# 03 The Gaseous State

## GUIDING QUESTIONS

- What is a mole? Why is it important in Chemistry?
- What is an ideal gas? What conditions are needed for a gas to behave ideally?
- What is the relationship between pressure, volume, temperature and amount of a gas?
- How do the individual components of a gas mixture contribute to the pressure of the mixture?

## LEARNING OUTCOMES

Students should be able to:

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

**3(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

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

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

**6(a)** define the terms *relative atomic, isotopic, molecular and formula mass* (Refer to Topic 1 Atomic Structure & Physical Periodicity for relative atomic and isotopic masses)

**6(b)** define the term *mole* in terms of Avogadro's constant

## REFERENCES


1. Peter Cann, Peter Hughes, *Chemistry*, 1st Edition, Hodder Education, Chapter 4
2. Silberberg, *Chemistry: The Molecular Nature of Matter and Change*, 3rd Edition, McGraw-Hill, Chapter 5
3. Burrows, Holman, Parsons, Pilling, Price, *Chemistry: Introducing inorganic, organic and physical chemistry*
4. http://www.chemguide.co.uk/physical/ktmenu.html#top

**LOOKING BACK**
In the gaseous state, the particles are far apart as compared to solid and liquid states and are in constant random motion. An element or compound that exists as a gas at room temperature generally have weak interactions between its particles. You should keep in mind how the structure and bonding of a substance impact on its physical properties such as melting and boiling points.

Early experiments on the macroscopic properties of gases led to an understanding of the laws that govern the macroscopic properties of gases and the development of the mole concept. In preparation for this chapter, you should recall the basics of mole concept that you have learnt previously (e.g. what is 1 mole of particles?). **Read Section 1: "*Gases*" before the lecture.**

## 1 GASES

### 1.1 Development of Mole Concept through Gas Experiments

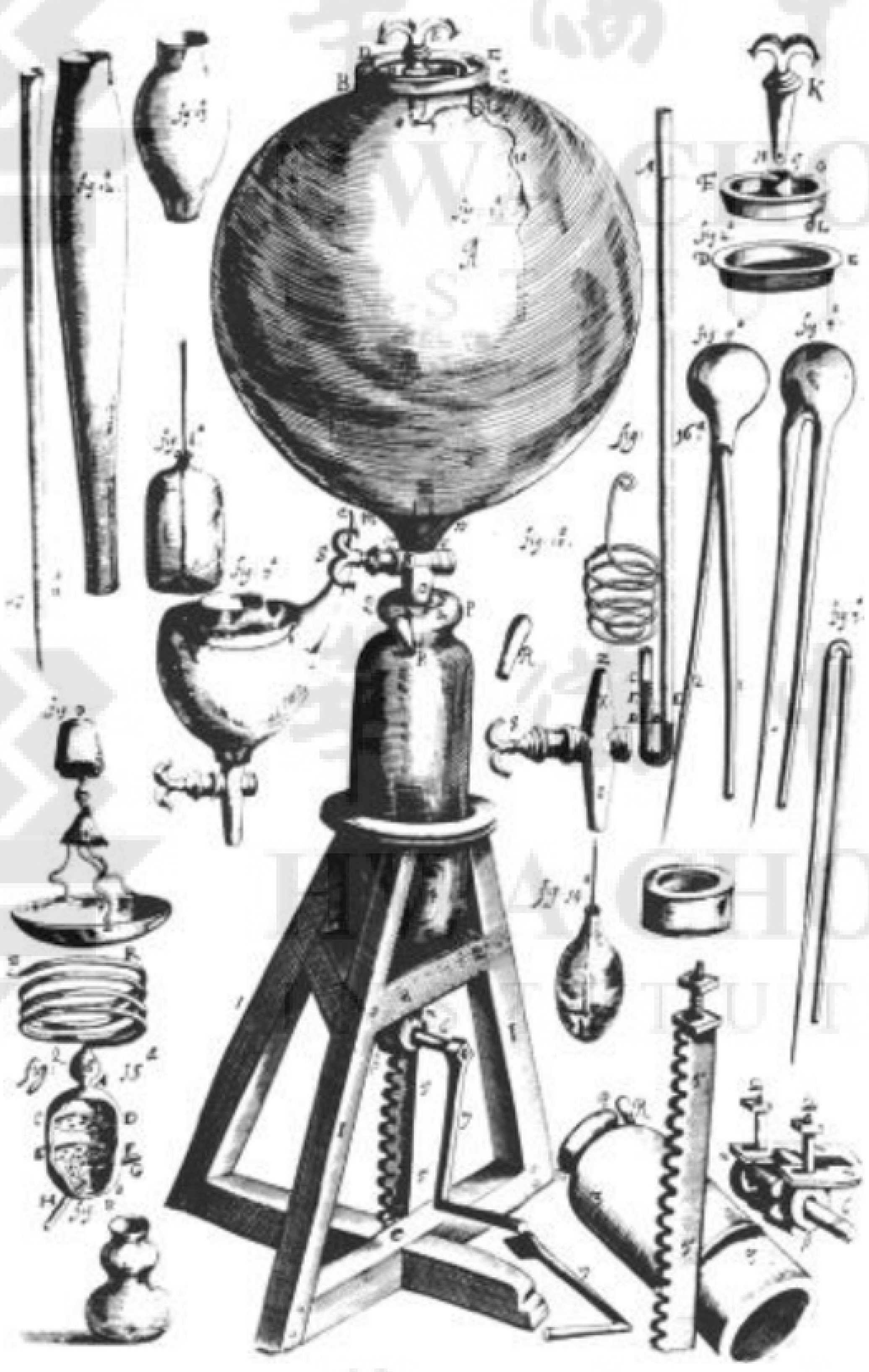


*Figure 1. Some apparatus used by Robert Boyle*

Some of the earliest scientific investigations concerning matter were performed by scientists trying to understand the physical and chemical properties of gases. It was these studies (~1650–1800 AD) that helped establish chemistry as a scientific discipline. The experiments of scientists such as Robert Boyle (1627 - 1691), Jacques Charles (1746-1823), and Gay-Lussac (1778-1850) led to our understanding of laws that govern the macroscopic properties of gases and we will learn these gas laws in *Section 3*.

Joseph Louis Gay-Lussac was a French chemist who studied how different volumes of gases combined during chemical reactions to make products. He determined that when different gases reacted, they would always do so in small whole number ratios (e.g., two volumes of hydrogen would react with one volume of oxygen in forming water) – the "Law of Combining Volumes of Gases". This was one of the greatest advancements of its time and helped form the basis for later atomic theory and how chemical reactions occur.

Amadeo Avogadro, an Italian physics professor, hypothesised the **Avogadro's Law** to explain Gay-Lussac's data.

**Avogadro's Law***:* Equal volumes of all gases, under the same temperature and pressure, contain the same number of particles (atoms or molecules).

From this hypothesis it followed that **relative molecular mass** of any two gases can be found by comparing the masses of equal volumes of the gases. Avogadro also astutely reasoned that simple gases were not formed of solitary atoms but were instead compound molecules of two or more atoms.

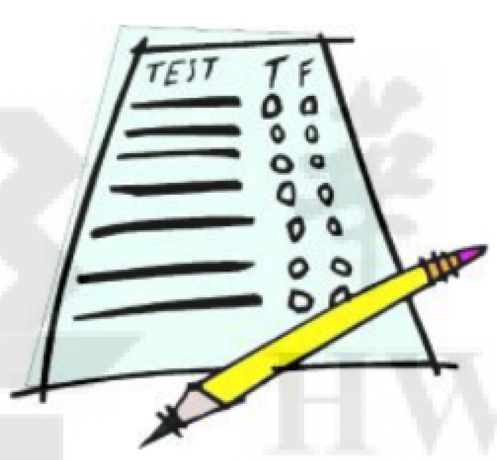
About fifty years later, an Italian scientist named Stanislao Cannizzaro championed Avogadro's hypothesis and used it to develop a set of atomic masses ($A_r$) for the known elements by comparing the masses of equal volumes of gas. Building on this work, an Austrian high school teacher named Johann Josef Loschmidt calculated the size of a molecule of air in 1865, and thus developed an estimate for the number of molecules in a given volume of air. While these early estimates have since been refined, they led to the concept of the **mole** and the discovery that the atomic mass of an element contains a precise number of atoms given by the **Avogadro constant** (named in recognition of Avogadro's contribution). With a clear understanding of how to measure atomic and molecular mass established, the concept of reacting ratios developed rapidly and we are now able to determine reaction stoichiometry with ease.

One ***mole*** contains exactly $6.02 \times 10^{23}$ (or Avogadro constant, L) elementary entities. (notation: η, unit: **mol**)

**Relative molecular mass, $M_r$**: $\dfrac{\textit{average}\text{ mass of one molecule of a substance}}{\frac{1}{12}\text{ x the mass of one atom of }^{12}\text{C}}$

**Note**:

- Due to the presence of isotopes, the word "average" is necessary in definition of $M_r$
- $M_r$ = sum of $A_r$ of all the atoms in the molecular formula
- $M_r$ has no units as it is a ratio of two masses




**Exam tip**

You are not required to remember the history of the development of mole concept for the examinations. However, you will need to define the important terms used in mole concept (those given in boxes above). The use of these terms in calculation will be covered in *Topic 4: "Reactions and Stoichiometry"*.

## 1.2 Units of Pressure

Pressure is defined as force exerted per unit area. Gas pressure is a gauge of the frequency and force of collisions between gas particles and the walls of the container that hold them. It is measured in a number of different units. One of the units is the millimetre of mercury, mmHg, which originates from measuring atmospheric pressure (760 mmHg) with a mercury barometer.

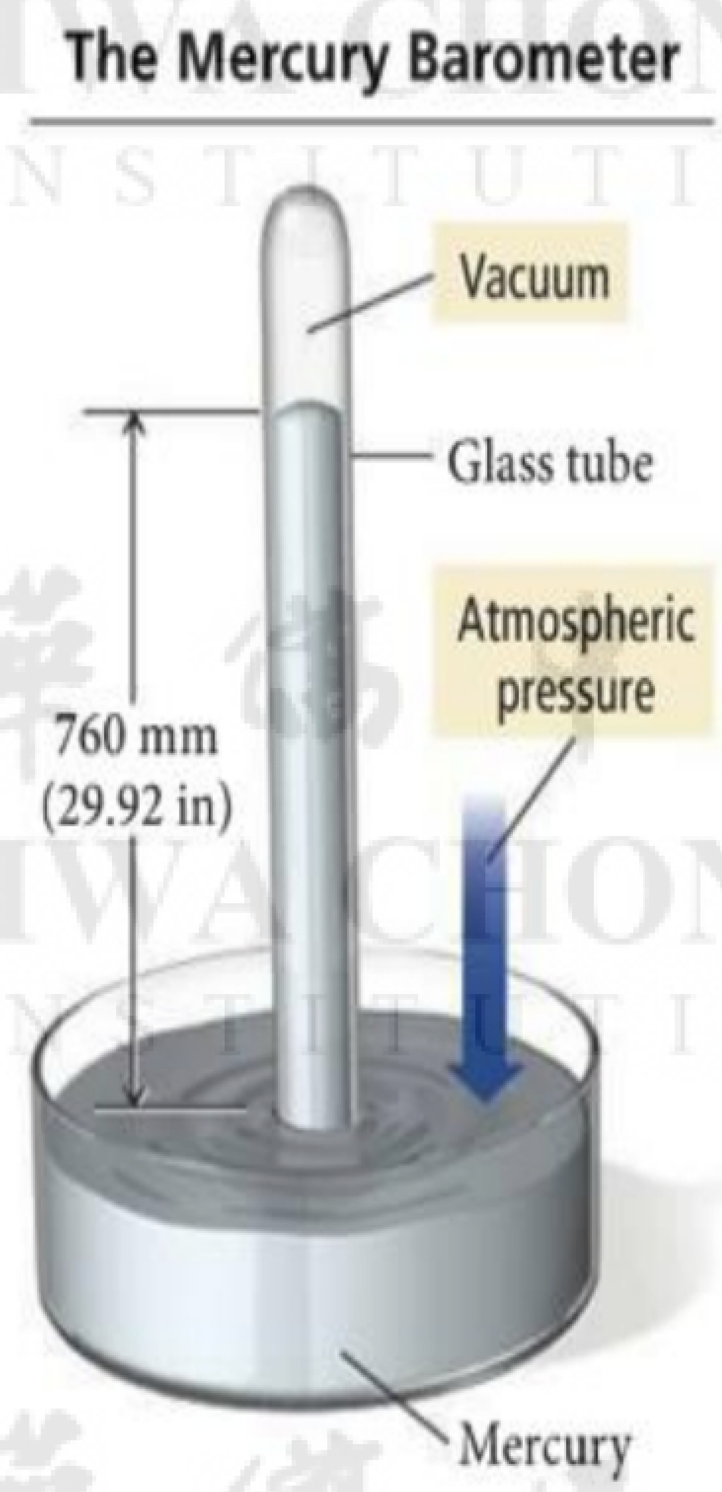


*Figure 2 – A mercury barometer at sea level*

The SI units of pressure is the pascal, Pa, defined as 1 newton, N, per square metre. This is a very common unit used in the A-level syllabus.

$$1 \text{ Pa} = 1 \text{ N m}^{-2}$$

It is a much smaller unit of pressure than the standard atmosphere (**atm**) and the **bar**, which are approximated to the following values for calculations:

1 atm = 101,325 Pa

1 bar = 100,000 Pa

## 1.3 Measuring standards for gas samples

Because the physical properties of a gas sample can vary greatly depending on several factors, we often have to specify the conditions under which the measurements were made.

**Molar volume**, $V_m$, of any gas is the volume occupied by 1 mole of the gas at a specified temperature and pressure. The common conditions used for gas measurements and molar volumes are summarised in the table below.

*Table 1. Molar volume and measurement conditions for gas samples*

| | **Measurement conditions used** | | |
|---|---|---|---|
| | Pressure | Temperature | Molar volume ($V_m$) |
| Standard temperature and pressure (s.t.p.) | 1 bar (100,000 Pa) | 273 K (0 °C) | 22.7 $dm^3 mol^{-1}$ |
| Room temperature and pressure (r.t.p.) | 1 atm (101,325 Pa) | 293 K (20 °C) | 24 $dm^3 mol^{-1}$ |

the Data book — You do not need to memorise the conditions and molar volumes for s.t.p. and r.t.p as they are listed on the first page of the Data Booklet!

