2022 JC1 H2 CHEMISTRY (9729)
CORE IDEA 2: STRUCTURE AND PROPERTIES
Topic 4: THE GASEOUS STATE

Name: ____ Civics Group: _________

Students should be able to:
(a) state the basic assumptions of the kinetic theory as applied to an ideal gas
(b) explain qualitatively in terms of intermolecular forces and molecular size:
  (i) the conditions necessary for a gas to approach ideal behaviour
  (ii) the limitations of ideality at very high pressures and very low temperatures
(c) state and use the general gas equation $pV = nRT$ in calculations, including the determination of M_r
(d) use Dalton's Law to determine the partial pressures of gases in a mixture

This topic is not included in the H1 Chemistry Syllabus.

Lecture Content

REFERENCES

1 **Chemistry (for CIE AS & A Level)** by Peter Cann & Peter Hughes

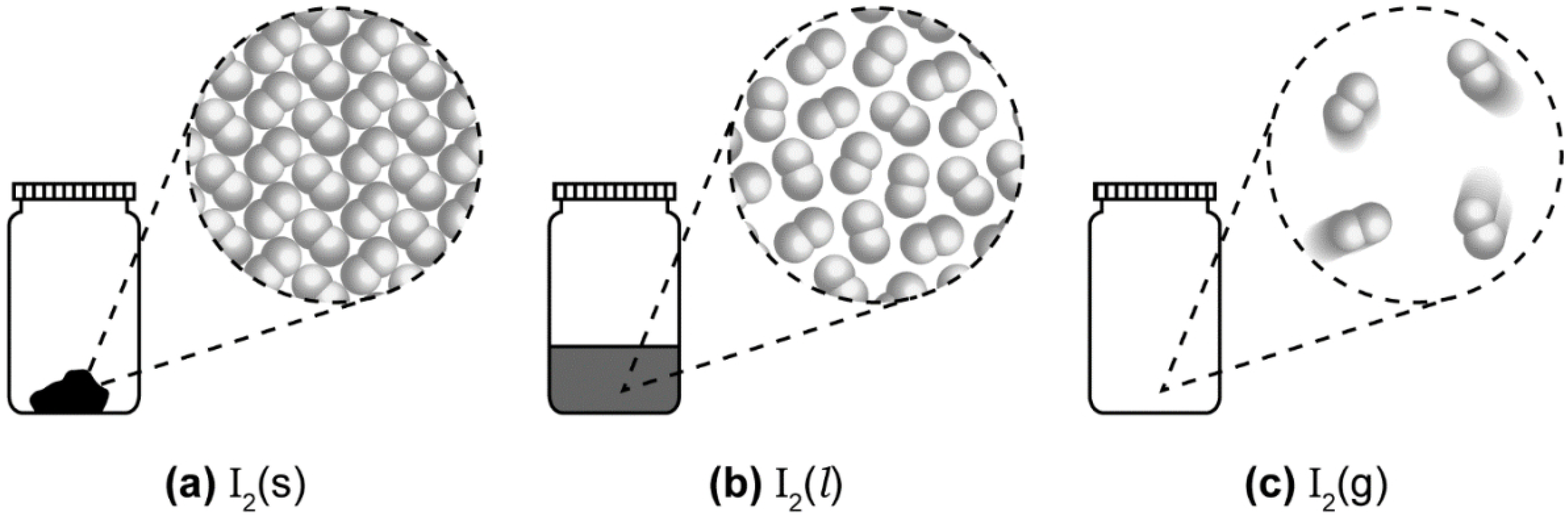
2 **Chemistry^3: Introducing Inorganic, Organic and Physical Chemistry**
by Andrew Burrows, John Holman, Andrew Parsons, Gwen Pilling & Gareth Price

3 **A-Level Chemistry** by E.N. Ramsden

1 Introduction

Gases tend to have the following physical properties:

- Gases have much lower density than solids or liquids.
- Gases assume the volumes and shapes of their containers.
- Gases are highly compressible, and their volumes change greatly when a pressure is applied.
- Gases exert pressure equally in all directions


(a) $I_2(s)$ **(b)** $I_2(l)$ **(c)** $I_2(g)$

S.I. Units and Common Units of Measurement for the Properties of Gases

The physical behaviour of a sample of gas can generally be described completely by four variables:

(a) Pressure exerted by the gas, ***p***

S.I. Unit	pascal	(Pa)	1 Pa = 1 N m^{-2}
Other commonly used units	atmosphere	(atm)	1 atm = 101 325 Pa
	bar	(bar)	1 bar = 10^5 Pa
	torr	(torr or mm Hg)	760 torr = 760 mm Hg = 1 atm = 101 325 Pa

(b) Volume occupied by the gas, ***V***

S.I. Unit	cubic metre	(m^3)	
Other commonly used units	cubic decimetre	(dm^3)	1 dm^3 = 10^{-3} m^3
	cubic centimetre	(cm^3)	1 cm^3 = 10^{-6} m^3
	litre	(L)	1 L = 1 dm^3 = 10^{-3} m^3
	millilitre	(mL)	1 mL = 1 cm^3 = 10^{-6} m^3

(c) Amount of the gas, ***n***

S.I. Unit	mole	(mol)

(d) Temperature of the gas, ***T***

S.I. Unit	kelvin	(K)	
Other commonly used units	degree Celsius	(°C)	T / °C + 273 = T / K

Self-Check 1A

Express the following quantities in their S.I. units.

(a) 2 atm (b) 500 mL (c) 22.7 dm^3 (d) 30 cm^3 (e) 25 ºC

Checkpoint

Section 1

☐ I know the S.I. units and common units of measurements for pressure (Pa), volume (m^3), amount (mol) and temperature (K).

☐ I know how to convert between the different units of measurement.

2 The Gas Laws

LO (c) state and use the general gas equation $pV = nRT$ in calculations, including the determination of M_r

Some of the first quantitative investigations were conducted in the 17th – 18th century to study the behaviour of gases. The relationship between the different macroscopic properties of gases (volume, temperature and pressure) are expressed via the different gas laws.

2.1 Boyle's Law

- The volume V of a fixed mass of gas at a **constant temperature** is **inversely proportional** to the pressure p of the gas.

$$V \propto \frac{1}{p}$$

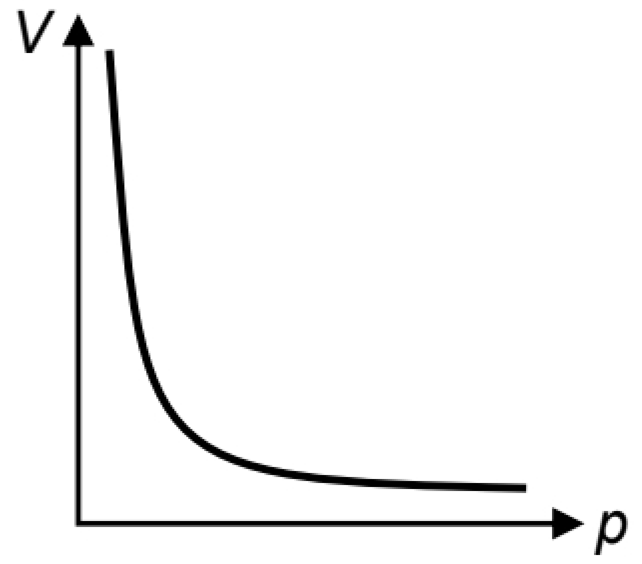
$$pV = k \quad \text{where } k \text{ is a constant}$$

- In other words, for a fixed mass (or amount) of gas at **constant temperature**, when its volume **increases**, its pressure **decreases**, and vice versa.

