

5 Hot Physics

This section gives an introduction to the areas of physics known as thermodynamics and statistical mechanics. These deal with the questions “What happens when things heat up or cool down?” and “Why?” respectively.

We start with a statement that will be very familiar – but then find that it leads us into new territory when explored further.

5.1 *The Conservation of Energy*

You will be used to the idea that energy can neither be used up nor created – only transferred from one object to another, perhaps in different forms.

For our purposes, this is stated mathematically as

$$dQ + dW = dU, \quad (1)$$

where ‘dX’ refers to ‘a small change in X’. Put into words, this states: “Heat entering object + Work done on the object = the change in its internal energy.” Internal energy means any form of stored energy in the object. Usually this will mean the heat it has, and will be measured by temperature. However if magnetic or electric fields are involved, U can also refer to electrical or magnetic potential energy.

Given that the conservation of energy must be the starting point for a study of heat, it is called the First Law of Thermodynamics.

Equation (1) can be applied to any object or substance. The most straightforward material to think about is a perfect gas, and so we shall start there. It is possible to generalize our observations to other materials afterwards.

Imagine some gas in a cylinder with a piston of cross-sectional area A. The gas will have a volume V, and a pressure p. Let us now do some work on the gas by pushing the piston in by a small distance dL. The force required to push the piston $F = p A$, and so the work done on the gas is $dW = F dL = p A dL$. Notice that AdL is also the amount by which the volume of the gas has been decreased. If dV represents the change in volume, $dV = -A dL$. Therefore $dW = -p dV$.

For a perfect gas in a cylinder (or in fact in any other situation), the First Law can be written a bit differently as:

$$dQ = dU + p dV \quad (2)$$

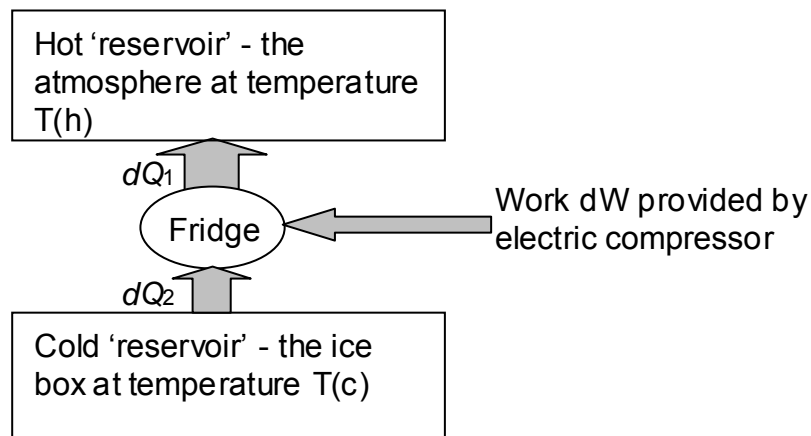
5.2 The Second Law

While the First Law is useful, there are certain things it can never tell us. For example – think about an ice cube sitting on a dish in an oven. We know what happens next – the ice cube melts as heat flows from oven to ice, warming it up until it reaches melting point. However the First Law doesn't tell us that. As far as it is concerned it is just as possible for heat to flow from the ice to the oven, cooling the ice and heating the oven.

We stumbled across our next law – called the second law of thermodynamics. This can be stated in several ways, but we shall start with this: **Heat will never flow from a cold object to a hotter object by itself.**

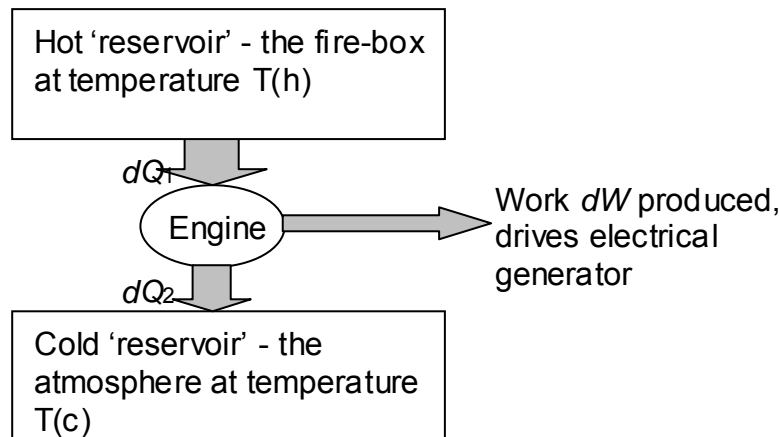
This helps us with the ice in the oven, but you may be wondering what the significance of the “by itself” is. Actually heat *can* be transferred from a cold object to a hotter one – that is what fridges and air conditioning units do. However they can only do it because they are plugged into the electricity supply. If you are prepared to do some work – then you can get heat out of a cold object and into a hotter one, but as soon as you turn the power off and leave it to its own devices, the heat will start flowing the other way again.

