6. The Gaseous State

6.1 Introduction

Many chemical reactions produce gases, so chemists often find it necessary to handle gases. Only a few coloured gases can be seen. Some can be detected by their odour the majority are colourless and odourless. The detection of such gases is by chemical reactions.

The volume of a gas does not tell how much of it is available because any sample of gas will fill its container. However, knowledge of the volume and pressure of a sample of gas gives useful information about the actual mass of the gas. The variations in the volumes, pressures and temperatures of ideal gases are subject to certain simple laws known as the **gas laws**. The laws of Boyle and Charles are two of such. These laws enable us to determine how one of the important properties (volume, pressure or temperature) of a gas under a given condition will change its properties, if a variation occurs in another one.

But why are most gases invisible and why do they exert pressure? What are Boyleâ€™s and Charles laws and why do gases obey them? What other laws do gases obey? The kinetic theory of gases answers these and other questions about gases.

6.2 The kinetic theory of gases

The kinetic theory assumes that gases are made up of tiny elastic particles (molecules), moving about in random motion at temperatures above the absolute zero degree (O Kelvin = - 273Â°C). The higher the temperature the higher the velocity of the molecules.

Demonstration:

Drop a tennis ball from a height of about 2 metres onto a scale pan of a compression balance. Note the movement of the scale pointer. Note also that the ball rebounces possibly to drop again on the scale pan.

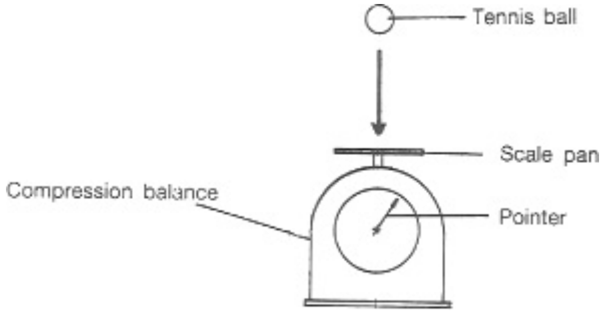

Figure 6.1 Compression balance

Like the tennis ball, the mobile molecules of a gas collide with the walls of their container and rebounce. They move in the opposite directions, after each collision. Force is exerted on the wall of the container as a result of each collision. This is responsible for the movement of the pointer in the demonstration above. Just as the reading of the scale depends on the mass and velocity of the ball, the force on the wall of a gas container depends on the mass and velocity of the gas molecules. Surely, if two balls strike the scale pan **at the same time, the magnitude of deflection of the pointer** will **be doubled.** Similarly the greater the number of molecules in the container the greater the force on the walls.

Assumptions of the kinetic theory

The kinetic theory makes the following assumptions about the molecules of a gas:

1. The molecules are so far apart and their sizes so small that the actual space which each molecule occupies is negligible compared to the distance between them.
2. The forces of attraction or repulsion between the molecules are negligible.
3. The molecules are in constant random motion in straight lines until they collide with each other or the wall of the containing vessel. These collisions are perfectly elastic, with the result that there is no loss of momentum on collision with the walls of their container or with each other.

Implications of the assumptions

The first assumption explains why gases are not visible if not coloured. Their molecules are very tiny and far apart. It also explains why gas samples can be compressed to smaller volumes. Compression involves bringing the molecules closer to one another. If the molecules are brought so closely together that inter-molecular attractive forces become high, the gas turns to liquid. The molecules are no longer free to move about freely but merely glide over each other.

The second assumption explains why a gas sample fills any space into which it is put. The lack of restriction means that the molecules can occupy any available space. The third assumption explains why gas molecules continue their motion indefinitely. If a gas molecule were to lose energy as a result of collision, it would eventually come to rest.

Calculation of pressure exerted by gas molecules

Imagine that there are *n* molecules of a gas in a cube of dimensions *1* cm. If one of these molecules moves with a velocity of c cm sec^{-1}, then the time it takes to move from a wall of the cube to an opposite wall and back will be

$$= \frac{2\ 1}{c} \text{ seconds}$$

The momentum of the molecule before collision with opposite wall is *mc,* if *m* is the mass of a molecule. The momentum after collision is mc since there is no loss of momentum. Change in momentum = ***mc â€“ (-mc)*** = 2 ***mc***.

The force on the wall is equal to the rate of change of momentum

$$i.e.\ F = \frac{\text{change in momentum}}{\text{time it takes for a change to occur}}$$

$$= \frac{2mc}{21/c}$$

$$= \frac{mc^2}{l}$$

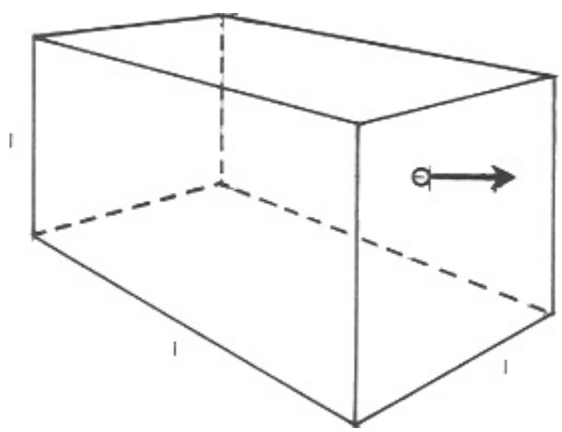

Figure 6.2 A cube containing *n* molecules of gas

Assuming that all the molecules move with the same velocity, at any point in time ⅓ of them will be moving along each of the three cartesian co-ordinates, x, y, and z.

The total force exerted on each wall will be $\frac{\frac{1}{3}nmc^2}{l}$.

But pressure $= \frac{\text{force}}{\text{area}}$

$\therefore$ Pressure on each wall $= \frac{\frac{1}{3}nmc^2/l}{l^2}$

$= \frac{\frac{1}{3}nmc^2}{l^3}$

Now, l^3 = volume (V) of the cube

Pressure on each wall $= \frac{\frac{1}{3}nmc^2}{V}$

Rearranging this equation, we have $PV = \frac{1}{3}nmc^2$, where P is the pressure.

The kinetic energy of a body in motion is given by Â½ mc^2. where m is the mass of the body, and c its velocity.

$PV = \frac{2}{3}n(\frac{1}{2}mc^2)$

i.e. $PV = \frac{2}{3}n \times$ k.e. of each molecule.

