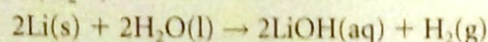


The volume of gaseous reactants and products in chemical reactions can be calculated using a similar strategy to that outlined earlier to calculate masses.

Worked example

What volume of hydrogen (H_2) is produced when 0.056 g of lithium (Li) reacts completely with water (H_2O):



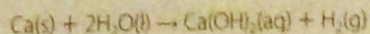
Assume the volume is measured at STP.

Solution

	Calculator values
Step 1 $2\text{Li(s)} + 2\text{H}_2\text{O(l)} \rightarrow 2\text{LiOH(aq)} + \text{H}_2\text{(g)}$ 2 moles 1 mole	
Step 2 2 moles of Li react to produce 1 mole of H_2 $n(\text{H}_2) = \frac{1}{2} n(\text{Li})$	
Step 3 $n(\text{Li}) = \frac{m}{M} = \frac{0.056}{6.94}$ $n(\text{H}_2) = \frac{1}{2} \left(\frac{0.056}{6.94} \right)$	= 0.008 069 164 = $0.5 \times 0.008 069 164$ = 0.004 034 582
Step 4 Translate into volume. Use $V = nV_{\text{molar}}$ $V(\text{H}_2) = nV_{\text{molar}} = \frac{1}{2} \left(\frac{0.056}{6.94} \right) \times 22\,400 \text{ cm}^3$ = 90 cm^3	= $0.004 034 582 \times 22\,400$ = 90.374 639 77

Exercise

17 Calcium reacts with water to produce hydrogen:



Calculate the volume of gas, measured at STP produced when 0.200 g of calcium reacts completely with water.

The gas laws

The gaseous state is the simplest state. All gases have the same molar volume and they respond in similar ways to changes in temperature, pressure and volume. The gas laws describe this behaviour.

Pressure

If you have ever pumped a bicycle tyre or squeezed an inflated balloon you have experienced the pressure of a gas. A gas produces a pressure when its particles collide with the walls of its container. An increase in the *frequency* or *energy* of these collisions will increase the pressure.



Pump gas molecules into a box and see what happens as you change the volume, add or remove heat, change gravity and more. Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.

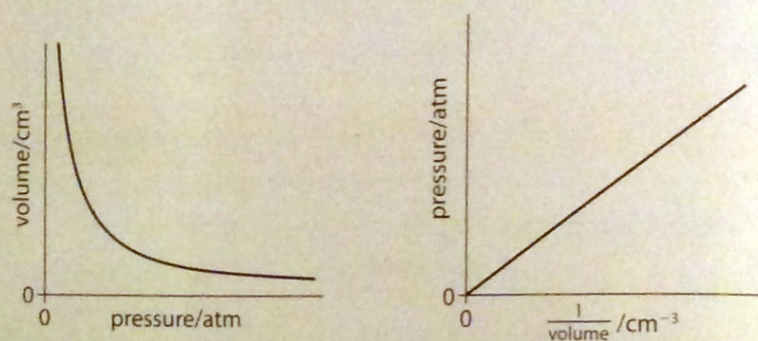
Relationship between volume and pressure for a gas

An increase in volume reduces the frequency of the collisions with the walls and so the pressure decreases. The relationship was studied experimentally by Robert Boyle in the 17th century. He found that if the temperature and amount of gas is kept constant, the pressure *halves* if the volume is *doubled*. The pressure is inversely proportional to the volume and the relationship can be expressed as:

$$P = \frac{k_1}{V}, \text{ where } k_1 \text{ is a constant.}$$

$$PV = k_1$$

Figure 1.8 The pressure of a gas is inversely proportional to the volume. A graph of P against $\frac{1}{V}$ produces a straight line through the origin.



