Antonine Physics A2

Topic 13 Thermal Physics

How to Use this Book

How to use these pages:

- This book intended to complement the work you do with a teacher, not to replace the teacher.
- Read the book along with your notes.
- If you get stuck, ask your teacher for help.
- The best way to succeed in Physics is to practise the questions.

There are many other resources available to help you to progress:

- Web-based resources, many of which are free.
- Your friends on your course.
- Your teacher.
- Books in the library.

This is an electronic book which you can download. You can carry it in a portable drive and access it from your school's computers (if allowed) as well as your own at home.

Thermal Physics studies the behaviour of flows of heat energy, and the way gases behave when they are heated. These ideas are fundamental to engineers as they design heat engines. Thermodynamics is an important part of Applied Physics.

Tutorials 13.04 and 13.05 are for the Cambridge Pre-U syllabus only. They can be used as an extension for students who are considering doing Physics at university level. 13.04 covers the Laws of Thermodynamics. 13.05 covers the Boltzmann factor.

Tutorial	**Title**	**Page**
13.01	Heat Flow	4
13.02	The Equation of State for an Ideal Gas	27
13.03	Molecular Kinetic Theory	44
13.04	The Laws of Thermodynamics	55
13.05	The Boltzmann Factor	73
	Answers	85

Topic 13

Thermal Physics

Tutorial 13.01 Heat Flow

All Syllabi

Contents

13.0101 Conduction
13.0102 Convection
13.0103 Radiation
13.0104 Heat Flow
13.0105 Thermometry
13.0106 Practical Thermometers
13.0107 Thermal Equilibrium
13.0108 Internal Energy
13.0109 Brownian Motion
13.0110 Specific Heat Capacity
13.0111 Specific heat with two materials
13.0112 Phases of matter
13.0113 Latent Heat

13.0101 Conduction

You will be familiar with conduction, convection, and radiation from GCSE. You did it in Year 10 (and you probably weren't listening?).

Conduction involves the flow of heat energy in a **solid material**. As well as the vibration of molecules, electrons are involved. This explains why metals are good conductors of heat. Materials that do not conduct electricity do not conduct heat well. Liquids and gases can conduct heat but are very poor at doing so.

Models of conduction are not easy and are well beyond the scope of these notes.

13.0102 Convection

This occurs in fluids (liquids and gases). It cannot happen in solid materials. The particles in a fluid near a heat source vibrate more strongly. Therefore, they move apart, to occupy more space (*Figure 1*). Therefore, the density decreases, and the fluid rises. As the particles rise higher, the heat is transferred to cooler particles. Therefore, the space occupied by the molecules decreases and the density rises. The denser fluid falls.

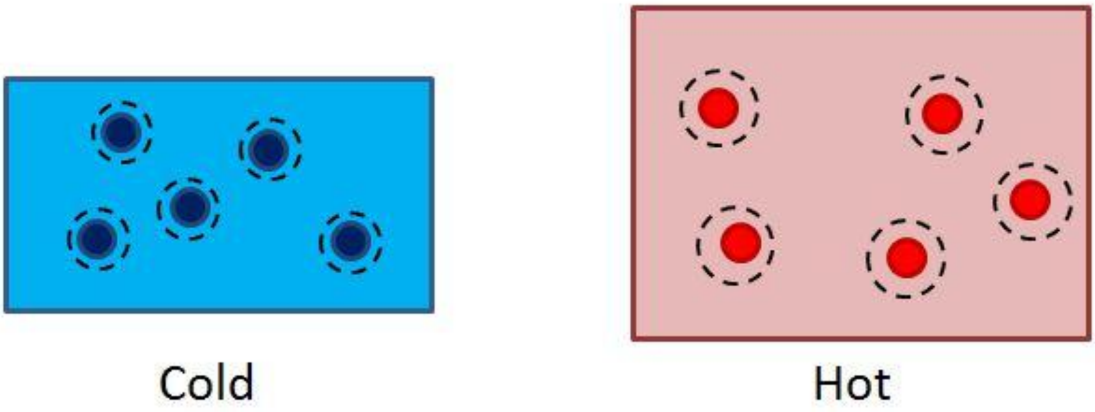


Figure 1 Hotter fluids occupy more space per particle

The particles themselves do not change density, just the fluid which consists of the particles.

13.0103 Radiation

All hot bodies radiate heat energy in the form of electromagnetic radiation. Thermal (**infra-red**) radiation behaves just like light:

- It consists of a stream of photons.
- It travels in straight lines.
- Its speed is 300 million m s^{-1} in a vacuum.
- It can be reflected and refracted.

Infra-red radiation has a wavelength of above 650 nm.

Shiny surfaces reflect infra-red radiation. Matt-black surfaces emit and absorb radiation particularly well.

Heat pipes are often found in computers to transfer the heat generated by the processors to the cooling fan. Here is a picture of some heat pipes in a laptop computer (*Figure 2*).

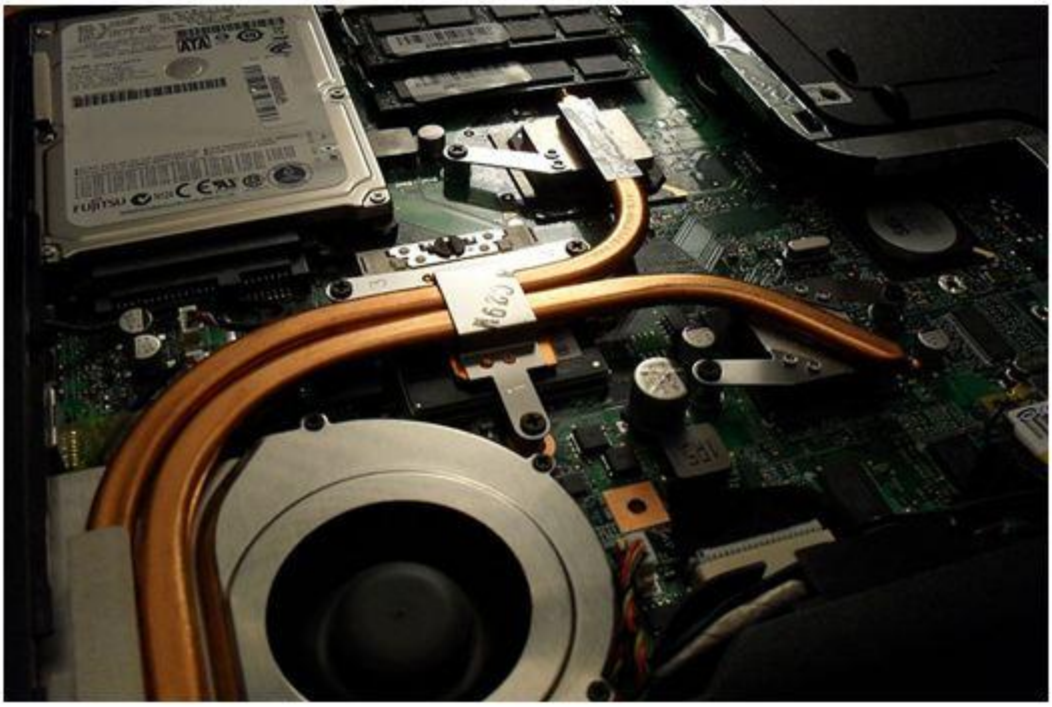


Figure 2 Heat pipes in a laptop computer

They use all three processes of heat transfer.

13.0104 Heat Flow

Heat is the **transfer of energy**, a flow of energy from a **hot** body to a **cooler** body (*Figure 3*). Heat is conducted by the movement of electrons as well as the vibration of molecules. Good conductors of electricity are good conductors of heat. Heat must not be confused with **internal energy**, caused by the **vibrations** of atoms or molecules within a body.

Figure 3 Heat flowing from hot to cold

If the heat source is removed, the object will **cool** by transferring heat energy to the surroundings.

13.0105 Thermometry (Irish and CIE Syllabuses)

Temperature is a representation of internal energy, not heat flow. The more internal energy there is, the higher the temperature.

The measurement of temperature is called **thermometry**. Temperature is remarkably difficult to measure, and it was only in the seventeenth and eighteenth centuries that a reliable method was established. Measurement depended on the even expansion of a liquid between two reference points. The most logical reference points are the **triple point of water** (when water exists as liquid water, ice, and water vapour) and the **boiling point** of water. These were proposed in 1742 by a Swedish astronomer and physicist, Anders **Celsius** (1701 - 1744). There were 100 steps between the two reference points - hence the term centigrade (Latin - one hundred steps). See *Figure 4*. Originally the zero reference point was at the boiling point of water, and the triple point of water was 100. The scale was reversed by Carl Linnaeus, who was the zoologist that gave us the system of naming species of animals and plants, to make the scale more practical.

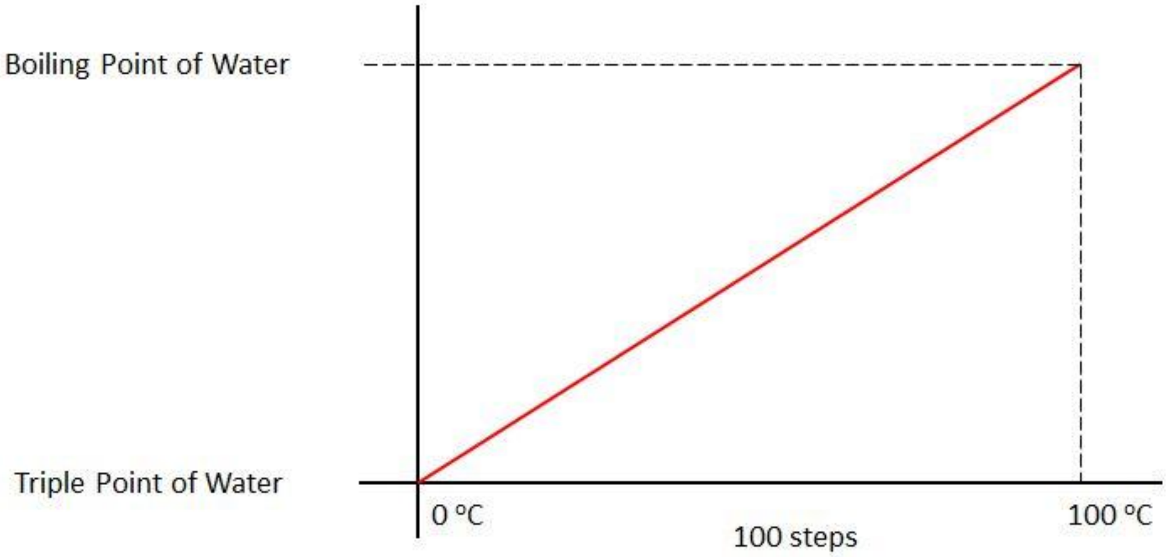


Figure 4 The Celsius scale

Gabriel Daniel Fahrenheit (1686 - 1736) lived in The Netherlands and had an enviable reputation as an expert glassblower. He used different reference points. His low temperature reference point was a mixture of ice, water, and ammonium chloride, which was the coldest thing he knew. His high temperature reference point was the boiling point of mercury. He had 300 steps between the two. Other reference points were the triple points of water (32 F) and the boiling point of water (212 F). There were 180 steps between the two.

For its practicality and simplicity, the **Celsius** steps are used by all scientists. The Fahrenheit scale is still used in the United States and some backward-looking news media in the UK. Most people in the UK and Ireland are now used to the Celsius scale.

Physicists now use the **Kelvin** scale, devised in 1848 by William Thomson, Lord Kelvin (1824 - 1908). It is an **absolute** scale, with the low temperature reference point being the temperature at which all molecular movement ceases. The Kelvin scale does not depend on any physical property. The **absolute zero** is written as 0 K which is -273.17 °C. Note that Kelvin temperatures are **never** written "°K". The Kelvin scale is shown in *Figure 5*.

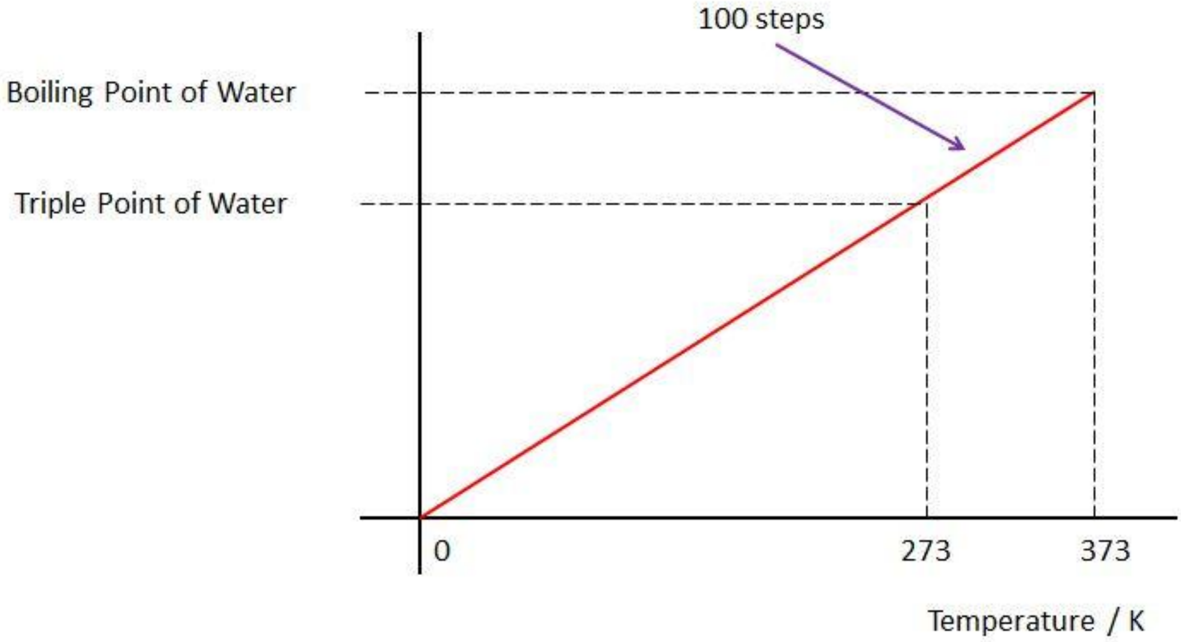


Figure 5 The Kelvin scale

Temperatures are never below **absolute zero**. It's totally impossible to have a temperature of -1 K (-274 °C).

Note that for most purposes, Celsius is the **practical** temperature scale, especially as we often take the temperature difference. **Celsius** temperatures are often given the code θ ("theta", a Greek lower case double letter 'th'). In certain cases, we have to use **absolute** temperatures. In this case we have to use the **Kelvin** Scale, given the physics code T:

$$T = \theta + 273.15$$ .... *Equation 1*

13.0106 Practical Thermometers

The picture shows a number of different kinds of thermometer. In this picture (*Figure* 6), there is a **spirit in a glass tube** thermometer that is widely used in school and college laboratories. There are also two weather stations that have an external thermometer.

Figure 6 Different kinds of thermometer

And this picture (*Figure 7*) shows the **sensors** for each base station. They are in the same place on a sheltered bird table in the garden. They connect to the weather stations using radio waves.

Figure 7 Temperature sensors for the weather stations in Figure 6

Notice that the readings from the outside sensors in the top picture are not quite the same. They are not too far out, but the picture shows that any two thermometers may not necessarily give the same reading. This can increase the **uncertainty** in the results of a temperature dependent quantity. These sensors can be **calibrated** to a reference to give as close to a true reading as possible. Thermometers that are accurately **calibrated** tend to be quite expensive.

Thermometers such as these depend on the variation of the **resistance** of a **thermistor** with temperature.

Another electrical method of measuring temperature is to use a **thermocouple** (*Figure 8*). The thermocouple generates a voltage when exposed to a **temperature difference**. A thermocouple is simply two wires of dissimilar metals that are joined together, as shown in the diagram:

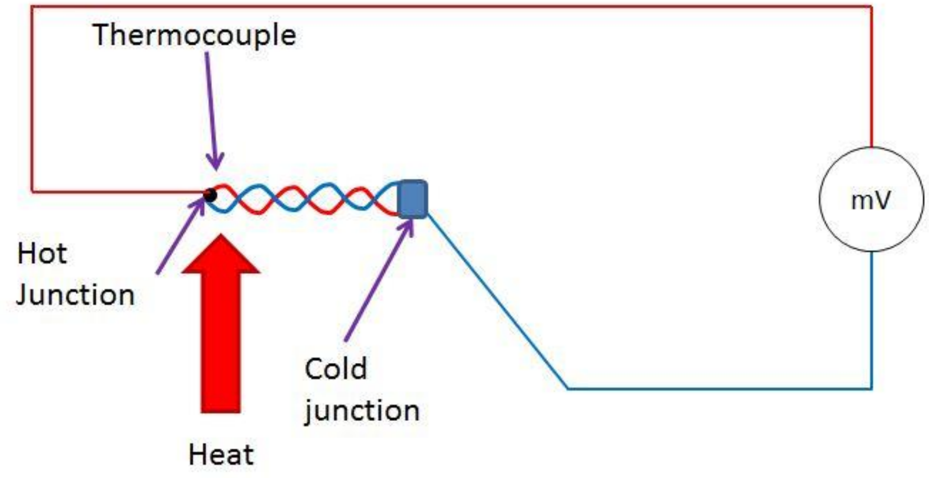


Figure 8 A thermocouple thermometer

The wires are joined together at the hot junction to ensure electrical contact. The heat is applied at the **hot junction**. The **cold junction** is left at room temperature. Along their length, the wires are **insulated** with a material that will resist the temperatures generated by the heat source. A **voltage** is generated, depending on the temperature. The voltage is shown on a **millivoltmeter**, of which the scale is calibrated not in volts, but in Celsius.

If both junctions are heated by the heat source, the voltage will be zero.

The sketch graph (*Figure 9*) shows the behaviour of two different thermocouples when exposed to temperatures between 0 °C to 1000 °C.

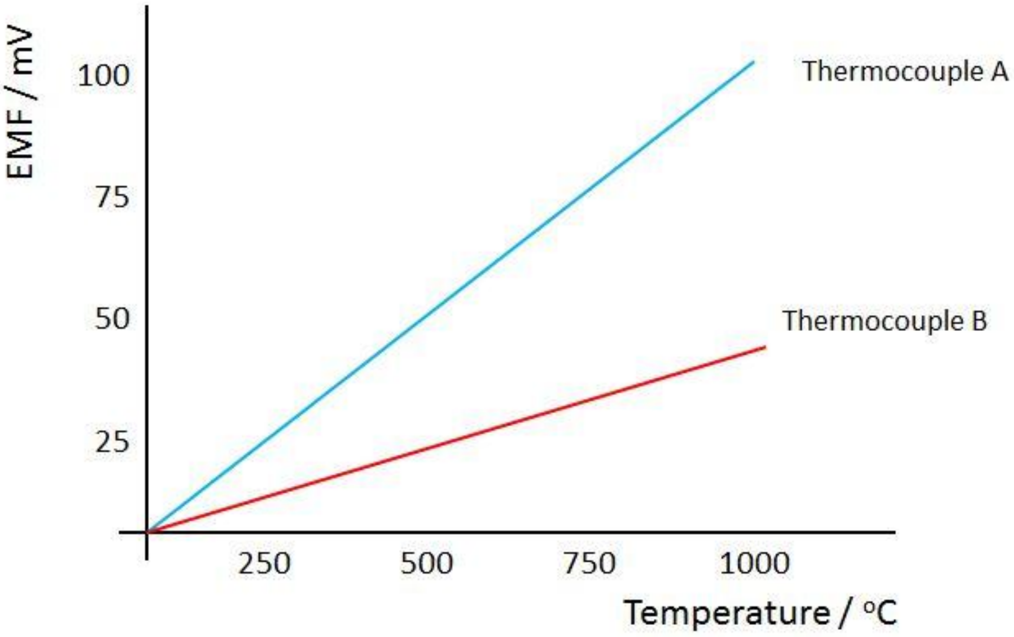


Figure 9 Graph showing the response of different thermocouples to increasing temperatures

The pairs of metals that are used include:

- Nickel-chromium and nickel alumel;
- Iron and constantan.

We can compare the **advantages** and **disadvantages** of thermocouples when compared with thermistors:

- Thermocouples have a wide range of temperatures at which they can operate (-200 °C to + 350 °C, or 100 °C to 1200 °C, depending on the type), while the temperature range of a thermistor is about -55 °C to 150 °C.
- Thermocouples tend to have a linear characteristic, making calibration easy, while thermistors are non-linear (the resistance can decrease exponentially with temperature).
- Thermistors are sensitive a small temperature changes, while thermocouples require a large temperature change to show a difference.
- Thermocouples are active devices; they generate a voltage. Thermistors are passive devices which require an external power supply to make them work.

- Thermocouples are accurate, and once calibrated, will retain their calibration. Thermistors will be accurate to +/- 1°C, which leads to uncertainty. They can be calibrated accurately, but this is a time consuming process, therefore expensive.
- Thermocouples don't need amplification circuitry while thermistors do.

Another important thing to do is to ensure good **thermal contact**, to ensure that you are measuring a temperature that is as close as possible to the true temperature.

Temperature sensors are used with **data-loggers**, which store the variation of temperature, and display the data on a graph. Other examples of practical thermometers include:

- clinical thermometers.
- the thermometer on a coffee machine.
- the temperature gauge in a car.

13.0107 Thermal Equilibrium

Suppose we heat a rod at one end and see how the temperature rises at the other. At the start, the rod will be hot at one end and cold at the other end. If we measure the temperature at the other end with a data-logger, we will see a graph like this (*Figure 10*).

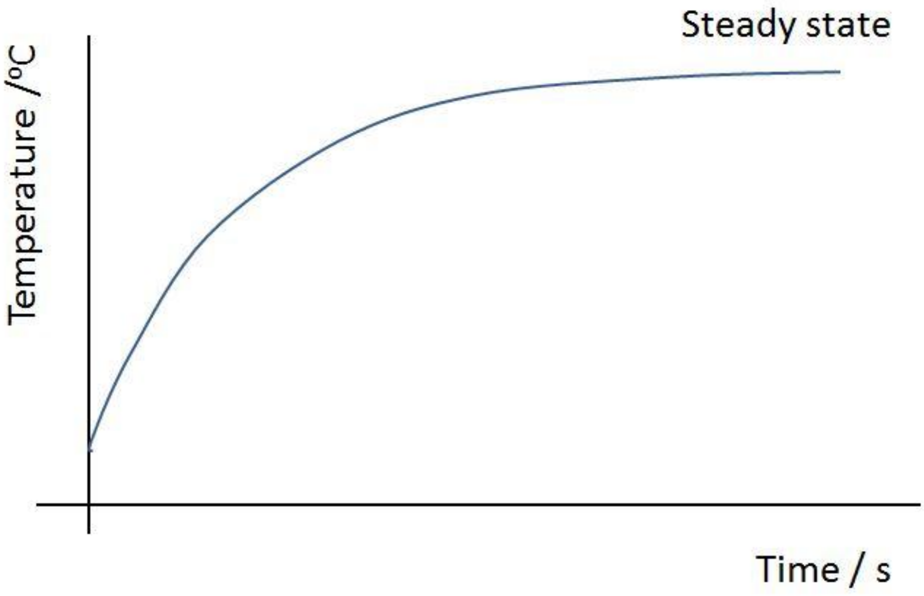


Figure 10 Steady state

When the heat flow into the rod is balanced by the heat flow out of the rod, we say that the system is in **steady state**. The temperature in the rod varies in a linear way along the length of the rod. This is called **Thermal Equilibrium**. The heat flowing into the system is the same as the heat flowing out.

Heat flows can be modelled in the same way as electric circuits:

- The **temperature difference** is equivalent to the voltage.
- The **heat flow** is equivalent to the current.
- The **thermal resistance** is equivalent to the electrical resistance.

13.0108 Internal Energy

We can increase the internal energy by:

- Transferring heat into the body
- Doing a job of work on the body.

Some houses have electric central heating using **night storage** heaters (*Figure 11*). These consist of a large metal box full of bricks, in which there are electrical elements. The elements are switched on at night. Electricity is cheaper at night, as power stations running at half load run less efficiently.