5.3 Heat Engines and Fridges



The fridge is shown diagrammatically above. It is a device which uses work dW (usually provided by an electric compressor) to extract heat dQ_2 from the ice-box (cooling it down), and pump it out into the surroundings (warming them up). However, by the conservation of energy, the amount of energy pumped out dQ_1 is bigger than the amount of energy removed from the ice-box. By convention $dQ_2 > 0$, and $dQ_1 < 0$, since heat flowing in is regarded as positive. The First Law therefore states that $dQ_1 + dQ_2 + dW = 0$.

The fridge is a device that uses work to move heat from cold objects to hot. The opposite of a fridge is a heat engine. This allows heat to flow its preferred way – namely from hot to cold – but arranges it to do some work on the way. Petrol engines, steam engines, turbo-generators and jet engines are all examples of heat engines.



It was Carnot who realised that the most efficient heat engine of all was a 'reversible' heat engine. In other words – one that got the same amount of work out of the heat transfer as would be needed to operate a perfect fridge to undo its operation.

In order to do this, it is necessary for all the heat transfers (between one object and another) to take place with as small a temperature difference as possible. If this is not done, heat will flow from hot objects to cold – a process which could have been used to do work, but wasn't. Therefore not enough work will be done to enable the fridge to return the heat to the hot object.

Carnot therefore proposed that the ratio of heat coming in from the hot object to the heat going out into the cold object has a maximum for this most-efficient engine. This is because the difference between heat in and heat out is the work done, and we want to do as much work as possible. Furthermore, he said that this ratio must be a function of the temperatures of the hot and cold objects only.

This can be stated as

$$\left| \frac{dQ_1}{dQ_2} \right| = f(T_1, T_2) \quad (3)$$

where T_1 is the temperature of the hot object, and T_2 is that of the cold object. More light can be shed on the problem if we stack two heat engines in series, with the second taking the heat dQ_2 from the first (at

temperature T_2), extracting further work from it before dumping it as heat (dQ_3) into a yet colder object at temperature T_3 .

The two heat engines separately and together give us the equations:

$$\begin{aligned} \left| \frac{dQ_1}{dQ_2} \right| &= f(T_1, T_2) & \left| \frac{dQ_2}{dQ_3} \right| &= f(T_2, T_3) & \left| \frac{dQ_1}{dQ_3} \right| &= f(T_1, T_3) \\ \Rightarrow f(T_1, T_3) &= f(T_1, T_2) \times f(T_2, T_3) & & & & (4) \\ \Rightarrow f(T_1, T_2) &= \frac{g(T_1)}{g(T_2)} \end{aligned}$$

5.3.1 Thermodynamic Temperature

However if $g(T)$ is a function of the temperature alone, we might as well call $g(T)$ the temperature itself. This is the thermodynamic definition of temperature.

To summarize: Thermodynamic temperature (T) is defined so that in a reversible heat engine, the ratio of heat extracted from the hot object (Q_1) to the heat ejected into the cold object (Q_2):

$$\left| \frac{Q_1}{Q_2} \right| = \frac{T_1}{T_2} \quad (5)$$

The 'kelvin' temperature scale obtained using the gas laws satisfies this definition. For this reason, the kelvin is frequently referred to as the unit of 'thermodynamic temperature'.

5.3.2 Efficiency of a Heat Engine

The efficiency of a reversible heat engine can then be calculated. We define the efficiency (η) to be the ratio of the work done (the useful output) to Q_1 (the total energy input). Therefore

$$\eta = \left| \frac{dW}{dQ_1} \right| = \frac{dQ_1 - |dQ_2|}{dQ_1} = 1 - \frac{T_2}{T_1}. \quad (6)$$

This, being the efficiency of a reversible engine, is the maximum efficiency that can be achieved. A real engine will fall short of this goal. Notice that for a coal-fired power station, in which T_1 (the temperature of the boiler) is frequently 840K, and T_2 (the temperature of the stream outside) is 300K; the maximum possible efficiency is

$$\eta = 1 - \frac{300}{840} = 64\% .$$

In practice the water leaves the turbo generator at 530K, and so the efficiency can't go any higher than

$$\eta = 1 - \frac{530}{840} = 37\% .$$

The design of modern large power stations is such that the actual efficiency is remarkably close to this value.