$= \frac{2}{3} \times$ k.e. of all the molecules.

6.3 Boyleâ€™s law

Molecules are known to acquire greater velocities at high temperatures and to move with low velocities at low temperatures. That is, their kinetic energy depends on temperature. At a constant temperature therefore, all molecules will possess the same kinetic energy. That is, at constant temperature, ⅔ k.e. is constant. This also implies that *PV* is constant at constant tenperature. Robert Boyle arrived at this law long before the kinetic theory was formulated. Boyleâ€™s law states that:

At constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.

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

or PV = constant

or $P_1V_1 = P_2V_2$

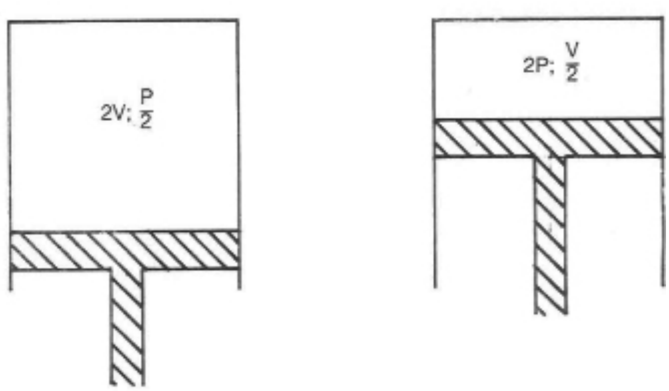

Figure 6.3 Boyleâ€™s law

Experiment 6.1 Investigating Boyleâ€™s law
Set up the apparatus shown in Figure 6.4

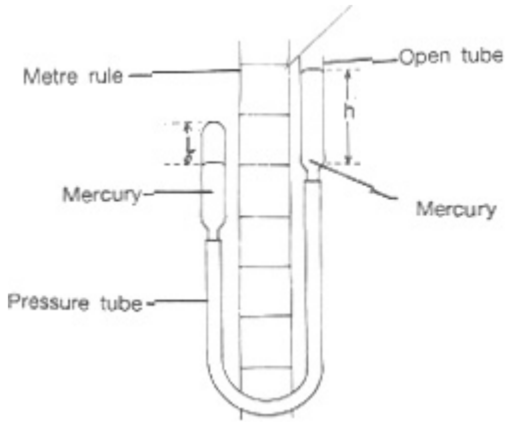

Figure 6.4 Boyleâ€™s law apparatus

Keeping the levels of mercury in the two tubes steady, take readings of l and h. Raise or lower the open tube to different heights and take corresponding l and h reading. Repeat this five times. Note the atmospheric pressure during the experiment. The pressure of the trapped air for each reading is equal to the atmospheric pressure plus h, if the mercury level in the open tube is above that in the closed tube; or minus h, if the level of mercury in the open tube is below that in the closed tube. Since the closed tube is of uniform, cross-section, the volume of air in it is proportional to the height, 1.

Calculate PV. for each set of readings. Record your readings as in Table 6.1

TABLE 6.1

l (cm)	h (cm)	P = (atm. pressure + h)	PV	$\frac{1}{P}$

Plot a graph of V against 1/P. A straight line graph passing through the origin is obtained. The slope of that graph is equal to PV.

The PV values in Table 6.1 should be constant, within the limits of experimental error.

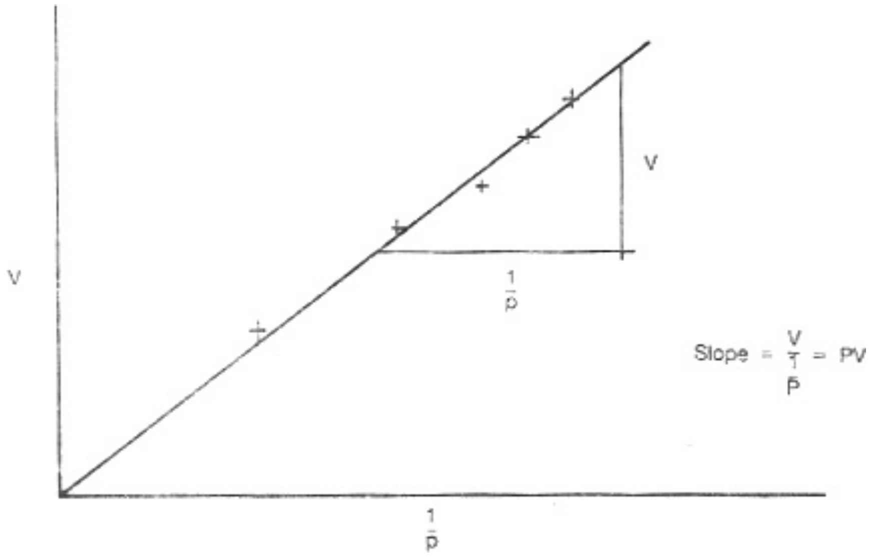

Figure 6.5 Graph of V against $\frac{1}{P}$

Worked Examples

(1) 345 dm^3 of air at atmospheric pressure is compressed to 23 atmospheres in a compression tube. What volume will it occupy in the tube?

Solution

Substituting in $P_1V_1 = P_2V_2$, we get

$1 \times 345 = 23 \times V_2$

$\therefore V_2 = \frac{345}{23} dm^3 = 15 dm^3$

That is, the volume occupied is 15 dm^3.

(2) If the air pressure at an altitude of 5 km above sea level is 4.8 Ã— 10^4 Nm^{-2}, (48000Nm^{-2}); what volume will 1kg of air occupy at that altitude if it occupies 0.75 m^3 at sea level? What will be the change in the density of the air? Assume that temperature remains constant. Atmospheric pressure of air at sea level is 105300 N m^{-2}.

Solution

Substituting in $P_1V_1 = P_2V_2$
$48000 \times V = 105300 \times 0.75$

$$\therefore V = \frac{105300 \times 0.75}{48000}$$
$$= 3.125m^3$$

Density of air at sea level $= \frac{1kg}{0.75m^3}$
$= 1.333kg\ m^{-3}$

Density at an altitude of 5km above sea level
$$= \frac{1kg}{3.125m^3}$$
$$= 0.3kg\ m^{-3}$$

Thus the density changes from 1.33 to $0.3kg\ m^{-3}$

Exercise 6A

If the volume of gas inside the cylinder of a car engine is reduced to 1/10 of the original volume, by how much is the pressure increased? Assume that temperature remains constant.