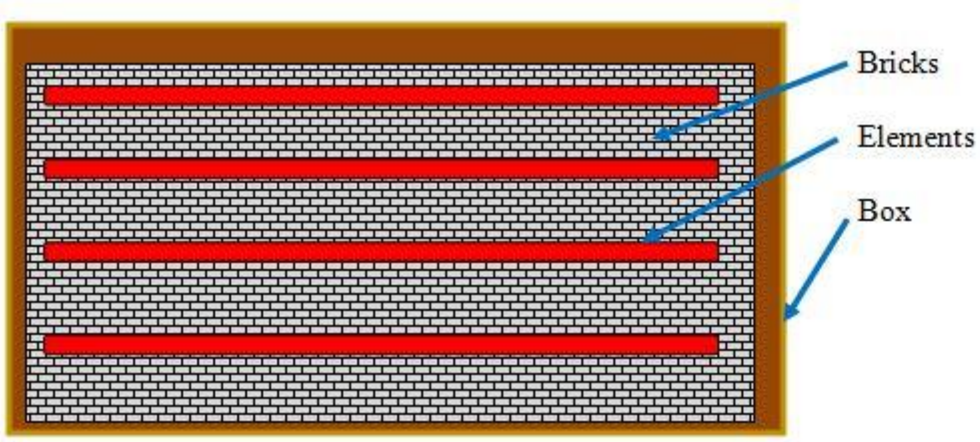


Figure 11 A night storage heater

The elements transfer electrical energy to heat. The heat flows into the bricks, increasing their internal energy. The temperature rises. When the electricity is turned off in the morning, the internal energy in the bricks is used to heat the room (*Figure 12*).

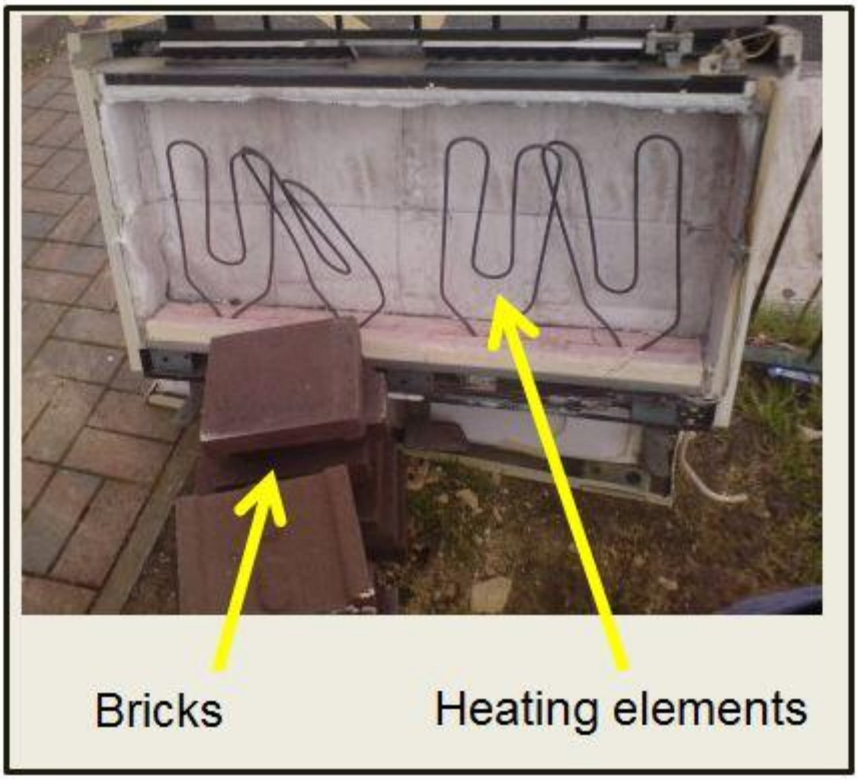


Figure 12 A night storage heater in bits

The rate of heat flow into the room can be controlled with flaps.

Internal energy is the **total energy** in the movement of the molecules in a body. The body itself might not seem to have potential or kinetic energy. If we look on the microscopic scale at an ideal monatomic gas, we can see that there are atoms travelling around in random directions at hundreds of metres per second. The energy is translational **kinetic** energy.

If we have gases that consist of molecules, we will also observe:

- translational kinetic energy of vibrations of bonds.
- rotational kinetic energy of the molecules as they spin.

If there are liquid and solid materials in the system, we have to take into account the potential energy contained within the bonds.

The internal energy is all of these energies, potential and kinetic, added together. The distribution of the energies in the molecules is random.

13.0109 Brownian Motion

Brownian motion can be used as a model to show the vibration of molecules (*Figure 13*).

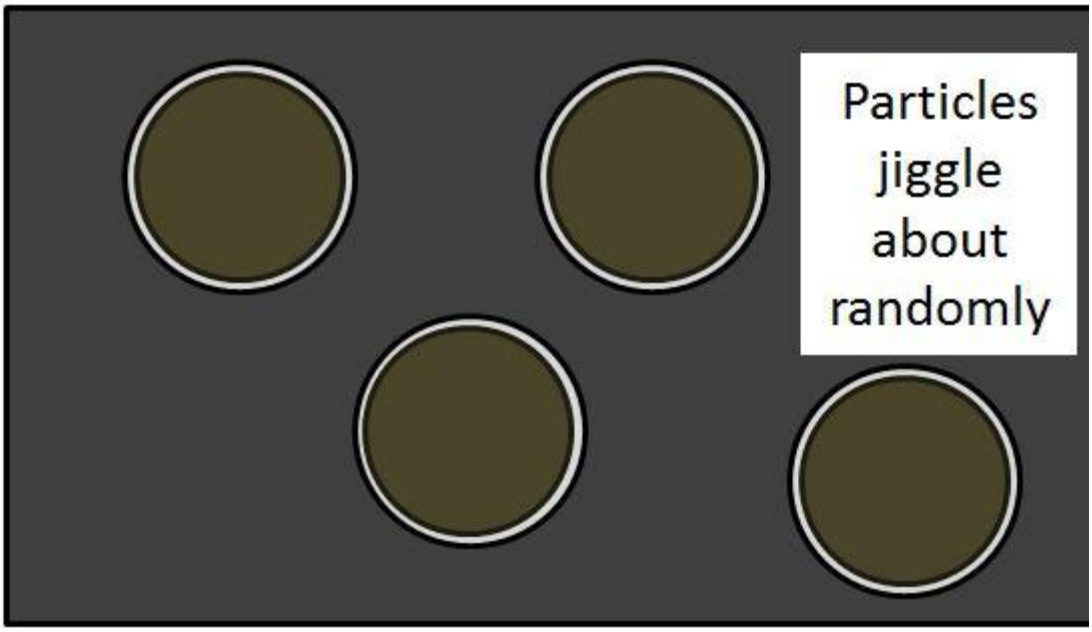


Figure 13 Brownian motion

If you look at smoke particles in a cell under the microscope, you can see the particles jiggling about randomly as they are bombarded by air molecules.

13.0110 Specific Heat Capacity

Specific Heat Capacity is the **quantity of heat** required to raise the **temperature** of a **unit mass** through a **unit temperature rise**. It is given the physics code c. The formula associated with this is:

Heat flow (J) = mass (kg) × specific heat capacity (J kg^{-1} K^{-1}) × temperature change (K)

$$\Delta Q = mc\Delta\theta$$

.... *Equation 2*

- ΔQ is the **flow of heat energy**.
- $\Delta\theta$ is the **temperature change**. It doesn't matter whether temperatures are in Kelvin or degrees Celsius. Since the steps are the same, the difference will be the same.
- Units for **specific heat** are **joules per kilogram per kelvin** (J kg^{-1} K^{-1}). It is important that the masses are in **kilograms**. Sometimes you might come across c in non-SI units of J g^{-1} K^{-1}, but it is important that it is converted. A material with a heat capacity of 1 J g^{-1} K^{-1} will have a capacity of 1000 J kg^{-1} K^{-1} in SI units.

In the exam:

Watch out for conversions. Make sure that your mass in the equation is in kilograms. It does not matter whether the temperature is in Celsius or Kelvin. The steps are the same, and it's the difference that matters.

Missing these conversions is a very common bear trap

We can measure the specific heat capacity of a metal in a simple experiment as shown in the diagram below (*Figure 14*):

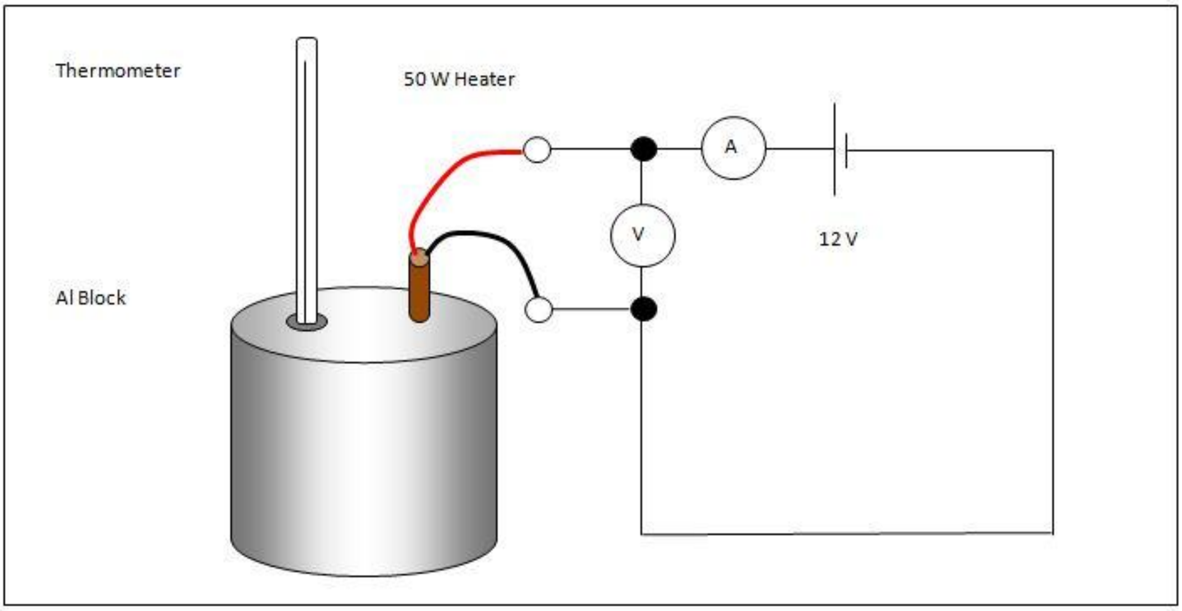


Figure 14 Finding the specific heat of an aluminium block

We measure the **voltage** and **current**, which gives us **power**. We should keep the voltage and current steady. We then measure the **temperature** and **time**.

We can easily work out the **energy** supplied by:

$$E = VIt \quad \text{………………}\textit{Equation 3}$$

We then need to plot the graph of temperature change against energy (*Figure 15*).

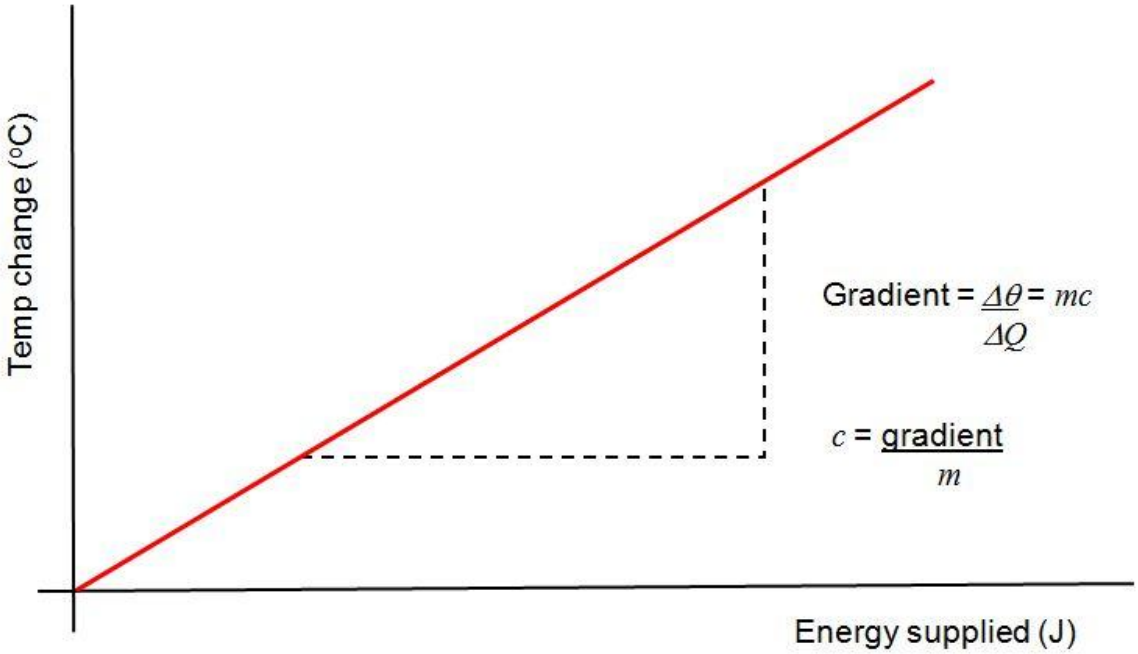


Figure 15 Finding the specific heat from a graph of temperature change against energy supplied

From this graph we can work out the specific heat from the gradient.

13.0111 Specific heat with two materials

You may well find yourself having to work with more than one material. An example of this may be:

- dropping a hot lump of metal into a beaker of water.
- taking into account the specific heat of a container, as oil is heated.

Although this may appear more complex, it's not that much harder than with a single material.

Suppose we have mass m_1 of a liquid of specific heat c_1 in a calorimeter (metal beaker) of mass m_2 and specific heat c_2. We want to change the temperature by $\Delta\theta$. To do this we need to supply ΔQ joules of energy (*Figure 16*).

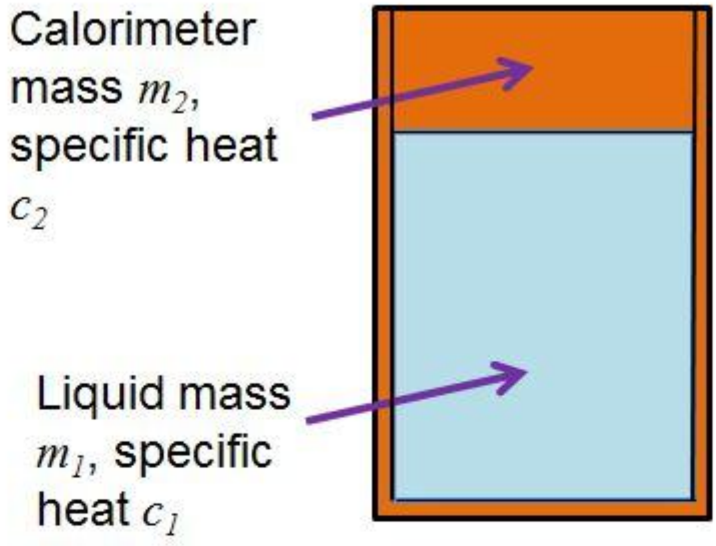


Figure 16 Working with two different specific heats

For the liquid:

$$\Delta Q_1 = m_1 c_1 \Delta\theta$$

.... *Equation 4*

For the calorimeter:

$$\Delta Q_2 = m_2 c_2 \Delta\theta$$

.... *Equation 5*

The total energy supplied is:

$$\Delta Q = \Delta Q_1 + \Delta Q_2$$

.... *Equation 6*

To reduce uncertainty, the calorimeter needs to be well insulated around its sides. It also needs to have a lid to reduce the heat loss by convection.

Here is a table of specific heat capacities of some materials:

Material	Specific Heat (J kg^{-1} K^{-1})
Aluminium	878
Copper	381
Iron	438
Lead	126
Ethanol	2410
Water	4200
Hydrogen	14150

The picture (*Figure 17*) shows some oil in a copper **calorimeter** (a metal beaker). As the oil gets hot, so will the calorimeter, so some energy will go to the oil, while some goes to the calorimeter. We will use this for the worked example:

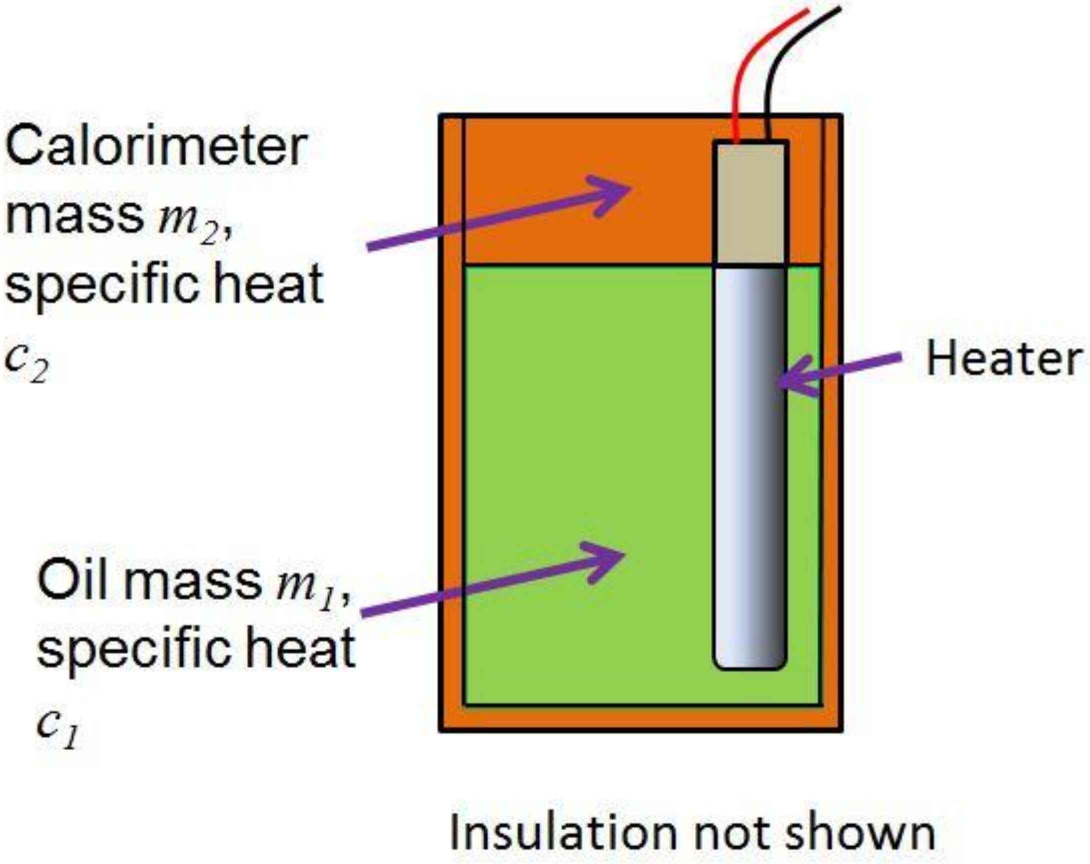


Figure 17 Oil being heated in a copper calorimeter

Worked Example

A copper calorimeter has a mass of 0.20 kg. Oil, of mass 0.12 kg, is placed into the calorimeter. The temperature of both the oil and the calorimeter is 20 °C. 15 kJ of energy is supplied to the oil and calorimeter, and the final temperature is 50 °C. What is the specific heat capacity of the oil? (c for copper = 381 J kg^{-1} K^{-1})

Answer

Formula:

$$\Delta Q = mc\Delta\theta$$

Calculate the energy taken by the calorimeter:

$$\Delta Q = 0.20\ \text{kg} \times 381\ \text{J kg}^{-1}\ \text{K}^{-1} \times 30\ \text{K} = 2286\ \text{J}$$

The remaining energy is used to heat the oil. So, take 2286 J from 15000 J

$$Q = 15000\ \text{J} - 2286\ \text{J} = 12714\ \text{J}$$

Now use this to calculate the specific heat capacity of the oil c' ("c-prime"):

$$c' = \frac{Q}{m\Delta\theta} = \frac{12714\ \text{J}}{0.12\ \text{kg} \times 30\ \text{K}}$$

$$c' = 3531 = \underline{\mathbf{3500\ J\ kg^{-1}\ K^{-1}}}$$

(data are to 2 significant figures, so 2 s.f. is appropriate)

Now let us see what happens if we drop a hot lump of metal into some cool liquid. The liquid will have a low starting temperature, while the metal has a high starting temperature. The key to solving a problem like this is the energy flow *DQ* from the metal is the same as the energy flow into the liquid. Let us look at that in the next example:

Worked Example

A lump of iron of mass 1.0 kg has a temperature of 500 K. It is dropped into 10 kg water which has a temperature of 300 K. Neglecting the heat capacity of the container, and assuming that the mass of water lost to steam is negligible, what is the final temperature of the iron and water? (Specific heat for iron = 438 J kg^{-1} K^{-1}. Specific heat for water = 4200 J kg^{-1} K^{-1}.)

The temperature change is NOT 200 K. The energy from the hot iron raises the temperature of the water. The energy going out of the iron means its temperature will fall.

Answer

The same energy leaves the iron as enters the water (Conservation of energy).

$$\Delta Q = 1.0 \text{ kg} \times 438 \text{ J kg}^{-1} \text{ K}^{-1} \times -\Delta\theta_1 = 10 \text{ kg} \times 4200 \text{ J kg}^{-1} \text{ K}^{-1} \times \Delta\theta_2$$

Now the end temperature is T. It will be the same for the iron and the water.

For the iron:

$$-\Delta\theta_1 = T - 500 \text{ K (it will be negative because it's a temperature drop)}$$

For the water:

$$\Delta\theta_2 = T - 300 \text{ K (it will be positive because it's a temperature rise)}$$

Now substitute:

$$1.0 \text{ kg} \times 438 \text{ J kg}^{-1} \text{ K}^{-1} \times -(T - 500 \text{ K}) = 10 \text{ kg} \times 4200 \text{ J kg}^{-1} \text{ K}^{-1} \times (T - 300\text{K})$$

$$438 \text{ J K}^{-1} \times (-T + 500 \text{ K}) = 42000 \text{ J K}^{-1} \times (T - 300\text{K})$$

$$-438\,T + 219\,000 \text{ J} = 42000\,T - 1.26 \times 10^7 \text{ J}$$

$$-42000\,T - 438\,T = -1.26 \times 10^7 \text{ J} - 2.19 \times 10^5 \text{ J}$$

$$42438\,T = 1.2819 \times 10^7 \text{ J}$$

T = **<u>302 K</u>** (to 3 significant figures).

In this case, it is important to use **absolute** temperatures. You will notice that the change in the temperature of the water is not very much. Water has a particularly high specific heat capacity, which means you need to put in a lot of heat to get even a small rise in temperature. That is why water is good at cooling things.

13.0112 Phases of Matter

From your GCSE work, you will know that solid materials have a **long range structure** that follows a regular pattern. There are bonds between all the atoms that determine the **crystal structure**. In liquids the molecules go about in small groups that can easily get past each other. In gases the molecules are on their own with a large distance between their neighbours.

When we heat a solid material, the temperature rises with the **heat flow** into the body of the material. However, when the material reaches its **melting point**, the temperature remains the same until all the solid has melted. The energy is still going in to break bonds. Once all the material is liquid, the temperature rises until the boiling point is reached. Then the temperature remains the same while all the bonds in the liquid are broken, and the liquid has boiled.

A change of state graph shows the idea of latent heat (*Figure 18*).