- Hence, for a given mass of gas under two different sets of conditions at constant temperature,

$$p_1V_1 = p_2V_2$$

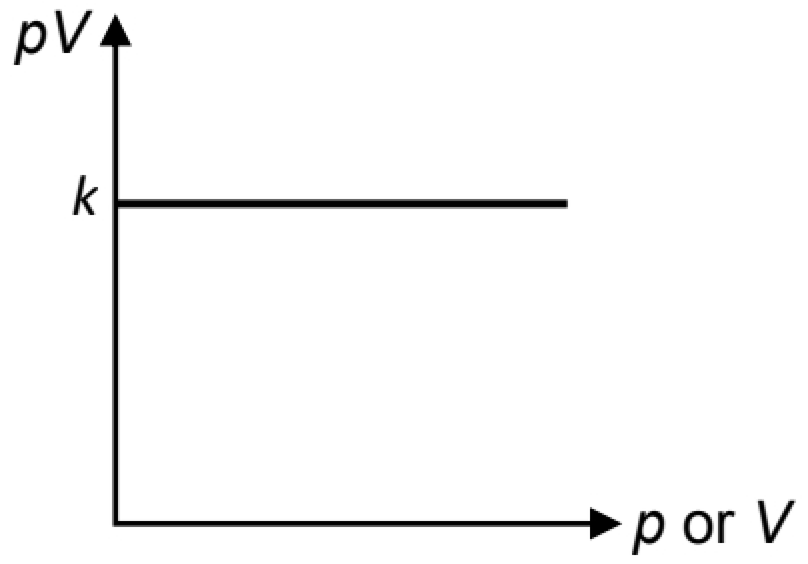
- Graphically, Boyle's Law can be represented in the following forms:



At constant T,

$$V = \frac{k}{p}$$

$\left(\text{Resembles } y = \frac{1}{x} \text{ graph}\right)$

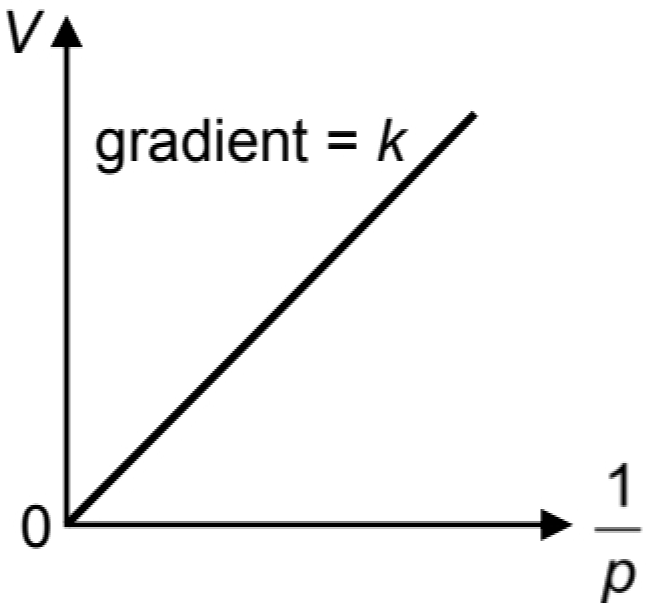


At constant T,

$$pV = k$$

Therefore, pV is independent of p or V.

(Resembles y = c graph)



At constant T,

$$V = k\left(\frac{1}{p}\right)$$

(Resembles $y = mx$ graph)

Example 2A

A balloon occupies a volume of 600 cm^3. Assuming that temperature remains constant, what volume will the balloon occupy if the surrounding pressure is reduced so that the pressure in it is reduced to one-third of its starting value?

2.2 Charles's Law

- The volume V of a fixed mass of gas at a **constant pressure** is **directly proportional** to its temperature T (in kelvin).

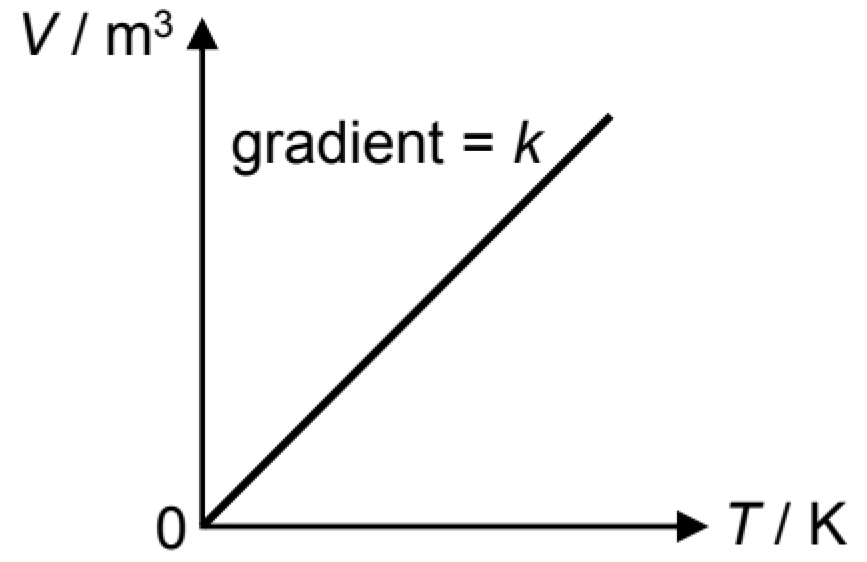
$$\boxed{\begin{array}{l} V \propto T \\ \dfrac{V}{T} = k \qquad \text{where } k \text{ is a constant} \end{array}}$$

- In other words, for a fixed mass (or amount) of gas at **constant pressure**, when its volume **increases**, its temperature **increases**, and vice versa

- For a given mass of gas under two different sets of conditions at constant pressure,

$$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$$

- Graphically, Charles's Law can be represented as such:



At constant p,

$$V = kT$$

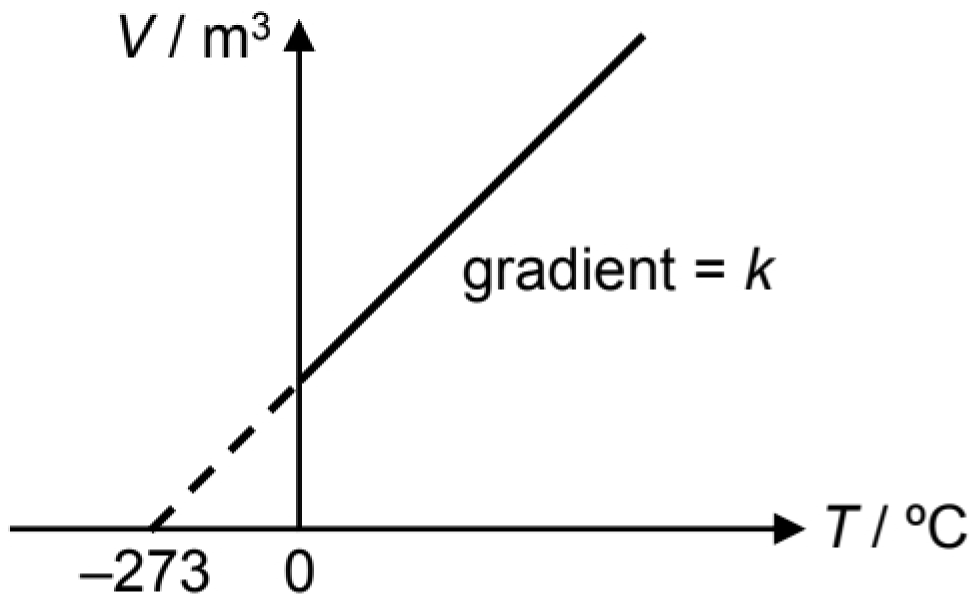
(Resembles $y = mx$ graph)

- The absolute temperature scale or Kelvin scale was defined based on the linear relationship between gas volume and temperature. The Kelvin scale starts at absolute zero (i.e. 0 K = –273 ºC). Each degree in this scale has the same size as a degree on the Celsius scale.

- To convert temperature from degree Celsius to kelvin,

$$\boxed{\mathbf{T\ /\ K = T\ /\ {}^{\circ}C + 273}}$$

- When gas volume is plotted against temperature in degree Celsius, the graph is as follows:



Note: *The relationship $V \propto T$ is only applicable when* ***temperature is expressed in kelvins*** *(NOT degree Celsius).*

Example 2B

32.0 cm^3 of carbon dioxide from a chemical reaction is collected in a syringe at 0 ºC and 1.00 atm. What would be its volume at r.t.p.?

2.3 Avogadro's Law

- Under the **same conditions of temperature and pressure**, equal volumes of all gases will contain equal numbers of molecules.

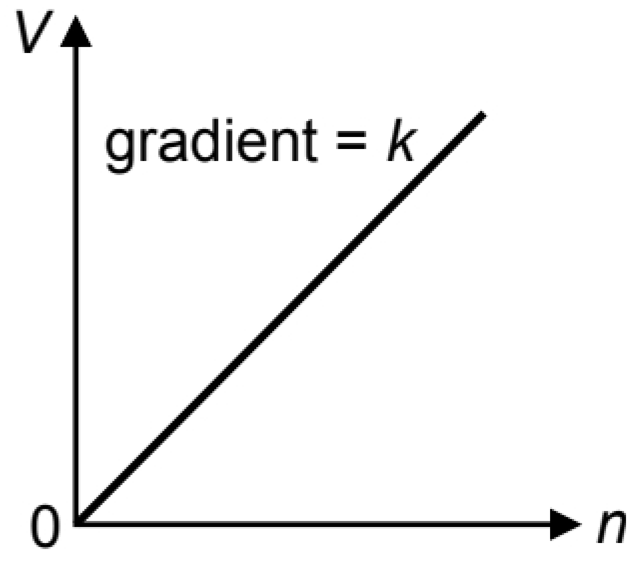
$$\boxed{V \propto n \qquad \text{where } n \text{ is the amount (in moles) of gas present}}$$

- For example, the number of O_2 molecules in 1 dm^3 of O_2 gas = the number of CO_2 molecules in 1 dm^3 of CO_2 gas.

- At constant temperature and pressure,

$$\boxed{\frac{V_1}{n_1} = \frac{V_2}{n_2}}$$

- Graphically, Avogadro's Law can be represented as:



At constant T and p,

$$V = kn$$

(Resembles $y = mx$ graph)

2.4 The Ideal Gas Equation

- Combining Boyle's law, Charles's law and Avogadro's law,

$$V \propto \frac{nT}{p}$$

therefore, $pV = nRT$ where R is the molar gas constant $(R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1})$

- An ideal gas is one whose behaviour follows the ideal gas equation exactly under any pressure and temperature.

Important: When using the ideal gas equation, each quantity needs to be expressed in its **S.I. unit**.

Example 2C

Calculate the molar volume of an ideal gas at 0 ºC and 1 bar (i.e. under standard temperature and pressure, s.t.p.).

Recall:
Molar volume of a gas, $\boldsymbol{V_m}$ (units: dm^3 mol^{-1})*, is the volume, in* dm^3*, occupied by 1 mole of the gas under a given set of temperature and pressure.*

Example 2D

A sample of gas was heated from 25 ºC until both its pressure and its volume doubled. What was the new temperature?

- Using the ideal gas equation, the relative molecular mass of the gas can be determined,

Since $n = \frac{m}{M}$,

$pV = \frac{m}{M}RT$ where m is the mass of the gas

M is the relative molecular mass of the gas

Example 2E

The volume occupied by 0.10 g of a gas is found to be 83.1 cm^3 (measured at 1.0 × 10^5 Pa and 27 ºC). Assuming that the gas behaves ideally, what is the relative molecular mass of this gas?

Example 2F

Determine the density of H_2S at 20 ºC and 2.00 atm, assuming that it behaves like an ideal gas under the stated conditions.

Self-Check 2B

1. When an evacuated glass bulb of volume 63.8 cm^3 was filled with a gas at 24 ºC and 99.5 kPa, its mass was found to increase by 0.103 g. Is the gas likely to be ammonia, nitrogen or argon? [Argon]

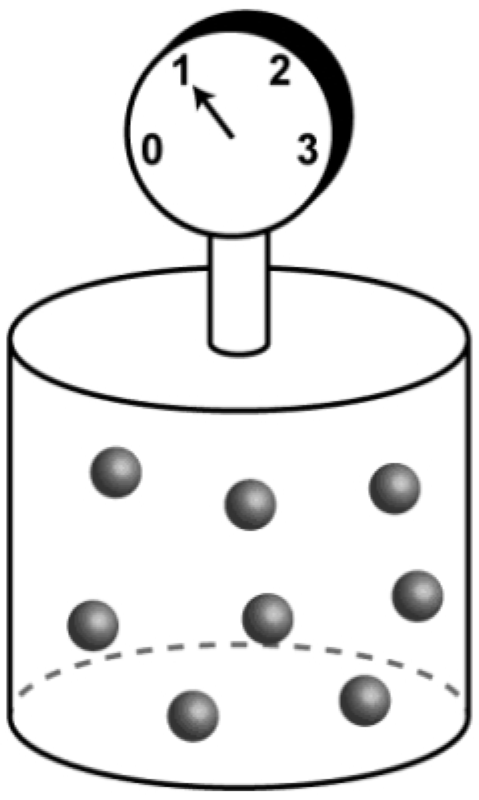
2. 1 cm^3 of ice was heated to 323 ºC at a pressure of 1 atm. Given that the density of ice is 1.00 g cm^{-3}, what was the volume of steam produced? [2.72 dm^3]

