EDEXCEL A LEVEL

CHEMISTRY

Includes AS level

1

GRAHAM CURTIS
ANDREW HUNT

DYNAMIC
LEARNING

Contents

www.youtube.com/megalecture

5 Formulae, equations and amounts of substance

5.1 Understanding chemical quantities

Chemists often need to measure how much of a particular chemical there is in a sample. Analysts in pharmaceutical companies, for example, test samples of tablets and medicines to check that they contain the right amount of a drug. Industrial chemists measure the amounts of substances they need for chemical processes. Laboratory chemists calculate the yield of product they expect when they mix measured quantities of the reactants for a synthesis. In these, and many other contexts, chemists have to be able to measure amounts of substances accurately.

Chemical amounts

In chemistry, the **amount of a substance** is measured in moles. Chemists use the unit 'mole' to measure an amount of substance containing a standard number of atoms, molecules or ions. The word 'mole' entered the language of chemistry at the end of the nineteenth century. It is based on the Latin word for a heap or a pile.

When chemists are determining formulae or working with equations, they need to measure amounts in moles. Chemists have balances to measure masses and graduated containers to measure volumes, but there is no instrument for measuring chemical amounts directly. Instead, chemists must first measure the masses or volumes of substances and then calculate the chemical amounts.

Molar masses

The key to working with chemical amounts in moles is to know the relative masses of different atoms. The accurate method for determining **relative atomic masses** involves the use of a mass spectrometer (Section 1.3).

One mole of an element has a mass that is equal to its relative atomic mass in grams. So, the mass of one mole of carbon is 12.0 g and the mass of one mole of copper is 63.5 g. These masses of one mole are called **molar masses** (symbol M). So, the molar mass of carbon, $M(C) = 12.0$ g mol^{-1} and the molar mass of copper, $M(Cu)$ = 63.5 g mol^{-1} (Figure 5.1).

Similarly the molar mass of the molecules of an element or a compound is numerically equal to its relative molecular mass. So, the molar mass of oxygen molecules, $M(O_2)$ = 32.0 g mol^{-1} and the molar mass of sulfuric acid, $M(H_2SO_4)$ = 98.1 g mol^{-1}. Likewise, the molar mass of an ionic compound is numerically equal to its relative formula mass. The molar mass of magnesium nitrate, $Mg(NO_3)_2$, is therefore 148.3 g mol^{-1} (Figure 5.2).

Key terms

Amount of substance is a physical quantity (symbol n) which is measured in the unit mole (symbol mol).

Key terms

Relative atomic mass, A_r, is the average mass of an element reletive to 1/12th of the mass of an atom of the isotope carbon-12. The values are relative so they do not have units.

Key terms

Molar mass is the mass of one mole of a chemical – the unit is g mol^{-1}. As always with molar amounts, the symbol or formula of the chemical must be specified.

www.youtube.com/megalecture

Figure 5.1 One mole amounts of copper, carbon, iron, aluminium, mercury and sulfur

Figure 5.2 One mole amounts of some ionic compounds

Amount in moles

The mole is the SI unit for amount of substance. The name of the quantity is 'mole'. Its unit is 'mol'. So,

12 g of carbon contains 1 mol of carbon atoms

24 g of carbon contains 2 mol of carbon atoms

240 g of carbon contains 20 mol of carbon atoms.

Notice that:

$$\text{amount of substance/mol} = \frac{\text{mass of substance/g}}{\text{molar mass/g mol}^{-1}}$$

It is important to be precise about the chemical **species** involved when measuring amounts in moles. In calcium chloride, $CaCl_2$, for example, there are two chloride ions, Cl^-, combined with each calcium ion, Ca^{2+}. So in one mole of calcium chloride there is one mole of calcium ions and two moles of chloride ions.

The Avogadro constant

Relative atomic masses show that one atom of carbon is 12 times heavier than one atom of hydrogen. This means that 12 g of carbon contains the same number of atoms as 1 g of hydrogen. Similarly, one atom of oxygen is 16 times as heavy as one atom of hydrogen, so 16 g of oxygen also contains the same number of atoms as 1 g of hydrogen.

In fact, the molar mass of every element (1 g of hydrogen, 12 g carbon, 16 g oxygen, and so on) contains the same number of atoms. This number is called the **Avogadro constant**, after the Italian scientist Amedeo Avogadro. Experiments show that the Avogadro constant, L, is 6.02×10^{23} mol^{-1}. Written out in full this is $602\,000\,000\,000\,000\,000\,000\,000$ atoms, molecules or ions per mole.