## 2 THE SIMPLE GAS LAWS AND IDEAL GAS LAW

Because most gases are difficult to observe directly, they are described through the use of four macroscopic properties.

- Pressure (**P**)
- Volume (**V**)
- Temperature (**T**)
- Number of moles of gas (**n**)

Simple gas laws are formulated to describe the relationship between pairs of the properties and hold to good approximations for all gases.

### 2.1 Simple Gas Laws

The simple gas laws describe the relationships between pairs of the above variables, when the other two variables are held constant.

In the early 1660s, the English scientist Robert Boyle found that at constant temperature, the volume of a fixed mass of gas (i.e. for n is constant) is *inversely proportional* to its pressure. The mathematical and graphical relationships of **Boyle's Law** are given below:

Mathematical relationship

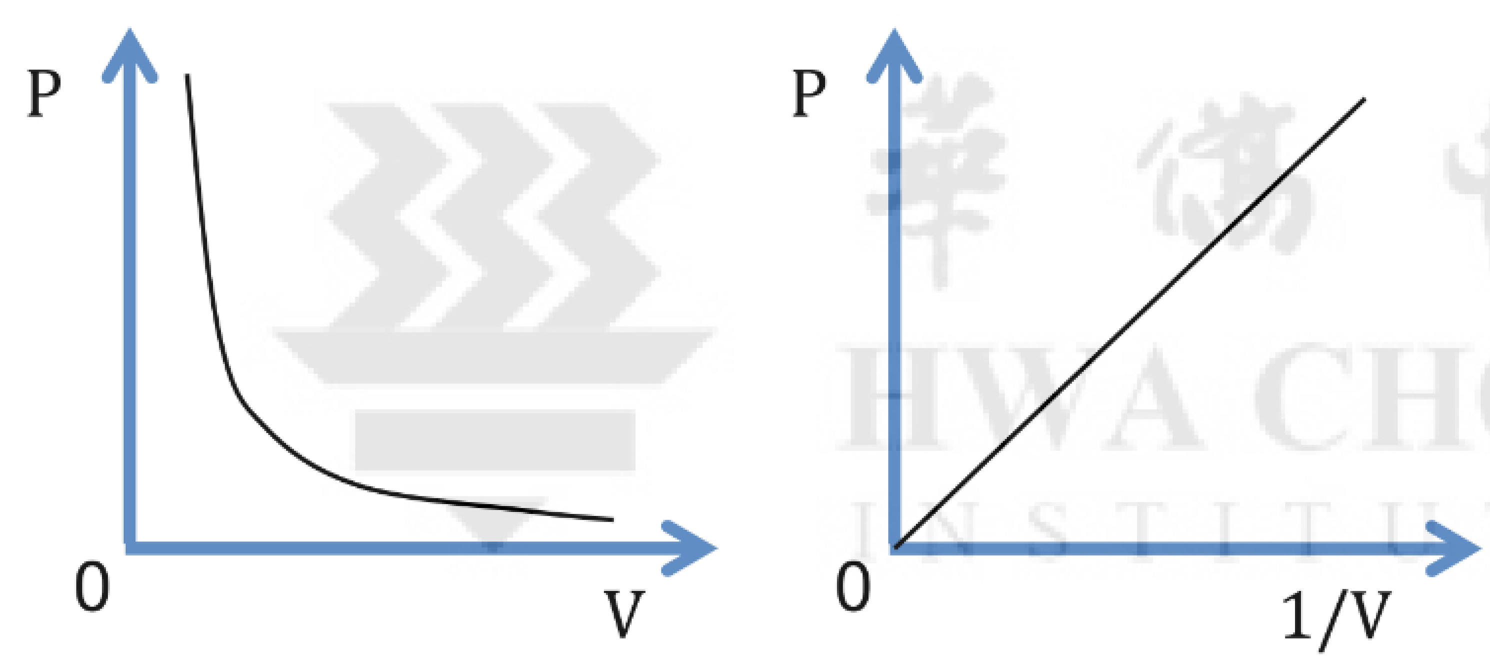
For n is constant and T is constant,

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

or

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

Graphical representation



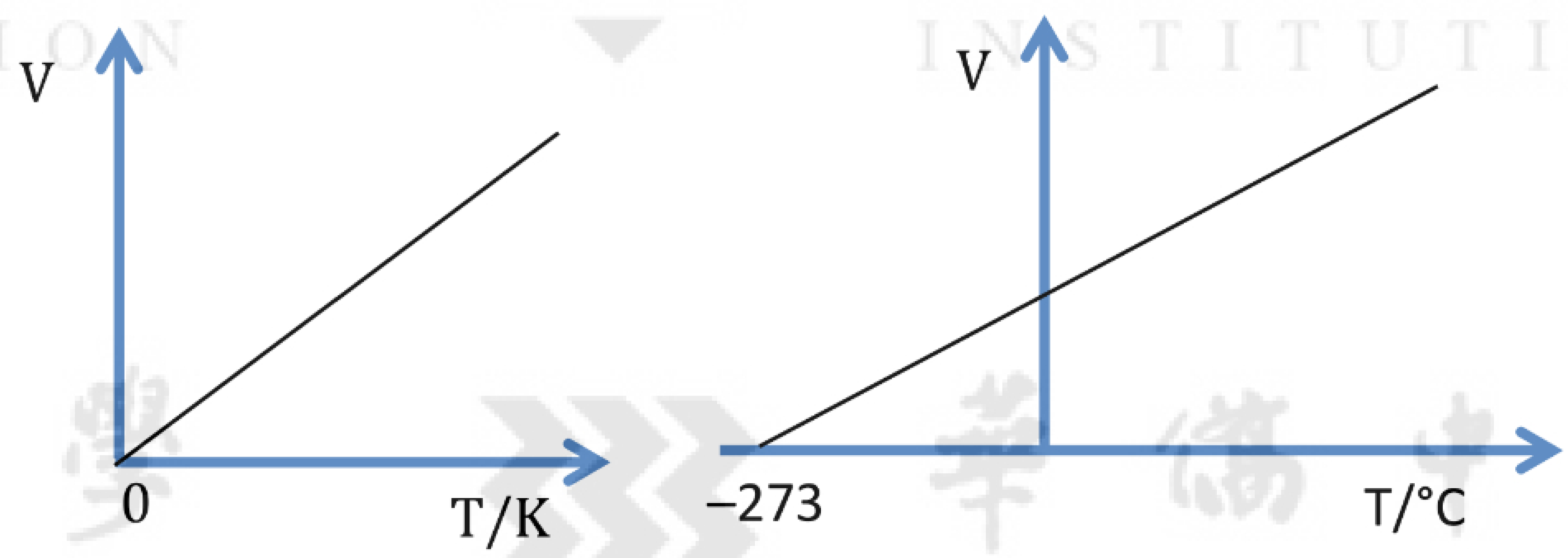

Later, in 1787, the French physicist Jacques Charles found that at constant pressure, the volume of a fixed mass of gas is *directly proportional* to its absolute temperature (measured in K). The mathematical and graphical relationships of **Charles' Law** are given below:

Mathematical relationship

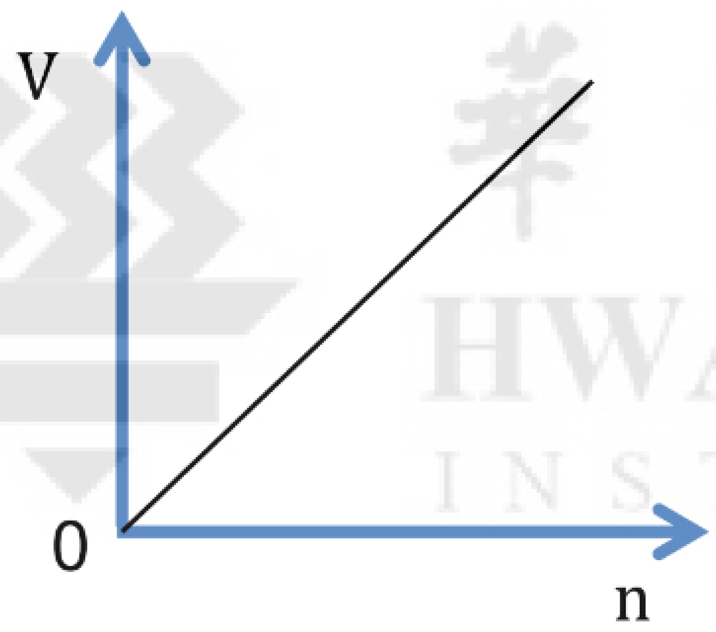
For n is constant and P is constant,

$$V \propto T$$

Graphical representation



In 1811, Amadeo Avogadro proposed that at constant temperature and pressure, the volume of a gas is *directly proportional* to the number of molecules (or number of moles of gas) present. The mathematical and graphical relationships of **Avogadro's Law** are given below:

| Mathematical relationship | Graphical representation |
|---|---|
| For T is constant and P is constant, $V \propto n$ |  |

Take note that at constant temperature and volume, the pressure of a gas is also *directly proportional* to the number of moles present.

**Self-practice 2.1**

Which of the simple gas laws is at work in each of the following examples?

(i) The bubbles exhaled by a scuba diver grow in size as the bubbles approach the surface of the ocean.

(ii) On collision, airbags in cars inflate rapidly. A sensor triggers the ignition of sodium nitride according to the following equation: $2NaN_3(s) \rightarrow 2Na(s) + 3N_2(g)$

(iii) The print head of a bubble jet printer contains 64 or 128 tiny nozzles. The tip of the nozzle is filled with ink which is then heated by an electronic heater. This vaporizes the ink and a bubble of vapor ink is then published on the paper. This bubble when published acts as a dot, of a letter or image.

## 2.2 The Ideal Gas Equation

By combining the three relationships given above, we get $V \propto \frac{nT}{P}$

We can replace the proportionality sign by incorporating a proportionality constant known as the *molar gas constant* (R):

$$V = R\left(\frac{nT}{P}\right) \xrightarrow{\text{Rearrange}} \boxed{\mathbf{PV = nRT}}$$

This equation is known as the **ideal gas equation**. It expresses the relationship among the four variables P, V, T and n for an **ideal gas**. An **ideal gas** is one which follows this equation exactly, under all conditions of pressure, volume and temperature. Refer to Section 4 for more information on the assumptions of the kinetic theory as applied to an ideal gas.

## Using the ideal gas equation in calculations

We can use the ideal gas equation to determine the value of any one of the four variables given the other three. However, the value and units of **R** must match the units of P, V, n and T chosen:

- T must be measured in K;
- n is usually expressed in moles;
- P and V can be expressed in a number of different units (shown in Table 2). In the A-level syllabus, we stick to SI units of Pa and $m^3$ respectively. When using these units, the corresponding value of **R** is **8.31 J $K^{-1}$ $mol^{-1}$**.

*Table 2. Table showing possible units of the four measurable variables when substituted in the ideal gas equation*

| Variable | Symbol | SI units | Other Units | Conversions |
|---|---|---|---|---|
| Pressure | P | Pa (pascal) or N $m^{-2}$ | atm , bar | 1 atm = 101325 Pa<br>1 bar = 100000 Pa |
| Volume | V | $m^3$ | $cm^3$ ; $dm^3$ | 1 $cm^3$ = $1 \times 10^{-6}$ $m^3$<br>1 $dm^3$ = 1000 $cm^3$ = $1 \times 10^{-3}$ $m^3$ |
| Temperature | T | K (kelvin) | *–nil–* | Absolute temperature (in K)<br>= temperature (in °C) + 273<br>0 K = –273 °C (absolute zero) |
| Amount | n | mol | *–nil–* | |

In the Data Booklet, the data given for **R,** called the molar gas constant, is **8.31 J $K^{-1}$ $mol^{-1}$.**

If we are to make **R** the subject of the ideal gas equation, its unit would be "Pa $m^3$ $mol^{-1}$ $K^{-1}$". How do we end up with "J $K^{-1}$ $mol^{-1}$" as the unit?

Recall that the joule is the SI unit of measurement of energy. It is equal to the work done in applying a force of one newton through a distance of one metre. Therefore, 1 J = 1 N m. Recall also that pressure is the force acting per unit area and therefore, 1 Pa = 1 N $m^{-2}$. Simple dimensional analysis will reveal the final unit of **R**.

**Lecture Exercise 2.1**

On the surface of Venus the temperature is 470 °C and the pressure is 1.00 atm. What is the volume occupied by 1.00 mol of an ideal gas under these conditions?

## 2.3 Applications of the Ideal Gas Equation

**Lecture Exercise 2.2**

**Calculating gas density and relative molecular mass using the Ideal Gas Equation**

The ideal gas law can be recast to determine other properties of gases, such as density and relative molecular mass. In the table below, express the ideal gas equation to make the specified parameter the subject of the equation.

| | Parameter | Useful link | Equation |
|---|---|---|---|
| i | Mass (m) in g | $n = \left(\frac{\text{mass}}{\text{molar mass}}\right) = \frac{m}{M_r}$<br>$\therefore PV = \left(\frac{m}{M_r}\right)RT$ | |
| ii | Concentration (c) in mol $m^{-3}$ | Concentration, $c = \frac{\text{no. of moles}}{\text{volume}} = \frac{n}{V}$<br>Rearranging ideal gas law:<br>$P = \left(\frac{n}{V}\right)RT$<br>$\therefore P = cRT$ | |
| iii | Relative molecular mass ($M_r$) | Rearrange equation for mass found in part i. | |
| iv | Density in g $m^{-3}$ | density, $\rho = \left(\frac{\text{mass}}{\text{volume}}\right) = \frac{m}{V}$<br>From i, $PV = \left(\frac{m}{M_r}\right)RT$<br>Rearranging, $P = \left(\frac{m}{V}\right)\frac{RT}{M_r}$<br>$\therefore P = \frac{\rho RT}{M_r}$ | |

**Self-practice 2.2**

In a syringe experiment, 0.10 g of a gas is found to occupy 83.1 $cm^3$ measured at standard temperature and pressure. What is the relative molecular mass of the gas?