5.4 Entropy

Now we need to take a step backwards before we can go forwards. Look back at the definition of thermodynamic temperature in equation (5). It can be rearranged to state

$$\frac{dQ_1}{T_1} = \frac{|dQ_2|}{T_2} \Rightarrow \frac{dQ_1}{T_1} + \frac{dQ_2}{T_2} = 0 \quad \text{REVERSIBLE.} \quad (7)$$

Remember that this is for the ideal situation of a reversible process – as in a perfect fridge or heat engine. Suppose, then, that we start with some gas at pressure p and volume V . Then we do something with it (squeeze it, heat it, let it expand, or anything reversible), and finally do some more things to it to bring it back to pressure p and volume V . The list of processes can be broken up into tiny stages, each of which saw some heat (dQ) entering or leaving the system, which was at a particular temperature T . The only difference between this situation, and that in (7) is that there were only two stages in the process for the simpler case. The physics of (7) should still apply, no matter how many processes are involved. Therefore providing all the actions are reversible we can write

$$\sum_{\text{complete cycle}} \frac{dQ}{T} = 0 \Rightarrow \oint \frac{dQ}{T} = 0 \quad \text{REVERSIBLE} \quad (8)$$

where the circle on the integral implies that the final position (on a p,V graph) is the same as where the gas started.

Now suppose that there are two points on the (p,V) graph which are of interest to us, and we call them A and B. Let us go from A to B and then back again (using a different route), but only using reversible processes. We call the first route I, and the second route II. Equation (8) tells us

$$\oint \frac{dQ}{T} = \int_A^B \frac{dQ_I}{T} + \int_B^A \frac{dQ_{II}}{T} = 0$$

$$\int_A^B \frac{dQ_I}{T} - \int_A^B \frac{dQ_{II}}{T} = 0 \quad \text{REVERSIBLE} \quad (9)$$

$$\int_A^B \frac{dQ_I}{T} = \int_A^B \frac{dQ_{II}}{T}$$

In other words the integral of dQ/T between the two points A and B is the same, no matter which reversible route is chosen. This is a very special property of a function – we label dQ/T as a function of state, and call it the entropy (S).

This means that the current entropy of the gas, like pressure, volume and temperature, is only a function of the state that the gas is in now – and does not depend on the preparation method.

5.5 Irreversible Processes and the Second Law

We must stress that entropy is only given by $\int dQ/T$ when the integral is taken along reversible processes in which there is no wastage of heat. Heat is wasted when it is allowed to flow from a hot object to a cold one without doing any work on the journey. This would be irreversible, since you could only get the heat back into the hot object if you expended more energy on it.

Let us make an analogy. Reversible processes are like a world in which purchasing prices and selling prices are the same. If you started with £100, and spent it in various ways, you could sell the goods and end up with £100 cash at the end.

Irreversible processes are like the real world in that a trader will want to sell you an apple for more than she bought it for. Otherwise she won't be able to make a profit. If you started with £100, and spent it, you would never be able to get the £100 back again, since you would lose money in each transaction. You may end up with £100 'worth of goods', but you would have to be satisfied with a price lower than £100 if you wanted to sell it all for cash.

Let us now return to the physics, and the gas in the piston. What does irreversibility mean here? We haven't lost any energy – the First Law has ensured that. But we have lost usefulness.

Equation (8) tells us that if we come back to where we started, and only use reversible processes on the way, the total entropy change will be zero. There is another way of looking at this, from the point of view of a heat engine.

Let us suppose that the temperature of the boiler in a steam engine is T_A . In a perfect heat engine, the cylinder will receive the steam at this temperature. Suppose Q joules of heat are transferred from boiler to cylinder. The boiler loses entropy Q/T_A , the cylinder gains entropy Q/T_A , and the total entropy remains constant.

Now let us look at a real engine. The boiler must be hotter than the cylinder, or heat would not flow from boiler to cylinder! Suppose that the boiler is still at T_A , but the cylinder is at T_C . We have now let irreversibility loose in the system, since the heat Q now flows from hot to cooler without doing work on the way.

What about the entropy? The boiler now loses Q/T_A to the connecting pipe¹⁶, but the cylinder gains Q/T_C from it. Since $T_C < T_A$, the cylinder gains more entropy than the boiler lost.

This is an alternative definition of the Second Law. Processes go in the direction to maximize the total amount of entropy.

5.6 Re-statement of First Law

For reversible processes, $dW = -p dV$, and $dQ = T dS$. Therefore the First Law (1), can be written as

$$T dS = dU + p dV . \quad (9)$$

We find that this equation is also true for irreversible processes. This is because T , S , U , p and V are all functions of state, and therefore if the equation is true for reversible processes, it is true for all processes. However care must be taken when using it for irreversible processes, since TdS is no longer equal to the heat flow, and pdV is no longer equal to the work done.

5.7 The Boltzmann Law

The Boltzmann Law is simple to state, but profound in its implications.

$$\text{Probability that a particle has energy } E \propto e^{-E/kT} \quad (10)$$

¹⁶ What's the pipe got to do with it? Remember that we said that change in entropy dS is only given by dQ/T for reversible processes. The passing of Q joules of heat into the pipe is done reversibly (at temperature T_A), so we can calculate the entropy change. Similarly the passing of Q joules of heat from pipe to cylinder is done reversibly (at T_C), so the calculation is similarly valid at the other end. However something is going on in the pipe which is not reversible – namely Q joules of heat passing from higher to lower temperature. Therefore we mustn't apply any $dS = dQ/T$ arguments inside the pipe.

where k is the Boltzmann constant, and is about 1.38×10^{-23} J/K. We also find that the probability that a system has energy E or greater is also proportional to $e^{-E/kT}$ (with a different constant of proportionality).