6.4 Charlesâ€™ law

From our assumptions and derivation we arrived at the relationship
PV = ⅔ k.e.
for a fixed mass of gas. Gas molecules acquire greater kinetic energy and move faster when temperature rises, but lose kinetic energy and move more slowly when temperature falls. That is, kinetic energy (k.e.) varies directly with temperature. Mathematically, we can write:
kinetic energy Î± T
or kinetic energy = kT, where k is a constant.

PV = ⅔ kT
or V/T = ⅔ k/P
But ⅔k/P is constant at constant pressure.
Therefore, V/T is constant at constant pressure.
Jacques Alexandre Charles discovered this law in 1787. Charlesâ€™ law states that:

the volume of a fixed mass of gas at constant pressure is directly proportional to its absolute temperature.

Mathematically $V \propto T$
or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

The **absolute temperature** (temperature in degrees kelvin, is equal to the celsius (Centigrade) temperature, plus 273.
O K = â€“273Â°C.

Theoretically all gases have zero volume at zero degree kelvin (absolute zero temperature). All gases however turn to liquid before that temperature is reached.

A fixed mass of gas contains a certain number of molecules. A rise in temperature is accompanied by a rise in the kinetic energy of the molecules. For pressure to remain constant the molecules must move a longer distance before they collide with the wall of their container. That is, volume will increase.

Experiment 6.2 Investigating Charlesâ€™ Law

Use the apparatus in Figure 6.6 for this experiment.

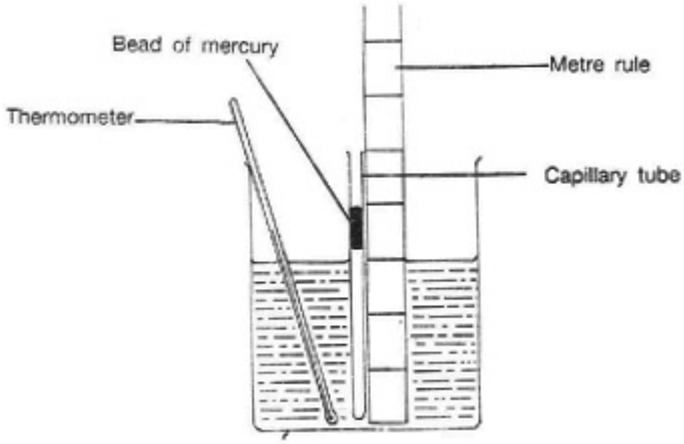

Figure 6.6 Charlesâ€™ law apparatus

Introduce a bead of mercury into a capillary tube sealed at one end. Immerse the capillary tube in a beaker of water as shown in Figure 6.6. Record the temperature of the water. With the aid of a metre rule record the volume of air trapped in the capillary tube by the bead of mercury. (The length of the column of air is proportional to its volume).

Put some ice-salt mixture into the beaker and again record the temperature and length of the column of trapped air.

Take the readings at various other temperatures while heating the beaker.

Plot a graph of volume (length of air column), against temperature. Extrapolate the graph to the temperature axis to obtain the temperature at zero volume.

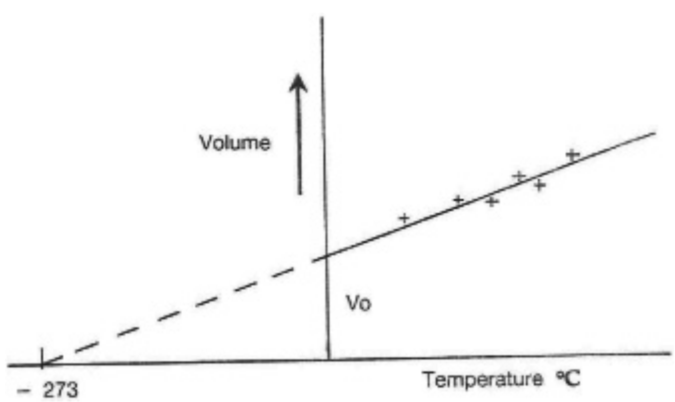

Figure 6.7 Graph of volume vs temperature

The graph intercepts the temperature axis at â€“273Â°C. The slope of the graph is equal to the constant, V/T. This slope, divided by V_0 (Volume at 0Â°C), gives the mean coefficient of expansion. This is expansion per degree rise in temperature. It is equal to 1/273. That is, for every Â°C rise in temperature the volume increases by 1/273 of the original volume.

Worked Example

105 cm^3 of hydrogen gas is liberated by the action of 0.3g of zinc on excess dilute tetraoxosulphate (VI) acid at 85Â°C. What volume would the gas occupy at room temperature of 25Â°C?

Solution

Substituting in $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

$$\frac{105}{(85 + 273)} = \frac{V_2}{(25 + 273)}$$

$$\frac{105}{358} = \frac{V_2}{298}$$

$$\therefore V_2 = \frac{105 \times 298}{358}$$

$$= 87.4 \text{ cm}^3$$

Exercise 6B

A certain gas sample has a volume of 50cm^3 at 27Â°C. If its pressure remains constant, what volume will it have at 37Â°C? What will be the decrease in its density if the mass of the gas is 0.025g?

6.5 The general gas equation

Refer back to the derivation of the equation

$PV = \frac{2}{3}$k.e. (Section 6.2)

Since kinetic energy (k.e.) is proportional to temperature, T, we got

$PV = \frac{2}{3}kT$, where k is a constant.

$$\frac{PV}{T} = \frac{2}{3}k$$

that is $\frac{PV}{T}$ is a constant.

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

This relationship is the ideal gas equation. It is more useful than either Boyleâ€™s or Charlesâ€™ law because it is more usual for all three variables, pressure, volume and temperature to change for gas samples. Use is made of this equation in determining the new volume, pressure or temperature of a gas when the original set of conditions have changed. It also enables us to calculate the quantity (mass and volume) of gaseous products obtained in reactions, by application of Avogadroâ€™s law.

When using the gas laws the temperature, T, must be in absolute (Kelvin) units, (that is Â°C + 273). The standard conditions of temperature and pressure (s.t.p.) are 0Â°C (273 K), and one atmosphere. (105325 N m^{-2} or 760 mm of mercury) respectively.

