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6.6 Molecular Kinetic Theory Model

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A Level Physics AQA

6.6 Molecular Kinetic Theory Model

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6.6.1 Gas Laws v Kinetic Theory

Gas Laws v Kinetic Theory

- There is a scientific distinction between the gas laws and kinetic theory

Gas Laws

- The gas laws are **empirical** in nature which means they are based on **observation** and **evidence**
- The gas laws include Boyle's Law, Charles's Law, Pressure Law and the ideal gas equation
- These are all based on observations of how a gas responds to changes in its environment, namely volume, pressure and temperature from experiment

Kinetic Theory

- Kinetic theory is based on **theory** (as stated in its name)
- This means it is based on **assumptions** and **derivations** from existing theories
- These are then used to explain why the gas laws behave the way they do

Ideal Gas Internal Energy

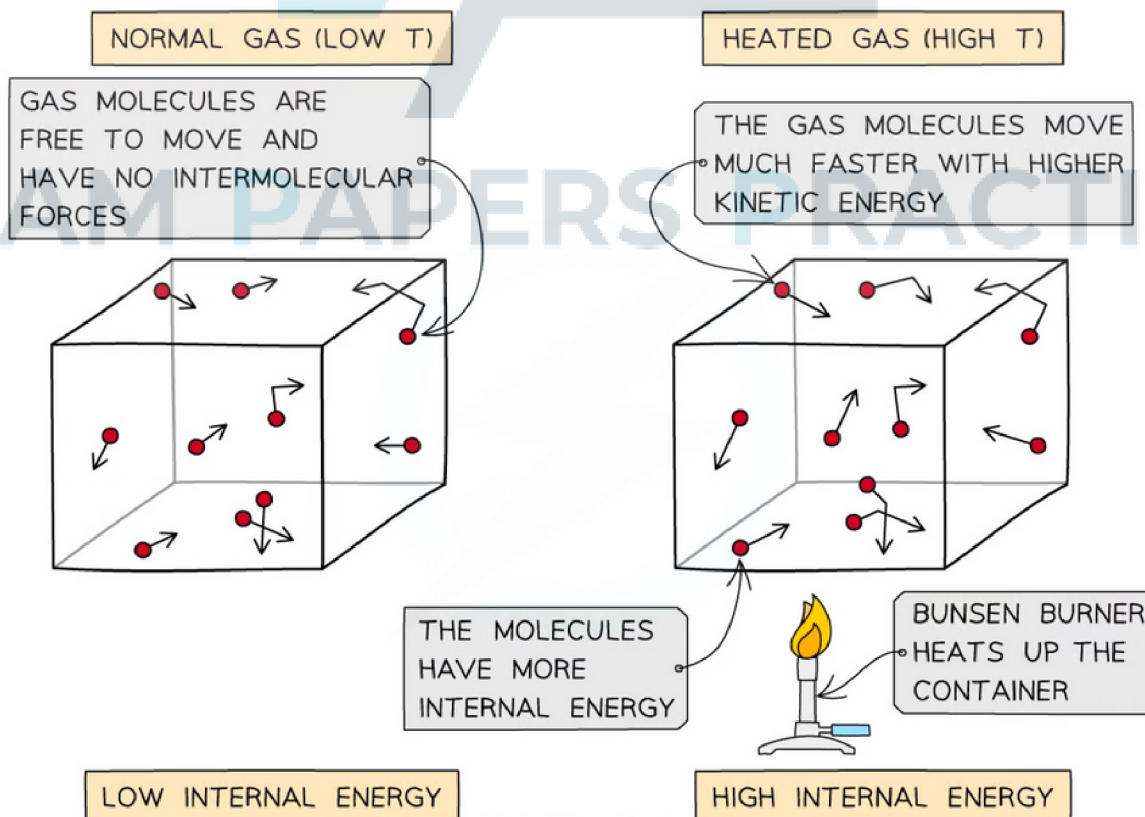
- The **internal energy** of an object is intrinsically related to its **temperature**
- When a container containing gas molecules is heated up, the molecules begin to **move around faster**, increasing their kinetic energy
- If the object is a solid, where the molecules are tightly packed, when heated the molecules begin to **vibrate** more
- Molecules in liquids and solids have both kinetic and potential energy because they are close together and bound by intermolecular forces
- However, ideal gas molecules are assumed to have **no intermolecular forces**
 - This means they have **no potential energy, only kinetic energy**
 - This means that the ideal gas internal energy is the **kinetic energy** of the atoms
- The (change in) internal energy of an ideal gas is equal to:

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

- Therefore, the change in internal energy is proportional to the change in temperature:

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

- Where:
 - ΔU = change in internal energy (J)
 - ΔT = change in temperature (K)



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

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

Step 1: Write down the relationship between internal energy and temperature

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

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

Step 2: Determine whether the change in temperature (in K) increases by three times

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

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

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

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

- Therefore, the temperature change, in Kelvin, does **not** increase by three times

Step 3: Write a concluding statement relating the temperature change to the internal energy

- The internal energy is directly proportional to the temperature
- The thermodynamic temperature has not trebled, therefore, neither has the internal energy
- **Therefore, the student is incorrect**



Exam 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**

6.6.2 Kinetic Theory of Gases Equation

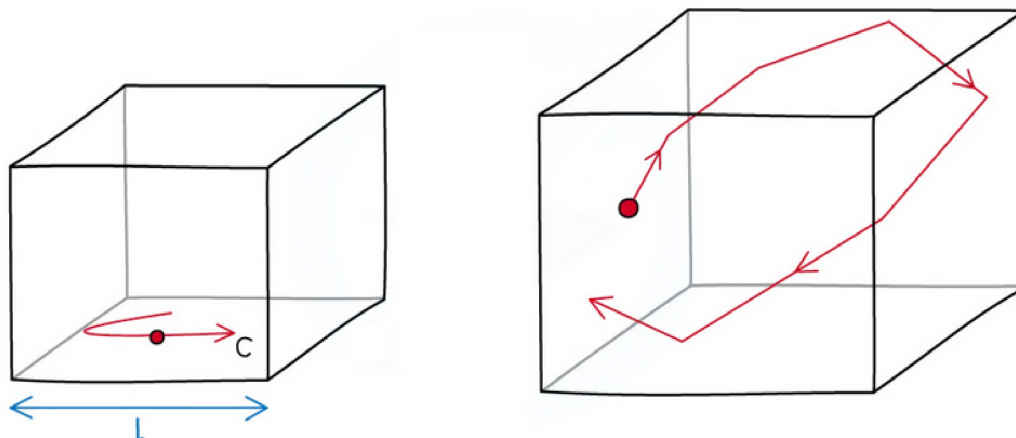
Kinetic Theory of Gases Equation

Assumptions in Kinetic Theory

- Gases consist of atoms or molecules randomly moving around at high speeds
- The kinetic theory of gases models the thermodynamic behaviour of gases by linking the **microscopic properties** of particles (mass and speed) to **macroscopic properties** of particles (pressure and volume)
- The theory is based on a set of the following assumptions:
 - Molecules of a gas behave as **identical** (or all have the same mass)
 - Molecules of gas are hard, **perfectly elastic** spheres
 - The **volume** of the molecules is **negligible** compared to the volume of the container
 - The **time** of a collision is **negligible** compared to the time between collisions
 - There are **no intermolecular forces** between the molecules (except during impact)
 - The molecules move in **continuous random motion**
 - **Newton's** laws apply
 - There are a **very** large number of molecules
- The number of molecules of gas in a container is very large, therefore the **average** behaviour (eg. speed) is usually considered