There is common sense here, because (10) is saying that greater energies are less likely; and also that the higher the temperature, the more likely you are to have higher energies.

Let's give some examples:

5.7.1 Atmospheric Pressure

The pressure in the atmosphere at height h is proportional to the probability that a molecule will be at that height, and is therefore proportional to $e^{-mgh/kT}$. Here, the energy E , is of course the gravitational potential energy of the molecule – which has mass m .

The proof of this statement is in several parts. Firstly we assume that all the air is at the same temperature. This is a dodgy assumption, but we shall make do with it. Next we divide the atmosphere into slabs (each of height dh and unit area), stacked one on top of the other. Each slab has to support all the ones above it. From the Gas Law ($pV = NkT$ where N is the number of molecules under consideration), and the definition of density ($Nm = \rho V$) we can show that $\rho = pm/kT$. Furthermore, if you go up by a small height dh , the pressure will reduce by the weight of one slab – namely $\rho g dh$. Therefore

$$\begin{aligned} \frac{dp}{dh} &= -\rho g = -\frac{pmg}{kT} \\ \Rightarrow p &= p_0 \exp\left(-\frac{mgh}{kT}\right) \end{aligned} \quad (11)$$

where p_0 is the pressure at ground level. We see that the Boltzmann Law is obeyed.

5.7.2 Velocity distribution of molecules in a gas

The probability that a molecule in the air will have x -component of its velocity equal to u_x is proportional to $\exp(-mu_x^2/2kT)$. Here the energy E is the kinetic energy associated with the x -component of motion.

From this statement, you can work out the mean value of u_x^2 , and find it to be:

$$\begin{aligned} \overline{u_x^2} &= \frac{\int x^2 \exp(-mx^2/2kT) dx}{\int \exp(-mx^2/2kT) dx} = \frac{\frac{1}{2}(2kT/m)^{3/2}}{(2kT/m)^{1/2}} = \frac{kT}{m} \\ \frac{1}{2} m \overline{u_x^2} &= \frac{1}{2} kT \end{aligned} \quad (12)$$

The mean kinetic energy is given by

$$\overline{K} = \frac{1}{2} m \overline{u^2} = \frac{1}{2} m (\overline{u_x^2} + \overline{u_y^2} + \overline{u_z^2}) = \frac{3}{2} kT \quad (13)$$

so the internal energy of a mole of gas (due to linear motion) is

$$U = N_A \overline{K} = \frac{3}{2} N_A kT = \frac{3}{2} RT \quad (14)$$

where $R \equiv N_A k$ is the gas constant. From this it follows that the molar heat capacity of a perfect gas¹⁷, $C_V = \frac{3}{2} R$.

5.7.3 Vapour Pressure

The probability that a water molecule in a mug of tea has enough (or more than enough) energy to leave the liquid is proportional to $\exp(-E_L/kT)$ where E_L is the energy required to escape the attractive pull of the other molecules (latent heat of vaporization per molecule).

5.7.4 Justification of Boltzmann Law

In this section, we introduce some statistical mechanics to give a taste of where the Boltzmann law comes from.

Suppose that you have N atoms, and P 'packets' of energy to distribute between them. How will they be shared? In statistical mechanics we assume that the energy will be shared in the most likely way.

In a simple example, we could try sharing 4 units of energy ($P=4$) among 7 atoms ($N=7$). Because the individual energy units are indistinguishable (as are the 7 atoms), the possible arrangements are:

- 1 atom with 4 energy units, 6 atoms with none
- 1 atom with 3 energy units, 1 with 1, 5 with none
- 2 atoms with 2 energy units, 5 with none
- 1 atom with 2 energy units, 2 with 1, 4 with none
- 4 atoms with 1 energy unit, 3 with none.

These are said to be the five macrostates of the system. We can work out how likely each one is to occur if the energy is distributed randomly by counting the ways in which each macrostate could have happened.

¹⁷ This is the heat capacity due to linear motion. For a monatomic gas (like helium), this is the whole story. For other gases, the molecules can rotate or vibrate about their bonds as well, and therefore the heat capacity will be higher.

For example, in the first case (all of the energy is given to one of the atoms), there are seven ways of setting it up – because there are seven atoms to choose from.

In the second case, we have to choose one atom to take 3 units (7 to choose from), and then choose one from the remaining six to take the remaining unit. Therefore there are $7 \times 6 = 42$ ways of setting it up.

