



4 The gaseous state

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- 4.2 Ideal gas behaviour and deviations from it
- 4.3 $pV = nRT$ and its use in determining a value for M_r

Learning Outcomes

Candidates 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

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4.1 Kinetic molecular model

- ✍ Matter exists in three states: solid, liquid and gas.
- ✍ The characteristics of these states are:
 - *Solids*: definite volume and shape, incompressible and have high densities
 - *Liquids*: definite volume, take the shape of its container, incompressible and have moderate to high densities
 - *Gases*: take up the volume and shape of its container, compressible and have low densities
- ✍ In solids, the particles are packed closely together in an orderly arrangement. Intermolecular forces are stronger than kinetic forces, allowing for vibration and rotation about a fixed position.
- ✍ In liquids, particles are slightly further apart as compared to that in solids, and are not arranged in an orderly manner. Intermolecular forces are of the same order of magnitude as kinetic forces, allowing for the particles to vibrate, rotate and move freely.
- ✍ In gases, particles are far apart and are allowed to vibrate, rotate and move freely. Kinetic forces are stronger than intermolecular forces.

Change of states

- ✍ At its *melting point*, a solid changes to a liquid. At its *boiling point*, a liquid changes to a gas. In *sublimation*, solid changes to a gas, bypassing the liquid phase.

Melting

- ✍ Sufficient energy must be provided to overcome the intermolecular forces in order to cause a solid to melt.
- ✍ Particles gain energy and vibrate faster with an increase in temperature till finally the particles are able to move around.
- ✍ The lattice structure then breaks down and the solid melts to form a liquid.
- ✍ The melting point of a solid is directly proportional to the strength of the forces holding the particles.

Vaporisation

- ✍ Molecules of liquid move around freely at different speeds. The faster moving molecules near the surface will have sufficient energy to overcome intermolecular forces to *evaporate*.



- ✍ With an increase in temperature or surface area, the rate of evaporation increases. A decrease in external pressure will also increase the rate of evaporation.
- ✍ Evaporation continues till no liquid remains in an open container.
- ✍ In a closed container, the vapour condenses as vapour molecules collide with the walls of the container and re-enter the liquid.
- ✍ A state of equilibrium is reached when the rate of evaporation equals the rate of condensation.

Vapour pressure

The **vapour pressure** of a liquid is the pressure exerted by the molecules which have escaped from the liquid.

- ✍ The maximum pressure exerted by the vapour in equilibrium with its liquid is the *saturated vapour pressure*.
- ✍ The identity of the liquid and the temperature will determine the magnitude of the saturated vapour pressure.
- ✍ *Boiling occurs* when the saturated vapour pressure is equal to the external pressure.

The **boiling point** of a liquid is the temperature at which its vapour is in equilibrium with the liquid at 1 atm.

- ✍ The boiling point is directly proportional to the strength of the intermolecular forces as well as the external pressure.
- ✍ As heat energy is required to break the intermolecular forces, the temperature remains constant at both the boiling and melting points.

Define

Ideal gas

An **ideal gas** is defined as a theoretical gas which follows the Ideal Gas Law.

- ✍ The term *ideal gas* implies that the gas particles:
- 1 have negligible volume or size.
 - 2 have negligible intermolecular forces of attraction.
 - 3 are in constant random motion.
 - 4 participate in collisions that are perfectly elastic and are of negligible duration.

Maxwell-Boltzmann curve

- ✍ Gas molecules traveling at different speeds collide with one another.
- ✍ The spread of molecular speed and molecular energy of gas molecules are shown by the *Maxwell-Boltzmann curve*.
- ✍ With an increase in temperature, the curve shifts right towards higher velocities and is flattened as there are more high speed molecules. In addition, the proportion of molecules with high energy increases.

Real gas

A **real gas** is defined as a gas which will not always show ideal behaviour.

- ✍ The extent and degree of deviation from ideal behaviour depends on:
- 1 type of gas (mass and intermolecular forces of attraction)
 - In a real gas, the gas particles have significant size and forces of attraction between the particles.
 - Polar molecules have stronger forces of attraction than non-polar molecules and thus have greater deviation from ideality.
 - 2 pressure
 - The higher the pressure, the greater is the deviation from ideality as the gas particles will be packed closely together, thus the volume



and forces of attraction between particles cannot be assumed to be negligible.

③ temperature

- At lower temperatures, the intermolecular attractions are not negligible as the gas particles do not have enough energy to overcome it.

📖 A real gas behaves most like an ideal gas at low pressures and high temperatures.