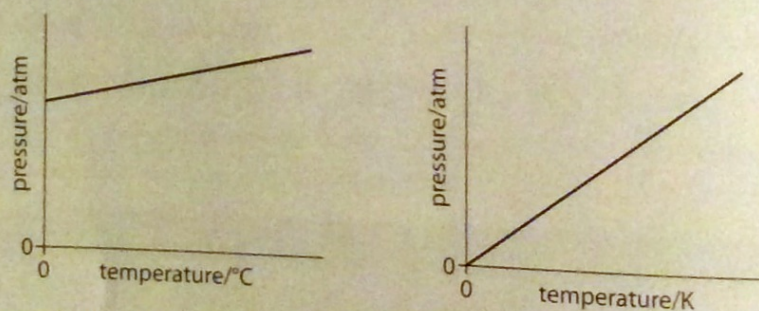
Investigate Boyle's Law using this simulation. Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.



Figure 1.9 The pressure is proportional to the absolute temperature. The pressure of the gas is zero at absolute zero when the particles are not moving (-273°C).

Relationship between temperature and pressure for a gas

You may have noticed that balloons have an increased tendency to 'pop' on hot summer days. An increase in temperature increases the average kinetic energy of the particles. The particles move faster and collide with the walls of the balloon with more energy and more frequency. Both factors lead to an increase in pressure. When the relationship is studied experimentally at constant volume, the following graphs are produced.



The pressure is proportional to the absolute temperature measured in kelvin (K). $P = k_2 T$, where k_2 is a constant.

Effect of temperature on the gas volume

Combining the two previous relationships we can predict how the volume changes with absolute temperature. Consider the following sequence:

- 1 The temperature is *doubled* at fixed volume.
- 2 The volume is *doubled* at fixed temperature.

The changes are summarized below.

	Step 1	Step 2	Overall change
temperature	doubled	fixed	doubled
volume	constant	doubled	doubled
pressure	doubled due to increase in temperature	halved due to increase in volume	no change

The volume and the temperature of the gas have both doubled at fixed volume. This relationship is sometimes called Charles' law and is represented below.

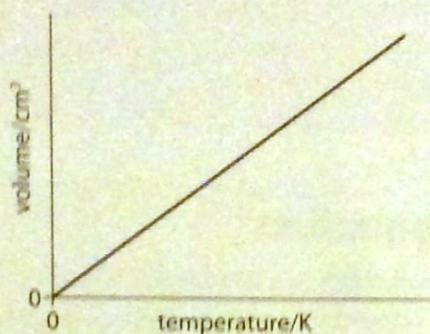


Figure 1.10 Charles' Law. The volume is proportional to the absolute temperature.

The volume of a gas is proportional to the absolute temperature.

$$V = k_3 T, \text{ where } k_3 \text{ is a constant}$$

The combined gas law

We can combine the three gas laws into one expression:

$$\begin{array}{l} V \propto T \\ P \propto \frac{1}{V} \end{array} \longrightarrow PV \propto T$$

$$P \propto \frac{1}{V} \qquad \frac{PV}{T} = \text{constant}$$

The response of a gas to a change in conditions can be predicted by a more convenient form of the expression:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

where 1 refers to the initial conditions and 2 the final conditions.

Worked example

What happens to the volume of a fixed mass of gas when its pressure and its temperature (in kelvin) are both doubled?

Solution

The pressure and temperature are both doubled: $P_2 = 2P_1$, $T_2 = 2T_1$:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Substitute for P_2 and T_2 :

$$\frac{P_1 V_1}{T_1} = \frac{2P_1 V_2}{2T_1}$$

P_1 and T_1 cancel from both sides:

$$V_1 = \frac{2V_2}{2}$$

$$V_1 = V_2$$

The volume does not change.



Would there have been the gas laws without the work of Charles or Boyle?

In science, the individual scientist is irrelevant and all scientists contribute to a common body of knowledge. This should be contrasted with the arts. There could have been no *Hamlet* without Shakespeare, no *Guernica* without Picasso.



$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

The temperature must be in kelvin.



▲ Blowing air molecules into a balloon increases the volume.