Similarly we can count the ways of rearranging for the other macrostates¹⁸:

- | | |
|---|----------|
| • 1 atom with 4 energy units, 6 atoms with none | 7 ways |
| • 1 atom with 3 energy units, 1 with 1, 5 with none | 42 ways |
| • 2 atoms with 2 energy units, 5 with none | 21 ways |
| • 1 atom with 2 energy units, 2 with 1, 4 with none | 105 ways |
| • 4 atoms with 1 energy unit, 3 with none. | 35 ways |

We can see that there is one macrostate clearly in the lead – where 4 atoms have no energy, 2 atoms have one energy unit, and 1 atom has two energy units. This macrostate is interesting because there is a geometric progression in the number of atoms (4,2,1) having each amount of energy.

It can be shown that the most likely macrostate will always be the one with (or closest to) a geometric progression of populations.¹⁹ In other

¹⁸ The calculation is made more straightforward using the formula $W = N! / (n_0! n_1! n_2! \dots)$ where W is the number of ways of setting up the macrostate, n_0 is the number of atoms with no energy, n_1 is the number of atoms with one unit of energy, and so on.

Here is one justification for this formula: $N!$ gives the total number of ways of choosing the atoms in order. The division by $n_0!$ prevents us overcounting when we choose the same atoms to have zero energy in a different order. A similar reason holds for the other terms on the denominator.

Alternatively, W = the number of ways of choosing n_0 atoms from $N \times$ the number of ways of choosing the n_1 from the remaining $(N - n_0) \times$ the number of ways of choosing the n_2 from the remaining $(N - n_0 - n_1)$ and so on. Thus

$$W = C_{n_0}^N C_{n_1}^{N-n_0} C_{n_2}^{N-n_0-n_1} \dots$$

$$= \frac{N!}{n_0!(N-n_0)!} \times \frac{(N-n_0)!}{n_1!(N-n_0-n_1)!} \times \frac{(N-n_0-n_1)!}{n_2!(N-n_0-n_1-n_2)!} \dots = \frac{N!}{n_0! n_1! n_2! \dots}$$

¹⁹ To show this, start with a geometric progression (in other words, say $n_i = A f^i$ where f is some number), and write out the formula for W . Now suppose that one of the atoms with i units of energy gives a unit to one of the atoms with j units. This means that n_i and n_j have gone down by 1, while n_{i-1} and n_{j+1} have each gone up by one. By comparing the old and

words, assuming that this macrostate is the true one (which is the best bet)²⁰, then the fraction of atoms with n energy units is proportional to some number to the power $-n$. The actual fraction is given by the formula $(1 + P/N)^{-1} \times (1 + N/P)^{-n}$. Assuming that the mean number of energy units per atom is large (so that we approximate the continuous range of values that the physical energy can take), this means that $1 + N/P \approx e^{N/P}$, and so the probability that an atom will have n units of energy is proportional to $e^{-Nn/P}$.

Suppose that each packet contains ε joules of energy. Then the energy of one atom (with n packets) is $E = n\varepsilon$, and the probability that our atom will have energy E as $e^{-NE/P\varepsilon}$. The mean energy per atom is $P\varepsilon/N$. Now we have seen that the average energy of an atom in a system is about kT , where T is the temperature in kelvins, and so it should not seem odd that the Boltzmann probability is $e^{-E/kT}$ where we replace one expression for the mean energy per atom $P\varepsilon/N$, with another kT .

5.8 Perfect Gases

All substances have an *equation of state*. This tells you the relationship between volume, pressure and temperature for the substance. Most equations of state are nasty, however the one for an ideal, or perfect, gas is straightforward to use. It is called the Gas Law. This states that

$$p V = n R T \quad (18)$$

$$p V = N k T \quad (19)$$

where p is the pressure of the gas, V its volume, and T its absolute (or thermodynamic) temperature. This temperature is measured in kelvins *always*. There are two ways of stating the equation: as in (18), where n represents the number of moles of gas; or as in (19), where N represents the number of molecules of gas. Clearly $N = N_A n$ where N_A is the Avogadro number, and therefore $R = N_A k$.

You can adjust the equation to give you a value for the number density of molecules. This means the number of molecules per cubic metre, and is given by $N/V = p/kT$. The volume of one mole of molecules can also be worked out by setting $n=1$ in (18):

new values of W , you can show that the new W is smaller, and that therefore the old arrangement was the one with the biggest W .

