temperatures using the Centigrade symbol, °C because it is familiar. I will continue to do so, but you should be aware of the distinctions between the various scales.

7.2 Thermodynamic Temperature

While Carnot introduced the idea of heat engines, it was Clausius and Kelvin who developed his ideas to the point where a more fundamental definition of temperature emerged, along with a new function of state, called *entropy*. I am going to adopt the traditional approach to this based upon heat engines, as I think that it follows more naturally from what has gone before, and is still the most widely known. I refer to

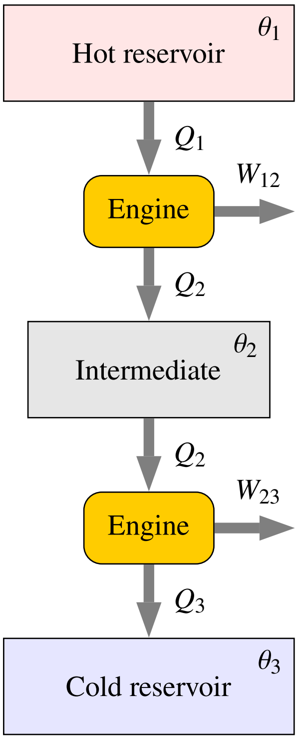

Figure 7.2 Two Carnot engines run between reservoirs at temperatures θ_1 and θ_3 via an intermediate stage at temperature θ_2.

Appendix A.1 for a more abstract approach, which the more mathematically inclined may prefer; it is not required material for this course however.

Carnot's theorem says that all reversible engines (henceforth "Carnot engines") running between the same two reservoirs have the same efficiency, regardless of their construction. Therefore we can say that the efficiency and the ratio of heat input to output is a function of the reservoir temperatures only

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2), \tag{7.5}$$

where θ_1 and θ_2 are the empirical temperatures of the hot and cold reservoirs respectively. The function f will depend upon the particular empirical temperature scale in use, but *its result,* Q_1/Q_2 *does not*, as long the reservoir temperatures do not vary. This is a strong hint that we might be able to come up with a system-independent definition of temperature based upon Carnot engines. To do so, let's look into the form of the function f. Consider the situation depicted in Fig. 7.2 which shows two Carnot engines (by which I mean reversible) running between reservoirs at empirical temperatures θ_1 and θ_3 via an intermediary at θ_2. The system is set up so that there is no net flow of heat into or out of the intermediate reservoir, in which case we can also think of the two engines combined into a single engine running straight from the top to the bottom reservoir and producing total work $W_{12} + W_{23}$. The ratios of heat input to output of the two engines considered separately and the two considered as one are given by:

$$\frac{Q_1}{Q_2} = f(\theta_1, \theta_2), \tag{7.6}$$

$$\frac{Q_2}{Q_3} = f(\theta_2, \theta_3), \tag{7.7}$$

$$\frac{Q_1}{Q_3} = f(\theta_1, \theta_3). \tag{7.8}$$

Therefore

$$f(\theta_1, \theta_3) = f(\theta_1, \theta_2) f(\theta_2, \theta_3). \tag{7.9}$$

Although θ_2 appears on the right-hand side, it does not on the left, and the only way that this can be true for arbitrary θ_2 is if the function f is of the form

$$f(\theta_1, \theta_2) = \frac{g(\theta_1)}{g(\theta_2)}, \tag{7.10}$$

where g is a function of the empirical temperature. Again, the form of g will depend upon the empirical temperature scale we are using, but its output for all bodies of the same temperature in the sense of being in thermal equilibrium must be the same, up to an arbitrary multiplicative constant, because of Carnot's theorem. Now comes the clever bit: let's use $T = g(\theta)$ for our temperature! We can then write

$$\boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}}. \tag{7.11}$$

where T_1 and T_2 are the "thermodynamic temperatures" of the reservoirs. This equation defines the ratio of thermodynamic temperatures of two reservoirs as the ratio of heats exchanged during the operation of a reversible engine running between them. This defines thermodynamic temperature up to a multiplicative constant. If a calibration point is defined, then the scale is uniquely determined. The triple point of water is defined to have $T = 273.16$ K, the number chosen so that there are 100 K between the ice and steam points, consistent with the standard usage of the Centigrade scale.

7.2.1 Temperature and Hotness

We know from the Second Law that if Q_1 is extracted from the hotter reservoir then some work can be obtained and therefore $Q_2 < Q_1$, which implies that $T_2 < T_1$. This implies that the hotter reservoir has the higher temperature, as expected. Note that there is an element of choice here. I could have equally well written

$$f(\theta_1, \theta_2) = \frac{T(\theta_2)}{T(\theta_1)}, \tag{7.12}$$

in place of Eq. 7.10 which would have reversed the ordering of temperature and hotness, although there would always be a one-to-one correspondence between the two properties in any scheme.

7.3 Efficiencies of Engines, Heat Pumps and Refrigerators

Eq. 7.11, which says that $Q_1/Q_2 = T_1/T_2$, leads immediately to expressions for maximum efficiency factors for engines, heat pumps and refrigerators. For an engine

$$\eta_E = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}. \tag{7.13}$$

Thus a heat engine running between the steam point ($T_1 = 373\,\mathrm{K}$) and the ice point ($T_2 = 273\,\mathrm{K}$) has a maximum efficiency of ~ 27%. It is clearly of advantage to raise the hot reservoir to the highest possible temperature.

For heat pumps we are interested in the reverse, i.e. the ratio of heat dumped to the hot reservoir to the work input

$$\eta_{\mathrm{HP}} = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}. \tag{7.14}$$

The point here is that for small temperature differences, one potentially has a huge gain. For instance to heat a house to 18°C with a river flowing by of temperature 8°C, $\eta_{\mathrm{HP}} = 29$! Real heat pumps fall a long way short of this ideal, and have large initial costs, which is why they are relatively rare. However, they are certainly used and can produce considerable savings in heating costs. If only "heat" as in hot water could be transported efficiently through pipes one could easily imagine power companies setting up heat pumps on the coast to supply cities with heating; the savings in energy usage could be enormous if this were possible.

Finally, in refrigerators we are interested in the amount of heat extracted from the cold reservoir per unit work

$$\eta_{\mathrm{R}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}. \tag{7.15}$$

This again can be much larger than unity, but we can always expect a considerable drop off in efficiency the larger the temperature difference.

7.4 Goodbye to T_{I}

In principle measurement of thermodynamic temperature is simple. One defines a reference temperature, e.g. the triple point of water, 273.16 K. Then to measure the temperature of any other object, one runs a reversible heat engine between the two and measures the heats Q_1 and Q_2. Then by the fundamental relation, $Q_1/Q_2 = T_1/T_2$, the temperature of the object follows. However, this is complex and in no way practical. Is there another way? The answer is yes, and in this section I will show that the thermodynamic temperature is in fact identical to the ideal gas scale. Although the latter is tricky to measure in practice, it is at least possible. The key to the proof is Carnot's cycle which works with an ideal gas. From this we can obtain an expression of the heat ratio involving the ideal gas scale, which leads to the direct equivalence of thermodynamic and ideal gas temperatures.

The heat Q_1 can be calculated from step 1 of the Carnot cycle, when the gas expands isothermally in contact with the hot reservoir (point A to point B, Fig. 6.5, section 6.5). As we saw in section 4.9.1, all heat absorbed in an isothermal expansion of an ideal gas is converted to work, so the work performed in this stage gives the heat absorbed Q_1. Therefore from Eq. 5.12 and putting $V_1 = V_A$, and $V_2 = V_B$, and $T_{\mathrm{I}} = (T_{\mathrm{I}})_1$, we get

$$Q_1 = n_m R (T_{\mathrm{I}})_1 \ln \frac{V_B}{V_A}. \tag{7.16}$$

(NB: there is a switch of sign here which inverts the ratio within the logarithm, because Q_1 equals the work done *by* the gas.) Similarly Q_2, the heat given up to the cold reservoir, comes from step 3 when the gas is isothermally compressed in contact with the cold reservoir (point C to D), in which case

$$Q_2 = n_m R (T_{\mathrm{I}})_2 \ln \frac{V_C}{V_D}. \tag{7.17}$$

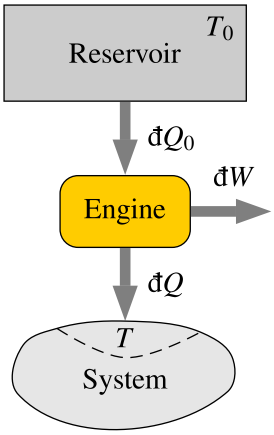

Figure 7.3 A Carnot engine is used to transfer heat to a system. The engine runs between a reservoir at temperature T_0 and a part of the system at temperature T.

Therefore

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{(T_\mathrm{I})_1}{(T_\mathrm{I})_2} \frac{\ln(V_B/V_A)}{\ln(V_C/V_D)}. \tag{7.18}$$

The middle term of this equation is just the definition of thermodynamic temperature. The equivalence between the thermodynamic and ideal gas scales is proved if we can show that the last term equals unity. We can do this if we remember that points B and C, and points D and A are connected by reversible adiabatics for which we know $T_\mathrm{I} V^{\gamma-1} = \text{const}$. Therefore

$$(T_\mathrm{I})_1 V_B^{\gamma-1} = (T_\mathrm{I})_2 V_C^{\gamma-1}, \tag{7.19}$$

$$(T_\mathrm{I})_1 V_A^{\gamma-1} = (T_\mathrm{I})_2 V_D^{\gamma-1}. \tag{7.20}$$

Dividing these two equations shows that $V_B/V_A = V_C/V_D$ and so

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} = \frac{(T_\mathrm{I})_1}{(T_\mathrm{I})_2}. \tag{7.21}$$

Therefore, the ideal gas temperature scale does indeed have a fundamental significance since it is identical to the thermodynamic temperature scale. From now on, there will be no more "T_I", but T instead.

Having finally dealt with temperature, I move on to entropy.

7.5 Entropy

Carnot's engine provides us with a means to deal quantitatively with the transfer of heat and will lead to a definition of a new function of state, entropy.

Consider the situation depicted in Fig. 7.3 which shows the transfer of an infinitesimal amount of heat $đQ$ to a system via a Carnot engine which does useful work $đW$. For each infinitesimal cycle of the Carnot engine the heat transferred from the reservoir is

$$đQ_0 = T_0 \frac{đQ}{T}. \tag{7.22}$$

The part of the system which connects to the Carnot engine is at temperature T, but we do not require the whole system to be at this temperature. We expect that T will change as the Carnot engine runs over many cycles and heat is exchanged between the system and the reservoir. By making each cycle infinitesimally small we can take T as fixed over the cycle. Thus, all the infinitesimal Carnot cycles are reversible, but the system can undergo any process, reversible or not. The system may do some work, but all heat transfer in or out of it is done via the Carnot engine.

