



## B.2 Thermodynamics

### Understandings

- The first law of thermodynamics
- The second law of thermodynamics
- Entropy
- Cyclic processes and  $pV$  diagrams
- Isovolumetric, isobaric, isothermal, and adiabatic processes
- Carnot cycle
- Thermal efficiency



### Nature of science

#### Different viewpoints of the second law of thermodynamics

Thermodynamics is an area of physics which, through different scientific eras, has been shaped by a combination of practice and theory. When Sadi Carnot wrote his treatise about heat engines, he was a believer in the caloric standpoint – yet his ideas were sufficiently developed to influence the development of machines in the industrial revolution. Clausius, Boltzmann, Kelvin, and Gibbs were all responsible for different statements of the second law of thermodynamics – a law that has a fundamental impact on whether or not a process, allowed by the first law of thermodynamics, can actually occur.



### Applications and skills

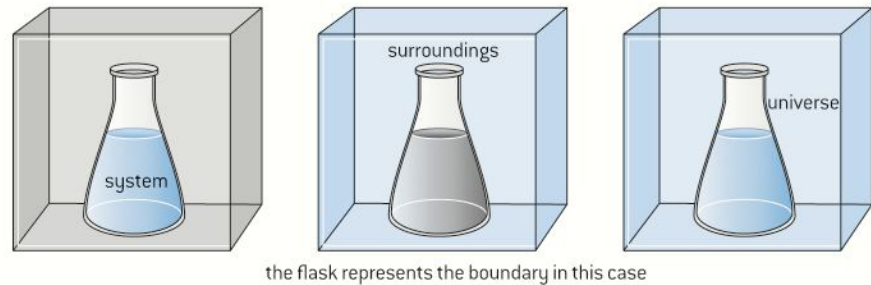
- Describing the first law of thermodynamics as a statement of conservation of energy
- Explaining sign convention used when stating the first law of thermodynamics as  $Q = \Delta U + W$
- Solving problems involving the first law of thermodynamics
- Describing the second law of thermodynamics in Clausius form, Kelvin form and as a consequence of entropy
- Describing examples of processes in terms of entropy change
- Solving problems involving entropy changes
- Sketching and interpreting cyclic processes
- Solving problems for adiabatic processes for monatomic gases using  $pV^{\frac{5}{3}} = \text{constant}$
- Solving problems involving thermal efficiency

### Equations

- First law of thermodynamics:  $Q = \Delta U + W$
- Internal energy:  $U = \frac{3}{2}nRT$
- Entropy change:  $\Delta S = \frac{\Delta Q}{T}$
- Equation of state for adiabatic change:  
 $pV^{\frac{5}{3}} = \text{constant}$  (for monatomic gases)
- Work done when volume changes at constant pressure:  $W = p\Delta V$
- Thermal efficiency:  $\eta = \frac{\text{useful work done}}{\text{energy input}}$
- Carnot efficiency:  $\eta_{\text{Carnot}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$

### Introduction

When using thermodynamics, there is a convention that we talk about the body that we are interested in as being the **system**. Everything else that may have an impact on the system is known as the **surroundings**. The system is separated from the surroundings by a **boundary** or **wall**. Everything including the system and the surroundings is called the **universe**.



▲ Figure 1 Thermodynamic system and surroundings.

As we saw in Topic 3, James Joule showed that work done on a system or energy transferred to the system because of temperature differences result in the same outcome: the internal energy of that system increases.

The nature of the way the system changes and how that energy reveals itself depends on whether or not the phase of the substance changes. When there is no change of state the most apparent effect is the increase in the mean random kinetic energy of the particles; when there is a change of state the increase in the potential energy is the most significant effect.

Remember that *the internal energy of a system is the total of the potential energy and the random kinetic energy of all the particles making up the system.*

We often simplify discussion by considering the system to be an ideal gas. In this case the internal energy is entirely kinetic and we can use the relationship derived in Sub-topic 3.2. This showed that, for  $n$  moles of an ideal gas, the internal energy  $U$  is related to the absolute temperature  $T$  by the equation  $U = \frac{3}{2} nRT$ , where  $R$  is the universal molar gas constant.