Derivation of the Kinetic Theory of Gases Equation

- When molecules rebound from a wall in a container, the change in momentum gives rise to a force exerted by the particle on the wall
- Many molecules moving in random motion exert forces on the walls which create an average overall **pressure** (since pressure is the force per unit area)
- Take a single molecule in a cube-shaped box with sides of equal length L
- The molecule has a mass m and moves with speed c , parallel to one side of the box
- It collides at regular intervals with the sides of the box, exerting a force and contributing to the pressure of the gas
- By calculating the pressure this one molecule exerts on one end of the box, the total pressure produced by a total of N molecules can be deduced



A single molecule in a box collides with the walls and exerts a pressure

1. Determine the change in momentum as a single molecule hits a wall perpendicularly

- One assumption of the kinetic theory is that molecules **rebound elastically**
 - This means there is no kinetic energy lost in the collision
- If the particle hits one side of the wall and rebounds elastically in the opposite direction to their initial velocity, their final velocity is $-c$
- The change in momentum is therefore:

$$p = mc$$

$$\Delta p = \text{final } p - \text{initial } p = -mc - (+mc) = -mc - mc = -2mc$$

- Where:
 - Δp = change in momentum (kg m s^{-1})
 - m = mass of the molecule (kg)
 - c = speed of the molecule (m s^{-1})

2. Calculate the number of collisions per second by the molecule on a wall

- The time between collisions of the molecule travelling to the opposite facing wall and back is calculated by travelling a distance of $2L$ with speed c :

$$\text{Time between collisions} = \frac{\text{distance}}{\text{speed}} = \frac{2L}{c}$$

- **Note:** c is **not** taken as the speed of light in this scenario

3. Calculate the force exerted by the molecule on the wall

- The force the molecule exerts on one wall is found using Newton's second law of motion:

$$\text{Force} = \text{rate of change in momentum} = \frac{\Delta p}{\Delta t} = \frac{2mc}{\frac{2L}{c}} = \frac{mc^2}{L}$$

- The change in momentum is $+2mc$ since the force on the molecule from the wall is in the opposite direction to its change in momentum

4. Calculate the total pressure for one molecule

- The area of one wall is L^2
- The pressure is defined as the force per unit area:

$$p = \frac{\text{Force}}{\text{Area}} = \frac{\frac{mc^2}{L}}{L^2} = \frac{mc^2}{L^3}$$

- This is the pressure exerted from **one molecule** in a particular direction

5. Consider the effect of N molecules moving randomly in 3D space

- The pressure equation still assumes that all the molecules are travelling in the same direction and collide with the same pair of opposite faces of the cube
- In reality, all molecules will be moving in three dimensions equally and randomly
- By splitting the velocity into its components c_x , c_y and c_z to denote the amount in the x, y and z directions, c^2 can be defined using Pythagoras' theorem in 3D:

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

- Since there is nothing special about any particular direction, it can be deduced that:

$$c_x^2 = c_y^2 = c_z^2$$

- Therefore, c_x^2 can be defined as:

$$c_x^2 = \frac{1}{3} c^2$$

- Where c^2 is the sum of the squared speeds of all the molecules

$$c^2 = c_1^2 + c_2^2 + c_3^2 + \dots + c_N^2$$

6. Consider the speed of the molecules as an average speed

- Each molecule has a different speed and they all contribute to the pressure
- Therefore, the square root of the average of the square velocities is taken as the speed instead
- This is called the **root-mean-square speed** or c_{rms}
- c_{rms} is defined as:

$$c_{rms} = \sqrt{\frac{c_1^2 + c_2^2 + c_3^2 \dots c_N^2}{N}}$$

- Therefore

$$N(c_{rms})^2 = c_1^2 + c_2^2 + c_3^2 + \dots + c_N^2$$

7. Consider the volume of the box

- The box is a cube and all the sides are of length l
 - This means L^3 is equal to the volume of the cube, V
- Substituting $N(c_{rms})^2$ and L^3 back into the pressure equation obtains the equation:

$$p = \frac{1}{3} \frac{Nm(c_{rms})^2}{L^3} = \frac{1}{3} \frac{Nm(c_{rms})^2}{V}$$