Now we take the system through a "large" cycle, encompassing infinitely many complete cycles of the Carnot engine, returning everything to its initial state, so that the internal energy (of system plus Carnot engine) is unchanged. Hence the total heat Q_0 extracted from the reservoir is equal to the work done by the system and the Carnot engine. By the Kelvin-Planck statement of the Second Law these must be less than or equal to zero or we would have converted heat completely into work with no other effect. Therefore

$$Q_0 = \oint đQ_0 = T_0 \oint \frac{đQ}{T} \leq 0, \tag{7.23}$$

where the circles through the integral signs indicates that the system executes a cycle. Since $T_0 > 0$ we deduce that

$$\boxed{\oint \frac{đQ}{T} \leq 0}. \tag{7.24}$$

This is *Clausius' inequality* and is a very important relation in thermodynamics. As usual, $đQ$ is the heat transferred to the system. It's worth noting carefully the significance of T in the above result. In a general (irreversible) cycle, the different parts of the system might not be in thermal equilibrium with each other and it might be impossible to define a temperature for the system as a whole. T appeared in the argument above as the temperature of the Carnot engine as heat is transferred across the boundary of the system. So, *T is the temperature at which heat is supplied to the system.*

If the cycle is reversible, then by running it in reverse we exchange every $đQ$ with $-đQ$ so that $\oint đQ/T \geq 0$. But if this and 7.24 are simultaneously true we must have

$$\oint \frac{đQ_R}{T} = 0, \tag{7.25}$$

where the subscript R denotes reversible. Clausius's inequality becomes an equality for *reversible changes.*

This last equation implies the existence of a new function of state, in a way similar to that in which the First Law implies the existence of internal energy, U. Consider for example Fig. 7.4 in which a system is taken through a cycle. If done reversibly we can write

$$\oint \frac{đQ_R}{T} = \left(\int_A^B \frac{đQ_R}{T}\right)_1 + \left(\int_B^A \frac{đQ_R}{T}\right)_2 = 0, \tag{7.26}$$

where the subscripts on the brackets around the integrals refer to the path traversed. Therefore switching the limits on the second integral we have

$$\left(\int_A^B \frac{đQ_R}{T}\right)_1 = \left(\int_A^B \frac{đQ_R}{T}\right)_2. \tag{7.27}$$

In other words, the value of this integral is *independent of the path taken.* This is the same as the First Law in which the work done is independent of the path if no heat is involved (adiabatic). Therefore in a similar way, there must be a *function of state*,

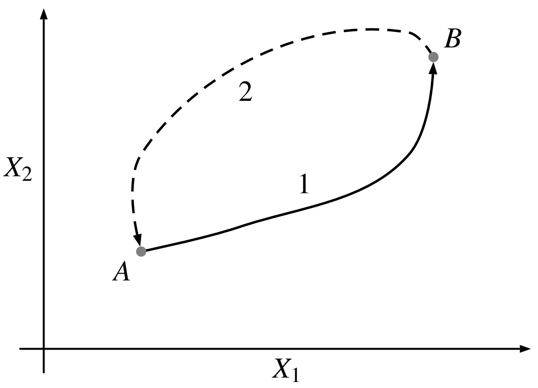

Figure 7.4 A system is taken through a cycle from A to B via path 1 and then back to A via path 2. Done reversibly, this establishes the existence of entropy; see text for how it does so.

S, such that

$$S_B - S_A = \int_A^B \frac{đQ_R}{T}. \tag{7.28}$$

The new function of state is called the *entropy*. The fundamental equation for a change of entropy of a system is then

$$\boxed{dS = \frac{đQ_R}{T}}, \tag{7.29}$$

where the R is a reminder that this only applies to *reversible* transfer of heat and T is the temperature at which heat is supplied to the system. An immediate consequence of this is that if a change is reversible *and* adiabatic as well ($đQ = 0$), then $dS = 0$. Therefore

> the entropy of a system is constant for reversible, adiabatic changes. Entropy is a "label" that uniquely defines reversible adiabatics.

This can in fact be shown very directly from the Second Law, as shown in Appendix A.1, although to obtain the relation of Eq. 7.29 requires some rather abstract analysis.

Now consider that path 1 in Fig. 7.4 is *irreversible* (so it can't really be drawn on the diagram because the system does not pass through a continuous set of equilibrium states!) while path 2 remains reversible. Then from Clausius's inequality, Eq. 7.24, I can write

$$\oint \frac{đQ}{T} = \left(\int_A^B \frac{đQ}{T}\right)_1 + \left(\int_B^A \frac{đQ_R}{T}\right)_2 \leq 0. \tag{7.30}$$

Using Eq. 7.28, the second term can be written

$$\left(\int_B^A \frac{đQ_R}{T}\right)_2 = S_A - S_B \tag{7.31}$$

and therefore in general

$$S_B - S_A \geq \int_A^B \frac{đQ}{T}, \tag{7.32}$$

or for an infinitesimal heat transfer

$$\boxed{đQ \leq T\, dS}, \tag{7.33}$$

where T is the temperature at which heat is supplied to the system. This is Clausius' inequality in a different form, and is a very important relation. For reversible heat transfer, it becomes an equality.

7.6 The Increase of Entropy and Heat Death of the Universe

For an isolated system $đQ = 0$, so Clausius' inequality in the form of Eq. 7.33 shows that

$$\mathrm{d}S \geq 0. \tag{7.34}$$

In words, the entropy of an isolated system *can never decrease*. This is a very remarkable result, as it imposes a direction in which processes can occur. Applied to the Universe as a whole, the entropy will carry on increasing until it can no longer do so, by which point the Universe will be in a state of equilibrium and it will no longer be possible to extract work from any process. This is the so-called *heat death* of the Universe that was much discussed in the 19th century.

The increase of entropy gives us another way to decide whether a process is reversible or not:

$$\boxed{\text{reversible processes do not change the total entropy of the Universe}}$$

7.7 Calculations Involving Entropy

Entropy will be an unfamiliar concept to you. One way to become happy with it is to carry out lots of example calculations of entropy changes. I will now do just this. One thing to realise is that you are free to assume reversible changes for the separate components of a system because entropy is a function of state. It does not matter how you calculate the change as long as the system begins and ends in an equilibrium state. Therefore, you might as well make things simple and do things reversibly when you can.

7.7.1 Heat Engines

The setup of a heat engine makes it particularly simple to calculate entropy changes. The hot reservoir has heat Q_1 *removed* so

$$\Delta S_1 = -\frac{Q_1}{T_1}. \tag{7.35}$$

Similarly

$$\Delta S_2 = \frac{Q_2}{T_2}. \tag{7.36}$$

When the engine completes a cycle, the entropy change of the Universe is:

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}. \tag{7.37}$$

If the engine is reversible, then $Q_1/T_1 = Q_2/T_2$ and $\Delta S = 0$, as expected. If the engine is not reversible then it is less efficient, or equivalently Q_2 is larger for a given Q_1 than in the case of a reversible engine, and $\Delta S > 0$, as expected again. Irreversible engines are therefore entropy source.

7.7.2 Entropy Change during a Change of Phase

The change of a liquid to a gas or solid to liquid is called a change of phase. As we know this involves "latent heat", heat absorbed at constant temperature. This implies that an increase of entropy has occurred. This is particularly simple to calculate because there is no change in temperature. To boil mass m of liquid requires input of

$$Q = mL, \tag{7.38}$$

where L is latent heat of vaporisation, at temperature T_b. Therefore

$$\Delta S_l = \frac{mL}{T_b}. \tag{7.39}$$

In this case, an entropy increase is associated with increasing disorder. Note that it is only the entropy of the substance that has increased; the entropy of the Universe could stay constant if the process was carried out reversibly because then you would have *supplied* heat Q at temperature T_b, and so the entropy of the surroundings would have dropped by ΔS_l.

7.7.3 Hot objects placed in water

Suppose you heat a lump of iron to temperature T_{Fe}, and then place it into a large quantity of water of temperature T_{W}. The final temperature will be $\approx T_{\mathrm{W}}$, and as we have seen such a process is irreversible. We therefore expect the total entropy to increase.

We need to calculate the change in entropy of the water and the iron. The change for water is relatively easy. Its temperature is constant, but heat $Q = m_{\mathrm{Fe}}C_{\mathrm{Fe}}(T_{\mathrm{Fe}} - T_{\mathrm{W}})$ flows into it from the iron, giving a change in entropy of

$$\Delta S_{\mathrm{W}} = m_{\mathrm{Fe}}C_{\mathrm{Fe}}\frac{T_{\mathrm{Fe}} - T_{\mathrm{W}}}{T_{\mathrm{W}}}, \tag{7.40}$$

because the temperature of the water hardly changes. The iron is trickier because as it loses heat, it cools down so the temperature T that we use in the relation $\mathrm{d}S = đQ_R/T$ changes all the time. We therefore need to integrate. Remembering that $đQ = m_{\mathrm{Fe}}C_{\mathrm{Fe}}\,\mathrm{d}T$, then

$$\Delta S_{\mathrm{Fe}} = \int_{T_{\mathrm{Fe}}}^{T_{\mathrm{W}}} \frac{m_{\mathrm{Fe}}C_{\mathrm{Fe}}\,\mathrm{d}T}{T} = -m_{\mathrm{Fe}}C_{\mathrm{Fe}}\ln\frac{T_{\mathrm{Fe}}}{T_{\mathrm{W}}}. \tag{7.41}$$

The total entropy change of the Universe is then

$$\delta S = \Delta S_{\mathrm{W}} + \Delta S_{\mathrm{Fe}} = m_{\mathrm{Fe}}C_{\mathrm{Fe}}\left(\frac{T_{\mathrm{Fe}} - T_{\mathrm{W}}}{T_{\mathrm{W}}} - \ln\frac{T_{\mathrm{Fe}}}{T_{\mathrm{W}}}\right). \tag{7.42}$$

One can show that the term in brackets is indeed positive (or zero if $T_{\mathrm{Fe}} = T_{\mathrm{W}}$), as expected, so the entropy of the Universe does indeed increase in this irreversible process.

7.7.4 Isothermal Expansion of Gas

During the isothermal expansion of an ideal gas, the heat absorbed equals the work performed *by* the gas. Therefore

$$đQ_R = T\,\mathrm{d}S = P\,\mathrm{d}V, \tag{7.43}$$

and so

$$\Delta S_{\text{gas}} = \int_{V_1}^{V_2} \frac{P\,\mathrm{d}V}{T}. \tag{7.44}$$

From the ideal gas law, $PV = n_m RT$, and so

$$\Delta S_{\text{gas}} = n_m R \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} = n_m R \ln \frac{V_2}{V_1}. \tag{7.45}$$

If carried out reversibly there is an exactly compensating decrease in the entropy of the surroundings. However, since entropy is a function of state, this formula is correct regardless of how the volume change is carried out, as long as we start and end in equilibrium at temperature T.

7.7.5 Joule Expansions

Joule expansions are classic examples of irreversible changes. In this case no heat is transferred, so the surroundings do not change their entropy. However, in expanding from V_1 to V_2, the entropy of the gas does change according to the equation of the previous section

$$\Delta S = n_m R \ln \frac{V_2}{V_1}. \tag{7.46}$$

This is therefore the change of entropy of the Universe, and since $V_2 > V_1$, then $\Delta S > 0$ as expected.

7.8 Generating Entropy

Any irreversibility generates entropy; entropy is *not* conserved. An example is the Sun, which is a huge entropy source. The Sun generates 4×10^{26} W at a temperature of $T = 15 \times 10^6$ K at its centre. This corresponds to an entropy generation rate of

$$\frac{4 \times 10^{26}\,\mathrm{W}}{15 \times 10^6\,\mathrm{K}} = 2.67 \times 10^{19}\,\mathrm{J\,K^{-1}\,s^{-1}}. \tag{7.47}$$

All this power is radiated at its surface at a temperature of 5700 K, so entropy is generated at

$$\frac{4 \times 10^{26}\,\mathrm{W}}{5700\,\mathrm{K}} = 7.02 \times 10^{22}\,\mathrm{J\,K^{-1}\,s^{-1}}, \tag{7.48}$$

at the surface. Between the core and the surface irreversible heat transfer processes have generated more entropy. Still more is generated when the radiation reaches Earth, is absorbed and then re-radiated at about 300 K.

