Thermodynamics

Unit 1

Contents

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1.2 Work, heat and the first law of thermodynamics (page 9)	• Give the definitions of isothermal, isobaric, isochoric and adiabatic processes and draw their associated p–V diagrams. • Calculate work and heat for ideal gas processes. • State the first law of thermodynamics. • Identify the appropriate form of the first law of thermodynamics for isobaric, isochoric and isothermal processes. • Describe ways of changing the internal energy of a gas. • Apply thermodynamics laws to solve simple numerical problems. • Solve problems involving calculations of pressure, temperature or volume for a gas undergoing adiabatic changes. • Define molar heat capacity. • Distinguish between molar heat capacity at constant pressure and at constant volume. Show their relationship based on Mayer's equation. • Show that the molar heat capacity at constant pressure is greater than the molar heat capacity at constant volume. • Evaluate $C_p - C_v$ and $\frac{C_p}{C_v}$ for an ideal gas. • Indentify the value of $\frac{C_p}{C_v}$ for atomic gases and monatomic gasses. • Use $TV^{\gamma-1}$ = constant for adiabatic processes to solve problems.
1.3 Kinetic theory of gases (page 21)	• State the assumptions made to define an ideal gas. • Describe the kinetic theory of gases, including the importance of Brownian motion and diffusion. • Define r.m.s. velocity of a gas and the mean free path for a gas particle. • Use the expression for the pressure of an ideal gas in terms of its density and mean square speed of molecules to solve problems. • Solve problems to determine p, V, T or r.m.s. speed of gas molecules for an ideal gas, given relevant data. • State Graham's law of diffusion and use it to solve related problems. • State Dalton's law of partial pressure and use it to solve related problems.

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Section	Learning competencies
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1.5 Heat engines and refrigerators (page 37)	• Describe the fundamental principles of heat engines and refrigerators. • Solve problems involving heat flow, work and efficiency in a heat engine. • Identify that all real heat engines lose some heat to their surrondings. • Investigate the physical principles that all heat engines and refrigerators must obey.

Figure 1.1 *Sadi Carnot was born in Paris in 1796. He was the first person to start thinking about how to better the steam engines that were proving so valuable during the Industrial Revolution.*

Another title for this unit could be "The universe and everything in it". Thermodynamics is a grand topic. Historically, it has humble roots in the Industrial Revolution of the 19th century and the rise of the steam engine as a way of harnessing the power of nature to meet the needs of mankind. The term is derived from the Greek words *therme*, meaning heat, and *dynamis*, meaning power. Following the subsequent discovery of the atom, this new branch of physics has grown to help us now understand the interaction between energy and matter on a multitude of spatial scales: from the interaction between individual atoms, through all processes and events that occur in our own everyday surroundings, to stars, galaxies and even the universe as a whole.

As physicists, our role is often to take a reductionist approach: that is, to reduce the world around us to more simple, more fundamental situations that allow us to use the basic laws we have at our disposal to solve specific problems. **Thermodynamics** is different. For example, we might wish to work out the effect of heating a gas in a sealed container. Alternatively, we might squash the gas. We could work out that the pressure of the gas on the walls of the container would increase in both cases by applying the laws of Newtonian mechanics to every molecule in the gas. **Newton's laws** are very simple but this would be an extremely time-consuming process. Instead, the laws of thermodynamics provide us with solutions to these problems whilst requiring knowledge of only large-scale quantities of the gas such as volume, temperature and pressure.

As they do not depend on the specific details of the systems being studied, the laws of thermodynamics are extremely powerful tools that allow us to predict the behaviour of systems like machines, engines and, in particular, gases. These same laws also help to provide us with answers to deep questions like:

- Why does the "arrow of time" only ever point in one direction?
- How will the universe end?
- What will happen to an object if you keep cooling it down?

KEY WORDS

thermodynamics *the study of energy conversion between heat and other forms of energy*

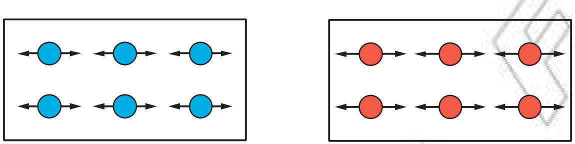
Newton's laws *laws describing the relationship between the forces acting on a body and its motion due to those forces*

1.1 Thermal equilibrium and definition of temperature

By the end of this section you should be able to:

- Define the terms atomic mass, mole, molar mass and Avogadro's number. Use their relationship to solve related problems.
- Define the zeroth law of thermodynamics.
- Determine the relationship between temperature and energy transfer and thermal equilibrium.
- State what is meant by an absolute scale of temperature.
- Draw phase diagrams to determine the triple point of a substance.
- Differentiate between the critical point and the boiling point of a substance.

Before we can learn the laws of thermodynamics and be able to apply them successfully, we must first be confident of our understanding of the particle model of matter, and terms such as heating and thermal equilibrium. Temperature is more difficult to define and we will encounter a number of different ways to approach temperature in this unit.



cold – molecules vibrate a bit

hot – molecules vibrate faster and are slightly further apart

Figure 1.2 *Temperature is related to the average random kinetic energy of particles in a substance.*

Atoms and moles

In order to understand temperature and heat at the particle level we need to use and understand the terms moles and molar mass.

The mole (unit, mol) is a measure of number of discrete particles in a substance (solid, liquid or gas). From definition:

- 1 mol = 6.02×10^{23} particles

1 mol of helium gas contains 6.02×10^{23} particles of helium. However care must be taken when dealing with more complex substances. Each water molecule contains two hydrogen atoms and one oxygen atom (H_2O). 1 mol of water contains 6.02×10^{23} molecules of water. This equates to 6.02×10^{23} atoms of oxygen and 1.20×10^{24} atoms of hydrogen (as there are two hydrogen atoms in each water molecule).

DID YOU KNOW?

6.02×10^{23} is called Avogadro's number (N_A); it is defined as the number of particles in 12 g of carbon-12.

The relationship between the number of moles, the number of particles and Avogadro's number is shown below:

- $N = nN_A$

where

N = number of particles

n = number of moles

N_A = Avogadro's number, 6.02×10^{23} mol^{-1}

Discussion activity

It is often helpful to know the mass of 1 mol of a substance. This is called the molar mass. One mole of carbon-12 has a **molar mass** of 12 g or 0.012 kg. Uranium-238 has a molar mass of 238 g or 0.238 kg. If you know the number of moles of a substance and the molar mass of you can calculate the mass of the substance.

- $m = nM$

where

m = mass of substance

n = number of moles

M = molar mass

This equation can be combined with the previous one to give:

- $n = \frac{N}{N_A} = \frac{m}{M}$

From this the mass of each particle (m_p) can be calculated using:

- $m_p = \frac{M}{N_A}$

or

- $m_p = \frac{m}{N}$

KEY WORDS

molar mass *the mass of one mole of a substance*

kinetic energy *the energy possessed by an object as a result of its motion*

thermal energy *the energy possessed by an object resulting from the movement of its particles*

internal energy *the sum of the random distribution of kinetic and potential energies associated with the molecules within a system*

zeroth law *two bodies that are separately in thermal equilibrium with a third body must be in thermal equilibrium with each other*

thermal equilibrium *condition in which two bodies are at the same temperature and there is no net transfer of energy between them*

Worked example 1.1

A block of pure carbon-12 contains 4.2 mol particles. Calculate:

a) the number of particles in the block

b) the mass of the block

c) the mass of each carbon-12 atom.

a) • $N = nN_A$	*Use the relationship between number of moles and Avogadro's number*
• $N = 4.2 \times 6.02 \times 10^{23}$	*Substitute the known values*
• $N = 2.5 \times 10^{24}$ particles	*Solve the equation*
b) • $m = nM$	*Use the relationship between number of moles and Molar mass*
• $m = 4.2 \times 0.012$	*Substitute the known values*
• $m = 0.05$ kg	*Solve the equation*
c) • $m_p = \frac{M}{N_A}$	*Use the relationship between number of moles and Molar mass*
• $m_p = \frac{0.012}{6.02 \times 10^{23}}$	*Substitute the known values*
• $m_p = 2.0 \times 10^{-26}$ kg	*Solve the equation*

What causes thermal energy transfer?

The particle model of matter is a way of visualising what individual particles are doing inside a substance. In solids, particles are vibrating. In liquids and gases, the particles are moving more freely. In all cases, the particles have kinetic energy; this causes them to collide with their neighbours. As a result, energy is distributed throughout the substance. There is a range of different particle speeds and directions within the substance: so many, in fact, that we say that the motion is random. However, on average if the particles in the substance are vibrating faster we would say that the substance is hotter – the temperature is higher.

Temperature is something that we all have experience of. If we place two bodies of different temperatures in contact, then the particles at the boundary will collide and the kinetic energy of particles is transferred backwards and forwards between the objects. A ‘body’ is another word for an object. On average, the particles in the hotter body have more **kinetic energy** than those in the colder body, so there is a net transfer of **thermal energy** from the hotter body to the colder body. This process is referred to as heating. This is the only way that the word heat can be used. A body does not contain or possess heat. This is just the same as an electrical component, which does not contain or possess electrical current. Instead we will use the term **internal energy** to describe the total energy that is internal to bodies.

- Temperature is a measure of the average random kinetic energy of particles in a body, and is used to determine in which direction there will be a net energy flow when two bodies are close to one another.

Activity 1.1: Hot and cold water

Place one hand in a bucket of cold water and the other hand in a bucket of warm water. Think about what is happening to the particles in your hand and in the water. In which direction is heat transfer taking place and why?

What is the zeroth law?

The zeroth law of thermodynamics states that:

“Two bodies that are separately in thermal equilibrium with a third body must be in thermal equilibrium with each other.”

When two bodies are in **thermal equilibrium** then there is no net transfer of energy between them.

From our everyday experience, the zeroth law may seem obvious, but it provides us with a way of defining temperature: it is the property of a body that determines whether it is in thermal equilibrium with other bodies. This also enables accurate calibration between thermometers of different kinds.

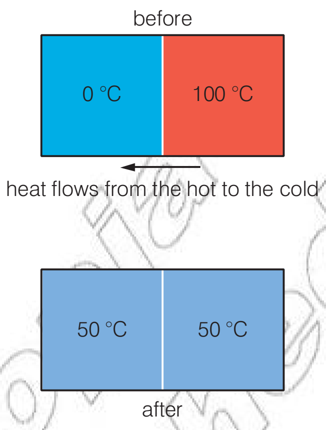


***Figure 1.3** Heat flows from the hotter body to the colder body until the temperatures are equal.*

DID YOU KNOW?

Historically, of the four laws of thermodynamics, the first to be derived was the so-called **second law**. The **first law** came next. The **third law** was only formulated in 1912 and the **zeroth law**, although very important, was developed as something of an afterthought.

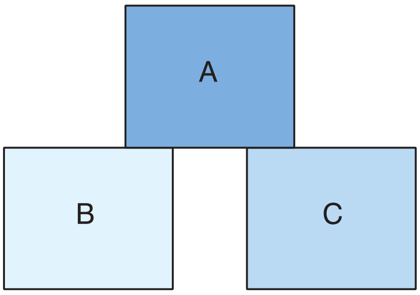


***Figure 1.4** If A is in thermal equilibrium with B, and C is in thermal equilibrium with B, then A is also in thermal equilibrium with C.*

DID YOU KNOW?

The term **steady state** can be confused with the term thermal equilibrium. Steady state indicates that a situation is not changing with time. There may be a constant temperature difference between two bodies so there may be a steady non-zero net flow of energy between them. Thermal equilibrium implies steady state, but the reverse is not true.

KEY WORDS

steady state *a situation that is not changing with time*

DID YOU KNOW?

The Kelvin temperature scale is referred to as 'absolute' as it is independent of any other property of a substance.

Figure 1.6 *The triple point of water is the temperature (and pressure) at which all three phases (ice, water and water vapour) coexist in thermal equilibrium.*

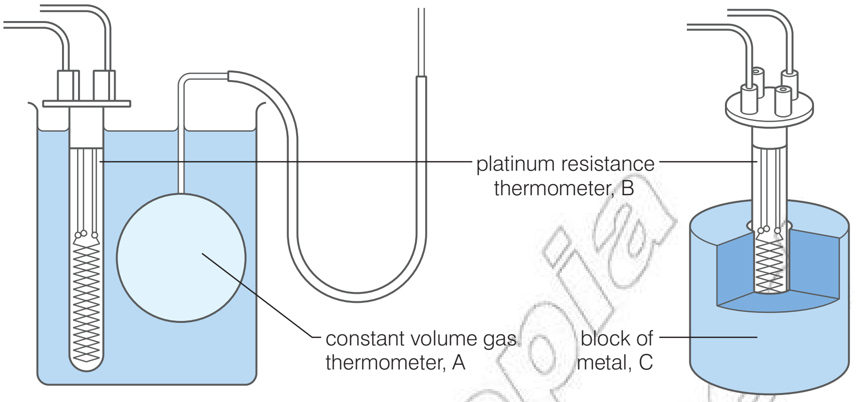


Figure 1.5 *The constant volume gas thermometer, A, indicates a consistent water temperature T and the platinum resistance thermometer, B, indicates a consistent water temperature of $T + \Delta T$. When the platinum resistance thermometer is then placed in contact with the block of metal it indicates a consistent temperature of $T + \Delta T$. The water, the block of metal and the two thermometers are therefore all in thermal equilibrium.*

The thermodynamic temperature scale

The accurate and reliable measurement of temperature has always posed problems for scientists. An international conference in 1947 decided that the absolute temperature scale that should be used was the thermodynamic, or ideal gas, temperature scale measured in kelvin (K). **Absolute zero**, the temperature at which all the random motion of particles in a substance ceases, is defined as 0 K and the triple point of water, the temperature at which all three states of water can coexist, is defined as 273.16 K. In relation to the Celsius temperature scale, t, the **thermodynamic scale**, T, is then given by:

$$T(\text{K}) = t(°\text{C}) + 273.15$$

	Absolute temperature (K)	Celsius temperature (°C)
Absolute zero	0.00	−273.15
Triple point of water	273.16	0.01
Ice point	273.15	0.00
Steam point	373.15	100.00
Room temperature	293	20

Table 1.1 *Important temperatures in units of kelvin and degrees Celsius.*

Activity 1.2: Celsius and kelvin

Research the temperature of a range of objects (e.g. the surface of the Sun, a healthy human body temperature, etc.) and express these in °C and in K.

Discussion activity

The third law of thermodynamics is not a law in the same way as the others. But for completeness, it states: "no object can reach a temperature of **absolute zero** in a finite number of steps." Can you explain why this is true?

KEY WORDS

absolute zero *the temperature at which all random motion of particles in a substance ceases*

thermodynamic scale *an absolute measurement of temperature*

phase (of matter) *point at which all the physical properties within a material are uniform*

phase diagram *graph of pressure against temperature for a given substance*

Phases of matter

A **phase** of matter is when all the physical properties within a material are uniform. At a given phase of matter a material will have the same density and refractive index.

Take the example of some ice cubes in a glass of water. The ice cubes are at one phase, the water is at another and there is a third phase just above the water as it evaporates.

States of matter are classifications of the distinct phases of matter based on their large-scale properties. For example, a solid phase is the state in which the substance maintains a fixed volume and a fixed shape, whereas the liquid phase is one where the substance can change to take the shape of its container.

Changing the pressure or temperature of a substance will affect its phase. Plotting a graph of pressure against temperature is often called a **phase diagram**.

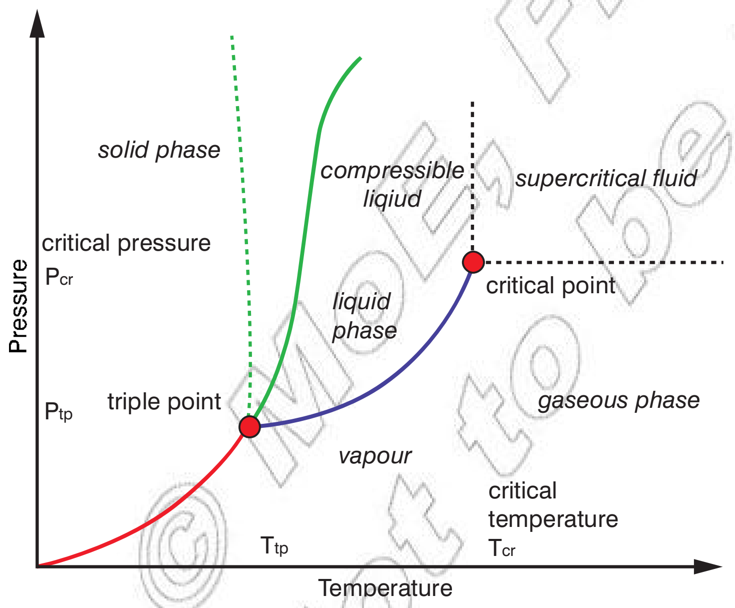


Figure 1.7 *A phase diagram showing different states of matter*

From the graph there are clear boundaries between different phases and two points of particular interest.