**[27.3]**

**Self-practice 2.3**

A sample of *m g* of an organic compound is vaporised in a gas syringe and occupies *V* $cm^3$ at *T* K and *P* bar. What is the relative molecular mass of the compound, $M_r$? (*N00/III/6*)

**A** $M_r = \frac{m \times 22700 \times T}{P \times V \times 273}$

**B** $M_r = \frac{m \times 22700 \times (T + 273)}{P \times V \times 273}$

**C** $M_r = \frac{m \times 22700 \times 273 \times P}{V \times T}$

**D** $M_r = \frac{m \times 22700 \times 273 \times P}{V \times (T + 273)}$

## 2.4 Combined Gas Equation

The combined gas equation is useful for changes to gas systems where the **amount of the gas, n, is kept constant**.

Since n and R are constants,

$$\frac{PV}{T} = nR \qquad \Rightarrow \frac{PV}{T} = \text{constant}$$

Because $\frac{PV}{T}$ is a constant, it follows that for any change in condition, the expression will give the same value.

$$\frac{P_1V_1}{T_1} = \text{constant} = \frac{P_2V_2}{T_2}$$

$$\boxed{\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}}$$

where $P_1$, $V_1$ and $T_1$ relate to the gas in its initial condition, and $P_2$, $V_2$ and $T_2$ relate to the gas in its final condition. Temperature values must *only be in K* for the expression to be valid.

The combined gas equation can be further reduced to:

| | |
|---|---|
| $P_1V_1 = P_2V_2$ | if temperature is constant |
| $P_1 / T_1 = P_2 / T_2$ | if volume is constant and |
| $V_1 / T_1 = V_2 / T_2$ | if pressure is constant |

***Useful tip***:

- Because these relationships do not make use of the gas constant R, it is possible to use *any units of pressure or volume*, as long as they are consistently used for initial and final values.

**Lecture Exercise 2.3**

**Making use of the combined gas equation**

An air bubble rises from the bottom of the sea, where the temperature is 6.0 °C and pressure is 8.4 atm, to the water surface. The water surface has a temperature of 24.0 °C at 1.0 atm. Calculate the volume of the bubble in $cm^3$, to 2 decimal places, if its initial volume is 0.030 $cm^3$.

***Strategy***:
An air bubble contains a *fixed mass of gas* (assuming it doesn't combine with other air bubbles on the way up) so n is constant. We need to determine the final volume of the gas sample when both pressure and temperature change. We need to use $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$.

***Working and solution***:

***Note***:
Here, values of pressure and volume can be directly used (with the units given in the question), without being converted to SI units, as we are using a direct proportionality relationship which does not require the use of the gas constant R, nor finding the exact amount of gas (in moles).

**Self-practice 2.4**

A 400 $cm^3$ mixture of petrol vapour and air is taken into the cylinder of a car engine at 200 °C and a pressure of 100 kPa. The piston compresses this gaseous mixture to 50.0 $cm^3$.
Find the pressure of the compressed gas if temperature is constant. [Assume that the gases do not react]

**[800 kPa]**

## 2.5 Graphical Relationships for Ideal Gases

The graphical relationships for simple gas laws are introduced in *section 2.1*. In this section, we will attempt to predict the graphical relationship between other variables, based on manipulation of the ideal gas equation **PV = nRT**. Figure out which of the four variables are constants, and rearrange this equation in the form $y = mx + c$.

**Lecture Exercise 2.4**

**Situation 1**

For a fixed amount of gas kept at a constant temperature, sketch a graph of PV against P and PV against V.

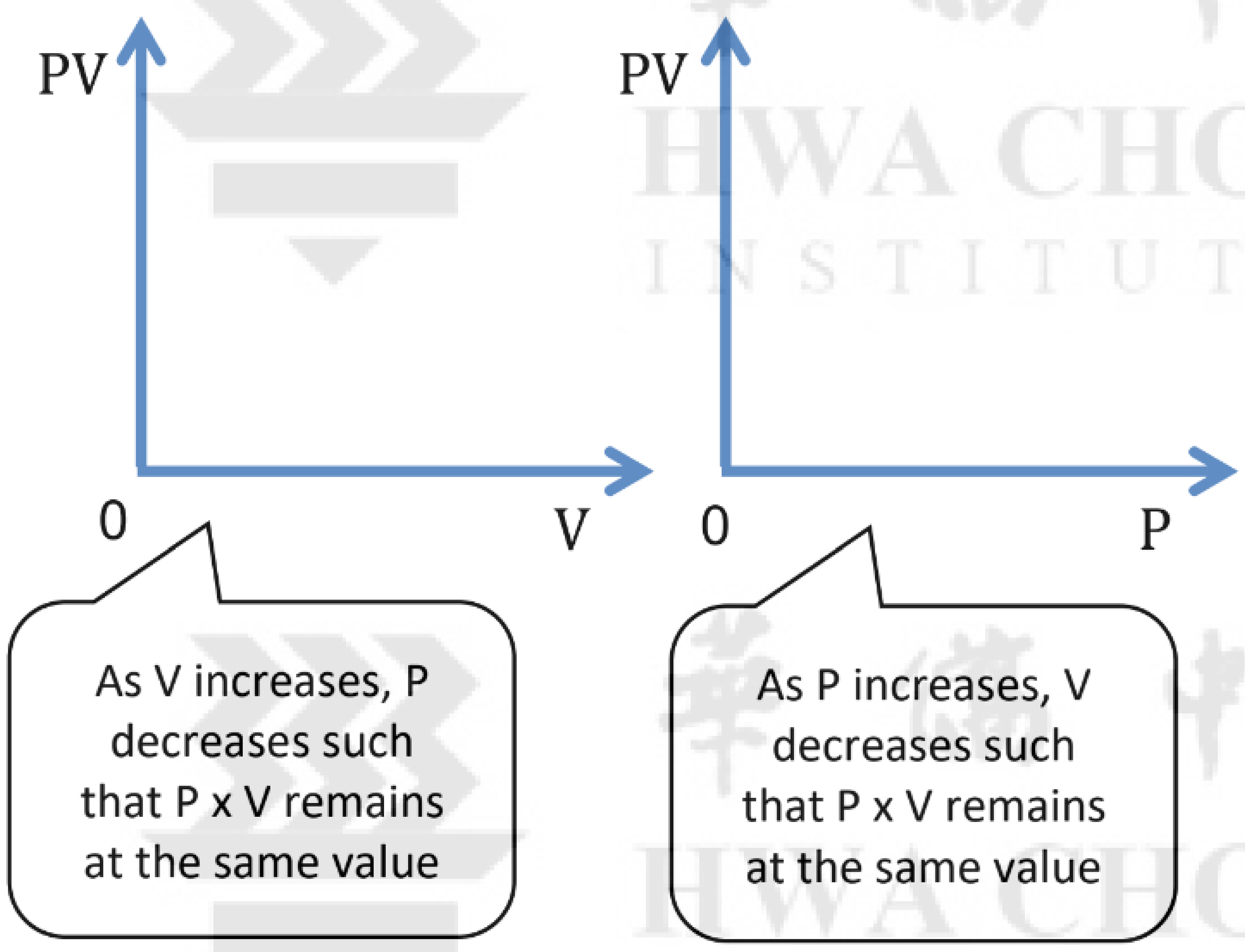
↑ n is constant ↑ T is constant

***Working:***

There is no need to rearrange the ideal gas equation as the variables are in the right place.

PV = nRT (nRT: constant)

$\Longrightarrow$ PV = constant



**Situation 2 (Charles' Law)**

For a <u>fixed amount of gas</u> kept in a <u>fixed pressure</u>, sketch a graph of V against T.

(fixed amount of gas → n is constant; fixed pressure → P is constant)

***Working:***

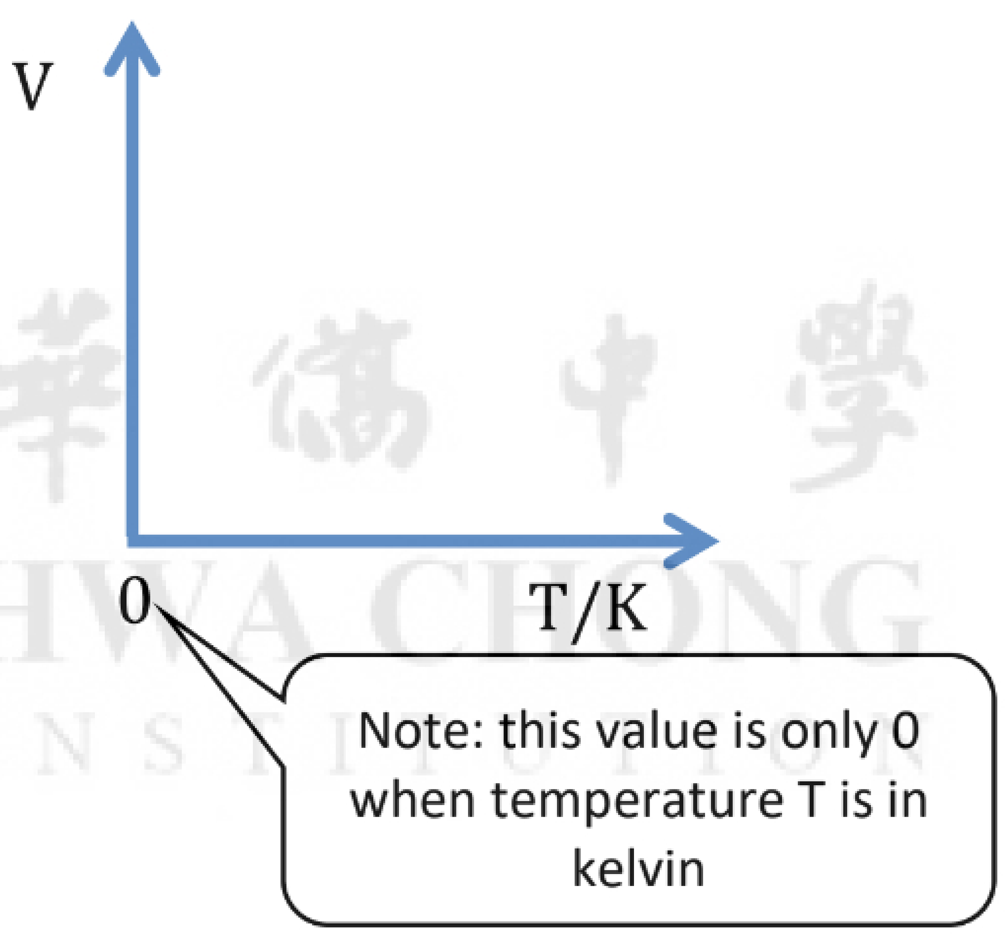
$PV = nRT$ (P and nR are constant) $\Rightarrow V = \left(\frac{nR}{P}\right)T$ ($\frac{nR}{P}$ is constant)