Worked Example

What volume will 100 cm^3 of hydrogen, measured at 25Â°C and 120000 N m^{-2} pressure occupy at s.t.p?

Solution

Substitute in $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{120000 \times 100}{(273 + 25)} = \frac{105325 \times V_2}{273}$$

$$\therefore V_2 = \frac{120000 \times 100 \times 273}{105325 \times 298}$$

$$= 104.37 \text{ cm}^3$$

Exercise 6C

What volume will 22.4 dm^3 of oxygen, measured at s.t.p. occupy at 25Â°C and 1.12 Ã— 10^5 (i.e. 112000) N m^{-2}? The standard pressure is 105325 N m^{-2}.

6.6 Daltonâ€™s law of partial pressures

This law enables us to add and subtract pressures as we do masses, It states that:

The total pressure exerted by a mixture of gases which do not react is equal to the sum of the partial pressure each gas would exert if it alone occupied the volume occupied by the mixture.

The kinetic theory of gases explains this law perfectly well. Since the gases in the mixture do not react, the molecules of each gas behave as if the other gas molecules were not present. Their rates of collision with the walls of the container, and hence the pressures they exert, are not affected by the presence of the other gas molecules.

When gases are collected over water, the total pressure exerted equals the pressure of the gas plus the water vapour pressure at the temperature of collection, since the gas is collected along with water vapour. To get the pressure of the gas alone, we subtract the water vapour pressure.

Worked Example

If 600cm^3 of oxygen was collected over water from the decomposition of 2.45g of potassium trioxochlorate(V) at 1 atmosphere pressure (105325 N m^{-2}) and 25Â°C, calculate the volume of the dry gas at standard temperature and pressure, (s.t.p.). The water vapour pressure at 25Â°C is 1663 N m^{-2}.

Solution

Pressure of the dry oxygen = (105325 â€“ 1663) N m^{-2}

= 103662 Nm^{-2}

Substituting in $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

we have,

$$\frac{103662 \times 600}{(273 + 25)} = \frac{105325 \times V_2}{273}$$

$$\therefore V_2 = \frac{103662 \times 600 \times 273}{105325 \times 298}$$

$$= 590.5cm^3$$

Exercise 6D

Which is denser, wet carbon(IV) oxide or the dry gas? Explain your answer. Which will have the greater pressure 100 cm^3 of wet carbon(IV) oxide at 25Â°C or 100 cm^3 of the dry gas at the same temperature?

6.7 Grahamâ€™s law of diffusion

Grahamâ€™s law is a direct deduction of the kinetic theory of gases. If gas molecules are in constant random motion we would expect the heavy molecules to move more slowly than lighter ones. What one molecule gains in mass, it loses in velocity. The law which illustrates this is named after Thomas Graham (1805 â€“ 1869). Grahamâ€™s law of gaseous diffusion states that:

the rates at which gases diffuse are inversely proportional to the square roots of their vapour densities.

That is,

$$r \propto \frac{1}{\sqrt{d}}$$

$$\text{or} \quad \frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$

Where r_1 and d_1 are the respective rate of diffusion and density of one gas; and r_2, d_2 the rate of diffusion and density of a second gas.

Since the molar mass of a gas is its vapour density multiplied by 2, the law offers us a method of determining the molar mass of gaseous compounds. If the rate of diffusion of a gas of known vapour density is determined, and the rate of diffusion of an equal volume of an

unknown gas is also determined, then the molar mass of the unknown gas can be calculated. The shorter the time taken to diffuse through a given distance, the higher the rate of diffusion. Therefore, the lighter gas diffuses out within a shorter time.
We can write that,

$$\frac{r_1}{r_2} = \frac{t_2}{t_1} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$$

Experiment 6.3 Comparing the rates of diffusion of hydrogen and carbon(IV) oxide

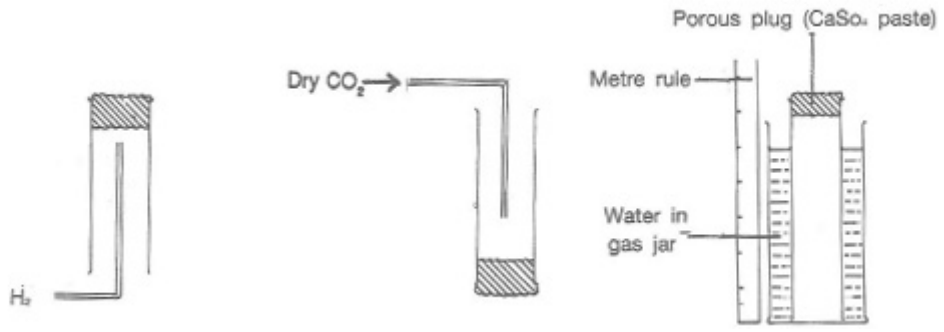

Figure 6.8 Rates of diffusion of hydrogen and chlorine

Make a paste of calcium tetraoxosulphate(VI) in water. Use this paste to plug one end of a glass tube that is about 20cm long. Leave overnight to set.

Fill the glass tube with hydrogen. Immerse the glass tube, with the plugged end up, into a gas jar containing water. By means of a metre rule, record the time it takes for water to rise to a height of 5, 10, and 15 cm, into the glass tube as the gas diffuses out through the porous plug. Repeat the experiment with carbon(IV) oxide.
Find the ratio:

time for water to rise, 10cm as H_2 diffuses
time for water to rise, 10cm as CO_2 diffuses

Is the ratio equal to $\frac{\sqrt{\text{molar mass of } H_2}}{\sqrt{\text{molar mass of } CO_2}}$

i.e. $\frac{\sqrt{2}}{\sqrt{44}}$?

Calculate the ratios for a rise of water level of 5 and 15cm.
Do the results agree with the theoretical prediction?

Worked Examples

1. A glass tube fitted at one end with a disc of porous material and

open at the other, was filled with nitrogen and inverted in a larger beaker of water as shown in the Figure 6.9. After some time the water in the tube rose to the level of that in the beaker.