Triple point

As we've already mentioned this is the specific temperature and pressure where all three states of matter are able to exist in thermal equilibrium.

Critical point (sometimes called a critical state)

The critical point occurs where the critical temperature and critical pressure of a substance meet. Above this point clear phase boundaries cease to exist. For water the critical point is around 647 K and 22 MPa. The properties of the gas and liquid phases merge together giving only one phase at the critical point. The substance forms a supercritical fluid. Above the critical temperature it is not possible to form a liquid, regardless of any increase in pressure.

The critical point is different to the boiling point of a substance. The boiling point of a substance is usually meant to mean the boiling point at standard atmospheric pressure. However, in Figure 1.7 the actual boiling point of a substance depends on the surrounding pressure. From the phase diagram the substance has a number of boiling points following the curving blue line. The lower the pressure, the lower the boiling point.

The critical point only occurs at one specific temperature and pressure.

Summary

- 1 mol = 6.02×10^{23} particles
- The zeroth law of thermodynamics: two bodies that are separately in thermal equilibrium with a third body must be in thermal equilibrium with each other.
- Temperature defines the direction of net energy transfer between two bodies.
- When two bodies are in thermal equilibrium then there is no net transfer of energy between them and they are both at the same temperature.
- The absolute temperature scale: $T(\mathrm{K}) = t(°\mathrm{C}) + 273.15$

Review questions

1. Convert the following to degrees Celsius:
   a) the boiling point of helium, 4.25 K
   b) the freezing point of gold, 1340 K.
2. Convert the following to kelvin:
   a) the freezing point of mercury, –39 °C
   b) the average temperature of the universe, –270.42 °C.
3. In Figure 1.5, why was it necessary to say that the readings on the thermometers were consistent?
4. Sketch a phase diagram labelling and explaining any key points.

1.2 Work, heat and the first law of thermodynamics

By the end of this section you should be able to:

- Give the definitions of isothermal, isobaric, isochoric and adiabatic processes and draw their associated p–V diagrams.
- Calculate work and heat for ideal gas processes.
- State the first law of thermodynamics.
- Identify the appropriate form of the first law of thermodynamics for isobaric, isochoric and isothermal processes.
- Describe ways of changing the internal energy of a gas.
- Apply thermodynamics laws to solve simple numerical problems.
- Solve problems involving calculations of pressure, temperature or volume for a gas undergoing adiabatic changes.
- Define molar heat capacity.
- Distinguish between molar heat capacity at constant pressure and at constant volume. Show their relationship based on Mayer's equation.
- Show that the molar heat capacity at constant pressure is greater than the molar heat capacity at constant volume.
- Evaluate $C_p - C_v$ and $\frac{C_p}{C_v}$ for an ideal gas.
- Identify the value of $\frac{C_p}{C_v}$ for atomic gases and monatomic gasses.
- Use $TV^{\gamma-1}$ = constant for adiabatic processes to solve problems.

KEY WORDS

caloric *a 19th century representation of heat as an invisible fluid*

In the early 19th century, steam engines were becoming more popular and were replacing traditional methods of doing work, for example, moving objects and people from one place to another. Sadi Carnot and many other scientistists of the time believed that heat was like an invisible, massless fluid – it was then called '**caloric**'. The steam engine, according to Carnot, worked like a water mill with caloric running 'downhill' from the boiler to the condenser and, in the process, driving the shafts of the engine.

Twenty years later, James Prescott Joule, working in his father's brewery in England, showed that the temperature of a body could be increased just by doing mechanical work on it. He called this process the 'mechanical equivalent of heat'. His work showed that the idea of heat as a fluid running 'downhill' was false. He also paved the way for a greater understanding of energy and temperature leading to the first law of thermodynamics.

KEY WORDS

Carnot's principle *a principle that sets a limit on the maximum efficiency any possible engine can obtain*

system *a body that is the subject of study and that may be solid, liquid or gas*

surroundings *the environment that is around a system and in thermal contact with it*

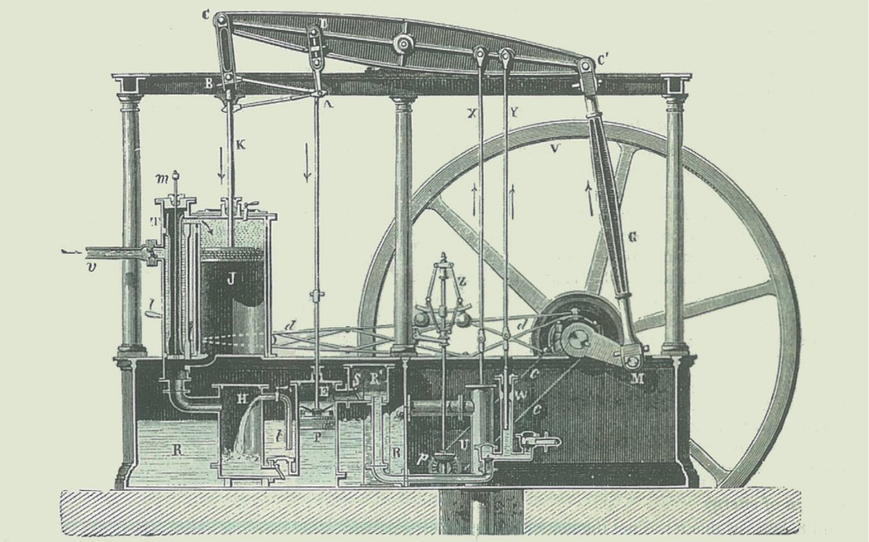


Figure 1.8 *An example of an early steam engine. Just like the amount of water stays constant as it flows through a water mill, so Carnot thought that the total amount of caloric was unchanged as it ran through a steam engine. This part of his idea was later shown to be incorrect but* ***Carnot's principle*** *is still used today to determine the maximum efficiencies of boilers and turbines in power stations.*

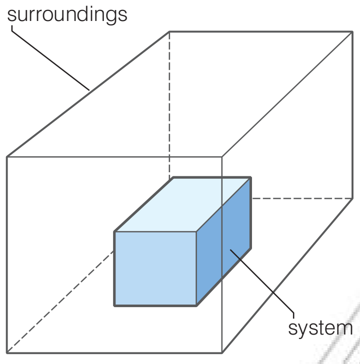


Figure 1.9 *A representative diagram of a system and its surroundings*

What exactly is internal energy?

In the topic of thermodynamics we always study a **system** in relation to its **surroundings**. The system is another word for a body that may be solid, liquid or gas, complex or simple. It is the 'thing' that we are interested in. The surroundings might be the table an object is resting on and the atmosphere around it, or it may be the entire universe. It is that which surrounds the system and is in thermal contact with it.

It seems common sense that if we heat a system then that system will become hotter. But is this always true? What if the system was a small beaker of water at room temperature placed above a candle flame? Its temperature will increase until it reaches 100 °C, but the temperature will then stay constant as the water boils. Clearly we have transferred energy to the water at a constant rate. At the start of the heating process the energy transferred increased the average random kinetic energy of the molecules in the water. But during the phase change from liquid to gas, work was done on individual molecules to move them apart against their intermolecular attraction. The internal energy of the steam at 100 °C is greater than that of the same mass of water at 100 °C.

- The internal energy of a system is the sum of the random distribution of kinetic and potential energies associated with the molecules within that system.

Discussion activity

What about ideal gases? Within an ideal gas, there are no intermolecular forces except during collisions, so the internal energy is equal to the sum of random kinetic energies of the particles only.

What about melting ice? When ice melts, the water molecules in the liquid phase are closer to each other, on average, than the molecules in the solid phase. However, energy is still required in order to break the hydrogen bonds that exist between the molecules in ice, and so the internal energy still increases.

What is the first law of thermodynamics?

The work of Joule mentioned at the start of this section led to the idea that energy as a quantity is conserved whenever any process takes place. This notion is expressed most often as the ‘law of conservation of energy’, which is a simplification of **the first law of thermodynamics**. The first law states that:

“The increase in internal energy of a system is equal to the sum of the energy entering the system through heating, and the work done on the system.”

When defining the three quantities, particular attention must be paid to the sign of each quantity. These have the following definitions:

ΔU = *increase* in internal energy of the system

ΔQ = the amount of energy transferred to the system by heating it (that is, by means of a temperature gradient)

ΔW = the amount of work done on the system

The first law of thermodynamics is therefore written as:
$\Delta U = \Delta Q + \Delta W$

KEY WORDS

the first law of thermodynamics *the increase in internal energy of a system is equal to the sum of the energy entering a system through heating, and the work done on the system*

adiabatic *a process that involves no energy transfer into or out of a system as a result of heating*

The bicycle pump

An **adiabatic** process involves no energy transfer into or out of a system as a result of heating. For example, if we push the plunger of a bicycle pump very rapidly whilst blocking the hole at the end of the pump with our finger, the air inside the pump is compressed. The mechanical work done *on* the air results in an *increase* in the internal energy of the air. As there is no phase change, the average potential energy of the molecules stays constant but the average random kinetic energy of the molecules increases; evidence of this is an increase in the temperature of the air. As the compression takes place rapildy, there is a negligible time in which energy transfer to the surroundings by heating can occur, and the process is nearly adiabatic. Of course, after the compression is complete, the temperature gradient between the system and its surroundings will result in an energy transfer *from* the system, resulting in a *decrease* in the internal energy of the air (and the warming of the pump, the surrounding air and your hand).

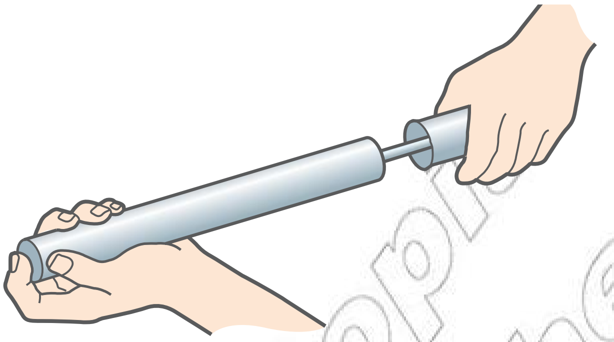


Figure 1.10 *Compressing the air in a bicycle pump*

KEY WORDS

isothermal *a process which involves no change in the temperature of the system*

An **isothermal** process involves no change in the temperature of the system. In these types of processes heating of the system or by the system must be allowed to occur. In practice, this means that the process must occur extremely slowly, also called quasistatically, so that a tiny temperature gradient can be set up allowing the flow of heat into or out of the system. If we were to ensure that the bicycle pump were made of metal, to allow the fast transfer of energy out of the system through heating, and we push the plunger in very slowly whilst blocking the hole at the end of the pump with our finger, the compression of the air inside the pump is very nearly isothermal.

- An adiabatic process involves no transfer of energy into or out of the system as a result of a temperature gradient.
- An isothermal process involves no change in the temperature of the system.

How can we calculate the increase in the internal energy of a system?

1. *Heating the system*. For example, if we transfer energy to a volume of water in a beaker by heating the beaker using a Bunsen flame. If no work is done on or by the system then $\Delta W = 0$ and:

$$\Delta U = \Delta Q = mc\Delta T$$

where m is the mass of the water, c is the specific heat capacity of the water and ΔT is the *increase* in the temperature of the water.

2. *Doing electrical work on the system*. For example, if we pass an electric current, I, through a wire by placing a potential difference, V, across the wire for a time, Δt. If the process was adiabatic then $\Delta Q = 0$ and:

$$\Delta U = \Delta W = VI\Delta t$$

3. *Doing mechanical work on the system*. For example, if we depress a frictionless plunger in a sealed syringe containing helium gas by a distance, Δx, using a constant force, F. If the process was adiabatic then $\Delta Q = 0$ and:

$$\Delta U = \Delta W = F\Delta x$$

Alternatively, if we know that the volume of the helium was changed by an amount ΔV, whilst the pressure on the gas remained at a constant value, p, then we can calculate the change in internal energy using:

$$\Delta U = \Delta W = -p\Delta V$$

The negative sign is necessary as a decrease in volume of the gas results in work being done on the gas and a subsequent increase in internal energy.

Discussion activity

Can you show that the expressions for mechanical work, $F\Delta x$ and $p\Delta V$, are equivalent?

Remember: doing work on a system is very different to heating it. Working is an ordered process that has nothing to do with a temperature gradient. It does not matter whether the system is hotter or colder than its surroundings. You can still do work on it by applying a force over a certain distance. Heating, on the other hand, is a random process that can only transfer energy down a temperature gradient.

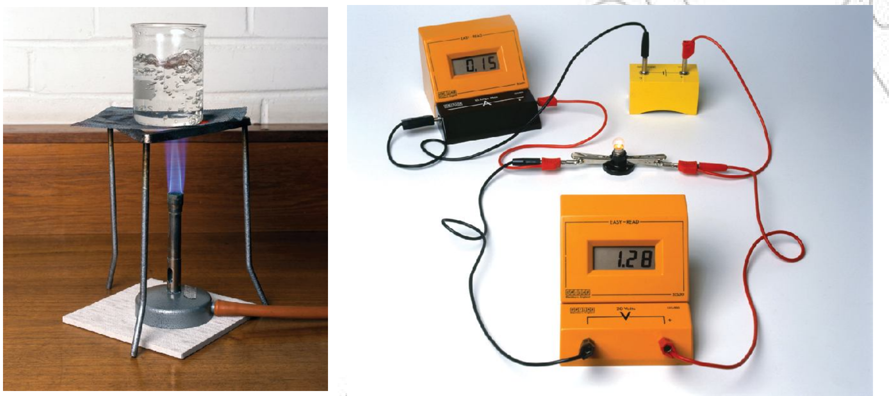


***Figure 1.11** Examples of how to increase the internal energy of a system: (a) heating a volume of water; (b) passing an electric current through a wire inside a bulb*

Discussion activity

Insulated systems allow no transfer of energy by heating. **Isolated** systems do not interact with their surroundings so their internal energy remains constant. Very few objects, including those in space, are truly isolated. Perhaps the only isolated system in existence is the entire universe. If the internal energy of the universe is constant then where did all the energy come from originally?

KEY WORDS

insulated *a system that allows no transfer of energy by heating*

isolated *a system that does not interact with its surroundings, hence its internal energy remains constant*

Discussion activity

How is the first law of thermodynamics related to the law of heat exchange that we have studied previously? Which law is more general? As a reminder, the law of heat exchange states that, for an isolated system:

$$\sum Q_{\text{lost}} + \sum Q_{\text{gained}} = 0$$

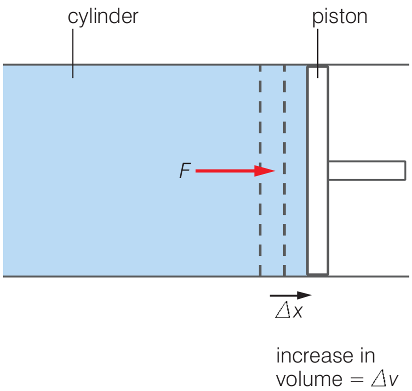


Figure 1.12 *Expansion of ammonia gas in a cylinder*

Example calculation using the first law of thermodynamics

Imagine ammonia gas expanding rapidly within a cylinder forcing a frictionless piston to move a distance of 5.0 cm, as shown in Figure 1.12. The process is isobaric, that is, the pressure of the gas remains constant, at 130 kPa. The mass of the gas is 650 mg and the area of the piston in contact with the gas is 3.0×10^{-3} m². What happens to the temperature of the ammonia?

