



# HL IB Physics

  
Your notes

## Thermodynamics

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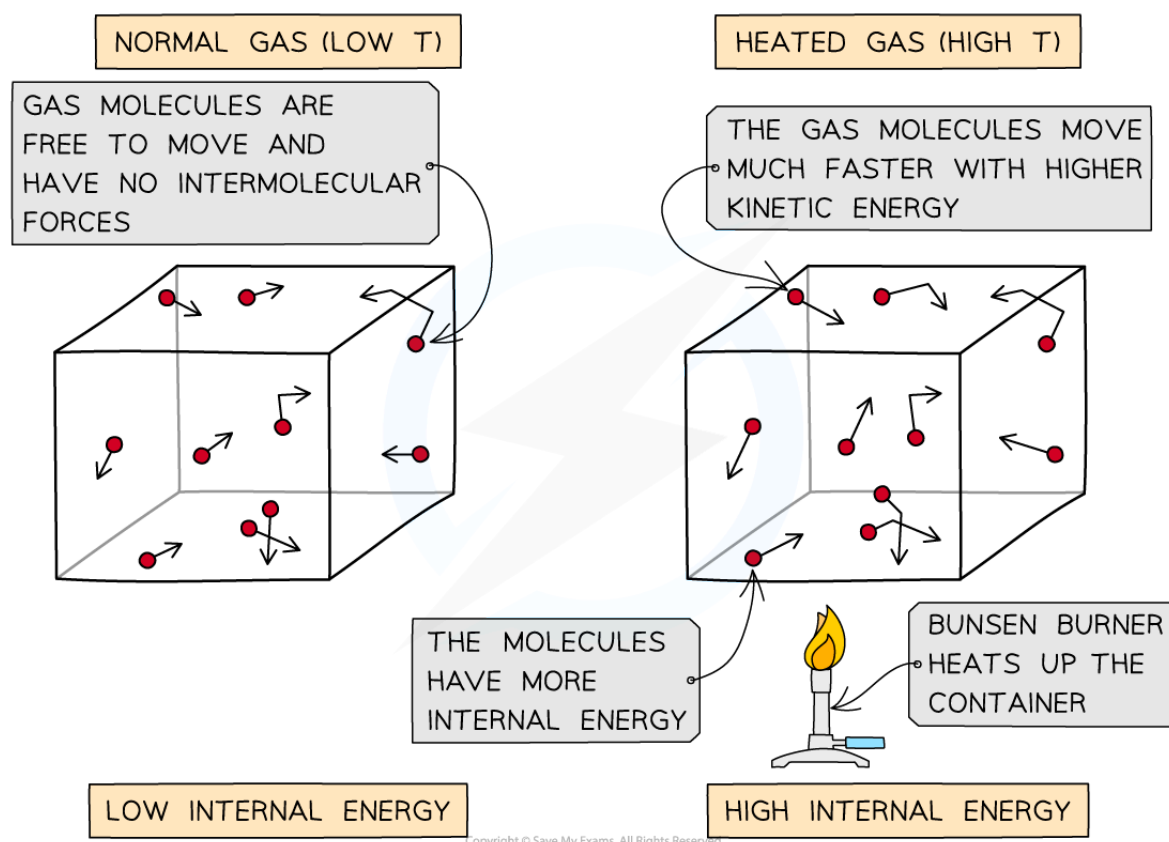
## Thermodynamic Systems (HL)

### Change in Internal Energy

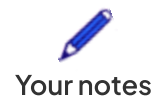
- The change in the internal energy  $\Delta U$  of an object is intrinsically related to a change in its temperature  $\Delta T$

$$\Delta U \propto \Delta T$$

- When a container containing gas molecules is heated up, the molecules begin to **move around faster**, increasing their kinetic energy
  - In a solid, where the molecules are tightly packed, molecules begin to **vibrate** more as they are heated
  - Molecules in liquids and solids have **both** kinetic and potential energy because they are close together and bound by intermolecular forces
- However, the molecules in an ideal gas are assumed to have **no intermolecular forces**
  - This means they do **not** possess potential energy, **only** kinetic energy



As the container is heated up, the gas molecules move faster with higher kinetic energy and therefore higher internal energy



- The (change in) internal energy of an ideal gas is equal to:

$$\Delta U = \frac{3}{2} N k_B \Delta T$$

- Where
  - $\Delta U$  = change in internal energy (J)
  - $k_B$  = Boltzmann constant
  - $\Delta T$  = change in temperature (K)
  - $N$  = number of particles
- Another form of this equation related to the translational kinetic energy of the **particles** is

$$\Delta U = \frac{3}{2} n R \Delta T$$

- Where:
  - $n$  = number of moles of gas (mol)
  - $R$  = molar gas constant

### Worked example

A student suggests that, when an ideal gas is heated from 50°C to 150°C, the internal energy of the gas is tripled.

State and explain whether the student's suggestion is correct.

**Answer:**

- The change in internal energy of an ideal gas is directly proportional to its change in temperature

$$\Delta U \propto \Delta T$$

- The temperature change is the **thermodynamic** temperature i.e. Kelvin
- The temperature change in degrees (from 50°C to 150°C) increases by three times
- The temperature change in Kelvin is:

$$50^\circ\text{C} + 273.15 = 323.15 \text{ K}$$

$$150^\circ\text{C} + 273.15 = 423.15 \text{ K}$$

$$\frac{423.15}{323.15} = 1.3$$

- The temperature change, in Kelvin, does **not** increase by three times, therefore, neither does the internal energy
- **Hence, the student is incorrect**



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### Worked example

An ideal gas expands at constant pressure. The following data are available:

amount of gas = 126 mol

initial temperature of gas =  $-23.0^{\circ}\text{C}$

final temperature of gas =  $+27.0^{\circ}\text{C}$

Determine the change in internal energy of the gas during this expansion.

**Answer:**

- The change in internal energy of a gas is equal to

$$\Delta U = \frac{3}{2}nR\Delta T$$

- Where

- Amount of gas,  $n = 126$  mol
- Gas constant,  $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$
- Change in temperature,  $\Delta T = 27 - (-23) = 50^{\circ}\text{C}$

$$\Delta U = \frac{3}{2} \times 126 \times 8.31 \times 50$$

$$\Delta U = 7.85 \times 10^4 \text{ J}$$

### Examiner Tip

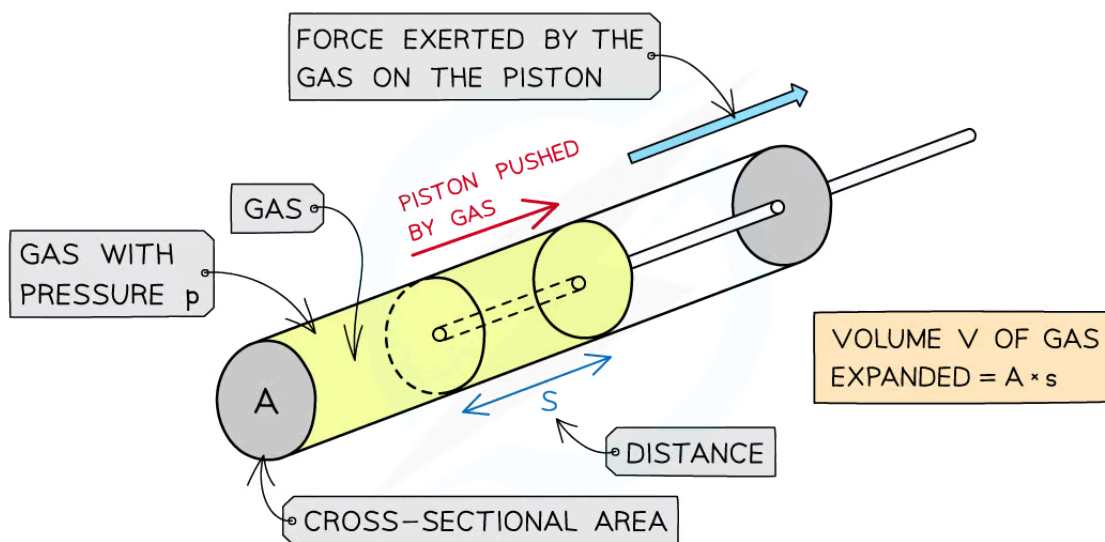
If an exam question about an ideal gas asks for the **total internal energy**, remember that this is equal to the **total kinetic energy** since an ideal gas has **zero potential energy**



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## Work Done by a Gas

- When a gas **expands**, it **does work** on its surroundings by exerting pressure on the walls of the container it's in
- For a gas inside a piston, the force exerted by the gas pushes the piston outwards
  - As a result, work is done **on** the piston **by** the gas
- Alternatively, if an external force is applied to the piston, the gas will be **compressed**
  - In this case, work is done **on** the gas **by** the piston



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**The expansion of the gas does work on the piston by exerting a force over a distance,  $s$**

- Assuming the volume of gas is kept at **constant** pressure, this means the force  $F$  exerted by the gas on the piston is equal to:

$$p = \frac{F}{A} \quad \Rightarrow \quad F = pA$$

- Where  $A$  = cross-sectional area of the cylinder ( $\text{m}^2$ )
- The definition of work done is:

$$W = Fs$$

- Where  $s$  = displacement in the direction of force (m)
- The displacement  $s$  of the gas multiplied by the cross-sectional area  $A$  is equal to the increase in volume  $\Delta V$  of the gas:

$$W = pAs$$

- This gives the equation for the work done when the volume of a gas changes at constant pressure:

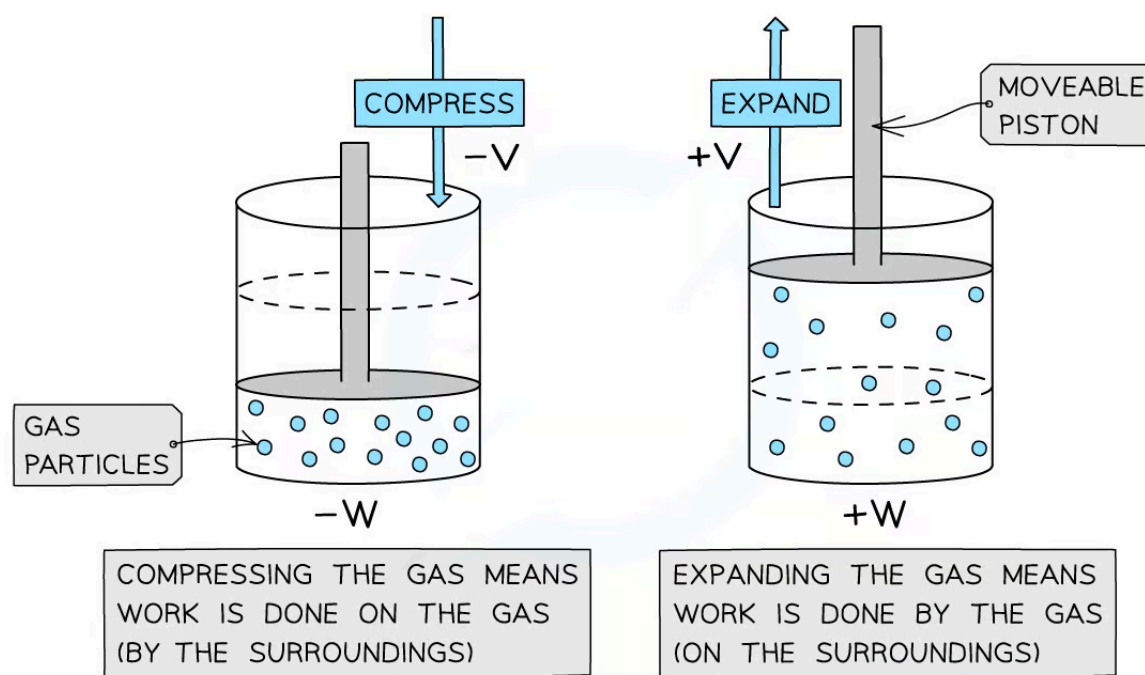
$$W = p\Delta V$$

- Where:

- $W$  = work done (J)
- $p$  = pressure of the gas (Pa)
- $\Delta V$  = change in the volume of the gas ( $\text{m}^3$ )
- This equation assumes that the surrounding pressure does not change as the gas expands
  - This is true if the gas is expanding against the pressure of the atmosphere, which changes very slowly

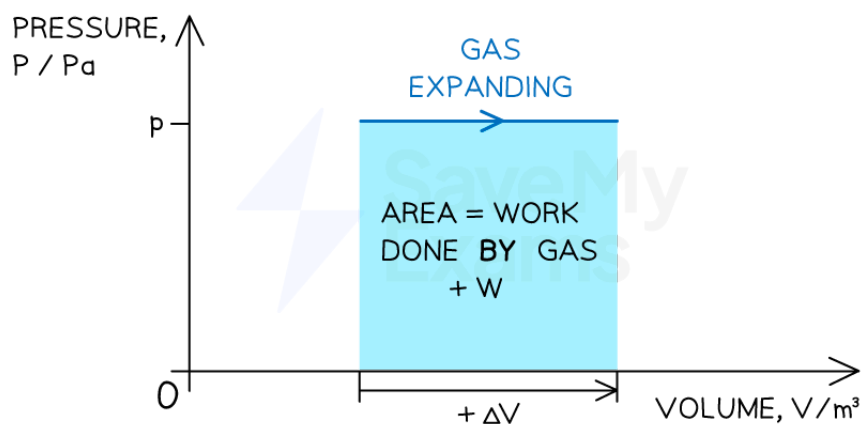
## p-V diagrams

- Pressure-volume (p-V) diagrams are often used to represent changes in the **state of a gas** in thermodynamic processes



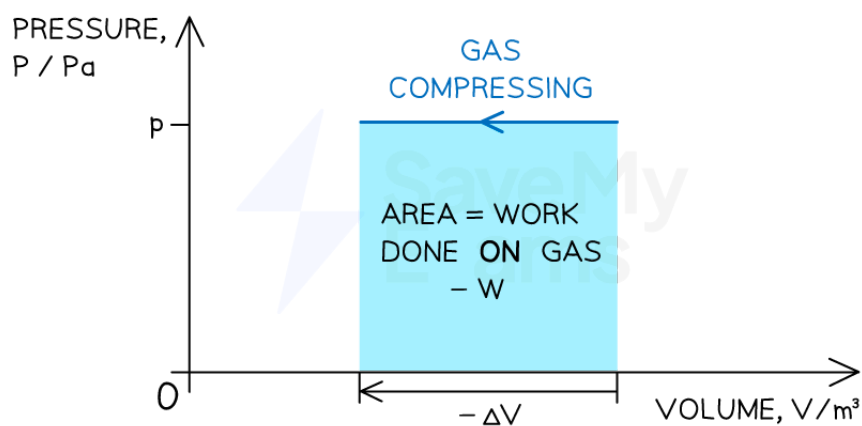
**Positive or negative work done depends on whether the gas is compressed or expanded**

- When a gas **expands** (at constant pressure) **work done is positive**
  - Volume increases  $+\Delta V$
  - Work is done **by** the gas  $+W$



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- When a gas is **compressed** (at constant pressure) **work done  $W$  is negative**
  - Volume decreases  $-\Delta V$
  - Work is done **on** the gas  $-W$

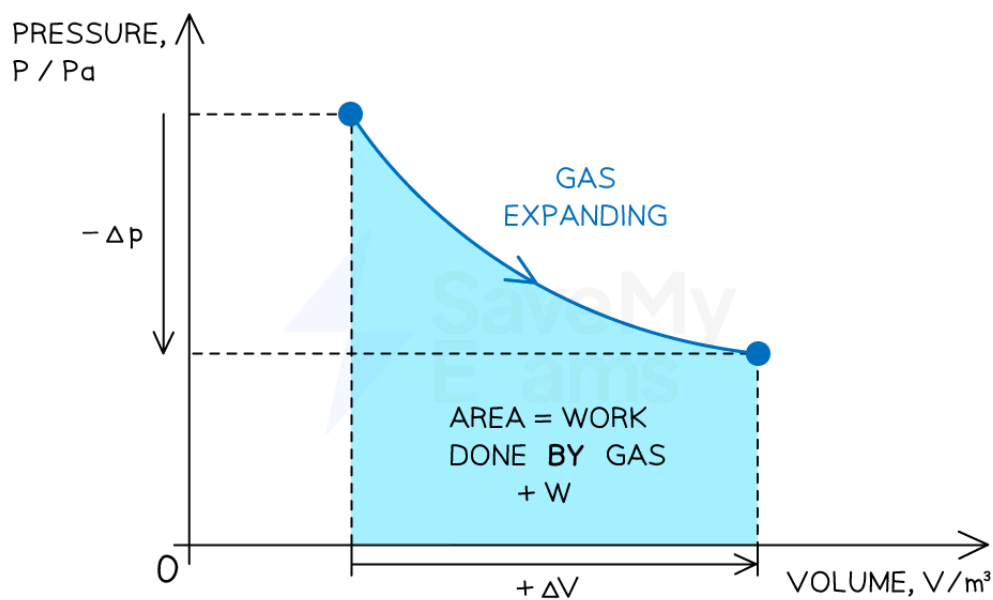


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- When both the volume and pressure of gas **changes**  
**The work done can be determined from the area under a p-V diagram**



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### Worked example

When a balloon is inflated, its rubber walls push against the air around it.

Calculate the work done when the balloon is blown up from 0.015 m<sup>3</sup> to 0.030 m<sup>3</sup>.

Atmospheric pressure = 1.0 × 10<sup>5</sup> Pa.

**Answer:**

- The work done by a gas is equal to

$$W = p \Delta V$$

- Where the change in volume is

$$\Delta V = \text{final volume} - \text{initial volume} = 0.030 - 0.015 = 0.015 \text{ m}^3$$

- Therefore, work done is

$$W = (1.0 \times 10^5) \times 0.015 = 1500 \text{ J}$$

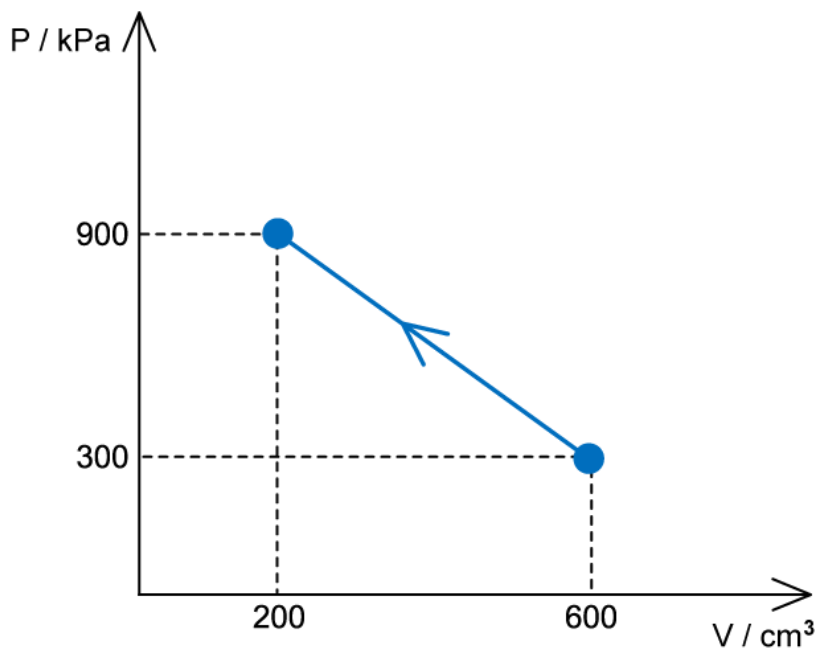




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### Worked example

An ideal gas is compressed, as shown on the graph below.



- For this change, state and explain whether work is done on the gas or by the gas
- Determine the value of the work done and state whether it is positive or negative

**Answer:**

**(a)**

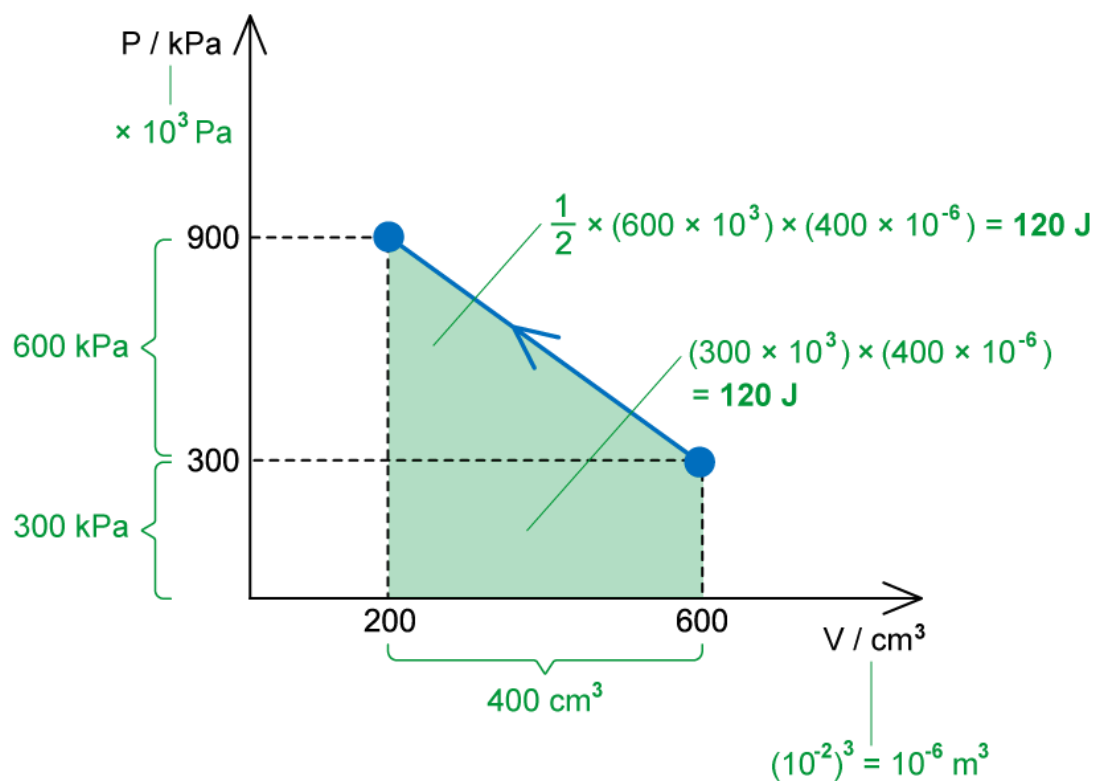
- The volume decreases, therefore, work is done **on the gas**

**(b)**

- The work done is equal to the area under the p-V diagram



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$$W = \frac{1}{2}(600 \times 10^3)(400 \times 10^{-6}) + (300 \times 10^3)(400 \times 10^{-6})$$

$$W = -240 \text{ J}$$

- When volume decreases, the work done is **negative**

### Examiner Tip

The pressure  $p$  in the work done by a gas equation is not the pressure of the gas but the pressure of the surroundings. This is because when a gas expands, it does work **on** the surroundings.