3. A fluoride ***X*** is formed when krypton reacts with fluorine. Given that 0.100 g of ***X*** occupies 104 cm^3 at 2.00 × 10^4 Pa and 305 K, what is the relative molecular mass and molecular formula of ***X***? [121.9; KrF_2]

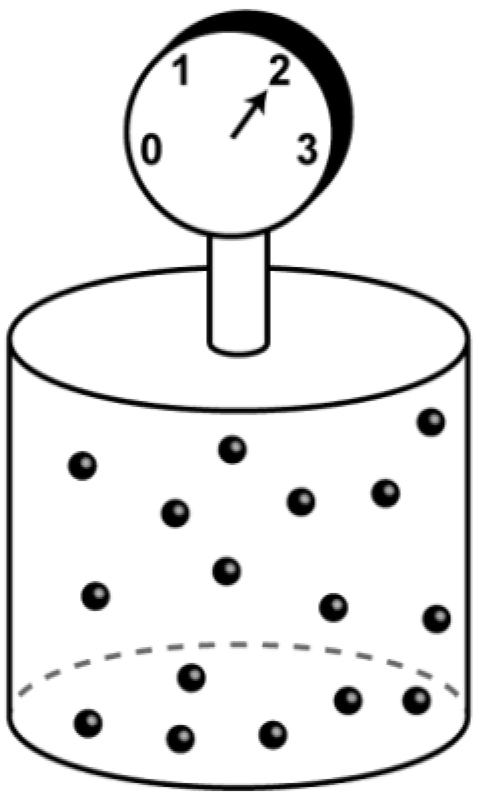
2.5 Dalton's Law of Partial Pressures

LO (d) use Dalton's Law to determine the partial pressures of gases in a mixture

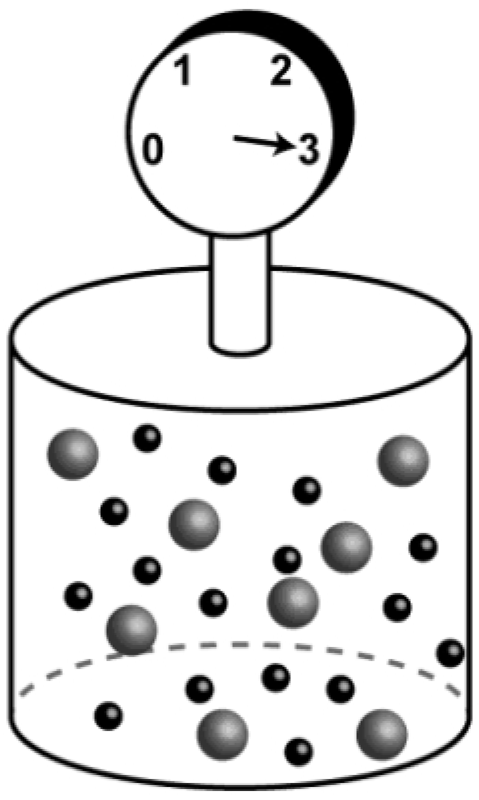
- In **a mixture of gases that do not react with one another**, each gas behaves as if it was the only gas present.



Gas A only
pressure = p_A



Gas B only
pressure = p_B



Mixture of **Gases A and B**
pressure = $p_A + p_B$

each gas in the mixture exerts the same pressure as if it were the only substance in the container

> **Dalton's Law** states that in a mixture of gases which do not react chemically, the total pressure is the sum of the partial pressures of the components.
>
> $$p_{\text{total}} = p_A + p_B + p_C + \cdots + p_N = \sum_{i=A}^{i=N} p_i$$
>
> where p_i is the partial pressure of any component, i, in the mixture

- The **partial pressure** is the pressure that would be exerted if the gas was alone in the container. We can determine the partial pressure of each component gas using its **mole ratio**.

- Assuming a non-reacting mixture of gas **A** and gas **B** contained in a volume, V, at temperature, T,

partial pressure of gas **A**: $p_A = \dfrac{n_A RT}{V}$

partial pressure of gas **B**: $p_B = \dfrac{n_B RT}{V}$

total pressure, $p_{\text{total}} = p_A + p_B = \dfrac{n_A RT}{V} + \dfrac{n_B RT}{V}$

$$= \frac{(n_A + n_B)RT}{V}$$

Mole Fraction and Partial Pressure

- The **mole fraction** of a component A, χ_A, in a mixture is the ratio of the number of moles of A to the total number of moles of all components present in the mixture. Mathematically, this is shown as:

$$\boxed{\chi_A = \frac{\text{amount of component A}}{\text{total amount of all components in mixture}} = \frac{n_A}{n_{total}}}$$

- If there is a non-reacting mixture of gas A and gas B in a container, then:

$$\begin{aligned}\frac{p_A}{p_{total}} &= \frac{n_A RT}{V} \div \frac{(n_A + n_B)RT}{V} \\ &= \frac{n_A}{n_A + n_B} \\ &= \chi_A \ (\text{where } \chi_A \text{ is the mole fraction of gas A})\end{aligned}$$

- The **partial pressure** of gas A is thus:

$$\boxed{p_A = \chi_A \times p_{total}}$$

Example 2G

A mixture of 0.5 mol of helium, 2.0 mol neon and 2.5 mol of argon has a total pressure of 100 kPa. What is the partial pressure of each gas in the mixture?

Example 2H

Flask X contains 1 dm^3 of helium at 2 kPa pressure and Flask Y contains 2 dm^3 of neon at 1 kPa pressure. If the flasks are connected at constant temperature, what is the final pressure?

Checkpoint

Section 2

☐ I appreciate Boyle's Law, Charles' Law and Avogadro's Law and how they combine to give the ideal gas equation.

☐ I know how to state and use the ideal gas equation $pV = nRT$ in calculations, using the relevant S.I. units for each term.

☐ I know how to derive the relative molecular mass and density of a gas using the ideal gas equation.

☐ I know how what Dalton's Law is, and how use it to calculate and determine the partial pressures of gases in a gaseous mixture

☐ I know how to represent graphically, different gas relationships using $pV = nRT$ as a basis. (e.g. when $V \propto \frac{1}{p}$, $V \propto T$ and $V \propto n$.)

3 The Kinetic Molecular Theory of Gases

LO (a) state the basic assumptions of the kinetic theory as applied to an ideal gas.

The ideal gas equation was obtained using an *empirical* approach by combining the experimentally determined gas laws (Boyle's Law, Charles's Law, Avogadro's Law). While it enables us to determine what happens to a gas when conditions change, it does not tell us what is happening at the molecular level, and why.