(Specific heat capacity of ammonia at constant pressure = 2.2 kJ/kg K)

The change in volume of the gas

$$= 3.0 \times 10^{-3}\ \text{m}^2 \times 0.050\ \text{m}$$
$$= 1.5 \times 10^{-4}\ \text{m}^3$$

The mechanical work done by the gas on the piston

$$= p\Delta V$$
$$= 1.3 \times 10^5\ \text{Pa} \times 1.5 \times 10^{-4}\ \text{m}^3$$
$$= 19.5\ \text{J}$$

As the process occurs rapidly it is nearly adiabatic, $\Delta Q = 0$ and the first law of thermodynamics reduces to:

$$\Delta U = \Delta W = -p\Delta V$$
$$= -19.5\ \text{J}$$

Since work was done by the gas on its surroundings the internal energy of the gas has decreased. Assuming no change of phase of the gas, we can now find out by how much the temperature of the gas has decreased:

$$\Delta U = mc\Delta T$$
$$-19.5\ \text{J} = 6.5 \times 10^{-4}\ \text{kg} \times 2200\ \text{J/kg K} \times \Delta T$$
$$\Delta T = -14\ \text{K}$$

The temperature of the ammonia gas has decreased by 14 K.

Activity 1.3: Temperature of a rubber band

Carry out the following practical where the system being studied is a short piece of rubber band. For each step, write down whether the temperature of the rubber increased or decreased. Also, for each step, write down whether the values for ΔU, ΔQ and ΔW are negative, zero or positive.

1. Place the rubber band against your lower lip and stretch it *quickly*.
2. Keep the rubber band stretched against your lower lip for 10 seconds.
3. Still holding the rubber against your lip, *quickly* allow it to return to its original length, but keep hold of it!
4. Keep the rubber band in contact with your lower lip for 10 seconds.

The first law for different thermodynamic processes

Isobaric

During an **isobaric process** the pressure of the system remains constant. Any work done by the system will result in an increase in volume. For example, imagine a gas expanding at constant pressure.

The yellow area represents the work done. This is given by:

- $\Delta W = p\Delta V$

Substituting this into the first law equation gives:

- $\Delta U = \Delta Q + \Delta W$
- $\Delta U = \Delta Q + p\Delta V$

Remember the $+\Delta W$ represents work done on the system. In the case of the expanding gas, work is being done by the system and the equation would be written as:

- $\Delta U = \Delta Q - p\Delta V$

KEY WORDS

isobaric process *a process in which the pressure of a gas remains constant*

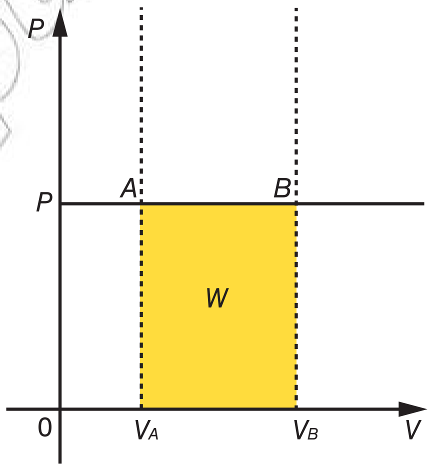


Figure 1.13 *A simple p–V digram for an isobaric process*

Isochoric

If the volume of the system remains constant then there is no mechanical work down on the system. Since $\Delta W = p\Delta V$, if $\Delta V = 0$, ΔW must also equal 0. The first law equations for an isochoric process would be written as:

- $\Delta U = \Delta Q + \Delta W$
- $\Delta U = \Delta Q + 0$
- $\Delta U = \Delta Q$

Activity 1.4 Thermodynamic processes

Draw a table showing the different forms of the first law for the four processes described.

Isothermal

If the process occurs at constant temperature then there is no change in the internal energy of the system so $\Delta U = 0$. The first law equations for an isothermal process would be written as:

- $\Delta U = \Delta Q + \Delta W$
- $0 = \Delta Q + \Delta W$
- $\Delta Q = -\Delta W$

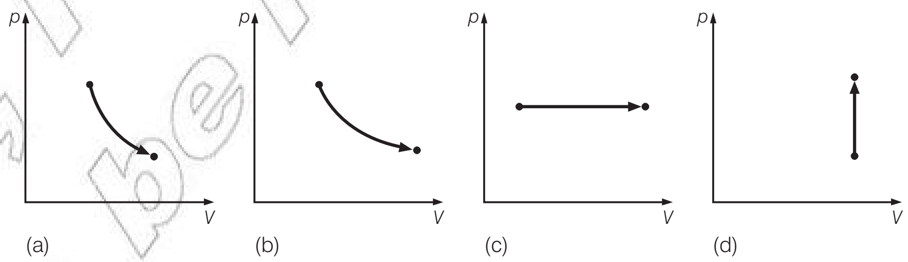
Adiabatic

During an adiabatic process there is no heat transfer into or out of the system, therefore $\Delta Q = 0$. The first law equations for an adiabatic process would be written as:

- $\Delta U = \Delta Q + \Delta W$
- $\Delta U = 0 + \Delta W$
- $\Delta U = \Delta W$

What general expressions can we derive for a gas when it is heated?

If the system we are investigating is a gas then pressure, p, and volume, V, are two important properties of that gas and we often represent the processes that change the state of the gas using a p–V graph. Examples of adiabatic, isothermal, isobaric and isochoric processes are provided in Figure 1.14.



(a) (b) (c) (d)

Figure 1.14 *p–V graphs of a gas under (a) adiabatic expansion; (b) isothermal expansion; (c) isobaric expansion; and (d) an isochoric increase in pressure. An isochoric process is one where the volume of the gas is constant.*

In each case the work done is represented by the area under the line. If the gas is doing work (i.e. the arrow is moving to the right) this area should be expressed as $-\Delta W$.

The physics of the gas phase is more accessible than that of the liquid or solid phase. So it is helpful to apply, in detail, the first law of thermodynamics to gases to try to understand more about the relationship between energy and temperature through the concept of heat capacity. When a gas is heated, we can use the **molar heat capacity**, the heat capacity per unit mole, to calculate the increase in temperature of the gas. As we shall see, we actually require two different quantities depending on the conditions under which the

KEY WORDS

molar heat capacity *the heat capacity per unit mole of a substance* heating takes place: the **molar heat capacity at constant pressure**, C_p, and the **molar heat capacity at constant volume**, C_V. Both have units of J/mol K.

Discussion activity

Why do we only require one value for the molar heat capacity of a liquid or a solid?

Note...

Lower case "c" is commonly used for specific heat capacity, heat capacity per unit mass, whereas upper case "C" is used for molar heat capacity.

When n moles of gas are heated resulting in a temperature rise of ΔT we can write:

$$C_p = \frac{\Delta Q_p}{n\Delta T}$$

and

$$C_V = \frac{\Delta Q_V}{n\Delta T}$$

where ΔQ_p is the energy transferred to the gas at constant pressure by heating and ΔQ_V is the energy transferred to the gas at constant volume by heating. If the gas is kept at constant pressure (approximately true for small changes in volume) then we know that it expands when heated and so does work on its surroundings. If the gas is kept at constant volume then no work is done by the gas. Using the first law of thermodynamics:

$$\Delta U = \Delta Q + \Delta W = \Delta Q - p\Delta V$$

so

at constant pressure: $\Delta Q_p = \Delta U + p\Delta V$

at constant volume: $\Delta Q_V = \Delta U$

From the above equations it can be seen that in order to produce an equal increase in internal energy, and a subsequent increase in temperature, a greater amount of energy must be transferred by heating a gas at constant pressure than by heating a gas at constant volume. This is because, at constant pressure, energy must also be supplied to enable the gas to do work in, for example, pushing a piston back against a restraining force. It is therefore always true that:

$$C_p > C_V$$

Quantitatively, we can also write:

$$\Delta Q_p = \Delta Q_V + p\Delta V$$

and substituting in our definitions of molar heat capacities we obtain:

$$C_p n\Delta T = C_V n\Delta T + p\Delta V$$

We will derive the ideal gas equation in the next section but it is:

$$pV = nRT \quad \text{(where } R = \text{molar gas constant)}$$

If the pressure is constant then a change in temperature of an ideal gas will produce a change in volume given by:

$$p\Delta V = nR\Delta T$$

substituting this we get: $C_p n\Delta T = C_V n\Delta T + nR\Delta T$

which reduces to: $C_p - C_V = R$

This relationship is called **Mayer's equation.**

So for gases that behave in an ideal fashion, C_p is always larger than C_V by an amount equal to the molar gas constant, 8.3 J/mol K. Table 1.2 provides the molar heat capacities of some real gases, showing increasing departure from ideal behaviour.

KEY WORDS

Mayer's equation *the difference between the specific heat of a gas at constant pressure and its specific heat at constant volume is equal to the molar gas constant*

We will show in the next section that the increase in internal energy of one mole of an ideal gas when heated at constant volume, producing a temperature increase of ΔT, is equal to $\frac{3}{2}R\Delta T$. We have already seen that $\Delta U = \Delta Q_V = C_V n\Delta T$ so, for one mole of gas with constant volume, the increase in internal energy is also equal to $C_V\Delta T$. Equating these two expressions we see that for an ideal gas $C_V = \frac{3}{2}R$ and hence $C_p = \frac{5}{2}R$. The ratio of C_p to C_V is commonly written as the symbol γ. For an ideal gas:

$$\gamma = \frac{C_p}{C_V} = \frac{5}{3}$$

Worked example 1.2

When heating one mole of a certain gas at constant volume, an energy transfer of 200 J produces an increase in temperature of 10 K. What temperature increase would there be if the same amount of gas was heated in the same way at constant pressure?

1. As the amount of energy transferred by heating is the same we can say that $\Delta Q_V = \Delta Q_p$ so:

   $$C_v n\Delta T_v = C_p n\Delta T_p$$

   where ΔT_v and ΔT_p are the temperature increases of the gas at constant volume and constant pressure, respectively.

2. Rearranging this equation we obtain:

   $$\frac{\Delta T_p}{\Delta T_v} = \frac{C_v}{C_p} = \frac{3}{5}$$

   and so the temperature increase of the gas at constant pressure is 0.6 x 10 K or 6 K.

Gas	c_p/Jmol^{-1} K^{-1}	c_v/Jmol^{-1} K^{-1}	($c_p - c_v$)/Jmol^{-1} K^{-1}
Nitrogen	29.0	20.7	8.3
Hydrogen	28.1	19.9	8.2
Carbon dioxide	36.6	28.2	8.4
Chlorine	34.2	25.1	9.1
Ammonia	37.2	27.8	9.4

***Table 1.2** Molar heat capacities of some real gases.*
Nitrogen shows behaviour that is closest to that of an ideal gas.

As discussed, for an ideal gas:

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3}$$

This equation is also valid for monatomic gases like helium and neon. However for diatomic gases such as nitrogen (N_2) and oxygen (O_2) this value slightly different.

	Monatomic (ideal) gases	Diatomic gases
$\gamma = \frac{C_p}{C_v}$	5/3 = 1.67	7/5 = 1.4

For a reversible, adiabatic process, it is also true that:

$TV^{\gamma-1}$ = constant

and

pV^{γ} = constant

where

T = absolute temperature in kelvin

V = volume of gas in m^3

p = pressure of gas in Pa

Therefore it follows that:

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

and

$p_1V_1^{\gamma} = p_2V_2^{\gamma}$

Worked example 1.3

A piston contains oxygen at 280 K occupying a volume of 0.25 m^3. The cylinder is compressed adiabatically to 0.14 m^3, find the increase in temperature of the gas.

Oxygen is a diatomic gas so $\gamma = 1.4$, using $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$ substituting in known values gives:

- $(280 \times 0.25)^{1.4-1} = (T_2 \times 0.14)^{1.4-1}$
- $\sqrt[(1.4-1)]{70} = \sqrt[(1.4-1)]{0.14T_2}$ *Solving the left hand side and rooting by the power*
- $70 = 0.14T_2$
- $T_2 = \frac{70}{0.14}$ *Rearranging to make T_2 the subject gives*
- $T_2 = 500$ K

Summary

- The first law of thermodynamics states that: $\Delta U = \Delta Q + \Delta W$, where ΔU is the *increase* in internal energy of the system, ΔQ is the amount of energy transferred to the system by heating it and ΔW is the amount of work done *on* the system.
- The internal energy of a gas can be increased by heating it or by doing mechanical work on it.
- When heating a system: $\Delta Q = mc\Delta T$
- When doing mechanical work on a gas: $\Delta W = -p\Delta V$
- In an isothermal process the temperature of the system remains constant.
- In an adiabatic process there is no transfer of energy into or out of the system by heating.
- For any gas: $C_p > C_V$.
- For an ideal gas: $C_p - C_v = R$ and $\frac{C_p}{C_V} = \frac{5}{3}$.

Review questions

1. In points 2 and 3 on page 12 (how to calculate the increase in internal energy of a system), the processes were adiabatic. How could this have been nearly achieved in practice in the two example situations?
2. Some fire extinguishers contain carbon dioxide stored under very high pressure. Use the first law of thermodynamics to explain why some carbon dioxide solidifies as 'dry ice' when released from such a fire extinguisher.
3. A lump of lead with mass 0.50 kg is dropped from a height of 20 m onto a hard surface. It does not rebound but remains there at rest for a long period of time.

   What are:

   a) ΔQ, (b) ΔW and (c) ΔU for the lead during this process?

   d) What is the temperature change in the lead immediately after the impact? [specific heat capacity of lead = 128 kJ/kg K]
4. 1000 cm^3 of air at 20 °C and 101.35 kPa is heated at constant pressure until its volume doubles.

   a) Use the ideal gas equation to calculate the final temperature of the gas.

   b) Calculate the work done by the gas as it expands.

1.3 Kinetic theory of gases

By the end of this section you should be able to:

- State the assumptions made to define an ideal gas.
- Describe the kinetic theory of gases, including the importance of Brownian motion and diffusion.
- Define of r.m.s. velocity of a gas and the mean free path for a gas particle.
- Use the expression for the pressure of an ideal gas in terms of its density and mean square speed of molecules to solve problems.
- Solve problems to determine P, V, T or r.m.s. speed of gas molecules for an ideal gas, given relevant data.
- State Graham's law of diffusion and use it to solve related problems.
- State Dalton's law of partial pressure and use it to solve related problems.

As we have started to look at gases in more detail at the end of the previous section, and before we move on to understand the workings and implications of the second law of thermodynamics, we will take an in-depth look at gases. In particular, we will derive equations that describe the macroscopic quantities and then the microscopic quantities of a gas. By quantitatively comparing these two quantities some remarkably simple and satisfying relationships will be found. In order to allow us to do this, we must make various assumptions about the gas, namely that it is 'ideal'. This is nearly true for a large number of gases as long as the pressure is not too high and the temperature is not too low.

What are the gas laws and the ideal gas equation?

From Figure 1.15 overleaf, the three gas laws may be summarised as follows;

Boyle's law: pV = constant (if T is constant)

Charles' law: $\frac{V}{T}$ = constant (if p is constant)

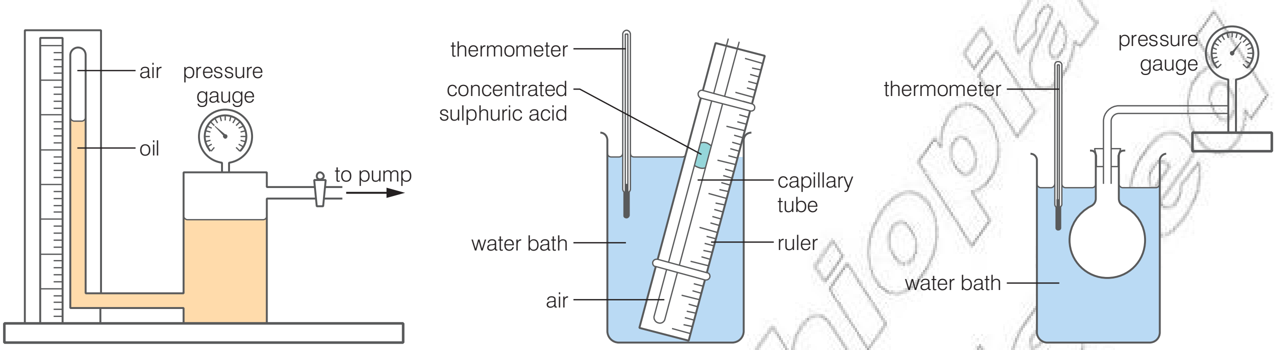
Pressure law: $\frac{p}{T}$ = constant (if V is constant)

It is worth remembering that:

- these are empirical laws, obtained by experiment, and
- any calculation in thermodynamics must contain temperature given in kelvin, that is, we must use the ideal gas temperature scale at all times.