Use this simulation to investigate the gas laws. Now go to www.heinemann.co.uk/hotlinks, insert the express code 4259P and click on this activity.



● **Examiner's hint:** Make sure that you use the correct units when using the ideal gas equation. SI units should be used when $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$. P should be in units of N m^{-2} (Pa), V in units of m^3 and T in units of K.

Exercises

- 18 The temperature in kelvin of 4.0 dm^3 of hydrogen gas is increased by a factor of three and the pressure is increased by a factor of four. Deduce the final volume of the gas.
- 19 The molar volume of a gas at STP is 22.4 dm^3 . Use the combined gas equation to show that the molar volume of gas is 24 dm^3 at RTP.

The ideal gas equation

The combined gas equation refers to a fixed mass of gas. When you blow into a balloon you increase the number of particles and this increases the volume. When you pump up a bicycle tyre the added gases cause the pressure to increase. The number of moles can be included in the combined gas equation to give the ideal gas equation.

$\frac{PV}{nT} = R$ where R is the gas constant. When SI units are used R has the value $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$.

Gases which follow this equation exactly are called **ideal gases**. Real gases deviate from the equation at high pressure and low temperature owing to the effects of inter-particle forces.

Worked example

A helium party balloon has a volume of 18.0 dm^3 . At room temperature (25°C) the internal pressure is 1.05 atm . Calculate the number of moles of helium in the balloon and the mass needed to inflate it.

Solution

$$PV = nRT$$

$$n = \frac{PV}{RT}$$

Convert data into SI units:

$$P = 1.05 \text{ atm} = 1.05 \times 1.01 \times 10^5 \text{ Pa (see Table 2 in the IB Data booklet)}$$

$$V = 18.0 \text{ dm}^3 = 18.0 \times 10^{-3} \text{ m}^3, T = 25^\circ\text{C} = (25 + 273) \text{ K} = 298 \text{ K}$$

$$n = \frac{1.05 \times 1.01 \times 10^5 \times 18.0 \times 10^{-3}}{(8.31 \times 298)} = 0.771 \text{ mole (calculator value: 0.770 842 924)}$$

$$\text{Mass} = nM = 0.771 \times 4.00 = 3.08 \text{ g}$$

Measuring the molar mass

The ideal gas equation can be used to find the molar mass of gases or volatile liquids.

$$PV = nRT$$

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

$$PV = \left(\frac{m}{M}\right) RT \text{ when } m \text{ is in g}$$

$$M = \frac{mRT}{PV}$$

$$\text{Density } \rho = \frac{m}{V}$$

$$M = \frac{\rho RT}{P}, \text{ when density is in } \text{g m}^{-3}$$

Worked example

A sample of gas has a volume of 432 cm^3 and a mass of 1.500 g at a pressure of 0.974 atm and a temperature of 28°C . Calculate the molar mass of the gas.

Solution

$$M = \frac{mRT}{PV}$$

Convert into SI units (the mass should be kept in g).

$$\begin{aligned} T &= 273 + 28 \text{ K}, P = 0.974 \times 1.01 \times 10^5 \text{ Pa}, V = 432 \times 10^{-6} \text{ m}^3 \\ &= \frac{1.500 \times 8.31 \times (273 + 28)}{(0.974 \times 1.01 \times 10^5 \times 432 \times 10^{-6})} \\ &= 88.3 \text{ g mol}^{-1} \text{ (calculator value: } 88.286 \text{ } 581 \text{ } 48) \end{aligned}$$

Exercise

- 20 The density of a gaseous hydrocarbon with the empirical formula C_3H_7 is found to be 2.81 g dm^{-3} at 100°C and 1.00 atm . Calculate the molar mass of the hydrocarbon and find its molecular formula.

1.5 Solutions

Liquids

Like gases it is often more convenient to measure the volume of a liquid instead of its mass. Unlike gases however there is no direct relationship between the volume of a liquid and its amount. The mass can be calculated from the volume if the density is known.