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📖 Different real gases deviate to a different extent from ideal gas behaviour. Polar molecules deviate more from ideality as compared to non-polar molecules due to the stronger forces of attraction.

📖 Significant attractive forces are present in a real gas, decreasing the force with which the molecule collides with the wall. This results in a reduction in pressure.

📖 With an increase in atomic size and number of electrons, there will be an increase in the intermolecular attractive forces.

Worked Example

Example 1

- State and explain whether the expansion of gas into a region of low pressure is exothermic or endothermic.
- Explain why gases like carbon dioxide can be liquefied by increasing the pressure.
- Explain why gases can only be liquefied by pressure alone if the temperature is lower than the critical temperature.

Solution:

- When air is expanded into a region of lower pressure, it is an endothermic process. This is because at low pressure, the molecules are further apart from one another and energy is required to overcome intermolecular attractions. Thus it is endothermic. (ans)
- When pressure is increased, the gaseous particles become closer to one another. There will come a point when the pressure is so high such that the particles can no longer move around freely. The gas has condensed into a liquid. (ans)
- Since the average kinetic energy of a gas is dependent on the temperature, as temperature increases, the average kinetic energy will increase until the particles cannot be held within the volume of the liquid even though the increase in pressure is pushing the particles together. The temperature at which this occurs is the critical temperature. The increase in intermolecular attraction is not enough to hold the particles within a fixed volume due to their high kinetic energies of the particles above the critical temperature.

The critical temperature varies for different gases. Generally, gases with low intermolecular forces will have a lower critical temperature than gases with higher intermolecular forces. (ans)





4.3

$pV = nRT$ and its use in determining a value for M_r

General gas equation

- The **general gas equation** is derived by combining the three gas laws (Boyle's law, Charles law and Avogadro's law).

$$pV = nRT$$

where p = pressure in Pa
 V = volume in m^3
 n = no. of moles of gas
 R = universal gas constant ($8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)
 T = temperature in K

- At 0 K, the gas will have no volume in theory.
- The pressure exerted by a gas increases with an increase in the number of particles and temperature of the gas.

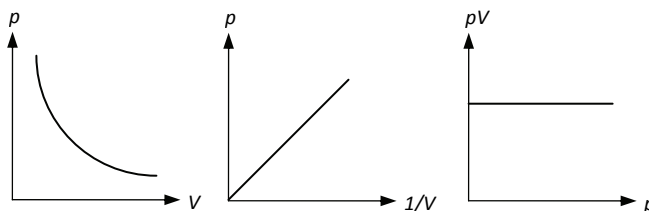
- The *general gas equation* can also be used to find the M_r of a gas.

Since $n = \frac{m}{M}$ where m = mass in g
 M = molar mass

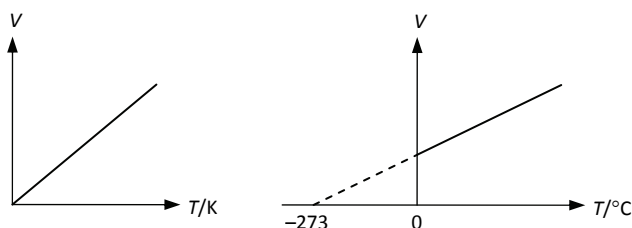
$$pV = nRT \Rightarrow pV = \frac{m}{M}RT \Rightarrow M = \frac{m}{pV}RT = \rho \frac{RT}{p} \quad \text{where } \rho = \frac{m}{V}$$

- An ideal gas will obey the *general gas equation*.

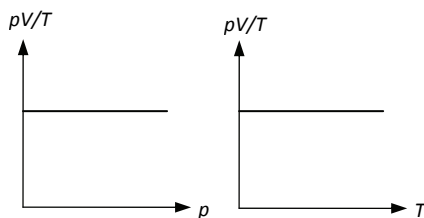
- At constant temperature, $pV = \text{constant}$ or $V \propto \frac{1}{p}$. (Boyle's law)



- At constant pressure, $\frac{V}{T} = \text{constant}$ or $V \propto T$. (Charles' law)



- At constant temperature, $\frac{PV}{T} = \text{constant}$. (Avogadro's law)



Gas diffusion

Gas diffusion is the inter-mixing of two or more gases to form a homogeneous mixture without any chemical change.

- It is able to occur as gases move randomly and fill empty spaces.
- The rate of diffusion increases with an increase in temperature and decreases with an increase in gas density.

Partial pressure

Partial pressure is the pressure a gas would exert if it alone occupied a container.