## The first law of thermodynamics

The internal energy of a system may change as any combination of (i) doing work on the system (or allowing the system to do work on the surroundings) and (ii) transferring energy to or from the system as a result of a difference in temperature. Saying this amounts to stating the conservation of energy. There are a variety of versions of the equation for the first law of thermodynamics and each has its merits – they will all be self-consistent and understandable but you will need to make sure that you read the definition of each of the terms in the equation. The preferred version of the equation for the IB Physics syllabus is written as:

$$Q = \Delta U + W$$

When each of these quantities is **positive**:

- $Q$  represents the energy transferred **from** the surroundings to the system because the surroundings are at a higher temperature than the system
- $\Delta U$  represents the **increase** in the internal energy of the system (this is not simply a change, it is an increase)
- $W$  represents the work done **by** the system as it expands and pushes back the surroundings.

When each of these quantities is **negative**:

- $Q$  represents the energy transferred **from** the system to the surroundings because the system is at a higher temperature than the surroundings



- $\Delta U$  represents the **decrease** in the internal energy of the system
- $W$  represents the work done **on** the system as the surroundings compresses it.

### Worked example

A system's internal energy falls by 200 J as a result of energy transfer and work being done. The system does 500 J of work on the surroundings.

- State and explain whether the system is at a higher or lower temperature than its surroundings.
- Calculate the amount of energy transferred causing the reduction in internal energy.

### Solution

- The system must gain energy in order to be able to do this amount of work and so its temperature must be below that of the surroundings.
- Using the first law of thermodynamics  $Q = \Delta U + W$ ,  $\Delta U$  must be negative and  $W$  must be positive.

$$Q = -200 + 500 = 300\text{J}$$

So 300 J are transferred to the system from the surroundings.



## Nature of science

### Human metabolism and the first law

Let us consider a human body as a thermodynamic system. When we eat, our internal energy increases because we are taking in food in the form of chemical potential energy. When there is no energy transfer because of temperature differences this must be a process which is related to work – although we will not discuss the biochemistry here.

So, using the first law with no energy transfer:

$$0 = \Delta U + W$$

As  $\Delta U$  is positive this means that  $W$  is negative.

The chemical energy in the food we eat does three main things: it allows us to do work on

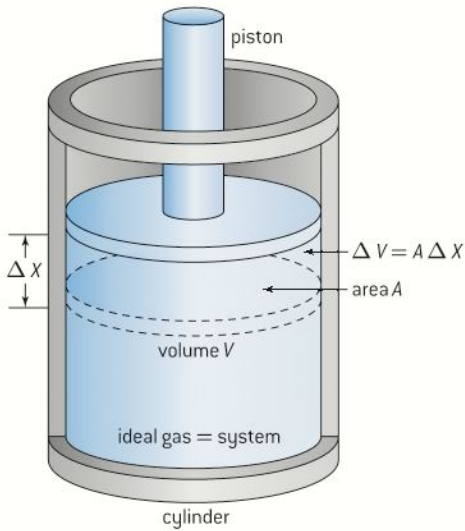
our surroundings, it allows us to transfer energy to the (usually) cooler surroundings and the remainder is stored in our bodies (as fat). With a well-adjusted, balanced diet the build up of fat and change in internal energy is zero and the food we eat allows us to stay warm and do work and be active. So the ideal system is to make the net change in the internal energy of our bodies zero – eat too much and we will build up fat ( $\Delta U$  is positive), eat too little and we will lose weight ( $\Delta U$  is negative). In reality, human metabolism is much more complicated than this, but the first law of thermodynamics does represent a model that has many more applications than the gases we will now focus on.

## Using the first law for ideal gases

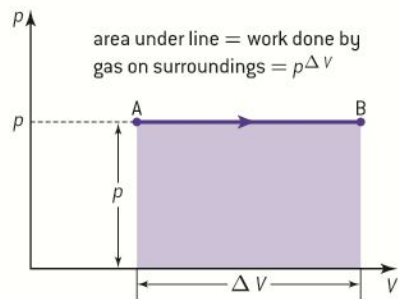
When discussing the changes that can be made to the state of the gas, it is usual to consider an ideal gas enclosed in a cylinder by a moveable piston. The gas represents the system, the cylinder and the piston represent the boundaries or walls. Everything else becomes the surroundings.