In the laboratory the volume of a liquid can be measured using different apparatus depending on the precision required. When the volume is known, volumetric flasks or pipettes are used. A 25 cm^3 pipette has a typical uncertainty of $\pm 0.75 \text{ cm}^3$ and a 250 cm^3 volumetric flask has an uncertainty of $\pm 0.15 \text{ cm}^3$. A burette is used when the volume is unknown. A 50 cm^3 burette has a typical uncertainty of $\pm 0.1 \text{ cm}^3$. The uncertainty of measurements is discussed in more detail in Chapter 11.

$$\text{Density } \rho = \frac{\text{mass } (m)}{\text{volume } (v)}$$

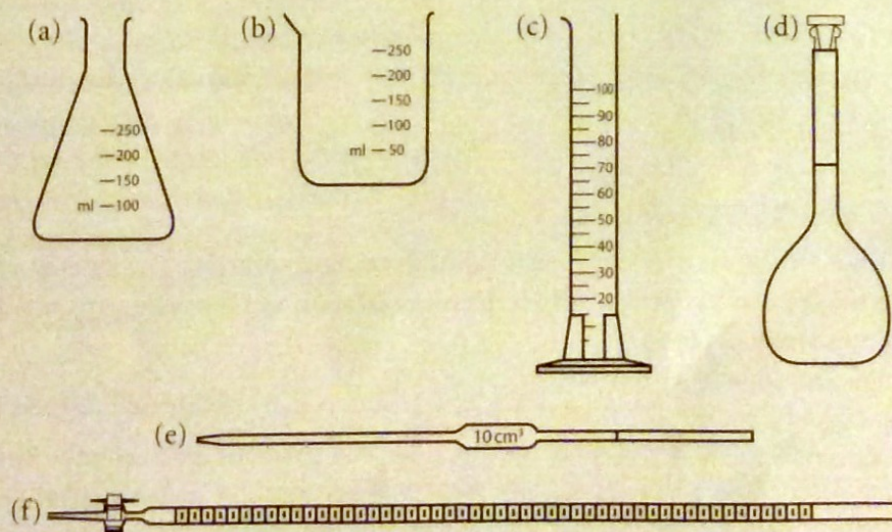


Figure 1.11 Different pieces of glassware used in the lab. (a) Conical or Erlenmeyer flask (250 cm^3). The shape makes it easy to mix liquids as the flask can be easily swirled. (b) Beaker (250 cm^3). (c) Measuring cylinder (100 cm^3). (d) Volumetric flask (250 cm^3). (e) Pipette (10 cm^3). (f) Burette (50 cm^3). The beaker and the conical flask are not generally used for measuring volume.

Solutions

The discussion so far has focused on pure substances but chemists often carry out reactions in **solution**. Solutions are mixtures of two components. The less abundant component is the **solute** and the more abundant the **solvent**. The solute can be solid, liquid or gas but the solvent is generally a liquid. Salt water is a solution with salt as the solute and water the solvent. Solutions in water are particularly important. These are called **aqueous** solutions and are given the state symbol (aq).

Concentration

The composition of a solution is generally expressed in terms of its **concentration**. As more and more solute dissolves in the solvent, the solution becomes more and more concentrated. When the solvent cannot dissolve any more solute, it is **saturated**.

The concentration is generally expressed in terms of the mass or amount of solute dissolved in 1 dm³ of solution. The units are either g dm⁻³ or mol dm⁻³. One mole of sodium chloride for example has a mass of 22.99 + 35.45 g = 58.44 g. When this amount of solute is added to water to make a 1 dm³ solution, the concentration can either be expressed as 58.44 g dm⁻³ or 1.00 mol dm⁻³. Square brackets are used to represent concentrations, so this can be written [NaCl] = 1.00 mol dm⁻³. Concentrations in mol dm⁻³ are generally used in solving problems involving chemical equations.

$$\text{Concentration} = \frac{\text{number of moles } (n)}{\text{volume of solution } (V)}$$

The volume is in dm³.