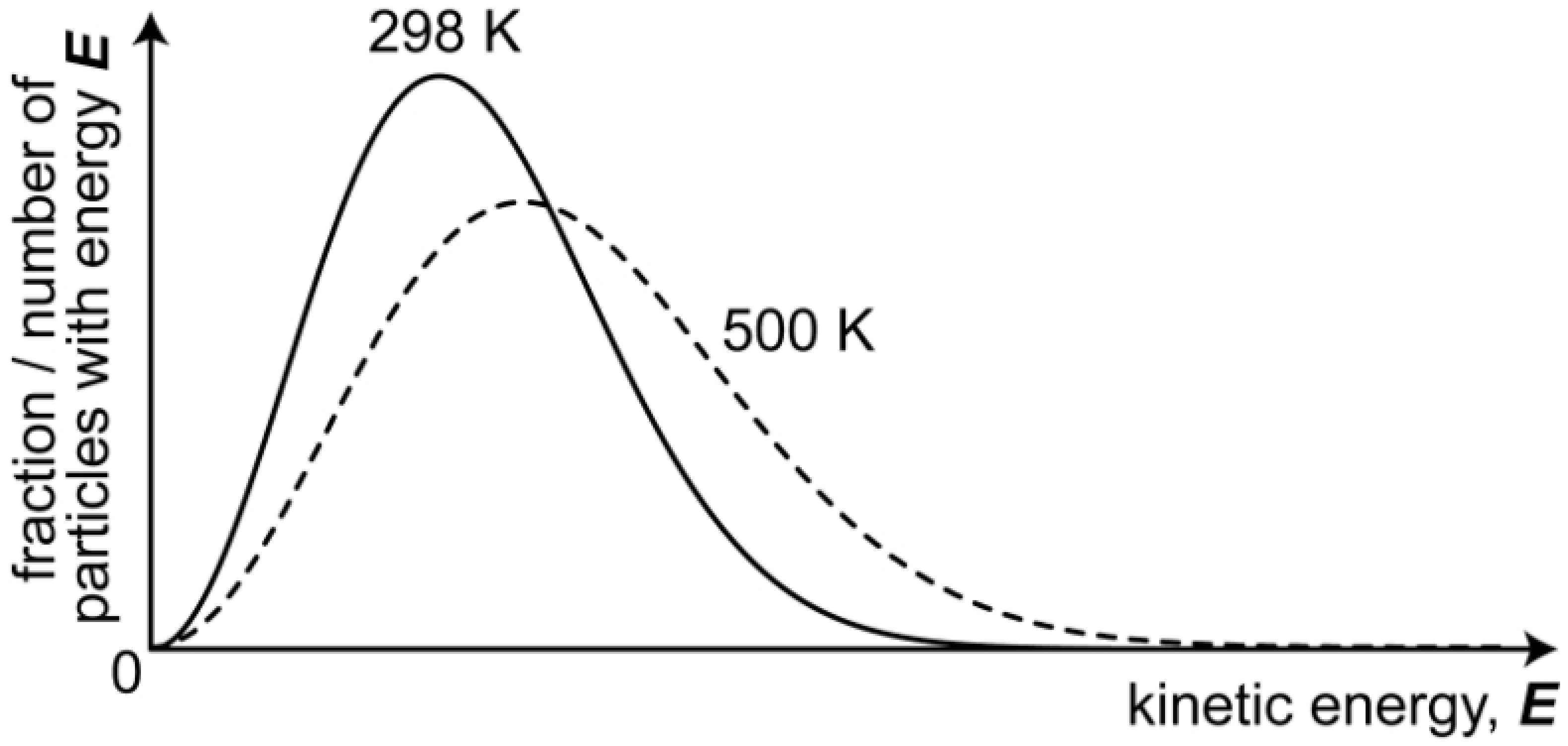
In the 19th century, a group of scientists including Ludwig Boltzmann and James Clerk Maxwell developed the **kinetic molecular theory of gases** to try to explain gas behaviours as described by the gas laws and the ideal gas equation. This theory is based on a model that assumes that:

1. The **gas particles have no volume**, *i.e.* they are point masses.
2. There are **no forces of attraction between gas particles**.
3. When the particles collide, the **collision is perfectly elastic**. i.e., the particles bounce apart after they collide with **no loss of kinetic energy**.
4. The gas particles are in **constant random** motion.

As a result, the average kinetic energy of the particles is proportional to the **temperature (in Kelvin)**.

A Maxwell-Boltzmann distribution curve shows how energy is distributed among the particles in a system. The total area under a Maxwell-Boltzmann distribution curve is proportional to the total number of particles present. At a given temperature, the particles have a range of kinetic energies.

When temperature increases from 298 K to 500 K, the particles have a larger range of kinetic energy and the average kinetic energy of the gaseous particles increases. As such, the Maxwell-Boltzmann distribution curve at the higher temperature broadens and flattens out.



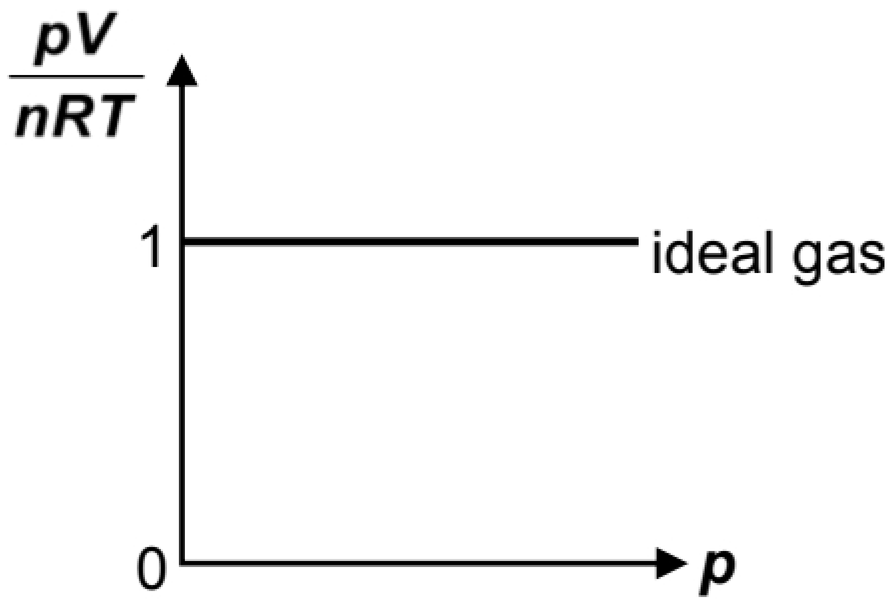
You will learn more about the Maxwell-Boltzmann distribution curve under ***Topic 6: Reaction Kinetics***.

4 The Behaviour of Real Gases

LO (b) explain qualitatively in terms of intermolecular forces and molecular size:
  (i) the conditions necessary for a gas to approach ideal behaviour
  (ii) the limitations of ideality at very high pressures and very low temperatures

- For an ideal gas, $\frac{pV}{nRT}$ will have a constant value of 1 (since $pV = nRT$).