### Calculating the work done in an isobaric change

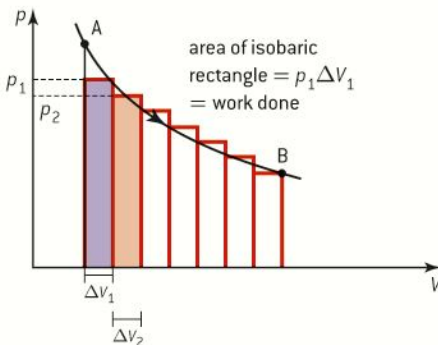
An **isobaric** change is one which occurs at **constant pressure**. Consider an ideal gas at a pressure  $p$  enclosed in a cylinder of cross-sectional area  $A$ . When the gas expands it pushes the piston a distance  $\Delta x$  so that the volume



▲ Figure 2 Work done by an ideal gas.



▲ Figure 3 Work done in an isobaric change.



▲ Figure 4 Work done in a non-isobaric change.

### Note

Isothermal changes normally take place very slowly and the boundary between the system and the surrounding must be a good conductor of energy.

of the gas increases by  $\Delta V (= A\Delta x)$ . When energy is supplied to the gas from the surroundings the pressure can remain constant at value  $p$ . The work done by the gas on the surroundings during this expansion will be  $W$ . The force  $F$  of the gas on piston =  $pA$ . This means that the work done during expansion =  $F\Delta x = pA\Delta x = p\Delta V$ .

$$W = p\Delta V$$

This will be a positive quantity because the system is doing work on the surroundings. When the gas is compressed  $W$  will be negative.

Figure 3 shows a  $p$ - $V$  graph for an isobaric change. The area under the graph is equal to the work done. The arrow on the line connecting the end points AB shows that the gas is expanding and doing work on the surroundings – an arrow in the opposite direction would show a compression.

Applying the first law of thermodynamics to this, we get  $Q = \Delta U + p\Delta V$ . This could result in any number of possibilities but they must be consistent with this equation;  $Q$  must be positive for an expansion and negative for a compression. For example, supplying 20 J to the gas could increase the internal energy by 19 J and allow the gas to do 1 J of work or increase the internal energy by 19.1 and do 0.9 J of work etc.

The equation of state for an isobaric change is  $\frac{V}{T} = \text{constant}$ .

## Work done for non-isobaric changes

When changes do not occur at constant pressure we can still calculate the work done from the area under a  $p$ - $V$  graph. We can make the assumption that the pressure will be unchanged over a small change in volume and, therefore, we approximate the overall change to a series of small isobaric changes as shown in figure 4.

The area of the first constant pressure rectangle =  $p_1 \Delta V_1 = W_1$

The area of the second rectangle would be  $p_2 \Delta V_2 = W_2$ , etc.

Therefore, the total work done =  $\sum_n W_n = \sum_n p_n \Delta V_n$  for  $n$  rectangles – this is the area under the curve. So for any  $p$ - $V$  graph the area under the curve will give the work done – this depends on the path taken and not just on the end points.

## Isothermal changes

Isothermal changes are those that occur **resulting in the internal energy of the system staying constant**. The internal energy of an ideal gas consists of the sum of the mean random kinetic energies of the particles of gas. The mean kinetic energy is proportional to the temperature of the gas. An isothermal change, therefore, means that there is **no change in the temperature of the system**.

Using the first law of thermodynamics  $Q = \Delta U + W$  with  $\Delta U = 0$ , this leaves  $Q = W$ . As there is no change in internal energy, the energy transferred to the system because of a temperature difference between the system and the surroundings  $Q$  will allow the system to do work  $W$  on the surroundings. As  $W = p\Delta V$  this can only mean that the gas is expanding – the direction arrow on the graph should go from A to B.



The other possibility is that  $-Q = -W$  so the energy transferred from the system to the surroundings is equal to the work done on the system by the surroundings. In this case the gas is being compressed – the direction arrow on the graph should go from B to A.

We saw in Topic 3 that when the temperature does not change  $pV = \text{constant}$ . This is the equation of the line on a  $p$ – $V$  graph for an isothermal change. The lines are known as isotherms. As shown in figure 6, changes at higher temperatures will always produce isotherms that are further from the origin than those at lower temperatures. For a given volume the pressure will always increase in moving from a low temperature isotherm to one at higher temperature.

## Adiabatic changes

This is the name given to a change in which **no energy is transferred** between the system and the surroundings. This does not mean that the system and the surroundings are always at the same temperature, although that could be so, but it is more likely that there is a well-insulated barrier between them. Adiabatic changes usually happen very quickly, which means that there is no time for the energy to transfer.