Square brackets are used to represent concentrations.



Worked example

A solution of sodium hydroxide has a concentration of 8.00 g dm⁻³. What is its concentration in mol dm⁻³?

Solution

To find number of moles use: $n = \frac{m}{M}$

$$M = 22.99 + 1.01 + 16.00 = 40.00 \text{ g}$$

$$n = \frac{8.00}{40.00} = 0.200$$

$$[\text{NaOH}] = \frac{n}{V} = \frac{0.200}{1.00} = 0.200 \text{ mol dm}^{-3}$$

Worked example

Calculate the concentration of a 0.0400 mol dm⁻³ solution of sodium carbonate Na₂CO₃ in g dm⁻³

Solution

To find the mass use: $m = nM$

$$M = (22.99 \times 2) + 12.01 + (3 \times 16.00) \text{ (calculator value: 105.99)}$$

$$m = nM = 0.0400 \times ((22.99 \times 2) + 12.01 + (3 \times 16.00)) \text{ (calculator value: 4.2396)}$$

$$[\text{Na}_2\text{CO}_3] = 4.24 \text{ g dm}^{-3}$$

Standard solutions

A solution of known concentration is called a **standard solution**. The amount of solute needed can be calculated from the concentration and the volume required

$$\text{concentration} = \frac{n}{V} \text{ (dm}^3\text{)}$$

$$n = \text{concentration} \times V \text{ (dm}^3\text{)}$$

if the volume is in cm³

$$n = \frac{\text{concentration} \times V \text{ (cm}^3\text{)}}{1000}$$

The mass needed can then be calculated from $m = nM$.

Worked example

Calculate the mass of copper(II) sulfate pentahydrate, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, required to prepare 500 cm^3 of a $0.400 \text{ mol dm}^{-3}$ solution.

Solution

$$\begin{aligned}n &= \text{concentration} \times \frac{V}{1000} \\&= 0.400 \times \frac{500}{1000} \text{ (calculator value: 0.2)} \\m &= nM \\M &= 63.55 + 32.06 + 4(16.00) + 5(16.00 + (2 \times 1.01)) \\&\text{(calculator value: 249.71)}\end{aligned}$$

Note there are five moles of H_2O in one mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ crystals.

$$\begin{aligned}m &= nM = \left(0.400 \times \frac{500}{1000}\right) \times (63.55 + 32.06 + 4(16.00) \\&\quad + 5(16.00 + (2 \times 1.01))) = 49.8 \text{ g (calculator value: } 249.71 \times 0.2 = 49.942)\end{aligned}$$

$$\text{Number of moles (n)} = \frac{\text{concentration} \times \text{volume (V)}}{1000}$$

Exercise

- 21 Calculate the mass of potassium hydroxide needed to prepare 250 cm^3 of a $0.200 \text{ mol dm}^{-3}$ solution.

Titration

Standard solutions are used to find the concentration of other solutions. The analysis of composition by measuring the volume of one solution needed to react with a given volume of another solution is called **volumetric analysis**. One of the most important techniques is **titration**. Typically, a known volume of one solution is measured into a conical flask using a pipette. The other solution is then added from a burette to find the equivalence point – the volume when the reaction is just complete. In acid–base reactions the equivalence point can be detected by the colour change of an **indicator**.



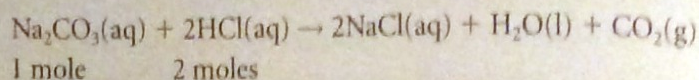
A pipette is used to measure a known volume of liquid accurately. Burettes and conical flasks, which are also used in the titrations, are in the background.

Worked example

What volume of hydrochloric acid with a concentration of 2.00 mol dm^{-3} would have to be added to 25.0 cm^3 of a $0.500 \text{ mol dm}^{-3}$ sodium carbonate solution to produce a neutral solution of sodium chloride?