- This is the pressure parallel to the x (or y or z axis)
- Multiplying both sides by the volume V gives the final **Kinetic Theory of Gases Equation:**

$$pV = \frac{1}{3}Nm(c_{rms})^2$$

- Where:
 - p = pressure (Pa)
 - V = volume (m^3)
 - N = number of molecules
 - m = mass of one molecule of gas (kg)
 - c_{rms} = root mean square speed of the molecules ($m\ s^{-1}$)
- The equation can also be written using the density ρ of the gas:

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

- Rearranging the equation for pressure p and substituting the density ρ gives the equation:

$$p = \frac{1}{3}\rho(c_{rms})^2$$

? Worked Example

An ideal gas has a density of $4.5\ kg\ m^{-3}$ at a pressure of $9.3 \times 10^5\ Pa$ and a temperature of $504\ K$.

Determine c_{rms} of the gas atoms at $504\ K$.

Step 1: Write out the equation for the pressure of an ideal gas with density

$$p = \frac{1}{3}\rho(c_{rms})^2$$

Step 2: Rearrange for mean square speed

$$(c_{rms})^2 = \frac{3p}{\rho}$$

Step 3: Substitute in values

$$(c_{rms})^2 = \frac{3 \times (9.3 \times 10^5)}{4.5}$$

Step 4: Calculate the square root to find c_{rms}

$$c_{rms} = \sqrt{\frac{3 \times (9.3 \times 10^5)}{4.5}} = 787.4 = 790\ m\ s^{-1}\ (2\ s.f.)$$



Exam Tip

Make sure to revise and understand each step for the whole of the derivation as you may be asked to derive all, or part, of the equation in an exam question. Ensure you also write the appropriate commentary instead of simply stating equations in your answers to get full marks.

Also, make sure to memorise **all** the assumptions for your exams, as it is a common exam question to be asked to recall them.



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6.6.3 Average Molecular Kinetic Energy

Average Molecular Kinetic Energy

- An important property of molecules in a gas is their **average kinetic energy**
- This can be deduced from the ideal gas equations relating pressure, volume, temperature and speed
- Recall the ideal gas equation:

$$pV = NkT$$

- Also, recall the equation linking pressure and mean square speed of the molecules:

$$pV = \frac{1}{3}Nm(c_{rms})^2$$

- The left-hand side of both equations are equal (pV)
- This means the right-hand sides are also equal:

$$\frac{1}{3}Nm(c_{rms})^2 = NkT$$

- N will cancel out on both sides and multiplying by 3 on both sides too obtains the equation:

$$m(c_{rms})^2 = 3kT$$

- Recall the familiar kinetic energy equation from mechanics:

$$\text{Kinetic energy} = \frac{1}{2}mv^2$$

- Instead of v^2 for the velocity of one particle, $(c_{rms})^2$ is the average speed of all molecules
- Multiplying both sides of the equation by $\frac{1}{2}$ obtains the **average molecular kinetic energy** of the molecules of an ideal gas:

$$E_k = \frac{1}{2}m(c_{rms})^2 = \frac{3}{2}kT$$

- Where:
 - E_k = kinetic energy of a molecule (J)
 - m = mass of one molecule (kg)
 - $(c_{rms})^2$ = mean square speed of a molecule ($m^2 s^{-2}$)
 - k = Boltzmann constant
 - T = temperature of the gas (K)
- **Note:** this is the average kinetic energy for only **one** molecule of the gas
- A key feature of this equation is that the mean kinetic energy of an ideal gas molecule is proportional to its thermodynamic temperature

$$E_k \propto T$$

- The Boltzmann constant k can be replaced with

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

- Substituting this into the average molecular kinetic energy equation means it can also be written as:

$$E_k = \frac{1}{2}m(c_{rms})^2 = \frac{3}{2}kT = \frac{3RT}{2N_A}$$



Worked Example

Helium can be treated as an ideal gas. Helium molecules have a root-mean-square (r.m.s.) speed of 730 m s^{-1} at a temperature of $45 \text{ }^\circ\text{C}$. Calculate the r.m.s. speed of the molecules at a temperature of $80 \text{ }^\circ\text{C}$.