Combining the three gas laws gives:

$$\frac{pV}{T} = \text{constant}$$



Boyle's law
Gas (usually air) is trapped in a glass tube by light oil. Pressure is exerted on the oil by a pump, which compresses the gas. Pressure is measured with a gauge and volume by the length of the air column.

Charles' law
Gas (usually air) is trapped in a capillary tube by a bead of concentrated sulphuric acid (this ensures that the air column is dry). The gas is heated in a water bath, and the volume measured by the length of the column.

Pressure law
Gas (usually air) is trapped in a flask and heated in a water bath, or an oil bath if temperatures above 100 °C are required. Pressure is measured with a pressure gauge.

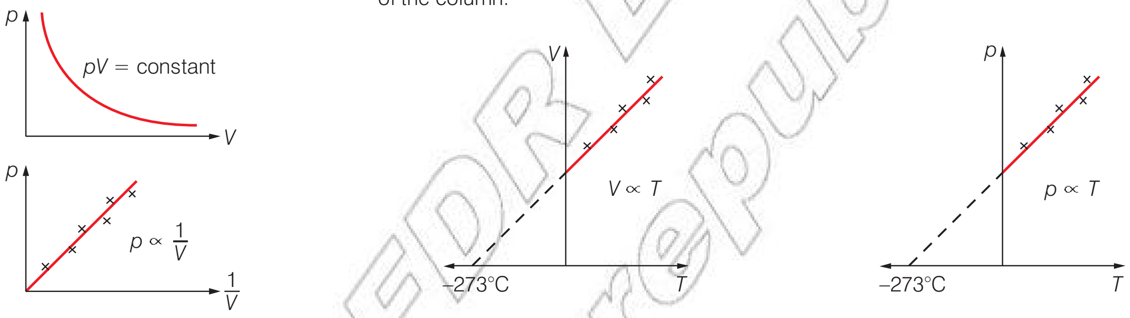


***Figure 1.15** Investigating the gas laws*

KEY WORDS

molar gas constant *a constant value given by the pressure times the volume of a gas divided by its absolute temperature*

Avogadro's constant *the number of particles in one mole of a substance*

Experiments also show that for a given pressure and temperature, doubling the amount of gas doubles the volume. The constant may therefore be written as nR where n is the number of moles of particles in the gas and R is the **molar gas constant**, which has a value of approximately 8.3 J/mol K. One mole of 'something' represents 6.0×10^{23} of that something and this number is also referred to as **Avogadro's constant**, N_A.

The equation of state for an ideal gas describes for us the way that a fixed amount of gas behaves as the macroscopic quantities of pressure, volume and/or temperature vary and it is written as:

$$\frac{pV}{T} = nR$$

or

$$\boldsymbol{pV = nRT}$$

Worked example 1.4

At sea level, atmospheric pressure is 1.0×10^5 Pa, temperature is 300 K and the density of air is 1.2 kg/m^3. What is the density of air at the top of Mount Everest where the temperature is 250 K and atmospheric pressure is 3.3×10^4 Pa?

1. The solution is made easier by dealing with a fixed mass of gas, say 1 kg.

   At sea level: volume of 1 kg of air $= \dfrac{1 \text{ kg}}{1.2 \text{ kg/m}^3}$

   $= 0.83$ m^3

   so: $p_1 = 1.0 \times 10^5$ Pa $\quad T_1 = 300$ K $\quad V_1 = 0.83$ m^3
2. At the top of Everest:
   $p_2 = 3.3 \times 10^4$ Pa $\quad T_2 = 250$ K $\quad V_2 =$ to be calculated
3. As the mass of gas stays fixed (we are dealing with 1 kg of air in each case) we can write the ideal gas equation as:

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

4. Substituting in all the above values we obtain: $V_2 = 2.1$ m^3. This means that the density of our 1 kg mass of air is 1 kg/ 2.1 m^3 which is 0.48 kg/m^3.

Dalton's law of partial pressures

The equation of state of an ideal gas also explains two laws that were formulated in the early 19th century. Firstly, **Avogadro's law** states that "equal volumes of all gases at the same temperature and pressure contain the same number of molecules".

Secondly, **Dalton's law of partial pressures** states that "the total pressure of a mixture of gases, which do not interact chemically, is equal to the sum of the partial pressures, i.e. to the sum of the pressure that each gas would exert if it alone occupied the volume contacting the mixture." To show this is the case, suppose we have a volume V that contains n_1 moles of a gas with a partial pressure p_1 and n_2 moles of a gas with a partial pressure p_2. If the gas mixture is in thermal equilibrium at temperature T then:

$$p_1V = n_1RT \quad \text{and} \quad p_2V = n_2RT,$$

and dividing these equations gives $\dfrac{p_1}{p_2} = \dfrac{n_1}{n_2}$

By substituting in Dalton's law in the form $p = p_1 + p_2$ we obtain equations for the two partial pressures:

$$p_1 = p\left(\frac{n_1}{n_1 + n_2}\right) \text{ and } p_2 = \left(\frac{n_2}{n_1 + n_2}\right)$$

KEY WORDS

Avogadro's law *equal volumes of all gases at the same temperature and pressure contain the same number of molecules*

Dalton's law of partial pressures *the total pressure of a mixture of gases, which do not interact chemically, is equal to the sum of the pressures that each gas would exert if it alone occupied the volume containing the mixture*

Activity 1.5: Partial pressures

If air is taken to consist of 80% nitrogen and 20% oxygen, what are the partial pressures of these two gases at an atmospheric pressure of 101 kPa?

The kinetic theory of gases

KEY WORDS

Brownian motion *the apparently random movement of particles in fluids, caused by the impacts of molecules of the fluid*

Since 1827, when Robert Brown observed the so-called **Brownian motion** of pollen grains suspended in water, it has been known that liquids and gases contain tiny particles that are moving at high speed. Nowadays, the dancing, zigzag motion of smoke particles as they are bombarded by light and very fast air molecules can be easily observed through a microscope. Einstein showed in 1905 that this motion provided evidence for the existence of atoms; it also leads us to look at gases in a more microscopic and methodical way, to see what we can find out about the kinetics of the tiny particles that make up a gas.

Step 1: To start with, consider a single particle, mass m, travelling at velocity c in a box as shown in Figure 1.16. The particle collides elastically with the shaded wall and rebounds with a velocity $-c$. The change in the particle's momentum is $2mc$.

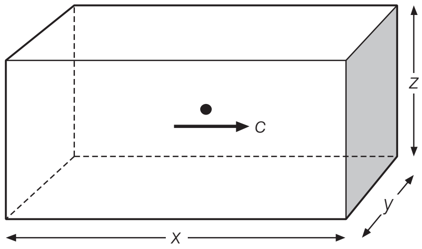


Figure 1.16 *Our starting point for deriving a mathematical relationship between the motion of particles in a gas and the pressure they exert*

Step 2: The particle bounces backwards and forwards within the box, exerting a force on the shaded wall many times but only for a short duration each time. As the box has a length X, the time between two successive collisions with the shaded wall is equal to $\frac{2x}{c}$.

Step 3: Newton's second law states that force is equal to the change of momentum divided by the time taken. In each time interval $\frac{2x}{c}$ the wall will cause a change in momentum of the particle of $2mc$. The average force on the particle by the wall is therefore $\frac{mc^2}{x}$.

Step 4: Newton's third law tells us that as the wall has exerted a force on the particle, the particle has exerted an equal and opposite force on the wall. The average force exerted on the wall over a series of impacts therefore equals $\frac{mc^2}{xyz}$. See Figure 1.17.

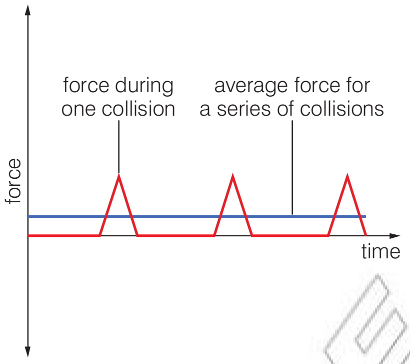


Figure 1.17 *The impulse on the shaded wall is represented by the area under a force–time graph. This is the same whether we consider a series of instantaneous forces or a small but continuous force.*

Step 5: As pressure is equal to force divided by area and the area of the shaded wall is xz, the average pressure on the shaded wall due to the motion of the single particle is $\frac{mc^2}{V}$. The volume, V, of the box is equal to xyz so the pressure can be written as $\frac{mc^2}{x}$.

Step 6: In reality, there will be N particles in the box moving in random directions. On average, one-third of the particles will be colliding with the shaded wall and the opposite wall and a third will be colliding with each of the other pairs of facing walls. The total average pressure on the shaded wall is therefore $\frac{Nmc^3}{3V}$.

A much more rigorous statistical approach should be used but the result of such an analysis provides the same result as the one that we have used here. As this expression is independent of direction it gives us the total average pressure on any of the walls that make up the container of the gas and it now makes sense to refer to particle speeds rather than velocities.

Step 7: The total mass of the gas is Nm so we can replace $\frac{Nm}{3}$ with the density of the gas, ρ. The total average pressure is now $\frac{\rho c^2}{3}$.

Step 8: We need one final, important alteration. As we have a collection of a very large number of particles there will exist a range of speeds for the particles. As it is the mean pressure that we can measure for any gas then our expression can only provide us with information on the mean of all the squares of the speeds of the particles. We call this the **mean square speed**, $\langle c^2 \rangle$.

To conclude, the pressure, p, of an ideal gas can be written in terms of the microscopic quantities of the gas as:

$$p = \tfrac{1}{3}\rho\langle c^2 \rangle$$

where ρ = the density of the gas and $\langle c^2 \rangle$ = the mean square speed of all the particles.

KEY WORDS

mean square speed *the average value of the squares of the speeds of particles in a gas*

What are the assumptions made in the kinetic theory of gases?

The kinetic theory of gases applies only to ideal gases that have the following properties:

1. The internal energy of the gas is made up of random kinetic energies of particles only. There is no potential energy component. Another way of saying this is that there is no interaction between particles or between particles and the wall except during collisions, all of which are instantaneous.
2. Collisions between particles and between particles and walls are perfectly elastic (there is no loss of kinetic energy during any collision).
3. The volume occupied by the particle is negligible compared to the volume of the gas as a whole.
4. The distribution of velocities of particles is random. That is, the average distribution of velocities over time is the same in all directions. This requires that the number of particles, N, is very large.
5. Newton's laws can be applied to all collisions.

Although no gas is ever perfectly ideal, the results of the above model compare well with that of real gases as long as the gas is well away from the conditions at which it would liquefy.

Activity 1.6: Assumptions in the kinetic theory of gases

Discuss with a partner each assumption in turn. Assess the validity of each assumption for a range of different gases at different temperatures (for example, helium at 4 K, the atmosphere at 280 K and a gas burning in air at 600 K).

KEY WORDS

root-mean-square speed *the square root of the mean of all the squares of the speeds of the particles in a gas*

How fast are molecules in the air moving right now?

Using our model we cannot find out information on the velocities of individual particles or even the range of velocities. We can only work out $<c^2>$.

Taking the density of air at approximately 25 °C as 1.18 kg/m^3 and atmospheric pressure at sea level as 101 kPa:

$$<c^2> = \frac{3p}{\rho}$$

$$= \frac{3 \times 1.01 \times 10^5 \text{ Pa}}{1.18 \text{ kg/m}^3}$$

$$= 2.57 \times 10^5 \text{ m}^2/\text{s}^2$$

By taking the square-root of the mean square speed we do not obtain the mean speed but, instead, the **root-mean-square speed**,

$$c_{\text{rms}} = \sqrt{<c^2>} = 507 \text{ m/s}$$

It is amazing that we can so easily work out a microscopic property of a gas like the root-mean-square speed of its particles just by knowing two macroscopic quantities of the gas (pressure and density). And the speed is rather large. Try to imagine that, on average, air molecules are striking the skin on your nose at this very moment at over 500 m/s!

Activity 1.7: Mean square speed and root mean square speed

Convince yourself that $<c>$ is different from c_{rms} by calculating the value of both quantities for the following group of velocities: 400 m/s, 450 m/s, 750 m/s, 300 m/s, 500 m/s, 600 m/s. You will find that they are similar but c_{rms} is always greater. Why?

Discussion activity

Refer to Table 1.3. Why does it make sense that c_{rms} is always larger than c_{sound}?

Gas	c_{rms} (m/s)	c_{sound} (m/s)
Helium	1500	1020
Nitrogen	567	356
Carbon dioxide	452	270

Table 1.3 *Values of the root-mean-square speed of particles,* c_{rms}*, and the speed of sound,* c_{sound}*, for a number of gases at room temperature and pressure.*

Brownian motion and diffusion

Brownian motion is the apparently random movement of particles in a fluid. It was first observed by the Scottish botanist Robert Brown. He observed pollen grains suspended in water would 'jiggle' around when seen under a microscope.

The first good explanation for this motion was suggested by J. Desaulx in 1877. He said:

"In my way of thinking the phenomenon is a result of thermal molecular motion in the liquid environment (of the particles)."

This turned out to be true. The particle in the fluid (liquid or a gas) was being constantly bombarded from all sides by molecules of the fluid. If the particle is very small, because the impacts are seemingly random on occasion it gets more hits on one side than the other. This gives rise to a net force and causes the particle to accelerate in the direction this net force. These small movements are what make up Brownian motion.

The term **mean free path** (often given the symbol λ) of the particle was used to describe the average distance covered by the particle between successive impacts. In a gas, the lower the pressure of the gas, or the lower the temperature, the greater the mean free path.

KEY WORDS

mean free path *the average distance covered by a particle between impacts in Brownian motion*

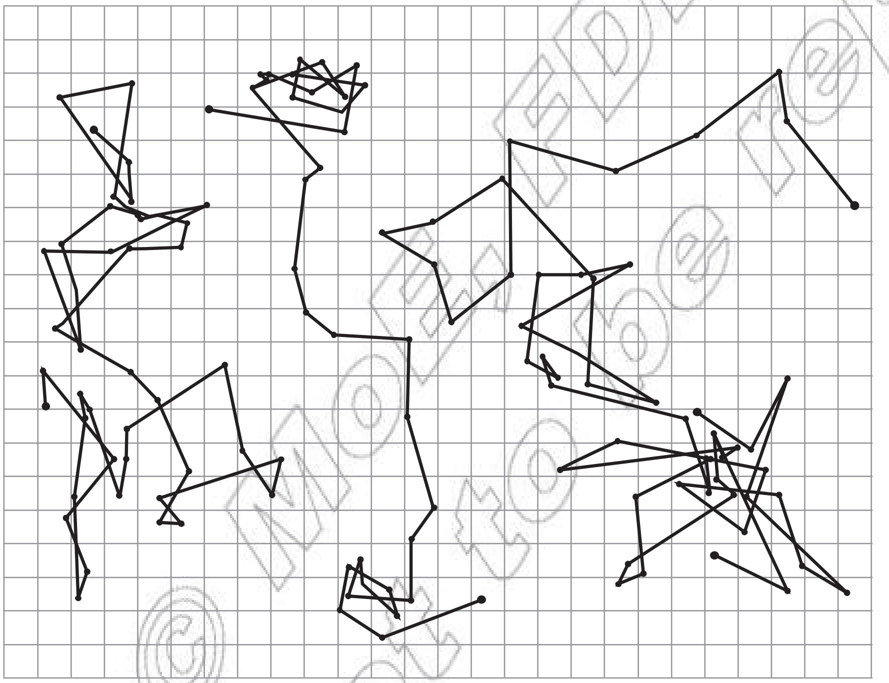


Figure 1.18 *Three tracings of the motion of particles seen under the microscope*

Einstein was the first to come up with an acceptable mathematical model for these movements. He was able to show that this motion can be predicted directly from the kinetic model of thermal equilibrium. This was confirmed experimentally, providing clear evidence for not only the atomic/particle nature of fluids but also the statistical nature of the second law of thermodynamics.

KEY WORDS

diffusion *the process where particles in a fluid spread from a region of high concentration to a lower one*

Graham's law *the rate of diffusion of a gas is inversely proportional to the square root of its density*

Einstein also produced a statistical analysis of **diffusion**. This is the process where particles in a fluid spread from a region of high concentration to a lower one. You can see this if you add a drop of orange juice to a glass of water. The concentrated orange drop slowly diffuses throughout the rest of the water. Einstein was able to provide a mathematical explanation for this process.

The ideas developed from Einstein's ideas on Brownian motion and diffusion lead to the kinetic theory models already discussed earlier in this chapter.