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## First Law of Thermodynamics (HL)

### The First Law of Thermodynamics

- The first law of thermodynamics is based on the principle of conservation of energy
- When energy is put into a gas by heating it or doing work on it, its internal energy must increase:  
**energy supplied by heating = change in internal energy + work done on the system**

- The first law of thermodynamics is therefore defined as:

$$Q = \Delta U + W$$

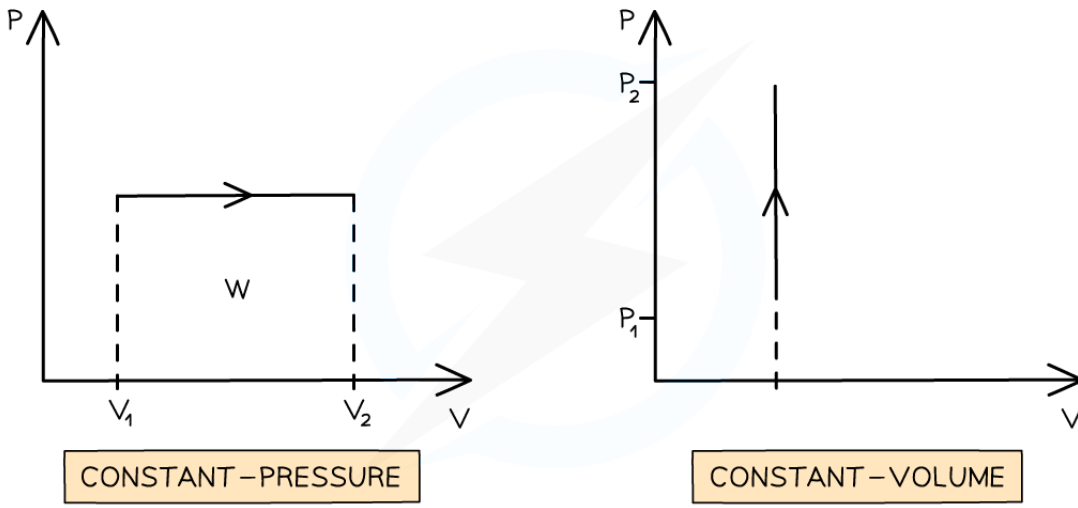
- Where:
  - $Q$  = energy supplied to the system by heating (J)
  - $\Delta U$  = change in internal energy (J)
  - $W$  = work done by the system (J)
- The first law of thermodynamics applies to **all** situations, not just to gases
  - There is an important sign convention used for this equation
- A **positive** value for internal energy ( $+\Delta U$ ) means:
  - The internal energy  $\Delta U$  **increases**
  - Heat  $Q$  is **added** to the system ( $+Q$ )
  - Work  $W$  is done **on** the system ( $-W$ )
- A **negative** value for internal energy ( $-\Delta U$ ) means:
  - The internal energy  $\Delta U$  **decreases**
  - Heat  $Q$  is **taken away** from the system ( $-Q$ )
  - Work  $W$  is done **by** the system ( $+W$ )

### Graphs of Constant Pressure & Volume

- Graphs of pressure  $p$  against volume  $V$  can provide information about the work done and internal energy of the gas
  - The work done is represented by the area under the line
- A constant pressure process is represented as a **horizontal line**
  - If the volume is increasing (expansion), work is done **by** the gas (on the surroundings) and internal energy decreases ( $\Delta U = q - W$ )
  - If the arrow is reversed and the volume is decreasing (compression), work is done **on** the gas and internal energy increases ( $\Delta U = q + W$ )
  - The volume of the gas is made smaller, so more collisions between the molecules of the gas and the walls of the container occur. This creates a higher pressure.
- A constant volume process is represented as a **vertical line**
  - In a process with constant volume, the area under the curve is **zero**
  - Therefore, no work is done when the volume stays the same



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**Work is only done when the volume of a gas changes**



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### Worked example

The volume occupied by 1.00 mol of a liquid at 50°C is  $2.4 \times 10^{-5} \text{ m}^3$ . When the liquid is vaporised at an atmospheric pressure of  $1.03 \times 10^5 \text{ Pa}$ , the vapour occupies a volume of  $5.9 \times 10^{-2} \text{ m}^3$ .

The latent heat to vaporise 1.00 mol of this liquid at 50°C at atmospheric pressure is  $3.48 \times 10^4 \text{ J}$ .

For this change of state, determine the increase in internal energy  $\Delta U$  of the system.

**Answer:**

#### Step 1: List the known quantities

- Thermal energy,  $Q = 3.48 \times 10^4 \text{ J}$
- Atmospheric pressure,  $p = 1.03 \times 10^5 \text{ Pa}$
- Initial volume =  $2.4 \times 10^{-5} \text{ m}^3$
- Final volume =  $5.9 \times 10^{-2} \text{ m}^3$

#### Step 2: Calculate the work done $W$

- The work done by a gas at constant pressure is

$$W = p\Delta V$$

- Where the change in volume is:

$$\Delta V = \text{final volume} - \text{initial volume} = (5.9 \times 10^{-2}) - (2.4 \times 10^{-5}) = 0.059 \text{ m}^3$$

- Since the volume of the gas increases, the work done is positive

$$W = (1.03 \times 10^5) \times 0.059 = 6077 = 6.08 \times 10^3 \text{ J}$$

$$W = +6.08 \times 10^3 \text{ J}$$

#### Step 3: Substitute the values into the equation for the first law of thermodynamics

- From the first law of thermodynamics:

$$\Delta U = Q - W$$

$$\Delta U = (3.48 \times 10^4) - (6.08 \times 10^3) = 28720 \text{ J}$$

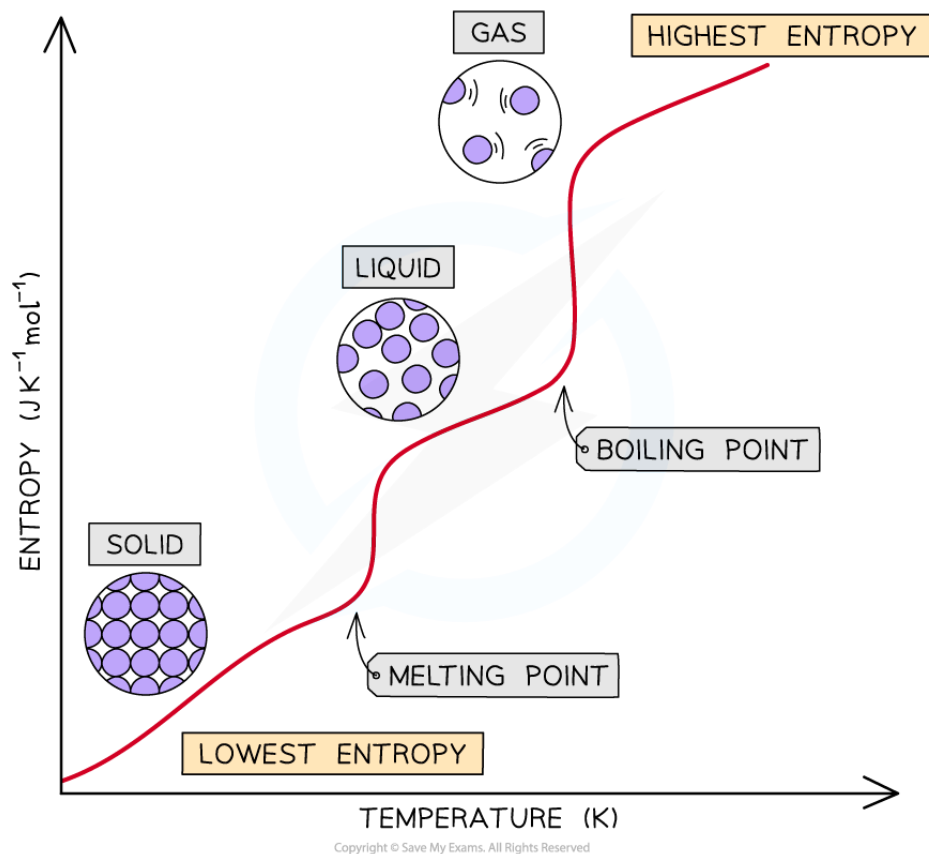


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## Entropy (HL)

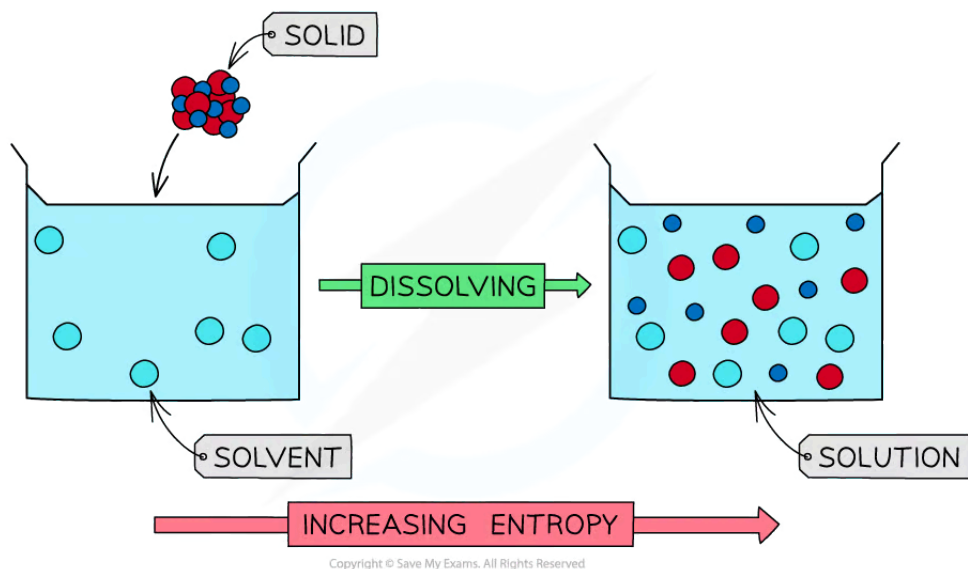
### Entropy

- The entropy  $S$  of a given system is a measure of the number of possible arrangements of the particles and their energies
  - In other words, it is a measure of how **disordered** a system is
  - When a system becomes more disordered, its entropy will **increase**
- The order of entropy for the different states of matter from **most** disordered to **least** is:  
**gas > liquid > solid**
- The entropy of a substance changes during a **change in state**
- Entropy **increases** when a substance **melts** (solid  $\rightarrow$  liquid) or **boils** (liquid  $\rightarrow$  gas)
  - Increasing the temperature of a substance causes the particles to **vibrate** more
  - The particles in a gas can now freely move around and are far apart from each other
  - The entropy increases as the particles become more disordered
- Similarly, entropy **decreases** when a substance **condenses** (gas  $\rightarrow$  liquid) or **freezes** (liquid  $\rightarrow$  solid)
  - The particles are brought together and become arranged more regularly
  - The particles become less able to move as they become more ordered
  - There are fewer ways of arranging the energy, hence the entropy decreases

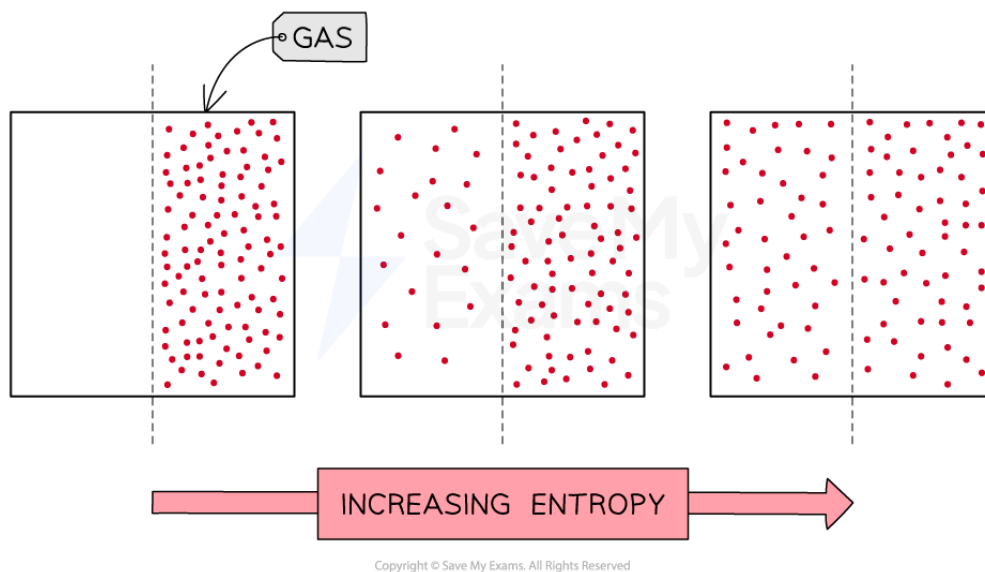


*The entropy of a substance increases when the temperature is raised as particles become more disordered*

- Entropy can also increase when
  - A solid **dissolves** in a solvent
  - A gas **diffuses** in a container
- In both cases, entropy **increases** because:
  - The particles become more spread out
  - There is an increase in the number of ways of arranging the energy



**When a solid is dissolved in a solvent to form a dilute solution, the entropy increases as the particles become more disordered**







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### Worked example

A freezer door is opened while switched on and placed in a sealed room.