- Each gas exerts its own pressure in a mixture of gases.
- Partial pressure of a gas = mole fraction \times total pressure
- In a mixture of two gases C and D,

$$\text{Partial pressure of gas C} = \frac{n_C}{(n_C + n_D)} \times p_T$$

where n_C = no. of moles of gas C

n_D = no. of moles of gas D

p_T = total pressure

Dalton's Law

Dalton's Law states that in a mixture of unreacting gases, the total pressure is equal to the sum of the partial pressures of all the gases in the mixture.

- Each gas exerts its own pressure in a mixture of gases.
- The partial pressures of the remaining gases remain the same even after the removal of one of the gases.



Example

A mixture of gases at 200 kPa consists of 50% NH₃, 30% H₂ and 20% N₂ by volume. Calculate the partial pressures of each gas.

$$\text{Partial pressure of NH}_3 = \left(\frac{50}{100}\right) \times 200 = 100 \text{ kPa (ans)}$$

$$\text{Partial pressure of H}_2 = \left(\frac{30}{100}\right) \times 200 = 60 \text{ kPa (ans)}$$

$$\text{Partial pressure of N}_2 = \left(\frac{20}{100}\right) \times 200 = 40 \text{ kPa (ans)}$$



Gas displacement

- ✍ Gas including evaporated water molecules is collected in the laboratory preparation of gas.
- ✍ The total pressure of the gas collected (including evaporated water molecules), $p_T = p_{\text{gas}} + p_{\text{water}}$.
- ✍ In the event when the water level in the collection flask is the same as that outside of it, $p_T = p_{\text{atm}}$, and $p_{\text{gas}} = p_{\text{atm}} - p_{\text{water}}$.
- ✍ p_{atm} is taken by a barometer.

Example

In an experiment, 250 cm³ of hydrogen gas was collected by gas displacement at 25°C. Given that the $p_{\text{atm}} = 98.5 \text{ kPa}$ and the $p_{\text{water}} = 3.18 \text{ kPa}$, calculate the volume of dry hydrogen under standard conditions (273 K and 101.3 kPa).

$$\begin{aligned} p_{\text{hydrogen}} &= p_{\text{atm}} - p_{\text{water}} \\ &= 98.5 - 3.18 \\ &= 95.3 \text{ kPa} \end{aligned}$$

$$\frac{(P_{\text{atm}} V_{\text{atm}})}{T_{\text{atm}}} = \frac{(P_{\text{hyd}} V_{\text{hyd}})}{T_{\text{hyd}}}$$

$$\begin{aligned} V_{\text{hyd}} &= \left[\frac{(95.3 \times 250)}{(25 + 273)} \right] \times \left(\frac{273}{101.3} \right) \\ &= 215 \text{ cm}^3 \text{ (ans)} \end{aligned}$$



Worked Examples

Example 1

Derive the general gas equation.

Solution:

Boyle's law states that at constant temperature, the volume of a given mass of gas is inversely proportional to the applied pressure.

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

Charles' law states that at constant pressure, the volume of a given mass of gas is proportional to its temperature in K.

$$V \propto T$$

From the two laws,

$$V \propto \frac{T}{p} \Rightarrow \frac{pV}{T} = \text{constant}$$

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

Avogadro's law states that equal volume of gases at the same temperature and pressure contains an equal number of molecules, implying that the volume of a gas, at constant temperature and pressure, is directly proportional to the amount of gas in moles.

$$V \propto n$$

Combining the above three gas laws, the relationship $V \propto \frac{nT}{p}$ can be obtained.

$$V = R \left(\frac{nT}{p} \right) \Rightarrow pV = nRT \text{ where } R \text{ is the proportionality constant. (ans)}$$



Example 2

- Calculate the volume occupied by 5.00 g of water at 25°C under a pressure of 4000 Pa.
- If the pressure is raised to 4500 Pa at constant temperature, calculate the new volume.

Solution:

$$(a) n = \frac{5}{(16+2)} = 0.27778 \text{ mol (5 sf)}$$

$$T = 273.15 + 25 = 298.15 \text{ K}$$

$$pV = nRT$$

$$4000V = 0.27778 \times 298.15 \times 8.314$$

$$V = 0.172 \text{ m}^3 \text{ (3 sf) (ans)}$$



(b) Let V_2 be the new volume.

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

$$p_1 V_1 = p_2 V_2$$

$$4000 \times 0.172 = 4500 \times V_2$$

$$V_2 = 0.153 \text{ m}^3 \text{ (3 sf) (ans)}$$



Example 3

When 5.2 g of a substance was completely vaporized at 25°C and 35000 Pa, 0.006 m³ of vapour was produced. Calculate the relative molecular mass of the substance.