Graham's law of diffusion

The r.m.s. speed of molecules has an effect on how fast they diffuse through, for example, a cotton wool plug. It is not the velocity of the bulk motion of the gas that is important here but instead the diffusion of the gas through the porous plug is a result of the motion of individual molecules within the gas. **Graham's law** states that "the rate of diffusion of a gas is inversely proportional to the square root of its density", which we will explain below.

Using $pV = nRT$, two gases at a given temperature and pressure with equal volumes of a gas contain equal numbers of molecules so the density of each gas is just directly proportional to the molecular mass of its constituent particles. For two different gases denoted by subscripts 1 and 2: $m_1/m_2 = \rho_1/\rho_2$. From kinetic theory, the molecules in each gas at the same temperature possess the same average kinetic energy, so:

$$\frac{<c_1^2>}{<c_2^2>} = \frac{m_2}{m_1}$$

and therefore:

$$\frac{<c_1^2>}{<c_2^2>} = \frac{p_2}{p_1}$$

leading to:

$$\frac{\sqrt{<c_1^2>}}{\sqrt{<c_2^2>}} = \sqrt{\frac{p_2}{p_1}}$$

This explains why the rate of diffusion in a gas – which is dependent on the r.m.s. speed of molecules – is inversely proportional to the square root of the density of the gas.

Worked example 1.5

The r.m.s. speed of molecules in a container of helium gas at 332 K is 1440 m/s. What is the r.m.s. speed of molecules of hydrogen gas in the same container at he same temperature and pressure?

Avogadro's law tells us that the number of molecules of hydrogen is the same as the number of molecules of helium. The ratio of densities of the two gases therefore depends only on the ratio of the molecular masses. The mass of a helium molecule is twice the mass of a hydrogen molecule so $\rho_H = \rho_{He}/2$. Therefore:

$$\text{r.m.s. speed of molecules in the hydrogen gas} = \sqrt{2} \times 1440 \text{ m/s}$$
$$= 2036 \text{ m/s}$$

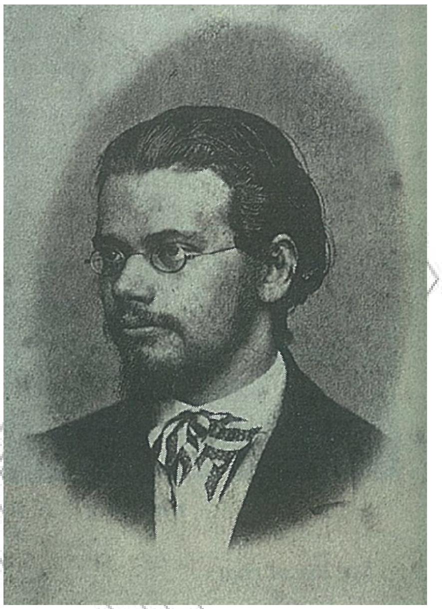


Figure 1.19 Ludwig Boltzmann (1844–1906)

KEY WORDS

kinematics of particles *study of the motion of particles within a gas*

Boltzmann constant *the gas constant for one particle in a gas*

What if we compare these two world views?

We now have two equations that describe the behaviour of a gas. The first is a result of experimental study of gases. The second is based on a model of the **kinematics of particles** in the gas. Let us see what else we can find out about gases from these two equations:

Equation 1: $pV = nRT$

Equation 2: $p = \frac{1}{3}\rho\langle c^2\rangle = \dfrac{\frac{1}{3}Nm\langle c^2\rangle}{V}$

Equating pV in both Equation 1 and Equation 2:

$$\tfrac{1}{3}Nm\langle c^2\rangle = nRT$$

From the definition of a mole: $N = nN_A$, where $N_A = 6.0 \times 10^{23}$, so:

$$\tfrac{1}{3}m\langle c^2\rangle = \frac{RT}{N_A}$$

Defining the average kinetic energy of a particle as $\langle E_k\rangle = \frac{1}{2}m\langle c^2\rangle$, we can state that:

$$\langle E_k\rangle = {}^{3}/_{2}kT \text{ (where } k = \frac{R}{N_A}\text{)}$$

The constant k is called the **Boltzmann constant** and it is effectively the gas constant for one particle in a gas (as opposed to R which is the gas constant for one mole of gas). The value of k is 1.38×10^{-23} J/K.

Again, we have an expression that can tell us a microscopic quantity of a gas, the average kinetic energy of its particles, from, in this case, a single macroscopic quantity, the Kelvin temperature. This seems remarkable until you go back and see how we originally defined temperature in section 1.1. However, we must remember that the above quantitative relationship is only true for an ideal gas.

DID YOU KNOW?

The Boltzmann constant is named after an Austrian physicist named Ludwig Boltzmann who contributed a great deal to the study of thermodynamics, including the work on the kinetic theory of gases. Unfortunately, Boltzmann's theories of the behaviour of matter were not generally accepted at the time, even ridiculed, and he committed suicide. Seventy years after his death, Zartmann and Ko showed that the distribution of velocities in the molecules of a gas agreed with his predictions, as shown in Figure 1.20.

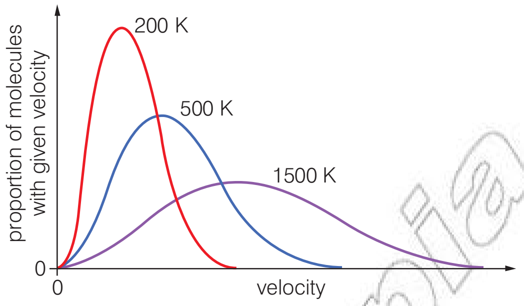


Figure 1.20 *The distribution of molecular speeds within a gas changes and the average speed of molecules increases as the temperature of the gas increases.*

In addition, as this is an ideal gas the internal energy is equal to the sum of all the random kinetic energies of its particles. The internal energy of one mole of gas, U, can therefore be written as:

$$U = N_A\langle E_k\rangle = {}^3/_2RT$$

Summary

- The ideal gas equation: $pV = nRT$.
- With all the assumptions of an ideal gas, the kinetic theory of gases states that $p = {}^1/_3\,\rho\,\langle c^2\rangle$.
- The r.m.s. speed is the square root of the mean of all the squares of the speeds.
- The average kinetic energy of a molecule in an ideal gas $= {}^3/_2\,kT$.

Review questions

1. An ideal gas is sealed within a container at a temperature of 17 °C and a pressure of 101 kPa. The container is heated until the temperature of the gas reaches 100 °C. A valve in the container is then opened to allow gas to escape until the pressure falls back to 101 kPa at 100 °C.
   a) Calculate the pressure in the gas just before the valve is opened.
   b) Calculate the fraction of the initial mass of gas that was lost as a result of opening the valve.
2. Calculate:
   a) the average kinetic energy of a nitrogen molecule at 20 °C
   b) the average kinetic energy of an oxygen molecule at 20 °C
   c) the internal energy of one mole of nitrogen gas at a pressure of 50 kPa occupying a volume of 5.0×10^4 cm^3.
3. Estimate the number of impacts that air molecules make with the palm of your hand each second, assuming that air consists entirely of nitrogen (molar mass = 0.028 kg).

1.4 Second law of thermodynamics, efficiency and entropy

By the end of this section you should be able to:

- State the second law of thermodynamics.
- Appreciate that the second law of thermodynamics places sharp constraints on the maximum possible efficiency of heat engines and refrigerators.
- Distinguish between reversible and irreversible processes.
- Define entropy as a measure of disorder and state the second law of thermodynamics in terms of entropy.

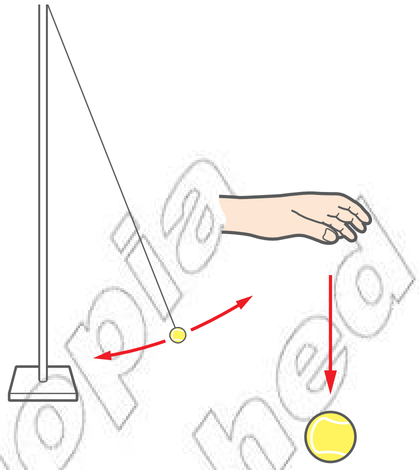


***Figure 1.21** Considering the direction of time: (a) a simple pendulum in motion; (b) a tennis ball falling towards the floor and bouncing a number of times*

Imagine we viewed a short film of the two situations shown in Figure 1.21. Now imagine we viewed the same two films running backwards. Would we notice any change?

For the pendulum, we would not notice any difference. Energy would still flow from the gravitational potential form to the kinetic form and back again. It would appear that the physics of the pendulum system is the same whether time moves forwards or backwards.

However, watching a tennis ball bouncing to ever greater heights would seem very odd indeed. Despite satisfying the law of conservation of energy, the idea that with every bounce the ball absorbs energy through heating and so rebounds with a greater kinetic energy than it struck the floor with, goes against our everyday experience. Of course, if the film of the pendulum lasted longer it, too, would only make sense with time flowing forwards (the amplitude of the swings cannot increase over time).

This apparent gap in our description of the universe will now be filled by the second law of thermodynamics. The second law provides a necessary direction to time and, importantly, places limits on the efficiency of systems and how they behave.

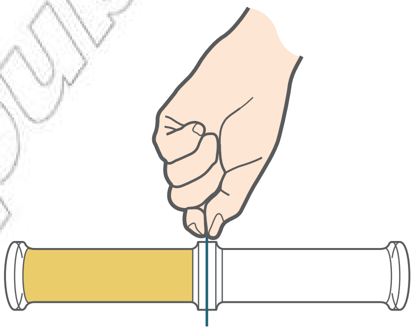


***Figure 1.22** Two glass cylinders separated by a glass cover slide. In the left-hand cylinder is bromine gas. In the right-hand cylinder is air.*

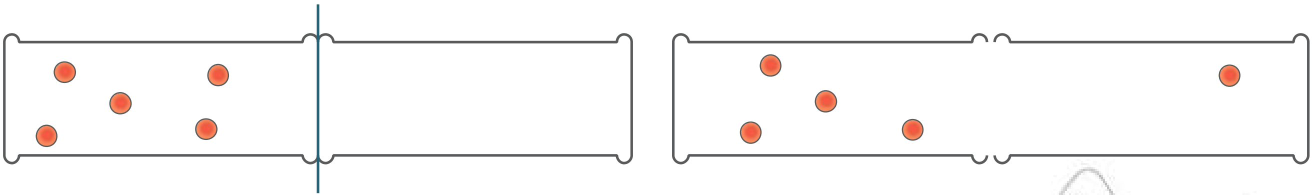
Entropy and the second law of thermodynamics

As we have already seen, the concept of energy cannot be used to determine the possible direction of time as the sum of all energies in an isolated system does not change with time. Instead we need the concept of **entropy**. We will introduce this new quantity using the example of bromine gas in a cylinder as in Figure 1.22.

Imagine that the cover slide is removed and the bromine gas is left to diffuse for a long time. When we next look we expect to see that the bromine gas has spread evenly within both cylinders. We would certainly not expect to see this process happen in reverse, for all the bromine molecules to end up in the left cylinder only. But would it be possible? In order to investigate this possibility let us deal with a simpler situation where there are only five molecules, as shown overleaf in Figure 1.23.

KEY WORDS

entropy *a measure of the amount of disorder in a system*



the five particles all start off in the left-hand jar

once the cover slip is removed, the particles are free to move between the jars

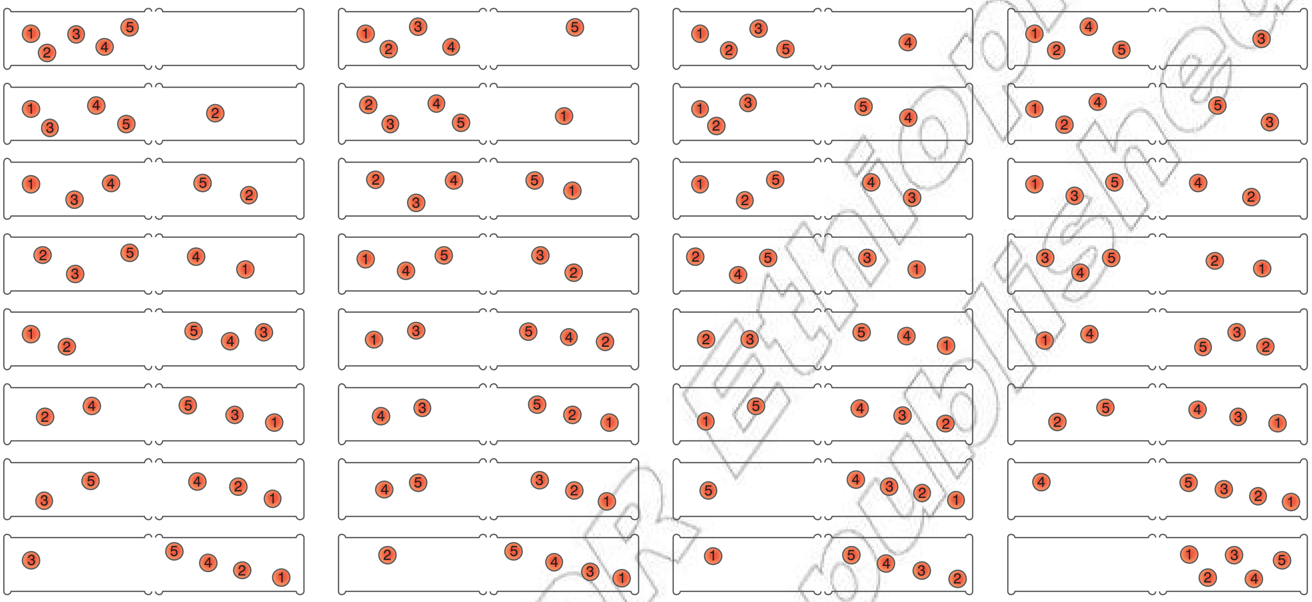


Figure 1.23 To start with, all five bromine molecules are certain to be in the left-hand cylinder. Once the cover slip is removed each particle is in one of two states: either in the left-hand cylinder or in the right-hand cylinder. The number of possible ways in which the five particles might be distributed between the cylinders is therefore $2 \times 2 \times 2 \times 2 \times 2$*, written as* 2^5*. The probability of all the particles being in the left-hand cylinder is therefore 1 in* 2^5*, or 1 in 32.*

KEY WORDS

disorder *chaos or a lack of order or arrangement*

quanta *the set amounts by which atoms can increase or decrease their energy*

Entropy is a measure of the amount of **disorder** (or chaos) in a system and the measure of disorder is equal to the number of ways that the system *may* be arranged. Before the cover slide was removed from our simple system it was very *ordered* as there was only one possible arrangement for the five particles: they were all in the left-hand cylinder. The entropy of the system was small. After the cover slide was removed, the amount of disorder in the system, and hence its entropy, increased as there were then 32 possible arrangements for the particles. The particles may all briefly move back into the left-hand cylinder but the entropy will still be higher as there are still 32 possible arrangements for the particles.

The second law of thermodynamics states that:

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

In a more realistic situation like our sample of bromine gas in Figure 1.22, there may be of the order of 10^{22} molecules present. This means that after the cover slide is removed, the increase in entropy will be very great. How likely is it that all the bromine molecules will end up back in the left-hand cylinder? The probability is 1 in $2^{10^{22}}$. To put this in context, if we observed electronically the cylinders at a rate of 1 MHz then, on average, in order to observe all the molecules in the left-hand cylinder we would have to wait for a time equivalent to *N* times the age of the universe. In order to write the number *N* you would have to write down a "1" and then write down the following group of zeroes a billion, billion, billion times: 000,000,000,000,000,000,000,000,00 0,000. If you think about it, you really would not want to try this experiment for real! So we are justified in saying that the particles in the gases will *always* spread out and that the entropy (and disorder) of the system will *always* increase.

Discussion activity

If W is equal to the amount of disorder in a system, that is, the number of possible arrangements within the system, then the entropy, S, of that system is given by the expression $k \ln(W)$, where k is the Boltsmann constant. In units of J/K, can you work out the entropy of the bromine gas in Figure 1.23 after the cover slide is removed?

How is entropy related to energy and heat?

The same ideas about entropy and the second law of thermodynamics are not just true in prescribing the direction of time when observing particles in a gas. They also describe how photosynthesis occurs, how many machines work (such as photocopiers, for example) and why energy tends to spread out through the process of heating.