Applying the first law of thermodynamics to a system undergoing an adiabatic change gives:

$Q = \Delta U + W$  but, as  $Q = 0$ , this can mean either  $\Delta U = -W$  (an increase in internal energy occurs because of work being done on the system) or  $-\Delta U = W$  (a decrease in internal energy occurs because the system is doing work on the surroundings). For an ideal monatomic gas the equation for an adiabatic change takes the form:

$$pV^{\frac{5}{3}} = \text{constant}$$

This can be written as  $p_1V_1^{\frac{5}{3}} = p_2V_2^{\frac{5}{3}}$  when there is a constant temperature.

As the gas is an ideal gas the equation

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

also applies to an adiabatic change.

Dividing  $p_1V_1^{\frac{5}{3}} = p_2V_2^{\frac{5}{3}}$  by  $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

gives

$$T_1V_1^{\frac{2}{3}} = T_2V_2^{\frac{2}{3}}$$

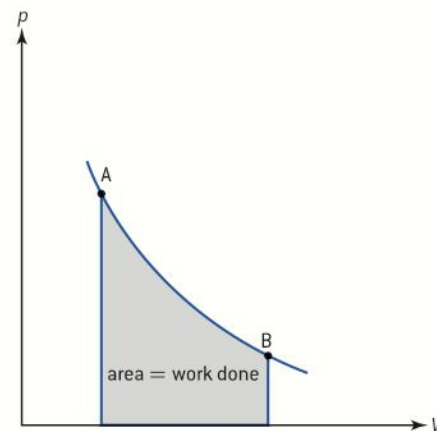
In the  $p$ – $V$  equation for an adiabatic change  $V$  is raised to a power of greater than one. This means that for an adiabatic change the line will be steeper than that for an isothermal change – as shown in figure 7.

The area under the adiabatic change, as for all other changes, will be the work done. The direction of the arrow will determine whether work is done on or by the gas.

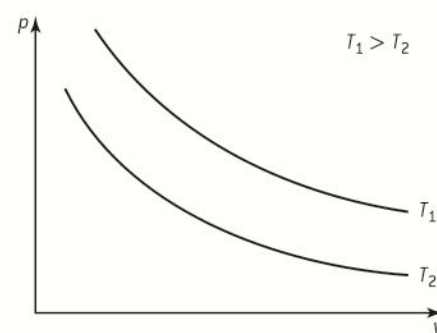
## Isovolumetric changes

These changes occur at constant volume and, therefore, mean that **no work can be done** by or on the system.

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



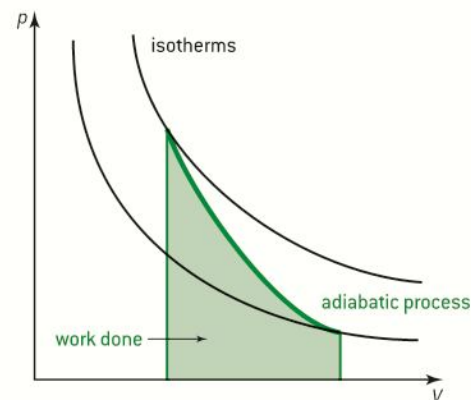
▲ Figure 5 Work done in an isothermal change.



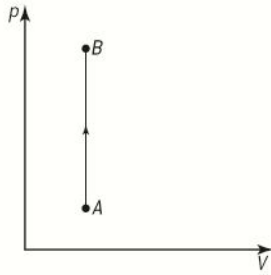
▲ Figure 6 Isotherms at different temperatures.

### Note

You don't need to derive the equations for adiabatic changes. The exponent for  $V$  does vary if the gas molecules are diatomic (two atom molecules) or polyatomic (three or more molecules in the atom). The value is actually the ratio of the principal molar specific heats but, as this is not going to be examined, we leave you to do further research on this.



▲ Figure 7 Adiabatic and isothermal changes.



▲ Figure 8 Isovolumetric change.

With no change in the volume, the first law of thermodynamics becomes  $Q = \Delta U$  (when the energy transferred to the system increases the internal energy) or  $-Q = -\Delta U$  (when the energy transferred from the system decreases the internal energy).

Figure 8 shows an isovolumetric change on a  $p$ - $V$  graph. In this case the change shows an increase in temperature (moving to a higher isotherm on an isothermal graph).