- An ideal gas (one which obeys the ideal gas equation under all conditions) is hypothetical in nature. All real gases do not obey the ideal gas equation. Deviations from the ideal gas behaviour can be observed by plotting $\frac{pV}{nRT}$ versus p.



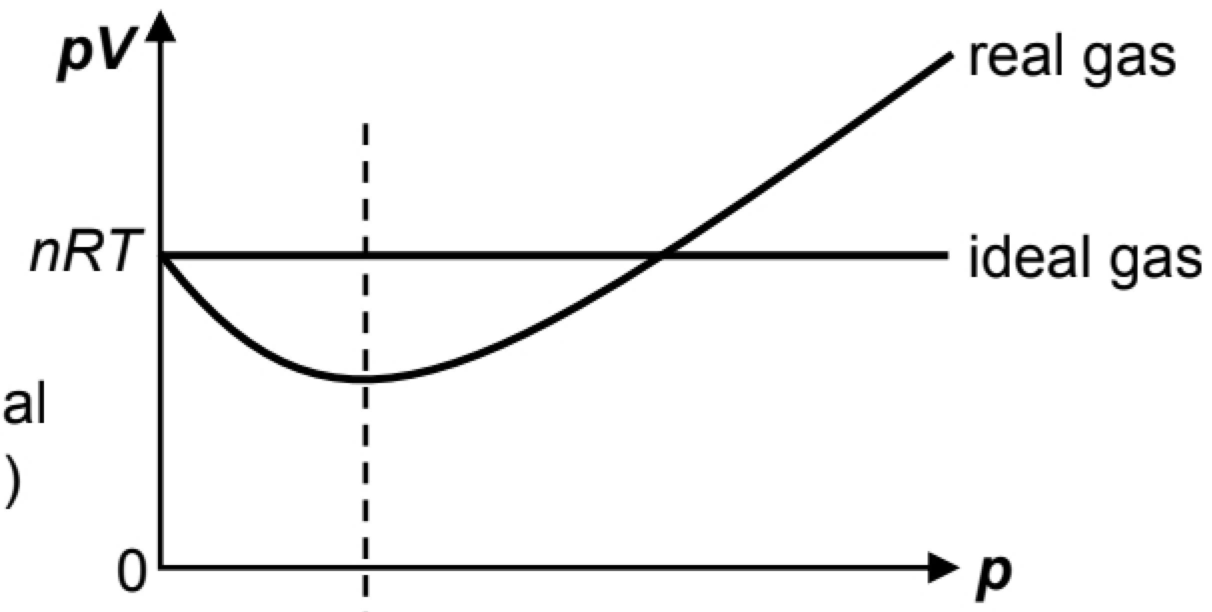
- Deviation from ideality is due to:
  1) **Intermolecular forces of attraction** between gas particles becoming more significant.
  2) **Volume of each gas particle relative to total volume occupied by the gas** becoming more significant.

  (Recall assumptions of kinetic molecular theory of gases outlined in Section 3)

- Real gases **deviate** most from ideal gas behaviour at **high pressure** and **low temperature**.

4.1 Effect of High Pressure

(For a constant amount of a real gas, at constant temperature.)



pV **of real gas decreases with increasing *p***

- In real gases, **intermolecular forces of attraction are significant** (assumption 2)
- When a molecule is about to strike the wall of the container, it is attracted by molecules surrounding it
- Molecule slows down and hits wall with smaller force
- Hence, **pressure** exerted is **lower** than that in an ideal gas, pV is lower
- IMF becomes more significant at higher p as the molecules are closer together
- Hence pV **decreases** with increasing p

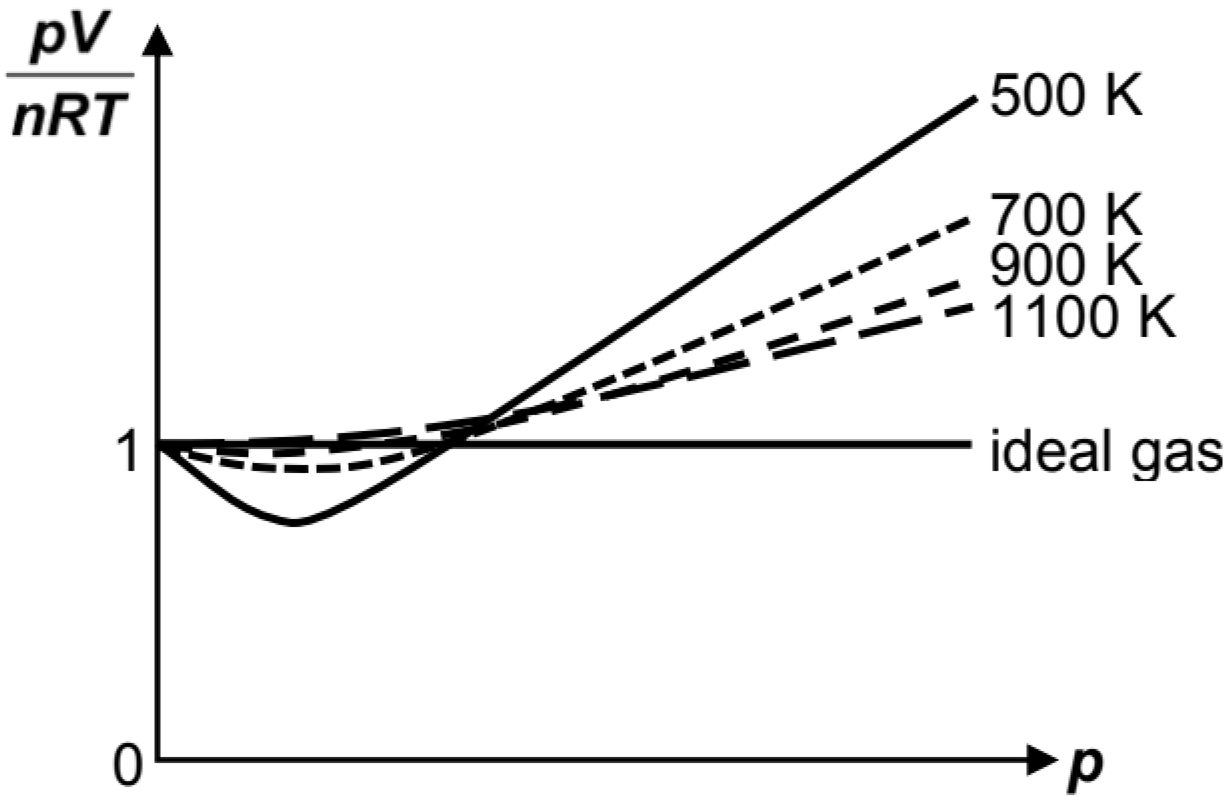
pV **of real gas increases with increasing *p***

- In real gases, **size of gas molecules are significant** (assumption 1)
- Hence, the **volume** occupied by a real gas is **larger** than that occupied by an ideal gas, pV is higher
- The volume of the gas molecules **compared** to the volume occupied by the gas becomes more significant as the volume occupied by the gas becomes smaller at higher p
- Hence pV **increases** with increasing p
- This factor dominates at high p

Note: The volume, V, here is the volume of the container that the gas is contained. It is not referring to the volume of the gas particles!