Just as the spreading out of particles in Figure 1.23 represented an increase of entropy, the spreading out of random kinetic energy through heating also represents an overall increase in entropy. In the early 20th century it was found that atoms can only increase or decrease their energy in set amounts, called **quanta**. It is the behaviour of quanta, tiny packets of energy, that is similar to the behaviour of particles in a gas. If all the quanta that exist in a system are held by a small number of atoms then the number of possible arrangements of those quanta is small. However, if the same number of quanta were distributed amongst a larger number of atoms then, although the total energy of the system is the same, the number of possible arrangements (and therefore the entropy) increases. This is why energy in an isolated system tends to spread out over time: the entropy of the system must not decrease. This explains why the tennis ball cannot bounce to ever greater heights and why a smashed bowl does not spontaneously turn into an undamaged bowl.

You may suggest that, in Figure 1.23, we somehow pick up the five theoretical particles, one by one, and place them back in the left-hand cylinder and seal it, and that this will reduce the disorder in the cylinders. It will, but the cylinders are not then an isolated system. By doing mechanical work on the particles you must, in the process, have caused a heating effect elsewhere that would have caused a larger increase of entropy than the decrease in entropy of the particles. Ultimately, the system in question encompasses the entire universe, hence the definition of the second law of thermodynamics.

DID YOU KNOW?

Computer processor chips run hot. This is not merely due to resistance heating as a result of the flow of electric current. In addition, heating must occur in order to counteract the decrease in entropy that the chip is causing by processing data: in other words ordering that data.

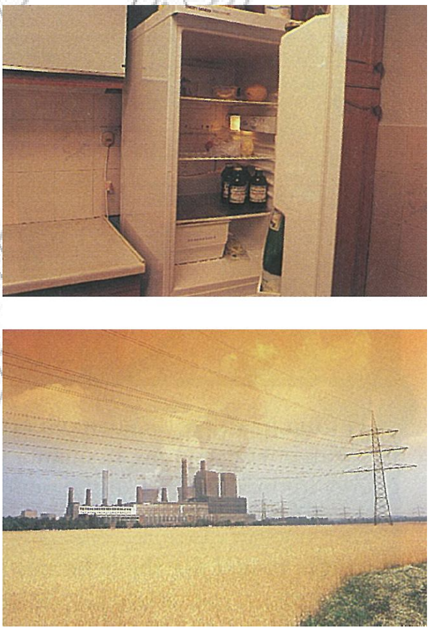


***Figure 1.24** The second law of thermodynamics can also be written as "the spontaneous transfer of energy from a cooler body to a hotter body is not possible". As we shall see in the following section, a refrigerator is an example of a heat pump where, by doing work on the system, energy is transferred from a colder body to a hotter body. This appears to directly contradict the second law. But it does not, as the transfer is not spontaneous. Somewhere else in the world a lump of coal is burned to provide the necessary electricity and the burning coal increases the entropy of the universe by a greater amount than the refrigerator decreases it.*

KEY WORDS

heat engine *a device designed to do useful mechanical work*

heat source *a device or body that supplies heat*

heat sink *a body which absorbs heat from other bodies with which it is in thermal contact*

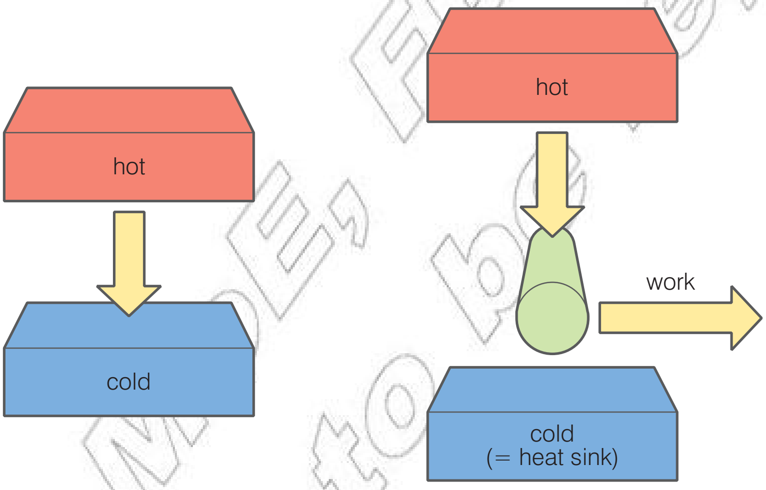
Why can we not build a power station that is perfectly efficient?

As we shall discover in more detail in the following section, even if we removed all sources of friction and electrical resistance from within a power station, its efficiency would still be far less than 100%. This is explained by the second law of thermodynamics.

A **heat engine** is any device that is designed to do useful mechanical work by taking energy from a hot body, often called the **heat source**. A power station is an example of a heat engine. As described in detail in Figure 1.25, the second law of thermodynamics can also be written in the form:

"the complete conversion of energy from a hot source into work is not possible."

Instead, it is necessary to transfer some of the random kinetic energy of the particles to a colder body, often called a **heat sink**. The heat sink is also necessary in order to draw the energy from the hot source. This places very strict limits on the efficiency of heat engines of any kind in our universe. Nothing can be 100% efficient and many heat engines struggle to achieve a theoretical maximum efficiency of even 50%. As we shall soon see, it is the relative temperatures of the heat source and the heat sink that determine how much work can be done as a proportion of the energy input.



When a hot object comes into contact with a cooler one, there is a net flow of energy from the the hot body to the cooler one simply because there are more ways of arranging the quanta when this happens

If energy is removed from a heat source (i.e. a hot body). the entropy of the body decreases. If all this energy is then converted into work, the overall change in entropy is a decrease, which contravenes the second law

If a small amount of energy is allowed to flow into the heat sink, the rise in entropy of the heat sink can offset the drop in entropy of the heat source – so the second law is satisfied

Figure 1.25 *An explanation of why heat engines can never be perfectly efficient. The green cylinder represents the heat engine.*

Discussion activity

The temperature differences that exist between astronomical objects in the universe can be thought of as doing work. For example, the temperature difference between the Sun and the Earth can be considered to power life itself. As the entropy of the universe must always increase what do you think the universe will eventually be like?

What processes can we reverse and why is this important?

When we discussed ideal gases in the previous section, it was clear that no gas is truly ideal but many gases were close enough to ideal, and the assumptions of an ideal gas simplified the theory enough, that the derivation of the kinetic theory of gases was a necessary and worthwhile process. The discussion of thermodynamic reversibility is of similar merit.

- A reversible process is one that can be reversed by means of an infinitesimally small change in a property of the system without a transfer of energy.

Due to the need for an infinitely small change, the system must be at rest during the entire process and the process will therefore take an infinite amount of time. Perfectly **reversible** processes are impossible. However, if the system can respond to a change in its state faster than the change is occurring then a process may be approximately reversible.

For a process to be reversible it must also be right on the limit of the second law of thermodynamics: there must be no change in entropy. For if a process causes an increase in entropy of the system then clearly the exact reverse process could not happen. Despite being a practical impossibility, a reversible heat engine therefore has the maximum possible efficiency allowed by the Second Law of Thermodynamics. It transfers *just* enough energy to the heat sink to maintain the same total entropy and so transfers the maximum amount of useful work.

Just like an angry word said in haste, every process that occurs in the universe is actually **irreversible**, either because it has caused entropy to increase or because a finite change in the system occurred. Milk stirred into coffee does not then spontaneously collect together in the cup. All of the water on a towel does not spontaneously return to the surface of your hand.

When we look at real heat engines we require them to run in a **cycle**. This is where a system is taken through a series of different states and then finally returns to its original state. In this way, the engine can do a large amount of useful work over a large number of repeated cycles. In order to be able to predict the outcome of using

KEY WORDS

irreversible *a process that cannot be reversed, either because entropy has increased or because there has been a finite change in the system*

reversible *a process that can be reversed by means of an infinitesimally small change in a property of the system without a transfer of energy*

Cycle *an interval of time over which a system is taken through a series of different states before returning to its original state*

Activity 1.8: Irreversible processes

With your partner, describe the following processes at a molecular level and hence why they are irreversible: (a) ice cubes melting in a glass of water; (b) a heater warming the air in a room; and (c) clothes drying in a breeze. Remember that if a system did undergo a reversible process, as no change in entropy occurs, then it would be equivalent to time standing still.

a cyclical heat engine, the whole process needs to be reversible, or, at least, nearly reversible. If it was not then the pressure, volume and temperature of the system will be different after each complete cycle and this would make the analysis of the situation very complicated.

Summary

- Entropy is a measure of the amount of disorder in a system.
- The second law of thermodynamics states that no process is possible in which there is an overall decrease in the entropy of the universe.
- A reversible process can be reversed by means of an infinitesimally small change in a property of the system without a transfer of energy.
- As well as defining the direction of time, the second law of thermodynamics implies that no process or cycle is perfectly reversible and no heat engine or refrigerator can be perfectly efficient.

Review questions

1. The concept of 'negentropy' has been suggested – it is a measure of the order in a system. Do you agree with the statement "In our lives, we do not so much consume energy as consume negentropy". Give your reasons.
2. A table tennis ball is placed on the hot plate of an oven hob and gently heated. At some point, all the kinetic energy transferred to the particles in the ball results in all the particles moving upwards at the same time and the ball jumps into the air.
   a) Does this contradict the first law of thermodynamics? Explain why.
   b) Does this contradict the second law of thermodynamics? Explain why.
   c) Is the ball likely to jump in the air? Explain why.
3. When heating occurs at a constant temperature, the change in entropy that occurs is equal to Q/T, where Q is the amount of energy transferred and T is the temperature. Referring to Figure 1.25, can you explain how it is possible for a heat engine to transform some of the energy from the hot source into work and for the total entropy of the system to still increase?

1.5 Heat engines and refrigerators

By the end of this section you should be able to:

- Describe the fundamental principles of heat engines and refrigerators.
- Solve problems involving heat, work and efficiency in a heat engine.
- Identify that all real heat engines lose some heat to their surroundings.
- Investigate the physical principles that all heat engines and refrigerators must obey.

What is a heat engine?

We briefly mentioned heat engines in the previous section. A heat engine is a device that transforms heat energy into mechanical work. Obvious examples include petrol, diesel and jet engines; however, a power plant (such as a nuclear power plant) could be considered to be a heat engine, as could the toy drinking bird in Figure 1.26.

Figure 1.26 ***The drinking bird is an example of a heat engine; the temperature difference between the room and the cooler water drives the bird.***

The drinking bird is a heat engine that uses the temperature difference between the room and the water to convert heat energy to mechanical work.

Like all heat engines, the drinking bird works through a thermodynamic cycle (more on these in a moment). The bird starts off vertical with a wet foam head. It then runs through the following process:

1. The water evaporates from the foam head; this evaporation lowers the temperature of the glass head.
2. This temperature drop causes some of the vapour in the head to condense. The lower temperature and condensation cause the pressure to drop in the head (from the ideal gas law).
3. As there is now a small pressure difference between the head and the base, liquid is drawn up the tube.
4. As liquid flows into the head, the bird becomes unbalanced and tips over.
5. When it tips, the head re-enters the water and becomes wet again. At the same time the bottom end of the neck tube rises above the surface of the liquid. A small bubble of vapour rises up the tube through this gap, displacing liquid as it goes. This causes liquid to flow back to the bottom bulb. This equalises the pressure.
6. With the liquid back in the bottom bulb the bird tips back to the vertical; the process then repeats.

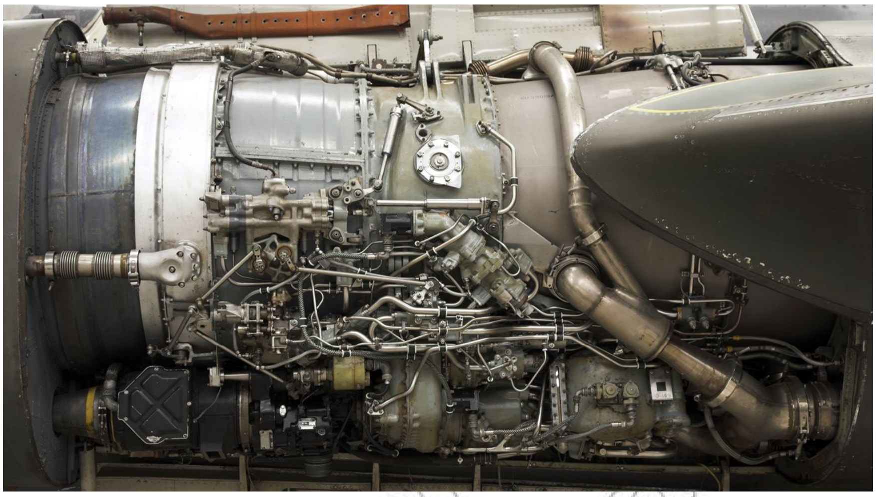


Figure 1.27 A more obvious heat engine

All heat engines require this temperature gradient to function. Often through more complex thermodynamic processes the heat engine extracts some of the thermal energy flowing from a hotter region to a colder one and coverts this into mechanical work. This may be seen in the simple schematic below:

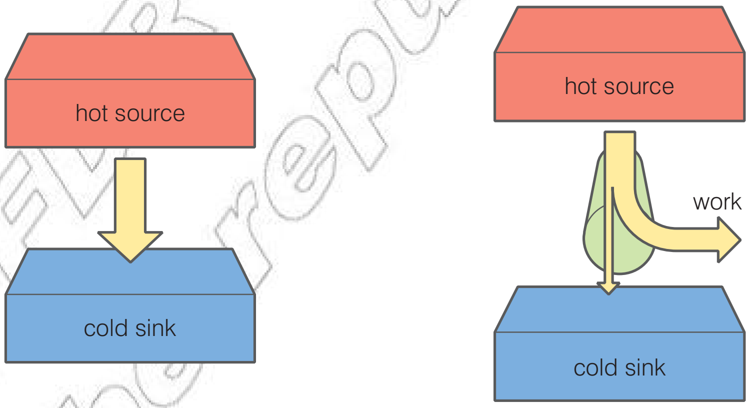


Figure 1.28 A simple schematic of a heat engine

Here the heat engine is represented by the green cylinder. Thermal energy is transferred through the engine from a hot source to a cold sink (also referred to as a heat sink). As mentioned previously, the cold sink is necessary in order to 'draw' the energy from the hot source. Processes inside the engine then convert some of this thermal energy into work.

The operation of heat engines is bound within the first and second law of thermodynamics. The first law involves the application of conservation of energy to the system. This often involves work done on or by gases within the engine.

As previously mentioned the second law can also be written in the form:

- The complete conversion of energy from a hot source into work is not possible.

The second law therefore sets limits on the maximum theoretical efficiency of any heat engine (more on this later).

How do heat engines work?

Most heat engines use thermodynamic processes and involve gases doing work. Previously in section 1.2 we looked at isobaric, adiabatic and isothermal expansion along with isochoric pressure increases. These processes are important in the operation of most heat engines and may be seen represented on a pressure vs. volume graph, as shown in Figure 1.29.

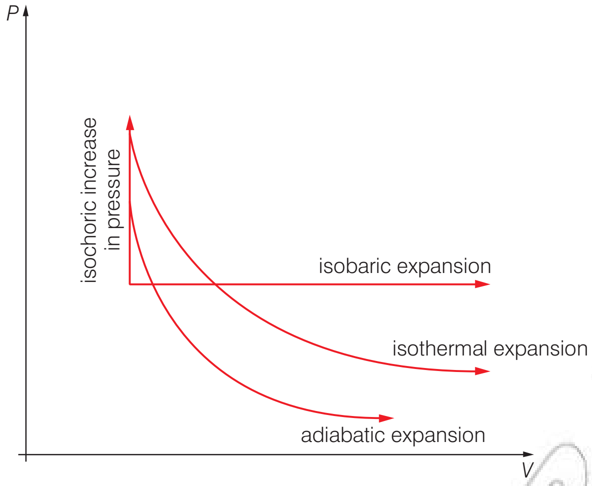


Figure 1.29 *p–V diagrams for various processes*

Table 1.4 *Summary of some thermodynamic processes*

Process	Meaning
Adiabatic	No heat transfer (heating or cooling results from pressure change – work is either done on or by the gas)
Isochoric	Constant volume (also called isometric)
Isothermal	Constant temperature
Isobaric	Constant pressure

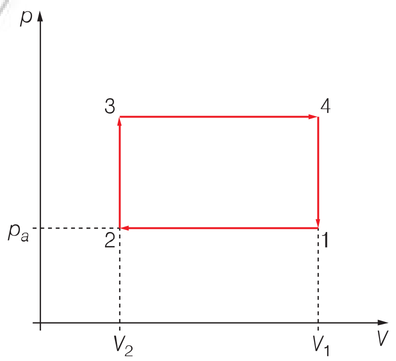


Figure 1.30 *A simplified p–V cycle*

Two or more of these processes are combined to form a simple cycle. As this cycle repeats, work is continuously extracted from the heat transferred from the hot source to the cold sink.