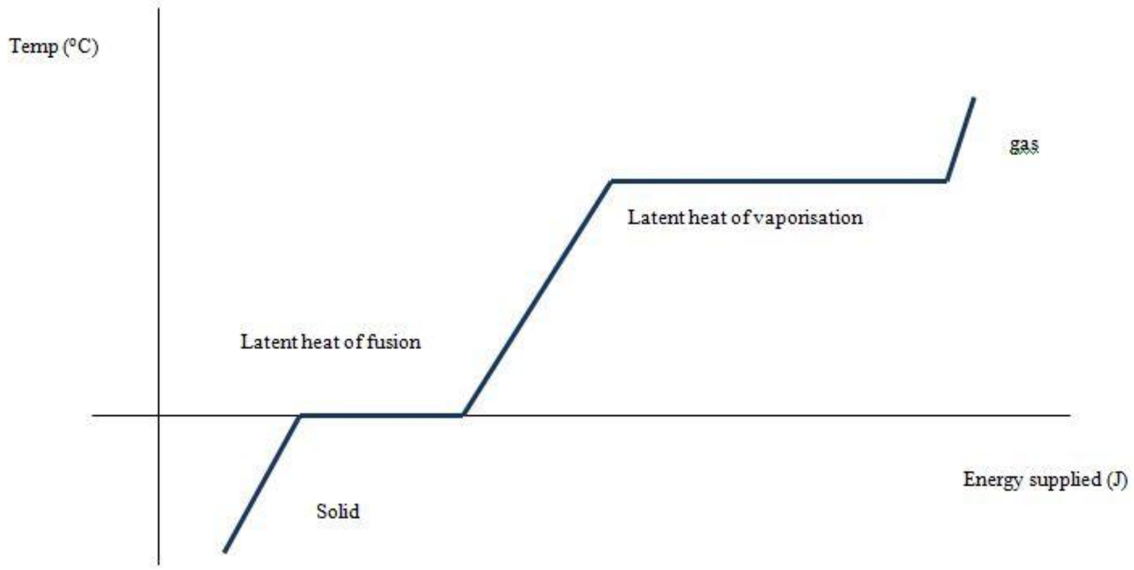


Figure 18 Changes of state

The **rise in temperature** is a reflection of the **increase in internal energy**. In simple terms, internal energy is about vibration of molecules. The greater the vibration of molecules, the higher the internal energy. When materials **change state**, work has to be done to break bonds between molecules. Also, most materials expand, so work has to be done against external forces. So, the latent heat represents the sum of these two:

- breaking of bonds.
- expansion of the material.

While the material is changing state, there no increase in internal energy, so the temperature stays the same.

The reverse is true. As a gas **condenses**, heat is given out. This heat can be made to do a job of work. However, as the gas condenses, there is no change in temperature. Nor is there a change in temperature as the liquid **freezes** to a solid.

While most work has been done on water (as it's very common and convenient to use), the same models can be applied to other substances. Investigating iron would not be easy, as it melts at over 1000 °C and boils at about 3000 °C.

13.0113 Latent Heat

The **specific latent heat** is the energy to change the state of a unit mass of liquid without a temperature change. There is a value for specific latent heat during:

- fusion, or melting
- vaporisation, or boiling.

Whichever of these latent heats we are using, the calculation is the same. The code for latent heat is L.

Energy flow = mass × specific latent heat.

$$\Delta Q = mL \qquad \text{.............. } \textit{Equation 7}$$

The units are **Joules per kilogram** (J kg^{-1}).

For water, the specific latent heat of fusion, L_m = 334 000 J kg^{-1}. The specific latent heat of vaporisation is rather higher, L_v = 2.3 x 10^6 J kg^{-1}.

Hot materials can do jobs of work, which is studied in detail in a discipline called **Thermodynamics** (see the option Applied Physics). The steam engine below (*Figure 19*) is an example of how hot fluids are used to do very large amounts of work.

Figure 19 Much heat is lost as waste from this steam engine

You can also see that a considerable amount of heat is being lost as waste steam.

Tutorial 13.01 Questions

13.01.1

Professor Turner warned his first year university class, "*...it is internal energy. If I catch any of you calling it 'heat', I will personally come out and thump you.*"

Can you explain the difference so that none of his students will get into trouble with the professor?

13.01.2

Water has a specific heat capacity of 4200 J kg^{-1} K^{-1}. What is the amount of energy that is needed to bring 1.5 kg water to the boil from 20 °C?

13.01.3

Here are the results of an experiment:

Joulemeter reading at the start	31225 J
Joulemeter reading at the end	43120 J
Temperature at the start	23 °C
Temperature at the end.	58 °C
Mass of the material	1.25 kg
Time taken	250 s

(a) Which piece of data is irrelevant?

(b) What is the specific heat capacity of the material?

13.01.4

(Harder) Calculate how much energy is needed to melt, bring to the boil, and boil away 0.5 kg water. How long would this take a 2 kW kettle?

Tutorial 13.02 The Equation of State for an Ideal Gas

All Syllabi

Contents

13.021 The Ideal Gas	13.022 Ideal Gas Equation
13.023 The Mole	13.024 Investigating Boyle's and Charles' Law

13.021 The Ideal Gas

We will be looking at gases and their behaviour under different conditions. The behaviour of **ideal** gases is quite easily predictable. However real gases tend to behave slightly differently, especially those that consist of molecules. So the ideal gas we will consider is:

- monatomic (the molecules are single atoms, for example Ar).
- at low temperature.
- at low pressure.

There is no interaction between the molecules of an ideal gas except for collisions, which are always **perfectly elastic**. Helium is a good example of an ideal gas.

13.022 Ideal Gas Equation

There are three **gas laws**:

- Boyle's Law
- Charles' Law
- Pressure Law

These gas laws led to several important concepts in Physics. Boyle's Law and Charles' Law are **required practicals**.

Boyles Law (*Figure 20*)

Pressure is inversely proportional to the volume

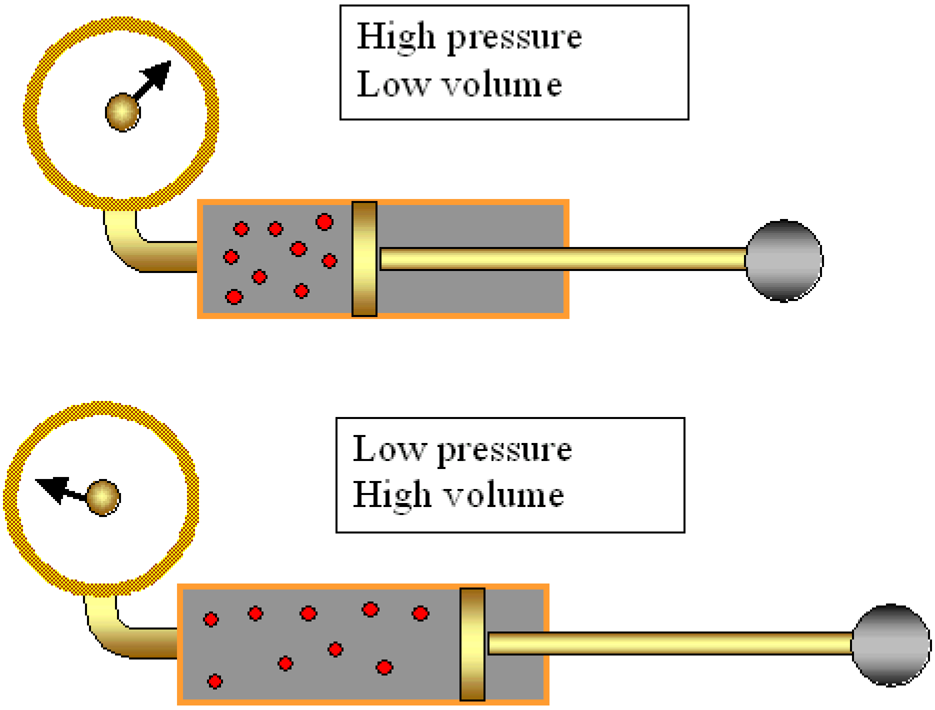


Figure 20 Boyles's Law

We can plot the data as a graph (*Figure 21*).

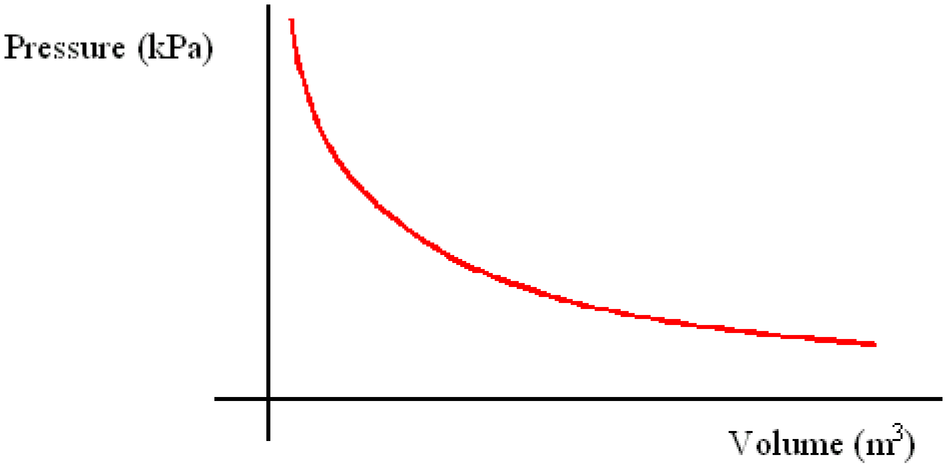


Figure 21 Graph of pressure against volume (Boyle's Law)

We can see that the data fit into a pattern called a **hyperbola**. If, however we plot **pressure** against **1/volume** we get a **linear** (straight line) graph that shows direct proportionality (*Figure 22*).

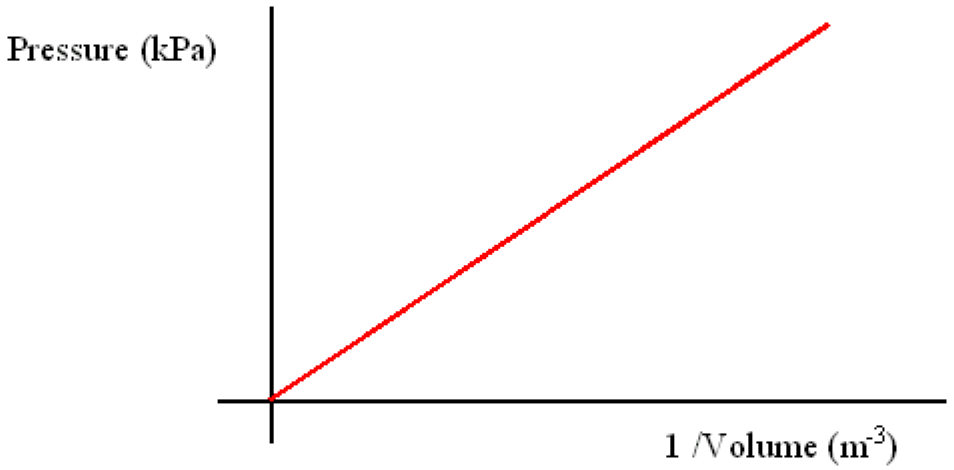


Figure 22 Pressure against 1/volume

Since the line goes through the origin, we say that the two quantities are directly proportional.

So we can say that

$$P \propto 1/V$$ ………….. *Equation 8*

Therefore:

$$P = k/V$$ ……………… *Equation 9*

where k is a constant.

Rearranging:

$$PV = \text{constant}$$ .... *Equation 10*

The picture below shows a data-logging experiment for Boyle's Law (*Figure 23*)

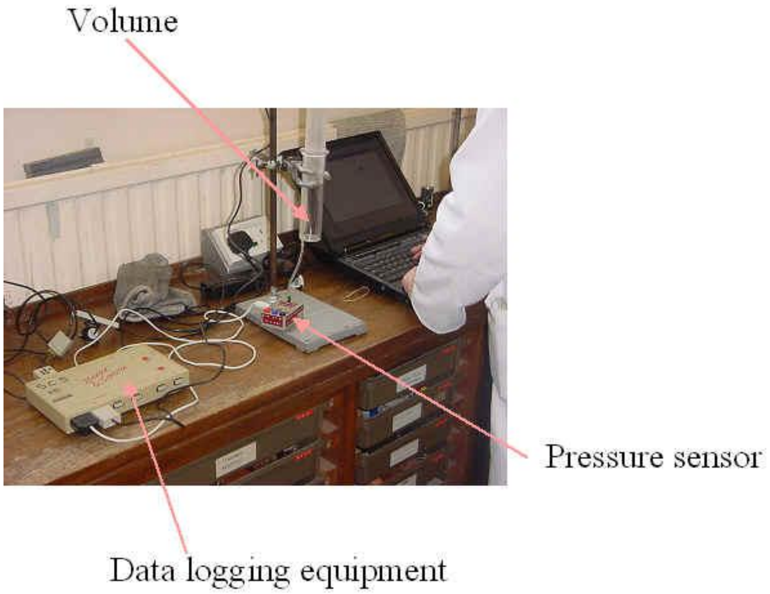


Figure 23 Data logging experiment for Boyle's Law

Charles' Law

The volume of an ideal gas is proportional to its Kelvin temperature.

The traditional way was to use a small drop of concentrated sulphuric acid in a capillary tube and heat it in water, watching it move up the capillary as the temperature got higher. Getting good thermal contact is quite difficult in the experiment, so there is quite a lot of uncertainty. We can use data logging equipment to show the experiment (*Figure 24*).

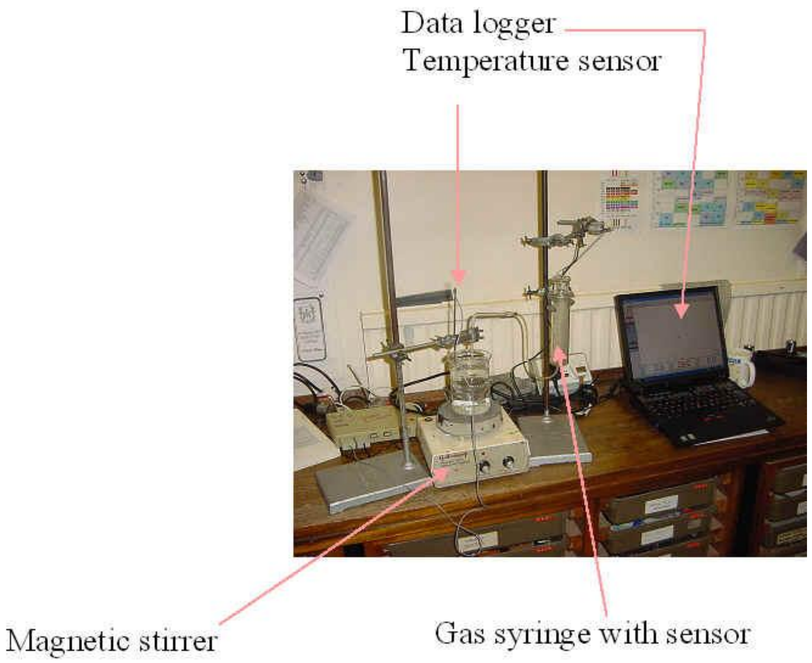


Figure 24 Data-logging for Charles' Law

Whichever way we get the data, the ideal graph is like this (*Figure 25*).

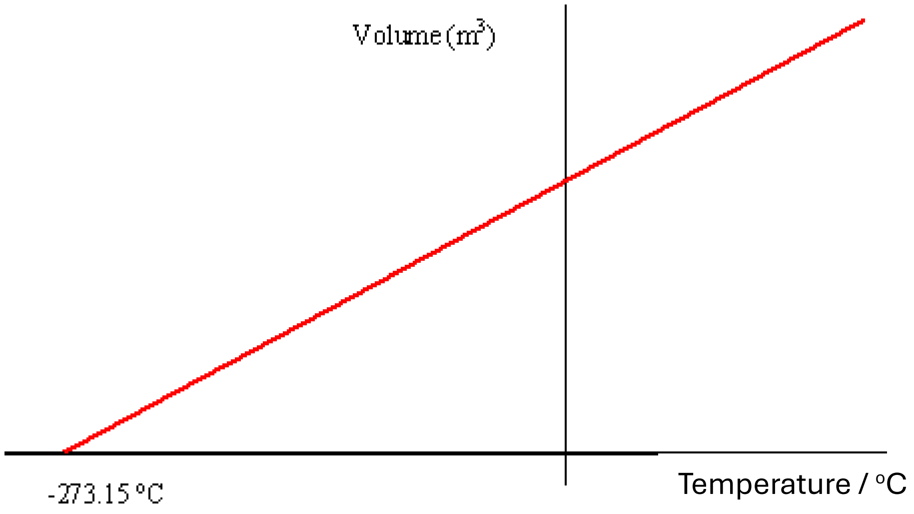


Figure 25 Graph of volume against temperature for Charles' Law

Whatever the gas we use, we find that the line always, without exception passes through the temperature axis at a very particular value, **-273.15 °C**. This led to the concept of absolute zero, discovered by William Thomson, Lord Kelvin (1824 - 1907). If we plot from the absolute zero point, 0 Kelvin, we get (*Figure 26*):

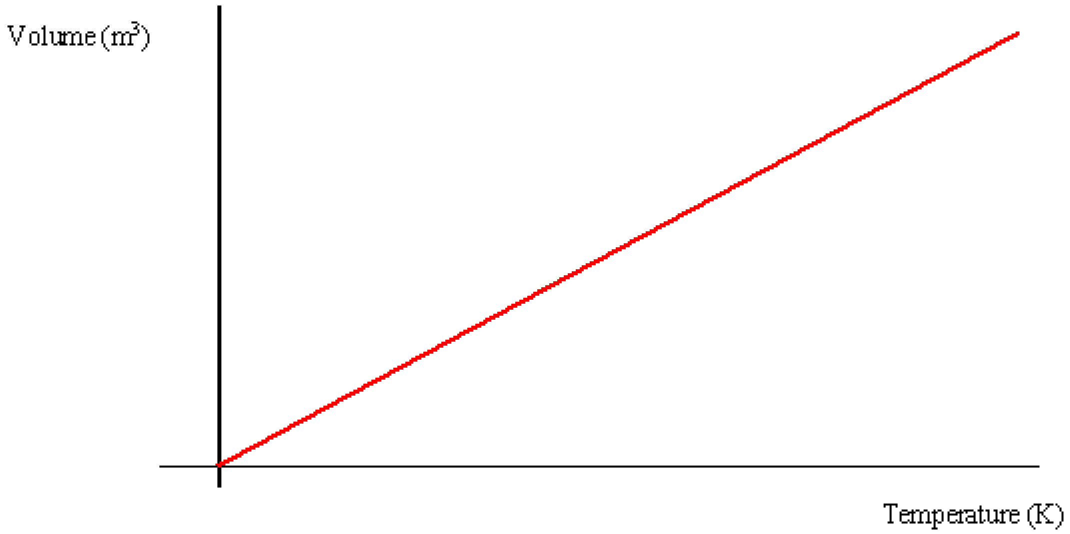


Figure 26 Volume against Kelvin temperature for Charles' Law

This allows us to say:

$$V \propto T \text{ ……………. Equation 11}$$

Therefore:

$$V = kT \quad \text{……………} \; \textit{Equation 12}$$

where k is a constant

Rearranging:

$$V/T = \text{constant} \quad \text{…………..} \; \textit{Equation 13}$$

To convert from Celsius to Kelvin, we use the following equation:

$$T = \theta + 273 \quad \text{…………..} \; \textit{Equation 14}$$

where:

- T is the temperature in K.
- θ is the temperature in °C.

It is not possible to get below 0 K. You cannot get -274 °C. At 0 K all molecular motion stops completely.

The Pressure Law:

This law tells us that pressure is proportional to the Kelvin temperature. The traditional way to demonstrate this is with a large glass sphere immersed in water, connected to a manometer, a rather low tech (but remarkably accurate) way of detecting small differences in gas pressure (*Figure 27*).

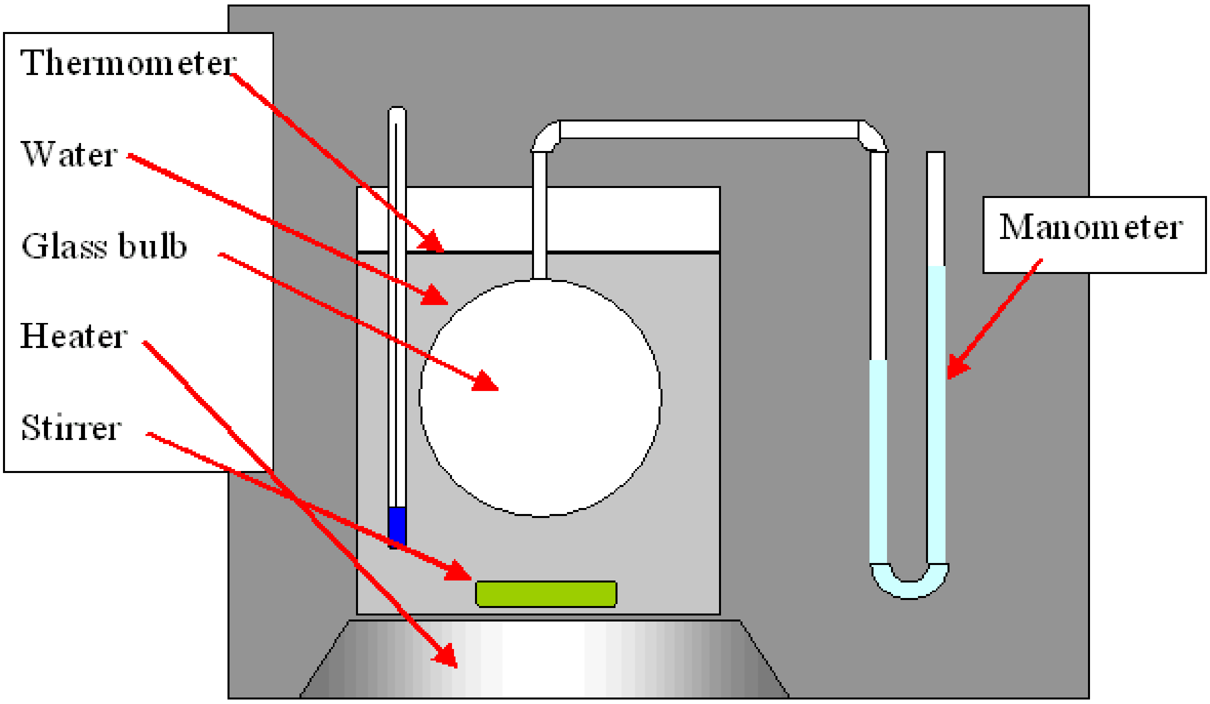


Figure 27 Demonstrating the Pressure Law

We can demonstrate the same using data-logging equipment like this:

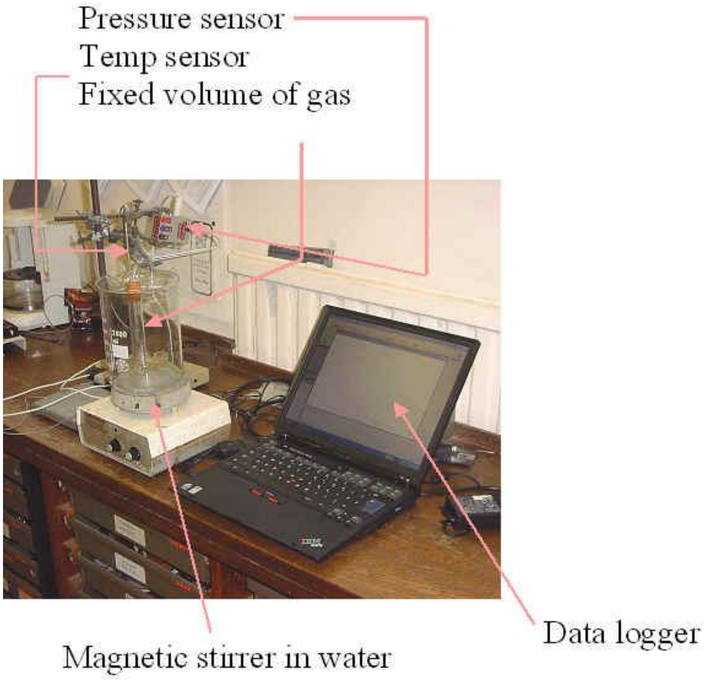


Figure 28 Datalogging for the Pressure Law

We can show this on a graph like this (*Figure 29*):

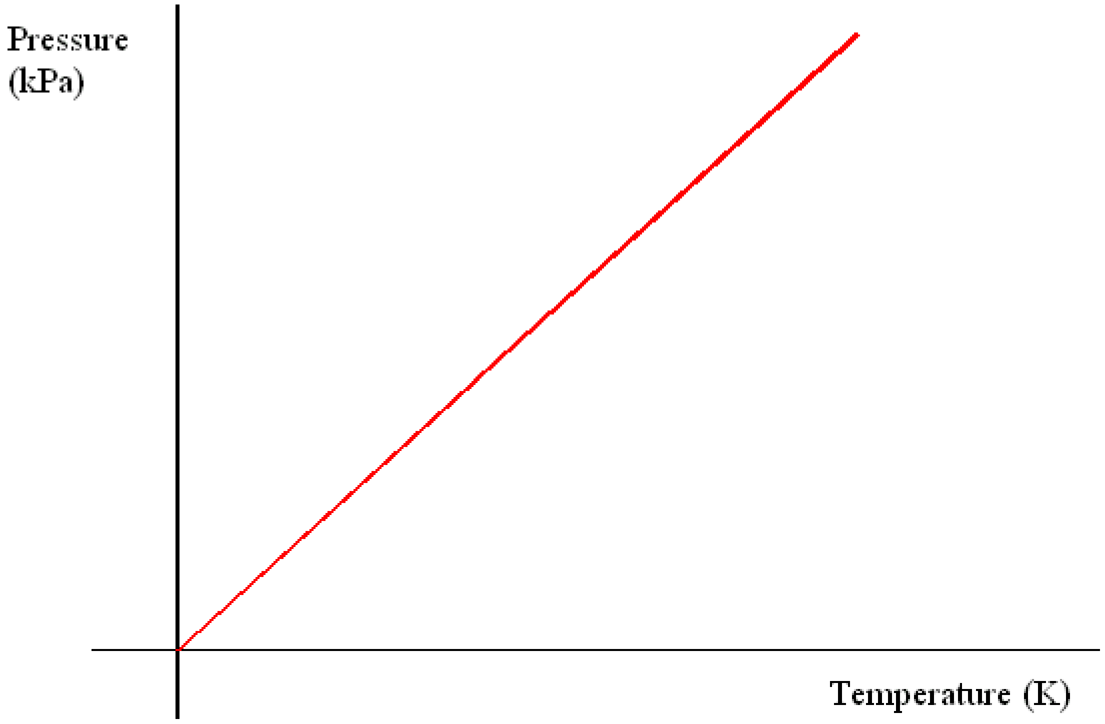


Figure 29 Graph of Pressure against temperature for the Pressure Law

So we can write:

$$P \propto T \quad \text{………….. } \textit{Equation 15}$$

Therefore

$$P = kT \quad \text{………….. } \textit{Equation 16}$$

Rearranging:

$$P/T = \text{constant} \quad \text{…………… } \textit{Equation 17}$$

Equations 10, 13 and *17* can be combined to give:

$$\frac{PV}{T} = \text{constant} \quad \text{…………… } \textit{Equation 18}$$

From the gas laws we can write:

$$pV = RT$$ …………… *Equation 19*

Notice that this constant is given the code R, rather than k.