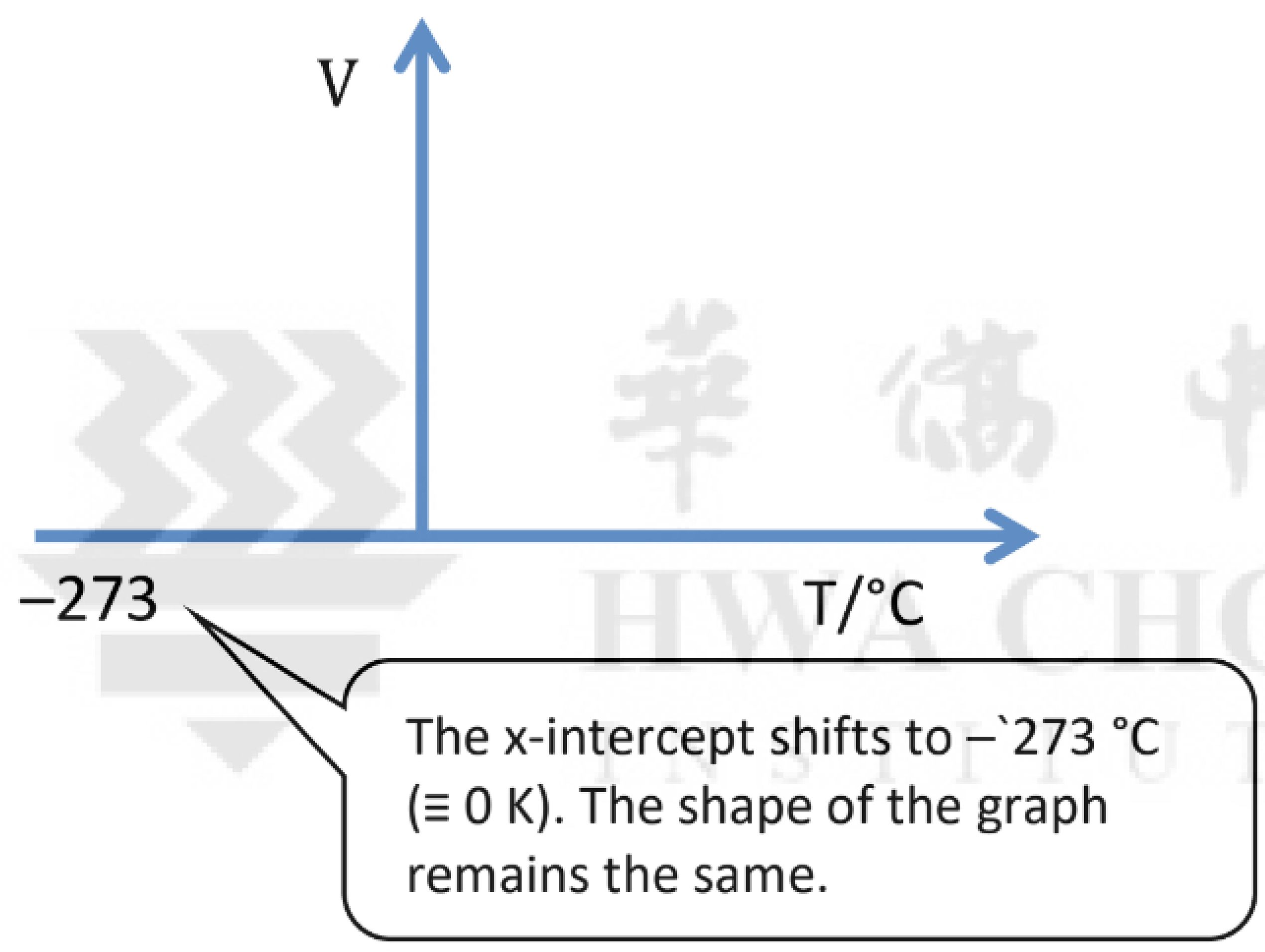
Or

$V \propto T$

$V = kT + 0$

$y = mx + c$



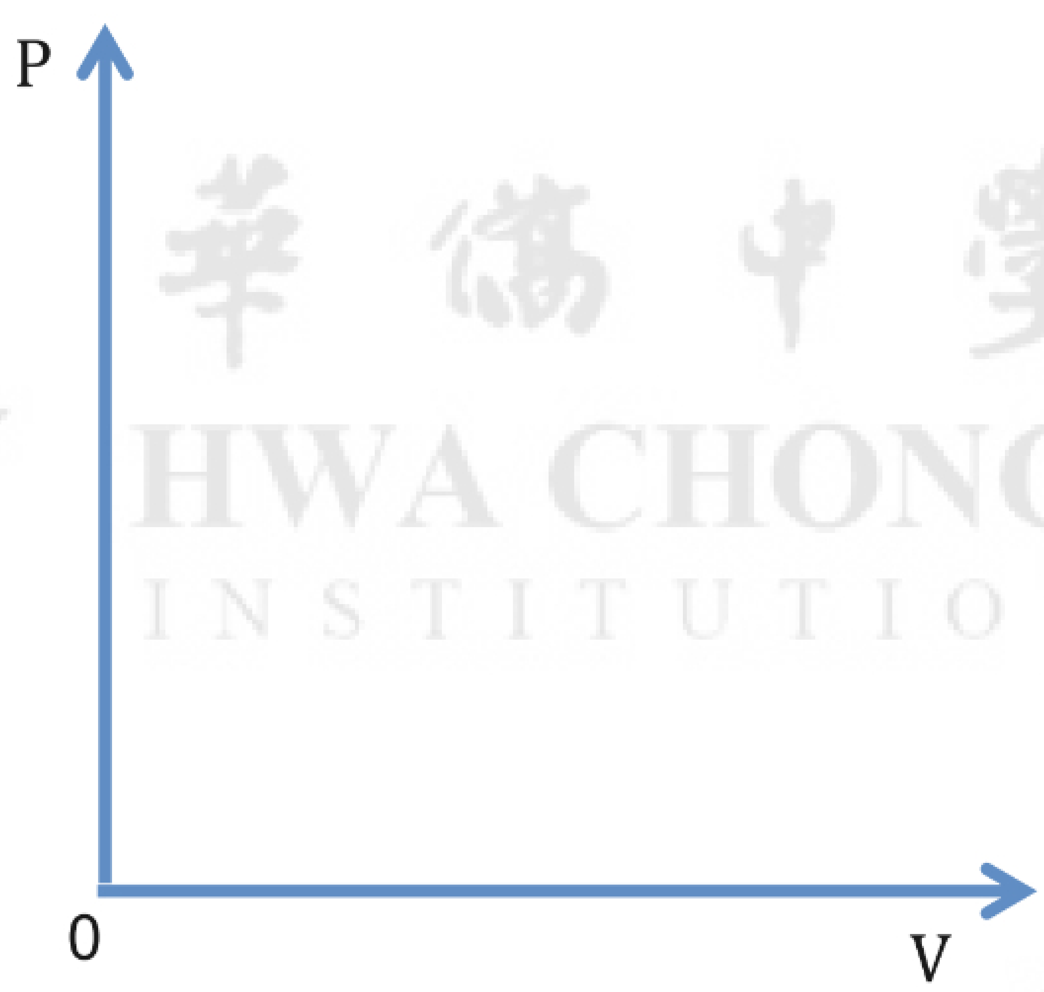




**Situation 3 (Extension of Boyle's Law)**

For a <u>fixed amount of gas</u> at two different temperatures ($T_2$ is higher than $T_1$), sketch on the same axes, the graphs of P against V.

***Working:***

Recall that for a fixed mass of gas at a constant temperature, the volume of the gas is <u>*inversely proportional*</u> to its pressure (*section 3.1*). This is known as Boyle's Law.




At the vertical line (where volume is a given value), the equation can be rearranged to give

$P = \left(\frac{nR}{V}\right)T$

$\Rightarrow P \propto T$

Hence, a higher temperature will result in a higher pressure.

**Self-practice 2.5**

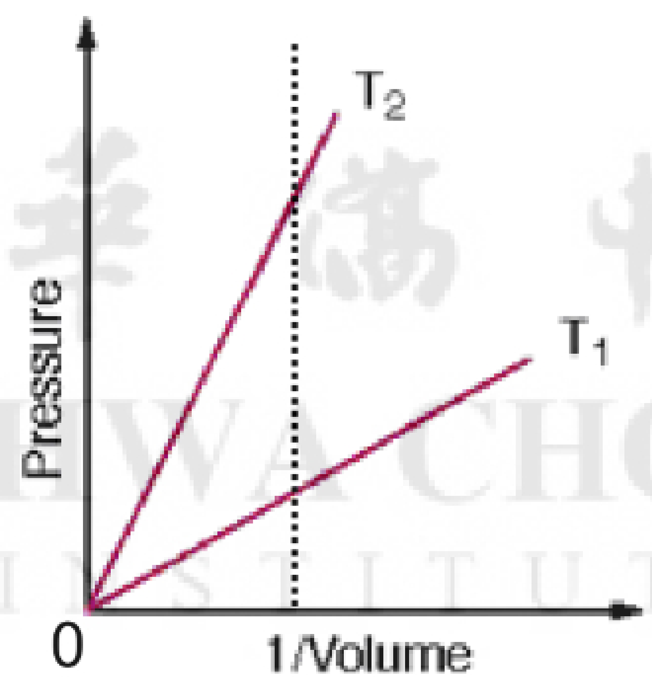
**Interpreting graphs**

Each of the following graphs represents plots for an ideal gas at two different conditions. In each case, you should be able to identify the variable with the higher value.

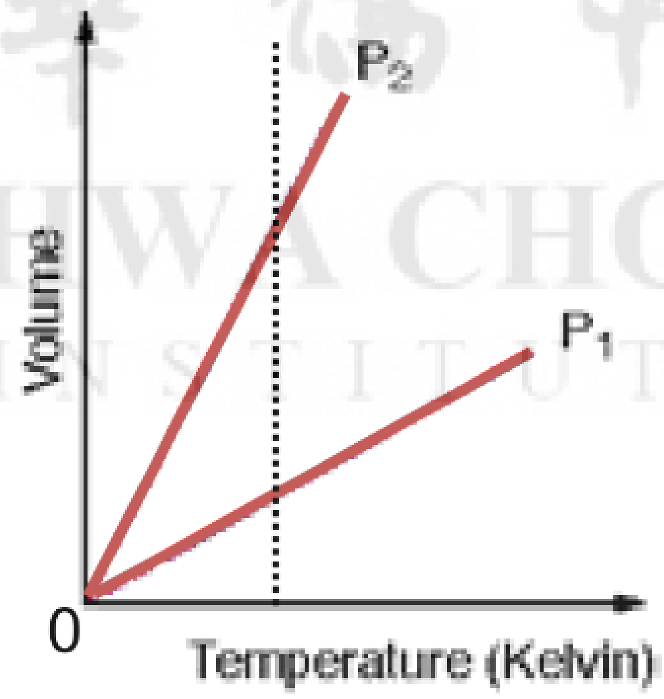
***Strategy:***

1. Consider for a given value of a variable (taken to be the x-axis variable for consistency) by drawing a vertical line.
2. Then compare how the other variable would change under the two different conditions given by looking at where the line you've drawn cuts the graphs.

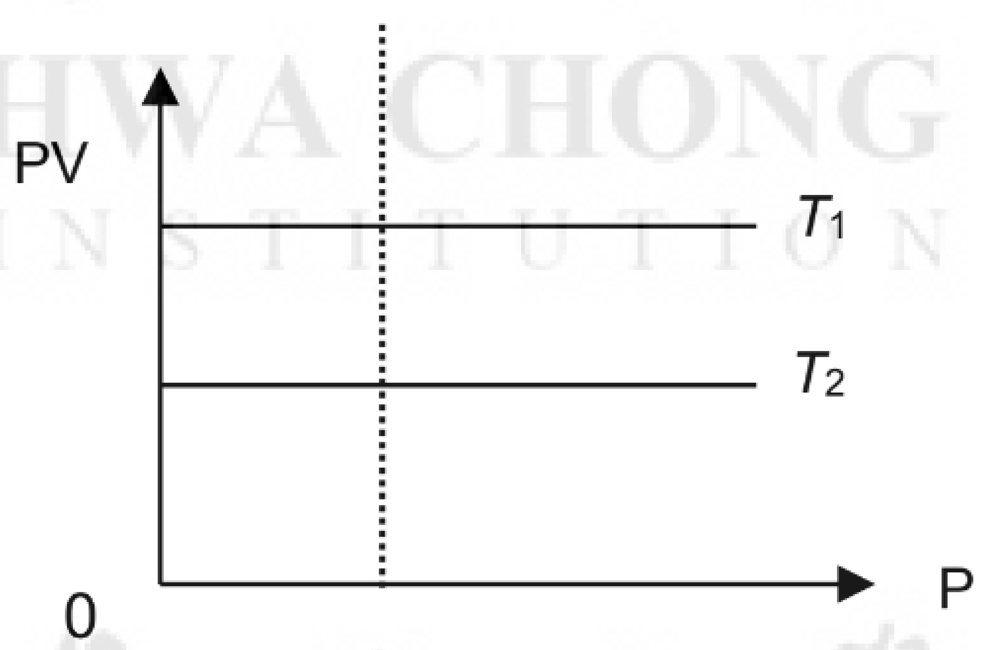
**(a)** Which temperature is higher, $T_1$ or $T_2$?




**(b)** Which pressure is higher, $P_1$ or $P_2$?



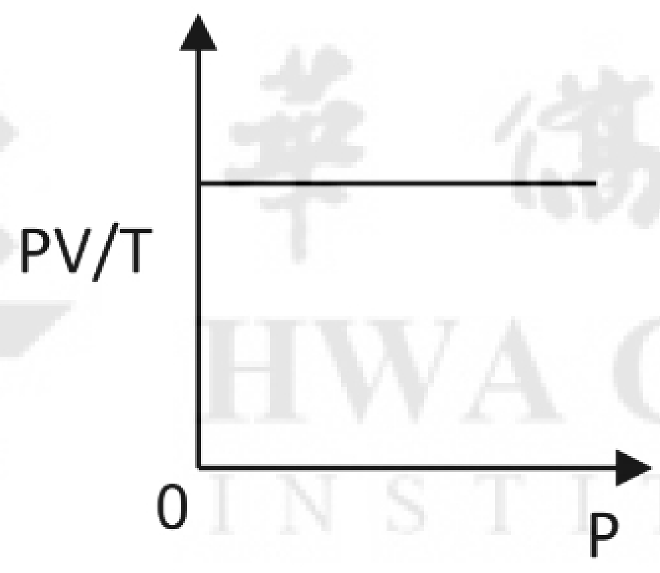

**(c)** Which temperature is higher, $T_1$ or $T_2$?



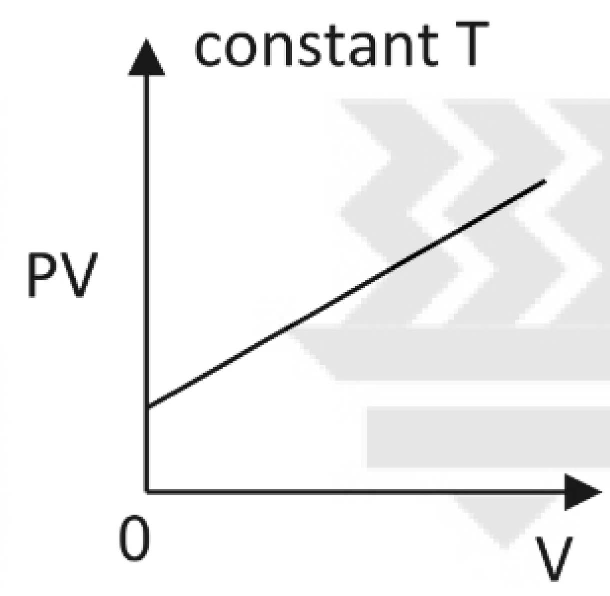
**Self-practice 2.6**

Which graph correctly describes the behaviour of a fixed mass of an ideal gas?

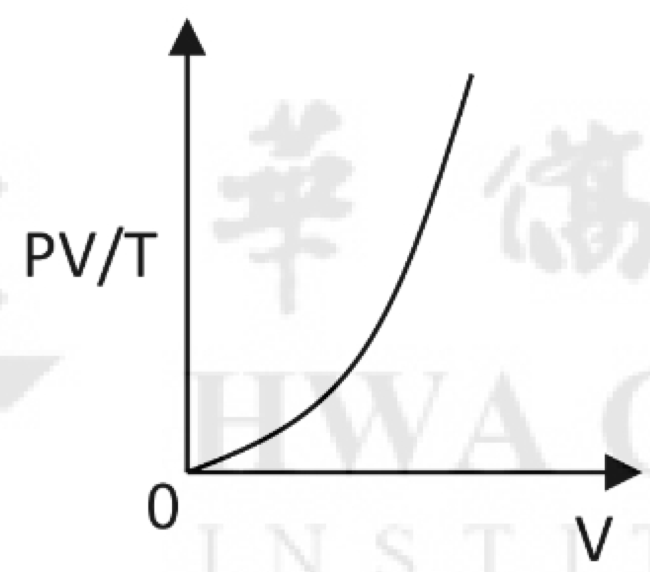
**A**



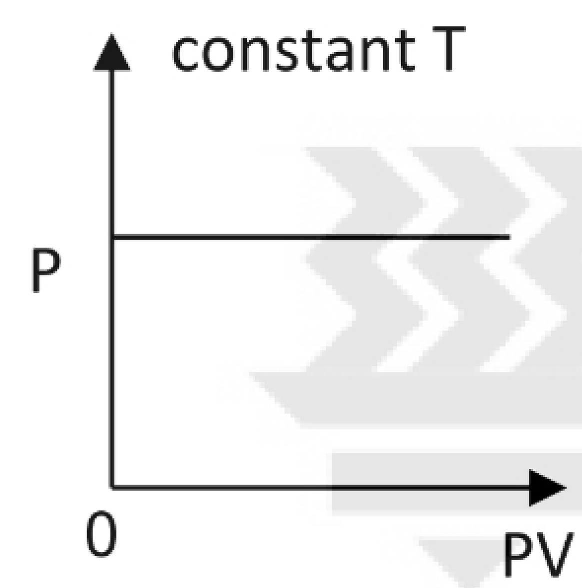

**B**




**C**




**D**



## 3 GAS MIXTURES AND PARTIAL PRESSURES

If a mixture of non-reacting gases is confined in a container, each gas occupies the volume (V) of the container and exerts its own pressure (P) on the walls of the container as if it alone were present. This observation is known as **Dalton's law of partial pressures**, and the pressure exerted by a particular gas in a mixture is referred to as its **partial pressure**.