7.9 Statistical Interpretation of Entropy

Entropy shows in which direction processes can occur and distinguishes reversible adiabatics, but *just what is it*? A question like this is almost always best answered at a microscopic level. For example, temperature is related microscopically to the mean energy per particle, an easy concept to take on board. This is even more the case with entropy. The Joule expansion is probably the easiest way to see this.

The increase of entropy during a Joule expansion indicates that it is irreversible. In other words, gas molecules in a box of volume V will *never* spontaneously all move to volume $V/2$. But surely this is nonsense isn't it? If you had only 2 molecules, there would be a 25% chance at any one time that both were in, say, the left-hand half of the box — nothing irreversible about that. How about N molecules? The chance of finding all of these in the left-hand side of the box is $1/2^N$. For large N, this is *tiny*! There are 2^N more ways to arrange N molecules in the whole box than in only half of it. This number is typically *enormous*! To see how big, note that

$$2^N = 10^{(\log 2)N} = 10^{0.3N}. \tag{7.49}$$

For gas at STP, for which $N \approx 2.5 \times 10^{25}$ m^{-3}, we therefore find that occupation of the whole of a cubic metre is approximately

$$10^{10^{25}} \tag{7.50}$$

times larger than occupation of half a cubic metre. Compare this with the age of the Universe, which is of order 10^{17} seconds. If you looked at the box once every second for the age of the Universe, the chance that you would find all the gas on one side is of order

$$10^{17-10^{25}}. \tag{7.51}$$

The "17" is tiny compared to 10^{25}. Thus a "Joule compression" will not happen in the age of the Universe, or even many, many, many times the age of the Universe. For practical purposes, it will indeed *never* happen.

We can investigate this some more. Let us count the number of ways in which we can distribute N molecules into two halves of a box.[2] At the microscopic level, each molecule can be in either the left or right half (but not both), and there are 2^N possibilities in total: these are the distinct *microstates*. However, at a macroscopic level, all that matters is how many molecules are in each half: we can label these *macrostates* by the number or fraction of the molecules in, say, the right half of the box (since the total number is fixed). The number of ways in which we can have n molecules out of N on the right is simply the number of combinations of n distinguishable objects drawn from N, which is

$$\frac{N!}{(N-n)!\,n!}. \tag{7.52}$$

If there are $N = 10$ molecules in total, for example, there are 11 possible macrostates, with microstates distributed as follows:

macrostate		
right	left	number of microstates
0	10	1
1	9	10
2	8	45
3	7	120
4	6	210
5	5	252
6	4	210
7	3	120
8	2	45
9	1	10
10	0	1

---

[2] You can think of these molecules as *classically* identical, meaning that they all have the same properties, but can be individually distinguished.

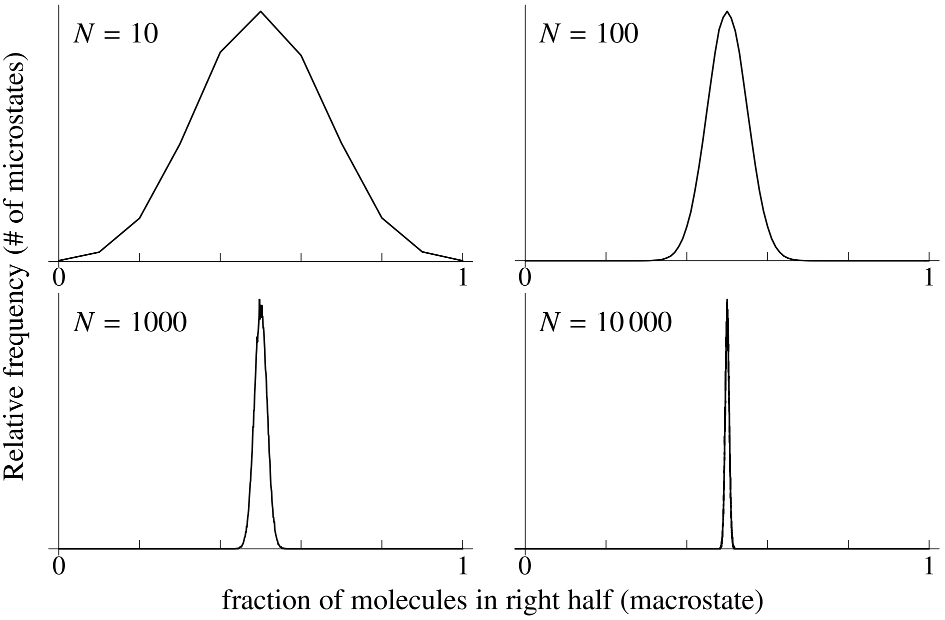

Figure 7.5 Multiplicity distributions for states of $N = 10$, 100, 1000 and 10 000 molecules distributed in two halves of a box.

With just 10 molecules we can begin to see that there are more microstates corresponding to macrostates with equal or nearly equal numbers of molecules in the two halves. As N increases it becomes less and less probable to have anything other than (almost) equal numbers in the two halves. I have illustrated this in Fig. 7.5. I considered using, in turn, $N = 10$, 100, 1000 and 10 000 molecules. In each case I did 100 000 trials of distributing the N molecules at random and with equal probability into the two halves of a box. For each set of trials I counted how often each macrostate (expressed as the fraction of molecules ending up in the right half) occurred. The results are presented as four graphs of the relative frequencies with which each macrostate occurred. What you can see is that as N increases, there is a sharper and sharper peak centred at 50% occupancy. This should make it easy to believe that with $N \approx 10^{23}$ molecules you essentially *always* find a macrostate with equal occupancy in the two halves of the box.

All this suggests that entropy may be related to the number of ways of arranging molecules, which is known as the *multiplicity*, W. The multiplicity of a macrostate is the number of microstates which correspond to it. For N molecules expanding from volume V_1 to V_2 (so V_1 and V_2 label the macrostates), the multiplicity changes by

$$\frac{W_2}{W_1} = \left(\frac{V_2}{V_1}\right)^N . \tag{7.53}$$

Very large numbers are easier to handle by taking their logarithm. The natural log of the multiplicity increase is given by

$$\ln\frac{W_2}{W_1} = N\ln\frac{V_2}{V_1}. \tag{7.54}$$

This is very closely related to the relation of Eq. 7.46. Indeed if we suppose that $S = k\ln W$, we have

$$\begin{aligned}\Delta S &= S_2 - S_1 = k(\ln W_2 - \ln W_1)\\ &= k\ln\frac{W_2}{W_1} = kN\ln\frac{V_2}{V_1} = n_m N_A k\ln\frac{V_2}{V_1} = n_m R\ln\frac{V_2}{V_1},\end{aligned} \tag{7.55}$$

using Eq. 7.54, and that there are N_A molecules in a mole. This is exactly the same as Eq. 7.46. The relation

$$\boxed{S = k \ln W} \tag{7.56}$$

is one of the most famous in physics. It was proposed by Boltzmann and is carved on his gravestone. It gives a very intuitive idea of entropy as a measure of the number of microscopic arrangements or *microstates* of a system, always subject to constraints on energy, volume, etc.

Boltzmann's relation is part of the foundation of statistical mechanics and makes it clear why reversible mechanical laws nevertheless lead to macroscopic irreversibility. All this is fairly clear for volume changes, but also applies to temperature increases. This however is much more difficult to deal with.

Boltzmann's interpretation makes the reason for the ever-increasing entropy of the Universe simple: the Universe is always changing to a more probable configuration, in the sense of more available microstates. The new configurations are *so much more probable* that the change is irreversible. The chance of the entropy of the Universe decreasing by as little as $0.000001\,\mathrm{J\,K^{-1}}$ is so tiny as to make the chance of being hit by a meteorite enormous by comparison.

7.10 Summary

In the hands of Clausius and Kelvin, Carnot's theorem led to the definition of an absolute, as opposed to empirical, temperature scale. At the same time a new function of state was recognised, called entropy. The key relation to remember for the entropy change of a system absorbing heat $đQ$, with the heat transfer occurring at temperature T, is Clausius' inequality in the form $\mathrm{d}S \geq đQ/T$. When the change is reversible, this reduces to $\mathrm{d}S = đQ_R/T$ where T is the temperature of the system.

The important consequence of Clausius' inequality is that the entropy of an isolated system always increases. This mysterious function is simplicity itself when viewed microscopically, following Boltzmann: a system always tends towards states of greater multiplicity given external constraints.

8

Thermodynamic Potentials

At this point I have more-or-less finished with the introduction of fundamental new physics, and we move onto applications. Even so we will need to develop new material to make straightforward use of entropy and the like. Thus in this chapter I will introduce what are called thermodynamic potentials which are of great importance in chemistry and biochemistry. I begin with an equation that summarises the First and Second Laws in one go.

8.1 The Central Equation of Thermodynamics

There is no commonly accepted description of the important equation I am now going to introduce, I will call it the *central equation of thermodynamics*. We have learned that the First Law can be written as

$$đQ = \mathrm{d}U - đW, \tag{8.1}$$

and that for reversible pressure work we can write

$$đQ_R = \mathrm{d}U + P\,\mathrm{d}V. \tag{8.2}$$

Now we also learnt in the last chapter that we can write

$$đQ_R = T\,\mathrm{d}S, \tag{8.3}$$

and therefore we have

$$\boxed{T\,\mathrm{d}S = \mathrm{d}U + P\,\mathrm{d}V}\,. \tag{8.4}$$

This is the *central equation*. It has a wonderful property: although derived for reversible changes only, it applies *generally*. This is because all variables are functions of state, so the method of change is immaterial. However, it is essential that the system starts and ends in equilibrium so that it is meaningful to talk about pressure, temperature and entropy.

8.2 Entropy of an Ideal Gas

I have already discussed the entropy change of an ideal gas during a Joule expansion, but now I can use the central equation to derive a more general relation. For one mole of ideal gas we have $P = RT/V$ and $\mathrm{d}U = C_V\,\mathrm{d}T$ (internal energy a function of temperature only). Therefore we can write Eq. 8.4 as

$$\mathrm{d}S = C_V\frac{\mathrm{d}T}{T} + R\frac{\mathrm{d}V}{V}. \tag{8.5}$$

This can immediately be integrated to give

$$S = S_0 + C_V \ln T + R \ln V, \tag{8.6}$$

where S_0 is a constant of integration (note that this constant is not determined in classical thermodynamics but is by statistical thermodynamics). This relation shows that the entropy of an ideal gas increases with both T and V. In other words increasing temperature must increase the number of available states, which it does because more energy states become available for the atoms. Remembering that for a monatomic gas

$$C_V = \frac{3}{2}R = \frac{3}{2}N_A k,$$

Boltzmann's relation $S = k \ln W$ implies that

$$W \propto T^{3N_A/2},$$

or $\propto T^{3/2}$ for one atom. This is a relation that can be explained by statistical thermodynamics.

8.3 Thermodynamic Potentials

Changes can only occur if the entropy of the Universe increases. For instance, we might have two chemicals mixed in a vessel. whether these react or not depends upon whether the entropy of the Universe increases as a result of their reaction. Similarly some elements, such as tin and sulphur, and perhaps most famously of all, carbon (graphite and diamond), can exist in multiple forms or "allotropes". Which is the stable one again depends upon whether the entropy of the Universe increases as one form converts to another. Note that this only means that change *can* occur, not that it *will* occur because potential barriers can make such reactions very slow indeed.