Step 1: Write down the equation for the average kinetic energy

$$E_k = \frac{1}{2}m(c_{rms})^2 = \frac{3}{2}kT$$

Step 2: Determine the relation between c_{rms} and the temperature T

Since m and k are constant, $(c_{rms})^2$ is directly proportional to T

$$(c_{rms})^2 \propto T$$

Therefore

$$c_{rms} \propto \sqrt{T}$$

Step 3: Change the proportionality into an equation

$$c_{rms} = a\sqrt{T}$$

where a is the constant of proportionality

Step 4: Calculate the constant of proportionality

Substitute the values given already for a temperature and corresponding c_{rms} for helium

$c_{rms} = 720 \text{ m s}^{-1}$ at a temperature of $45 \text{ }^\circ\text{C}$

$$T = 45 \text{ }^\circ\text{C} + 273.15 = 318.15 \text{ K}$$

$$a = \frac{c_{rms}}{\sqrt{T}} = \frac{720}{\sqrt{318.15}}$$

Step 5: Calculate c_{rms} at $T = 80 \text{ }^\circ\text{C}$ by substituting the value of a

$$T = 80 \text{ }^\circ\text{C} + 273.15 = 353.15 \text{ K}$$

$$c_{rms} = \frac{720}{\sqrt{318.15}} \times \sqrt{353.15} = 758.57 = \mathbf{760 \text{ m s}^{-1} \text{ (2 s.f.)}}$$



Exam Tip

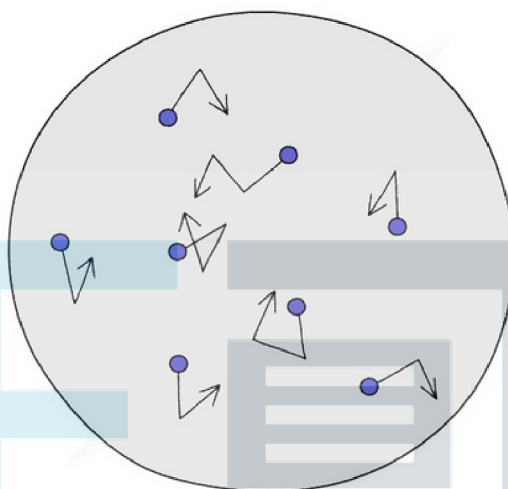
Keep in mind this particular equation for kinetic energy is only for **one** molecule in the gas. If you want to find the kinetic energy for all the molecules, remember to multiply by **N**, the total number of molecules. You can remember the equation through the rhyme 'Average K.E is three-halves kT'.

6.6.4 Brownian Motion

Brownian Motion

- Brownian motion of particles is the phenomenon when:

Small particles (such as pollen or smoke particles) suspended in a liquid or gas are observed to move around in a random, erratic fashion



Brownian motion is the erratic motion of small particles when observed through a microscope

- Brownian motion:
 - Can be observed under a microscope
 - Provides evidence for the existence of molecules in a gas or liquids
- The particles are said to be in random motion, this means that they have:
 - A range of speeds
 - No preferred direction of movement
- The observable particles in Brownian motion are significantly bigger than the molecules that cause the motion
 - In most cases, these were observed as smoke particles in air
 - The air particles cause the observable motion of the smoke particles that we see
 - This means that the air particles were small and light and the smoke particles were large and heavy
- The collisions cause larger particles to change their speed and directions randomly
 - This effect provides important evidence concerning the behaviour of molecules in a gas, especially the concept of pressure
- The small molecules are able to affect the larger particles in this way because:
 - They are travelling at a speed much higher than the larger particles
- They have a lot of momentum, which they transfer to the larger particles when they collide