The equation of state for an isovolumetric change is  $\frac{p}{T} = \text{constant}$ .

### Worked example

- Distinguish between an *isothermal* process and an *adiabatic* process as applied to an ideal gas.
- An ideal gas is held in a cylinder by a moveable piston and energy is supplied to the gas such that the gas expands at a constant pressure of  $1.5 \times 10^5$  Pa. The initial volume of the cylinder is  $0.040 \text{ m}^3$  and its final volume is  $0.12 \text{ m}^3$ . The total energy supplied to the gas during the process is  $7.5 \times 10^3 \text{ J}$ .
  - State and explain the type of change that the gas undergoes.
  - Determine the work done by the gas.
  - Calculate the change in internal energy of the gas.

### Solution

- An *isothermal* process is one that takes place at constant temperature (and constant internal energy) so there is an interchange of energy

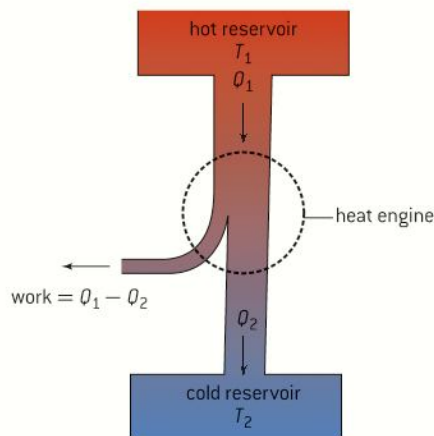
transferred because of the temperature difference between the gas and the surroundings and work done one on the other.

An *adiabatic* process is one in which there is no energy exchanged between the system and the surroundings. This means that changes in the internal energy (and hence temperature) occurs because of work done by or on the ideal gas.

- As the pressure does not change the gas undergoes an isobaric expansion.
  - Work done = area under the  $p$ - $V$  graph for the change ( $= p\Delta V$ )  $= 1.5 \times 10^5 (0.12 - 0.04) = 1.2 \times 10^4 \text{ J}$
  - Using the first law of thermodynamics  $Q = \Delta U + W$   
 $\Delta U = Q - W$  because only  $7.5 \times 10^3 \text{ J}$  is supplied to the gas and  $12.0 \times 10^3 \text{ J}$  of work is done, the internal energy must fall by  $4.5 \times 10^3 \text{ J}$

## Cycles and engines

Work can be converted into internal energy effectively through frictional forces. Work done by friction is usually undesirable because it increases the temperature of the system (good) and the surroundings (bad). The reverse process of continuously converting energy into work is more difficult to achieve, but it can be done using a **heat engine** that operates through a cycle of changes. In 1824 the French physicist and engineer, Sadi Carnot, published the first description of a heat engine; in this he described what has come to be known as the "Carnot cycle". The principle of a heat engine is to take in energy at a high temperature, reject energy at a low temperature and use the remainder of the energy to do work on the system as illustrated in figure 9.



▲ Figure 9 The principle of a heat engine.

We can think of the system as being a gas enclosed in a cylinder with a frictionless moveable piston. When energy  $Q_1$  is supplied to the gas from a hot reservoir at temperature  $T_1$ , the gas expands and moves the piston, doing work. This will stop as soon as the gas pressure is equal to that of the surroundings. The gas now needs to be returned to its original state before it can do further work. This can only happen if some of the energy ( $Q_2$ ) that was initially absorbed is rejected to a cold reservoir at lower temperature  $T_2$ .



The thermal efficiency  $\eta$  of the heat engine will be given by:

$$\eta = \frac{\text{useful work done}}{\text{energy input}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$$

In the Carnot cycle we imagine a completely friction-free engine that is able to take a gas through a cycle of two isothermal and two adiabatic changes as shown in figure 10.

Starting at point A where the gas is at its highest temperature  $T_1$ , it expands isothermally to B by absorbing energy  $Q_1$ . The internal energy of the gas does not change so all the energy absorbed is doing work.

The gas now expands adiabatically to C where the temperature falls to  $T_2$ . No energy is now being absorbed but the gas still does work on the surroundings by losing some internal energy.

During the expansion ABC the area under the two expansion curves gives the work done on the surroundings.

At C the gas now needs work being done on it so it is compressed isothermally to D and rejects energy  $Q_2$ . The internal energy does not change so the work done on the gas is all rejected as energy.