Framed in these terms, it seems odd that we need to account for the entire Universe in determining whether a change will occur, but it is simply because reactions do not usually occur in isolation. Plain $\Delta S > 0$ for a system only applies if we can mechanically and thermally isolate it, but thermal isolation for ever cannot be achieved and so we must at least be able to deal with the effect heat transfer has. This leads naturally to the definition of some new functions of state. Luckily they are just combinations of ones already encountered.

I will start with the quantity called enthalpy. In what follows, a subscript 0 on a quantity refers to its value in the surroundings, while plain variables refer to the system of interest.

8.3.1 Enthalpy

If a reaction occurs in a vessel of constant volume, then the First Law tells us that the heat *given off*, $-Q$, is simply related to the change of internal energy by

$$-Q = -\Delta U. \tag{8.7}$$

However, it is often easier to perform reactions at constant pressure, when we need to account for any change in volume. Thus consider a change of a system in *pressure equilibrium* with its surroundings, i.e. $P = P_0$, at least at the start and end of the change, although not necessarily while the change occurs. From the First Law we have

$$\Delta U = Q - P_0 \Delta V, \tag{8.8}$$

and so the heat given off, $-Q$, is now

$$-Q = -(\Delta U + P_0 \Delta V). \tag{8.9}$$

Now since $P = P_0$, a constant, at the start and end, we can write

$$-Q = -(\Delta U + P\Delta V) = -\Delta(U + PV) = -\Delta H, \tag{8.10}$$

where

$$\boxed{H = U + PV} \tag{8.11}$$

is a *function of state* called the *enthalpy*. $-\Delta H$ is the heat given off in chemical reactions at constant pressure. If you look at thermodynamic data tables, you are far more likely to see the enthalpy listed than the internal energy, even though the latter is more fundamental. The PV term in the enthalpy corrects for work done during any volume change. Just as we have seen that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V,$$

it is obvious that

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

Thus most "specific heat capacities" are really "specific enthalpy capacities", although the difference is large only for gases.

Thermodynamic data books include "enthalpies of formation", ΔH_f, from standard forms of elements. Thus the enthalpy of formation of the elements themselves is defined as zero. For instance, both hydrogen in the form of H_2, and oxygen as O_2 have $\Delta H_f = 0$. Water on the other hand (H_2O) has $\Delta H_f = -242\,\text{kJ mole}^{-1}$, and the formation of 1 kg of water from hydrogen and oxygen releases $242/0.018 = 13.4\,\text{MJ}$ of heat (molar mass of water = 18 g).

Example 8.1 The enthalpies of formation of carbon monoxide (CO) and carbon dioxide (CO_2) are $-110.5\,\text{kJ mole}^{-1}$ and $-393.5\,\text{kJ mole}^{-1}$ respectively. How much heat is produced per mole of carbon monoxide when it is burnt to produce carbon dioxide?

Answer 8.1 One mole of CO plus half a mole of O_2 produces one mole of CO_2. The enthalpy of formation of O_2 is zero by definition, and therefore the heat released is given by

$$-\Delta H = -(\Delta H_f(CO_2) - \Delta H_f(CO)) = 283 \text{ kJ mole}^{-1}.$$

8.3.2 Helmholtz Free Energy

I now look at a quantity of great importance in physics as it connects the microscopic and macroscopic properties of substances. Consider once more a reaction taking place at *constant volume* and let it be in *temperature equilibrium* at the start and finish. We have already seen that the heat given off is given by $-Q = -\Delta U$, but now I want to consider when such a reaction *can* take place spontaneously (that is without any intervention to make it happen).

We know that we must obey

$$\Delta S_{\text{universe}} = \Delta S_{\text{surroundings}} + \Delta S \geq 0. \tag{8.12}$$

We have to include the surroundings now because the reaction is not thermally isolated, and therefore the condition is not the plain-and-simple $\Delta S \geq 0$ that applies in the adiabatic $đQ = 0$ case.

The temperature of the surroundings does not change while heat Q transfers from it to the system, and so

$$\Delta S_{\text{surroundings}} = -\frac{Q}{T_0}. \tag{8.13}$$

(We are not including anything else that may be happening in the Universe!) We have in fact rederived Clausius's inequality since the previous two statements combine to give $Q \leq T_0\,\mathrm{d}S$, however it is less clear what is going on if one starts from this point.

Now from the First Law, $Q = \Delta U$ (no work in this case), and so we get

$$\Delta S - \frac{\Delta U}{T_0} \geq 0. \tag{8.14}$$

Now since $T = T_0$ a constant at the start and finish, we can write (multiplying through by T)

$$T\Delta S - \Delta U \geq 0. \tag{8.15}$$

or, equivalently,

$$\Delta F \leq 0, \tag{8.16}$$

where, the *Helmholtz free energy* F, is another function of state and is defined by

$$\boxed{F = U - TS}. \tag{8.17}$$

I have shown that changes (e.g. chemical reactions) at constant volume and temperature only occur spontaneously if $\Delta F \leq 0$. Equilibrium is reached therefore when F is a *minimum* at which point $\mathrm{d}F = 0$. The TS part of F is the usual entropy part that gives $\Delta S \geq 0$ for a thermally isolated system. The internal energy part enters to account for the heat transferred from the surroundings, in terms of the equivalent entropy change of the surroundings. Above all it is *entropy* which determines whether a change is possible or not, and F provides a convenient way of accounting for it.

One can see that changes are favoured either if $\Delta U < 0$ (the reaction gives off heat), or if $\Delta S > 0$ (there is an increase in entropy). In some cases both conditions are met, in others neither condition is met. Then there are the interesting in-between cases where perhaps $\Delta U > 0$ (the reaction absorbs heat) but $\Delta S > 0$. Then whether it occurs depends upon the temperature, becoming more favourable as the temperature is increased. Many such reactions occur: for instance the solution of ammonium nitrate in water is endothermic (it absorbs heat) but it goes ahead anyway because of the large increase in entropy (of the system) that results. This it must do to offset the decrease in the entropy of the surroundings that has occurred as a result of the absorption of heat.

8.3.3 Gibbs Free Energy

As usual, experimentally it is easier to operate under conditions of constant pressure rather than constant volume. All the reasoning of the previous section hold true except where we set $Q = \Delta U$, we must now set $Q = \Delta H$ as explained in section 8.3.1. Therefore rather than $F = U - TS$ as the function that determines whether changes can occur, we get

$$\Delta G \leq 0, \tag{8.18}$$

where

$$\boxed{G = H - TS = U - TS + PV}\,. \tag{8.19}$$

G is a function of state called the *Gibbs free energy*. It is named in honour of Willard Gibbs who almost single-handedly developed these ideas. Again, G is a minimum in equilibrium, when $\mathrm{d}G = 0$ for all possible changes.

The internal energy U, the enthalpy $H = U + PV$, the Helmholtz free energy $F = U - TS$ and the Gibbs free energy $G = U - TS + PV$ are collectively called the "thermodynamic potentials" because like potential energy, they are minimised in equilibrium. It is important to realise that which one is minimised depends upon the constraints. In practice F and especially G are the most useful in this respect.

8.3.4 Why "Free Energy"?

There is a very nice interpretation of F and G: the maximum amount of work that can be obtained during a change of a system of constant volume V and temperature T is $-\Delta F$, whereas it is $-\Delta G$ when T and P are constant (at the start and end of the change, not necessarily in between). It will suffice to show this for the Gibbs free energy, G. From the first law, the work we can extract from a system, $-W$ is given by

$$-W = -\mathrm{d}U + Q. \tag{8.20}$$

If the volume changes, then we lose some of this in work against the surroundings, $P_0 \Delta V$, and so can extract useful work

$$W_{\mathrm{use}} = -W - P_0\,\mathrm{d}V = -\mathrm{d}U - P_0\,\mathrm{d}V + Q. \tag{8.21}$$

Now from Clausius' inequality, $Q \leq T_0\,\mathrm{d}S$, and therefore

$$W_{\mathrm{use}} \leq -\mathrm{d}U - P_0\,\mathrm{d}V + T_0\,\mathrm{d}S. \tag{8.22}$$

Now, as usual, at the beginning and the end, $T_0 = T$ and $P_0 = P$ and therefore we can write

$$W_{\mathrm{use}} \leq -\mathrm{d}(U - TS + PV) = -\mathrm{d}G. \tag{8.23}$$

Therefore, as claimed $-\Delta G$ is the maximum amount of work that can be obtained. I will go through an example of this later in this chapter.

8.4 Natural Variables

The thermodynamic potentials have a different use, as they can provide expressions useful for manipulating the partial derivatives that abound in thermodynamics. This also provides what is probably the easiest way to remember their definitions (i.e. $F = U - TS$ etc). You first need to remember the "central equation", $T\,\mathrm{d}S = \mathrm{d}U + P\,\mathrm{d}V$, which can be written as

$$\mathrm{d}U = T\,\mathrm{d}S - P\,\mathrm{d}V. \tag{8.24}$$

We know that because of the equation of state one needs only have two independent variables. In this case the "natural" ones are S and V, i.e. $U = U(S, V)$. Now from mathematics we know that

$$\mathrm{d}U = \left(\frac{\partial U}{\partial S}\right)_V \mathrm{d}S + \left(\frac{\partial U}{\partial V}\right)_S \mathrm{d}V. \tag{8.25}$$

This applies *because U is a function of state!* Therefore comparing the expression from physics with that from maths we can write down some new relations:

$$T = \left(\frac{\partial U}{\partial S}\right)_V, \tag{8.26}$$

and

$$P = -\left(\frac{\partial U}{\partial V}\right)_S. \tag{8.27}$$

Actually, these are not especially useful since it is not immediately obvious how one takes a derivative with respect to entropy. It might have been better had it been $S\,\mathrm{d}T$ rather than $T\,\mathrm{d}S$. Consider then subtracting $\mathrm{d}(TS)$ from Eq. 8.25. Then, since

$$\mathrm{d}(TS) = T\,\mathrm{d}S + S\,\mathrm{d}T, \tag{8.28}$$

we get

$$\mathrm{d}U - \mathrm{d}(TS) = \mathrm{d}(U - TS) = -S\,\mathrm{d}T - P\,\mathrm{d}V, \tag{8.29}$$

or, recognising the Helmholtz free energy F,

$$\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V. \tag{8.30}$$

We now have a function of state on the left again, but with natural variables T and V, i.e. $F = F(T, V)$. We can then deduce, as with the expression for $\mathrm{d}U$, that

$$S = -\left(\frac{\partial F}{\partial T}\right)_V, \tag{8.31}$$

and

$$P = -\left(\frac{\partial F}{\partial V}\right)_T. \tag{8.32}$$

Now these equations *are* useful because it tuns out that F can be calculated rather directly in statistical thermodynamics. Starting with a microscopic model one can calculate an expression for F, and then having done so, calculate the pressure and entropy, and then $U = F + TS$, etc.

The subtraction of "$\mathrm{d}(TS)$" was not random: we must end up with a function of state on the left and only 2 dependent variables on the right. F then emerges naturally. We cannot for instance subtract $\mathrm{d}(PS)$ because it would not leave two terms on the right. Neither could we simply subtract $T\,\mathrm{d}S$ because then the left-hand side would not be a "perfect differential" i.e. a differential of a function because $\mathrm{d}U - T\,\mathrm{d}S \neq \mathrm{d}X$, where X is a function of state.