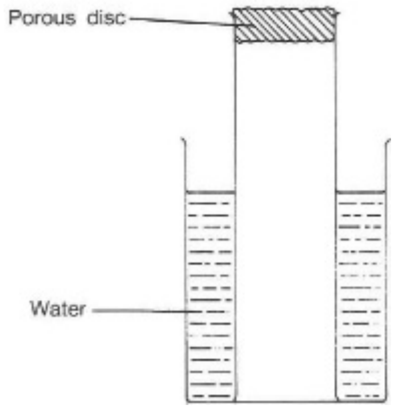

Figure 6.9

The experiment was repeated with hydrogen and methane.

(a) Explain why the water rose inside the tube

(b) Calculate the relative molecular masses of

(i) N_2, (ii) H_2 and (iii) CH_4

(H = 1, N = 14, C = 12)

(c) In which of the experiments would you expect the level of water to rise most slowly? Explain your reasoning.

(WAEC)

Solution

(a) Water rises inside the tube because gas diffuses out of it through he porous disc. The rate at which water rises in the tube is the same as the rate at which gas diffuses out. When the pressure inside the tube is equal to atmospheric pressure the level of water stops rising in the tube. At that time the rate of diffusion of gas out of the tube is equal to the rate of diffusion of gas into it from outside:

(b) The relative molecular masses of nitrogen, hydrogen and methane are (2 Ã— 14) :(2 Ã— 1): 12 + (4 Ã— 1)

= 28 : 1 : 16 respectively.

(c) The rate at which water rises in the tube is equal to the rate of diffusion of each gas.

From Grahamâ€™s law, rate of diffusion of each gas is proportional to the reciprocal of gas vapour density.

∴ The rates are proportional to the reciprocal of the densities or the relative molecular masses of the gases (since density is proportional to molar mass).

∴ Relative rates of diffusion of the three gases are:

$$= \frac{1}{\sqrt{28}} : \frac{1}{\sqrt{2}} : \frac{1}{\sqrt{16}}$$

$$= \frac{1}{5.1} : \frac{1}{1.4} : \frac{1}{4}$$

$$= 0.196 \quad 0.7 \quad 0.25$$

Therefore the level of water rises most slowly when nitrogen is in the tube.

2. If it takes 3 seconds for hydrogen sulphide to diffuse from one corner of a laboratory where it is produced to another corner, how long will it take sulphur(IV) oxide to traverse the same distance?

Solution

Substitute in $\frac{t_1}{t_2} = \frac{\sqrt{M_1}}{\sqrt{M_2}}$

Molar mass of H_2S $= (1 \times 2) + 32 = 34$

Molar mass of SO_2 $= 32 + (16 \times 2) = 64$

$$\frac{3}{t_2} = \frac{\sqrt{34}}{\sqrt{64}}$$

$$t_2 = \frac{3 \times \sqrt{64}}{\sqrt{34}} = \frac{3 \times 8}{5.83} = 4.115 \text{ seconds.}$$

It takes 4.12 seconds for sulphur(IV) oxide to traverse the same distance.

Exercise 6E

100 cm^3 of oxygen diffuses through a porous pot in 3 seconds. How long will it take 150 cm^3 of sulphur(IV) oxide to diffuse through the same pot?

6.8 Gay Lussacâ€™s law of combining volumes

Henry Cavendish was a pioneer worker in the study of ratio of combining volumes of gaseous reactions. He established that at constant temperature and pressure, hydrogen combines with half its volume of oxygen to form water. Gay Lussac carried on the work with hydrogen and chlorine, and with carbon(II) oxide and oxygen. From his results he stated the law which today bears his name.

$2H_2(g)$	$+$	$O_2(g)$	$\rightarrow$	$2H_2O(g)$
2 volumes		1 volume		2 volumes (Cavendish)
$H_2(g)$	$+$	$Cl_2(g)$	$\rightarrow$	$2HCl(g)$
1 volume		1 volume		2 volumes (Gay Lussac)
$2\,CO(g)$	$+$	$O_2(g)$	$\rightarrow$	$2CO_2(g)$
2 volumes		1 volume		2 volumes (Gay Lussac)

Gay Lussacâ€™s law states that:

When gases combine chemically, they do so in volumes which bear a simple ratio to one another, and to the volume of the product if gaseous, temperature and pressure remaining constant.

Experiment 6.4 Reproducing Cavendishâ€™s Experiment With Hydrogen and Oxygen

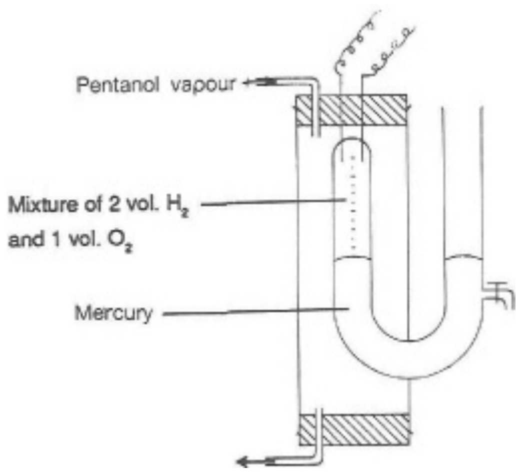

Figure 6.10 Apparatus for Cavendishâ€™s Experiment

This experiment need not be carried out. Two platinum wires are sealed into a closed end of a U-tube. That end of the U-tube is graduated to react volumes. Hydrogen and oxygen are first put into the U-tube in a volume ratio of 2:1. The gaseous mixture is trapped with mercury as shown in Figure 6.10. The closed end of the U-tube is enclosed in a jacket through which pentanol vapours are passed. By running out some mercury from the tap, the pressure of the gaseous mixture is reduced. The open end of the U-tube is corked so that mercury does not spill over when the gaseous mixture reacts. The volume of the mixture is recorded and a spark of electricity passed through the gap between the two platinum wires. This explodes the mixture so that they react. Because the explosion takes place at reduced pressure no harm is done. After the explosion the apparatus is allowed to cool. The passage of pentanol vapour ensures that the steam formed by the explosion does not condense. The levels of mercury in both arms of the U-tube are then adjusted and made equal and the volume of steam produced recorded. It should be two-third of the volume of the gaseous mixture.

After recording this volume, the passage of pentanol vapours is stopped and the steam allowed to condense. As the vapour condenses, mercury rises to the top of the closed end of the U-tube an fills it up, showing that no gas was left. That is, the two volumes of hydrogen reacted with one volume of oxygen to form two volumes of steam. So the ratio of reacting volumes of hydrogen and oxygen, and of steam formed is 2:1:2.