The value of the constant depends on how much gas is being considered. If we are looking at one mole of gas (which we will define later), then the constant is the **universal molar gas constant**. This is given the code R and has the value **8.31 J mol^{-1} K^{-1}**.

For n moles of a gas, we can write:

$$pV = nRT$$

…………. *Equation 20*

Where:

- p - pressure (Pa)
- V - volume (m^3)
- n - number of moles
- R - molar gas constant (**8.31 J mol^{-1} K^{-1})**
- T - Temperature (K)

This is called the **equation of state of an ideal gas**. In this equation, SI units must be used, i.e. volume in m^{-3}, pressure in Pa. Temperature must be in **Kelvin** (K). 0 K = -273 °C.

The temperature quoted in degrees Celsius is commonly set as a bear trap. Make sure you don't fall into it.

A more useful version of the ideal gas equation is this:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

.... *Equation 21*

The term p_1 stands for pressure in container 1 while p_2 stands for pressure in container 2. The same is true for the volume and the temperature.

13.023 The Mole

The **mole** is defined as**:**

the same number of particles of a substance as there is in 12 g of ^{12}C.

This number is called the **Avogadro constant**, and is given the codes L or N_A.

L = 6.02 x 10^{23} mol^{-1}

The molar mass M_m is the **mass of 1 mole** of the substance. Chemists quote this in grams per mole; for physics we need to convert to kilograms per mole by dividing by 1000 (or multiplying by 10^{-3}).

A rule that is important for chemists is that equal numbers of moles occupy the same volume of space. 1 mole of any gas occupies 0.0224 m^3 at **Standard Temperature and Pressure** (STP), where temperature is 273 K and pressure is 1.01×10^5 Pa.

13.024 Investigating Boyle's and Charles' Law

This is a **required practical** (Number 8). We have discussed the theory in the notes above. Apparatus that is suitable for investigating Boyle's Law is like this (*Figure 30*).

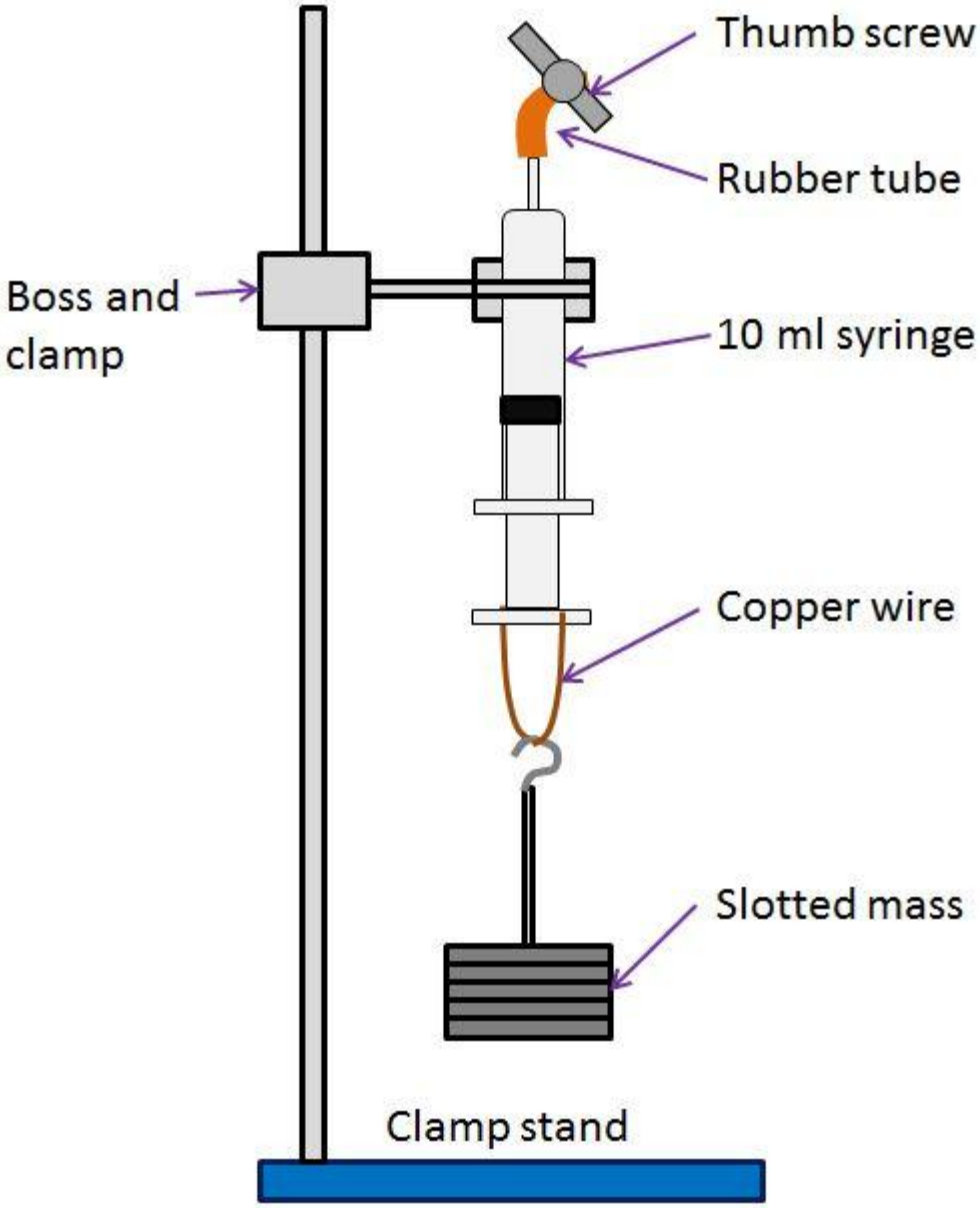


Figure 30 Investigating Boyles Law

You need to follow a procedure like this:

- Clamp the clamp stand to the bench to stop it rocking.
- Use a micrometer to measure the diameter of the plunger. Convert the reading into metres.
- Calculate the area of the plunger. ($A = \pi D^2/4$).

- Replace the plunger and draw in about 4 to 5 cm^3 of air.
- Place the rubber tubing over the nozzle. Tighten up the thumbscrew clip (pinch-clip).
- Clamp the syringe. This should not be too tight, as it will distort the syringe and could make it stick. It should not be too loose either, because the weight of the slotted masses could pull it away from the clamp.
- The slotted masses should be attached to the plunger using a loop of copper wire which can be wrapped around the plunger. (I have found that string can easily come undone, which is a bit of a pain.)
- Move the plunger up and down to make sure it moves freely.
- Add 200 g at a time to a maximum of 1000 g and measure the new volume.
- Do at least one more set of repeat readings.

You will need to covert the mass to weight, using g = 9.81 N kg^{-1}. You will then need to get the pressure using:

$$p = \frac{F}{A}$$

.... *Equation 22*

You then need to subtract this from the standard atmospheric pressure (= 100 kPa). This is the pressure you will plot on a graph of $1/V$ against P. This should be a straight line passing through the origin.

Having done this experiment with my students, I would say that you would be lucky to get a good straight line. The plungers on cheap 10 ml syringes tend to be rather sticky. If your school or college has a class set of glass gas syringes, you will get better results. However, if you break one, it's expensive! The risk of this is reduced by holding the syringe horizontally, and running the string over a bench pulley (*Figure 31*).

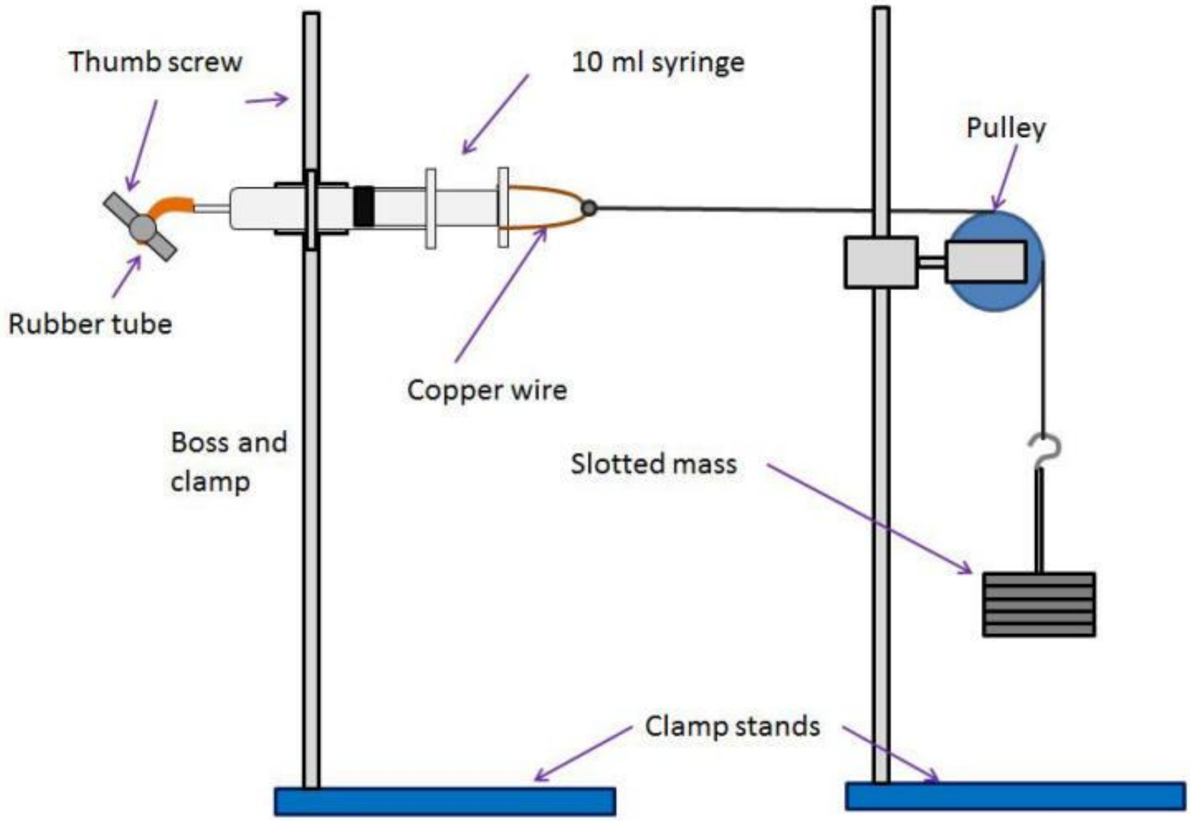


Figure 31 An alternative set up for Boyle's Law investigation

Charles' Law

The capillary tube will be set up for you. If it isn't you will be given instructions on how to do it by your tutor. (I would be highly surprised if this were the case. In the vast majority of schools and colleges, the technician or tutor would do this.)

The apparatus below has a small bead of concentrated sulphuric acid in the capillary tube. Concentrated sulphuric acid is highly dangerous. You will need to wear gloves, a lab coat, and goggles. You must keep your face well away from the apparatus.

The apparatus is shown in *Figure 32*.

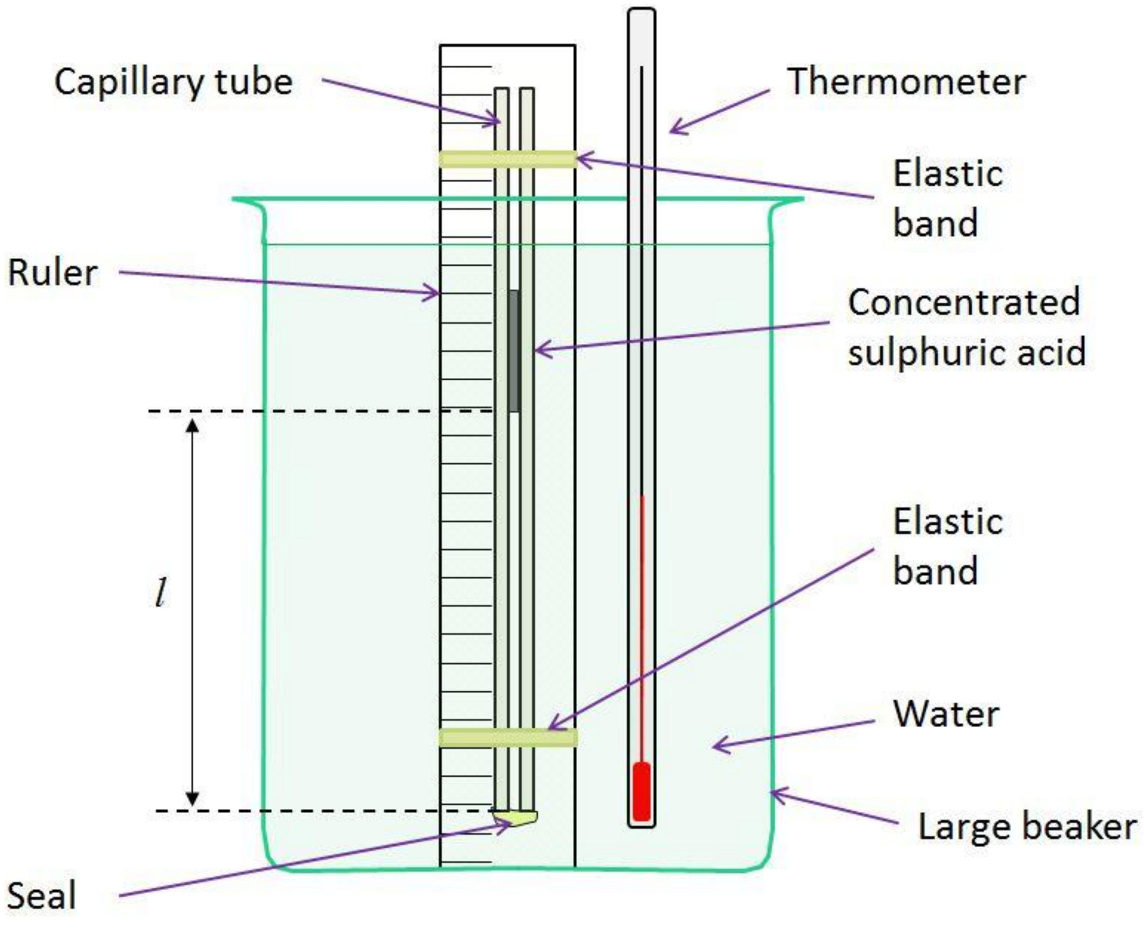


Figure 32 Investigating Charles' Law

You will need to do the following:

- Fill the beaker from a kettle.
- Stir the water **with a glass rod** (I was always taught <u>not</u> do do this with the thermometer).
- Read the value of length of the air sample, l, and the temperature on the thermometer, θ.
- Allow the water to cool, taking readings every 5 °C fall. You can speed up the process by removing a little of the water with a syringe, and placing the same amount of cold water.
- Plot a graph of l against θ.

You may want to heat the water up with an immersion heater instead. This would allow you more control of the temperature, so that you could do repeats.

You can then use your graph to calculate the value of absolute zero. Your graph will look something like this (*Figure 33*).

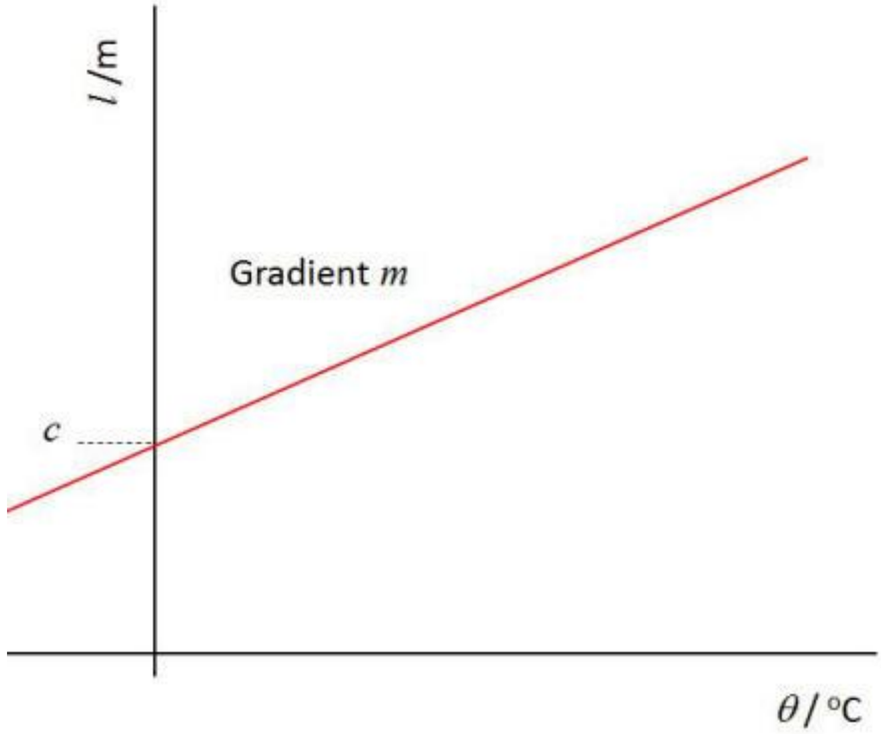


Figure 33 Graph of length against temperature

You need to work out the gradient, m. The equation will be:

$$l = m\theta + c$$

.... *Equation 23*

At absolute zero, $l = 0$. Therefore:

$$0 = m\theta_0 + c$$

.... *Equation 24*

Therefore:

$$\theta_0 = \frac{-c}{m}$$

.... *Equation 25*

This, hopefully, should be -273 °C as shown on this graph (*Figure 34*).

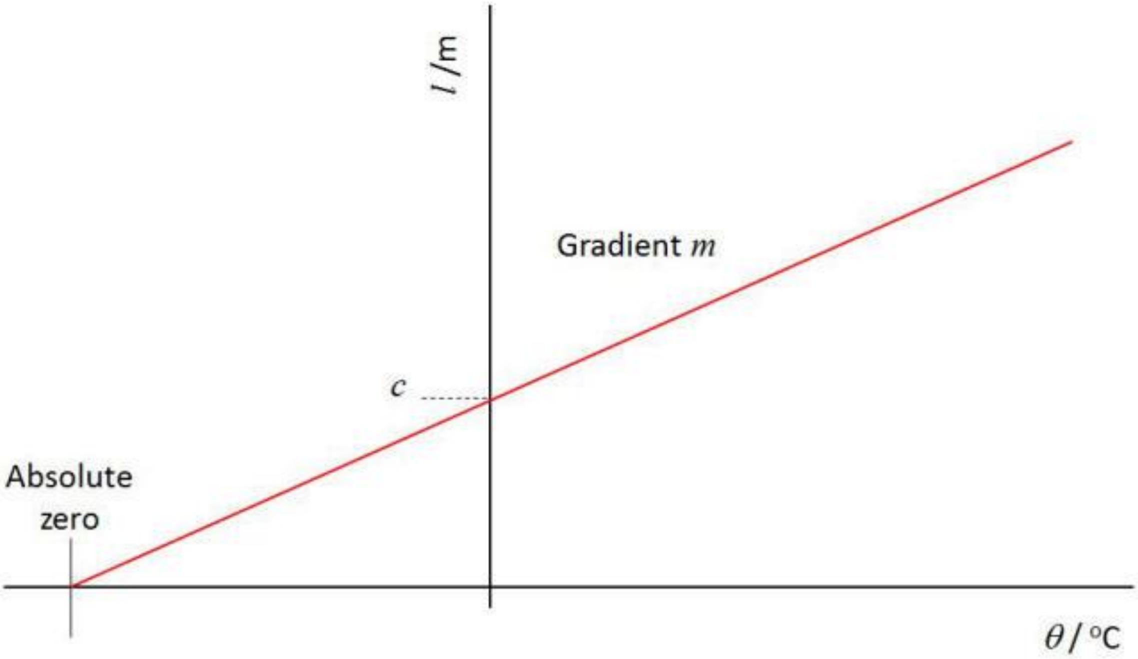


Figure 34 Extended Charles' Law graph showing absolute zero

Tutorial 13.02 Questions

13.02.1

Why is air not an ideal gas?

13.02.2

What is the volume of 2 moles of helium atoms at a temperature of 20 °C and a pressure of 100 kPa?

13.02.3

A SCUBA* diver is deep underwater at a point where the pressure is 3.03×10^5 Pa, and the temperature is 10 °C. The volume of her lungs is 3.0 litres. She spots a dangerous animal and rises very rapidly to the surface where the temperature of the water is 20 °C and the air pressure is 1.01×10^5 Pa. What is the volume of air in her lungs now?

*SCUBA stands for Self-Contained Underwater Breathing Apparatus.

13.02.4

A sealed container of volume 0.8×10^{-3} m^3 contains gas at a temperature of 320 K and a pressure of 1.5×10^6 Pa. Calculate:

a) The number of moles and molecules of the gas.

b) The mass of the gas if its molar mass is 32.0×10^{-3} kg

c) The mass of a single molecule of gas.

Tutorial 13.03 Molecular Kinetic Theory

All Syllabi

Contents

13.031 Molecular Kinetic Theory Model	13.032 Pressure Exerted by an Ideal Gas
13.033 Internal Energy and Kinetic Energy	

13.031 Molecular Kinetic Theory Model

The model, which we will study in this tutorial, tells us how gases behave. The topic fits quite well with mechanics because you need to understand about collisions to make sense of the Kinetic Theory model. It may be worth revising these ideas in Mechanics.

In mechanics we have been looked at big things, like tennis balls, cars, people, to name but a few. This can be referred to as the **macroscopic level**. In this piece of work we will go down to the molecular level, where things are very small. We call this the **microscopic** level.

A Scottish botanist, Robert Brown, first suggested that gases were in a state of random motion. He observed that pollen particles seem to jiggle about for no apparent reason. We can see the same by observing smoke particles under a microscope. The random jerky movement of the particles is called **Brownian motion** and is due to the continuous and random bombardment by air molecules (*Figure 35*).