Having done this once, it is easy to repeat the process. For instance P and V can be swapped by adding $\mathrm{d}(PV)$. If we do this to Eq. 8.25 we get

$$\mathrm{d}H = \mathrm{d}(U + PV) = T\,\mathrm{d}S + V\,\mathrm{d}P, \tag{8.33}$$

and equivalent relations

$$T = \left(\frac{\partial H}{\partial S}\right)_P, \tag{8.34}$$

and

$$V = \left(\frac{\partial H}{\partial P}\right)_S . \tag{8.35}$$

If we now subtract $\mathrm{d}(TS)$ from $\mathrm{d}H$, we get

$$\mathrm{d}G = \mathrm{d}(H - TS) = -S\,\mathrm{d}T + V\,\mathrm{d}P, \tag{8.36}$$

and equivalent relations

$$S = -\left(\frac{\partial G}{\partial T}\right)_P , \tag{8.37}$$

and

$$V = \left(\frac{\partial G}{\partial P}\right)_T . \tag{8.38}$$

Notice how the dependent variables match those discussed earlier. For instance G applies for reactions at constant T and P, and indeed the natural variables for G are T and P.

8.5 Example of Use of Gibbs Free Energy

I finish this chapter with an example of the use of the Gibbs free energy G.

Example 8.2 The density of graphite is 2.25×10^3 kg m^{-3} while that of diamond is 3.51×10^3 kg m^{-3}. Measured at 298 K, the enthalpy of formation of graphite is 0, while that of diamond is $\Delta H_f = 1.897$ kJ mole^{-1}. The difference in entropies of diamond and graphite is

$$S_d - S_g = -3.36\,\mathrm{J\,K^{-1}\,mole^{-1}}.$$

(a) What is ΔG going from graphite to diamond at 298 K?

(b) Is diamond or graphite the stable form of carbon at 298 K and 1 atm?

(c) Assuming that graphite and diamond are incompressible, at what pressure are they in equilibrium at 298 K?

Answer 8.2 (a) Starting from $G = H - TS$, then

$$\begin{aligned}\Delta G &= G_d - G_g = H_d - H_g - T(S_d - S_g)\\ &= 1897\,\mathrm{J\,mole^{-1}} - 298\,\mathrm{K} \times (-3.36\,\mathrm{J\,K^{-1}\,mole^{-1}}) = 2898\,\mathrm{J\,mole^{-1}}.\end{aligned}$$

(b) Since $\Delta G > 0$, graphite is the stable form. Diamond can change spontaneously to graphite at 298 K since then $\Delta G < 0$, but we don't see it happen because of a large activation energy.

(c) We use the relation $\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P$ (Eq. 8.36), from which

$$\mathrm{d}(G_d - G_g) = (V_d - V_g)\,\mathrm{d}P.$$

One mole of carbon has mass 0.012 kg, so the molar specific volumes are $V_g = 0.012\,\mathrm{kg\,mole^{-1}}/2250\,\mathrm{kg\,m^{-3}} = 5.333 \times 10^{-6}\,\mathrm{m^3\,mole^{-1}}$ and $V_d = 3.419 \times 10^{-6}\,\mathrm{m^3\,mole^{-1}}$. Therefore

$$\mathrm{d}(G_d - G_g) = -1.91 \times 10^{-6}\,\mathrm{m^3\,mole^{-1}}\,\mathrm{d}P.$$

Therefore the difference in G decreases with pressure, and will reach zero when $\mathrm{d}P = 2898\,\mathrm{J\,mole^{-1}}/1.91 \times 10^{-6}\,\mathrm{m^3\,mole^{-1}} = 1.5 \times 10^9\,\mathrm{N\,m^{-2}}$, or 15,000 atmospheres. Above this pressure, diamond is the stable form of carbon at 298 K.

8.6 Summary

The thermodynamic potentials are accounting tricks: the fundamental property is always that the total entropy of the Universe increases. However, they are very convenient and you can find extensive tables for many different substances. F and G are the driving force of reactions. In this sense they are potentials. The Gibbs free energy G in particular is very useful in the study of chemical reactions and can be thought of as the driving force of chemical reactions.

9

Phase Equilibria

When ice and water or water and its vapour exist together, we refer to each different state as a *phase*. The existence of distinctly different phases for the same set of molecules is a familiar and yet marvellous phenomenon which has fascinated people for many years. I will now apply thermodynamic potentials to the equilibrium between phases. As usual, classical thermodynamics can tell you what will happen, but not why. Later on we will see that the existence of phases is a result of interatomic forces, but that will require delving down to the microscopic scale once more.

9.1 The Clausius–Clapeyron Equation

Consider two phases in equilibrium (e.g. liquid/vapour). They clearly have the same temperature T and pressure P. These are the independent variables of the *Gibbs free energy*, G. Thus it turns out that it is useful to consider a situation in which the liquid/vapour system is in temperature and pressure equilibrium with its surroundings for which we know that G is a minimum. Now consider the *specific* Gibbs free energies of the phases, i.e. G per unit mass or per mole, g_1 and g_2, with the lower-case denoting the specific quantity as opposed to its so-called *extensive* counterpart. We can write

$$G = m_1 g_1 + m_2 g_2, \tag{9.1}$$

and at equilibrium $\mathrm{d}G = 0$ so

$$\mathrm{d}G = m_1\,\mathrm{d}g_1 + m_2\,\mathrm{d}g_2 + g_1\,\mathrm{d}m_1 + g_2\,\mathrm{d}m_2. \tag{9.2}$$

However since T and P are constant, and $g = g(T, P)$, we have $\mathrm{d}g_1 = \mathrm{d}g_2 = 0$, so

$$\mathrm{d}G = g_1\,\mathrm{d}m_1 + g_2\,\mathrm{d}m_2. \tag{9.3}$$

Finally $\mathrm{d}m_1 = -\mathrm{d}m_2$, from conservation of mass, so we have

$$g_1 = g_2. \tag{9.4}$$

Thus the condition that two phases are in equilibrium is that their specific Gibbs free energies are the same. One could start from a system of constant volume for which $\mathrm{d}F = 0$, however one finds the same result, i.e. that $g_1 = g_2$, *not* that $f_1 = f_2$. This is because one cannot say that $\mathrm{d}f_1 = \mathrm{d}f_2 = 0$ because $f = f(T, V)$, and the volume V

of a given phase can change. In fact one has to impose $dV_1 + dV_2 = 0$, which brings in a PV term which gets us back to G again. The fact that T and P are constant for multi-phase systems is the reason why it is usually G that it most useful.

Now let's consider what happens if we alter T and P. Then we must have

$$\mathrm{d}g_1 = \mathrm{d}g_2, \tag{9.5}$$

in order to maintain equilibrium between the phases. But we know that

$$\mathrm{d}G = -S\,\mathrm{d}T + V\,\mathrm{d}P, \tag{9.6}$$

(Eq. 8.36) and so we have (using lower-case letters for specific quantities)

$$-s_1\,\mathrm{d}T + v_1\,\mathrm{d}P = -s_2\,\mathrm{d}T + v_2\,\mathrm{d}P, \tag{9.7}$$

where s_1, v_1, s_2, v_2 are the *specific* entropies and volumes of the two phases, i.e. per unit mass or per mole. This equation shows that, in order to maintain equilibrium between the phases, a change in temperature must be matched by a change in pressure. Therefore we can work out the rate of change of pressure with temperature which is simply

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{s_2 - s_1}{v_2 - v_1}. \tag{9.8}$$

Latent heat L converts unit mass of phase 1 to phase 2 so that

$$s_2 - s_1 = \frac{L}{T}, \tag{9.9}$$

therefore

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{L}{T(v_2 - v_1)}}. \tag{9.10}$$

This is known as the *Clausius-Clapeyron equation* and tells you how the vapour pressure of a liquid changes with temperature and how the melting point of solids and the boiling point of liquids changes with pressure. I will now show this explicitly for water.

9.1.1 Melting Point of Ice

The latent heat of fusion of ice is $L = 335 \times 10^3\,\mathrm{J\,kg^{-1}}$, while the specific volumes are $v_2 = v_W = 10^{-3}\,\mathrm{m^3\,kg^{-1}}$ and $v_1 = v_I = 1.09 \times 10^{-3}\,\mathrm{m^3\,kg^{-1}}$ for water and ice respectively (the volume per unit mass is simply the inverse of the density: ice is less dense than water and hence has a larger specific volume). Putting these figures into the Clausius-Clapeyron equation gives

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{335 \times 10^3\,\mathrm{J\,kg^{-1}}}{273\,\mathrm{K} \times (1.00 - 1.09) \times 10^{-3}\,\mathrm{m^3\,kg^{-1}}} = -13.6 \times 10^6\,\mathrm{N\,m^{-2}\,K^{-1}}. \tag{9.11}$$

This equations shows that if the external pressure increases by 134 atmospheres, the melting point of ice *drops* by 1 K. It is the fact that ice is *less* dense than water that determines the sign of the change. Most solids are denser than their equivalent liquids and their melting point increases with pressure.

The decrease of melting point with pressure for ice is thought to be important for the movement of glaciers: any obstruction to the flow of ice will cause an increase of pressure and hence melting. It is also commonly said to be of importance to skating because of the melting caused by the pressure of the skate. However, taking a contact area of 2×10^{-5} m^2 for an 80 kg skater gives a pressure of about 400 atm, which would decrease the melting point by about 3°C. This is not enough to explain melting for figure skaters who like the ice to be at −5.5°C and ice-hockey players who like it to be at −9°C. In fact, skating is possible at temperatures down to −30°C. Estimates of frictional heating also cannot explain the melting. It is nowadays thought that the surface of ice actually has a liquid or liquid-like layer on it so it is naturally very slippery.

9.1.2 Boiling Point of Water

The latent heat of evaporation of water is $L = 2.257 \times 10^6\,\mathrm{J\,kg^{-1}}$, while the specific volumes of steam and water are $v_2 = v_S = 1.673\,\mathrm{m^3\,kg^{-1}}$ and $v_1 = v_W = 1.043 \times 10^{-3}\,\mathrm{m^3\,kg^{-1}}$, so

$$\frac{\mathrm{d}P}{\mathrm{d}T} = \frac{2.257 \times 10^6}{373(1.673 - 1.043 \times 10^{-3})} = 3619\,\mathrm{N\,m^{-2}\,K^{-1}}. \qquad (9.12)$$

This shows the rate at which the vapour pressure of water increases with temperature. Alternatively, given that the boiling point is defined by the point at which the vapour pressure of a liquid equals the surrounding atmospheric pressure, this equation can tell you how the boiling point changes with pressure. For instance, on top of Everest, the pressure is ≈ 66,000 N m^{-2} lower than normal, so the boiling point of water is 66000/3619 = 18°C lower. Such a reduction significantly lengthens cooking times (the chemical processes of cooking involves activation energies and temperature-sensitive Boltzmann factors, $e^{-E_A/kT}$). This is also the principle behind pressure cookers where the increased pressure raises the cooking temperature.