Experiment 6.5 Reproducing Gay Lussacâ€™s Experiment With Hydrogen and Chlorine

This experiment may not be performed.

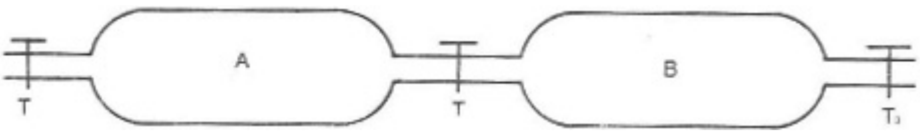

Figure 6.11 Apparatus for Gay Lussacâ€™s experiment

A and B are bulbs of equal volume (Figure 6.11). A is filled with dry hydrogen and B with dry chlorine. Taps T_1 and T_3 are closed while tap T_2 is opened. The set-up is left inside a room to avoid direct sunlight, for two to three days till the gases react completely. In direct sunlight, there would be an explosion.

At the end of the reaction one end of the apparatus is lowered into mercury and the tap at that end opened. Mercury does not rise inside the bulb, showing that no change in volume accompanied the reaction. The tap is closed and the apparatus brought out. One end is next lowered into water and the tap at that end opened. Water rushes in and fills the two bulbs. The hydrogen chloride gas formed is very soluble in water. Since the bulbs are filled with water, there must have been no hydrogen or chlorine left at the end of the reaction. (Although chlorine is soluble in water it is not as soluble as hydrogen chloride to make water rush inside the tube). Thus one volume of hydrogen is found to react with one volume of chlorine to produce two volumes of hydrogen chloride. That is, the ratio of volumes of the reactants and product is 1:1:2.

Gay Lussacâ€™s law on its own is not very useful. It becomes very important only when combined with Avogadroâ€™s law.

6.9 Avogadroâ€™s law

It was reasonable to expect one volume of hydrogen to react with one volume of chlorine to produce two volumes of hydrogen chloride since the volumes may be assumed to be additive. But it was not clearly understood how two volumes of hydrogen react with one volume of oxygen to give two volumes of steam. Same was the case for one volume of nitrogen which reacts with three volumes of hydrogen to give two volumes of ammonia.

To explain these reactions Avogadro put up a hypothesis which is now accepted as a scientific law. It states that:

> **equal volumes of all gases under the same conditions of temperature and pressure, contain the same number of molecules.**

The implication of Avogadroâ€™s hypothesis (law) is that atoms unite to form molecules. Molecules, not atoms, are the composite particles of gases (except for the noble gases). An application of Avogadroâ€™s law to volumes of reacting gases helps us to write equations for the reactions. For example, if we find out that two volumes of carbon(II) oxide react with one volume of oxygen to produce two volumes of carbon(IV) oxide, we can convert this ratio directly into an equation as the ratio of number of molecules. This is because equal volumes represent equal numbers of molecules. Thus we write:

$2CO + O_2$ â†’ $2CO_2$

Worked Example

10 cm^3 of ethane was exploded with 60 cm^3 of oxygen. If 15cm^3 of oxygen was in excess and 20 cm^3 of CO_2 was formed, write the equation of the reaction. All volumes were measured at the same temperature and pressure.

Solution

Volume of oxygen used = (60 − 15)cm^3 = 45 cm^3.
Volume of ethane = 10 cm^3
Volume of carbon(IV) oxide produced = 20 cm^3.

Changing the volumes to numbers of molecules we write

$$10\,C_2H_6(g) + 45\,O_2(g) \rightarrow 20\,CO_2(g) + ?\,H_2O(g)$$

Divide through by 5.

$$2C_2H_6(g) + 9O_2(g) \rightarrow 4CO_2(g) + ?H_2O(g)$$

To get a total of 12 hydrogen atoms on the right hand side as on the left, write 6 as the coefficient of H_2O. Hence the equation is

$$2C_2H_6(g) + 9O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

Exercise 6F

Given that 20 cm^3 of nitrogen reacts with 60 cm^3 of hydrogen to produce 40 cm^3 of ammonia, all measured at 25Â°C and 760 mm of mercury, what is the formula of ammonia?

6.10 Relationship between molar mass and vapour density

Consider carbon(IV) oxide and hydrogen at s.t.p. From Avogadroâ€™s law, we shall show later that 22.4 dm^3 is the volume of 1 mole of carbon(IV) oxide; 22.4 dm^3 is also the volume of 1 mole of hydrogen. Therefore the mass of 22.4 dm^3 of carbon(IV) oxide at s.t.p. is the molar mass of carbon(IV) oxide; and the mass of 22.4 dm^3 of hydrogen is also the molar mass of hydrogen.

$$\therefore \frac{\text{Mass of 22.4 dm}^3\text{ of } CO_2}{\text{Mass of 22.4 dm}^3\text{ of } H_2} = \frac{\text{Relative molecular mass of } CO_2}{\text{Relative molecular mass of } H_2}$$

$$\therefore \frac{\text{Mass of 1 dm}^3\text{ of } CO_2 \text{ at s.t.p.}}{\text{Mass of 1 dm}^3\text{ of } H_2 \text{ at s.t.p.}} = \frac{\text{Relative molecular mass of } CO_2}{\text{Relative molecular mass of } H_2}$$

Now, mass of 1 dm^3 of CO_2 at s.t.p. = 1.96g,
and mass of 1dm^3 of H_2 at s.t.p. = 0.09g

$$\therefore \frac{\text{Relative molecular mass of } CO_2}{\text{Relative molecular mass of } H_2} = 1.96/0.09 = \mathbf{22.0}$$

The ratio, $\dfrac{\text{relative molecular mass of a gas}}{\text{relative molecular mass of hydrogen}}$

is equal to the vapour density (V.D.) of the gas.

Vapour density (V.D.) is defined as: **the number of times a given volume of a gas or vapour is heavier than an equal volume of hydrogen under the same conditions of temperature and pressure**.