Finally, the gas is further compressed adiabatically from D back to A. The work done on the gas is all used to increase the internal energy in returning the gas to temperature  $T_1$ .

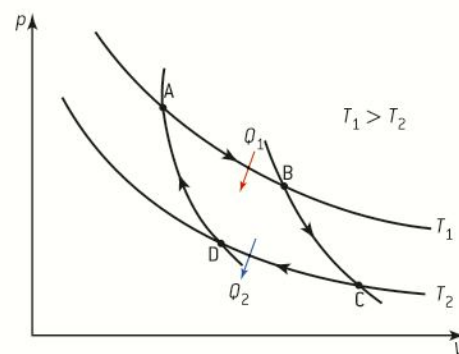
During the compression CDA the area under the two compression curves gives the work done by the surroundings on the gas. **The area enclosed by the curve is the net work done by the gas on the surroundings in one cycle.**

The Carnot heat engine is said to be reversible. This is a theoretical concept in which, at any part in the cycle, the system can be returned to a previous state without any energy transference – this must be done infinitely slowly and means that the system returns exactly to its initial state at the end of the cycle. It can be shown that, for the Carnot cycle (and all reversible heat engines), that the thermal efficiency is given by

$$\eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

This is written in the IB Physics Syllabus as

$$\eta_{\text{Carnot}} = 1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}$$



▲ Figure 10 The Carnot cycle.

### Note

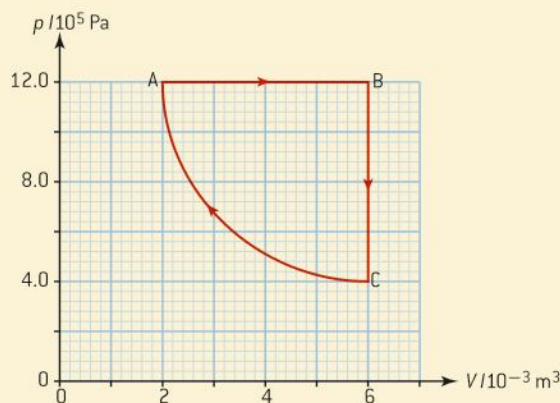
- Temperatures used here must be in kelvin.
- This is the equation for the maximum efficiency of a heat engine.
- The maximum efficiency is increased by raising the temperature of the hot reservoir and/or by lowering the temperature of the cold reservoir.
- The maximum efficiency can never equal 100% as this would mean that the cold reservoir was at absolute zero or else the hot reservoir was at an infinitely high temperature – neither of these requirements is possible.
- In practice thermodynamic cycles can be achieved but none will be more efficient than the Carnot cycle.

### Worked example

A quantity of an ideal gas is used as the working substance of a heat engine. The cycle of operation of the engine is shown in the  $p$ - $V$  graph opposite. Change CA is isothermal.

The temperature of the gas at A is 300 K.

- a) During the change AB the change in internal energy of the gas is 7.2 kJ.
- Calculate the temperature, at B, of the gas.
  - Determine the amount of energy transferred during change AB.



- b) State why, for the change BC, the change in the internal energy of the gas is numerically the same as that in AB.
- c) Calculate:
- the net work done in one cycle
  - the efficiency.

### Solution

- a) (i) For an ideal gas  $\frac{pV}{T} = \text{constant}$

$$\begin{aligned} \text{As pressure is constant } \frac{V_A}{T_A} &= \frac{V_B}{T_B} \Rightarrow T_B \\ &= \frac{V_B \times T_A}{V_A} = \frac{6.0 \times 10^{-3} \times 300}{2.0 \times 10^{-3}} = 900 \text{ K} \end{aligned}$$

$$\begin{aligned} \text{(ii) } W &= p\Delta V \\ &= 12.0 \times 10^5 \times (6.0 \times 10^{-3} - 2.0 \times 10^{-3}) \\ &= 4.8 \text{ kJ} \end{aligned}$$

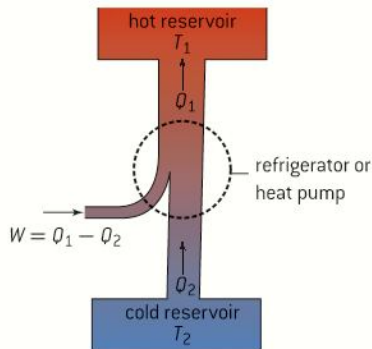
The increase in internal energy = 7.2 kJ  
so the energy transferred to the gas must equal  $4.8 + 7.2 = 12.0$  kJ.