4.2 Effect of Low Temperature

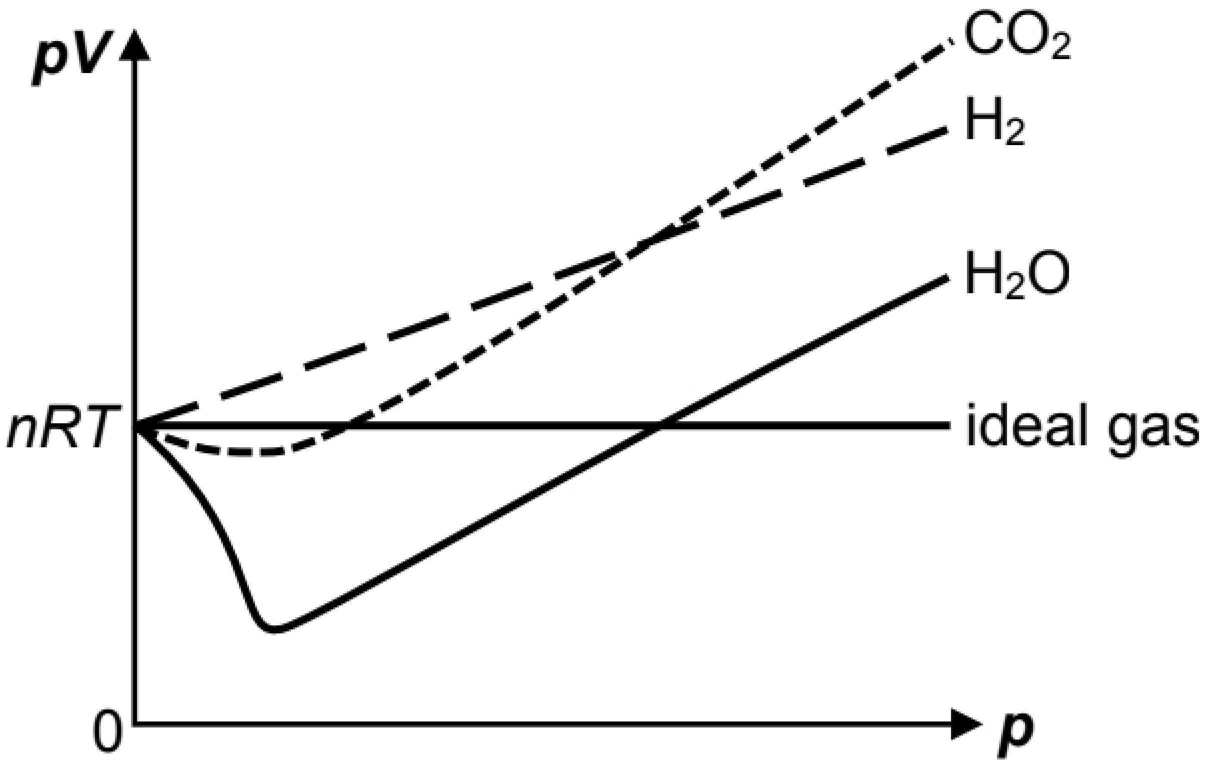
For a constant amount of a real gas, in this case, CO_2, at varying temperatures:



- At low temperatures, **<u>kinetic energy of the gas particles decreases</u>** and the particles move slower. This causes the **<u>intermolecular forces of attraction between the particles to be significant</u>** (assumption 2 is no longer valid). The **<u>number of collision and force exerted on wall of container will decrease</u>,** *pV* is smaller than that of an ideal gas. Hence at lower temperatures, there will be greater deviation from ideality.

4.3 Effect of Strong Intermolecular Forces

- Under the same conditions, different gases deviate from ideal gas behaviour to different extents due to **differences in the strengths of the intermolecular forces of attraction**.



- **Strong hydrogen bonds** exist between H_2O molecules while **weak instantaneous dipole–induced dipole interactions** exist between H_2 and CO_2 molecules.

- The hydrogen bonds between H_2O molecules **are stronger** as compared to the instantaneous dipole-induced dipole interactions between H_2 and CO_2 molecules (assumption 2 less valid for H_2O). Hence H_2O deviates more from ideality compared to H_2 and CO_2 at **low pressures**.

- However, at **high pressures**, CO_2 deviates more from ideality compared to H_2 and H_2O as volume of the CO_2 molecule is larger than that of H_2 and H_2O molecules (assumption 1 less valid for CO_2).

See <u>Appendix 3</u> for further discussion on deviations from the ideal gas laws.

Example 4A

Rank the following gases in order of decreasing ideality, with the most ideal first. Explain the reasons for your order.

CH_4 HF HCl

Checkpoint

Section 3

☐ I know the basic assumptions of the kinetic molecular theory of gases as applied to an ideal gas. There are 3 more important assumptions:

(i) gas particles have no volume, *i.e.* point masses,

(ii) gas particles have no intermolecular forces of attraction, and,

(iii) gas particles are in constant random motion.

**Be specific and make references to "gas particles" or "gas molecules" in the assumptions. (Do not simply state "gas".)*

Section 4

☐ I can explain the reasons when a real gas deviates from ideal gas behaviour due to real gas particles possessing:

(i) intermolecular forces of attraction,

(ii) volume.

☐ I can explain when real gases deviate from ideal gas behaviour the most at high temperature and low temperature.

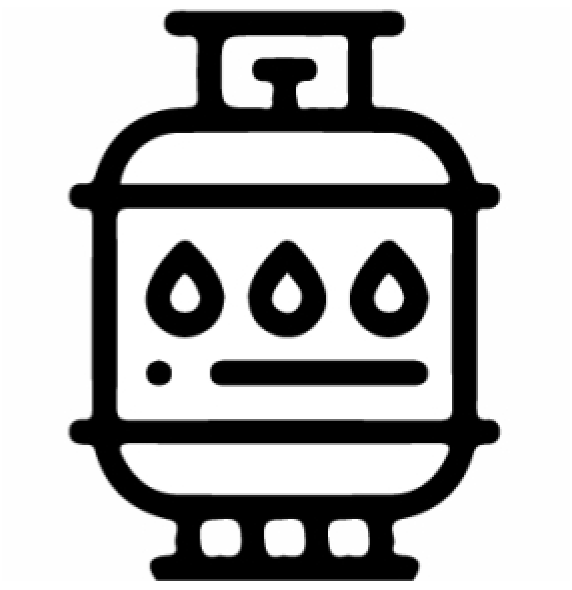
5 Real Life Applications

Why is it important to know how gases behave under different conditions?

Find out the answers to the questions below to understand how important the gas laws are!

Why must scuba divers return to the surface very slowly at the end of their dive?

Why must trucks transporting propane (a highly flammable gas) be subjected to weight tests before they travel during the summer months?



Why might it not be a good idea to bring a bag of chips onboard an aeroplane?

Why do we find it harder to breathe at high altitudes?