That is, the vapour density of carbon(IV) oxide is 22.0

$$\text{Since V.D.} = \frac{\text{mass of a volume of gas}}{\text{mass of an equal volume of hydrogen}}$$

$$\begin{aligned}\text{i.e. V.D.} &= \frac{\text{mass of 1 volume of gas}}{\text{mass of 1 volume of hydrogen}}\\ &= \frac{\text{mass of n molecules of gas}}{\text{mass of n molecules of hydrogen}}\\ &= \frac{\text{mass of 1 molecule of gas}}{\text{mass of 1 molecule of hydrogen}}\\ &= \frac{\text{mass of 1 molecule of gas}}{\text{mass of 2 atoms of hydrogen}}\end{aligned}$$

(since a hydrogen molecule is diatomic)

But the ratio

$$\frac{\text{Mass of 1 molecule of a gas}}{\text{Mass of 1 atom of hydrogen}} = \textbf{relative molecular mass of a gas}$$

$\therefore$ V. D. = ½ relative molecular mass

or 2 V. D. = relative molecular mass.

Worked Examples

1. If a balloon (of negligible mass) filled with dry hydrogen weighs 30g but weighs 900g when filled with the vapour of an organic compound, calculate

   (i) the vapour density and

(ii) the relative molecular mass of the organic compound.

Solution

$$V.D. = \frac{\text{mass of a volume of vapour}}{\text{mass of an equal volume of } H_2}$$
$$= 900/30 = 30$$

Relative molecular mass = 2 V. D. = 2 Ã— 30 = 60

2. The mass of 500 cm^2 of a gas. measured at 25Â°C and 750 mm of mercury pressure is 0.75g. Calculate the relative molecular mass of the gas. The density of hydrogen is 0.09g dm^2 at s.t.p.

Solution

To convert the 500 cm^3 of gas to volume at s.t.p. substitute in

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

$$\text{Thus } \frac{750 \times 500}{(25 + 273)} = \frac{760 \times V_2}{273}$$

$$\therefore V_2 = \frac{750 \times 500 \times 273}{760 \times 298}$$
$$= 452.2\ cm^3$$

452.2cm^3 of gas at s.t.p. weighs 0.75g

$\therefore$ 1000 cm^3 weighs $\frac{0.75}{452.2} \times 1000g = 1.66g$

$\therefore$ V. D. of the gas = 1.66/0.09 = 18.45

$\therefore$ Relative molecular mass of the gas = 2 V.D. = 36.9

Exercise 6g

Calculate the molar mass of a gas if 315 cm^3 of it measured at 25Â°C and 740 mm of mercury pressure weighs 0.4g.

6.11 The mole, Avogadro number and gram molecular volume

Calculations of the volumes at s.t.p.occupied by the molar masses of different gases, using densities of the gases shows a remarkable revelation. Table 6.2 illustrates the calculations for three gases.

TABLE 6.2

Formula of gas	Density (g dm^{-3})	Molar mass (g)	Molar volume (cm^3)
H_2	0.09	2	22410
O_2	1.43	32	22380
CO_2	1.96	44	22440

From the table we see that the volume occupied at s.t.p. by the molar mass of every gas is constant. That constant is taken to be 22400cm^3, (or 22.4 dm^3) It is known as the molar volume.

From Avogadroâ€™s law this volume for all gases contains the same **number of molecules. The number of molecules contained in 22.4 dm^3 of every gas measured at s.t.p. is 6.02 Ã— 10^{23};** this is known as the **Avogadro number** (Avogadro constant). **The molar mass of every gas contains the Avogadro number of molecules, and occupies 22.4 dm^3 at s.t.p.**

The atomic mass of every element also contains the Avogadro number of atoms. The Avogadro number of particles (molecules, atoms or ions) is known as the mole. The mole is the amount of the compound, element or ions which contains the same number of particles (molecules, atoms or ions) as there are atoms in 12g of ^{12}C isotope.

Worked example

If 575 cm^3 of gas measured at 18Â°C and 98000 Nm^{-2} pressure weighs 1g. Calculate its molar mass. Take atmospheric pressure as 101300 Nm^{-2}.

Solution

Convert the volume at 18Â°C and 98000 Nm^{-2} pressure to volume at s.t.p.

$$\frac{575 \times 98000}{(273 + 18)} = \frac{V \times 101300}{273}$$

$$\therefore V = \frac{575 \times 98000 \times 273}{291 \times 101300} \text{cm}^3$$

$$= 510 \text{ cm}^3$$

510 cm^3 weighs 1g.

$\therefore$ 22400 cm^3 weighs $\frac{1}{510} \times 22400$g

43.9 g

That is, molar mass = 43.9g.

Chapter Summary

Law	The gas law Statement	Mathematical expression
1. Boyleâ€™s	At constant temperature, pressure varies inversely with volume.	PV = constant, or $P_1V_1 = P_2V_2$
2. Charlesâ€™	At constant pressure, volume varies directly with temperature.	$\frac{V}{T}$ = constant $\frac{V_1}{T_1} = \frac{V_2}{T_2}$
3. Ideal gas equation		$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$
4. Daltonâ€™s	The partial pressure of a gas in a mixture is the pressure the gas would exert if it alone filled the space.	$P = P_1 + P_2 + P_3$ where P_1, P_2, P_3 are partial pressures.
5. Grahamâ€™s	The rate of diffusion of a gas is inversely proportional to the square root of its vapour density.	$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$
6. Avogadroâ€™s	Equal volumes of gases at the same temperature and pressure, contain the same number of molecules .	
7. Gay Lussacâ€™s	Volumes of gases which take part in a chemical reaction bear a simple ratio to one another and the volume of the product, if gaseous, provided temperature and pressure are constant.	

Gram molecular volume **(G.M.V.)** = 224 dm^3 at s.t.p.
This is the volume of 1 mole of every gas at s.t.p.

Kinetic theory of matter: Above the absolute zero temperature all particles of matter are in constant motion. The theory explains the gas laws and the phenomena uf melting, boiling and evaporation.

Assessment

1. How many molecules are present in 100cm^3 of hydrogen collected at 298K and 12000 N m^{-2} pressure? The standard temperature and

pressure are 273K and 101 325 N m^{-2} respectively.