A very simple cycle may involve just four stages. This may be seen in Figure 1.30.

If we consider each part of the cycle in turn we can see how work might be extracted from the system.

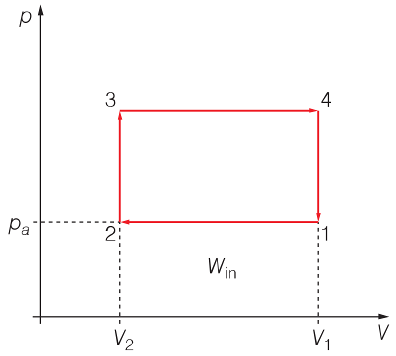


Figure 1.31 *The work done on the gas (W_{in}) as it is compressed at constant pressure*

1 to 2

The volume of the gas inside the engine is reduced at constant pressure (isobaric). This may achieved through a slow compression, allowing heat to flow out of the system or more commonly by rapidly cooling the system.

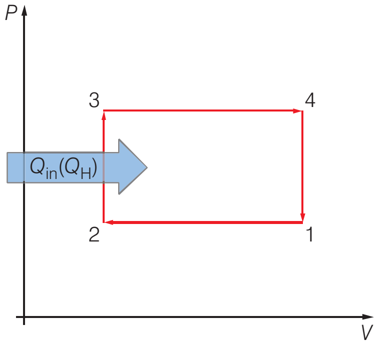


***Figure 1.32** Adding heat causes an isochoric pressure increase.*

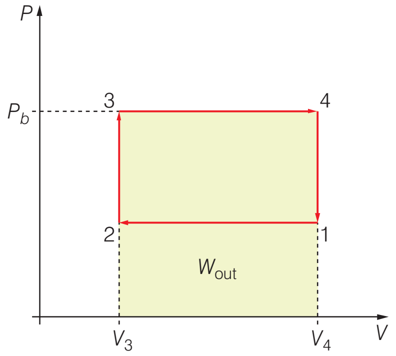


***Figure 1.33** The work done by the gas (W_{out}) as it expands at constant pressure*

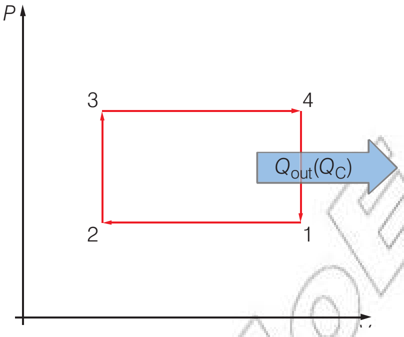


***Figure 1.34** Removing heat causes an isochoric pressure decrease.*

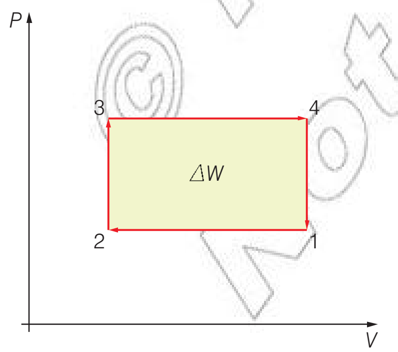


***Figure 1.35** The net work done is equal to the area of the enclosed cycle*

You should recall the work done on the gas at constant pressure is given by:

- $\Delta W = p\Delta V$

In terms of the quantities in Figure 1.31:

- $W_{in} = p_a(V_1 - V_2)$

This is equal to the area under the line 1–2, as shown in the diagram.

As this is an example of an isobaric process there must be no increase in temperature. If we apply the first law of thermodynamics we get:

- $\Delta U = \Delta Q + \Delta W$
- $0 = \Delta Q + p_a(V_1 - V_2)$
- $\Delta Q = -p_a(V_1 - V_2)$

ΔQ is the heat flow out of the system.

2 to 3

Heat is then allowed into the system (Q_H or Q_{in}). This is often achieved by igniting a fuel air mix. This may cause a rapid increase in pressure, whilst the volume remains constant.

Again considering the first law of thermodynamics:

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

In this case as there is no change in volume then no work is done on or by the gas and so all of the heat energy goes into increasing the internal energy of the gas:

- $\Delta U = Q_{in}$

This gives rise to an increase in temperature and so an increase in pressure.

3 to 4

The gas may then expand and as it does so it does work on its surroundings. This is very much an idealised example as heat would also need to be put in at this stage in order to keep the pressure constant.

The work done by the gas as it expands is equal to the area under the line 3–4, as shown in Figure 1.33.

4 to 1

Heat energy is then extracted from the system at constant volume. This leads to a drop in pressure and the system returns to its starting point. This process then repeats or 'cycles'. In each cycle, the work extracted is given by the area enclosed by the cycle.

The larger this area the greater the amount of work extracted per cycle.

Remember, this is a very simplified example of how processes may be combined to form a simple cycle.

Examples of real heat engines

Real heat engines combine the different thermodynamic processes in much more complex ways. We shall look at two examples of real engines in more detail: petrol engines and diesel engines. In both cases we will take an idealised engine and discuss the processes involved and how work is extracted from the system.

DID YOU KNOW?

Nikolaus August Otto was a German engineer and inventor. He is credited as the designer of the first internal combustion engine, which efficiently burnt fuel directly inside a piston.

Petrol engine

Inside a petrol engine fuel is burnt inside a piston. This piston moves up and down and extracts some the thermal energy as mechanical work. This is then usually used to turn a driveshaft and subsequently turn the wheels on a vehicle.

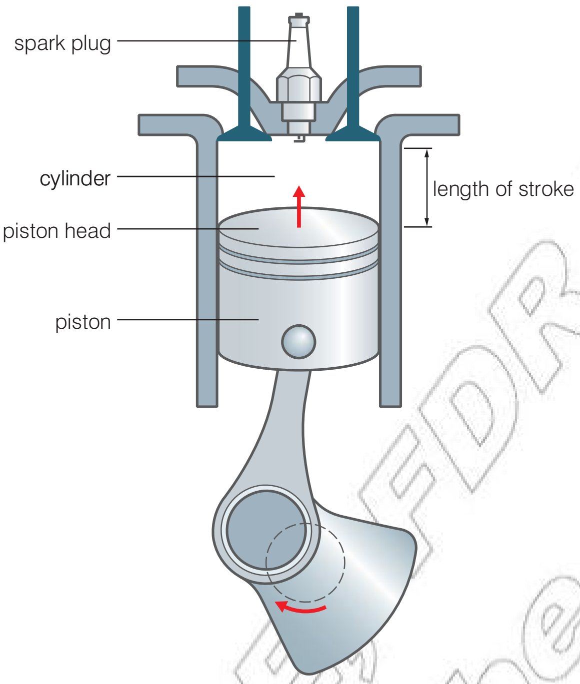


Figure 1.36 A diagram of a simple piston from a petrol engine

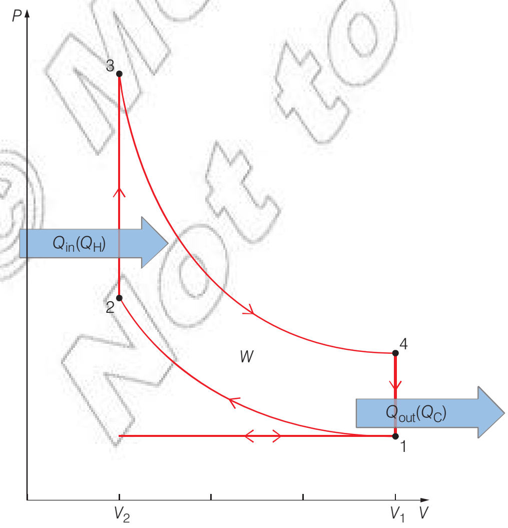


Figure 1.37 An idealised Otto cycle (petrol engine)

DID YOU KNOW?

Most petrol engines employ a four stroke process. The strokes are induction, compression, power and exhaust. Can you match them to the ideal Otto cycle $p-V$ diagram?

The cycle responsible for the extraction of work from a petrol engine is referred as the Otto cycle. The diagram in Figure 1.37 shows an idealised $p-V$ diagram for the Otto cycle.

Starting on the bottom left of the diagram the volume of the gas inside the piston is V_2.The piston is pulled down (due to the rotation of the shaft) and a fuel air mix is drawn in through the open inlet valve. The pressure remains constant and the volume of gas inside the cylinder increases to V_1.

The valve is closed and the piston moves back up, compressing the gas back to V_2. This process happens quickly and so the compression is adiabatic, no heat flows out of the gas. This results in an increase in temperature (and so pressure) as work is done on the gas. This can be seen in the line 1–2.

At 2 the fuel air mix is ignited by a spark from the spark plug. Combustion occurs very quickly and as a result the process can be considered to be isochoric, the volume of the gas remains constant. There is a significant amount of heat realised in this process (Q_{in} or Q_{H}). This heat increases the temperature and so the pressure of the gas inside the piston. This can be seen in the line 2–3.

Between 3 and 4 work is done by the gas as it forces this piston down. This again happens very quickly without any heat flowing out of the system and so it is an adiabatic change. The volume of the gas increases back to V_1 and the pressure drops.

Heat then flows out of the system (Q_{out} or Q_c) and the temperature of the gas drops causing a drop in pressure back to the original pressure. This can be seen in the line 4–1.

The final part of the cycle involves the piston moving back up, but this time the exhaust valve is open and so the pressure remains constant as the waste gases are expelled. We are now back at the bottom left and the process starts again.

Just like our simplified earlier example the difference between the work done by the gas and the work done on the gas is the area enclosed by the cycle. The power of the engine is then found as the product of this difference and the number of cycles per second.

This is very much an idealised Otto cycle. There are no friction losses, the combustion is isochoric (i.e. happens almost instantaneously) and there is no heat entering or leaving the gas between 1–2 and 3–4. In reality there are a number of losses through each part of the cycle. All real heat engines transfer additional thermal energy to their surroundings at every stage.

A more realistic cycle may be seen in Figure 1.38.

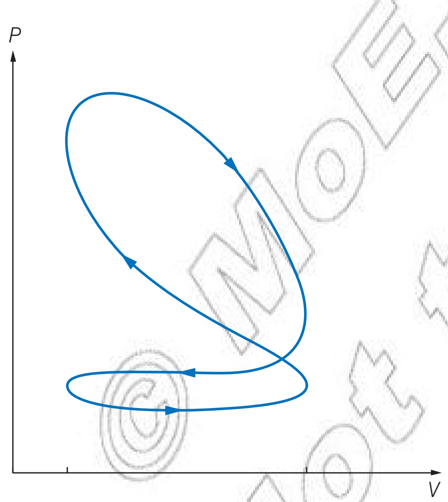


Figure 1.38 A more realistic Otto cycle

Diesel engine

Just like a petrol engine fuel is burnt inside a piston. This piston moves up and down and extracts some the thermal energy as mechanical work. This is then usually used to turn a driveshaft and subsequently turn the wheels on a vehicle. However, there are a few key differences in the process.

There are two obvious differences when looking at the diesel piston when compared to the petrol one. Firstly, there is no spark plug; the fuel–air mix is ignited in a different way. Secondly, the pistons are usually longer in a diesel engine for reasons that will become apparent.

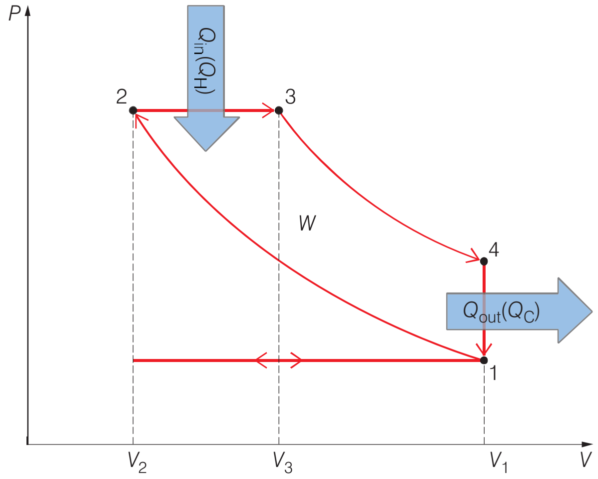


Figure 1.40 *An idealised diesel cycle*

The diagram in Figure 1.40 shows an idealised *p*–*V* diagram for a diesel cycle.

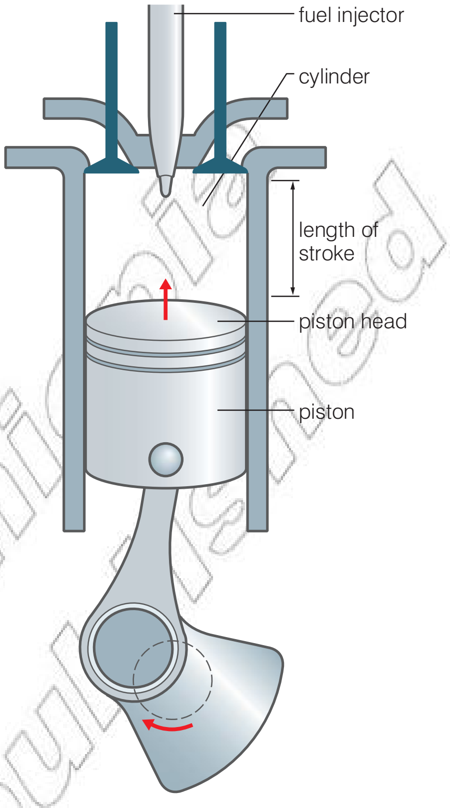


Figure 1.39 *A simple piston in a diesel engine*

Again starting on the bottom left of the diagram the volume of the gas inside the piston is V_2. The piston is pulled down (due to the rotation of the shaft), air is drawn in through an open inlet valve but no fuel is present at this stage. The pressure remains constant and the volume of gas inside the cylinder increases to V_1.

The valve is closed and the piston moves back up, compressing the gas back to V_2. This process happens quickly and so the compression is adiabatic, no heat flows out of the gas. This can be seen in the line 1–2. As the piston is longer the air inside the piston is compressed much more than inside a petrol piston. This results in more work done on the gas and so a much larger increase in temperature.

At 2, diesel is squirted into the piston from the injector. The air is so hot the diesel ignites and begins to push the piston back down. The volume increases to V_3 but the pressure remains constant (isobaric). There is a significant amount of heat realised in this process (Q_{in} or Q_H).

At 3, all the diesel has combusted and work is done by the gas as it continues to force this piston down. This again happens very quickly without any heat flowing out of the system and so it is an adiabatic change. The volume of the gas increases back to V_1 and the pressure drops.

The rest of the process is the same as the petrol engine. Heat then flows out of the system (Q_{out} or Q_c) and the temperature of the gas drops causing a drop in pressure back to the original pressure. This can be seen in the line 4–1. The piston then moves back up with the exhaust valve is open and so the pressure remains constant as the waste gases are expelled. We are now back at the bottom left and the process starts again.

The key difference between a diesel engine and a petrol one is the process for adding heat to the system. In a diesel engine it is isobaric, whereas in a petrol engine it is isochoric.

Other examples

There are many other examples of cycles employed by heat engines; these are summarised in Table 1.5. It is important to note there are two main groups.

The first group involves the burning of the fuel inside the working piston – internal combustion.

The second group involves burning a fuel in a chamber. The heat from this process is then transferred to a working fluid (such as steam) via a heat exchanger. This fluid is then transferred to the piston. As the heating does not take place inside the piston this is referred to as external combustion.

Table 1.5 *The various engine cycles*

Cycle	Compression of gas	Heat input	Expansion of gas	Heat output	Combustion
Otto (petrol engines)	adiabatic	isochoric	adiabatic	isochoric	internal
Diesel	adiabatic	isobaric	adiabatic	isochoric	internal
Brayton (jet engines)	adiabatic	isobaric	adiabatic	isobaric	internal
Carnot	adiabatic	isothermal	adiabatic	isothermal	external
Stirling	isothermal	isochoric	isothermal	isochoric	external
Ericsson	isothermal	isochoric	isothermal	isobaric	external
Rankine	adiabatic	isochoric	adiabatic	isobaric	external

Efficiency of a heat engine

Just like any machine the efficiency of a heat engine may be determined by considering the energy input and the useful energy output.