The Avogadro constant is the number of atoms, molecules or formula units in one mole of any substance. So, one mole of oxygen (O_2) contains 6.02×10^{23} O_2 molecules and two moles of oxygen (O_2) contains $2 \times 6.02 \times 10^{23}$ O_2 molecules.

The number of atoms, molecules or formula units =
amount of chemical/mol × the Avogadro constant/mol^{-1}

Tip

Section MiC.5 of the maths chapter on page xx gives advice on how to work out the value of maths equations with brackets and combinations of multiplication and addition.

Key terms

The term **species** is a useful collective noun used by chemists to refer generally to atoms, molecules or ions.

Tip

Section MiC.4 of the maths chapter on page xx gives help with substituting values into mathematical formulae.

Key terms

The **Avogadro constant** is the number of atoms, molecules or ions in one mole of a substance. The constant has the unit mol^{-1}.

5.1 Understanding chemical quantities   3

Again, it is vital to specify the chemical species concerned in calculating the amount of a substance or the number of particles in a sample of a substance. For example, 2 g of hydrogen contains 2 mol of hydrogen (H) atoms (12.04×10^{23} atoms) but only 1 mol of hydrogen (H_2) molecules (6.02×10^{23} molecules).

Test yourself

1 What is the amount, in moles, of:
  a) 20.05 g of calcium atoms
  b) 3.995 g of bromine atoms
  c) 159.8 g of bromine molecules
  d) 6.41 g of sulfur dioxide molecules
  e) 10 g of sodium hydroxide, NaOH?

2 What is the mass of:
  a) 0.1 mol of iodine atoms
  b) 0.25 mol of chlorine molecules
  c) 2 mol of water molecules
  d) 0.01 mol of ammonium chloride, NH_4Cl
  e) 0.125 mol of sulfate ions, SO_4^{2-}?

3 How many moles of:
  a) sodium ions are there in 1 mol of sodium carbonate, Na_2CO_3
  b) bromide ions are there in 0.5 mol of barium bromide, $BaBr_2$
  c) nitrogen atoms are there in 2 mol of ammonium nitrate, NH_4NO_3?

4 Use the Avogadro constant to calculate:
  a) the number of chloride ions in 0.5 mol of sodium chloride, NaCl
  b) the number of oxygen atoms in 2 mol of oxygen molecules, O_2
  c) the number of sulfate ions in 3 mol of aluminium sulfate, $Al_2(SO_4)_3$.

Key terms

An **empirical formula** shows the simplest whole number ratio of the atoms of different elements in a compound; for example, CH_4 for methane and CH_3 for ethane.

Tip

Section MiC.3 of the maths chapter on page xx gives help with calculations involving ratio and proportion.

5.2 Finding empirical formulae

Although the formulae of most compounds can be predicted, the only sure way of determining the formula of a substance is by experiment. This has been done for all common compounds and their formulae can be checked in tables of data.

'Empirical' evidence is information based on experience or experiment, so chemists use the term **empirical formulae** for formulae calculated from the results of experiments.

An experiment to find an empirical formula involves measuring the masses of elements which combine in the compound. From these masses, it is possible to calculate the number of moles of atoms which react, and hence the ratio of atoms which react. This gives an empirical formula which shows the simplest whole number ratio for the atoms of different elements in a compound.

www.youtube.com/megalecture

Example

Analysis of 20.1 g of an iron bromide sample showed that it contained 3.80 g of iron and 16.3 g of bromine. What is its empirical formula?

Notes on the method

The molar masses of the elements come from a table of data.

Convert the masses in grams to amounts in moles by dividing by the molar masses of the atoms of the elements.

Divide the amounts by the smaller of the amounts to find the simplest whole number ratio.

Answer

	iron	bromine
Combined masses	3.80 g	16.3 g
Molar mass	55.8 g mol^{-1}	79.9 g mol^{-1}
Combined moles of atoms	$\dfrac{3.80\,g}{55.8\,g\,mol^{-1}} = 0.0681\,mol$	$\dfrac{16.3\,g}{79.9\,g\,mol^{-1}} = 0.204\,mol$
Ratio of combined atoms	$\dfrac{0.0681}{0.0681} = 1.00$	$\dfrac{0.204}{0.0681} = 2.996 = 3.00$

Simplest whole number ratio of atoms is 1:3

So, the empirical formula is $FeBr_3$.

Percentage composition

Sometimes, the results of an analysis of a compound show the percentages of the different elements, rather than their masses. This is the **percentage composition** of the compound. The empirical formula of the compound can be calculated from these results.

Example

What is the empirical formula of copper pyrites which has the analysis 34.6% copper, 30.5% iron and 34.9% sulfur?