The entropy of the room

- A. equals zero
- B. increases
- C. decreases
- D. does not change

**Answer: B**

- A freezer is a heat pump, so thermal energy is transferred from inside the freezer and released at the back of the freezer
- While it runs with the door open, the internal energy of the contents of the freezer decreases
- The entropy of the contents of the freezer **decreases** because they are colder
- But the entropy of the room **increases** because it is hotter

## Real Isolated Systems

- In thermodynamics, the distinction between **reversible** and **irreversible** processes at the macroscopic level is very important
- A reversible process is defined as:  
**A process where there is no overall change in entropy as the system and its surroundings are returned to their original states**
- Whereas, an irreversible process is defined as:  
**A process which results in an increase in entropy as the system and its surroundings cannot return to their original states**
- Processes in **real isolated systems** are almost always irreversible and consequently, the entropy of a real isolated system always increases

## Non-Isolated Systems

- While the entropy of an isolated system must always increase, the entropy of a non-isolated system can decrease
- An isolated system is defined as
  - **A system in which neither matter nor energy can be transferred in or out**
- Whereas in a non-isolated system, matter and energy can be transferred in or out
  - In other words, a non-isolated system can be thought of as one which is part of a larger isolated system
- This means that the entropy of a non-isolated system can decrease locally, but this is compensated by an equal, or greater increase in the entropy of the surroundings



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## Calculating Changes in Entropy (HL)

### Calculating Changes in Entropy

- At a constant temperature  $T$ , the change in entropy on a **macroscopic** level can be calculated using the equation

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

- Where:
  - $\Delta S$  = change in entropy ( $\text{J K}^{-1}$ )
  - $\Delta Q$  = heat given to or removed from the system (J)
  - $T$  = temperature of the system (K)
- When heat is given to a system ( $\Delta Q$  = positive), **entropy increases**

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

$$\Delta Q > 0$$

$$\Delta S > 0$$

- When heat is removed from a system ( $\Delta Q$  = negative), **entropy decreases**

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

$$\Delta Q < 0$$

$$\Delta S < 0$$

- For a reversible process that returns the system to its original state, **entropy is constant**

$$\Delta Q = 0$$

$$\Delta S = 0$$

### Entropy & Microstates

- The entropy of a system, on a **microscopic** level, can be calculated using the equation

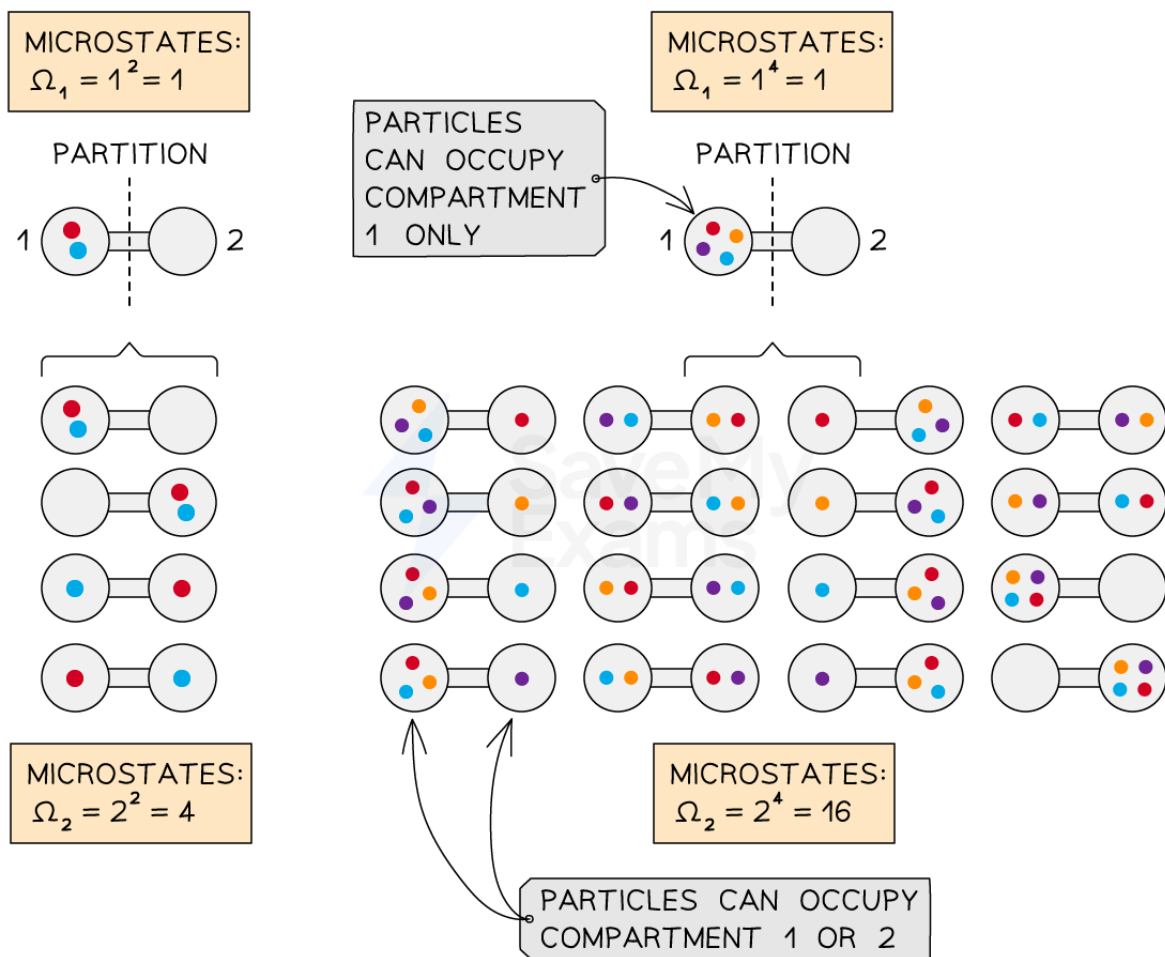
$$S = k_B \ln \Omega$$

- Where:
  - $S$  = entropy of a system of microscopic particles ( $\text{J K}^{-1}$ )
  - $k_B$  = the Boltzmann constant
  - $\Omega$  = the number of possible microstates of the system

- Similarly, the change in entropy when the number of microstates increases from  $\Omega_1$  to  $\Omega_2$  is given by

$$\Delta S = k_B \ln \frac{\Omega_2}{\Omega_1}$$

- A **microstate** describes one state or possible arrangement of the particles in the system
  - A state can be defined by any microscopic or macroscopic property that is known about the system e.g. positions or velocities of molecules, energy, volume etc.
- An example that helps illustrate this is a two-compartment container which holds  $N$  distinguishable particles (i.e. each particle can be identified individually)
- Initially, all  $N$  particles are sealed in one of two compartments



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**The number of possible microstates describes the number of different possible arrangements of particles in a system**

- When the particles are confined to one compartment, we know the location of all the particles



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- Therefore, the number of microstates (possible arrangements) in the initial volume is  $\Omega_1 = 1^N = 1$
- It is **always** equal to 1, for example, when  $N = 2$  or  $N = 4$ :  $\Omega_1 = 1^2 = 1^4 = 1$
- Once the partition is removed, the particles can spread out and occupy either one of the two compartments
  - The number of microstates (possible arrangements) in the final volume is  $\Omega_2 = 2^N$
  - For example, when  $N = 2$ , the particles can be arranged  $2^2 = 4$  **different ways**
  - Or, when  $N = 4$ , the particles can be arranged  $2^4 = 16$  **different ways**
- The change in the entropy is therefore:

$$\Delta S = k_B \ln \left( \frac{\Omega_2}{\Omega_1} \right) = k_B \ln \left( \frac{2^N}{1^N} \right)$$

$$\Delta S = k_B \ln (2^N)$$

- It follows that the number of possible microstates can be equated to macroscopic properties of the gas, such as its **volume** increasing from  $V$  to  $2V$
- As the gas expands, the space it can occupy **doubles**, hence it gains an amount of entropy equal to:

$$\Delta S = Nk_B \ln (2V) - Nk_B \ln (V)$$

$$\Delta S = Nk_B \ln \left( \frac{2V}{V} \right) = Nk_B \ln (2)$$

- This gives the same result as above:

$$\Delta S = k_B \ln (2^N)$$

### Examiner Tip

Entropy is an incredibly important topic in physics and underpins many fundamental ideas from quantum mechanics to the determination of the Schwarzschild radius of a black hole, so don't worry if you feel a bit lost at first as it is quite a challenging concept to get your head around initially!