Solution

Step 1



Step 2

$$\frac{n(\text{HCl})}{n(\text{Na}_2\text{CO}_3)} = \frac{2}{1}$$

$$n(\text{HCl}) = 2n(\text{Na}_2\text{CO}_3)$$

Step 3

$$n(\text{Na}_2\text{CO}_3) = \frac{\text{concentration} \times V}{1000} = \frac{(25.0 \times 0.500)}{1000}$$

$$n(\text{HCl}) = \frac{2.00 \times V(\text{HCl})}{1000}$$

Substitute these amounts in the equation in step 2:

$$2.00 \times \frac{V(\text{HCl})}{1000} = 2 \left(\frac{25.0 \times 0.500}{1000} \right)$$

Find the unknown volume.

Step 4

$$V(\text{HCl}) = \frac{2 \times 25.0 \times 0.500}{2.00} = 12.5 \text{ cm}^3$$

Calculations involving solutions and gases**Worked example**

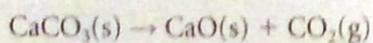
Calculate the volume of carbon dioxide produced when 1.00 g of calcium carbonate reacts with 20.0 cm³ of hydrochloric acid. Assume the volume of the gas is measured at 273K and 1 atm.

Solution

	Calculator values
Step 1 $\text{CaCO}_3(\text{s}) + 2\text{HCl}(\text{aq}) \rightarrow \text{CaCl}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$ 1 mole 2 moles	
Step 2 1 mole of CaCO ₃ (s) reacts with 2 moles of HCl to produce 1 mole of CO ₂	
Step 3 $M(\text{CaCO}_3) = 40.08 + 12.01 + (3 \times 16.00)$ $n(\text{CaCO}_3) = \frac{1.00}{(40.08 + 12.01 + (3 \times 16.00))} = 0.0100$ $n(\text{HCl}) = \frac{[\text{HCl}] \times V(\text{HCl})}{1000}$ $= \frac{2.00 \times 25.0}{1000} = 0.0500$	= 100.09 = $\frac{1}{100.09}$ = 0.009 991 008 0.05
0.0100 moles of CaCO ₃ reacts with 2(0.0100) mol of HCl to produce a theoretical yield of 0.0100 mole of CO ₂ . CaCO ₃ is the limiting reactant and HCl is in excess.	
Step 4 $n(\text{CO}_2) = n(\text{CaCO}_3)$ $n(\text{CO}_2) = \frac{1.00}{(40.08 + 12.01 + (3 \times 16.00))}$ $V(\text{CO}_2) = nV_{\text{molar}}$ $= 22.4 / (40.08 + 12.01 + (3 \times 16.00)) \text{ dm}^3$ $= 0.224 \text{ dm}^3 = 224 \text{ cm}^3$	= $\frac{1}{100.09}$ = 0.009 991 008 = 0.009 991 008 × 22.4 = 0.223 798 581

Worked example

Calcium carbonate decomposes on heating:



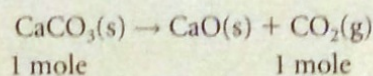
What is the maximum volume (measured at RTP in dm^3) of CO_2 produced when 25 g of CaCO_3 is heated?

- A 3.0 dm^3
- B 6.0 dm^3
- C 9.0 cm^3
- D 12 dm^3

Solution

As this is a multiple choice question it should be answered without a calculator. You can use less precise values (the data is given only to 2 significant figures) for the relative atomic masses. This makes the arithmetic easier.

Step 1



Step 2

1 mol of $\text{CaCO}_3(\text{s})$ produces 1 mol of CO_2 .

Step 3

$$n(\text{CaCO}_3) = \frac{25}{(40 + 12 + 3(16))} = 0.25$$

$$n(\text{CO}_2) = 0.25 \text{ mol}$$

'Translate' back into volume. Use $V = nV_{\text{molar}}$

Step 4

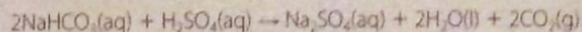
$$V(\text{H}_2) = 0.25 \times 24 \text{ dm}^3 = 6.0 \text{ dm}^3$$

Solution = B

● **Examiner's hint:** In Paper 1 you can find the best solution with less precise relative atomic mass values. This makes the calculation easier and saves time. For papers 2 and 3 estimate the answer before you use a calculator. This will help you spot careless mistakes.