**Definition:**
In a mixture of gases, the pressure exerted by any individual gas on the sides of a container is known as the **partial pressure** of the gas.

**Definition:**
**Dalton's law of partial pressures** states that *the total pressure of a mixture of gases is the sum of the partial pressures of the constituent gases.*

In other words, if we let $P_{total}$ be the total pressure of a gas mixture, we can write Dalton's law of partial pressures as:

$$P_{total} = P_a + P_b + P_c + \cdots$$

where $P_a$, $P_b$, $P_c$... are the partial pressures of the individual gases *a*, *b*, *c*... respectively.

Since T and V are constant, the partial pressure of each component is directly dependent on (and proportional to) the amount of each gas in the mixture. So, for gases *a, b, c, etc…*

$$P_a = n_a\left(\frac{RT}{V}\right) \qquad P_b = n_b\left(\frac{RT}{V}\right) \qquad P_c = n_c\left(\frac{RT}{V}\right) \qquad \text{… and so on}$$

Combining these into the expression for $P_{total}$, we get:

$$\begin{aligned} P_{total} &= n_a\left(\frac{RT}{V}\right) + n_b\left(\frac{RT}{V}\right) + n_c\left(\frac{RT}{V}\right) + \cdots \\ &= (n_a + n_b + n_c + \cdots)\left(\frac{RT}{V}\right) \\ &= n_{total}\left(\frac{RT}{V}\right) \end{aligned}$$

Dividing the expression for $P_a$ by that for $P_{total}$, and rearranging:

$$P_a = \left(\frac{n_a}{n_{total}}\right) P_{total}$$

where $\left(\frac{n_a}{n_{total}}\right)$ is called the **mole fraction**, sometimes represented by the Greek letter *chi*, χ, or:

$$P_a = \chi_a P_{total}$$

Thus, in a gas mixture, the **partial pressure of any individual gas is directly proportional to its mole fraction** in the mixture.

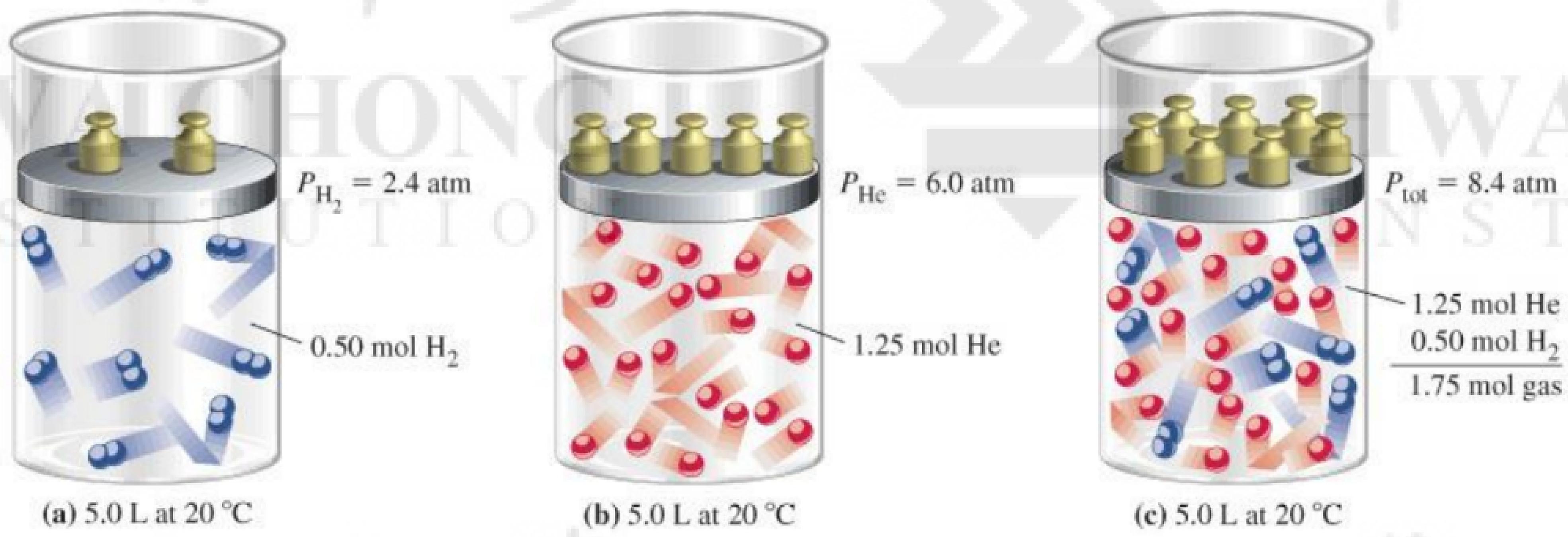



*Figure 3 – Illustration of Dalton's Law of Partial Pressures*

**Definition:**
For a mixture of gases, the ratio of the amount (or number of moles) of an individual gas to the total amount of gas is known as its **mole fraction**.

**Lecture Exercise 3.1**

**Finding total pressure of a gas mixture and individual partial pressures of the gases**
Two moles of oxygen and one mole of nitrogen are contained in a cylinder with a volume of 10.0 $dm^3$ at 298 K. What is the total pressure? What is the partial pressure of oxygen?

***Strategy***:
Oxygen and nitrogen do not react under these conditions. The total pressure will simply be dependent on the total number of moles of gas, and the ideal gas equation can be used to calculate it. The partial pressure of oxygen depends on its mole fraction in the gas mixture.

***Working and solution***:
Since we are using the ideal gas equation, convert all values to SI units, and calculate $n_{total}$:

$V = 10.0 \times 10^{-3}\ m^3$; $T = 298\ K$; $n_{total} = 3\ mol$

Rearranging the combined gas law to solve for $P_{total}$, and subsequently for $P_{O_2}$:

**Lecture Exercise 3.2**

Flask **Q** contains 1.00 $dm^3$ of helium at a pressure of 2.00 kPa and flask **R** contains 2.00 $dm^3$ of neon at a pressure of 3.00 kPa. If the flasks are connected at constant temperature, what is the final pressure of the system?

**Self-practice 3.1**

A 12.5 dm$^3$ scuba diving tank is filled with a heliox mixture containing 24.2 g of He and 4.32 g of $O_2$ at 298 K. Calculate the total pressure and the partial pressures of helium and oxygen in the mixture.

**[ $P_{total}$ = 1.23 x 10$^6$ Pa; $P_{He}$ = 1.20 x 10$^6$ Pa; $P_{O_2}$ = 2.67 x 10$^4$ Pa]**

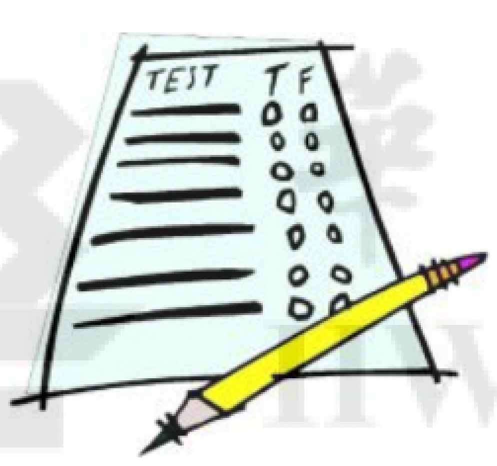
## 4 ASSUMPTIONS ABOUT IDEAL GASES

The kinetic theory of gases is a model used to describe the microscopic behaviour of gas particles and their interactions. This theory was developed in reference to **ideal gases** (refer to *section 2.2*), though it can be applied reasonably well to real gases. The following assumptions are about ideal gases:

1. The size of the gas particles is so small compared to the space between them that we can assume that the particles themselves have negligible volume. In other words, **the gas particles have negligible volume compared to the volume of the container**.

2. The **intermolecular forces of attraction** between gas particles are **negligible**.

3. **Collisions** between gas particles, and their collisions with the walls of the container, are **perfectly elastic;** i.e. there is no net loss or gain of kinetic energy during collision.




**Exam tip**

In the A-level examinations, you may be asked to recall the assumptions of the Kinetic Molecular Theory as applied to ideal gases. Assumptions 1 and 2 are the most important ones, particularly for the discussion on how real gases deviate from ideal behaviour.

If you are required to state more than 2 assumptions, assumption 3 can be included.

**Self-practice 4.1**

Argon exists in the atmosphere as a monoatomic inert gas.

**(a)** Using the Data Booklet, calculate the volume of an argon atom, indicating the units clearly. [Given: volume of a sphere is $^4/_3\pi r^3$, where r is its radius]

**(b)** Calculate the total combined volume of one mole of argon atoms.

**(c)** If the gas volume of 1 mole of argon is 24 dm$^3$ at room temperature and pressure, calculate the percentage of the total volume occupied by the argon atoms themselves.

**(d)** Based on your answer in (c), comment on whether it is justified to assume that argon at room conditions behaves ideally. State the relevant assumption applied to an ideal gas.

**[(a) 2.96 x 10$^{-29}$ m$^3$; (b) 1.78 x 10$^{-5}$ m$^3$ (or 1.78 x 10$^{-2}$ dm$^3$); (c) 0.0741%]**

### 4.1 Conditions for real gases to behave ideally

- At low pressures, the gaseous molecules are relatively far apart. The volume of the molecules themselves is negligible compared to the volume of the container. Thus, real gas molecules at low pressure can be approximated to have negligible volume. Also, intermolecular forces are negligible as the particles are far apart. Hence their behaviour at low pressures would approach that of ideal gases.

- At high temperatures, gas particles have enough kinetic energy to overcome intermolecular forces, which can thus be considered insignificant. As such, the behavior of real gases approach ideal gas behavior at high temperatures.

## 5 REAL GASES AND DEVIATION FROM IDEAL BEHAVIOUR

Based on the reasons given in Section 4.1, real gases would therefore deviate from ideal behaviour at high pressures and low temperatures.

Under these conditions, the following two assumptions about ideal gases are no longer valid, namely:

1) The gas particles have negligible volume compared to the volume of the container; and
2) The intermolecular forces of attraction between gas particles are negligible.

The behaviour of some real gases is compared with that of an ideal gas in Figure 4. In general, deviations from ideal behaviour become greater at higher pressures.

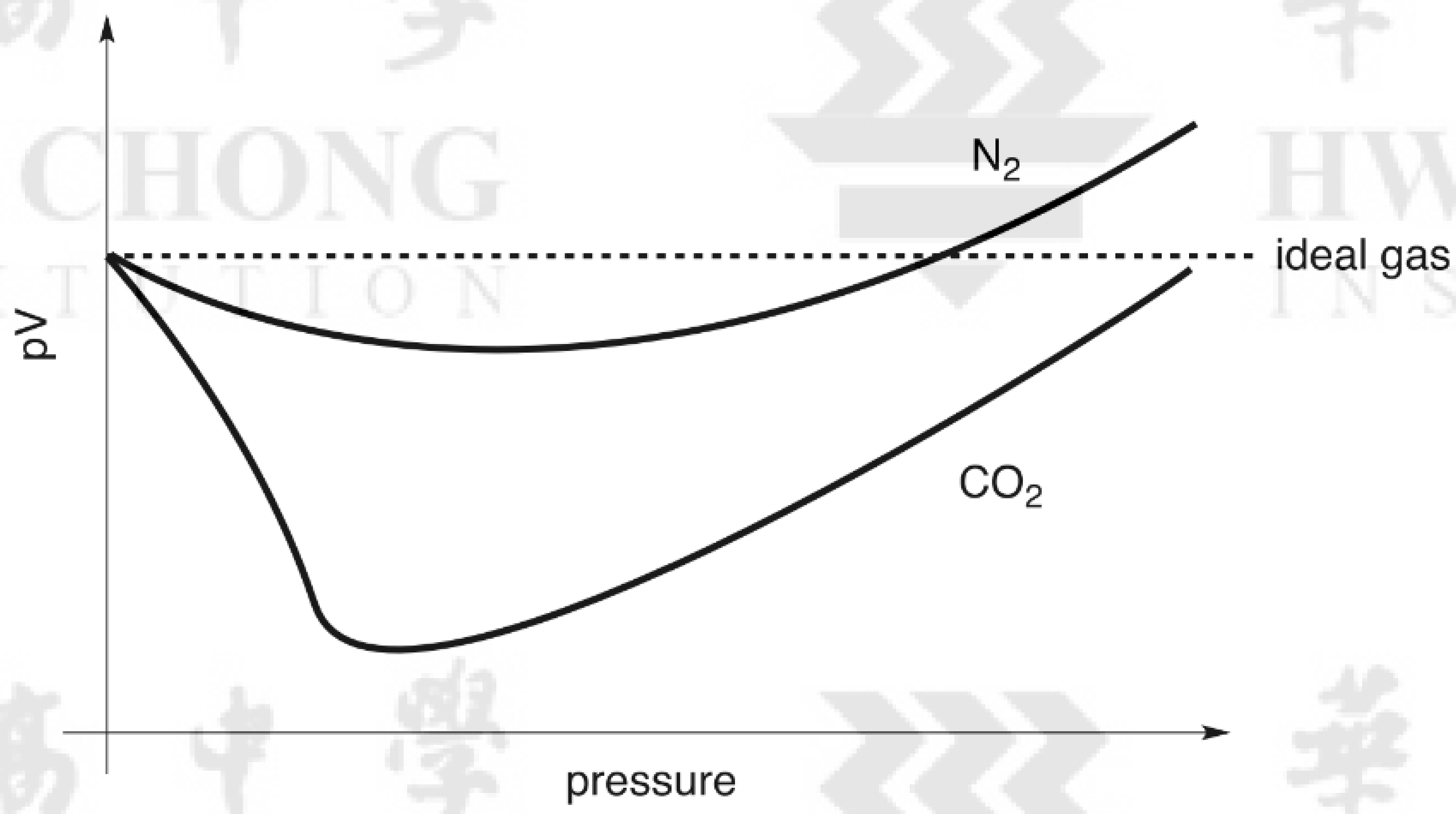



*Figure 4. Effect of pressure on the behaviour of several real gases at 300 K*

Figure 4 also shows how different gases deviate differently from ideal behaviour. Molecules with stronger intermolecular forces will violate assumption 2 and show greater deviation. For example, $CO_2$ has a larger electron cloud and hence stronger dispersion forces than $N_2$, hence $CO_2$ deviates more from ideal behaviour.