You might find it useful to think of microstates as a way of quantifying the **certainty** of information we have about the system

For example:

- A solid has **lower entropy** than a gas because we can be more certain about the location of the atoms in the solid
- A gas at a higher temperature (or pressure or volume) has a **higher entropy** than a similar gas at a lower temperature (or pressure or volume) because we become less certain about the location of the atoms by further increasing the possible locations they could occupy



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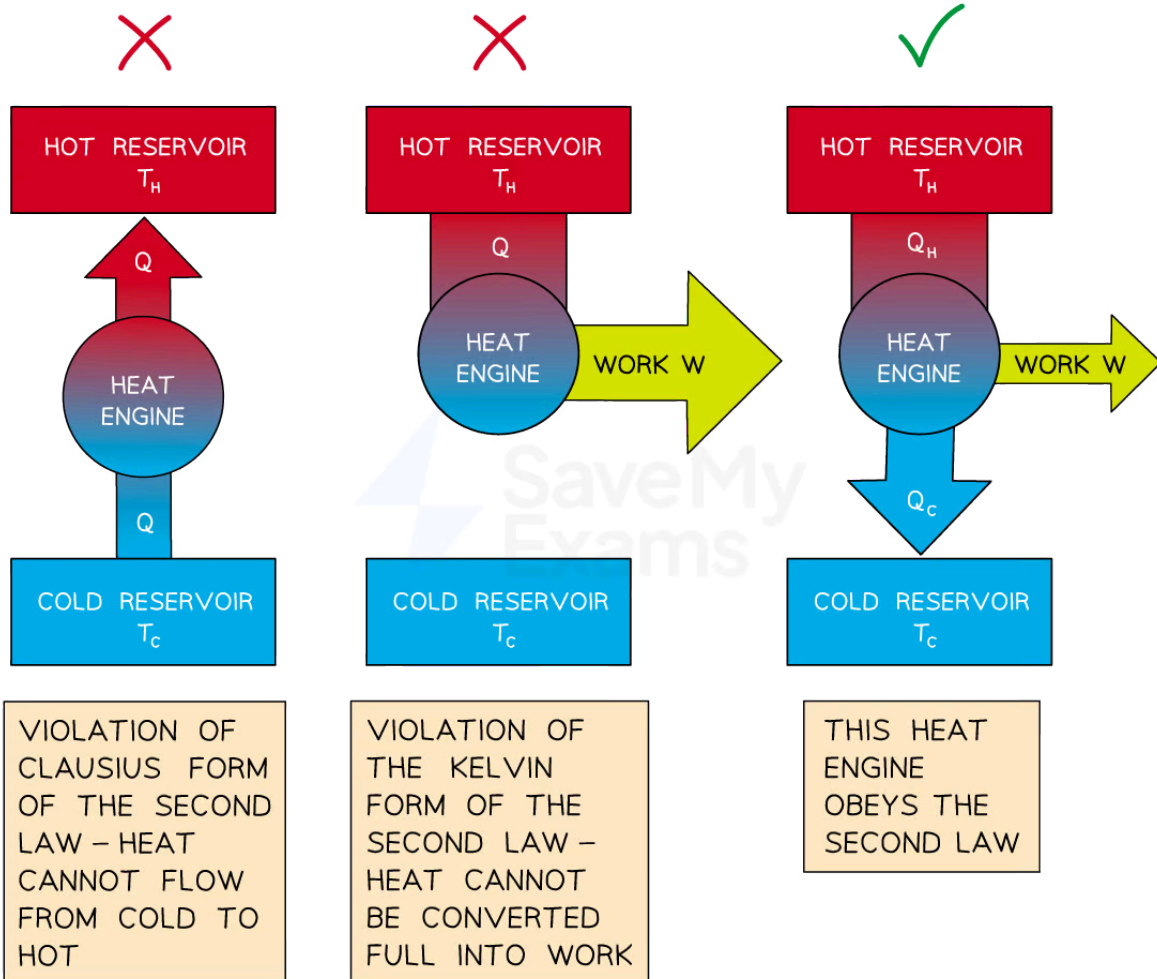


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## Second Law of Thermodynamics (HL)

### Second Law of Thermodynamics

- The second law of thermodynamics states  
**In every process, the total entropy of an isolated system always increases**
- In the case of a non-isolated system, it can be generalised to say that the entropy of the Universe must increase
- There are two alternative forms of this law which have slightly more practical applications
- The **Clausius form** of the second law states:  
**Thermal energy cannot spontaneously transfer from a region of lower temperature to a region of higher temperature**
- The use of the word 'spontaneously' is the key here, as heat pumps are an example of a way that heat can be transferred from a colder region to a hotter one by **doing work**
- This leads to the **Kelvin form** of the second law, which states  
**When extracting energy from a heat reservoir, it is impossible to convert it all into work**
- The different forms of the second law have significant implications for real-world applications, such as **heat engines**



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Two of these engines cannot exist as they violate the Clausius and Kelvin forms of the second law of thermodynamics





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## Thermodynamic Processes (HL)

### Thermodynamic Processes

- The four main thermodynamic processes are
  - Isovolumetric ( $W = 0$ )
  - Isobaric ( $\Delta p = 0$ )
  - Isothermal ( $\Delta T = 0$ )
  - Adiabatic ( $\Delta Q = 0$ )

#### Constant pressure (isobaric)

- An isobaric process is defined as:
  - A process in which no change in pressure occurs**
- This occurs when gases are allowed to expand or contract freely during a change in temperature
- When there is a change in volume  $\Delta V$  at a constant pressure  $p$ , work done  $W$  is equal to

$$W = p\Delta V$$

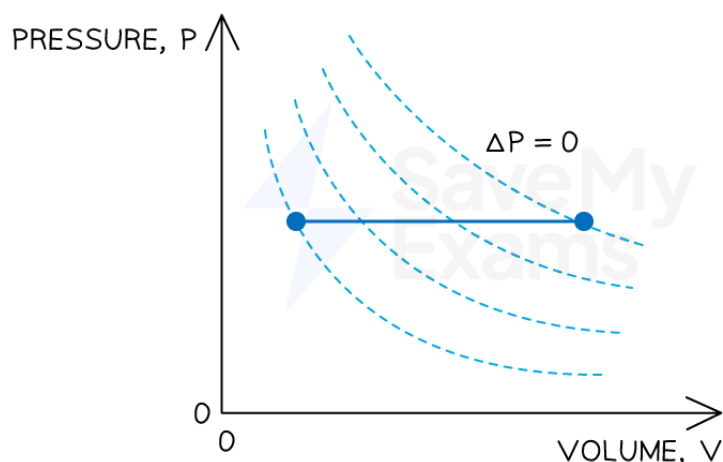
- From the first law of thermodynamics:

$$Q = \Delta U + W$$

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

- The  $\pm$  sign reflects whether work has been done on or by the gas as a result of the change in volume

ISOBARIC



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Representing an isobaric process on a  $p$ - $V$  diagram



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## Constant volume (isovolumetric)

- An isovolumetric process is defined as:

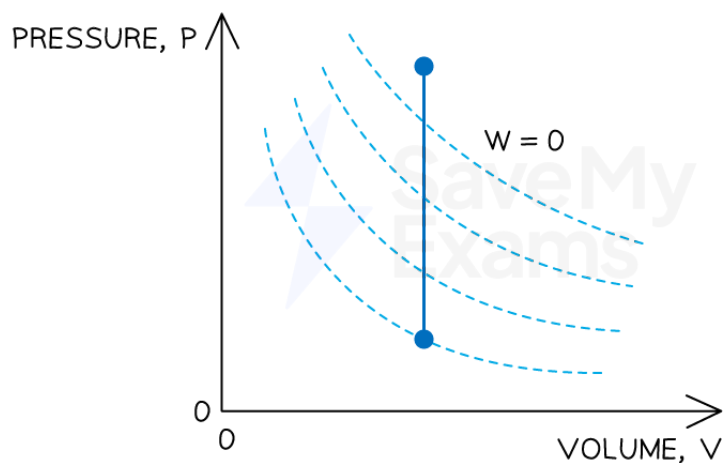
**A process where no change in volume occurs and the system does no work**

- If there is no change in volume, then there is no work done on or by the gas, so  $W = 0$
- Therefore, from the first law of thermodynamics:

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

$$Q = \Delta U$$

ISOVOLUMETRIC



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*Representing an isovolumetric process on a p-V diagram*

## Constant temperature (isothermal)

- An isothermal process is defined as:

**A process in which no change in temperature occurs**

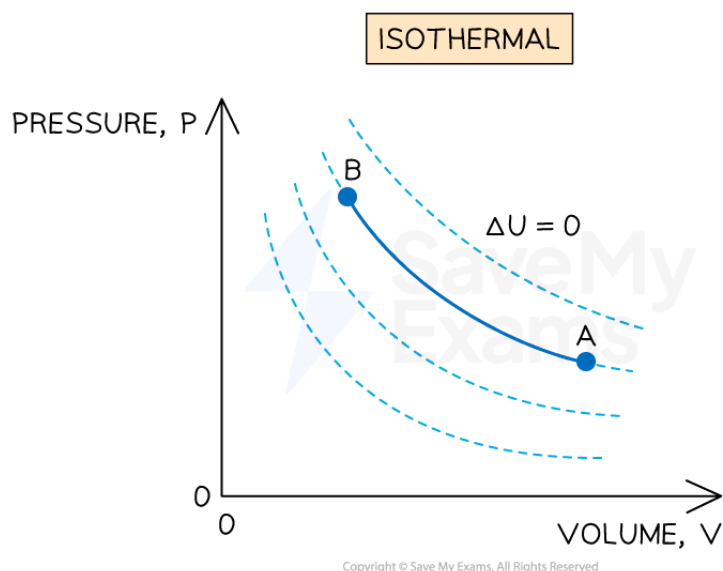
- If the temperature does not change, then the internal energy of the gas will not change, so  $\Delta U = 0$
- Therefore, from the first law of thermodynamics:

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

$$Q = W$$



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*Representing an isothermal process on a p-V diagram*

### Constant thermal energy (adiabatic)

- An adiabatic process is defined as:  
**A process where no heat is transferred into or out of the system**

- If there is no heat entering or leaving the system then  $Q = 0$
- Therefore, from the first law of thermodynamics:

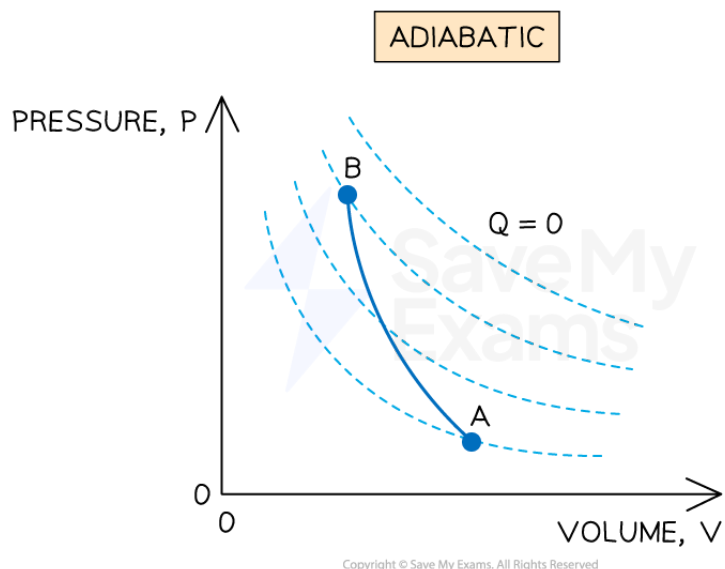
$$Q = \Delta U + W = 0$$

$$W = -\Delta U$$

- This means that all the work done is at the expense of the system's internal energy
- Hence, an adiabatic process will usually be accompanied by a change in temperature



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**Representing an adiabatic process on a p-V diagram**

## Entropy in Thermodynamic Processes

- At a constant temperature  $T$ , the change in entropy is related to heat by

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

- When heat is gained by a system ( $\Delta Q > 0$ ), entropy increases ( $\Delta S > 0$ )
- When heat is lost from a system ( $\Delta Q < 0$ ), entropy decreases ( $\Delta S < 0$ )
- For a reversible process ( $\Delta Q = 0$ ) that returns the system to its original state ( $\Delta S = 0$ )

Process		Heat gained or lost, $\Delta Q$	Change in entropy, $\Delta S$
Isothermal	Expansion	$\Delta Q > 0$ Heat gained = work done by gas	$\Delta S > 0$ Increases
	Compression	$\Delta Q < 0$ Heat lost = work done on gas	$\Delta S < 0$ Decreases



Your notes

Isobaric	Expansion	$\Delta Q > 0$ Heat gained = increase in internal energy + work done by gas	$\Delta S > 0$ Increases
	Compression	$\Delta Q < 0$ Heat lost = decrease in internal energy + work done on gas	$\Delta S < 0$ Decreases
Isovolumetric	Pressure rise	$\Delta Q > 0$ Heat gained due to temperature rise	$\Delta S > 0$ Increases
	Pressure drop	$\Delta Q < 0$ Heat lost due to temperature drop	$\Delta S < 0$ Decreases
Adiabatic	Expansion	$\Delta Q = 0$ Pressure & temperature decrease with no heat gained or lost	$\Delta S = 0$ No change
	Compression	$\Delta Q = 0$ Pressure & temperature increase with no heat gained or lost	$\Delta S = 0$ No change



Your notes

### Worked example

A quantity of energy  $Q$  is supplied to three ideal gases, **X**, **Y** and **Z**.