- b) The gas undergoes the same change in temperature and, as the gas is ideal, this means that the change in internal energy depends solely on the temperature.
- c) (i) We need to find the area enclosed by the cycle.

Each large square is equivalent to  $1.0 \times 10^{-3} \times 2.0 \times 10^5 \text{ J} = 200 \text{ J}$

Estimate that there are 14 large squares, making a total 2800 J or 2.8 kJ.

$$\text{(ii) } \eta = \frac{W}{Q_1} = \frac{2.8}{12} = 0.23 \text{ or } 23\%$$



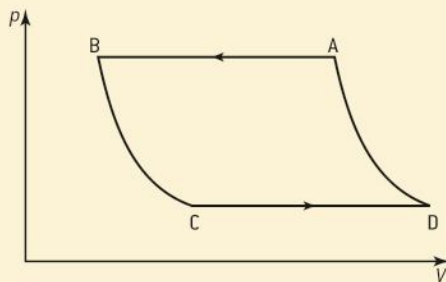
▲ Figure 11 The principle of a heat pump and refrigerator.

## Heat pumps and refrigerators

Heat pumps and refrigerators act in a similar manner to a heat engine working in reverse. They take in energy  $Q_2$  at a low temperature  $T_2$ , do work  $W$  on the working substance and reject energy  $Q_1$  at the high temperature  $T_1$ . Although they are very similar in their working the heat pump is designed to add energy to the high temperature reservoir (for example, the room being heated by extracting energy from the ground) whilst the refrigerator is designed to remove energy from the low temperature reservoir (the cool box). Air conditioning units are another example of heat pumps.

### Worked example

The diagram shows the relationship between the pressure  $p$  and the volume  $V$  of the working substance of a refrigerator for one cycle of its operation. The working substance is a volatile liquid which is made to vaporize and condense.



- a) The working substance at point C of the cycle is entirely in the liquid phase.
- Suggest the reason why both the changes from CD and AB are isothermal, isobaric changes.
- b) State during which process of the cycle energy is absorbed from the cold reservoir and during which process energy is transferred to the hot reservoir.
- c) State how the value of the work done during one cycle may be determined from the  $pV$  diagram.





### Solution

- a) Both changes are isobaric and isothermal because there is no pressure or temperature change. Each of the changes occurs because of a change of phase of the working substance. From C to D the liquid vaporizes and from A to B the vapour condenses.
- b) Energy is absorbed during C to D as the liquid needs energy to vaporize and it is ejected during A to B in order for the vapour to condense.
- c) The area enclosed by the cycle will always indicate the net amount of work – in this case it is work done on the system (working substance).

## The second law of thermodynamics

Although this is a fundamental law that has its origins in practical experiences, the second law of thermodynamics can be stated in a number of different ways. The first law of thermodynamics equates work to energy, the second law deals with the circumstances in which energy can be converted to work. Each of the statements is equivalent to the others and communicates an expression of the impracticability of reversing real thermodynamic processes.

The Clausius version of the second law can be stated as:

**It is impossible to transfer energy from a body at a lower temperature to one at higher temperature without doing work on the system.**

The Kelvin (or Kelvin-Planck) version states:

**It is impossible to extract energy from a hot reservoir and transfer this entirely into work.**

If the second law was not true it would be possible to power ships by energy extracted from the sea – this cannot be done because there needs to be a cold reservoir into which the difference between the energy extracted and the work done would be rejected. When, after a time, we return to full cup of coffee we do not expect to find it at a higher temperature than when it was made. Energy passes from the hot coffee to the cooler room until the two bodies are at the same temperature – if we wanted the coffee to heat up we would have to transfer energy to it using a heating coil or else do work on it by stirring it rapidly!

The internal energy of an object is related to the random motion of the molecules of the object. By trying to convert this internal energy into work we are trying to convert random motion into something more ordered. It is impossible to do this because we cannot take control over the individual motion of a colossal number of molecules.