9.2 Supersaturation

As a final example of phase equilibria, I consider supersaturation. This happens in several contexts, but the one I will look at is supersaturation of vapours. Consider cooling a vapour down. At some point when its pressure matches the saturated vapour pressure for the temperature in question, one expects condensation to occur. However, this is not always the case, and the vapour can carry on without condensation down to cooler temperatures, at least for a while. It is then known as supersaturated. To see why this can happen we have to look at the vapour pressure of small droplets which turns out to be higher than that of a flat liquid surface. The reason is to do with surface tension. Surface tension is a force that acts on the surfaces of liquids. One can think of the surface of a liquid as being like a stretched rubber sheet, most obvious when one sees insects walking on it. The difference is that the tension depends little upon area. Surface tension is measured in terms of a force per unit length, γ.

Now consider a spherical liquid drop of radius r. Around its equator surface tension provides a force of

$$2\pi r\gamma, \qquad (9.13)$$

holding the two halves of the drop together. Opposing this is a pressure ΔP acting over the cross-sectional area of the drop πr^2, therefore

$$\pi r^2 \Delta P = 2\pi r\gamma, \qquad (9.14)$$

and so surface tension raises the pressure inside a drop of radius r by

$$\Delta P = \frac{2\gamma}{r}. \tag{9.15}$$

This increase of pressure changes the specific Gibbs free energy of the liquid g_l, and therefore there has to be a compensating increase in vapour pressure. From the equation for dG (Eq. 8.36), at fixed temperature g_l is increased by $\Delta g_l = v_l \Delta P$, and therefore g_v must increase by the same amount so

$$\Delta g_v = v_v \Delta P_v = v_l \Delta P. \tag{9.16}$$

As a result the vapour pressure of a droplet of radius r is *larger* than that of a flat surface at the same temperature by an amount

$$\Delta P_v = \frac{v_l}{v_v}\frac{2\gamma}{r}. \tag{9.17}$$

It is this which allows vapours to be supersaturated because the saturated vapour pressure of droplets is such that they will not form until higher pressures than the normal saturated vapour pressure of a liquid surface. In fact since they have to start from a tiny radius, it is rather difficult to see how condensation happens as *easily* as it often does. The reason is thought to be the presence of condensation nuclei, such as charged particles and dust. The attractive forces of these lower g_l enough for condensation to get going. This idea was used in cloud and bubble chambers to show the tracks of charged elementary particles using the ions they produce as they travel through matter. It was also the principle of cloud seeding whereby people attempted to make rain occur by sprinkling salt crystals into clouds (experiments that were only partially successful). One can also see this in carbonated liquids such as cider and champagne: if you look carefully you will see that bubbles form only at certain sites which turn out to be either defects in the glass or dust particles. If you add sugar to fizzy drinks, you provide many nucleation sites and the bubbles emerge rapidly.

A last example of supersaturation is provided by hand warmers which contain a solution of sodium acetate in water. When sodium acetate dissolves in water, the reaction is endothermic, that is it absorbs heat. In reverse when crystallisation occurs, heat is realeased. Crystals of sodium acetate are dissolved by heating the solution. As it cools, the solution becomes supersaturated. Crystallisation starts only when a small metal disc is made to give a sharp click. Very quickly the whole solution crystallises, giving the required warmth.

9.3 Summary

In this chapter I have given just a hint of the application of Gibbs free energies to the equilibrium between phases. There are applications to the equilibrium of chemical reactions, and how it changes with pressure and temperature (of great importance in chemical engineering), as well as the mixing of liquids and the solution of salts.

10

Real Gases

I have so far exclusively used the ideal gas equation. This utterly fails to describe liquids and solids, but is not too bad for gases. Therefore one might hope that gases are the easiest type of matter to understand and should therefore be the first place to look for deviations from the ideal. The key point is the presence of interatomic forces which we have ignored up to now. I will show how a simple-minded approach leads to something called the van der Waals equation, which already contains some elements of the behaviour of real matter. In particular it offers some insight into the phenomenon of phases.

10.1 Interatomic Forces

Real atoms exert forces on each other. When very close they repel, as they must to keep the atoms separate, whereas at large distances the forces become weakly attractive. The repulsion can be viewed in terms of the electrostatic repulsion of the nuclei in combination with the Pauli exclusion principle which tends to counteract the possibility of the electrons gathering in between the nuclei and binding them together, except of course in chemical bonds. A classical picture for the long-range attraction is that fluctuations in the electron distribution give a dipole moment to an atom which induces a similar dipole moment in another atom and the two are attracted, rather as bits of dust can be attracted by an electrostatically-charged comb. The interaction between atoms can be represented by the potential energy $\phi(r)$ between atoms separated by distance r. The force f between atoms is related to the potential energy by $f = -\mathrm{d}\phi/\mathrm{d}r$ and $f > 0$ is repulsive, so the negative gradient at

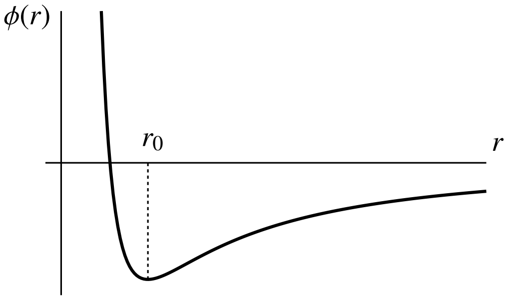

Figure 10.1 A schematic figure of the potential energy between two atoms as a function of distance between them. r_0 denotes the equilibrium separation.

short distance corresponds to repulsion. The form of the potential can be measured directly from experiments with atomic beams.

I will now show how interatomic forces can be taken into acount in an approximate manner.

10.2 The van der Waals Equation

The van der Waals equation is a modification of the ideal gas equation of state for the effects of interatomic forces. It is itself *approximate*. The effect of the short-range repulsive force shows up as an effective reduction in available volume, while the attractive part acts to reduce the pressure. Consider then N molecules in a volume V. Each molecule wipes out a small volume as far as the others are concerned. If we call this volume b, then we need to replace the normal volume by $V - Nb$. One estimate of b comes from considering the zone around a molecule in which no other centres of molecules can lie. For spherical molecules of radius r this is a sphere of radius $2r$, and volume $4\pi(2r)^3/3$. Correcting by a factor of two to avoid double counting (we are counting *pairs* of molecules and want to consider each pair only once), we find $b = 4v_m$ where v_m is the volume of one molecule. With the correction to the volume, the ideal gas equation (Eq. 1.10) is modified to

$$P(V - Nb) = NkT. \tag{10.1}$$

The reduced volume accounts for the short-range repulsion and increases the pressure for a given V. The attractive forces on the other hand act to reduce the pressure. Imagine a molecule hitting the wall of its container. It feels a general attractive force towards the rest of the molecules which will reduce its speed as it approaches the wall. Any forces exerted by atoms in the wall are irrelevant because if they attract for example, then while approaching atoms are accelerated towards the wall, an equal but opposite force is felt by the wall which is cancelled on average by the collision of the speeded-up atoms. The correction to P can be deduced as follows: the correction is proportional to the collision rate per unit area which is $\propto (N/V)$. The force decelerating each molecule will also depend upon the density of molecules, N/V, and thus we end with a correction factor of the form $(N/V)^2 a$ where a is a constant. This then leads to an equation of the form

$$\boxed{\left(P + N^2 \frac{a}{V^2}\right)(V - Nb) = NkT}. \tag{10.2}$$

This is the *van der Waals* equation. The constants a and b are the van der Waal's coefficients. The coefficient a depends upon the long-range attractive forces, while b depends upon the short-range repulsive forces which define the “size” of an atom. Very often rather than the number of molecules N, the number of moles n_m is used instead, which simply implies a re-scaling of a and b. The equation then looks like

$$\left(P + n_m^2 \frac{a}{V^2}\right)(V - n_m b) = n_m RT. \tag{10.3}$$

A slightly more sophisticated derivation goes as follows. The idea is to derive an expression for the Helmholtz free energy $F = U - TS$. We first correct U for the attractive forces. The potential of a molecule due to other molecules in a small volume $\mathrm{d}V$ at distance r is

$$\mathrm{d}u = \phi(r) n(r)\,\mathrm{d}V, \tag{10.4}$$

and assuming that the number density n is constant, except for $r < D$, the diameter of the molecules where $n = 0$, then

$$u = n \int_D^\infty \phi(r)\,\mathrm{d}V = -2an, \tag{10.5}$$

where the integral is set to $-2a$, a choice that will lead to the same expression in the end. Note that since the potential is negative at large r, the coeffcient a is positive. Therefore the total change in U is then

$$\Delta U = \frac{N}{2}(-2an) = -\frac{N^2 a}{V}, \tag{10.6}$$

where the factor of 2 prevents double counting of the the effect of each molecule. Therefore the total internal energy is given by

$$U = \frac{3}{2}NkT - \frac{N^2 a}{V}, \tag{10.7}$$

while the entropy is

$$\begin{aligned} S &= S_0 + n_m C_V \ln T + n_m R \ln(V - Nb), & (10.8)\\ &= S_0 + \frac{3}{2}Nk \ln T + Nk \ln(V - Nb), & (10.9) \end{aligned}$$

assuming a monatomic $C_V = 3R/2$. Therefore

$$\begin{aligned} F &= U - TS, & (10.10)\\ &= \frac{3}{2}NkT - \frac{N^2 a}{V} - \frac{3}{2}NkT \ln T + NkT \ln(V - Nb) - TS_0. & (10.11) \end{aligned}$$

Finally we deduce the pressure from

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{N^2 a}{V^2} + \frac{NkT}{V - Nb}, \tag{10.12}$$

which on re-arranging gives the van der Waals equation once more:

$$\left(P + \left(\frac{N}{V}\right)^2 a\right)(V - Nb) = NkT. \tag{10.13}$$

This approach is called a *mean field* theory. Although it is more complex than the argument in terms of forces, it is easier to generalise. Moreover, it is more obvious where it fails. For instance it is not the case that the number density is constant as a function of distance from a molecule. (The behaviour of number density with distance is a key way to describe the difference between gases, liquids and solids in fact.)

10.2.1 P–V Diagrams of a van der Waals Gas

Now let's see how the van der Waals equation differs from the ideal gas case. Put into simplest form for one mole, the van der Waals equation becomes

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT. \tag{10.14}$$

Note that as $V \to \infty$, this tends towards the ideal gas equation as expected. Fig. 10.2 shows a plot of isotherms of a van der Waals gas (curves of P versus V for a set

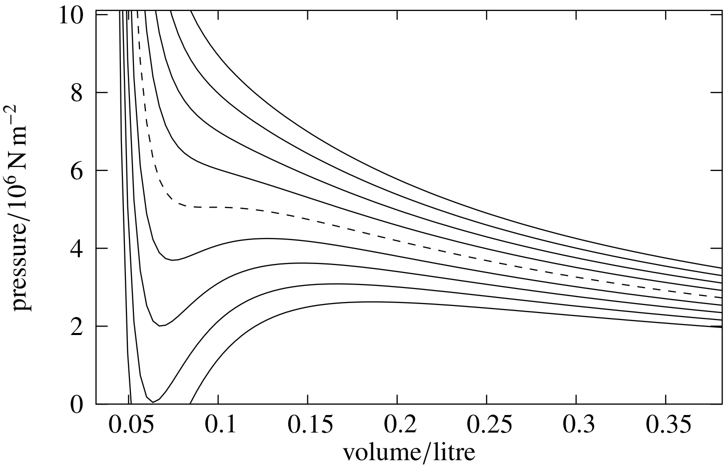

Figure 10.2 Isotherms of a van der Waals gas. The plot uses values $a = 0.138\,\mathrm{N\,m^4}$ and $b = 3.18 \times 10^{-5}\,\mathrm{m^3}$, appropriate for one mole of oxygen gas (O_2). The critical isotherm is drawn dashed, corresponding to a temperature of 155 K. The other isotherms are drawn in steps of 8 K for the temperature.

of constant temperatures). At small volumes these are very steep because of the b term, while at large volumes they tend to the ideal gas case. In between, some rather unexpected behaviour occurs with a kink developing and even negative pressures. The latter may seem impossible, but liquids are in fact able to support a certain level of negative pressure. In other words they can be in tension rather than compression. Still, although the van der Waals isotherms are somewhat closer to the behaviour of real gases than the ideal gas ones, the region of the kink is where the grossest deviations are seen and the behaviour of the van der Waals gas is in fact physically impossible in this region. To see why, consider the isotherm shown in Fig. 10.3. In the region BCD the pressure *increases* with increasing volume. This is unstable. Consider the two halves of a box filled by such a fluid. The slightest perturbation, which say caused the left-half to compress while the right-half expanded, would run away because as the left-half compressed its pressure would drop while the pressure in the right-half increased, so driving the process further still. Eventually once points B and D have been passed the normal P, V behaviour would return and eventually we would expect equilibrium to be reached with two fluids, one dense and one light, that is a liquid and a gas! These are marked at A and E in Fig. 10.3.