Gas **X** absorbs  $Q$  isothermally, gas **Y** isovolumetrically and gas **Z** isobarically.

Complete the table by inserting the words 'positive', 'zero' or 'negative' for the work done  $W$ , the change in internal energy  $\Delta U$  and the temperature change  $\Delta T$  for each gas.

	$W$	$\Delta U$	$\Delta T$
<b>X</b>			
<b>Y</b>			
<b>Z</b>			

**Answer:**

- **X:** Isothermal = constant temperature, no change in internal energy
  - Temperature:  $\Delta T = 0$
  - Internal energy:  $\Delta T \propto \Delta U$ , so,  $\Delta U = 0$
  - Work done:  $Q = \Delta U + W \Rightarrow Q = +W$
- **Y:** Isovolumetric = constant volume, no work done
  - Work done:  $W \propto \Delta V$ , so,  $W = 0$
  - Internal energy:  $Q = \Delta U + W \Rightarrow Q = +\Delta U$
  - Temperature:  $\Delta T \propto \Delta U$ , so,  $\Delta T > 0$
- **Z:** Isobaric = constant pressure
  - Work done:  $\Delta p = 0$ , so  $W = p\Delta V$ , so  $W > 0$
  - Internal energy:  $Q = \Delta U + W$ , so  $\Delta U > 0$
  - Temperature:  $\Delta T \propto \Delta U$ , so  $\Delta T > 0$

	$W$	$\Delta U$	$\Delta T$
<b>X</b>	positive	0	0
<b>Y</b>	0	positive	positive

z	positive	positive	positive
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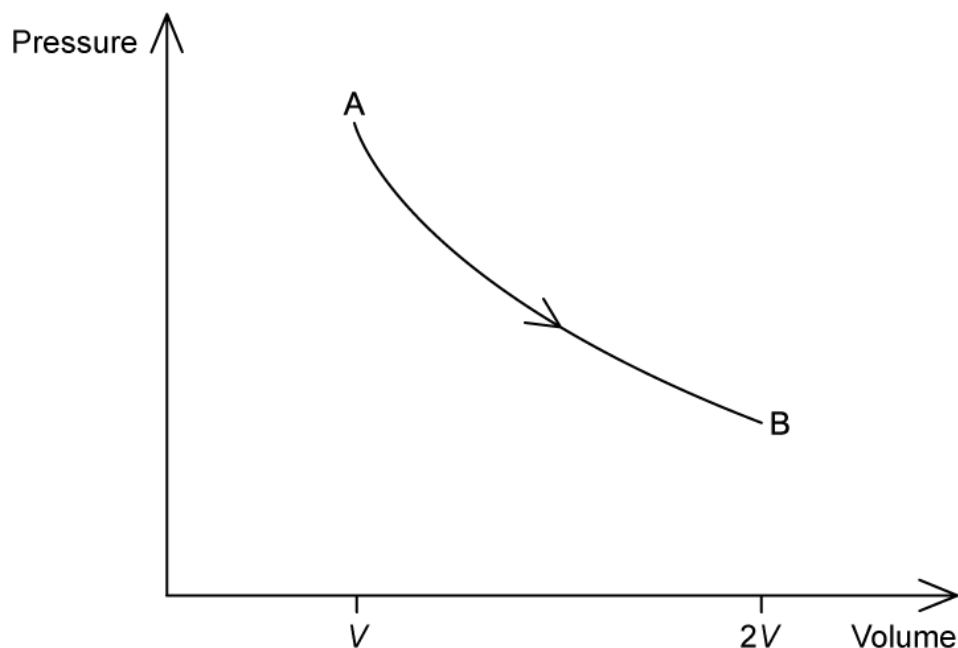
Your notes



Your notes

### Worked example

A heat engine operates on the cycle shown in the pressure–volume diagram. One step in the cycle consists of an isothermal expansion of an ideal gas from state A of volume  $V$  to state B of volume  $2V$ .



- (a) On the graph, complete the cycle ABCA by drawing curves to show
- an isovolumetric change from state B to state C
  - an adiabatic compression from state C to state A
- (b) State and explain at which point in the cycle ABCA the entropy of the gas is the largest.

**Answer:**

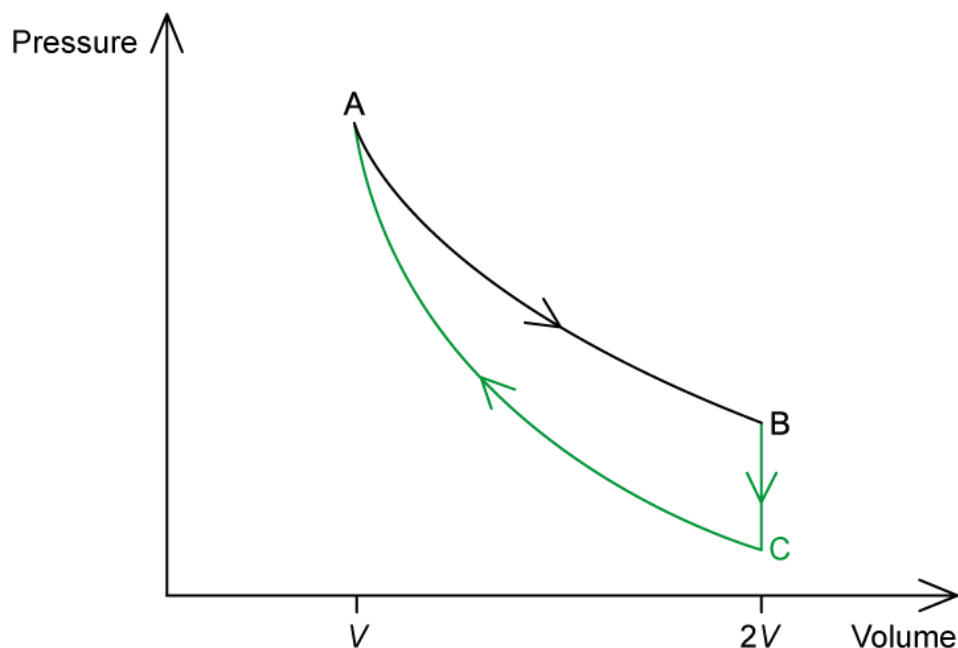
(a)

- **Isovolumetric** = constant volume, no work done
- Next step is a compression (where pressure increases), so this step should involve a **pressure drop**
  - Hence, B to C: line drawn vertically down
- **Adiabatic** = no heat supplied or removed, **compression** = work is done on the gas, volume decreases
  - Hence, C to A: line curves up to meet A





Your notes



(b)

- Entropy and heat (at a constant  $T$ ) are related by

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

- From state A to state B:
  - In an isothermal expansion, entropy **increases**
  - Because  $T = \text{constant}$  but the volume increases so work is done by gas,  $\Delta Q > 0$  so  $\Delta S > 0$
- From state B to state C:
  - In an isovolumetric change where pressure decreases, entropy **decreases**
  - Because temperature decreases, so energy has been removed,  $\Delta Q < 0$  so  $\Delta S < 0$
- From state C to state A:
  - In an adiabatic compression, entropy is **constant**
  - Because it is an adiabatic process,  $\Delta Q = 0$  so  $\Delta S = 0$
- Therefore, entropy is **greatest** at B

## Adiabatic Processes

- Adiabatic processes in monatomic ideal gases can be modelled by the equation

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

- Where:
  - $p$  = pressure of the gas (Pa)
  - $V$  = volume occupied by the gas ( $\text{m}^3$ )
- This equation can be used for calculating changes in pressure, volume and temperature for monatomic ideal gases

$$p_1 V_1^{\frac{5}{3}} = p_2 V_2^{\frac{5}{3}}$$

- Where:
  - $p_1$  = initial pressure (Pa)
  - $p_2$  = final pressure (Pa)
  - $V_1$  = initial volume ( $\text{m}^3$ )
  - $V_2$  = final volume ( $\text{m}^3$ )



Your notes



Your notes

### Worked example

An ideal monatomic gas expands adiabatically from a state with pressure  $7.5 \times 10^5$  Pa and volume  $1.8 \times 10^{-3} \text{ m}^3$  to a state of volume  $4.2 \times 10^{-3} \text{ m}^3$ .

Calculate the new pressure of the gas.

**Answer:**

- For an ideal monatomic gas undergoing an adiabatic change:

$$pV^{\frac{5}{3}} = C$$

$$p_1 V_1^{\frac{5}{3}} = p_2 V_2^{\frac{5}{3}}$$

- Where:

- Initial pressure,  $p_1 = 7.5 \times 10^5$  Pa
- Final pressure =  $p_2$
- Initial volume,  $V_1 = 1.8 \times 10^{-3} \text{ m}^3$
- Final volume,  $V_2 = 4.2 \times 10^{-3} \text{ m}^3$

$$p_2 = p_1 \left( \frac{V_1}{V_2} \right)^{\frac{5}{3}}$$

$$p_2 = (7.5 \times 10^5) \times \left( \frac{1.8 \times 10^{-3}}{4.2 \times 10^{-3}} \right)^{\frac{5}{3}}$$

New pressure:  $p_2 = 1.8 \times 10^5$  Pa



Your notes

### Worked example

An ideal monatomic gas is compressed adiabatically from a state with volume  $3.1 \times 10^{-3} \text{ m}^3$  and temperature 590 K to a state of volume  $2.1 \times 10^{-3} \text{ m}^3$ .

Calculate the new temperature of the gas.

**Answer:**

- For an ideal monatomic gas undergoing an adiabatic change:

$$pV^{\frac{5}{3}} = C$$

$$p_1 V_1^{\frac{5}{3}} = p_2 V_2^{\frac{5}{3}}$$

- From the ideal gas law:

$$pV = nRT \Rightarrow p = \frac{nRT}{V}$$

$$\left( \frac{nRT_1}{V_1} \right) V_1^{\frac{5}{3}} = \left( \frac{nRT_2}{V_2} \right) V_2^{\frac{5}{3}}$$

$$T_1 V_1^{\frac{2}{3}} = T_2 V_2^{\frac{2}{3}}$$

- Where:

- Initial temperature,  $T_1 = 590 \text{ K}$
- Final temperature =  $T_2$
- Initial volume,  $V_1 = 3.1 \times 10^{-3} \text{ m}^3$
- Final volume,  $V_2 = 2.1 \times 10^{-3} \text{ m}^3$

$$T_2 = T_1 \left( \frac{V_1}{V_2} \right)^{\frac{2}{3}}$$

$$T_2 = 590 \times \left( \frac{3.1 \times 10^{-3}}{2.1 \times 10^{-3}} \right)^{\frac{2}{3}}$$

$$\text{New temperature: } T_2 = 765 \text{ K}$$

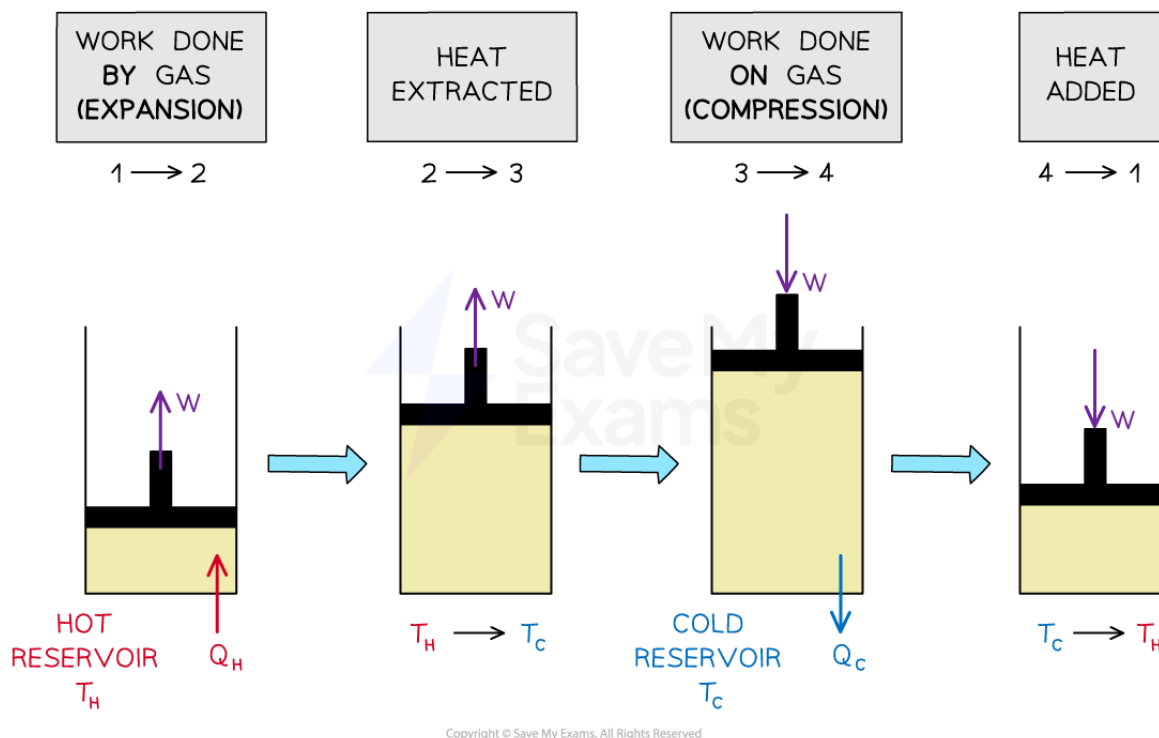


Your notes

## Heat Engines (HL)

### Heat Engines

- A heat engine is a device that converts **thermal energy** into **mechanical work**
- Heat engines operate through a series of thermodynamic processes which form a **closed cycle**
  - A closed cycle is one in which the system returns to its initial state
- A simple heat engine consists of a gas in a cylinder with a piston



*A simple heat engine converts thermal energy into mechanical work*

- The steps in the operation of a cyclic heat engine process are:
  - 1. Extract heat from a hot reservoir**
    - A hot reservoir (a source of thermal energy) at a high temperature  $T_H$  transfers heat  $Q_H$  into the engine
  - 2. Use some of the extracted heat to perform work**
    - The gas does mechanical work as it expands which pushes the piston out
  - 3. Release excess heat into a cold reservoir**
    - The gas is allowed to cool at constant volume, meanwhile, heat  $Q_C$  is released to the surroundings

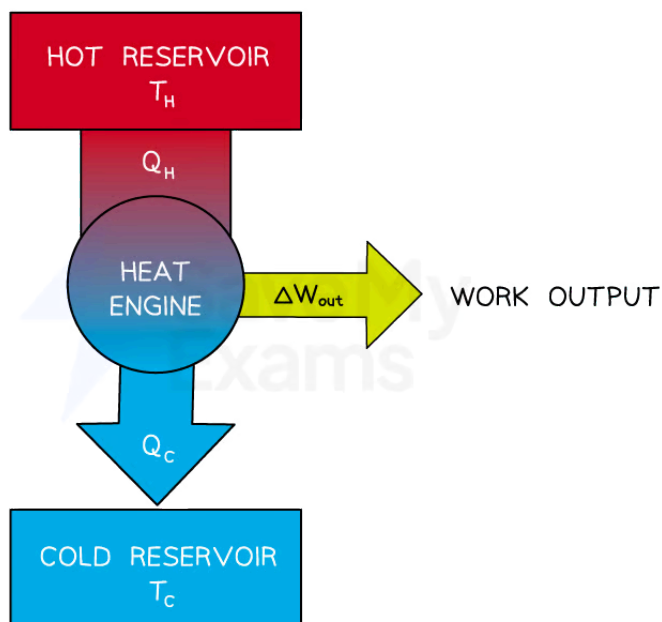


Your notes

- Some of the energy transferred into the engine is released into a cold reservoir (a sink for excess heat) at a lower temperature  $T_C$

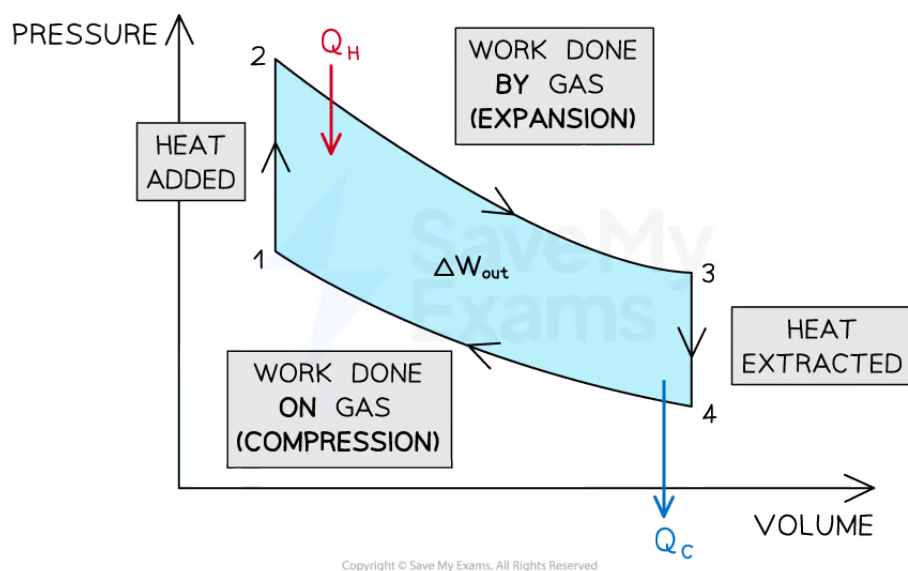
#### 4. Repeat cycle

- Once the heat has been extracted, the piston is pushed down to compress the gas back to its original state
- The process can then be repeated as many times as needed, continuously converting heat into mechanical work



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- For a cyclic heat engine process, the p-V diagram will form a closed loop
- The **area** inside the loop is equal to the **net work done** during one cycle



- The net work done by the engine is:

$$\Delta W_{out} = Q_H - Q_C$$

- Where:

- $\Delta W_{out}$  = useful work output of the heat engine (J)
- $Q_H$  = heat transferred from hot reservoir to engine (J)
- $Q_C$  = heat transferred from engine to cold reservoir (J)

## Efficiency of Heat Engines

- The goal of a heat engine is to transfer thermal energy into useful mechanical work as efficiently as possible
- The thermodynamic efficiency of a heat engine can be calculated using

$$\text{efficiency} = \frac{\text{useful work output}}{\text{total energy input}}$$

$$\eta = \frac{W_{out}}{Q_H} = \frac{(Q_H - Q_C)}{Q_H}$$

$$\eta = 1 - \frac{Q_C}{Q_H}$$

- Where:
  - $\eta$  = efficiency of a heat engine
  - $W_{out}$  = useful work output (J)
  - $Q_H$  = total energy input from the hot reservoir (J)
  - $Q_C$  = energy lost to the cold reservoir (J)



Your notes



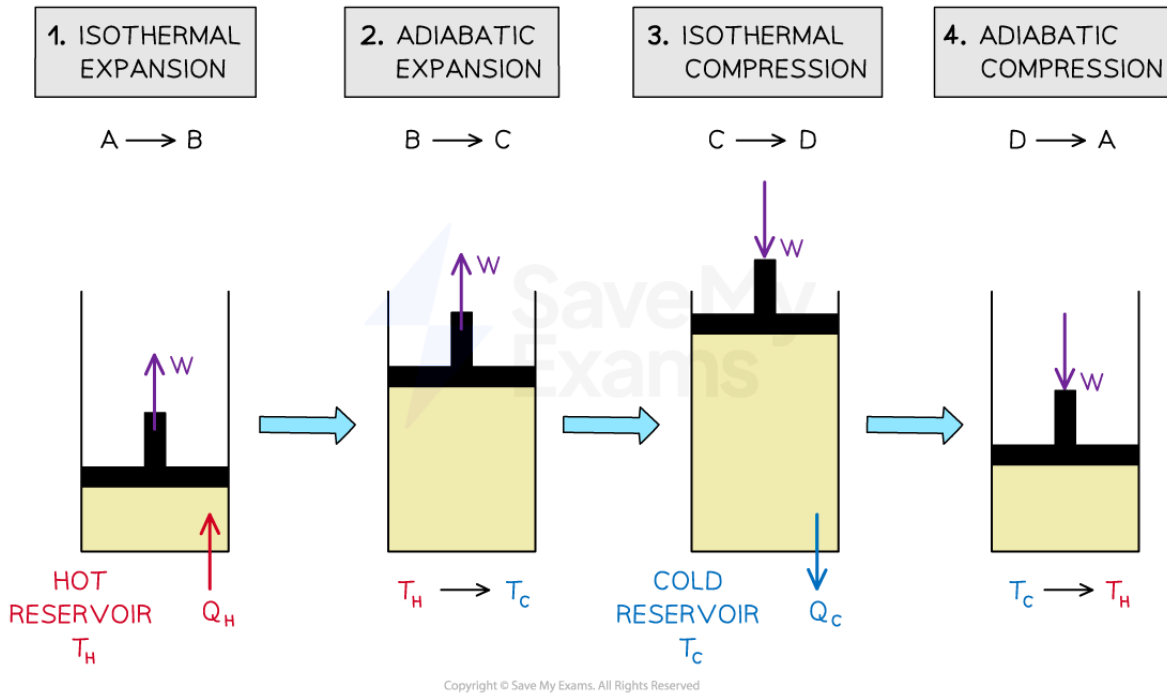


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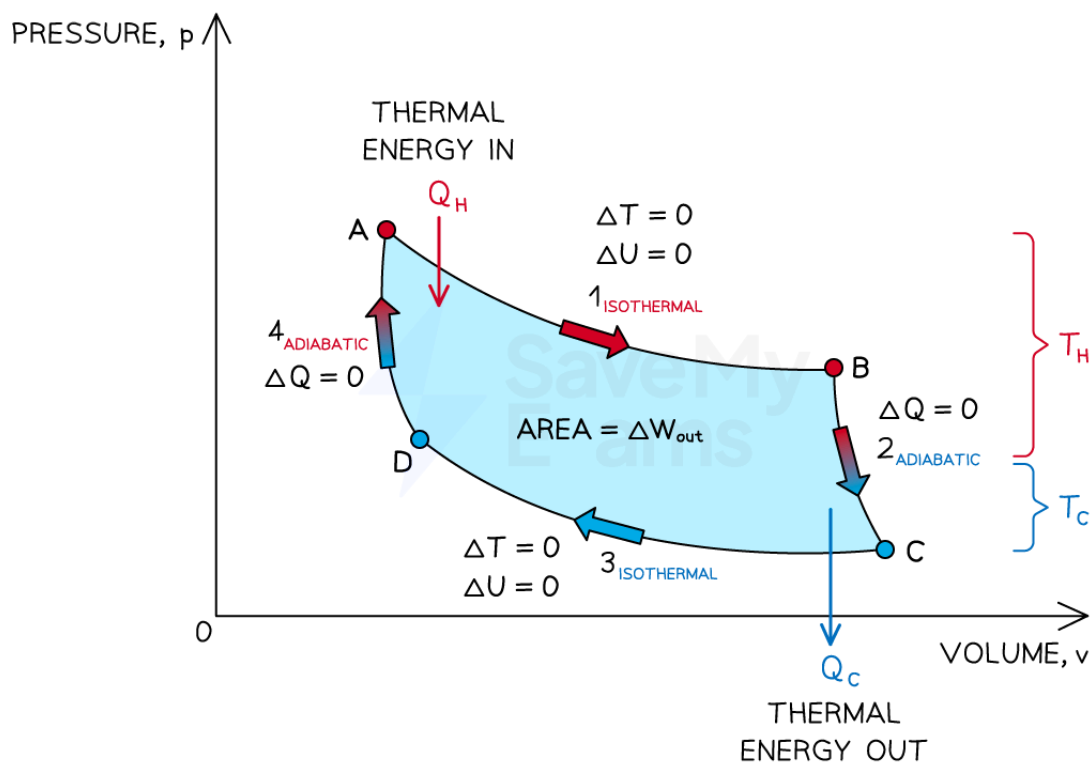
## The Carnot Cycle (HL)