The work of Einstein, Maxwell, and Boltzmann gave us the **kinetic theory,** as we know it today.

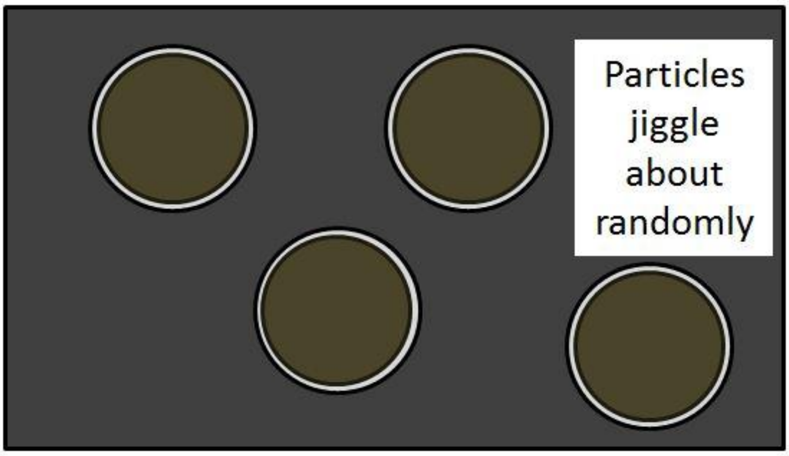


Figure 35 Brownian motion

13.032 Pressure Exerted by an Ideal Gas

Pressure is exerted by the impact of molecules on the sides of a container. We can use the idea to derive an expression for gas pressure. We must make the following **assumptions**:

The gas consists of a large number of **identical** molecules, such that the statistical treatments are meaningful.

- All **collisions** between molecules and the walls of the container are **perfectly elastic**.
- Intermolecular forces are **negligible**, as is gravity.
- Molecules move in **straight lines** and at **constant speed** between collisions.
- **Collision times** are **negligible** compared with time between collisions.
- **Volume** of the gas molecules is **negligible** compared to that of the gas.
- **Newton's laws of motion** are applicable.

Health Warning: The derivation of the kinetic theory equation is rather tedious but it's on the syllabus.

Here we go:

Stage 1 Momentum Change

Consider a large box, side l, full of molecules (*Figure 36*).

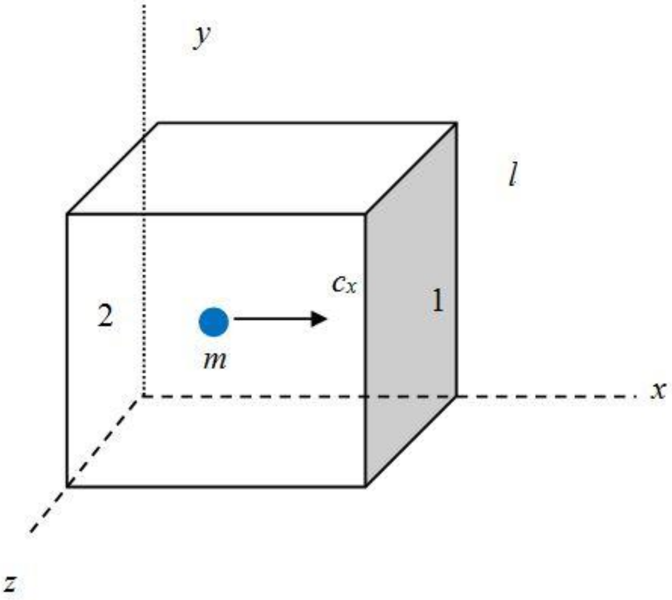


Figure 36 Box full of molecules

Now consider one molecule of mass m moving towards face 1 and the x-component of its velocity is c_x.

$\Rightarrow$ its momentum in the x direction is mc_x

At face 1 there is a perfectly elastic collision so that the momentum is reversed to $-mc_x$.

This results in a **momentum change** of:

$$mc_x - (-mc_x) = 2mc_x \text{ ……………… } \textit{Equation 26}$$

After colliding with face 1, the molecule travels a distance $2l$ before it collides again with face 1 again. This takes a time t, which is given by:

$$t = \frac{2l}{c_x} \text{ .... } \textit{Equation 27}$$

Stage 2 Impulse

So that we can get the pressure, we need to know the force. This can be worked out by Newton II, considering the **impulse**, which is the change of momentum (Δp).

$$\Delta p = F\Delta t \text{ ……….…. } \textit{Equation 28}$$

Rearranging gives us:

$$F = \frac{\Delta p}{\Delta t} \text{ ....} \textit{Equation 29}$$

Time interval is the time taken for the molecule to move up the box to the far end, bounce off and come back again.

Time = distance ÷ speed

$$t = \frac{2l}{c_x}$$

…………… *Equation 30*

Therefore, cobining *Equations 29* and *30*:

$$F = \frac{2mc_x}{2l/c_x} = \frac{m(c_x)^2}{l}$$

……………. *Equation 31*

Stage 3 Working out the pressure

Since *pressure* = *force* ÷ *area*, we can work out the pressure on face 1.

The area of face 1 = l^2.

$$p = \frac{F}{A} = \frac{m(c_x)^2/l}{l^2} = \frac{m(c_x)^2}{l^3}$$

………… *Equation 32*

Suppose we have N molecules of gas. The pressure will be:

$$p = \frac{m[(c_{x1})^2 + (c_{x2})^2 + (c_{x3})^2 + \cdots + (c_{xN})^2]}{l^3} = \frac{mN(c_x)^2}{l^3}$$

………….. *Equation 33*

Now l^3 is the volume V of the gas, so we can rewrite the equation:

"c - x-squared bar"

$$p = \frac{Nm\overline{c_x{}^2}}{V}$$

……………*Equation 34*

This can also be written as:

$$p = \frac{Nm < {c_x}^2 >}{V}$$

.... *Equation 35*

The term $<c_x{}^2>$ ("c-x-squared bar") is called the **mean square speed** of the molecules in the x direction. The bar is written over the c^2, as above in *Equation 34*. (Notice the different way of writing it in the text. You may see this in some books)

Stage 4 The Statistics

However the molecules are moving randomly in the container and very few would be moving exactly parallel to the x-axis. However we can consider each molecule's velocity to be the resultant of three components, c_x, c_y, and c_z.

As in two dimensions, the three components can be combined by Pythagoras to give the resultant velocity:

$$c^2 = c_x^2 + c_y^2 + c_z^2$$

.... *Equation 36*

Similarly we can combine the mean square velocities:

$$\overline{c^2} = \overline{c_x^2} + \overline{c_y^2} + \overline{c_z^2}$$

.... *Equation 37*

Since there are a large number of molecules we can assume that there are equal numbers moving in each of the co-ordinate directions:

$$\overline{c_x^2} = \overline{c_y^2} = \overline{c_z^2}$$

.... *Equation 38*

So we can write:

$$\overline{c^2} = 3\overline{c_x^2} \Rightarrow \overline{c_x^2} = 1/3\ \overline{c^2}$$

.... *Equation 39*

So our final equation becomes:

$$pV = \frac{1}{3}Nm\overline{c^2}$$

.... *Equation 40*

Which we can rewrite as:

$$p = \frac{1}{3}\frac{Nm\overline{c^2}}{V}$$

.... *Equation 41*

Stage 5 Density

However we can go further. Since Nm is the total mass of the gas and V is the volume, we can express the pressure in terms of the **density**.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{Nm}{V}$$

This gives us the equation:

$$p = \frac{1}{3}\rho\overline{c^2}$$

.... *Equation 42*

Maths Note

Be careful of the difference between the square of the mean $(<c>)^2$ ["c-bar squared"] and the mean square $<c^2>$ ["c-squared bar"].

Consider 1 + 2 + 3 = 6. The average is 2 and the square of the mean is 4. $(1^2 + 2^2 + 3^2) \div 3 = (1 + 4 + 9) \div 3 = 14 \div 3 = 4.67$, so there is quite a difference.

The **most probable speed** is that at which the greatest number of molecules are moving. The **mean speed** is the average value of all the speeds. The **root mean square speed** is the square root of the mean square speed of the molecules. They are slightly but significantly different.

13.033 Internal Energy and Kinetic Energy of Molecules

The internal energy of a material is the sum of its potential and kinetic energies. In an ideal gas the molecules are so far apart that intermolecular forces can be ignored. Therefore there is no potential energy. So all the energy is kinetic. The total kinetic energy is shared **randomly** throughout the molecules in the gas. Therefore there is a random distribution of the speeds of the molecules, which we can show on a graph (*Figure 37*).

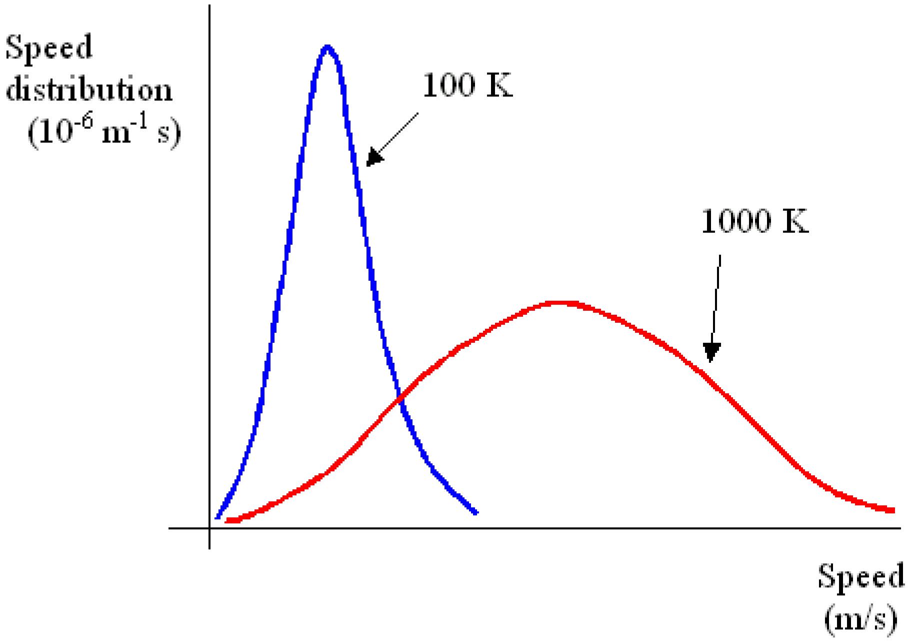


Figure 37 Speed distribution of molecules at 100K and 1000 K

If no energy is being transferred as heat between an object and its surroundings, we say that it is in **thermal equilibrium**. If a gas is in thermal equilibrium and it is not being compressed or expanded, the average kinetic energy will remain constant, so will the temperature.

We have seen that:

$$pV = nRT$$ (*Equation 20*)

and:

$$pV = \frac{1}{3}Nm\overline{c^2}$$

(*Equation 40*)

It does not take a genius to see that:

$$nRT = \frac{1}{3}Nm\overline{c^2}$$

.... *Equation 43*

We also know that kinetic energy,

$$E_\mathrm{k} = \frac{1}{2}mv^2$$

.... *Equation 44*

or:

$$E_\mathrm{k} = \frac{1}{2}mc^2$$

.... *Equation 45*

We can now rewrite our expression *Equation 43* as (since 2/3 ×1/2 = 1/3):

$$nRT = \frac{2}{3}N\left(\frac{1}{2}m\overline{c^2}\right)$$

.... *Equation 46*

We can rearrange this to write:

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}\frac{nRT}{N} = \frac{3}{2}\frac{RT}{N/n}$$

.... *Equation 47*

Since N is the total number of molecules and n is the number of moles, N/n will always be N_A, which is **Avogadro's number**, 6.02 $\times 10^{23}$ mol^{-1}.

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}\frac{RT}{N_A}$$

.... *Equation 48*

Now R/N_A is called **Boltzmann's constant** and is given the code k.

$$k = \frac{R}{N_A}$$

.... *Equation 49*

We can easily work out the value for k.

$$k = \frac{8.31\ \mathrm{J\ mol^{-1}K^{-1}}}{6.02 \times 10^{23}\mathrm{mol^{-1}}} = 1.38 \times\ 10^{-23}\ \mathrm{J\ K^{-1}}$$

.... *Equation 50*

So the equation now becomes:

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}kT$$

.... *Equation 51*

The translational kinetic energy of an ideal gas molecule is NOT dependent on what the gas is. It is only dependent on the temperature. So the kinetic energy of helium atoms is the same as the kinetic energy of xenon atoms at a given temperature.

Remember the bear trap. Temperature must be in Kelvin.

Tutorial 13.03 Questions

13.03.1

The observed speed of ten particles at a particular instant are shown in the table:

Number of Particles	1	2	4	1	1	1
Speed (m/s)	5.0	7.0	9.0	12.0	14.0	15.0

(a) What is the most probable speed?

(b) What is the mean speed?

(c) What is the rms speed of the molecules?

13.03.2

Nitrogen gas is kept in a closed container at a temperature of 27 °C and the pressure is 1.0×10^5 Pa. The density of nitrogen is 1.25 kg m^{-3}. Calculate:

(a) the rms speed of the molecules;

(b) the temperature at which the molecules travel twice as fast.

13.03.3

A cylinder of volume 0.25 m^3 contains nitrogen gas at a temperature of 17 °C and a pressure of 1.0×10^5 Pa. Molar mass of nitrogen = 0.028 kg mol^{-1}. Calculate:

a) The number of moles of gas in the cylinder

b) The rms speed of the gas molecules at 17 °C

c) The average translational kinetic energy of a nitrogen molecule;

d) The total kinetic energy of the gas in the cylinder. Give your answer to an appropriate number of significant figures.

Tutorial 13.04 The Laws of Thermodynamics

Cambridge Pre U

Contents

13.041 History of Thermodynamics	13.042 Language of Thermodynamics
13.043 Principles of Thermodynamics	13.044 The Zeroth Law of Thermodynamics
13.045 The First Law of Thermodynamics	13.046 The Second Law of Thermodynamics
13.047 Entropy	13.048 Entropy and Energy
13.049 Entropy and Cosmology	13.0410 The Third Law of Thermodynamics

This is quite a long tutorial. It is ONLY for students studying the Cambridge Pre U syllabus. It will NOT be examined at A-level. However, if you are going to study Physics at university, you may find this a useful introduction.

13.041 History of Thermodynamics

Thermodynamics is a branch of physics that links matter and energy. The science of thermodynamics has common rules that govern the interactions between matter and energy from the very large (**macroscopic**), for example a nebula formed by a supernova, to the everyday, for example the way a car uses its petrol or diesel, right down to the very small (**microscopic**), for example the energy in an atom. Thermodynamics was studied in the Industrial Revolution to find ways of making ways of making steam engines more efficient.

The first studies were carried out by a French engineer, Nicolas Léonard Sadi Carnot (1796 - 1832) and published in 1824. He introduced a concept of caloric, in which heat was an invisible fluid of zero mass. **Caloric** ran downhill from the boiler through a steam engine to the condensers. Energy could be extracted from the downhill flow, like a water mill extracting energy from the downhill flow of water in a river. Although caloric does not exist, Carnot's Principle is still valid. Its results are that there is a **maximum efficiency** for any heat engine (steam, turbine, or internal combustion engine. The maximum efficiency is determined by the **difference in** temperature of the source and the temperature of the coolant. Engineers often call this the **temperature gradient**.

Quantitative studies of heat flow was carried out by James Prescott Joule (1818 - 1889) in his father's brewery in Manchester. He disproved the existence of caloric and produced much of the groundwork for our understanding of the link between work, energy and temperature. Joule's work also laid the foundation for the Molecular Kinetic Theory.

Joule's work was developed further by William Thomson (1824 - 1907), better known as Lord Kelvin. Thomson's work was then taken even further by a German physicist, Rudolf Julius Emmanuel Gottleib (1822 - 1888), who is usually known by a Latin name, Clausius (it was a fashionable thing to do in those days). Both concluded that the quantity of energy remained the same in a steam engine, but its distribution changed irreversibly. Both Gottleib and Thomson's work led to two versions of the **Second Law of Thermodynamics**.

Ludwig Eduard Boltzmann (1844 - 1906) explained how the behaviour of particles on the microscopic scale could affect our understanding of flows of energy on the macroscopic scale. It was Boltzmann's work that led to the Molecular Kinetic Theory that we have seen in Tutorial 13.03.

13.042 Language of Thermodynamics

We need to be aware of some of the key ideas for us to make sense of Thermodynamics:

- **Energy** is the ability to do work.
- **Internal energy** is the result of motion of molecules. This can be due to movement of molecules (translational kinetic energy), and/or the vibration of intermolecular bonds.
- **Heat** is a flow of energy from a region of high internal energy to low internal energy.
- **Temperature** is a measure of internal energy, not heat.
- A **hot reservoir** is a region of high temperature.
- A **cold reservoir** is a region of low temperature.
- **Absolute zero** is the temperature at which all molecular movement ceases (-273.15 °C, or 0 K). It is impossible to have -1 K.
- **Entropy** is a concept in which energy becomes less useful. As entropy increases, energy gets more spread out and less useable.
- **Temperature gradient** the temperature per unit length. Units are K m^{-1}.

- **Thermal Equilibrium** is where the energy flow (heat) is **zero** between two reservoirs.
- **Efficiency** is the ratio between the work got out and the energy put in.
- A **diathermal** system allows heat to flow in and out.
- An **adiabatic** system keeps the heat in, so that there is no heat flow.

The idea of a temperature gradient is shown below (*Figure 38*).

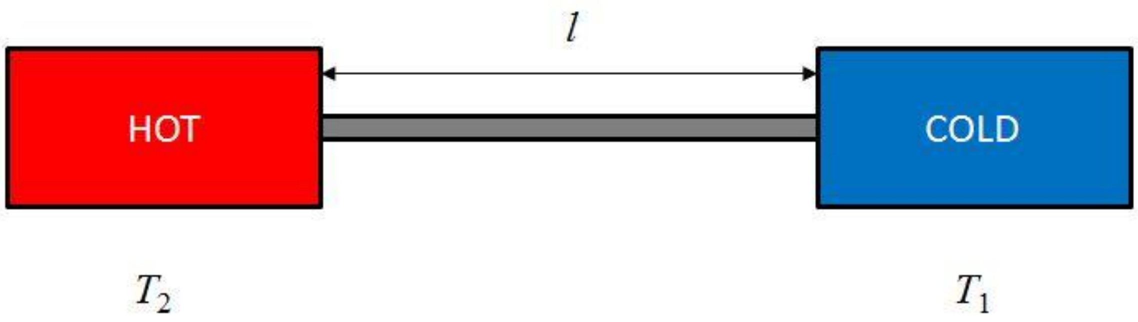


Figure 38 Temperature gradient between hot and cold

We can write an equation:

$$\text{Temperature Gradient} = \frac{T_2 - T_1}{l}$$

.... *Equation 52*

The units for a temperature gradient would be **Kelvin per metre** (K m^{-1})

13.043 Principles of Thermodynamics

- Heat flows from a hotter object to a colder object. It never happens the other way round.
- Work can be extracted from the heat flow.
- Total entropy must always increase. This means that energy gets more spread out.
- If entropy is decreased in one region, it must be at the expense of an increase in entropy elsewhere.
- There are three main laws of Thermodynamics.
- There can be no temperature lower than absolute zero. Absolute zero cannot be reached.

13.044 The Zeroth Law of Thermodynamics

The **Zeroth Law of Thermodynamics** was formulated after the First and Second Laws. It is considered to be more fundamental than the First and Second Laws. Hence it was called the Zeroth Law. It states:

If two bodies are each in thermal equilibrium with a third body, then they must be in thermal equilibrium with each other.

Consider the picture below (*Figure 39*).

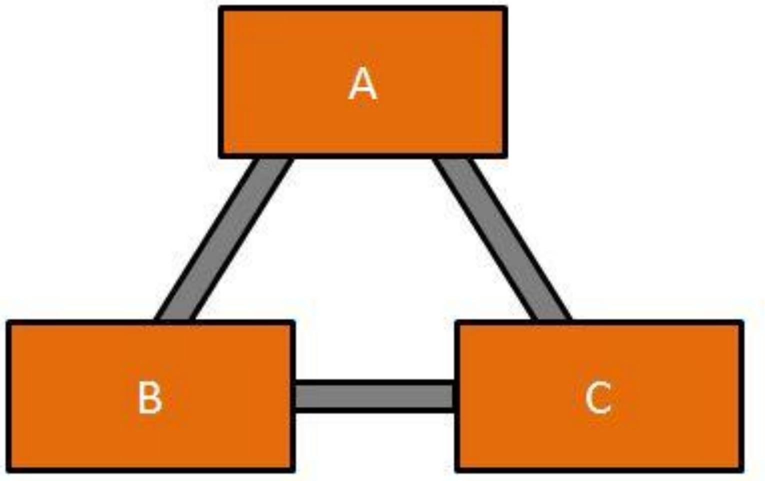


Figure 39 Objects in thermal equilibrium

A is in thermal equilibrium with C, and B is in thermal equilibrium with A. Therefore, B and C must be in thermal equilibrium. All will therefore be at the same temperature.

13.045 The First Law of Thermodynamics

Thermodynamics is the study of heat flows and how they can be put to work. **Engines** work by converting heat energy into movement energy, which can then do useful jobs of work for us. We need to look at a couple of key words. A **system** is the object of interest whose behaviour we are monitoring in relation to its **surroundings**. A flask containing gas is a system; the water bath in which the flask is placed is its surroundings. The diagram below helps to show the idea (*Figure 40*),

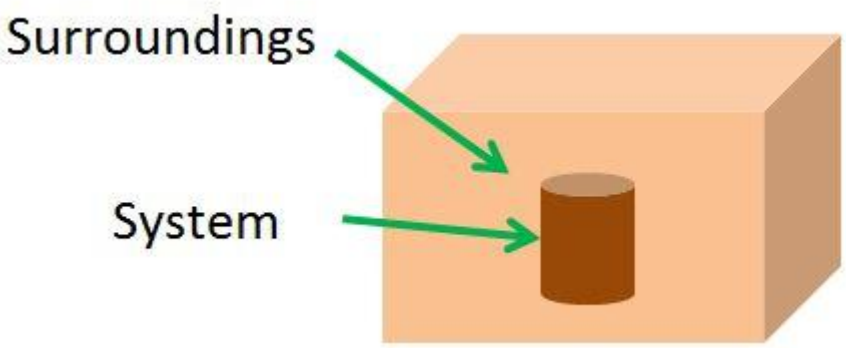


Figure 40 Key words in thermodynamics

The **Laws of Thermodynamics** were the results of work by nineteenth century physicists. Ironically the Second Law came before the First Law. Then a more fundamental law, the **Zeroth Law** was worked out.

In words the **First Law of Thermodynamics** is:

The change in internal energy of a system is equal to the sum of energy entering the system through heating and energy entering the system through work done on it.

We can write the first law in code:

$$\Delta Q = \Delta U + \Delta W$$

.... *Equation 53*

[ΔQ = heat entering the system; ΔU = increase in internal energy; ΔW - work done by the system]

The diagram here explains the idea (*Figure 41*).

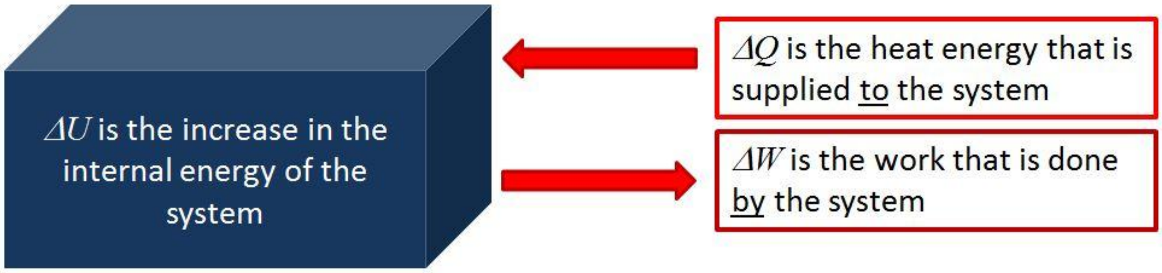


Figure 41 Heat being supplied to a system to get work out

Worked Example A lump of lead of mass 0.50 kg is dropped from a height of 20 m onto a hard surface. It does not bounce but remains at rest. What are ΔQ, ΔW, and ΔU?
Answer ΔQ = 0 J as zero heat is supplied to the system $\Delta U = mg\Delta h$ = 0.5 kg × 9.81 m s^{-2} × 20 m = 98 J ΔW = - 98 J as work is done on the system rather than by the system

If we compress a gas in a bicycle pump, we find it gets hot.