For molecules with similar electron cloud size, e.g. $NH_3$ ($M_r$ = 17.0) versus $CH_4$ ($M_r$ = 16.0), other intermolecular forces besides dispersion forces need to be considered. $NH_3$, with stronger hydrogen bonding, should deviate more from ideal behaviour than $CH_4$, with only intermolecular dispersion forces.

*Interesting to note*

*Liquefaction is a key property of real gases that is not predicted by the kinetic molecular theory of gases, as it requires the action of intermolecular forces (which the theory assumes to be negligible) in order to occur. In other words, ideal gases never condense into liquids!*

Figure 5 shows how one particular gas (nitrogen) behaves as a result of changing the temperature. The deviation is greatest at low temperatures.

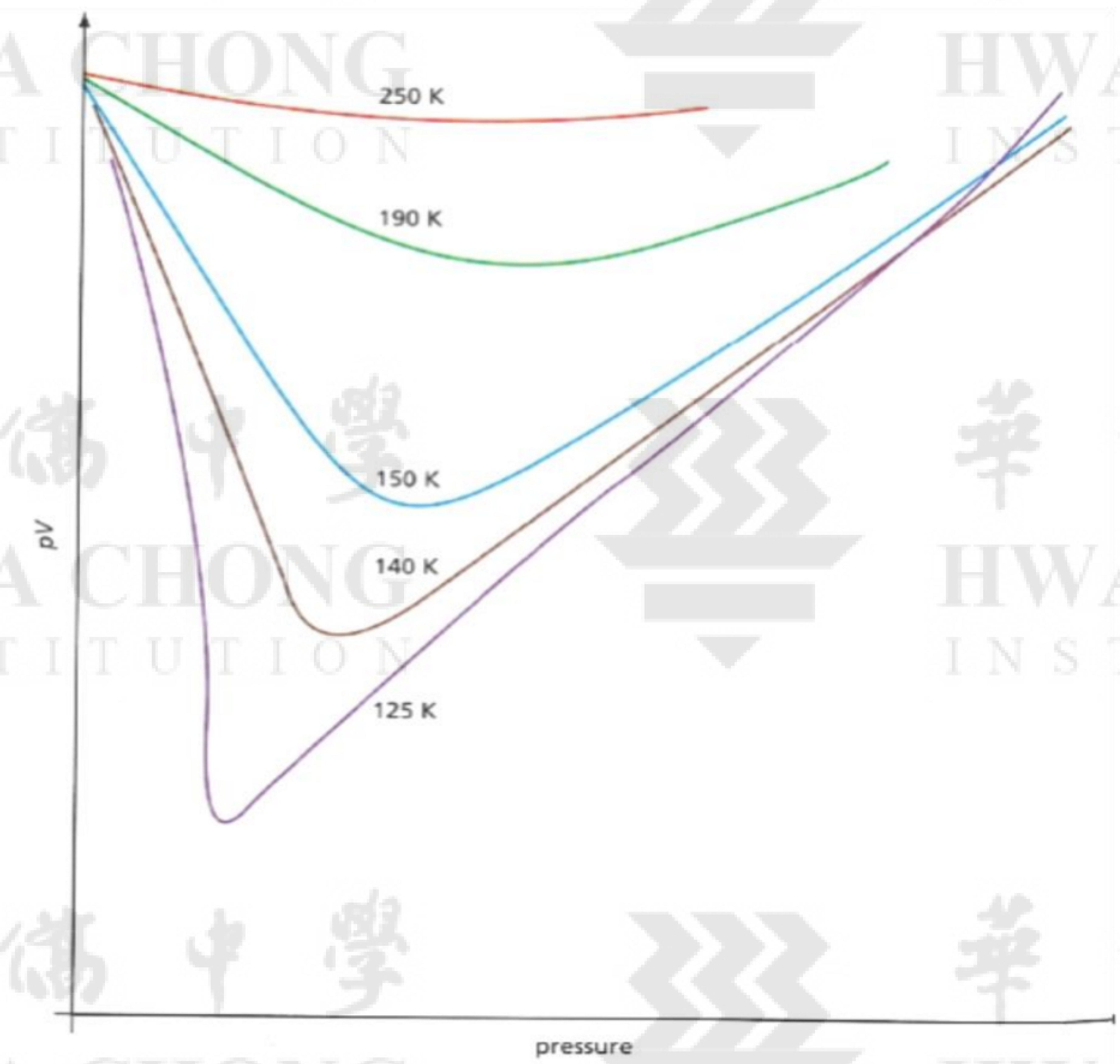


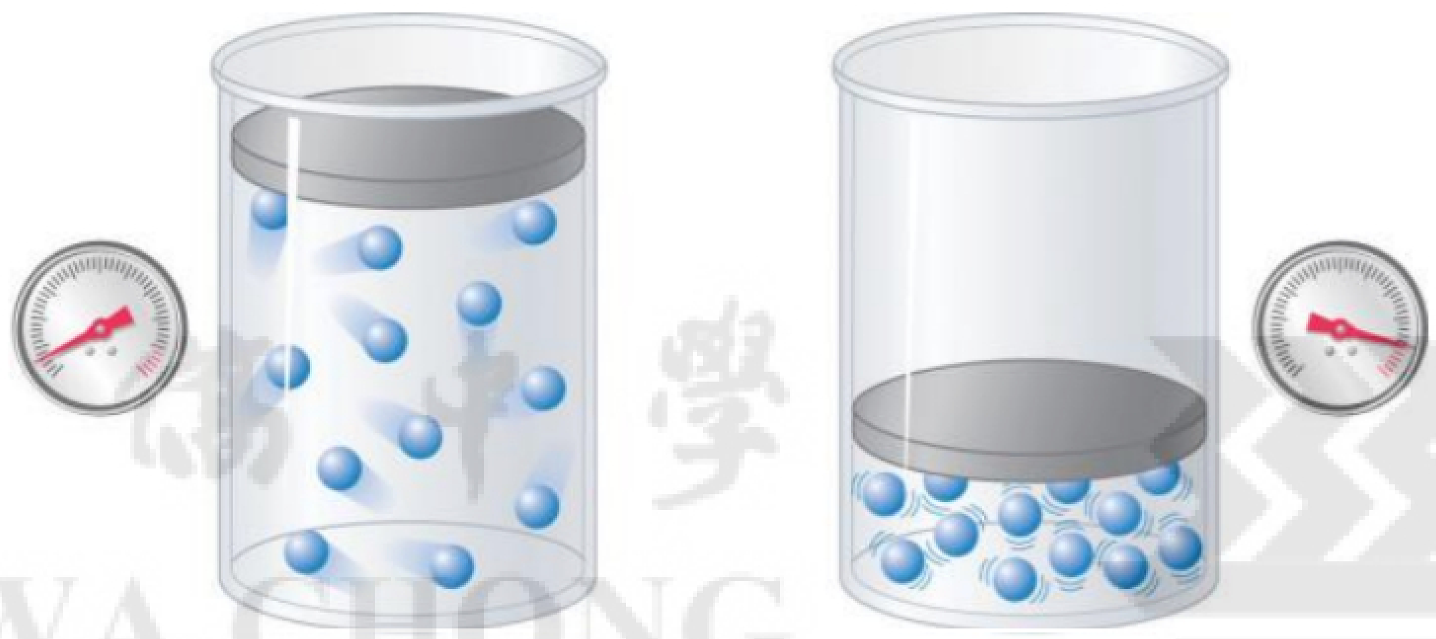

*Figure 5. Effect of temperature on the behaviour of nitrogen gas*

<u>Conclusion</u>: Real gases do not obey the ideal gas law, especially at high pressures and/or low temperatures.

### 5.1 Explaining deviations at high pressures

- The gas particles can no longer be considered to have negligible volume compared to the volume of the container.

At high pressures, the molecules take up a large portion of the volume of the container, resulting in a considerably smaller space in which the molecules can move. The volume of the molecules becomes an increasingly significant proportion of the volume of the container. Thus, it is no longer valid to assume that its volume is negligible, and so the gas deviates from ideal behaviour. (In fact, the total volume occupied by a real gas is actually greater than the volume predicted by the ideal gas equation.)



a) Low pressure b) High pressure

*Figure 7. Illustration of effect of non-zero particle size at low and high pressures*

### 5.2 Explaining deviations at low temperatures

- The intermolecular forces between gas particles become significant.

As temperature is lowered, the kinetic energy of the gas particles decreases, causing them to move more slowly and intermolecular forces to become more significant. This also causes collisions to become inelastic (such that assumption 3 is no longer valid either). Eventually, it reaches a point where the particles can no longer overcome the intermolecular forces, at which point real gases liquefy (condense to form a liquid) when cooled to below its boiling point.

## Did you notice?

Increasing the pressure on a real gas has opposite effects on the value of the product P × V. It increases the observed V, while decreasing the observed P. This effect is summarized in Figure 8 below:

- where the value of PV deviates below that of ideal gas, the effect of intermolecular forces dominates. The **stronger the intermolecular forces present, the greater the extent of deviation**;
- at higher pressures, where the value of PV deviates above that of ideal gas, the gas particles can no longer be considered to have negligible volume compared to the volume of the container

The competition between the two effects is responsible for the minimum observed in the plots of some of the gases.

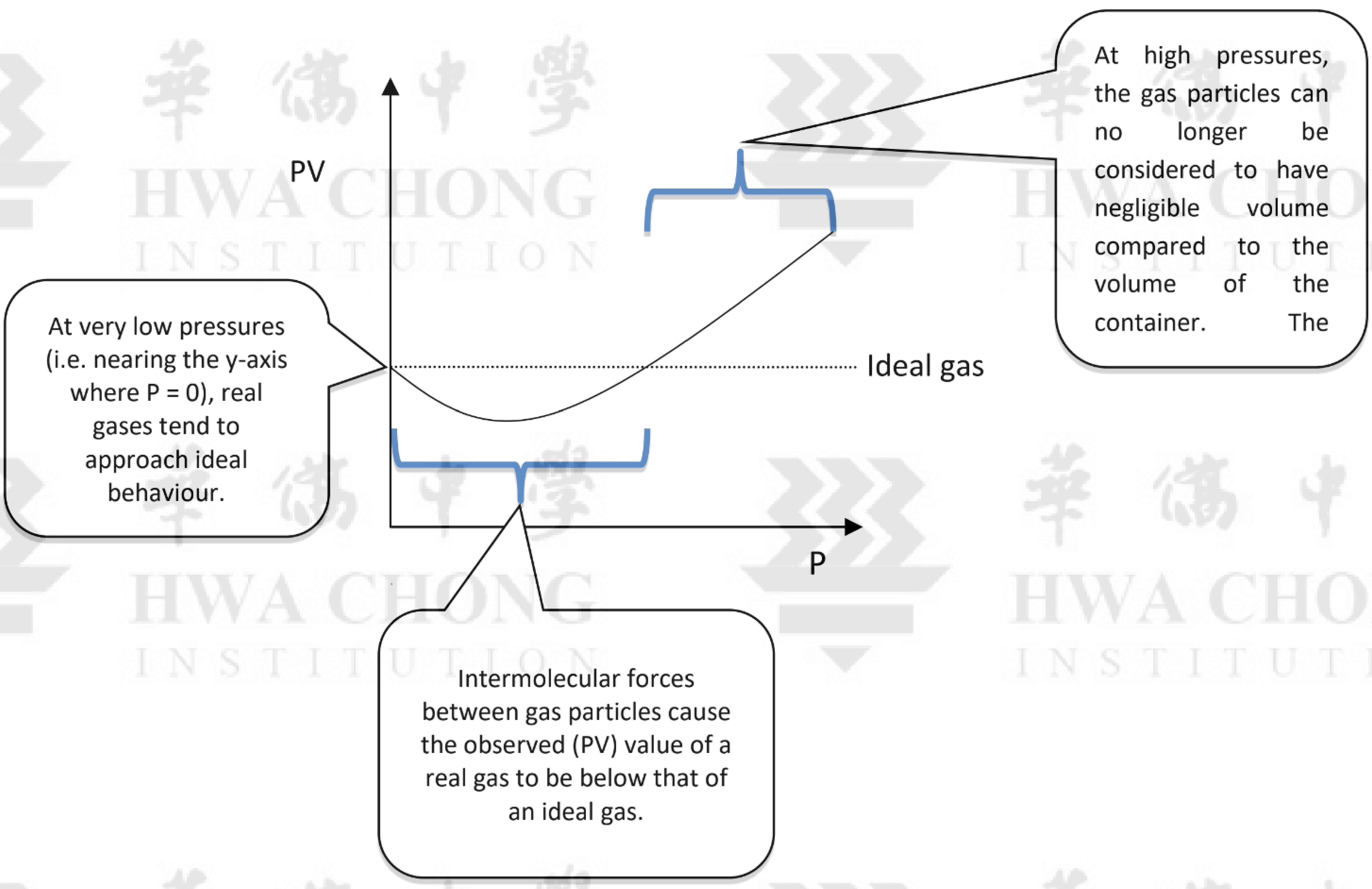
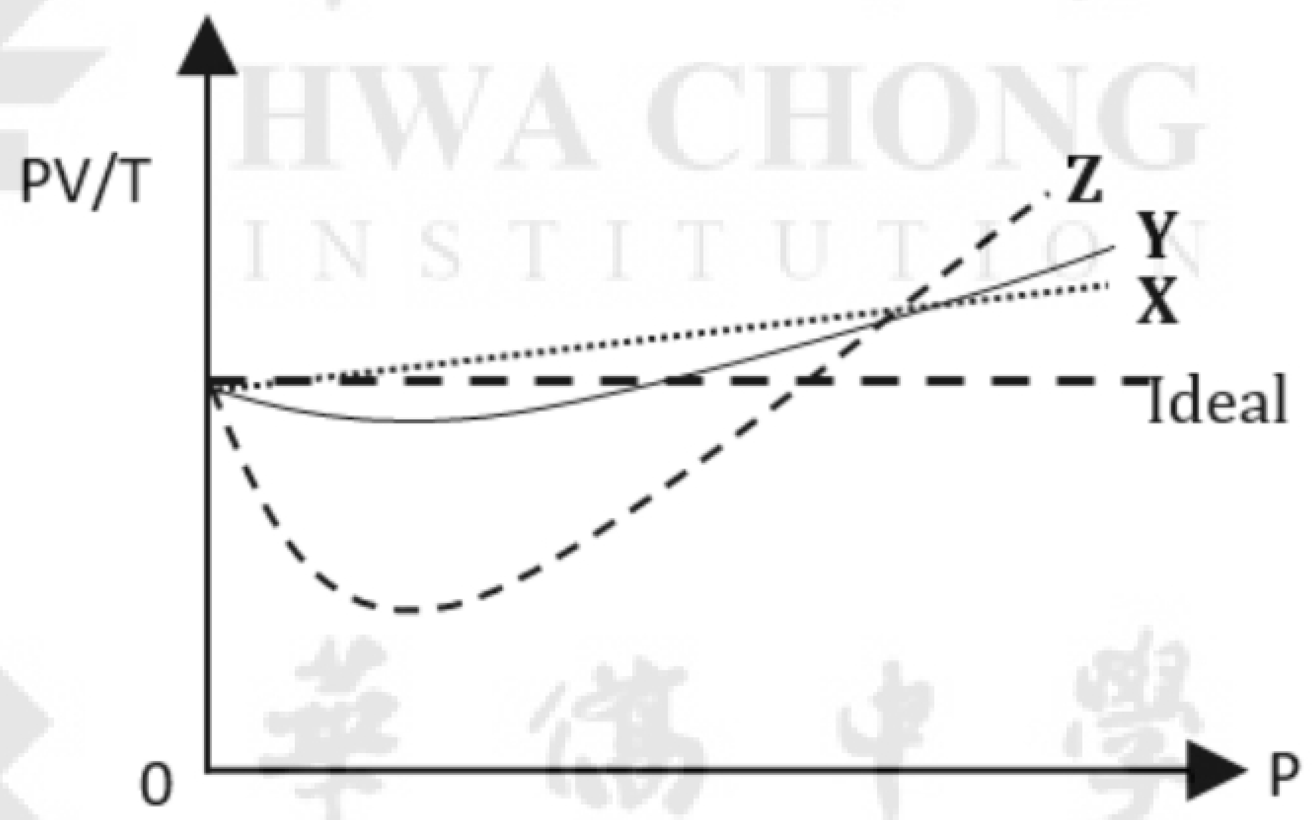