### The Carnot Cycle

- A thermodynamic system that runs at its greatest possible efficiency follows a cycle called the **Carnot cycle**



The four stage Carnot cycle of a gas in a piston



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***p-V diagram for the Carnot cycle. The enclosed area equals the work done after one cycle***

- The Carnot cycle is an idealised and reversible process
- It consists of four stages:
  - 1. Isothermal expansion**
    - The gas absorbs heat  $Q_H$  from a hot reservoir at temperature  $T_H$
    - Work is done by the gas as it expands i.e. volume increases, temperature is constant ( $\Delta T = 0$ )
    - Work done by the gas = heat gained  $Q_H$
  - 2. Adiabatic expansion**
    - The gas continues to expand
    - The gas does work on the surroundings as its volume increases and pressure decreases
    - The gas cools down from  $T_H$  to  $T_C$ , but no thermal energy is transferred ( $\Delta Q = 0$ )
  - 3. Isothermal compression**
    - The gas is compressed and transfers heat  $Q_C$  to a cold reservoir at temperature  $T_C$
    - Work is done on the gas as it is compressed i.e. volume decreases, temperature is constant ( $\Delta T = 0$ )

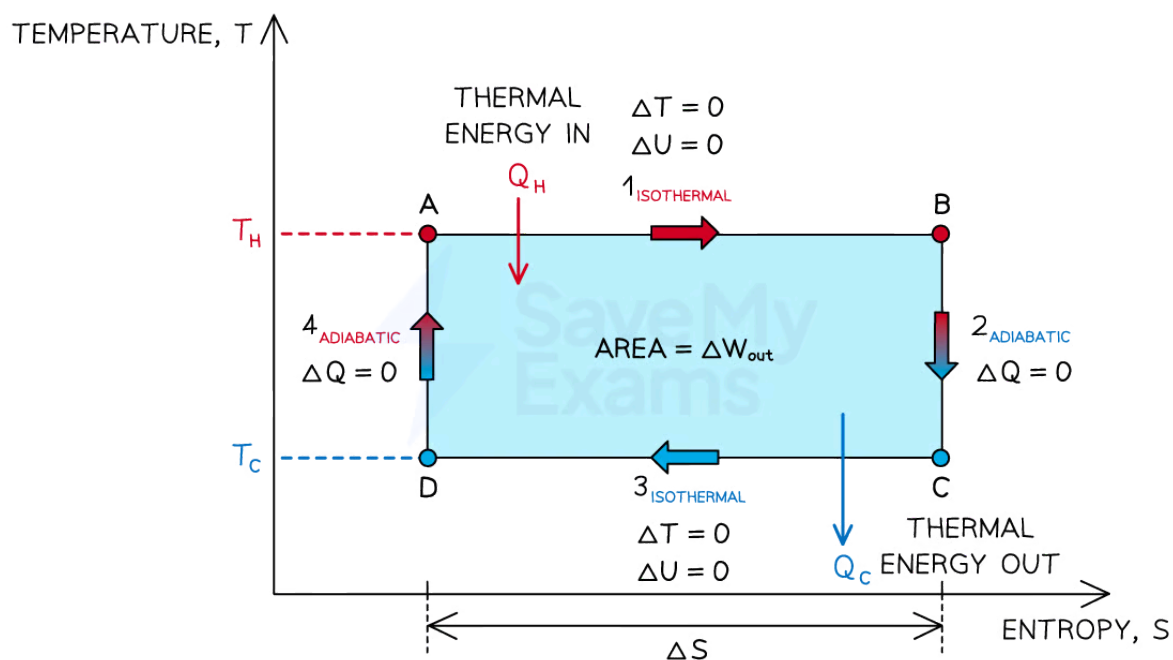


Your notes

- Work done on the gas = heat lost  $Q_C$

#### 4. Adiabatic compression

- The gas continues to be compressed
- Work is done on the gas as its volume decreases and pressure increases
- The gas heats up from  $T_C$  to  $T_H$ , but no thermal energy is transferred ( $\Delta Q = 0$ )
- At the end of the fourth stage, the gas has returned to its original state and the cycle can be repeated as many times as needed



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#### The variation of temperature and entropy throughout the Carnot cycle

- As the efficiency of a thermodynamic system increases, the **difference** between the temperatures of the hot and cold reservoirs increases
- The maximum theoretical efficiency of a heat engine using the Carnot cycle is:

$$\eta_C = 1 - \frac{T_C}{T_H}$$

- Where:
  - $\eta_C$  = maximum theoretical efficiency (Carnot cycle only)
  - $T_C$  = temperature in the cold reservoir (K)
  - $T_H$  = temperature in the hot reservoir (K)



Your notes

### Worked example

In an idealised heat engine, the hot and cold reservoirs are held at temperatures of  $T_H$  and  $T_C$  respectively.

Using the equation for the change in entropy

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

Show that the maximum theoretical efficiency of a heat engine is given by

$$\eta_C = 1 - \frac{T_C}{T_H}$$

**Answer:**

#### Step 1: Determine the change in entropy during isothermal expansion

- In isothermal expansion (AB): the gas absorbs heat  $Q_H$  from a hot reservoir at temperature  $T_H$
- Therefore, the increase in entropy is:

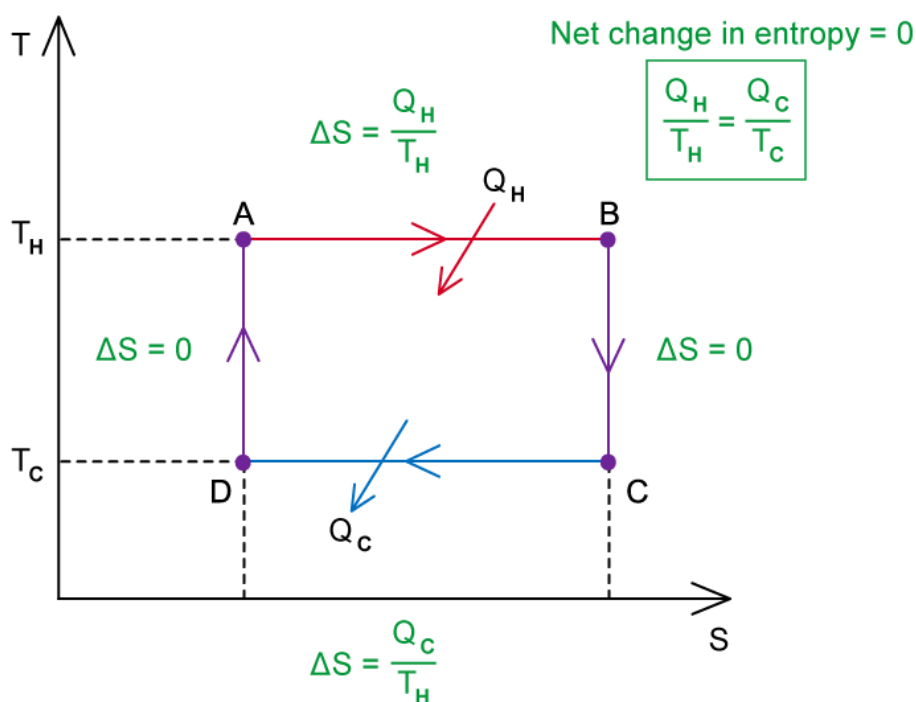
$$\Delta S_{AB} = \frac{Q_H}{T_H}$$

#### Step 2: Determine the change in entropy during isothermal compression

- In isothermal compression (CD): the gas transfers heat  $Q_C$  to a cold reservoir at temperature  $T_C$
- Therefore, the decrease in entropy is:

$$\Delta S_{CD} = -\frac{Q_C}{T_C}$$

#### Step 3: Consider the net change in entropy over the cycle



- During adiabatic expansion (BC) and compression (DA), entropy does not change as there is no thermal energy gained or lost

$$\Delta S_{BC} = \Delta S_{DA} = 0$$

- We know that the overall entropy of the system does not change in a cyclic process, therefore

$$\Delta S = \Delta S_{AB} + \Delta S_{BC} + \Delta S_{CD} + \Delta S_{DA}$$

$$\Delta S = \frac{Q_H}{T_H} + 0 + \left(-\frac{Q_C}{T_C}\right) + 0 = 0$$

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C} \Rightarrow \frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

#### Step 4: Substitute the expression into the equation for the efficiency of a heat engine

- The efficiency of a heat engine is given by:

$$\eta = \frac{\text{useful work}}{\text{input energy}} = \frac{W}{Q_H}$$

- Where useful work is  $W = Q_H - Q_C$

$$\eta = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

- Combining with the expression derived above gives:

$$\eta_C = 1 - \frac{T_C}{T_H}$$



Your notes

### Worked example

An engineer designs a heat engine that has an inlet temperature of 500 K and an outlet temperature of 300 K. The engineer claims that 100 kJ of thermal energy flows out of the hot reservoir and 25 kJ of thermal energy flows into the cold reservoir.

Determine, with reference to the second law of thermodynamics, whether this engine is thermodynamically possible.

**Answer:**

#### Step 1: Determine the efficiency of the proposed engine

- The efficiency of this engine would be

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

- Where:

- Heat transferred in,  $Q_H = 100$  kJ
- Heat transferred out,  $Q_C = 25$  kJ

$$\text{Efficiency} = 1 - \frac{25}{100} = 0.75 = 75\%$$

#### Step 2: Determine the maximum theoretical (Carnot) efficiency of the proposed engine

- A Carnot engine operating between the same temperatures would have an efficiency of

$$\eta_C = 1 - \frac{T_C}{T_H}$$

- Where:

- Inlet temperature,  $T_H = 500$  K
- Outlet temperature,  $T_C = 300$  K

$$\text{Carnot efficiency: } \eta_C = 1 - \frac{300}{500} = 0.4 = 40\%$$

#### Step 3: Discuss the proposed engine in relation to the second law

- The Clausius form of the second law states: it is impossible for heat to flow from a cooler body to a hotter body without performing work
- This law sets an upper limit on the maximum possible efficiency of the transfer of thermal energy to mechanical energy in a heat engine

- The maximum possible efficiency of the proposed engine is 40%, but the engineer is proposing an efficiency of 75% i.e. an efficiency greater than the Carnot efficiency
- This violates the Clausius form of the second law, hence **the proposed engine is impossible**



Your notes