Consider a cylinder of area A. A fluid is admitted at a constant pressure, p. It makes the piston move a distance, s (*Figure 42*).

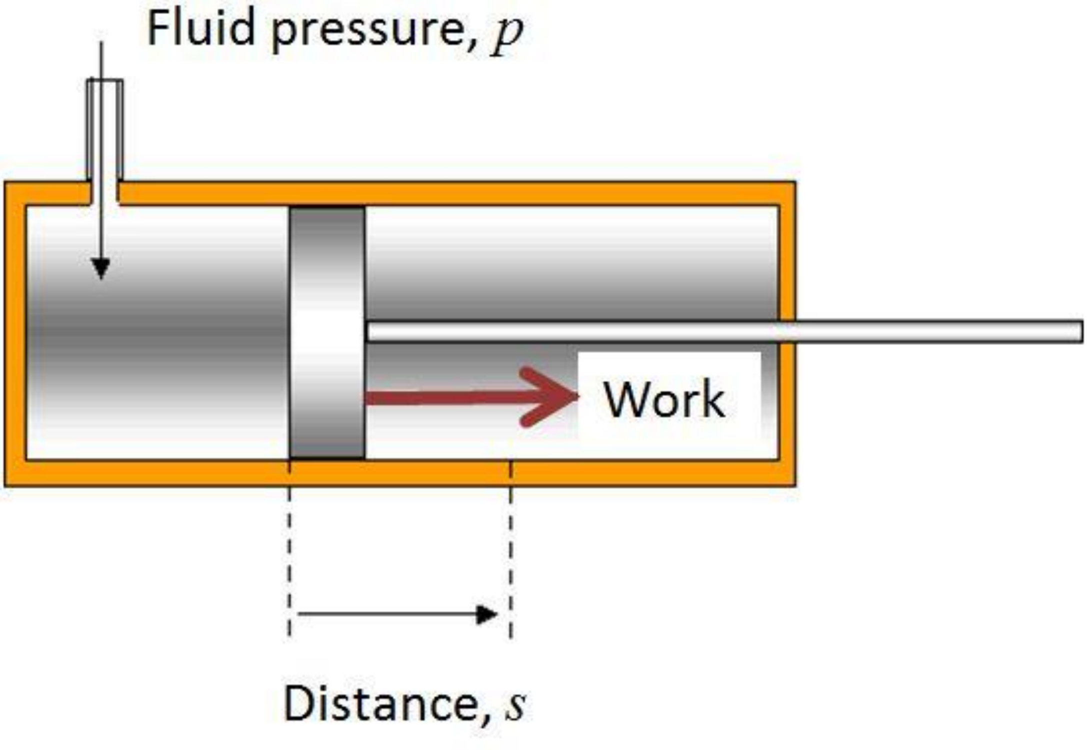


Figure 42 Fluid at a pressure p doing work on a cylinder

We know that:

Pressure (N m^{-2}) = force (N) ÷ area (m^2)

$$p = F/A$$ …………… *Equation 54*

Work done (J) = force (N) × distance moved (m)

$$W = F\Delta s$$ …………. *Equation 55*

Therefore

Force (N) = pressure (N m^{-2}) × area (m^2)

$$F = pA$$ ……….... *Equation 56*

Work done (J) = pressure (N m^{-2}) × area (m^2) × distance moved (m)

$$W = pA\Delta s$$ ……….. *Equation 57*

Area (m^2) × distance moved (m) = change in volume (m^3)

$$\Delta V = A\Delta s$$ ……… *Equation 58*

We can write, combining *Equations 57* and *58*:

Work done (J) = pressure (N m^{-2}) × change in volume (m^3)

In code:

$$\Delta W = p\Delta V$$ …………. *Equation 59*

This can be shown in a graph (*Figure 43*):

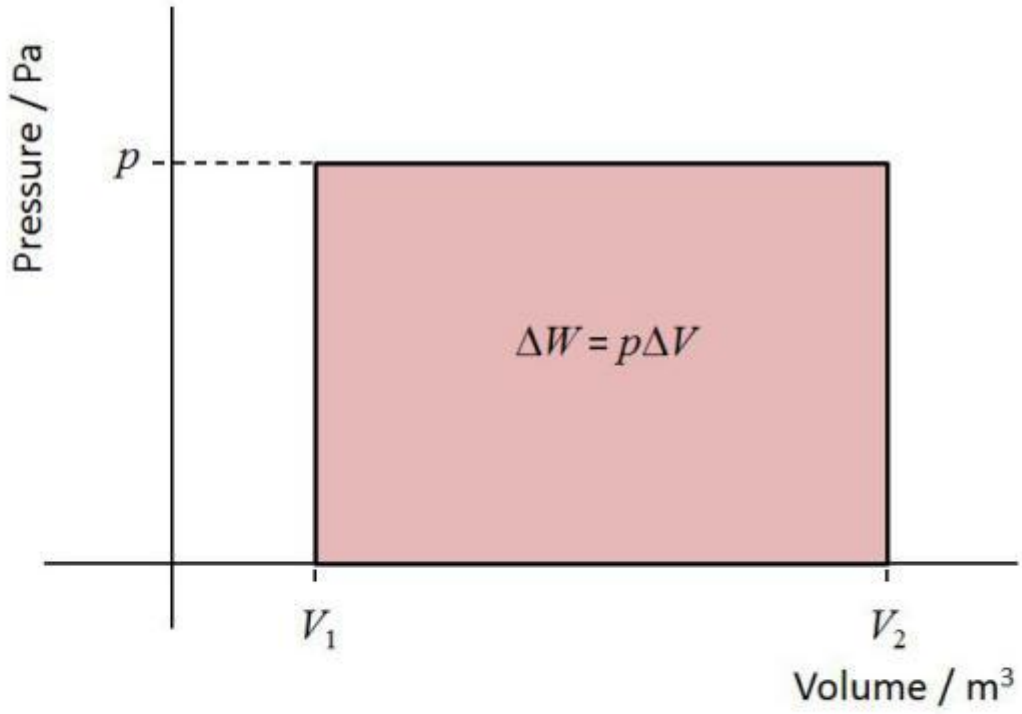


Figure 43 Graph of pressure against volume when work is done in a cylinder

The First Law of Thermodynamics has important implication in heat engines. These are discussed in Topic 14 C, Engineering Physics.

13.046 The Second Law of Thermodynamics

The **Second Law of Thermodynamics** states that it is impossible for any heat engine to be 100 % efficient:

No process is possible which results in the extraction of an amount of heat from a reservoir and its conversion to an equal amount of mechanical work.

This is the statement of the Second Law as described by Kelvin.

The Clausius (Gottlieb) version states:

No process is possible in which there is an overall decrease in the entropy of the universe.

The theory behind this is that **entropy** increases. In other words, all processes tend towards chaos (which might explain my physics lessons when I worked in schools). If you drop a pack of cards, they will scatter and the chances of their landing in a meaningful order are very small indeed.

Most energy is lost to the surroundings as **low grade heat**. We can show this in the diagram below (*Figure 44*):

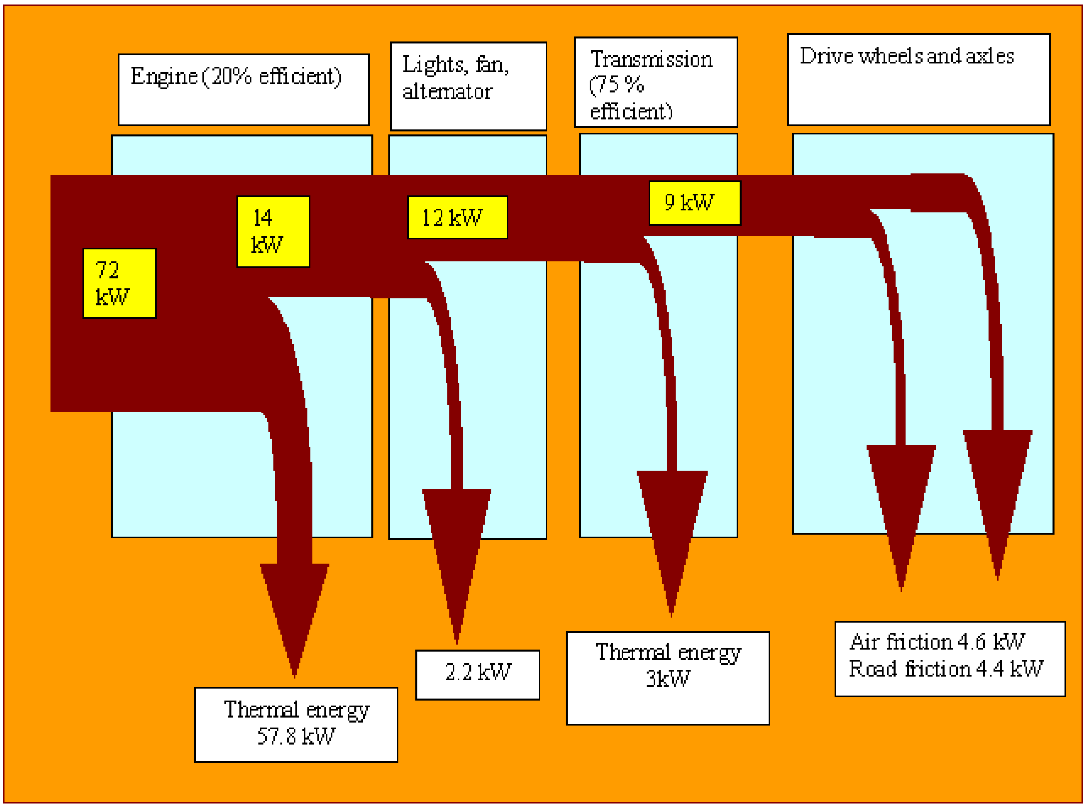


Figure 44 A Sankey diagram for a car going down a road

In this diagram, called a **Sankey Diagram**, we can see that of 72 kW of power from the fuel, only 9 kW are used in actually driving a car along a road. The rest is lost as low grade heat. As we said before, getting energy out of heat is remarkably difficult.

All heat engines work by extracting mechanical energy from a **temperature gradient**. A heat engine has to operate between the hot reservoir and the cold reservoir to satisfy the Second Law of Thermodynamics. Heat flows from hot to cold, never the other way round:

Heat won't pass from a cooler to a hotter.

You can try it if you like,

But you far better notta,

Because the cold in the cooler

Will get hotter as a ruler,

And that's a physical law!

[Michael Flanders and Donald Swan]

The engineering implications of the Second Law of Thermodynamics are discussed in Topic 14 D Engineering Physics.

13.047 Entropy

Diffusion is an example of how entropy increases. Suppose we have two gas jars. The one on the left has bromine (Br_2) molecules (*Figure 45*), while the one on the right has air molecules. We use bromine (an unpleasant smelling and toxic gas) as it is readily visible.

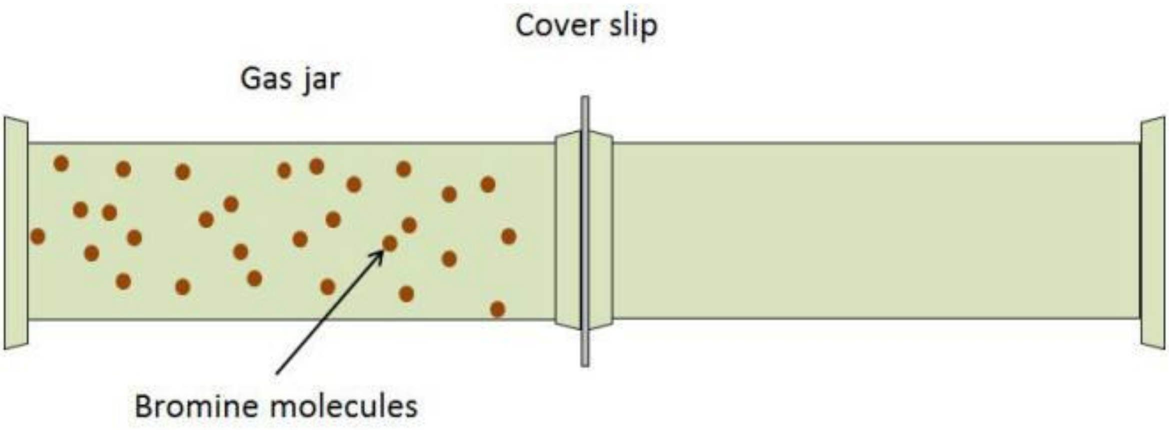


Figure 45 Showing entropy

We then remove the cover slip and watch the way the molecules diffuse. We assume that the molecules move randomly (*Figure 46*).

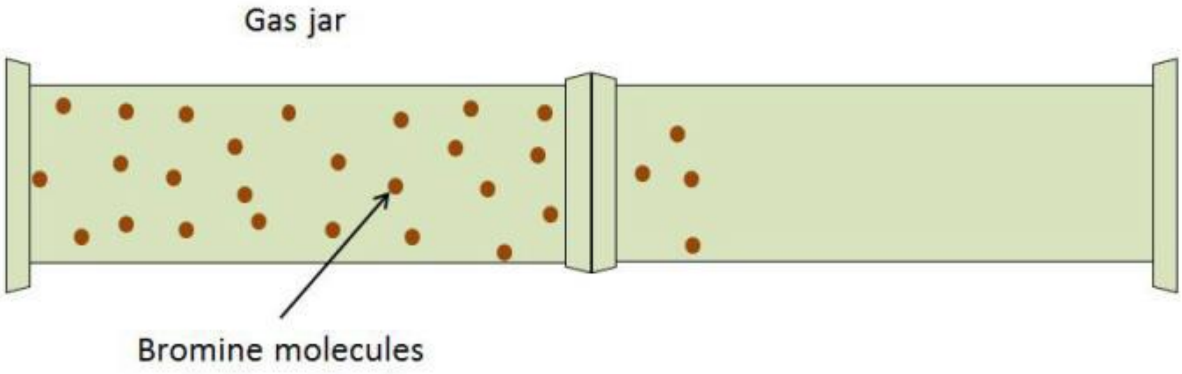


Figure 46 Diffusion of molecules

Eventually the molecules become evenly distributed (*Figure 47*).

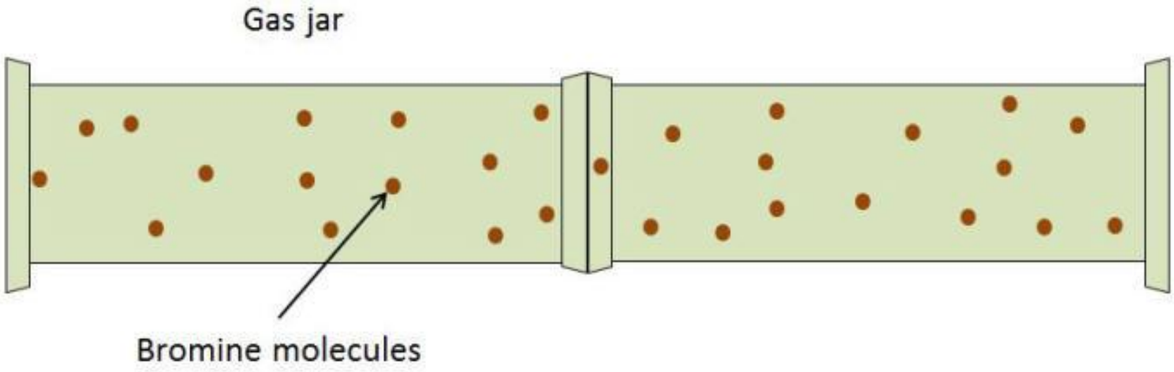


Figure 47 Even distribution of diffused molecules

It would be impossible to catch all the molecules and put them back all into the left-hand jar. In this example, there are 29 molecules. If there was just one molecule there would be a chance or probability of 1 in 2^1 (i.e., 0.5 or 2^{-1}) of the molecule being in the left hand jar. Similarly, if there are 4 molecules, the chances of all molecules being in just the left hand jar would be 1 in 16, or 2^{-4}.

If there are W molecules, the chances of all of them being in the left hand jar at the same time would be 2^{-W}.

Your answer to Question 13.04.6 is an average. Due to the random nature of molecular movement, the molecules could be all in the left hand jar in 10 seconds, or 300 years. On average, it would take about 17 years (and when it happened, you weren't there).

If 1 gram of bromine was placed in the gas jar, a back of the envelope calculation would show us that there would be about 10^{22} molecules. Thus, the probability of there being all the molecules back in the left hand jar is 2 to the power -10^{22}, which is infinitesimally small.

The **entropy** of a system is the property that tells us the number of possible arrangements of the molecules. It is given the physics code S and has the units J K^{-1}.

$$S = k \ln W \quad \text{.............. } \textit{Equation 60}$$

The constant k is the Boltzmann Constant:

$$k = 1.38 \times 10^{-23}\ \mathrm{J\ k^{-1}}$$

The graph (*Figure 48*) shows the even distribution of the molecules. The curves show the normal distributions for N = 10, 100, and 1000 molecules. For 10 molecules, there is a reasonable probability that most molecules are on the right. The more molecules there are, the chances that most molecules are to the right are reduced.

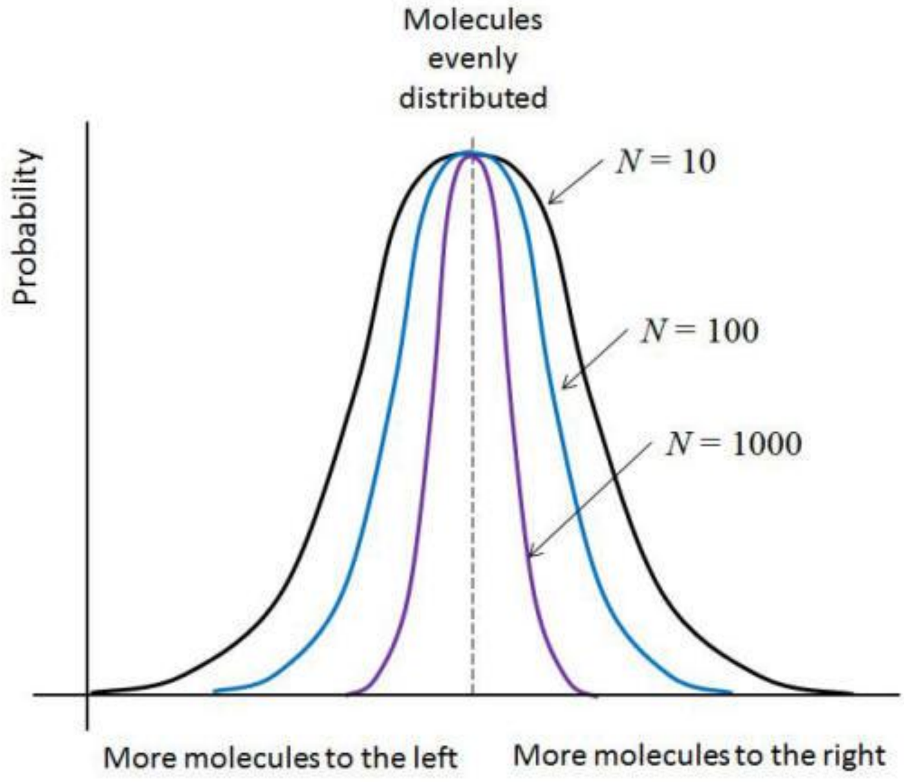


Figure 48 Probabilities of molecule distribution for N = 10, 100, 1000

The more molecules, the closer the distribution curve is to the central line. Therefore with 10^{22} molecules, the molecules are evenly distributed.

13.048 Entropy and Energy

Like molecules, energy spreads out. At high temperatures, the energy is **concentrated**. For a useful job of work to be done, we have to have a high concentration of energy. High concentrations of energy lead to high temperatures. In the last tutorial, we saw that:

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}kT$$

.... *Equation 61*

At high temperatures, molecules move about very quickly and can do a job of work. A fuel reacts in a boiler or engine to make a very high temperature, so a lot of work can be extracted. Then the energy becomes more spread out, eventually to heat up the environment. All heat engines work by extracting mechanical energy from a **temperature gradient**. A heat engine has to operate between the hot reservoir and the cold reservoir to satisfy the Second Law of Thermodynamics. Heat flows from hot to cold, never the other way round. We can show the heat flowing from a **hot reservoir** through a heat engine to a **cold reservoir** (*Figure 49*).

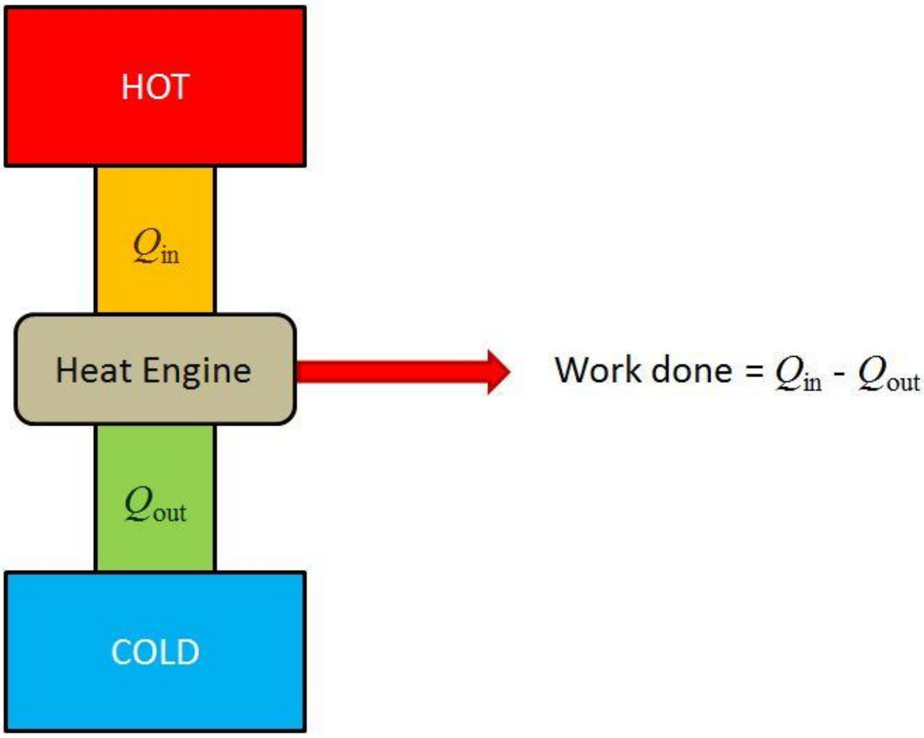


Figure 49 Heat doing work through a heat engine

All heat engines give up their energy to a **cold reservoir**. We can define the terms used on the diagram (*Figure 49*):

- Q_{in} = the heat flow from the hot reservoir to the engine
- Q_{out} is the heat flow from the engine to the cold reservoir.
- The work done by the heat engine is the difference between Q_{in} and Q_{out}.

Therefore:

$$W = Q_{\text{in}} - Q_{\text{out}} \quad \text{……………….. Equation 62}$$

Consider an engine in a car (*Figure 50*).