*Figure 8. Understanding the shape of a non-ideal gas curve*

**Lecture Exercise 5.1**

**Interpreting real gas behaviour from a plot PV/RT versus P**

The following curves represent the behaviour for equal amounts of three real gases and an ideal gas at a fixed temperature. Among the options given, what could the possible identities of real gases **X**, **Y** and **Z** be?



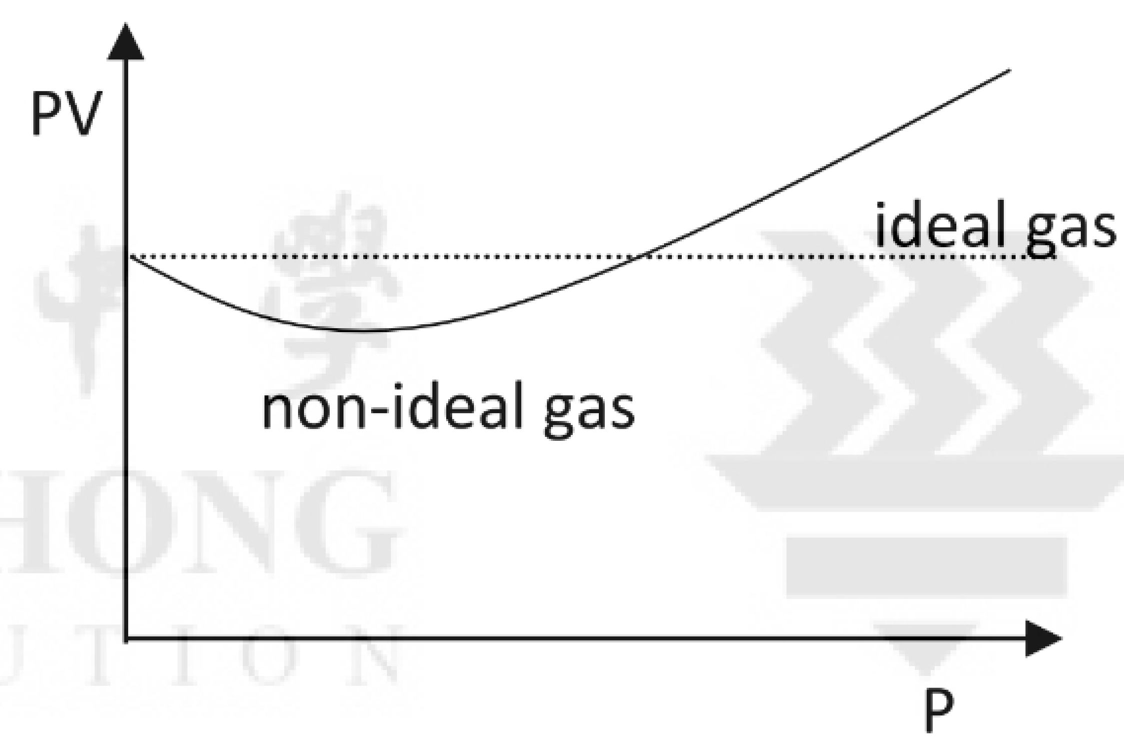

| | X | Y | Z |
|---|---|---|---|
| **A** | $NH_3$ | $N_2$ | $H_2$ |
| **B** | $H_2$ | $NH_3$ | $N_2$ |
| **C** | $N_2$ | $H_2$ | $NH_3$ |
| **D** | $H_2$ | $N_2$ | $NH_3$ |

***Working and solution:***

- The question mentions that 'equal amounts' of all gases are plotted – we therefore expect n to be the same, and thus their PV/T (which is = nR) values should also be the same when behaving ideally.
- Line Z has the greatest deviation below the ideal line and should represent the gas that has the strongest intermolecular forces, i.e. $NH_3$ (hydrogen bonding).
- Between the two remaining options, $N_2$ should show greater deviation (line Y) than $H_2$ (line X) as it has larger electron cloud (stronger dispersion forces)

**Self-practice 5.1**

The value of PV is plotted against P for two gases, an ideal gas and a non-ideal gas, where P is the pressure and V is the volume of the gas.




Which gas shows the greatest deviation from ideality?

| | | | |
|---|---|---|---|
| **A** | ammonia | **C** | methane |
| **B** | ethene | **D** | Nitrogen |

*[N2010/I/7]*

## 6 DISTRIBUTION OF MOLECULAR SPEEDS

The **average kinetic energy** of the gas particles is **directly proportional** to the **absolute temperature**. So at a particular temperature, all types of gaseous particles have the same average kinetic energy.

Although collectively the molecules in a gas sample have the **same *average* kinetic energy**, the individual molecules are moving at **different speeds**. There exists a distribution of speeds among the particles in a sample of gas. At a given temperature, heavier gases travel slower while lighter gases travel faster (recall: KE = ½mv$^2$). Figure 9 shows how the speed distribution varies with the molar mass of the gas for different gas samples at the same temperature.

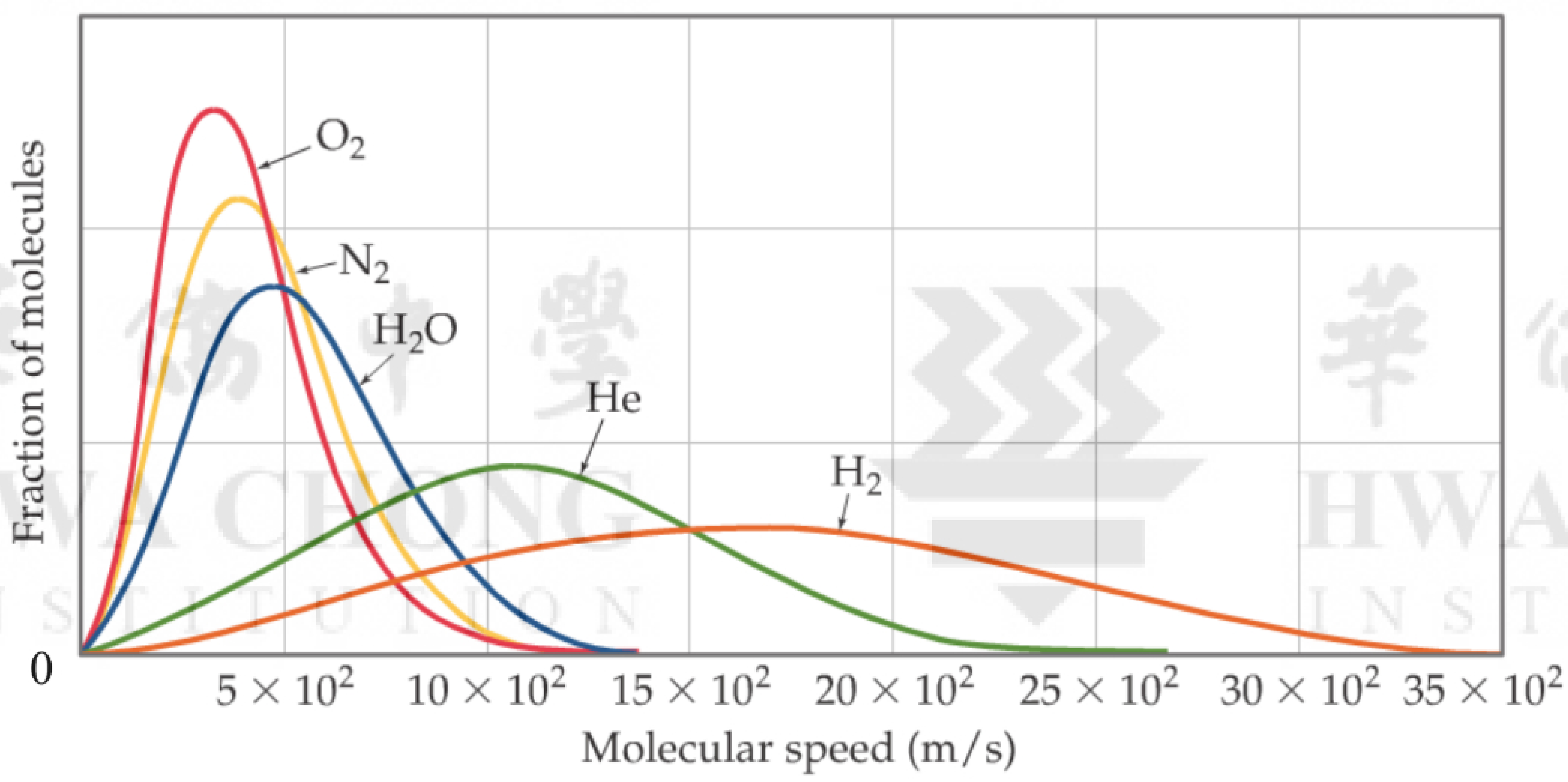



*Figure 9. Variation of speed distribution with molar mass at a given T*

For a gas sample at **different temperatures** as shown in Figure 10, the speed distribution of the molecules shifts toward higher speeds and becomes less sharply peaked as the temperature of the gas sample is increased. Even at low temperatures, a small number of molecules have high speed and kinetic energy. This number of molecules increases with temperature, while the number of molecules with low speed and kinetic energy becomes smaller but does not vanish.

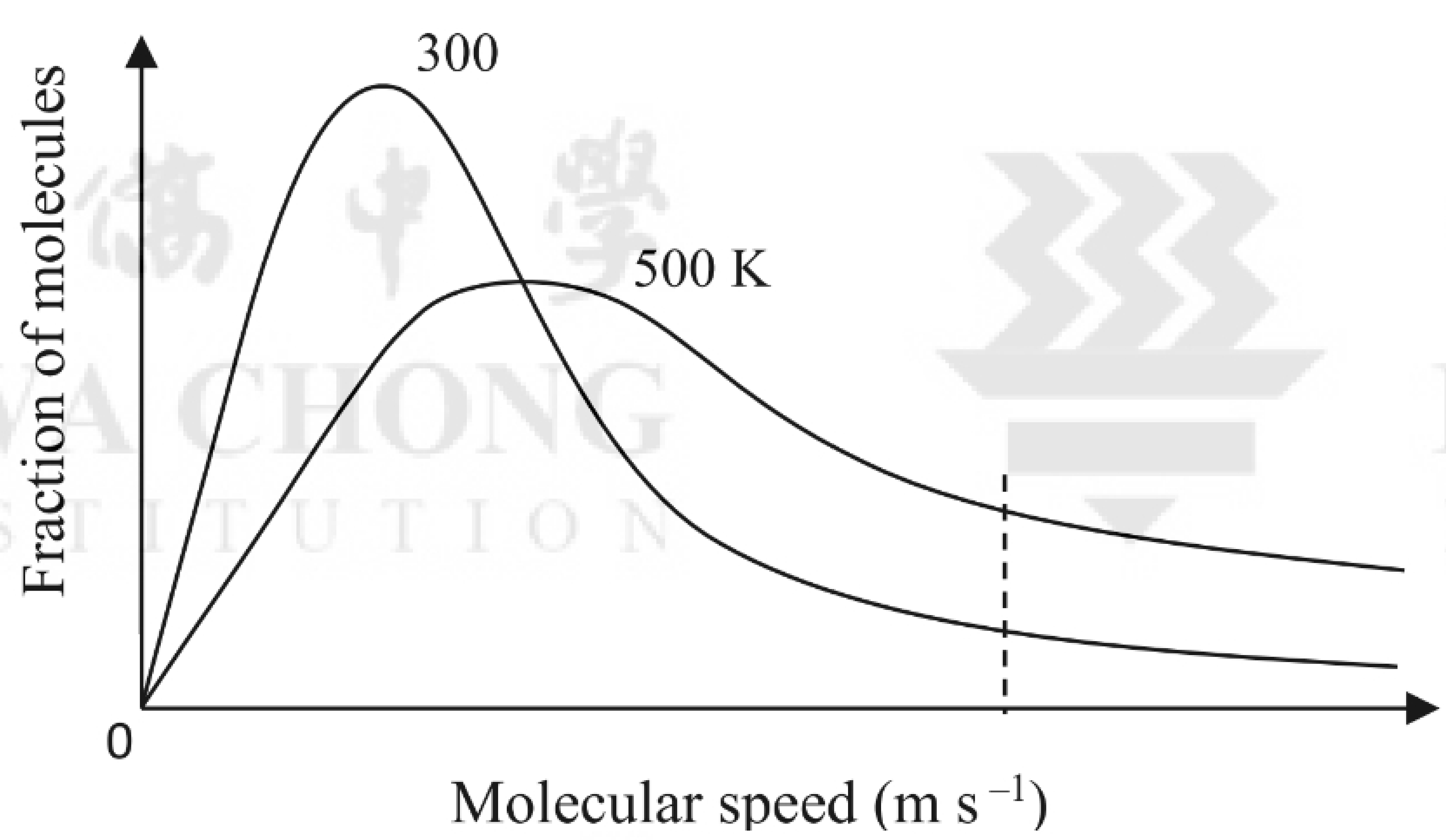



*Figure 10 – Variation of speed distribution with T* for a given gas sample

The above speed distributions are referred to as **Maxwell-Boltzmann distribution curves**, or simply, the **Boltzmann distribution curve**.