6.6.5 Evolving Models of Gas Behaviour

Evolving Models of Gas Behaviour

- Our knowledge and understanding of the behaviour of gases has changed significantly over time
- The gas laws were developed by many scientists over thousands of years

Democritus (2000 years ago)

- Ancient Greek and Roman philosophers, such as Democritus, had some ideas about gases, some of which are quite close to what we now know to be true
- Democritus thought that if you cut an object in half, and each half has the same properties as the original object, that you can continue to cut the object into smaller and smaller pieces until it can no longer be divided
- He named the infinitesimally small pieces of matter **atomos** meaning 'indivisible'
 - This is the etymology of the word 'atom'
- Both of the two most well-known Greek philosophers, Aristotle and Plato, rejected his theories
 - Due to their influence, Democritus's theories were not accepted until almost 2000 years later

Robert Boyle (1662)

- Robert Boyle discovered the relationship between pressure and volume at a constant temperature
- This came to be known as **Boyle's Law**

Guillaume Amontons (1699)

- Amontons, and later also by Joseph Louis Gay-Lussac (1809), discovered the relationship between the temperature and the pressure of a gas at constant volume
- This came to be known as the **Pressure Law**

Jacques Charles (1787)

- This was then followed by Charles who discovered the relationship between the volume of a gas and its temperature at constant pressure
- This came to be known as **Charles's Law**

Daniel Bernoulli (18th Century)

- Bernoulli assumed that gases were made up of tiny particles which sparked the beginning of kinetic theory
 - However, kinetic theory wasn't widely accepted for at least another couple of hundred years
- Bernoulli is also known for the **Bernoulli's Principle** of fluid dynamics, which is a statement of the conservation of energy appropriate for flowing fluids

Robert Brown (1827)

- Brown was an English botanist who discovered **Brownian Motion**, the random motion of particles in a fluid, which helped support kinetic theory
- This is because Brownian Motion gave evidence that air is made up of tiny atoms or molecules that move very quickly and randomly

Albert Einstein (1905)

- In Einstein's miracle year of 1905, he produced a paper on how **kinetic theory** was used to make predictions for **Brownian motion**
 - Only then did the atomic and kinetic theory of particles start to become more widely accepted
- His publication of Brownian Motion became one of his most cited papers of all time, due to its far-reaching implications in both chemistry and physics
- Scientific ideas are rarely accepted immediately and require a rigorous process **validation** process
- Other scientists must **repeat** experiments and obtain the same conclusions for a theory to be **accepted**
- The theory that gases are made up of randomly, fast-moving particles may seem obvious now, but the existence and nature of particles was ground-breaking in all the scientists and took many centuries to completely understand

EVOLVING MODELS OF GAS BEHAVIOUR

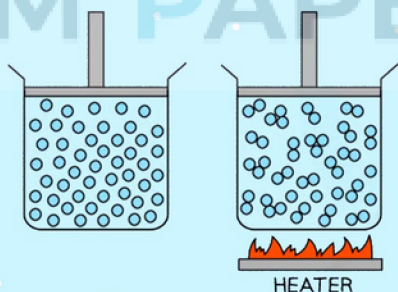


DEMOCRITUS
460 BCE – 370 BCE
'ATOMOS' – INDIVISIBLE
PIECES OF MATTER

2000 YEARS AGO



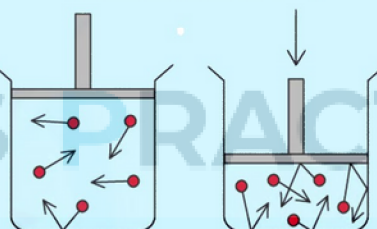
GUILLAUME AMONTONS
1663–1705
PRESSURE LAW



ROBERT BOYLE
1627 – 1691
BOYLE'S LAW

1662

1699



JACQUES CHARLES
1746–1823
CHARLE'S LAW

1787