²⁰ The bet gets better as the number of atoms increases. The combination (4,2,1) was the most popular in our example of $N=7$, $P=4$, however if you repeated the exercise with $N=700$ and $P=400$, you would find a result near (400,200,100) almost a certainty. In physics we deal with *huge* numbers of atoms in matter, so the gambling pays off.

$$V_m = \frac{RT}{p} \quad (20)$$

You can adjust this equation to give you an expression for the density. If the mass of one molecule is m , and the mass of a mole of molecules (the R.M.M.) is M , we have

$$\begin{aligned} \rho &= \frac{\text{Mass}}{\text{Volume}} = \frac{M}{RT/p} = \frac{Mp}{RT} \\ &= \frac{N_A mp}{N_A kT} = \frac{mp}{kT} \end{aligned} \quad (21)$$

Please note that this is the ideal gas law. Real gases will not always follow it. This is especially true at high pressures and low temperatures where the molecules themselves take up a good fraction of the space. However at room temperature and atmospheric pressure, the Gas Law is a very good model.

5.8.1 Heat Capacity of a Perfect Gas

We have already shown (in section 5.7.2) that for a perfect gas, the internal energy due to linear motion is $\frac{3}{2}RT$ per mole. If this were the only consideration, then the molar heat capacity would be $\frac{3}{2}R$. However there are two complications

5.8.1.1 *The conditions of heating*

In thermodynamics, you will see molar heat capacities written with subscripts – C_P and C_V . They both refer to the energy required to heat a mole of the substance (M kilograms) by one kelvin. However the energy needed is different depending on whether the volume or the pressure is kept constant as the heating progresses.

When you heat a gas at constant volume, all the heat going in goes into the internal energy of the gas ($dQ_V = dU$).

When you heat a gas at constant pressure, two things happen. The temperature goes up, but it also expands. In expanding, it does work on its surroundings. Therefore the heat put in is increasing both the internal energy and is also doing work ($dQ_P = dU + p dV$).

Given that we know the equation of state for the gas (18), we can work out the relationship between the constant-pressure and constant-volume heat capacities. In these equations we shall be considering one mole of gas.

$$\begin{aligned}
C_V &= \frac{dQ_V}{dT} = \frac{dU}{dT} \\
C_P &= \frac{dQ_P}{dT} = \frac{dU}{dT} + p \frac{dV}{dT} \\
&= C_V + p \frac{d}{dT} \left(\frac{RT}{p} \right) = C_V + R
\end{aligned} \tag{22}$$

5.8.1.2 The type of molecule

Gas molecules come in many shapes and sizes. Some only have one atom (like helium and argon), and these are called monatomic gases. Some gases are diatomic (like hydrogen, nitrogen, oxygen, and chlorine), and some have more than two atoms per molecule (like methane).

The monatomic molecule only has one use for energy – going places fast. Therefore its internal energy is given simply by $\frac{3}{2}kT$, and so the molar internal energy is $U = \frac{3}{2}RT$. Therefore, using equation (22), we can show that $C_V = \frac{3}{2}R$ and $C_P = C_V + R = \frac{5}{2}R$.

A diatomic molecule has other options open to it. The atoms can rotate about the molecular centre (and have a choice of two axes of rotation). They can also wiggle back and forth – stretching the molecular bond like a rubber band. At room temperature we find that the vibration does not have enough energy to kick in, so only the rotation and translation (the linear motion) affect the internal energy.

Each possible axis of rotation adds $\frac{1}{2}kT$ to the molecular energy, and so we find that for most diatomic molecules, $C_V = \frac{5}{2}R$ and $C_P = \frac{7}{2}R$.

5.8.1.3 Thermodynamic Gamma

It turns out that the ratio of C_P/C_V crops up frequently in equations, and is given the letter γ . This is not to be confused with the γ in relativity, which is completely different.

Using the results of our last section, we see that $\gamma=5/3$ for a monatomic gas, and $\gamma=7/5$ for one that is diatomic.

5.8.2 Pumping Heat

If a healthy examiner expects you to know about ideal gases and thermodynamics – you can bet that he or she will want you to be able to *do* thermodynamics with an ideal gas. In this section we show you how to turn a perfect gas (in a cylinder) into a reversible heat engine, and in doing so we will introduce the techniques you need to know.

5.8.2.1 Isothermal Gas Processes

As an introduction, we need to know how to perform two processes. Firstly we need to be able to get heat energy into or out of a gas without changing its temperature. Remember that we want a reversible heat engine, and therefore the gas must be at the same temperature as the hot object when the heat is passing into it. Any process, like this, which takes place at a constant temperature is said to be *isothermal*.

The Gas Law tells us (18) that $pV=nRT$, and hence that pV is a function of temperature alone (for a fixed amount of gas). Hence in an isothermal process

$$pV = \text{const} \quad . \quad \text{ISOTHERMAL} \quad (23)$$

Using this equation, we can work out how much we need to compress the gas to remove a certain quantity of heat from it. Alternatively, we can work out how much we need to let the gas expand in order for it to 'absorb' a certain quantity of heat. These processes are known as isothermal compression, and isothermal expansion, respectively.