Note the following about Maxwell-Boltzmann distribution curves:

1. The examples above use speed on the horizontal axis. However, since kinetic energy of a molecule is proportional to the square of its speed, the graph would have the same shape if kinetic energy (or sometimes, simply 'energy') were used on the x-axis instead.

2. Common labels for the vertical axis include number of (gas) particles (or molecules), proportion of particles, or fraction of particles.

3. The *area under the curve* generally represents the **total number of particles** in the sample. So for a fixed amount of sample at different temperatures, the area should remain the same even as the curve shifts.

4. The *peak* of each curve represents the **most probable speed** (or most probable kinetic energy, depending on the x-axis label). As the temperature increases, the peak decreases in height and shifts to the right as the distribution of molecular speeds becomes more spread out.

5. All curves start at the *origin* (0,0) because in a gas sample **there are no particles with zero speed** (or zero kinetic energy). In other words, all gas particles must be moving.
   [The only exception is at 0 K, absolute zero, which is the theoretical lowest possible temperature, one at which all particles have zero kinetic energy and particle motion stops.]

6. The curves **do not show a maximum speed** (or kinetic energy) value and run asymptotically along the x-axis – i.e. the curves do not intersect the x-axis again as there is theoretically no limit to the amount of speed (or energy) a particle can have.

**LOOKING AHEAD**

In this topic, you have learnt to describe the behaviour of a gas in macroscopic terms of pressure, volume, temperature and number of moles (ideal gas equation). This will set the foundation for your learning in subsequent topics so keep in mind the following questions:

1. How to calculate partial pressures of gaseous species in reactions? (This will be especially useful for Topic 7 Chemical Equilibria)
2. How do you use the principles of mole concept in stoichiometric calculations involving reacting masses, volumes of gases and concentrations of solutions? (Topic 4 Reactions and Stoichiometry)

**PLANNING FOR AN EXPERIMENT THAT INVOLVES GAS COLLECTION**

This type of experiment can be used to determine *concentration*, *percentage purity*, *rate of reaction* etc. Common reactions which can produce a gas are:

- Acid + metal → $H_2$
- Acid + carbonate → $CO_2$
- Catalysed decomposition of $H_2O_2$ → $O_2$
- $H_2O_2$ + oxidising agent → $O_2$
- Decomposition of solids (e.g. Group 2 carbonate → $CO_2$)

- You may be required to suggest the mass and/or volume of chemicals to react. These can be calculated based on your chosen capacity of your gas collection container (e.g. gas syringe, burette). Volume of container must be reflected in diagram or written clearly in the procedure.

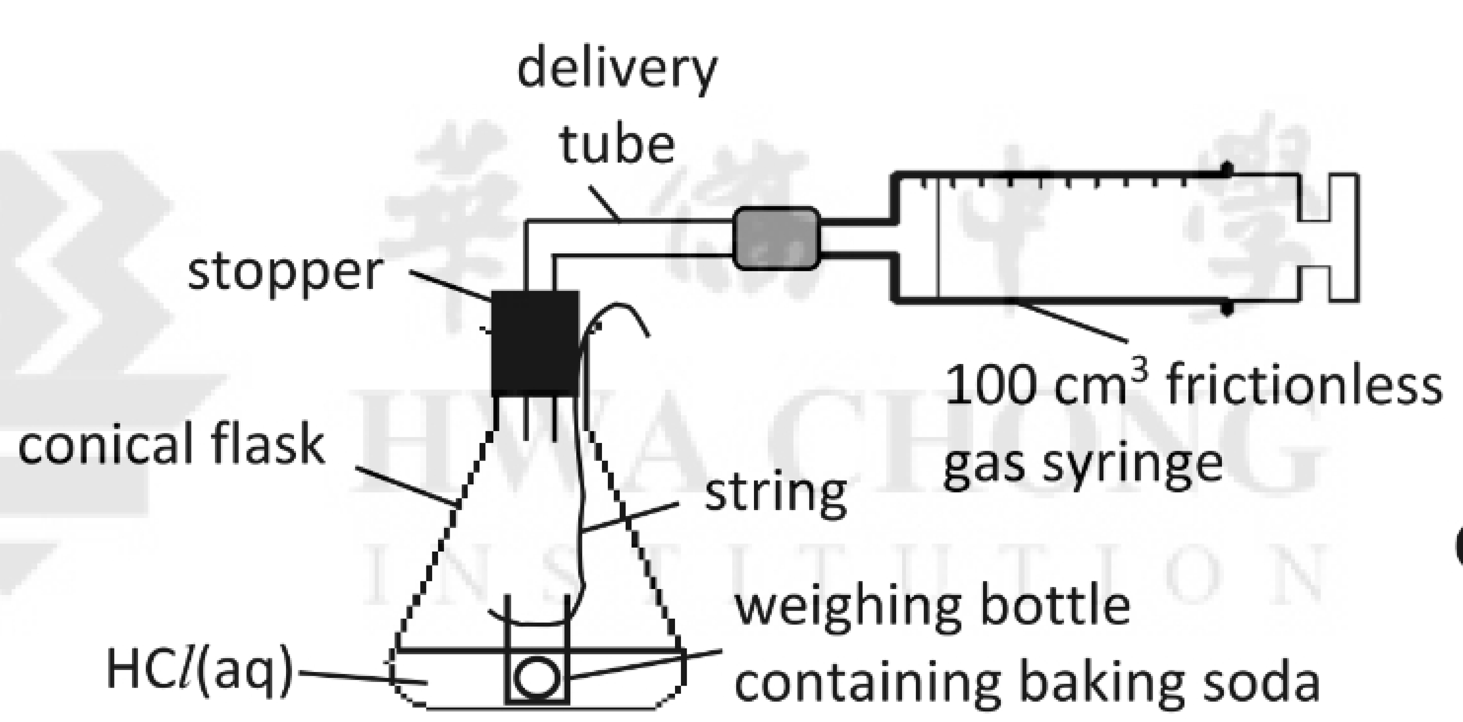
– The total volume of the reaction mixture should not exceed the capacity of your chosen reaction flask e.g. a 250 $cm^3$ conical flask.

– Ensure your proposed setup is a closed system (no loss of gas) and the chemicals are separated, ready to mix.

– The method of gas collection depends mainly on the solubility of the gas in water.
  - **Graduated gas syringe**: suitable for all gases. Typical capacity of gas syringe: 50 $cm^3$, 100 $cm^3$. The syringe must be graduated (draw markings in your diagram, or label *'graduated gas syringe'*).
  - **Downward-displacement of water** in an inverted burette (50 $cm^3$) or measuring cylinder (50 $cm^3$, 100 $cm^3$): suitable for gases that are sparingly soluble in water, e.g. $H_2$, $O_2$. A burette is more precise for measuring small volumes.

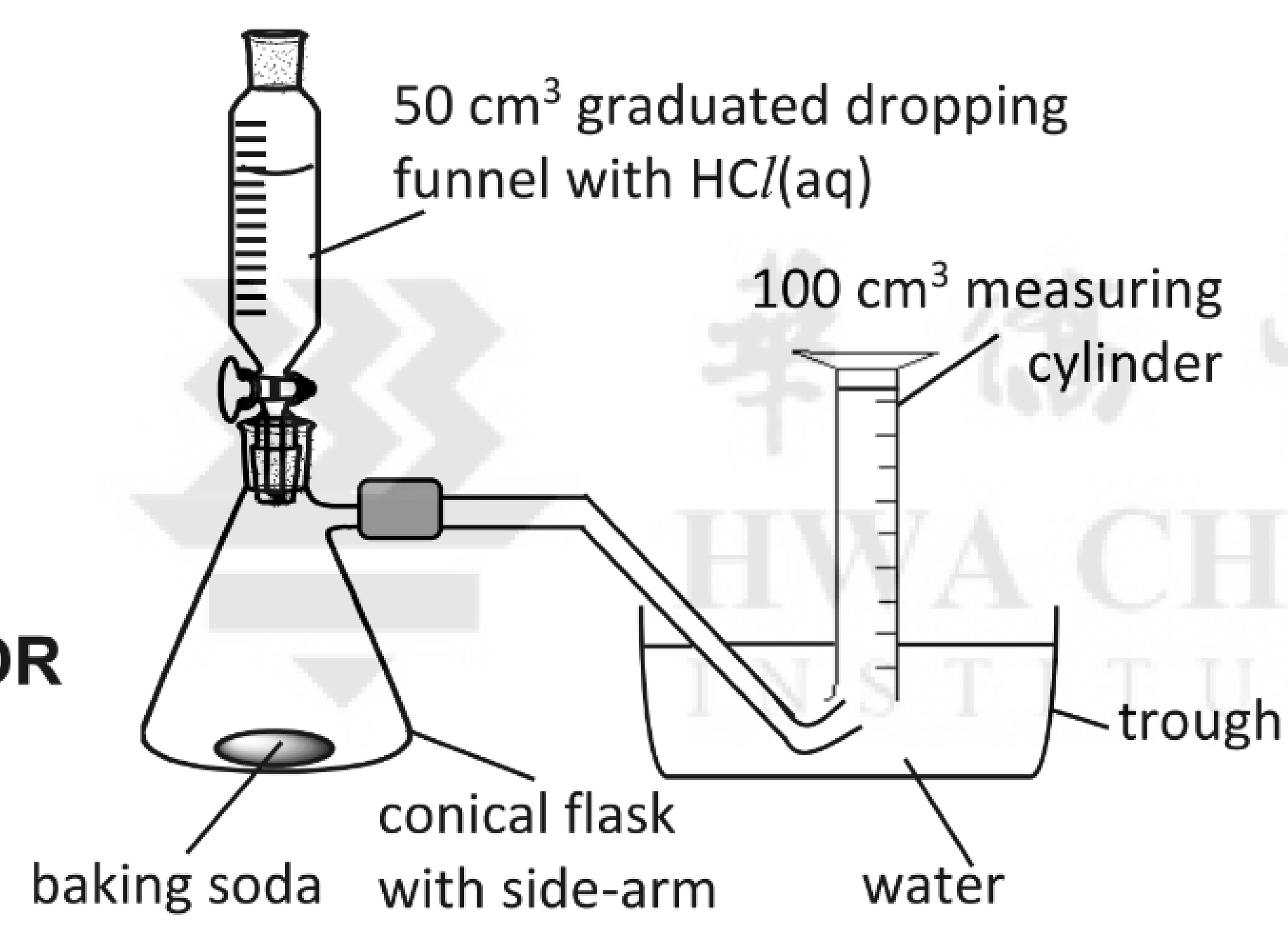
**Set-up**

A) Set–up with gas syringe




OR

B) Set-up with downward displacement of water



**Generic Procedure for (A)**

1. Using an electronic balance, weigh accurately about (mass) of (solid reactant) in a weighing bottle.

2. Using a measuring cylinder, transfer (volume) of (aqueous reactant) into a 250 $cm^3$ conical flask.

3. Carefully lower the weighing bottle containing (solid reactant) into the conical flask, ensuring the reactants do not mix. Insert the stopper to ensure a closed set-up.

4. Set up the apparatus as shown in the diagram (A).

5. Record the initial reading, $x$ $cm^3$, on the gas syringe.

6. Shake the conical flask to topple the weighing bottle, and continue swirling the conical flask to thoroughly mix the reactants.

7. When the volume reading has remained constant for a period of time, record the final reading, $y$ $cm^3$, on the gas syringe (or if it's for a kinetics experiment, "record volume of gas at appropriate time intervals"). The volume of gas collected is $(y - x)$ $cm^3$.

**Generic Procedure for (B)**

1. Using an electronic balance, weigh accurately about (mass) of (solid reactant) in a weighing bottle. Transfer the solid into a conical flask with side-arm. Reweigh the weighing bottle to account for any residual solid.

2. Set up the apparatus as shown in the diagram (B).

3. Fill a 50.0 $cm^3$ graduated dropping funnel with (aqueous reactant).

4. Record the initial reading, $x$ $cm^3$, on the (measuring cylinder/burette).

5. Take note of the initial reading on the graduated dropping funnel. Open the tap of the dropping funnel to add the (aqueous reactant) to the solid. When (volume) of (aqueous reactant) has been added, close the tap. Swirl the flask to thoroughly mix the reactants. (Note: There will be a corresponding volume of air displaced by the added liquid)

6. When bubbling through the (measuring cylinder/burette) has stopped, record the final reading, $y$ $cm^3$, on the (measuring cylinder/burette). The volume of gas collected is $(y - x - V_{displaced\ air})$ $cm^3$.

Note:

- It may sometimes be necessary to allow the set-up to equilibrate to room conditions, for example, if the reaction is highly exothermic. However, in a kinetics experiment where the volume of gas needs to be read at appropriate time intervals, it would not be possible to allow the set-up to equilibrate to room conditions (Refer to planning section in Topic 6 Reaction Kinetics.)
- If the reaction produces effervescence, it is possible to tell the reaction has stopped when no more effervescence is observed.