2. 300cm^3 of a gaseous hydrocarbon diffuses through a porous pot in 452 minutes. The same volume of hydrogen diffuses in 117 seconds under the same conditions. Calculate the molar mass of the hydrocarbon. If its empirical formula is CH_3, what is its formula?
3. What volume will 22.4 dm^3 of oxygen, measured at 25Â°C and 1.12 Ã— 10^5N m^{-2} occupy at a pressure of 1.053 Ã— 10^5 N m^{-2}?
4. A gas cylinder containing 13kg of butane has a capacity of 200 dm^3 at 26Â°C and 200 atmosphere pressure. What volume will the gas occupy. at s.t.p.?
5. 100 cm^3 of oxygen diffuses through a porous pot in 3 secs. How long will it take 150 cm^3 of sulphur(IV) oxide to diffuse through the same pot?
6. Define the term vapour density.
   A baloon filled with dry hydrogen weighs 30g but weighs 900g when filled with the vapour of an organic compound at the same temperature and pressure. What is the molar mass of the organic compound?
7. What is the apparent molar mass of air? (assume that air contains 78% of nitrogen, 21% of oxygen and 1% of argon).

$$\text{(Hint: apparent molar mass} = \frac{\text{total molar mass of the mixture}}{\text{total number of moles of mixture.)}}$$

8. (a) What mass of oxygen is required for the combustion of 13 kg of butane gas?
   (b) If air is 21% oxygen by volume what volume of air, measured at s.t.p. is required for the combustion of the butane?
   (c) What volume of carbon(IV) oxide is produced during the combustion?
9. A gas B at 300K and 1.013 Ã— 10^5 N m^{-2} is in a 5 dm^3 container. Another gas C at 300K and 3.039 Ã— 10^5 N m^{-2} is in a 5 dm^3 container. What will be the total pressure if
   (i) B and C are put into a 5 dm^3 vessel at 300K.
   (ii) B and C are put into a 10 dm^3 vessel at 300K?

(WAEC)

10. (a) State (i) two differences between solids and liquids, and
   (ii) two similarities between liquids and gases.
   (b) What are the constituent particles in each of the following solids:
   (i) sodium chloride
   (ii) iodine
   (iii) diamond?
   (c) When some solids are heated they pass directly into the

gaseous state.

(i) Name this process.

(ii) Give two examples of solids that will behave in this way.

(d) Describe and explain, in terms of the Kinetic Theory of matter, the transition:
Solid â†’ Liquid â†’ Gas

(WAEC)

Objective Questions

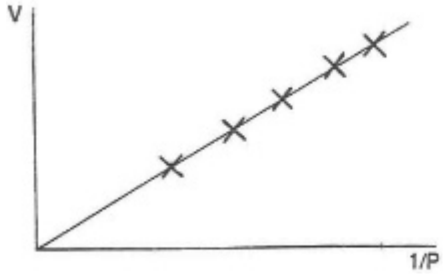

Figure 6.12

1. The graph in Figure 6.12 illustrates
   A. Charlesâ€™ law
   B. Boyles law
   C. Gay Lussacâ€™s law
   D. Grahams law
   E. Avogadroâ€™s law

2. In Boyleâ€™s law.
   A. T is constant while P varies directly with V.
   B. P is constant while V varies directly with T.
   C. V is constant while P varies directly with T.
   D. T is constant while V varies inversely with P.
   E. P is constant while V varies inversely with T.

3. Avogadro number is
   (i) The number of electrons flowing when 1 Faraday of electricity is passed.
   (ii) The number of atoms in the outermost shell of an atom.
   (iii) The number of molecules in the molar mass of a compound.
   (iv) The number of molecules in 22.4 dm^3 of any gas at s.t.p.
   A. (i) and (ii) only correct
   B. (i) and (iii) only correct
   C. (ii) and (iii) only correct
   D. (i), (iii) and (iv) only correct

E. (i), (ii), (iii) and (iv) correct.

4. A certain volume of a gas is found to weigh 4.4g. An equal volume of hydrogen weighs 0.2g. The molar mass of the gas is
(A) 44; (B) 22; (C) 28; (D) 64; (E) 32

5. If the standard pressure is 1.05 Ã— 10^5 N m^{-2} the volume 2 dm^3 of a gas at 300K will occupy at s.t.p. is

A. 3 dm^3
B. $\frac{2 \times 273}{300}$ dm^3
C. $\frac{2 \times 273 \times 1.05}{300}$ dm^3
D. $\frac{2 \times 300}{273 \times 1.05}$ dm^3
E. $\frac{2 \times 200}{273}$ dm^3

For questions 6 and 7 choose A if only (i) and (ii) are correct. Choose B, if only (iii) is correct;
Choose C if only (iii) and (iv) are correct; Choose D if only (i) and (iii) are correct; Choose E if (i), (ii), (iii) and (iv) are all correct.

6. The mass and number of molecules in 1 mole of different gases are as given in the table below:

Gas	**Mass**	**No. of Molecules**
(i) Hydrogen	1g	6.02 Ã— 10^{23}
(ii) Oxygen	16g	6.02 Ã— 10^{23}
(iii) Nitrogen	28g	6.02 Ã— 10^{23}
(iv) Carbon(IV) Oxide	44g	18.06 Ã— 10^{23}

7. Which of the following contains one mole of substance?
(i) 32g of sulphur
(ii) 22.4 dm^3 of oxygen, measured at s.t.p.
(iii) 22.4 dm^3 of hydrogen, measured at s.t.p.
(iv) 23g of sodium metal.

8. Which of the following gases has the Same volume under the same conditions as 8g of sulphur(IV) oxide?
A. 8g of hydrogen
B. 5.5g of carbon(IV) oxide
C. 7.1g of chlorine
D. 5g of nitrogen
E. 2g of helium

(WAEC)

9. 9.0g of aluminium powder reacts completely with excess sodium hydroxide solution. What is the volume of hydrogen evolved, measured at s.t.p.?

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$$

A. 22.4 dm^3
B. 11.2 dm^3
C. 5.6 dm^3
D. 2.8 dm^3
E. 1.4 dm^3

(WAEC)

10. If n and r_2 are the rates of diffusion of two gases with densities d_1 and d_2 respectively, Grahamâ€™s law can be expressed as

A. $\frac{r_1}{r_2} = \frac{d_1}{d_2}$
B. $\frac{r_1}{r_2} = \frac{d_2}{d_1}$
C. $\frac{r_1}{r_2} = \frac{\sqrt{d_2}}{\sqrt{d_1}}$
D. $\frac{r_1}{r_2} = \frac{\sqrt{d_1}}{\sqrt{d_2}}$
E. $\frac{r_1}{r_2} = \frac{d_1^2}{d_2^2}$

(WAEC)