- efficiency = useful work out / total work in

The diagram in Figure 1.41 shows the energies involved in a heat engine. The energy into the engine is Q_H and the useful work is W. Therefore the efficiency may be calculated using:

- efficiency = W / Q_H

By considering the law of conservation of energy we can express the efficiency in terms of Q_c and Q_H.

- energy from hot source = work done + energy to cold sink
- $Q_H = W + Q_c$

Therefore the useful work out of the engine may be found by:

- $W = Q_H - Q_c$

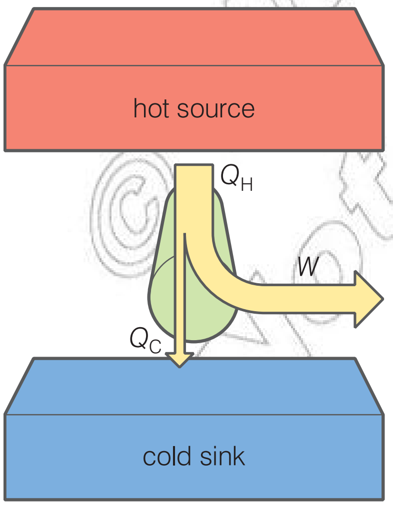


Figure 1.41 *The energies involved in a heat engine*

Applying the equation for efficiency we get:

- efficiency = useful work out / total work in
- $\eta = W / Q_H$
- $\eta = (Q_H - Q_c) / Q_H$

This may be expressed as:

- $\eta = 1 - (Q_c / Q_H)$

What is the maximum theoretical efficiency of a heat engine?

In order for heat energy to be drawn into the heat engine there must be temperature difference between the hot source and the cold sink. Some energy must always flow into the cold sink. This means Q_c can never be zero.

As a consequence the efficiency can never be 1 (i.e. 100% efficient).

As already discussed, this is confirmed by the second law of thermodynamics, which may be expressed as:

- **The complete conversion of energy from a hot source into work is not possible.**

However, the greater the absolute temperature difference between the hot source and cold sink, the greater the maximum theoretical efficiency.

- $\eta_{max} = 1 - (T_c / T_H)$

For example, the temperature inside a diesel engine may be 500 °C or 773 K. In this case the cold sink is the coolant in the engine. Assuming this is at 100 °C (373 K) the maximum theoretical efficiency will be:

- $\eta_{max} = 1 - (T_c / T_H)$
- $\eta_{max} = 1 - (373 / 773)$
- $\eta_{max} = 0.52$

However, no diesel engine is this efficient. A more common value is around 30% efficient (petrol engines have an even lower efficiency). The design of the engine results in several energy losses, mainly through friction. This results in additional heat being transferred to the surroundings.

However, the general principle is true that if the temperature difference between the hot source and cold sink is larger then the maximum theoretical efficiency increases.

In practice, increasing the temperature of the hot source causes significant problems in terms the material expansion of the components inside the engine. Engine designers are continuously researching new materials that can withstand higher temperatures in order to increase the efficiency of future engine designs.

Worked example 1.6

The heat input to a heat engine is 100 kJ. 25 kJ enters the cold sink. Determine the efficiency of the heat engine.

- $\eta = 1 - (Q_c / Q_H)$
- $\eta = 1 - (25\,000/100\,000)$
- $\eta = 0.75$ or 75%

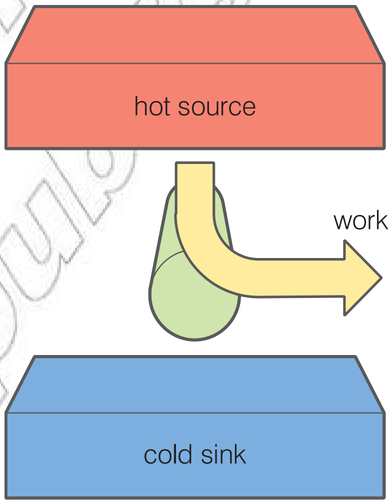


Figure 1.42 *Converting all the heat to work is forbidden by the second law.*

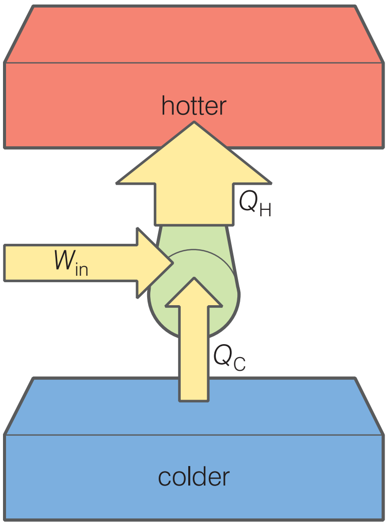


Figure 1.43 *A schematic of a heat pump*

Figure 1.44 *A refrigerator is a kind of heat pump.*

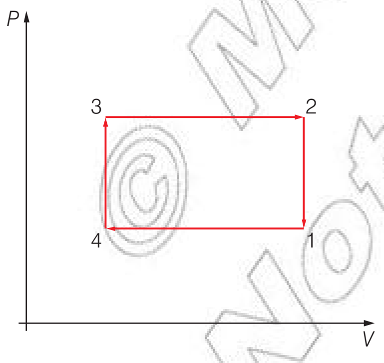


Figure 1.45 *A simple p–V diagram for a heat pump*

Refrigerators and heat pumps

Another way of stating the second law of thermodynamics is:

- **The spontaneous transfer of energy from a cooler body to a hotter body is not possible.**

This statement is most definitely true, in which case how it is possible for refrigerators to function? A bottle of water at room temperature goes into a cooler fridge and thermal energy is extracted from the water and transferred back to the room – which is at a higher temperature than the inside of the fridge.

It appears that the energy is flowing from a colder region to a hotter one, and it is! The key phrase here to consider is 'spontaneous transfer'. This means it does not happen without an additional input of energy.

A refrigerator is a kind of heat pump. A heat pump can be thought of as a heat engine running in reverse.

Work goes into the heat pump and this allows energy to flow from a colder region to a hotter one.

Imagine running the simple four-step cycle we looked at in heat engines running in reverse.

In this case there is more work done on the system than work done by the system. This net input of work (W_{in}) makes it possible for energy to be transferred from a colder region to a hotter one.

The energy transferred to the hotter region is given by:

- energy into hotter region = work input + energy from colder region
- $Q_H = W_{in} + Q_c$

How do refrigerators work?

Figure 1.46 shows a simple refrigerator. Inside every fridge there is a network of pipes containing a special fluid. The movement of this fluid around the fridge transfers thermal energy from inside the fridge (the colder region) to the surroundings (the hotter region).

Starting at the top left the liquid passes through an expansion valve. This is specially designed to force the liquid to change state into a gas and expand. This results in the gas doing work and so its temperature falls. The gas is pumped around the system, through the inside of the fridge.

Thermal energy flows from the inside of the fridge into the gas. This results in the temperature inside the fridge falling. This does not break the second law as the gas is much colder than the inside of the fridge.

Work is then done on the gas in order to compress it and turn it back into a liquid. This is the work put into the system (W_{in}). This causes an increase in temperature inside the fluid.

The fluid then passes through a series of pipes on the back of the refrigerator. As it is now hotter than the surroundings and so thermal energy is transferred to the room (Q_H).

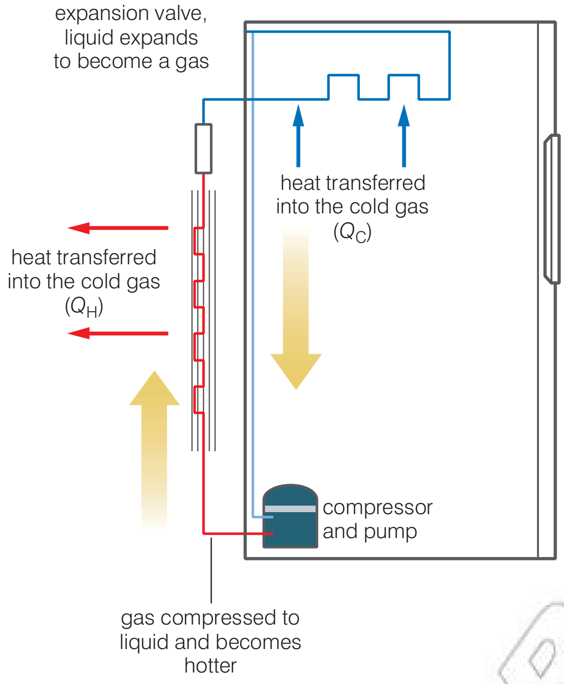


Figure 1.46 *A simple refrigerator*

Just like a heat engine, this process then cycles. The liquid passes through the expansion valve, turns into a gas and cools.

Summary

In this section you have learnt that:

- A heat engine converts some of the energy flowing from a hot source to a cold sink into mechanical work.
- Heat engines employ various thermodynamic processes to do mechanical work.
- The efficiency of a heat engine is given by $\eta = 1 - (Q_c / Q_H)$.
- All heat engines ‘waste’ energy in the form of heat transferred to their surroundings.
- The maximum theoretical efficiency of a heat engine is given by $\eta_{max} = 1 - (T_c / T_H)$.
- A heat pump allows thermal energy to be transferred from a colder region to a hotter one. This requires a net input of work.

Think about this...

What would happen to the temperature of a room if a refrigerator was left running with the door open?

Activity 1.9: Refrigerators

Sketch a simple p–V diagram for a refrigerator, labelling each section.

Every cycle results in energy being transferred from the colder region to the hotter one. The food stays cold, despite heat leaking in from the surroundings, most often when you open the door!

DID YOU KNOW?

Other examples of heat pumps include air conditioners and freezers.

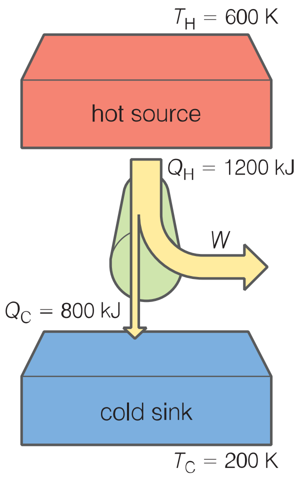


Figure 1.47 *For question 2*

Review questions

1. Describe what is meant by a heat engine.
2. Calculate the efficiency and the maximum theoretical efficiency of the heat engine in Figure 1.47.
3. Define the terms isochoric, adiabatic, isothermal and isobaric. Include a p–V diagram for each.
4. With the aid of a p–V diagram show how a net output of work may be produced from a cycle of thermodynamic processes
5. With reference to the second law of thermodynamics explain how refrigerators allow heat to be transferred from a colder region to a hotter one. Include a simple energy flow diagram with all key features labelled.

End of unit questions

1. The escape velocity from the Earth is approximately 11 km/s. This means that a gas molecule at the top of the atmosphere travelling outwards at 11 km/s will escape.
   a) The thermosphere, the layer of the upper atmosphere in which the Space Shuttle orbits, is at a temperature of about 1000 K. Calculate the mean kinetic energy of a molecule at this temperature.
   b) Calculate the r.m.s. speeds of (i) hydrogen, with molar mass 0.0020 kg/mol, and (ii) helium, with molar mass 0.040 kg/mol, at this temperature.
   c) If the r.m.s. speed of the molecules of a gas is greater than 0.2 of the escape velocity, then over the period of the Earth's existence all of the gas will have escaped from the atmosphere. Use this fact to explain whether we expect to find any hydrogen of helium in the atmosphere.
2. A meteorological balloon rises through the atmosphere until it expands to a volume of 1.0×10^8 m^3, where the pressure is 1.0×10^3 Pa. The temperature also falls from 17 °C to –43 °C. The pressure of the atmosphere at the Earth's surface is 1.0×10^5 Pa.
   a) What was the volume of the balloon at take-off?
   b) Before being released, the balloon was filled with helium gas of molar mass 4.0×10^{-3} kg/mol. Calculate (i) the number of moles of gas in the balloon, and (ii) the mass of gas in the balloon.
   c) When the balloon is filled at ground level, the internal energy of the gas is 1900 MJ. If the internal energy of the helium gas is equal to the random kinetic energy of all its molecules, estimate the internal energy of the helium when the balloon has risen to a height where the temperature is –43 °C.

3. a) Explain what is meant by *internal energy*. Hence suggest how the internal energy of a *real* gas differs from that of an *ideal* gas.

   b) Figure 1.48 shows the graph of the cooling curve of a substance between 250 °C and room temperature. Over which sections of the curve is:

      i) the internal energy of the substance decreasing?

      ii) the average random kinetic energy of the molecules decreasing?

      iii) the average random potential energy of the molecules almost constant?

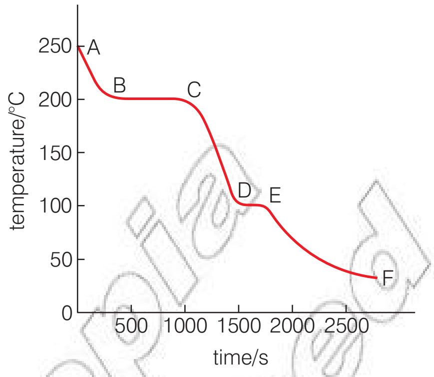


Figure 1.48

4. For every 10 m you descend below the surface of water, the pressure on you will increase by an amount equal to atmospheric pressure, 101 kPa. An air bubble in a lake has a volume of 20 mm^3 at a depth of 40 m. Predict what volume it will have just before it reaches the surface and write down the assumption that you have made in order to arrive at an answer.

5. Figure 1.49 shows curves (not to scale) relating pressure, p, and volume, V, for a fixed mass of an ideal monatomic gas at 300 K and 500 K. The gas is in a container fitted with a piston which can move with negligible friction.

   a) Show that the number of moles of gas in the container is 0.0201.

   b) Show that the volume of the gas at B on the graph is 1.67×10^{-3} m^3.

   c) Calculate the total internal energy of the gas in the container at point A on the graph.

   d) Explain how the first law of thermodynamics applies to the changes represented on the graph by (i) A to C, and (ii) A to B. Calculate the energy absorbed in each case by heating.

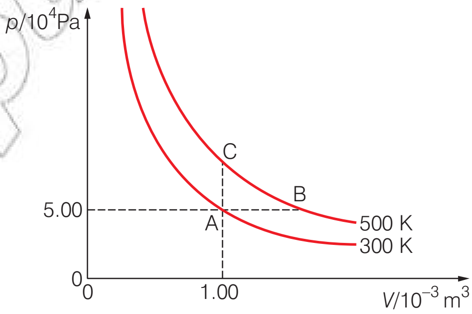


Figure 1.49

6. a) A perpetual motion machine would be able to produce a continuous output of work with no energy input. State the physical principle that makes this impossible.

   b) Figure 1.50 shows one suggestion put forward as a perpetual motion machine. The ball in position **A** would fall off the top of the water doing work on the pulley belt. At **B** it would move sideways doing no work and enter the bottom of the tank by a valve system which would prevent water from escaping. It would then float to the top ready to start again. Explain why this system will not behave as a perpetual motion machine.

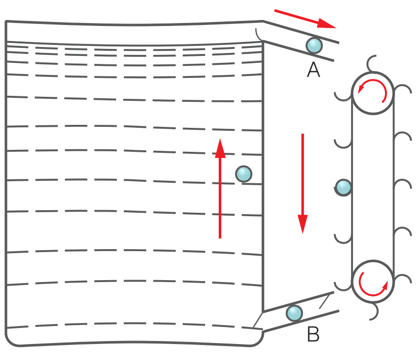


Figure 1.50

7. By tidying up your house last night, you will have decreased the amount of disorder present. In order for the second law of thermodynamics to still apply what did you do to the air in your house whilst you were tidying?

8. Sketch the p–V diagram for a petrol engine and describe each of the thermodynamic processes involved.

9. A smoke jack is another type of heat engine used to cook meat. Heat from a fire causes air to rise above the fire. This rising air causes a paddle wheel in the chimney to turn. This in turn rotates an animal being roasted above the fire.

   a) The temperature of the surrounding air is 15 °C and the fire is at a temperature of 350 °C. Calculate the maximum theoretical efficiency of the smoke jack.

   b) Sketch a simple diagram of a smoke jack and use this to indentify two places where the energy would be lost.

10. A heat engine operating between 100 °C and 700 °C has an efficiency equal to 40% of the maximum theoretical efficiency. How much energy does this engine extract from the hot reservoir in order to do 5000 J of mechanical work?