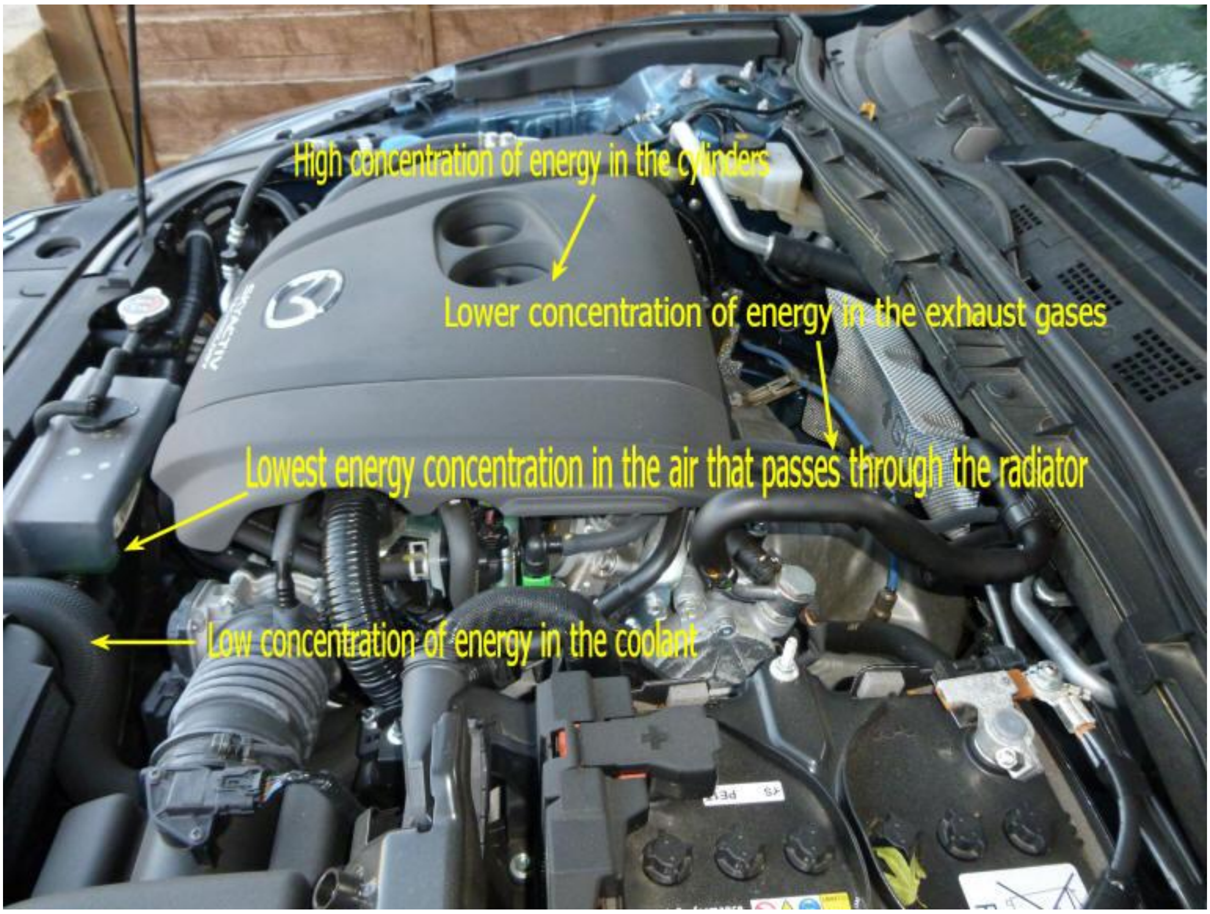


Figure 50 Energy concentration in a car engine

The fuel delivers energy in its most concentrated form, leading to a very high temperature when it is ignited by the spark plugs (this car uses petrol as a fuel). Some energy is extracted as the gases expand and make the crankshaft turn. Most of the energy is used to heat up the coolant, which is at a low temperature to maximise the temperature gradient. This makes the energy more spread out. Not much energy can be extracted from the coolant (some can be used to heat the car on a cold day). The coolant needs have its energy extracted from it by the flow of air through the radiator. The energy gets even more spread out and is useless. The exhaust gases are hot as they leave the engine. They can be harnessed to drive a turbocharger to increase the pressure in the inlet manifold of the engine. This makes the engine more powerful. (However, the downside to this is that turbocharged engines can be less reliable.)

The engine on this car does not have a turbocharger. It has a different method of managing the fuel that is to be burned. All the energy in the exhaust gases is lost to the environment.

13.049 Entropy and Cosmology

The entropy at the time of the Big Bang was extremely low. All the energy in the Universe was concentrated into an infinitesimally small space. Therefore, the temperature was extremely high. Since the lower the entropy, lower the probability of the event happening. We saw that with the 10^{22} molecules in the left-hand gas jar. Some theoretical physicists have concluded that since the entropy of the Big Bang was so low, the chances of the event happening was infinitesimally small. But it did happen. The evidence for the Big Bang is compelling (see Topic 14 A - Astrophysics).

The energy from the Big Bang has spread out to give the **Cosmic Background Radiation**, which gives the Universe an average temperature 2.7 K. Some places are hotter, like stars.

When all the stars in the Universe eventually die out and cool, astrophysicists believe they will evaporate into protons, electrons and photons.

Astrophysicists believe that this will happen in 10^{22} years, and that the temperature of the Universe will be down to 10^{-30} K. Not an appealing prospect if you don't like the cold. However, by the time it happens, we will be long since gone and forgotten.

Heat is work and work's a curse,

And all the heat in the Universe

Is gonna cool down.

That will mean no more work,

And there'll be perfect peace.

That's entropy, man!

[Michael Flanders and Donald Swan]

13.0410 The Third Law of Thermodynamics

Just above, we have seen that the temperature of the Universe will get down to 10^{-30} K. It is very nearly absolute zero, but not quite. The law states:

Absolute zero cannot be reached by a finite steps.

If we cool a body, there has to be an even cooler body to transfer the heat energy to. Even if the process takes many millions of steps over each of the 10^{22} years, there is still a finite number of steps to be taken.

Tutorial 13.04 Questions

13.04.1

What is internal energy?

13.04.2

Some air in a bicycle pump is compressed so that its volume decreases and its internal energy increases. If 25 J of work are done by the person compressing the air, and if 20 J of thermal energy leave the gas through the walls of the pump, what is the increase in the internal energy of the air?

13.04.3

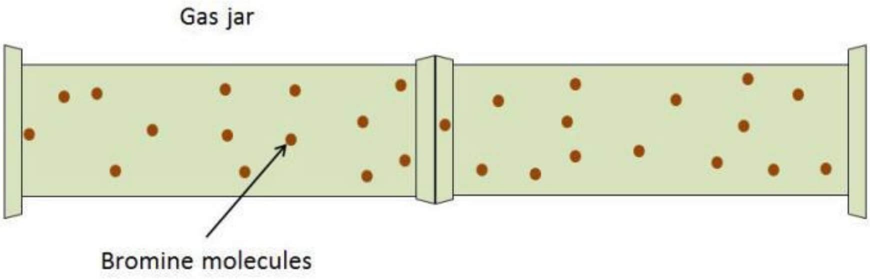
The bicycle pump is compressed and held so that no air inside is released. It is allowed to cool until the temperature of the air inside is the same as the air outside.

What happens if we release the pump?

13.04.4

A cylinder has an area of 0.125 m^2. Steam is admitted at a pressure of 1.5×10^6 Pa. The piston moves a distance of 0.20 m. What work is done?

13.04.5



If there are 29 molecules in the gas jars above, what is the chance of all the molecules being in the left hand jar at the same time?

13.04.6

Suppose we watched the 29 molecules once a second, show that it would take about 17 years for all 29 to be in the left hand jar at the same time.

13.04.7

If there are 10^{22} molecules in the two gas jars, calculate the entropy.

13.04.8

When all the stars in the Universe eventually die out and cool, astrophysicists believe they will evaporate into protons, electrons and photons.

Why not neutrons?

Tutorial 13.05 The Boltzmann Factor

Cambridge Pre U

Contents

13.051 Boltzmann Factor	13.052 Activation Processes
13.053 Creep	13.054 Semi-Conduction
13.055 Thermionic Emission	13.046
13.047	13.048
13.049	13.0410

(*Extension for Pre-U students*)

It is ONLY for students studying the Cambridge Pre U syllabus. It will NOT be examined at A-level. However, if you are going to study Physics at university, you may find this a useful introduction.

13.051 Boltzmann Factor

We have seen how the Kinetic Theory of Molecules is based on **statistical** assumptions. Molecules have a **range** of energies which can be due to their **translational kinetic energy**, or their **vibrational energy** (or both). Molecules can lose or gain energy due to **collisions**. In a large population of molecules, the **proportion** of molecules that have a certain value of energy will be **constant**, even if individual molecules gain or lose energy. Molecules have a **probability** of having a certain energy. Like all other probabilities, the probability must be within the range **0** to **1**. If the probability is 1, that means that every molecule has a particular energy (which is very unlikely).

Suppose n_ε is the number of molecules with a particular energy, ε. The total number of molecules is *N*. Therefore:

Proportion of molecules of energy ε = Number of molecule with energy ε ÷ total number of molecules

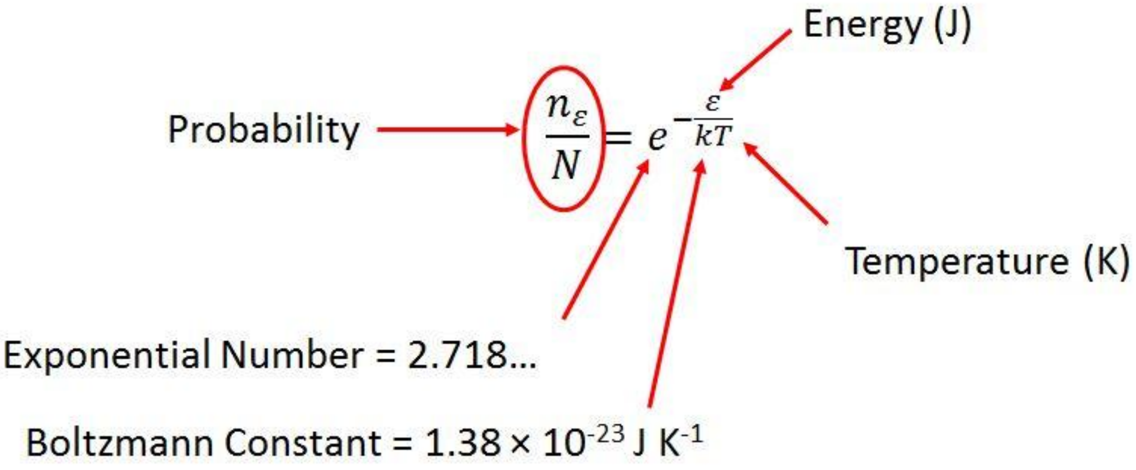
$$\text{Probabilty} = n_\varepsilon \div N \quad \text{……………… Equation 63}$$

This probability is called the **Boltzmann Factor**, given by the equation:

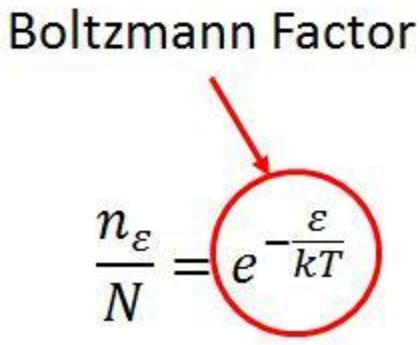
$$\frac{n_\varepsilon}{N} = e^{-\frac{\varepsilon}{kT}}$$

.... *Equation 64*

The terms are shown below:



The Boltzmann Factor is shown:



The Boltzmann Factor must not be confused with the Boltzmann Constant, *k*.

13.052 Boltzmann Factor and Activation Processes

In a chemical reaction, there is an **activation** energy. This means that the reactants have to have a certain energy before the reaction can happen. The idea is shown on this diagram (*Figure51*):

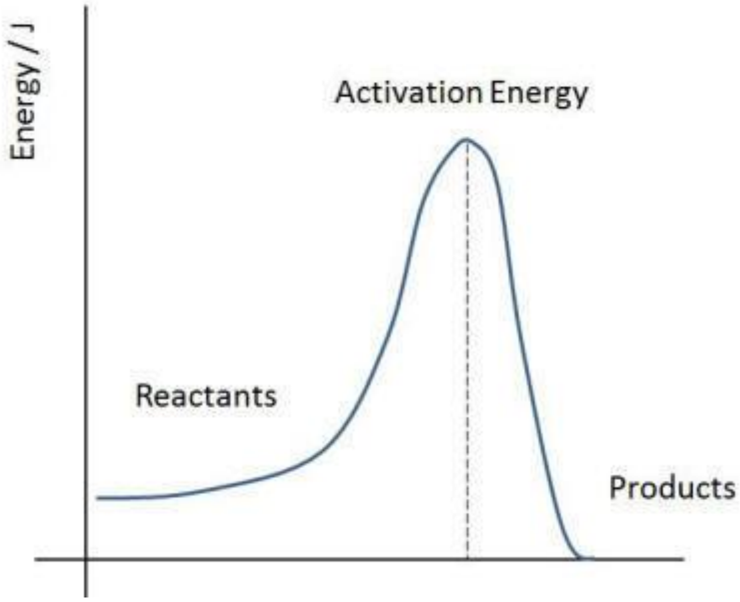


Figure 51 Activation energy in a chemical reaction

The reactants have to be lifted to the top of the energy hill. Then they can roll down the energy hill to make the products.

In many chemical reactions, we need to raise the energy of the reactants to initiate the reaction. We do this by increasing the temperature.

Suppose we have a reaction that has an activation energy of 5.0 kJ mol^{-1}. There is 1 mole of reactants. We can work out the average energy per reactant molecule:

$$\text{Energy} = 5000 \text{ J} \div 6.0 \times 10^{23} = 8.33 \times 10^{-21} \text{ J}$$

We can use this to calculate the probability of having molecules of this energy at room temperature (21 °C). 21 °C is 294 K.

Work out the the natural logarithm of the Boltzmann Factor:

$$\ln (n_\varepsilon/N) = -(8.33 \times 10^{-21}\text{ J} \div (1.38 \times 10^{-23}\text{ J K}^{-1} \times 294\text{ K}))$$

$$\ln (n_\varepsilon/N) = -(8.33 \times 10^{-21}\text{ J} \div 4.057 \times 10^{-21}\text{ J}) = -2.05$$

The Boltzmann factor is given by:

$$n_\varepsilon /N = e^{-2.05} = \underline{\mathbf{0.13}}$$

This would indicate that there would be a good chance of this reaction proceeding, especially as heat will be released as the reaction proceeds. However this does not take into account the probability of the collisions that are needed for a reaction, or that the collisions are in the right orientation. The **Arrhenius Equation** gives a better prediction:

$$K = Ae^{-\frac{\varepsilon_A}{kT}}$$

.... *Equation 65*

The terms are:

- K = rate constant of the reaction;
- A = pre-exponential factor, which depends on the reaction itself.

You are not expected to know this equation, but you can see its similarity to equation for the **Boltzmann Factor**.

Other activation processes include:

- Evaporation of liquids;
- Viscosity of fluids;
- Creep in ductile solid materials;
- Semi-conduction;
- Ionisation.

The structure of a **viscous** (gooey) fluid is that of a liquid, in that the molecules go about in small groups. The larger the small groups are, the more viscous the fluid is. There is a small, but finite, probability that an individual particle gets enough energy to break free of the group so that the fluid can flow (*Figure 52*).

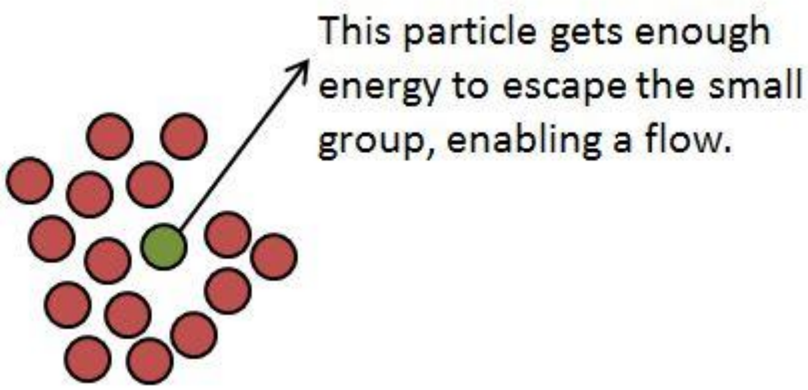


Figure 52 Molecule has sufficient energy to escape from a small group of molecules

Although glass seems solid, it is actually a very viscous fluid. The glass in a window that is a couple of hundred years old is noticeably thicker at the bottom that at the top (*Figure 53*).

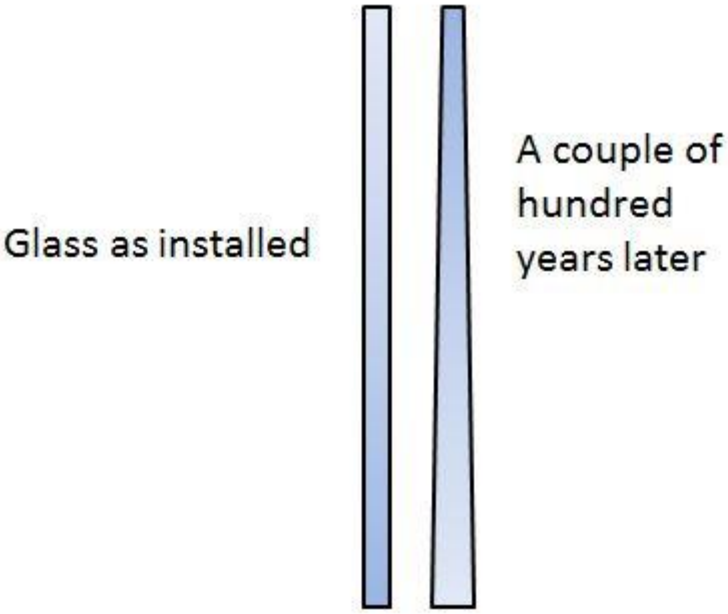


Figure 53 Glass is a very viscous fluid

13.053 Creep

This can be a serious problem in many engineering applications. If a material is subjected to a continuous stress, deformation can occur even though the stress itself may be lower than the yield stress. It is more marked in ductile materials like copper and lead. Lead is used as a roof covering on many old buildings like churches. The stress caused by the weight of the lead can pull the lead down the roof (*Figure 54*).

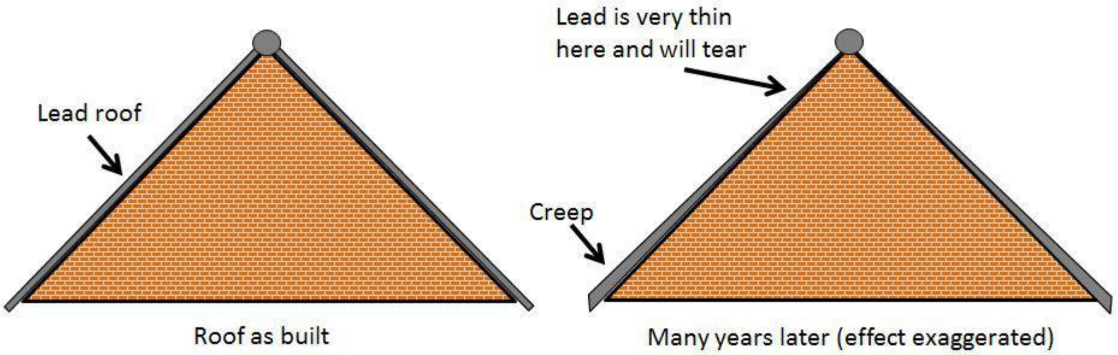


Figure 54 Creep on a roof

The church organ in York Minster (one of Europe's largest cathedrals) has had a major overhaul costing £2 million, in which the instrument has been completely dismantled. One problem identified is that many of the metal pipes have been subject to creep. They have shortened slightly and bulged at the bottom. This has caused them to go slightly out of tune. Since the pipes are shorter, their fundamental frequency will have slightly increased. To a musician their notes would be sharp. The pipes have been restored to their original dimensions so that they play true.

Creep is dependent on temperature, and materials like lead will creep at environmental temperatures. For many materials, creep happens at about 35 % of the Kelvin melting point.

In early day turbines, the forces acting on rapidly rotating blades could cause distortion by creep. If one blade fails as a result, it can shear off all of the others ("having a haircut"), which is highly expensive. In large power station turbines, the turbine rotors are very heavy. If the turbines are turned off, the shaft can sag due to creep, becoming slightly banana shaped. This can be prevented by slowly turning the shaft using a **barring motor** (*Figure 55*).

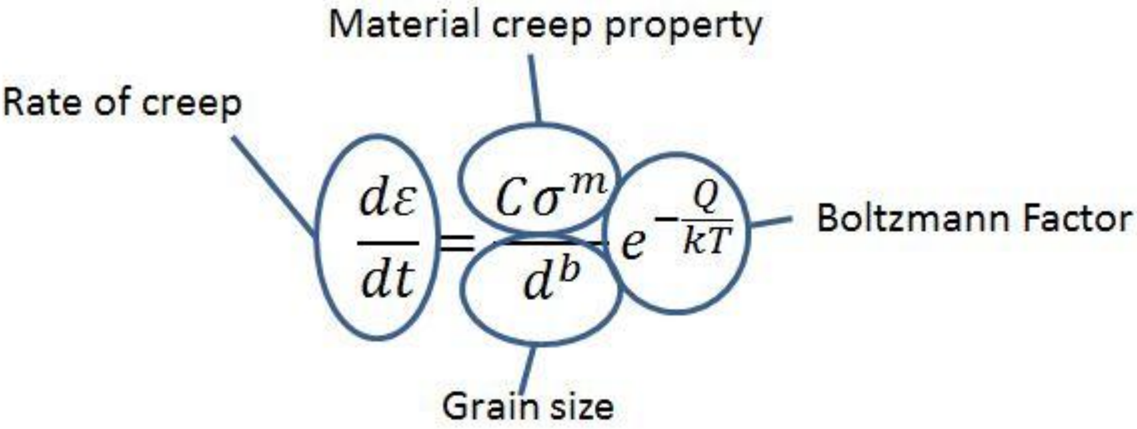
Figure 55 A barring motor in a power station alternator

A general equation for creep is shown below. You are not expected to know it.

$$\frac{d\varepsilon}{dt} = \frac{C\sigma^m}{d^b} e^{-\frac{Q}{kT}}$$

.... *Equation 66*

The meanings of the main components are shown:



The point of this diagram is to show the presence of the **Boltzmann Factor**. In the equation, Q is activation energy of the creep. The term ε is "epsilon", the physics code for strain. The other terms need not concern us here.

13.054 Boltzmann Constant and Semi-Conduction

Semi-conduction is described in Topic 4. Before you do this section, you may wish to review semi-conduction. We know that in a bipolar junction, there is a depletion layer that require there to be a certain voltage to overcome it. In the model in Electricity Tutorial 6, we talked about the depletion layer disappearing in forward bias. That is the usual model that is used by electronic engineers. However there is more to it, but it's not that complex.

The depletion layer disappears because the electrons have sufficient energy to jump into the conduction band and cross it. The electron energy required is:

$$\varepsilon = eV_{\mathrm{b}}$$

.... *Equation 67*

This is entirely consistent with **energy** being the product of **charge**, e (from the electron, 1.602 × 10^{-19} C) and the **bias voltage**, V_{b}. When the bipolar junction just conducts with a very small current, i_{b}, the equation is:

$$i_{\mathrm{b}} = ae^{-\frac{eV_{\mathrm{b}}}{kT}}$$

.... *Equation 68*

We can see the Boltzmann Factor in the equation:

$$i_{\mathrm{b}} = a\,\overset{\text{Boltzmann Factor}}{\boxed{e^{-\frac{eV_{\mathrm{b}}}{kT}}}}$$

The term a is a proportionality constant, a property of the semiconductor.

The Boltzmann factor is the probability that an electron will jump across the depletion layer. If the temperature is increased, the bigger the chance of an electron having the energy to jump over. This explains why semiconductors conduct a bigger current as their temperature rises.

13.055 Boltzmann Factor and Thermionic Emission

The most common way of accelerating electrons is to use an electron gun (*Figure 56*), in which current passes through a filament, which glows just like in a light bulb in Topics 2 and 3. The filament is connected to a source of electrons (the negative terminal of a high voltage source), called the **cathode**. Electrons are boiled off by a process of **thermionic emission**. They are attracted to a positively charged **anode**. Most hit the anode and go back to the source. Some go through a small hole in a narrow beam. (This was called the **cathode ray**.)