Solution:

$$pV = nRT$$

$$35000 \times 0.006 = \frac{(m \times 298.15 \times 8.314)}{M_r}$$

$$M_r = 11.804m$$

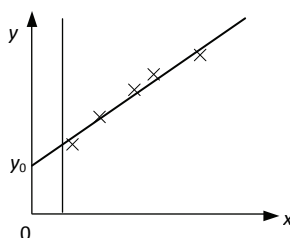
$$M_r = 11.804 \times 5.2$$

$$= 61.4 \text{ (3 sf) (ans)}$$



Worked Problems

Example 1



An experiment was conducted to find out how the pressure of a fixed mass of gas varies with its temperature when it is kept at constant volume. At the end of the experiment a graph was plotted as above. Which of the following statements are true?

- (a) The y -axis denotes pressure while the x -axis denotes temperature.
- (b) The gradient of the graph is equivalent to the volume of the gas.
- (c) y_0 refers to the temperature absolute zero, 0 K.

Solution:

(a) True. (ans)

(b) False. (ans)

$$\text{From Boyle's Law : } pV = nRT \Rightarrow p = \left(\frac{nR}{V}\right)T$$

The gradient refers to the value $\frac{nR}{V}$, and not the volume, V , itself.

(c) False. (ans)

Theoretically, at absolute zero the volume of an ideal gas would be zero and molecular motion would cease, causing pressure to be zero as well. Furthermore, in real life all gases would condense or solidify by the time it reaches absolute zero temperature.

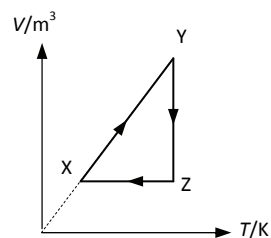
y_0 refers to the temperature 0°C instead.



Example 2

The graph above shows how the volume of a fixed mass of ideal gas varies according to its temperature. Determine if each of the following are correct descriptions of the pressure of the gas.

- (a) The gas pressure did not change from X to Y
- (b) The gas pressure decreased from Z to X
- (c) The gas pressure increased from Y to Z



Solution:

According to Boyle's Law, $pV = nRT$, where p is pressure, V is volume, T is temperature and n and R are constants.



Rearranging, we get $p = \frac{nRT}{V}$.

- (a) From X to Y, both volume and temperature increases. Thus the pressure remains unchanged.

The statement is correct. (ans)

- (b) From Z to X, the temperature decreased while the volume remained the same. Thus the pressure decreased.

The statement is correct. (ans)

- (c) From Y to Z, the temperature remains the same while the volume decreased. Thus the gas pressure increased.

The statement is correct. (ans)



Example 3

Cylinders of pressurized carbon dioxide were used to make carbonated drinks. One such cylinder, with an internal volume of 2.5 dm^3 , contains 2.2 kg of carbon dioxide. Calculate the pressure exerted by carbon dioxide inside the cylinder at room temperature (298 K). Suggest why this value obtained is different from the actual pressure of $2.2 \times 10^7 \text{ Pa}$ inside the cylinder.

Solution:

$$\begin{aligned} \text{No. of mol of carbon dioxide} &= \frac{(2.2 \times 10^3)}{[12.0 + 2(16.0)]} \\ &= 50 \end{aligned}$$

$$\begin{aligned} \text{Pressure exerted by carbon dioxide} &= \frac{(nRT)}{V} \\ &= \frac{(50 \times 8.31 \times 298)}{(2.5 \times 10^{-3})} \\ &= 4.95 \times 10^7 \text{ Pa} \end{aligned}$$

The actual pressure is lower than the calculated pressure inside the cylinder as carbon dioxide is not an ideal gas. The actual pressure is lower as carbon dioxide has a significant size and intermolecular forces of attraction. (ans)

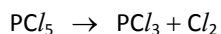


Example 4

At 340 K, pure PCl_5 gas has a pressure of 26.5 kPa in a flask. At 490 K, this is completely dissociated into $\text{PCl}_3(\text{g})$ and $\text{Cl}_2(\text{g})$. What is the pressure of the flask at 490 K?

Solution:

1 mol of PCl_5 dissociates to give 2 mol of gas by the equation:



Therefore the number of moles of gas is doubled at 490 K.

$$pV = nRT$$

$$\frac{n_1 T_1}{p_1} = \frac{n_2 T_2}{p_2}$$

$$p_2 = \frac{n_2 T_2}{n_1 T_1} \times p_1$$

$$= \frac{(2 \times 490)}{(1 \times 340)} \times 26.5$$

$$= 76.4 \text{ (3 sf) (ans)}$$