Suppose that the volume is changed from V_1 to V_2 , the temperature remaining T . Let us work out the amount of heat absorbed by the gas. First of all, remember that as the temperature is constant, the internal energy will be constant, and therefore the First Law may be stated $dQ=pdV$. In other words, the total heat entering the gas may be calculated by integrating pdV from V_1 to V_2 :

$$Q = \int p dV = \int \frac{nRT}{V} dV = [nRT \ln V]_{V_1}^{V_2} = nRT \ln \frac{V_2}{V_1} \quad (24)$$

This equation describes an isothermal (constant temperature) process only. In order to keep the temperature constant, we maintain a good thermal contact between the cylinder of gas and the hot object (the boiler wall, for example) while the expansion is going on.

5.8.2.2 Adiabatic Gas Processes

The other type of process you need to know about is the adiabatic process. These are processes in which there is no heat flow ($dQ=0$), and they are used in our heat engine to change the temperature of the gas in between its contact with the hot object and the cold object. Sometimes this is referred to as an isentropic process, since if $dQ=0$ for a reversible process, $TdS=0$, and so $dS=0$ and the entropy remains unchanged.²¹

²¹ While the terms 'isentropic' and 'adiabatic' are synonymous for a perfect gas, care must be taken when dealing with irreversible processes in more advanced systems. In this context dQ is not equal to TdS . If $dQ=0$, the process is said to be adiabatic: if $dS=0$, the process is

Before we can work out how much expansion causes a certain temperature change, we need to find a formula which describes how pressure and volume are related in an adiabatic process. Firstly, the First Law tells us that if $dQ=0$, then $0 = dU + p dV$. We can therefore reason like this for n moles of gas:

$$\begin{aligned} 0 &= dU + p dV \\ &= nC_V dT + p dV \end{aligned}$$

Now for a perfect gas, $nRT=pV$, therefore $nRdT = pdV + Vdp$. So we may continue the derivation thus:

$$\begin{aligned} nC_V dT &= \frac{C_V}{R} (pdV + Vdp) \\ 0 &= \frac{C_V}{R} (pdV + Vdp) + p dV \\ &= C_V (pdV + Vdp) + RpdV \\ &= C_p pdV + C_V Vdp \\ &= \gamma pdV + Vdp \\ &= \gamma \frac{dV}{V} + \frac{dp}{p} \end{aligned} \tag{25}$$

Integrating this differential equation gives

$$\begin{aligned} \gamma \ln V + \ln p + C &= 0 \\ pV^\gamma &= e^{-C} \quad . \text{ ADIABATIC} \\ pV^\gamma &= \text{const} \end{aligned} \tag{26}$$

Equation (26) is our most important equation for adiabatic gas processes, in that it tells us how pressure and volume will be related during a change.

We now come back to our original question: what volume change is needed to obtain a certain temperature change? Let us suppose we have a fixed amount of gas (n moles), whose volume changes from V_1 to V_2 . At the same time, the temperature changes from T_1 to T_2 . We may combine equation (26) with the Gas Law to obtain:

isentropic. Clearly for a complex system, the two conditions will be different. This arises because in these systems, the internal energy is not just a function of temperature, but also of volume or pressure.

$$\begin{aligned}
 pV^\gamma &= \text{const} \\
 pV V^{\gamma-1} &= \text{const} \\
 nRTV^{\gamma-1} &= \text{const} \quad . \\
 \frac{T_1}{T_2} \frac{V_1^{\gamma-1}}{V_2^{\gamma-1}} &= 1
 \end{aligned}
 \tag{27}$$

5.8.2.3 A Gas Heat Engine

We may now put our isothermal and adiabatic processes together to make a heat engine. The engine operates on a cycle:

1. The cylinder is attached to the hot object (temperature T_{hot}), and isothermal expansion is allowed (from V_1 to V_2) so that heat Q_1 is absorbed into the gas.
2. The cylinder is detached from the hot object, and an adiabatic expansion (from V_2 to V_3) is allowed to lower the temperature to that of the cold object (T_{cold}).
3. The cylinder is then attached to the cold object. Heat Q_2 is then expelled from the cylinder by an isothermal compression from V_3 to V_4 .
4. Finally, the cylinder is detached from the cold object. An adiabatic compression brings the volume back to V_1 , and the temperature back to T_{hot} .

Applying equation (24) to the isothermal processes gives us

$$\begin{aligned}
 Q_1 &= nRT_{\text{hot}} \ln \frac{V_2}{V_1} \\
 Q_2 &= nRT_{\text{cold}} \ln \frac{V_4}{V_3} \quad .
 \end{aligned}
 \tag{28}$$

Similarly, applying equation (27) to the adiabatic processes gives us

$$\begin{aligned}
 \frac{V_3}{V_2} &= \left(\frac{T_{\text{hot}}}{T_{\text{cold}}} \right)^{\gamma-1} \\
 \frac{V_4}{V_1} &= \left(\frac{T_{\text{hot}}}{T_{\text{cold}}} \right)^{\gamma-1} \quad . \\
 \Rightarrow \frac{V_3}{V_2} &= \frac{V_4}{V_1} \Rightarrow \frac{V_3}{V_4} = \frac{V_2}{V_1}
 \end{aligned}
 \tag{29}$$

Combining equations (28) and (29), gives us

$$\frac{Q_1}{Q_2} = -\frac{T_{hot}}{T_{cold}}, \quad (30)$$

$$\left| \frac{Q_1}{Q_2} \right| = \frac{T_{hot}}{T_{cold}},$$

where the minus sign reminds us that $Q_2 < 0$, since this heat was leaving the gas.