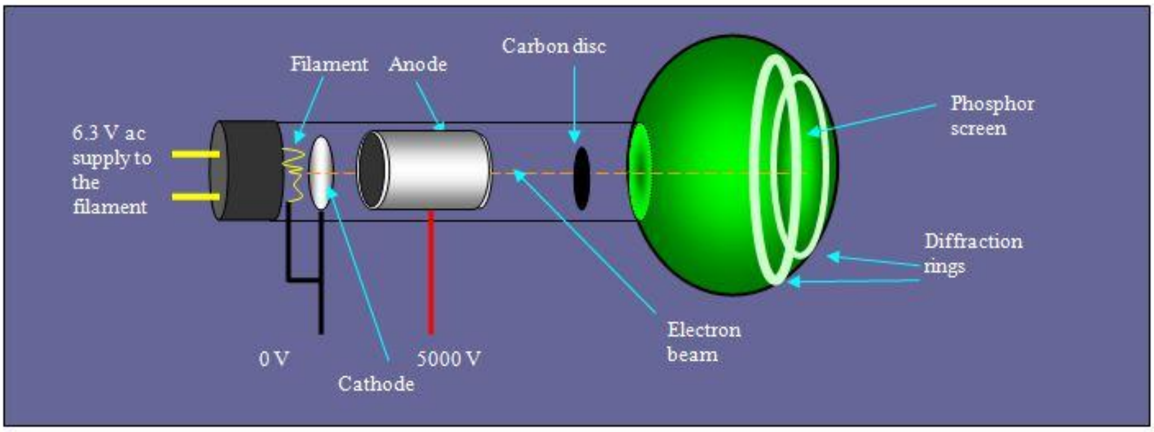


Figure 56 Electron gun

Since they are attracted by the very high potential difference, the electrons **accelerate**. Once they get to the anode (and pass out of the little hole), the electrons are moving very fast. All their energy is **kinetic**.

Thermionic emission is another **activation process** which works using the ideas of **probability**. It is quite hard to boil electrons off tungsten as it has a relatively high **work function** (Topic 3). The work function of tungsten is about 4.5 eV. This would reduce the probability of an electron being boiled off. To improve thermionic emission, the filament is coated with thorium, with a work function of 3.45 eV.

Thermionic emission can occur when an electron acquires energy of more than 3.45 eV. In the diagram below, we can see the model of a metal being a fixed lattice of positive ions in a sea of free moving electrons. One electron has gained enough energy to leap out of the metal (*Figure 57*).

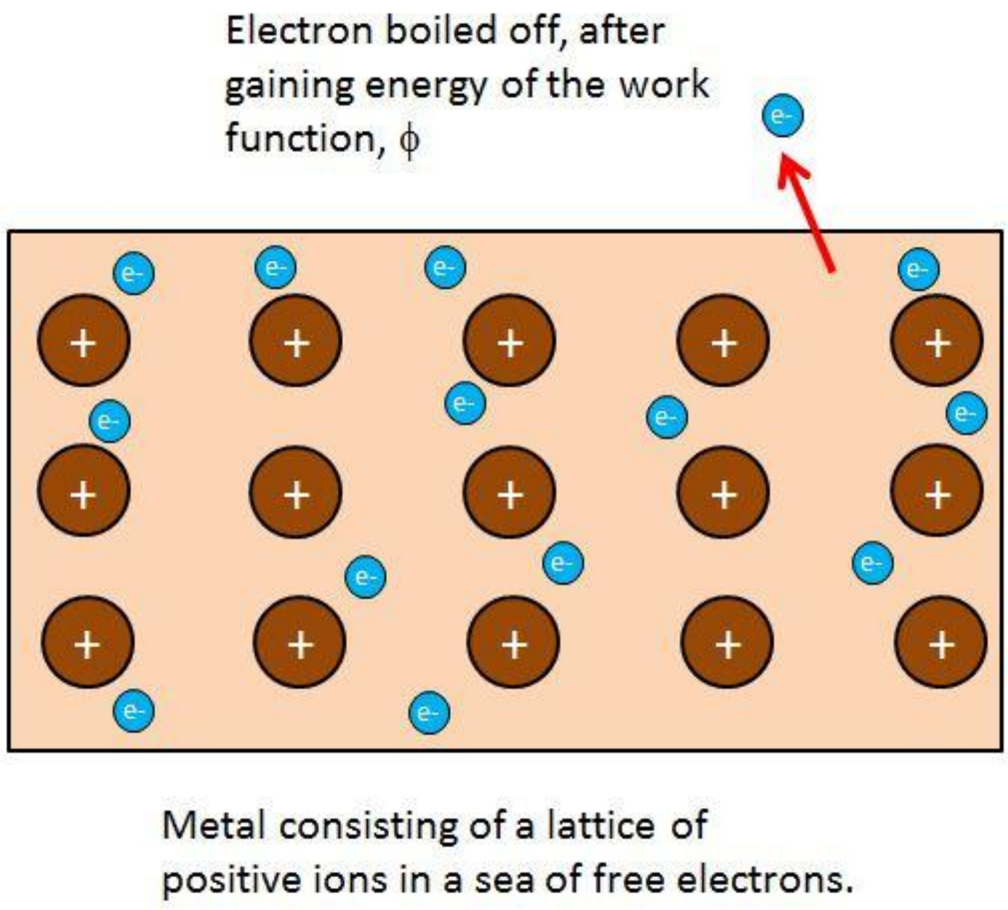


Figure 57 Thermionic emission

Experiment shows that the cathode current, I_c, depends on the Boltzmann factor. This is consistent with the probability of an electron escaping the metal, given by:

$$\text{Probability} = e^{-\frac{\phi}{kT}}$$

.... *Equation 69*

If the Kelvin temperature is low, then the probability is low. This explains why the filament has to be hot. Once the electrons are free of the filament, they are accelerated to the anode, as we saw above. The current is given by the following proportionality expression:

$$I_c \propto e^{-\frac{\phi}{kT}}$$

.... *Equation 70*

Experiment shows that the **current density**, J, (current per unit area) is given by:

$$J = AT^2 e^{-\frac{\phi}{kT}}$$

.... *Equation 71*

The proportionality constant is in two parts:

- The square of the Kelvin temperature;
- The **Richardson Constant**, *A*.

The equation above describes **Richardson's La**w, named after Owen Willans Richardson (1879 - 1959). The Richardson constant surprisingly does not depend on the material; it is a universal constant:

$$A = 1.2 \times 10^6 \text{ A m}^{-2} \text{ K}^{-2}$$

The Boltzmann Factor is important in **Statistical Mechanics**. You will study this at university.

Tutorial 13.05 Questions

13.05.1

The average translational kinetic energy of a molecule was found to be 6.0×10^{-21} J.

(a) If the temperature is 30 °C, calculate the Boltzmann Factor.

(b) Work out the number of molecules that are likely to have that energy, if there are 10 moles of molecules.

13.05.2

$$K = Ae^{-\frac{\varepsilon_{\mathrm{A}}}{kT}}$$

Identify the Boltzmann Factor in the equation above.

13.05.3

A bipolar junction just starts to conduct at 0.45 V. The diode is at 25 °C, and the proportionality constant, a, is 40 A.

(a) Calculate the Boltzmann Factor.

(b) Calculate the current, i_{b}.

13.05.4

A filament in an electron gun operates normally at a temperature of 1000 °C. The tungsten filament has a coating of thorium which has a work function of 3.45 eV.

(a) Show that the probability of an electron being boiled off is about 2×10^{-14}.

(b) Calculate the current density. Give the correct unit.

(c) The hole in the anode through which the electrons travel is 2.0 mm across. Calculate the anode current.

(d) Explain without a calculation why the thermionic emission will not happen at room temperature.

Answers to Questions

Tutorial 13.01

13.01.1

Internal energy is the energy contained by the molecules in a material. This energy is shown by the vibration of the atoms. Heat is a flow of energy through a material.

Internal energy can be stored (for example in a hot water bottle, or night storage heater)

Heat cannot be stored. For storage, heat is converted to **internal energy**.

13.01.2

Formula first:

$$Q = mc\Delta\theta$$

Temperature change = 100 - 20 = 80 ° C (= 80 K)

Energy = 1.5 kg × 4200 J kg^{-1} K^{-1} × 80 K

Energy = **<u>504 000 J</u>**

13.01.3

(a)

The time taken is only relevant if we are interested in power.

(b) Formula first:

$$Q = mc\Delta\theta$$

Temperature change = 58 ° C - 23° C = 35 ° C (= 35 K)

Energy = 43120 J - 31225 J = 11895 J

11895 J = 1.25 kg × Specific heat × 35 K

$$\text{Specific heat} = \frac{11895\ \text{J}}{1.25\ \text{kg} \times 35\ ^\circ\text{C}} = \underline{\mathbf{272\ J\ kg^{-1}\ K^{-1}}}$$

13.01.4

First we need to calculate the energy needed to melt the ice:

specific latent heat of fusion, L_m = 334 000 J/kg.

$\Delta Q = mL$ = 0.5 kg × 334 000 J kg^{-1} = 167 000 J

Next we need to find the energy supplied to bring the water to the boil:

Temp change = 100 °C - 0 °C = 100 °C (= 100 K)

$\Delta Q = mc\Delta\theta$ = 0.5 kg × 4200 J kg^{-1} K^{-1} × 100 K = 210000 J

Now we need to find out the energy needed to boil the water away:

specific latent heat of vaporisation is rather higher, L_v = 2.3 × 10^6 J kg^{-1}

$\Delta Q = mL$ = 0.5 kg × 2.3 × 10^6 J kg^{-1} = 1 150 000 J

Add them all together:

Total energy = 167 000 + 1 150 000 + 210000 = **1527000 J**

How long would this take a 2 kW kettle?

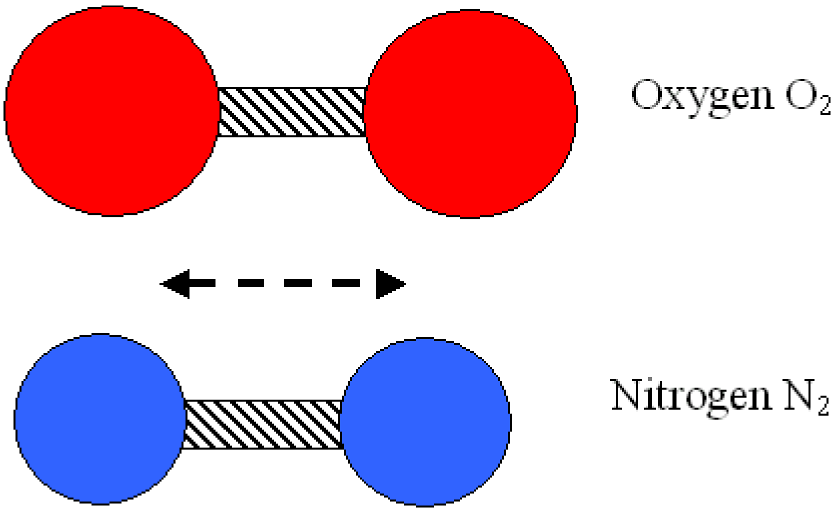
Power = energy / time

Time = energy / power = 1527000 J ÷ 2000 J s^{-1} = **763 s** (about 13 minutes)

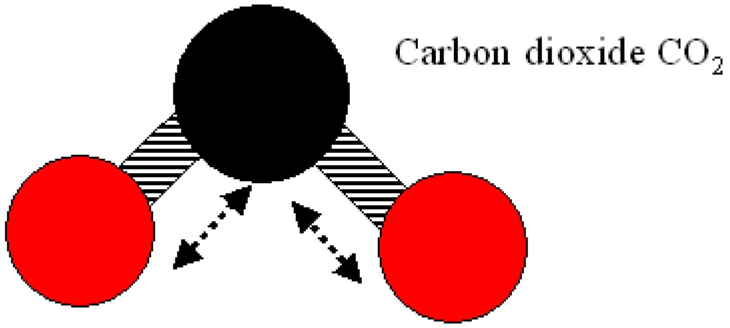
Tutorial 13.02

13.02.1

Air is a mixture of gases. Nitrogen and oxygen are both diatomic gases. This means that they consist of molecules of two atoms. Therefore, some energy is taken up in the vibration of the bond between the two atoms.



There are also molecules with three atoms such as carbon dioxide and water.



In these more energy would be taken up in the vibration of bonds.

Atmospheric pressure is 100 kPa, which is quite a high pressure, and the temperatures at which we are comfortable, about 290 K are quite high as far as gasses are concerned.

However, to a first approximation, we can model ideal gas behaviour with air.

13.02.2

Use $pV = nRT$

$$100\,000 \text{ Pa} \times V = 2 \text{ mol} \times 8.31 \text{ J mol}^{-1}\text{ K}^{-1} \times 293 \text{ K}$$

$$V = \frac{2 \text{ mol} \times 8.31 \text{ J mol}^{-1}\text{ K}^{-1} \times 293 \text{ K}}{100\,000 \text{ Pa}} = \frac{4870 \text{ J}}{100\,000 \text{ Pa}} = \mathbf{0.0487 \text{ m}^3}$$

Did you fall into the bear trap of not converting Celsius to Kelvin?

13.02.3

Use the formula:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

Put in the numbers:

$$\frac{3.03 \times 10^5 \text{ Pa} \times 3.0 \times 10^{-3} \text{ m}^3}{283\text{K}} = \frac{1.01 \times 10^5 \text{ Pa} \times V}{293 \text{ K}}$$

Rearranging:

$$V = \frac{3.03 \times 10^5 \text{ Pa} \times 3.0 \times 10^{-3} \text{ m}^3 \times 293 \text{ K}}{283 \text{ K} \times 1.01 \times 10^5 \text{ Pa}}$$

V = **9.32×10^{-3} m^3** = 9.32 litres (which would mean that they could burst).

Divers have to be very careful when coming to the surface. If the pressure reduces too quickly, nitrogen gas can form small bubbles in the blood that are at best extremely painful (the diver doubles up, hence "the bends"). At worst it can be fatal.

13.03.4

(a) Use $pV = nRT$

$$1.5 \times 10^{6}\ \text{Pa} \times 0.8 \times 10^{-3}\ \text{m3} = n \times 8.31\ \text{J mol}^{-1}\ \text{K}^{-1} \times 320\ \text{K}$$

$$n = \frac{1.5 \times 10^{6}\ \text{Pa} \times 0.8 \times 10^{-3}\ \text{m}^{3}}{8.31\ \text{J mol}^{-1}\ \text{K}^{-1} \times 320\ \text{K}} = \mathbf{0.451\ mol}$$

(b)

The mass of the gas if its molar mass is 32.0×10^{-3} kg

$$\text{mass of gas} = 0.451\ \text{mol} \times 32.0 \times 10^{-3}\ \text{kg mol}^{-1} = \underline{\mathbf{0.0144\ kg}}$$

(c) The mass of a single molecule of gas.

$$\text{Mass of 1 molecule} = \frac{32.0 \times 10^{-3}\ \text{kg mol}^{-1}}{6.023 \times 10^{23}\ \text{mol}^{-1}} = \underline{\mathbf{5.32 \times 10^{-26}\ kg}}$$

Tutorial 13.03

13.03.1

(a) What is the most probable speed?

The most probable speed is 9.0 m s^{-1} because there are the most molecules (4) travelling at that speed.

(b) What is the mean speed?

There are 10 molecules:

Mean speed =

$$\frac{(1 \times 5.0) + (2 \times 7.0) + (4 \times 9.0) + (1 \times 12.0) + (1 \times 14.0) + (1 \times 15.0)}{10}$$

$$= \frac{5 + 14 + 36 + 12 + 14 + 15}{10} = \frac{96}{10} = \mathbf{9.6\ m\ s^{-1}}$$

(c) What is the rms speed of the molecules?

$$\text{Mean square speed} = \frac{25 + 98 + 324 + 144 + 196 + 225}{10} = \frac{1012}{10}$$

$$= 101.2\ m^2\ s^{-2}$$

$$\text{Rms speed} = \sqrt{101.2} = \mathbf{10.1\ m\ s^{-1}}$$

13.03.2

(a) the rms speed of the molecules.

$$p = 1/3\ \rho\langle c^2\rangle$$

$$1.0 \times 10^5\ \text{Pa} = 1/3 \times 1.25\ \text{kg m-3} \times \langle c^2\rangle$$

$$\langle c^2\rangle = \frac{3 \times 1.0 \times 10^5\ \text{Pa}}{1.25\ \text{kg m}^{-3}} = 240\,000\ \text{m}^2\ \text{s}^{-2}$$

Rms speed = **490 m s^{-1}**

(b) the temperature at which the molecules travel twice as fast.

- The kinetic energy is proportional to the temperature. If we double the speed, the kinetic energy goes up by 4 times, therefore the temperature goes up 4 times.
- 27 °C = 300 K
- New temperature = **1200 K**

Did you forget to convert Celsius to Kelvin?

13.03.3

A cylinder of volume 0.25 m^3 contains nitrogen gas at a temperature of 17 °C and a pressure of 1.0×10^5 Pa. Molar mass of nitrogen = 0.028 kg mol^{-1}. Calculate:

a) The number of moles of gas in the cylinder

Use

$$pV = nRT$$

Rearrange:

$$n = \frac{pV}{RT} = \frac{1.0 \times 10^5\ \text{Pa} \times 0.25\ \text{m}^3}{8.3\ \text{J mol}^{-1}\ \text{K}^{-1} \times 290\ \text{K}} = \underline{\mathbf{10.4\ mol}}$$

b) The rms speed of the gas molecules at 17 °C

Use

$$p = 1/3\ \rho \langle c^2 \rangle$$

Work out density

$$\rho = \text{mass} \div \text{volume} = \frac{10.4\ \text{mol} \times 0.028\ \text{kg mol}^{-1}}{0.25\ \text{m}^3} = \frac{0.291\ \text{kg}}{0.25\ \text{m}^3} = 1.16\ \text{kg m}^{-3}$$

$$1.0 \times 10^5\ \text{Pa} = 1/3 \times 1.16\ \text{kg m}^{-3} \times \langle c^2 \rangle$$

$$\langle c^2 \rangle = \frac{3 \times 1.0 \times 10^5\ \text{Pa}}{1.16\ \text{kg m}^{-3}} = 2.59 \times 10^5\ \text{m}^2\ \text{s}^{-2}$$

RMS speed = $\underline{\mathbf{509\ m\ s^{-1}}}$

c) The average translational KE of a nitrogen molecule.

Average Kinetic energy per molecule = $3/2\ kT$

$= 3/2 \times 1.38 \times 10^{-23}\ \text{J K}^{-1} \times 290\ \text{K} = \underline{\mathbf{6.0 \times 10^{-21}\ J}}$

d) The total kinetic energy of the gas in the cylinder.

Total number of molecules = 10.4 mol × 6.02×10^{23} mol^{-1} = 6.26×10^{24}

Total kinetic energy = $6.26 \times 10^{24} \times 6.0 \times 10^{-21}$ = **<u>37 600 J</u>** = 38 000 J (2 s.f.)

Tutorial 13.04

13.04.1

Internal energy is a measure of the vibration of molecules in a material.

In a monatomic gas, it is a measure of kinetic energy of the atoms of gas.

In molecular gases, the internal energy is representative of the sum of kinetic energy of the molecules and the vibration of the bonds.

13.04.2

Energy supplied = increase in internal energy + work done by system

25 J = ΔU + 20 J

ΔU = **5 J**

13.04.3

The pump will spring back to where it was.

The gas will cool down, having gained its energy from the surroundings.

13.04.4

Work out the change in volume:

ΔV= 0.125 m^2 x 0.20 m = 0.025 m^3

Now use $\Delta W = p\Delta V$

DW = 1.5 x 10^6 Pa x 0.025 m^3 = **37 500 J**

13.04.5

Probability = 1/2^{29} = 1 ÷ 5.37 × 10^8 = **1.86 × 10^{-9}**

13.04.6

Time taken = 5.37 × 10^8 s

= 5.37 × 10^8 s ÷ (365 d y^{-1} × 86400 s d^{-1}) = **17 years**

(I am sure you have better things to do...)

13.04.7

Use:

$$S = k \ln W$$

S = 1.38 ×10^{-23} J K^{-1} × ln ($10^{22)}$ = 1.38 × 10^{-23} J K^{-1} × 50.66 = **6.99 × 10^{-22} J K^{-1}**

13.04.8

Neutrons are unstable, and decay by beta minus decay to protons.

On average, the decay time of an isolated neutron is about 8 minutes.

Tutorial 13.05

13.05.1

a) If the temperature is 30 °C, calculate the Boltzmann Factor.

Use:

$$\frac{n_\varepsilon}{N} = e^{-\frac{\varepsilon}{kT}}$$

Use natural logs:

$\ln(n_\varepsilon/N) = -(6.0 \times 10^{-21}\ \mathrm{J} \div (1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}} \times 303\ \mathrm{K})) = -1.43$

$n_\varepsilon/N = e^{-1.43} =$ **0.24** (2 s.f.)

Therefore 24 % of the molecules will have this energy.

b) The total number of molecules is 10 mol × $6.0 \times 10^{23}\ \mathrm{mol^{-1}} = 6.0 \times 10^{24}$.

Number of molecules that have energy 6.0×10^{-21} J $= 0.24 \times 6.0 \times 10^{24} =$ **1.4×10^{24}**

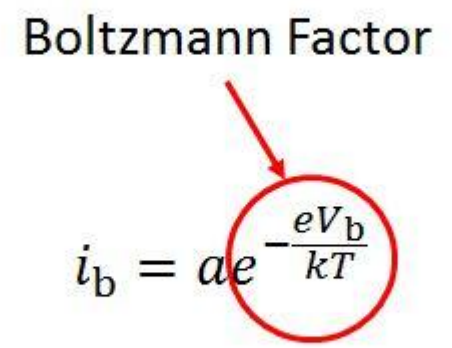
13.05.2

The Boltzmann Factor is shown in the ring.

$$K = Ae^{-\frac{\varepsilon_A}{kT}}$$

13.05.3

(a) The Boltzmann Factor is shown in the ring.



ln (Boltzmann factor) = $-((1.602 \times 10^{-19}\ \text{C} \times 0.45\ \text{V}) \div (1.38 \times 10^{-23}\ \text{J K}^{-1} \times 298\ \text{K}))$

$= -(7.209 \times 10^{-20}\ \text{J} \div 4.112 \times 10^{-21}\ \text{J}) = -17.5$

Boltzmann factor = $e^{-17.5}$ = **25.1×10^{-9}**

(b)

$i_b = 25.1 \times 10^{-9} \times 40 =$ **1.0×10^{-6} A** $= 1.0\ \mu\text{A}$

13.05.4

(a) Use:

$$\text{Probability} = e^{-\frac{\phi}{kT}}$$

Temperature = 1000 + 273 = 1273 K (Who put 1000 into their equation?)

$\ln(\text{Probability}) = -((1.602 \times 10^{-19}\ \text{J eV}^{-1} \times 3.45\ \text{eV}) \div (1.38 \times 10^{-23}\ \text{J K}^{-1} \times 1273\ \text{K}))$

$= -(5.52 \times 10^{-19}\ \text{J} \div 1.757 \times 10^{-20}\ \text{J}) = -31.4$

$\text{Probability} = e^{-31.4}$ = **2.31×10^{-14}** (which is about $2 \times 10^{-14\ \text{QED}}$)

(b) Use:

$$J = AT^2 e^{-\frac{\phi}{kT}}$$

$J = 1.2 \times 10^{6}\ \text{A m}^{-2}\ \text{K}^{-2} \times (1273\ \text{K})^2 \times 2.26 \times 10^{-14}$ = **$0.0439\ \text{A m}^{-2}$** $= 0.044\ \text{A m}^{-2}$ (2 s.f.)

(c)

$\text{Area} = \pi \times (1.0 \times 10^{-3})^2 = 3.14 \times 10^{-6}\ \text{m}^2$.

Current = current density × area

$I = 0.0439\ \text{A m}^{-2} \times 3.14 \times 10^{-6}\ \text{m}^2$ = **$1.38 \times 10^{-7}\ \text{A}$** $= 0.14\ \mu\text{A}$

(d)

If the temperature is room temperature, the probability of the emission is very low since the result of ϕ/kT is high. As probability is e to the power of a large negative number, the probability becomes very low.

The current density is the product of the Richardson Constant, the square of the temperature, and the probability. The square of a low temperature makes the current density extremely low.

(The figures (not needed) are $\text{Probability} = e^{-136} = 8.6 \times 10^{-60}$. $J = 1.2 \times 10^{-48}\ \text{A m}^{-2}$, not very high.)