What can we say about A and E? They must have the same temperature and pressure, which means they lie on the intersection of a horizontal line with the isotherm. We also have $g_\mathrm{A} = g_\mathrm{E}$, the usual condition for phase equilibrium. Since

$$\mathrm{d}g = -s\,\mathrm{d}T + v\,\mathrm{d}P, \tag{10.15}$$

if we integrate along the isotherm (for which $\mathrm{d}T = 0$) from A to E, we must have

$$g_\mathrm{E} = g_\mathrm{A} + \int_\mathrm{A}^\mathrm{E} v\,\mathrm{d}P, \tag{10.16}$$

and so

$$\int_\mathrm{A}^\mathrm{E} v\,\mathrm{d}P = 0. \tag{10.17}$$

For this reason I have drawn A and E at a pressure for which the shaded areas ABC and CDE are equal. This construction (usually known as the *Maxwell construction*) can be used to define the region where the liquid gas/separation is expected to occur.

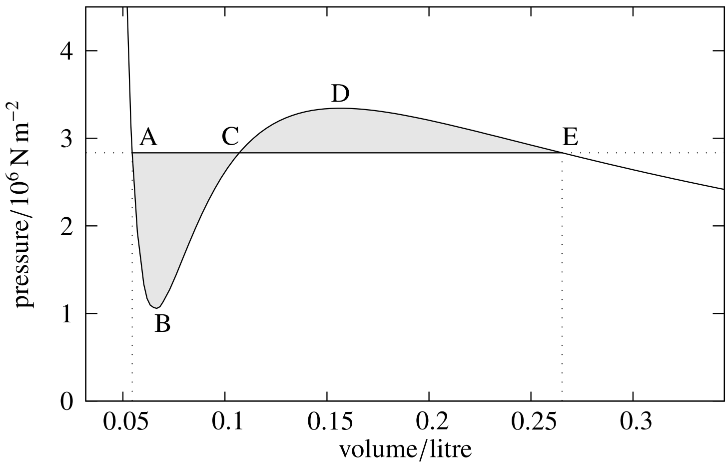

Figure 10.3 Isotherm of a van der Waals gas. The plot shows the $T = 135$ K isotherm for one mole of oxygen (O_2) with $a = 0.138$ N m^4 and $b = 3.18 \times 10^{-5}$ m^3. The equal-areas construction gives $P_A = P_E = 2.83 \times 10^6$ Pa, with $V_A = 0.055$ litre and $V_E = 0.265$ litre.

Referring to Fig. 10.2, we see that as the temperature rises (upper isotherms) there comes a point when there is no longer any kink. The critical isotherm is marked by a dashed line. At this point there will only be a single phase, and there will be no distinction between a liquid and a gas. This is known as the *critical point* and is a phenomenon observed in substances. This means there is a certain temperature above which no matter the pressure you will not see the formation of a separate liquid phase. At the critical point, which has a unique temperature and pressure, the gradient of pressure with respect to volume at constant temperature tends to zero, i.e.

$$\left(\frac{\partial P}{\partial V}\right)_T \to 0. \tag{10.18}$$

This means that huge density fluctuations occur and that one can see significant density gradients develop due to gravity even in a small container. The density fluctuations scatter light and the gas becomes milky white, a phenomenon known as *critical opalescence*.

The van der Waals equation provides a first understanding of the phenomenon of phases, but it is very crude. The surprise is that it works as well as it does.

10.3 Phase Diagrams

It is useful to represent phase equilibria on pressure–temperature, or P–T diagrams. This is because these are the natural variables for G and because we know that T and P are the same for all phases in equilibrium with one another (give or take surface tension effects in special cases). Fig. 10.4 shows the typical case. The lines indicate the values of pressure and temperature for which the various phases are in equilibrium. For solid–liquid equilibrium (the melting line), $g_s = g_l$, and one degree of freedom is lost. This implies that equilibrium is a line in a P–T diagram as shown. Similarly for the liquid–vapour (vaporisation) and the solid–vapour (sublimation) equilibria.

When all three phases are in equilibrium then $g_s = g_l = g_v$ which means there are no degrees of freedom. This also means that all three lines must meet at this point, which we have seen before as the triple point. The restriction on the specific

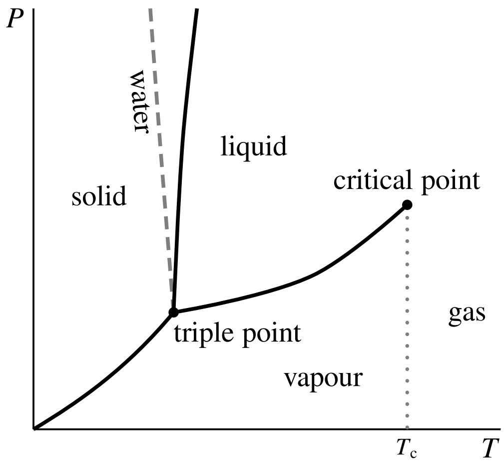

Figure 10.4 Phase diagram of a typical substance. The negative sloped dashed line shows the ice/water equilibrium which is unusual in this respect.

Gibbs free energies means that the triple point occurs at a unique temperature and pressure, which is why it makes a good temperature reference.

The key features of phase diagrams are:

- The slopes of the lines come from the Clausius-Clapeyron equation:

$$\frac{dP}{dT} = \frac{L}{T(v_2 - v_1)}.$$

  The water/ice slope is negative: can "squeeze" ice into water (Fig. 10.4).

- The liquid/vapour line *stops* at the *critical point*: there is no continuation. There is no equivalent point for the solid/liquid line; solids and liquids appear to be intrinsically different and there is no way to make a smooth transition between them.
- The solid/vapour transition is called *sublimation*; iodine gives a nice example of this, subliming as a purple gas when heated in its solid form.
- The three lines meet at the triple point.

10.3.1 P–V–T Surfaces

By adding a third axis, volume, to a P–T phase diagram we end up with a P-V-T surface. This is combining the phase diagram with a P–V indicator diagram. A simplified version of the P-V–T surface for water is shown in Fig. 10.5 on the next page.

10.4 Summary

The point of this chapter is that while classical thermodynamics can explain some of the features of phase diagrams, to understand the existence of phases we need to delve down to the microscopic level with the inclusion of interactions amongst atoms and molecules. The van der Waals equations shows how even the simplest inclusion of the effects of interactions introduces features that can be identified with phase changes. Nowadays computer models of great sophistication are run in an

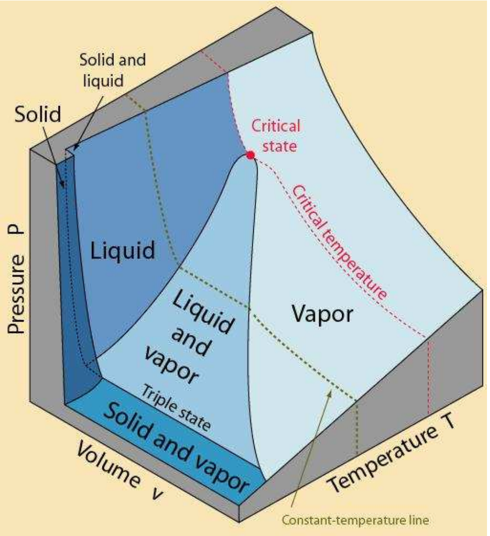

Figure 10.5 P–V–T surface for water. Image from http://hyperphysics.phy-astr.gsu.edu (Georgia State University, USA)

effort to explain the properties of matter. Liquids in particular remain a challenge. The van der Waals equation is one of several approximations to the behaviour of real gases, and makes the point that real gases are not ideal! The physics of phase changes has fascinated many of the greatest physicists and continues to be an area of great activity today.

A

Appendix

The material in this Appendix is *not examinable*.

A.1 Carathéodory's derivation of Entropy

The key consequence of the Second Law is the existence of the new function of state, entropy. However its derivation via heat engines seems convoluted and once it has been accomplished, heat engines hardly come into it. A different approach was developed by the Greek mathematician, Carathéodory. It is a more abstract method, and still not widely known, which is why I have adopted the traditional approach, which is still perfectly valid, and something that every physicist should have encountered. However, the more mathematical may prefer Carathéodory's approach which I outline in this appendix; elements of this approach may give everyone more insight into entropy, particularly the initial proof from the Second Law that there is a function of state that is constant on reversible adiabatics.

I first summarise the steps involved. I will begin by using the Second Law to establish the existence of a function of state which is constant on reversible adiabatics, which I call σ. From this one can show that $đQ_R = \lambda\,\mathrm{d}\sigma$, where $đQ_R$ is the amount of heat added to a system during a reversible change, and λ is another function of state. Next, one shows that λ is of the form $T(\theta)f(\sigma)$, where θ is the empirical temperature and T is a universal function of θ, i.e. the same function for every system. Identifying $\mathrm{d}S = f(\sigma)\,\mathrm{d}\sigma$, and calling the function T the thermodynamic temperature, one finally has $đQ_R = T\,dS$, as derived from heat engines.

A.1.1 Reversible Adiabatics

Fig. A.1 shows the track of a reversible adiabatic through a point A in a plot of internal energy U versus volume V (solid line). I will now show that there is only one such reversible adiabatic through any point. To see this, let the dashed line A to B be a hypothetical second adiabatic through A in addition to the one running from A to C. If this is the case, then starting from B, we can move to A and then to C along adiabatics. In the process $\Delta U < 0$, but since the change is adiabatic, $Q = 0$, so $W = \Delta U < 0$. Since W is the work done *on* the system, we have extracted work *from* the system. From point C we can return to B simply by adding heat $Q = -\Delta U$. We have then managed to return the system to its original state, and in the process we have converted heat completely into work. But this is impossible by the Kelvin-Planck statement of the second law, from which we deduce that the hypothetical

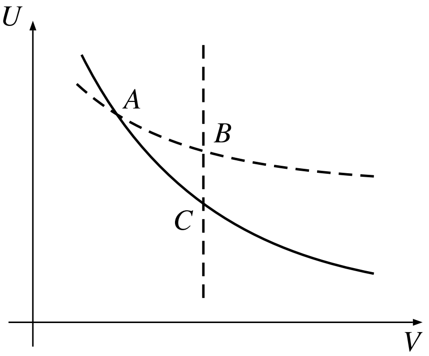

Figure A.1 The solid line represents the path of an adiabatic on a plot of internal energy U against the volume V. The dashed line shows a hypothetical adiabatic through point A

second adiabatic is impossible. This argument applies equally to the case of several state variables, e.g. magnetisation as well as volume (in which case the adiabatic becomes a surface rather than a line, but the same arguments apply).