Why does water boil at a lower temperature at higher altitudes?

APPENDIX

APPENDIX 1

Scientific Law vs. Theory

What are they? What is the difference?

In our everyday usage, the word “theory” sometimes means a guess or a hunch, and implies an explanation which is uncertain, while the word “law” is often used to refer to things that are immutable truths. In Science, these two terms have very specific meanings:

	What does it do?	Examples
Scientific Law	Describes or predicts **what will happen** based on a set of given conditions	Laws of motion (Isaac Newton), Law of universal gravitation (Isaac Newton), Law of conservation of mass (Antoine Lavoisier), Law of definite proportions (Joseph Proust)
Scientific Theory	Explains **why** things happen	Atomic theory, Big Bang theory, climate change, evolution by natural selection, plate tectonics

Changes to Laws & Theories in Science

Scientific knowledge is reliable and durable, but is subjected to revision in the light of new evidence from technological advancements. Scientific laws may be revised when new and unexpected observations are made. Scientific theories may also undergo changes over time – remember how the idea of the atom evolved from the time of the ancient Greeks? There can be multiple theories developed to explain a phenomenon, but only the one(s) that can explain most of the observations made will be favoured by scientists.

To find out more about the relationship between scientific laws and theories, check out:

What’s the difference between a scientific law and theory? (Video)

https://ed.ted.com/lessons/what-s-the-difference-between-a-scientific-law-and-theory-matt-anticole#watch

Fact vs. Theory vs. Hypothesis vs. Law… EXPLAINED! (Video)

https://youtu.be/lqk3TKuGNBA

Science at multiple levels (Webpage)

https://undsci.berkeley.edu/article/howscienceworks_19

APPENDIX 2

Using the Kinetic Molecular Theory of Gases to explain the behaviour of gases

1. **Gas Pressure**
   Gas molecules are in constant random motion within the container that the gas is in and collide with the walls of the container. When they do so, they exert a force which results in pressure being set up $\left(\text{pressure} = \dfrac{\text{force}}{\text{area}}\right)$.

2. **Boyle's Law**
   When the volume of the gas decreases, the distances between the gas molecules and the walls of the container are shorter. Hence, molecules collide with the walls more **frequently**, leading to greater pressure being exerted *by* the gas.

   When the pressure exerted *on* the gas increases, gas molecules are forced closer together, leading to a decrease in volume.

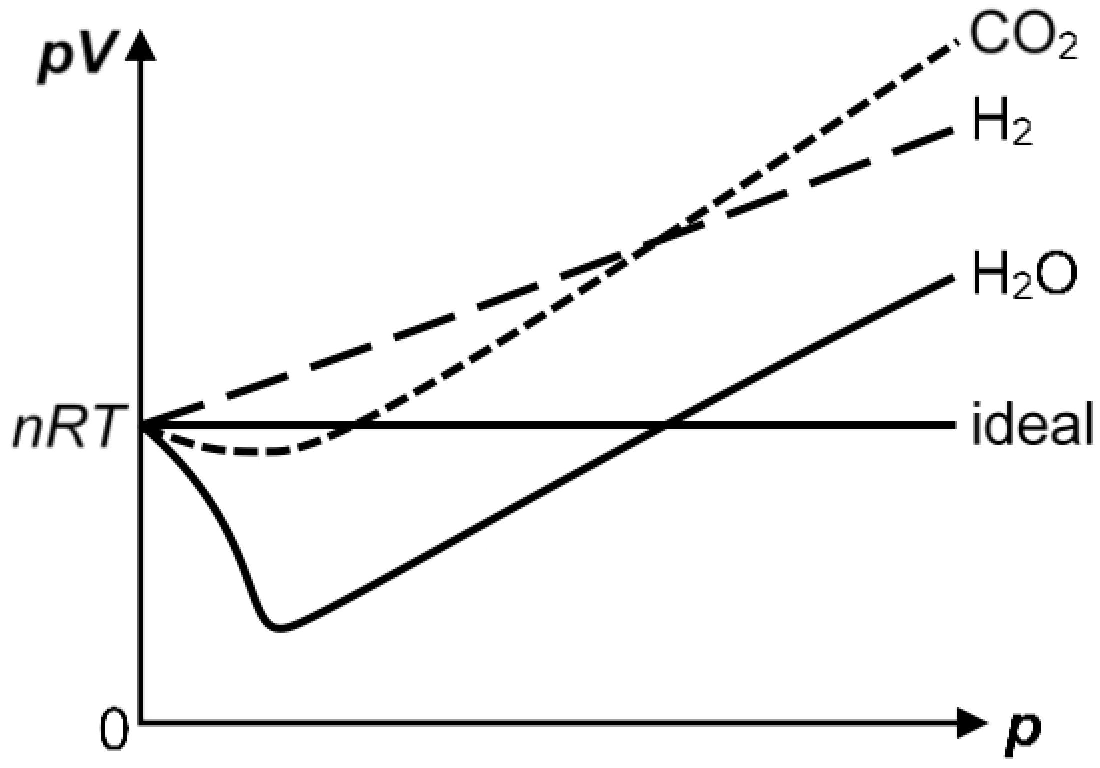
3. **Charles' Law**
   When temperature of the gas increases, the gas molecules have higher kinetic energy and move faster. They hit the walls of the container more frequently and with greater force, resulting in greater pressure being exerted by the gas. This results in the walls of the container moving outwards (i.e. increase in volume) until constant pressure is restored.

4. **Avogadro's Law/ Dalton's Law of Partial Pressure**
   The pressure exerted by the gas depends on the number of collisions per second, which is in turn proportional to the number of gas molecules present.

APPENDIX 3

Trend of the *pV–p* graph for a real gas

As we have discussed in the previous sections, the behaviours of real gases do not always obey the ideal gas equation, $pV = nRT$.



In 1873, Dutch physicist Johannes van der Waals successfully accounted for the behaviour of real gases by introducing two additional terms to the ideal gas equation, resulting in the **van der Waals equation**:

$$\left(p_{\text{measured}} + \underbrace{a\left(\frac{n}{V}\right)^2}_{\substack{\text{correction for}\\\text{intermolecular}\\\text{forces}}}\right)\left(V_{\text{measured}} - \underbrace{nb}_{\substack{\text{correction for}\\\text{volume of gas}\\\text{particles}}}\right) = nRT$$

The constants *a* and *b* differ for different gases: *a* correlates with the strength of the intermolecular forces between the gas particles, while *b* correlates with the size of the molecules. The smaller the constants are for a real gas, the more ideal it is. The van der Waals constants for some gases are listed in the table below:

gas	a / Pa m^6 mol^{-2}	b / 10^{-5} m^3 mol^{-1}
water vapour	0.5537	3.049
ammonia	0.4225	3.713
carbon dioxide	0.3658	4.286
carbon monoxide	0.1472	3.948
nitrogen	0.1370	3.87
hydrogen	0.02453	2.651
helium	0.00346	2.38

Do these values concur with what you have learnt so far about how much different gases deviate from ideality?