Exercise

- 22 25.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ sodium hydrogencarbonate solution was titrated with dilute sulfuric acid:



15.2 cm^3 of the acid was needed to neutralize the solution.

- (a) Calculate the concentration of the sulfuric acid.
- (b) Calculate the volume of carbon dioxide, measured at STP produced during the titration.

Practice questions

- 1 What amount of oxygen, O_2 , (in moles) contains 1.8×10^{22} molecules?

A 0.0030 B 0.030 C 0.30 D 3.0

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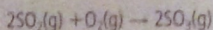
- 2 $\underline{\quad} \text{C}_2\text{H}_2(\text{g}) + \underline{\quad} \text{O}_2(\text{g}) \rightarrow \underline{\quad} \text{CO}_2(\text{g}) + \underline{\quad} \text{H}_2\text{O}(\text{g})$

When the equation above is balanced, what is the coefficient for oxygen?

A 2 B 3 C 4 D 5

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- 3 3.0 dm³ of sulfur dioxide is reacted with 2.0 dm³ of oxygen according to the equation below.

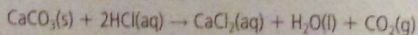


What volume of sulfur trioxide (in dm³) is formed? (Assume the reaction goes to completion and all gases are measured at the same temperature and pressure.)

- A 5.0 B 4.0 C 3.0 D 2.0

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- 4 What volume of 0.500 mol dm⁻³ HCl(aq) is required to react completely with 10.0 g of calcium carbonate according to the equation below?



- A 100 cm³ B 200 cm³ C 300 cm³ D 400 cm³

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- 5 The relative molecular mass of aluminium chloride is 267 and its composition by mass is 20.3% Al and 79.7% chlorine. Determine the empirical and molecular formulas of aluminium chloride. (4)

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- 6 27.82 g of hydrated sodium carbonate crystals, Na₂CO₃ · xH₂O, was dissolved in water and made up to 1.000 dm³. 25.00 cm³ of this solution was neutralized by 48.80 cm³ of hydrochloric acid of concentration 0.1000 mol dm⁻³.

- (a) Write an equation for the reaction between sodium carbonate and hydrochloric acid. (2)
 (b) Calculate the molar concentration of the sodium carbonate solution neutralized by the hydrochloric acid. (3)
 (c) Determine the mass of sodium carbonate neutralized by the hydrochloric acid and hence the mass of sodium carbonate present in 1.000 dm³ of solution. (3)
 (d) Calculate the mass of water in the hydrated crystals and hence find the value of x. (4)

(Total 12 marks)

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- 7 Describe in molecular terms the processes that occur when:
 (a) a mixture of ice and water is maintained at the melting point. (2)
 (b) a sample of a very volatile liquid (such as ethoxyethane) is placed on a person's skin. (2)

(Total 4 marks)

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- 8 The percentage composition by mass of a hydrocarbon is C = 85.6% and H = 14.4%.
 (a) Calculate the empirical formula of the hydrocarbon. (2)
 (b) A 100 g sample of the hydrocarbon at a temperature of 273 K and a pressure of 1.01 × 10⁵ Pa (1.00 atm) has a volume of 0.399 dm³.
 (i) Calculate the molar mass of the hydrocarbon. (2)
 (ii) Deduce the molecular formula of the hydrocarbon. (1)

(Total 5 marks)

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- 9 When a small quantity of strongly smelling gas such as ammonia is released into the air, it can be detected several metres away in a short time.
 (a) Use the kinetic molecular theory to explain why this happens. (2)
 (b) State and explain how the time taken to detect the gas changes when the temperature is increased. (2)

(Total 4 marks)

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