This means that every state of the system can be uniquely labelled by the reversible adiabatic that it lies upon. There is therefore some function of state which is constant along reversible adiabatics. Let this be called σ, the empirical entropy. Since σ is a function of state, we can write $U = U(\sigma, V)$, and therefore

$$\mathrm{d}U = \left(\frac{\partial U}{\partial \sigma}\right)_V \mathrm{d}\sigma + \left(\frac{\partial U}{\partial V}\right)_\sigma \mathrm{d}V, \tag{A.1}$$

Now when $\mathrm{d}\sigma = 0$, then by the definition of σ, the change is adiabatic and reversible, so $Q = 0$ and

$$\mathrm{d}U = đW_R = \left(\frac{\partial U}{\partial V}\right)_\sigma \mathrm{d}V, \tag{A.2}$$

and so substituting back in Eq. A.1, and writing

$$\lambda = \left(\frac{\partial U}{\partial \sigma}\right)_V, \tag{A.3}$$

for short, we have

$$\mathrm{d}U = \lambda\,\mathrm{d}\sigma + đW_R. \tag{A.4}$$

Therefore comparing with the first law, $\mathrm{d}U = đQ + đW$, we have

$$đQ_R = \lambda\,\mathrm{d}\sigma. \tag{A.5}$$

That is, amount of heat added in a reversible change equals a function of state, λ, times the change in the empirical entropy (λ is a function of state because any derivative of a function of state is also a function of state).

A.1.2 Thermodynamic Temperature

Now consider two systems, A and B, in thermal equilibrium with each other, and consider adding heat reversibly to each. If we add $đQ_A$ and $đQ_B$, then considering the two systems as a single large system, we have added

$$đQ = đQ_A + đQ_B, \tag{A.6}$$

to the combined system. Each of these terms obeys a relation of the form $đQ = \lambda\,\mathrm{d}\sigma$ so that

$$\lambda\,\mathrm{d}\sigma = \lambda_A\,\mathrm{d}\sigma_A + \lambda_B\,\mathrm{d}\sigma_B, \tag{A.7}$$

and so

$$\mathrm{d}\sigma = \frac{\lambda_A}{\lambda}\,\mathrm{d}\sigma_A + \frac{\lambda_B}{\lambda}\,\mathrm{d}\sigma_B. \tag{A.8}$$

But σ is a function of state so we can write $\sigma = \sigma(\sigma_A, \sigma_B)$. Now we look at the λ ratios which must also be functions of σ_A and σ_B. In general we can write

$$\begin{aligned}
\lambda_A &= \lambda_A(\theta, \sigma_A, X_1, X_2, \ldots), && \text{(A.9)}\\
\lambda_B &= \lambda_B(\theta, \sigma_B, Y_1, Y_2, \ldots), && \text{(A.10)}\\
\lambda &= \lambda(\theta, \sigma_A, \sigma_B, X_1, X_2, \ldots, Y_1, Y_2, \ldots), && \text{(A.11)}
\end{aligned}$$

where X_1, X_2 etc are whatever state variables are needed to define the state of system A, Y_1 etc define the state of system B, and θ is the common empirical temperature (the systems are in thermal equilibrium). However we have shown that the ratio λ_A/λ is a function of σ_A and σ_B only. Therefore λ cannot in fact depend upon Y_1, Y_2 etc because these do not enter into λ_A. Similarly we can use the other ratio to show that λ cannot depend upon X_1 etc, and therefore λ_A cannot depend upon X_1, X_2, etc, and λ_B cannot depend upon the Y values. Therefore the ratio λ_A/λ can be written

$$\frac{\lambda_A}{\lambda} = \frac{\lambda_A(\theta, \sigma_A)}{\lambda(\theta, \sigma_A, \sigma_B)}. \tag{A.12}$$

Again, we know that this ratio depends upon σ_A and σ_B only, so the dependence on the empirical temperature must factorise. We can therefore write

$$\begin{aligned}
\lambda_A &= T(\theta) f_A(\sigma_A), && \text{(A.13)}\\
\lambda_B &= T(\theta) f_B(\sigma_B), && \text{(A.14)}\\
& && \text{(A.15)}
\end{aligned}$$

where f_A and f_B are functions, which can be different for each system, but $T(\theta)$ is a *universal* function of temperature. “Universal” means it is the same for every system (at least subject to a constant multiplying factor which can be swept into the function f). If it was not, the dependence of θ would not drop out of the ratio.

We have now therefore learnt that

$$đQ_R = T(\theta) f(\sigma)\,\mathrm{d}\sigma. \tag{A.16}$$

Now defining two new functions, the entropy S such that $\mathrm{d}S = f(\sigma)\,\mathrm{d}\sigma$, and the “thermodynamic temperature” as T, we have

$$\boxed{đQ_R = T\,\mathrm{d}S}\,. \tag{A.17}$$

Thus a key result from the heat engine approach can be derived without recourse to heat engines. It is however a somewhat abstract approach, which is why I only include it for reference; it is not an examinable part of the course.

A.2 Maxwell Relations

Anyone giving a course on thermodynamics has to make a decision at some point: do I teach the Maxwell relations? These are the subject of innumerable rather tricky exam questions where it is quite easy to end up proving that $0 = 0$, resulting in blind panic. They offer no special new physical insight and therefore I have elected to make them *non-examinable*. Having said that, no-one can say that he or she has "done" thermodynamics, or even call her- or himself a physicist without having seen some Maxwell relations at least once, and seen a little of why they are useful.

Consider again the relation, equation 8.36, from section 8.4 on page 73,

$$dG = -S\,dT + V\,dP, \tag{A.18}$$

and the consequent identities,

$$S = -\left(\frac{\partial G}{\partial T}\right)_P, \tag{A.19}$$

and

$$V = \left(\frac{\partial G}{\partial P}\right)_T. \tag{A.20}$$

Now for *any* function $f(x, y)$, it is the case that

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}. \tag{A.21}$$

It is therefore the case that

$$\left.\frac{\partial}{\partial P}\right)_T \left(\frac{\partial G}{\partial T}\right)_P = \left.\frac{\partial}{\partial T}\right)_P \left(\frac{\partial G}{\partial P}\right)_T, \tag{A.22}$$

and therefore, that

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P. \tag{A.23}$$

This is a "Maxwell relation".What it does for us is convert a rather nasty quantity on the left hand side, to one that is easily measured on the right, since $(\partial V/\partial T)_P$ depends directly upon the expansivity of a substance.

There are equivalent Maxwell relations for the expressions for dU, dF and dH. If you get the hang of it, they are easy to derive; please *do not* try to remember them by rote. Although there are ways of trying to do so, I consider them to be an utter waste of brain power. In any case, as I said above, they are not examinable in this course.

I finish my discussion of them, with a classic illustration of their use, which will probably give you an idea of why I am not going to ask any questions on them. Still, read it through as it is good for your soul. Consider the heat capacity at constant volume, C_V. Since $đQ = T\,dS$ for reversible heat transfer, we can write

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V. \tag{A.24}$$

Similarly

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P. \tag{A.25}$$

We know that C_V is directly related to the internal energy via

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V, \tag{A.26}$$

so that by measuring it at a series of temperatures one could integrate to get U. Unfortunately, it is much easier to measure the heat capacity at constant *pressure* (imagine trying to keep the volume of a block of copper constant as you heated it).

Therefore it is useful to find a means of getting from C_P to C_V using other easily-measured quantities. We already saw the simple $C_P = C_V + R$ for one mole of ideal gas, but now we want a more general relation.

If we take $S = S(T, V)$, then

$$\mathrm{d}S = \left(\frac{\partial S}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial S}{\partial V}\right)_T \mathrm{d}V, \tag{A.27}$$

so that

$$\begin{aligned} C_P &= T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P, \\ &= C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P. \end{aligned}$$

The second of the two derivatives is measurable because the volume expansivity β, which is the fractional rate of increase in volume with temperature at constant pressure can be written as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P. \tag{A.28}$$

The first derivative is less obvious; we need to employ a Maxwell relation. Looking at the quantities on the bottom, we need a relation in which the independent variables are V and T. This is the one for $\mathrm{d}F$:

$$\mathrm{d}F = -S\,\mathrm{d}T - P\,\mathrm{d}V. \tag{A.29}$$

Going through the same process as before, we can immediately write the Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \tag{A.30}$$

so therefore we have

$$C_P = C_V + VT\beta\left(\frac{\partial P}{\partial T}\right)_V. \tag{A.31}$$

The new derivative is the rate at which pressure increases with temperature at constant volume. Hmmm, still not very easy: just how do you keep the volume of a solid constant? Instead, let's see if we can't re-express the new derivative as something simpler, but we won't use a Maxwell relation or we will end up where we started. We know from the equation of state that $P = P(T, V)$, so

$$\mathrm{d}P = \left(\frac{\partial P}{\partial T}\right)_V \mathrm{d}T + \left(\frac{\partial P}{\partial V}\right)_T \mathrm{d}V, \tag{A.32}$$

therefore on taking the derivative with respect to temperature at constant pressure, we get

$$0 = \left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P, \tag{A.33}$$

so

$$\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -V\beta\left(\frac{\partial P}{\partial V}\right)_T. \tag{A.34}$$

This is an example of something called the "cyclical rule"; like the Maxwell relations it is mathematical rather than physical. Therefore

$$C_P = C_V - V^2T\beta^2\left(\frac{\partial P}{\partial V}\right)_T. \tag{A.35}$$

The final derivative now *is* experimentally accessible because we can write

$$\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{(\partial V/\partial P)_T}, \tag{A.36}$$

(the usual rule for inverting derivatives), and the quantity on the bottom is related to the compressibility κ where

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T, \tag{A.37}$$

being the fractional decrease in volume as pressure is raised at constant temperature. Therefore, finally we have

$$C_P = C_V + \frac{VT\beta^2}{\kappa}. \tag{A.38}$$

This is the desired connection between the two heat capacities and other measurable quantities.

B

Constants and Numerical Data

Boltzmann's constant	k	=	$1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
Gas constant	R	=	$8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}$
Avogadro's number	N_A	=	$6.02 \times 10^{23}\,\mathrm{mol^{-1}}$
Atomic mass unit	u	=	$1.661 \times 10^{-27}\,\mathrm{kg}$
Water triple-point temperature	T_TP	=	$273.16\,\mathrm{K}$
Standard temperature and pressure (STP)			
temperature	T_stp	=	$273.15\,\mathrm{K}$
pressure	P_stp	=	$1.01 \times 10^5\,\mathrm{Pa} = 1\,\mathrm{atm}$
Density of air at STP	$\rho_\mathrm{air,STP}$	=	$1.293\,\mathrm{kg\,m^{-3}}$
Heat of fusion of H_2O (0°C, 1 atm)	L_fus	=	$333.5\,\mathrm{kJ\,kg^{-1}}$
Heat of vaporisation of H_2O (100°C, 1 atm)	L_vap	=	$2.257\,\mathrm{MJ\,kg^{-1}}$