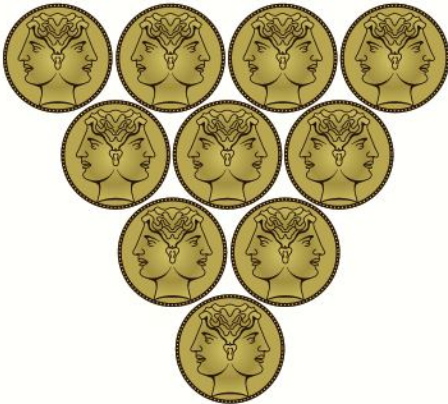
## Entropy

A third version of the second law of thermodynamics involves the concept of **entropy**  $S$ . This quantity can be defined (for a reversible change) in terms of the equation

$$\Delta S = \frac{\Delta Q}{T}$$

**Note**

- $T$  is always positive so when energy is absorbed by a system and  $\Delta Q$  is positive there will be a positive change in entropy – an increase. When energy is rejected by the system the entropy will decrease.
- For an adiabatic change  $\Delta Q = 0$  and so  $\Delta S = 0$
- A substance taken through a complete reversible cycle will undergo no change in entropy as  $\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{Q_2}{Q_1}$  this means  $\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$
- All heat engines reject energy to the surroundings and generate an overall increase in entropy of the universe.



▲ Figure 12 Ten coins all "heads up".

$\Delta S$  is the increase in entropy

$\Delta Q$  is the energy absorbed by the system

$T$  is the temperature in kelvin at which this occurs.

Entropy is a scalar quantity and has units of joule per kelvin ( $\text{J K}^{-1}$ )

**Worked example**

0.20 kg of ice at  $0^\circ\text{C}$  melts. The specific latent heat of fusion of water is  $3.3 \times 10^5 \text{ J kg}^{-1}$ . Calculate the change in entropy of the ice as it melts.

**Solution**

Energy needed to melt the ice =  $mL = 0.20 \times 3.3 \times 10^5 = 6.6 \times 10^4 \text{ J}$

$$\Delta S = \frac{\Delta Q}{T} = \frac{6.6 \times 10^4}{273} = 2.4 \times 10^2 \text{ J K}^{-1}$$

**Entropy as a measure of disorder**

We have now seen that for real processes the entropy of the universe increases – in fact this is another way of stating the second law of thermodynamics first suggested by Boltzmann.

Real processes always degrade the energy, i.e. change the energy from being localized to being more spread out. If some hot water is mixed with cold water in a completely insulated container there is no loss of energy, however, the opportunity to use the energy to do work is now restricted by having cold water. It is not a sensible proposition to separate the most energetic molecules to produce some hot water and some cold water from the mixture – the energy has changed from the localized situation in the hot water molecules to a situation where it is spread-out amongst all of the molecules.

Imagine having 10 coins all placed heads up on the table. The coins are picked up and shaken before being returned to the table, without looking to see where they are placed; some coins will, therefore, have heads up but others will have heads down. The coins have moved from an ordered state to a disordered state. There is a small likelihood  $\left(\left(\frac{1}{2}\right)^{10} = \frac{1}{1024}\right)$  that the coins would be replaced with all 10 heads up. By increasing the number of coins from 10 to 100 it decreases the likelihood of them all being heads up to 1 in  $1.3 \times 10^{30}$ , and, this really isn't likely to happen! The coin experiment mirrors nature in that a system does not naturally become more ordered. We have now seen that the entropy of a system naturally increases with the disorder of the system. This is not coincidental since it can be shown that *entropy is a measure of the disorder of a system*.



## TOK

**The arrow of time**

Many scientists have discussed increasing entropy as representing the "arrow of time". Because the disorder of a large system will increase with time, finding such a system with increased order would be equivalent to time going backwards. Perpetually increasing entropy is

contrary to Newton's laws of motion in which the change of state of a system is equally predictable whether we go forwards or backwards in time.

Does this statement of the Second law prevent the possibility of time travel?

**Worked example**

- a) State what is meant by an *increase in entropy* of a system.
- b) State, in terms of entropy, the second law of thermodynamics.
- c) When a chicken develops inside an egg, the entropy of the egg and its contents decreases. Explain how this observation is consistent with the second law of thermodynamics.

**Solution**

- a) When the entropy increases, there is an increase in the degree of disorder in the system.
- b) The total entropy of the universe increases.
- c) Entropy of the surroundings must increase more than the decrease of entropy in the developing egg. The energy generated by the biochemical processes within the egg becomes more spread out as a consequence of some passing into the surroundings.