To summarize this process, we have used a perfect gas to move heat from a hot object to a colder one. In doing this, we notice less heat was deposited in the cold object than absorbed from the hot one. Where has it gone? It materialized as useful work when the cylinder was allowed to expand. Had the piston been connected to a flywheel and generator, we would have seen this in a more concrete way.

We also notice that we have proved that the kelvin scale of temperature, as defined by the Gas Law, is a true thermodynamic temperature since equation (30) is identical to (5).

5.9 Radiation of Heat

And finally... there is an extra formula that you will need to be aware of. The amount of heat radiated from an object is given by:

$$P = \epsilon \sigma A T^4 \quad (31)$$

P is the power radiated (in watts), A is the surface area of the object (in m^2), and T is the thermodynamic temperature (in K).

The constant σ is called the Stefan-Boltzmann constant, and takes the value of $5.671 \times 10^{-8} \text{ W}/(\text{m}^2 \text{K}^4)$.

The amount radiated will also depend on the type of surface. For a perfect matt black (best absorber and radiator), the object would be called a *black body*, and the emissivity ϵ would take the value 1. For a perfect reflector, there is no absorption, and no radiation either, so $\epsilon=0$.

5.10 Questions

1. Calculate the maximum efficiency possible in a coal fired power station, if the steam is heated to 700°C and the river outside is at 7°C .
2. Mechanical engineers have been keen to build jet engines which run at higher temperatures. This makes it very difficult and expensive to make the parts, given that the materials must be strong, even when they are almost at their melting point. Why are they making life hard for themselves?

3. Two insulated blocks of steel are identical except that one is at 0°C, while the other is at 100°C. They are brought into thermal contact. A long time later, they are both at the same temperature. Calculate the final temperature; the energy change and entropy change of each block if (a) heat flows by conduction from one block to the other, and if (b) heat flows from one to the other via a reversible heat engine. ++
4. There is a 'rule of thumb' in chemistry that when you raise the temperature by 10°C, the rate of reaction roughly doubles. Use Boltzmann's Law to show that this means the activation energy of chemical processes must be of order 10^{-19} J. +
5. The amount of energy taken to turn 1kg of liquid water at 100°C into 1kg of steam at the same temperature is 2.26 MJ. This is called the latent heat of vaporization of water. How much energy does each molecule need to 'free itself' from the liquid?
6. By definition, the boiling point of a liquid is the temperature at which the saturated vapour pressure is equal to atmospheric pressure (about 100kPa). Up a mountain, you find that you can't make good tea, because the water is boiling at 85°C. What is the pressure? You will need your answer to q4. +
7. Estimate the altitude of the mountaineer in q5. Assume that all of the air in the atmosphere is at 0°C. +
8. Use the Gas Law to work out the volume of one mole of gas at room temperature and pressure (25°C, 100kPa).
9. What fraction of the volume of the air in a room is taken up with the molecules themselves? Make an estimate, assuming that the molecules are about 10^{-10} m in radius.
10. Estimate a typical speed for a nitrogen molecule in nitrogen at room temperature and pressure. On average, how far do you expect it to travel before it hits another molecule? Again, assume that the radius of the molecule is about 10^{-10} m. ++
11. The fraction of molecules (mass m each) in a gas at temperature T which have a particular velocity (of speed u) is proportional to $e^{-mu^2 / 2kT}$, as predicted by the Boltzmann law. However the fraction of molecules which have speed u is proportional to $u^2 e^{-mu^2 / 2kT}$. Where does the u^2 come from? ++
12. One litre of gas is suddenly squeezed to one hundredth of its volume. Assuming that the squeezing was done adiabatically, calculate the work done on the gas, and the temperature rise of the gas. Why is the adiabatic assumption a good one for rapid processes such as this?

13. A water rocket is made using a 2 litre plastic drinks bottle. An amount of water is put into the bottle, and the stopper is put on. Air is pumped into the bottle through a hole in the stopper. When the pressure gets to a certain level, the stopper blows out, and the pressure of the air in the bottle expels the water. If the bottle was standing stopper-end downwards, it flies up into the air. If you neglect the mass of the bottle itself, what is the optimum amount of water to put in the bottle if you want your rocket to (a) deliver the maximum impulse, or (b) rise to the greatest height when fired vertically. ++