Notes on the method

Follow the procedure in the example for finding an empirical formula. The percentages, in effect, show the combining masses in a 100 g sample of the compound.

Answer

	copper	iron	sulfur
Combining masses	34.6 g	30.5 g	34.9 g
Molar masses of elements	63.5 g mol^{-1}	55.8 g mol^{-1}	32.1 g mol^{-1}
Amounts combined	$\dfrac{34.6\,g}{63.5\,g\,mol^{-1}}$	$\dfrac{30.5\,g}{55.8\,g\,mol^{-1}}$	$\dfrac{34.9\,g}{32.1\,g\,mol^{-1}}$
	$= 0.545\,mol$	$= 0.546\,mol$	$= 1.09\,mol$

Simplest whole number ratio of amounts is 1:1:2

The empirical formula is $CuFeS_2$.

Key terms

Percentage composition is the percentage by mass of each of the elements in a sample of a compound.

www.youtube.com/megalecture

Test yourself

5 What is the empirical formula of the compound in which:

   a) 0.6 g carbon combines with 0.2 g hydrogen

   b) 1.02 g vanadium combines with 2.84 g chlorine

   c) 1.38 g sodium combines with 0.96 g sulfur and 1.92 g oxygen?

6 What is the empirical formula of the compound in which the percentages of the elements present are:

   a) 2.04% hydrogen, 32.65% sulfur and 65.31% oxygen

   b) 52.18% carbon, 13.04% hydrogen and 34.78% oxygen?

Activity

Finding the formula of red copper oxide

A group of students investigated the formula of red copper oxide by reducing it to copper using natural gas as shown in Figure 5.3.

The experiment was carried out five times, starting with different amounts of red copper oxide. The results are shown in Table 5.1.
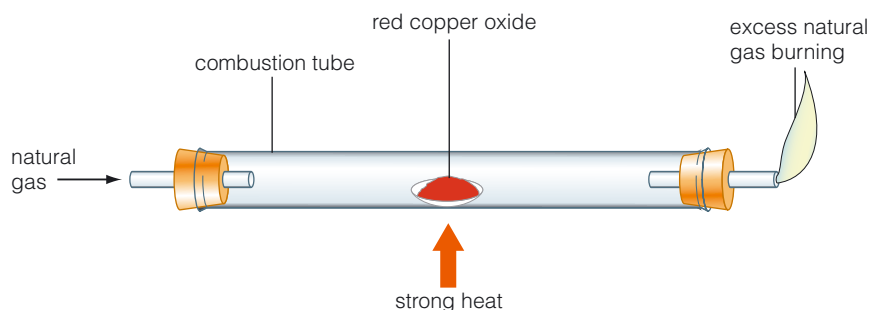

Figure 5.3 Reducing red copper oxide by heating in natural gas.

Table 5.1

Experiment number	Mass of copper in the oxide/g	Mass of red copper oxide/g
1	1.43	1.27
2	2.14	1.90
3	2.86	2.54
4	3.55	3.27
5	4.29	3.81

1 Look at Figure 5.3. What safety precautions should the students take during the experiments?

2 What steps should the students take to ensure that all the copper oxide is reduced to copper?

3 Start a spreadsheet program on a computer and open up a new spreadsheet for your results. Enter the experiment numbers and the masses of copper oxide and copper in the first three columns of your spreadsheet, as in Table 5.1.

4 a) Enter a formula in column 4 to work out the mass of oxygen in the red copper oxide used.

   b) Enter a formula in column 5 to find the amount of copper in moles in the oxide.

   c) Enter a formula in column 6 to find the amount of oxygen in moles in the oxide.

5 From the spreadsheet, plot a line graph of amount of copper (y-axis) against amount of oxygen (x-axis). Print out your graph. If you cannot plot graphs directly from the spreadsheet, draw the graph by hand.

6 Which of the points should be disregarded in drawing the line of best fit?

7 a) What, from your graph, is the average value of the ratio:

   $$\frac{\text{amount of copper/mol}}{\text{amount of oxygen/mol}} \ ?$$

   b) How much copper, in moles, combines with one mole of oxygen in red copper oxide?

   c) What is the formula of red copper oxide?

8 Give reasons why the student could claim that his answer for the formula of the oxide was valid?

9 Write a word equation, and then a balanced equation, for the reduction of red copper oxide to copper using methane (CH_4) in natural gas. (Hint: The only solid product is copper.)

5 Formulae, equations and amounts of substance

5.3 Amounts of gases

Gases and the gas laws

The Irish chemist Robert Boyle (1627–91) was one of the first people to investigate the effect of pressure on the volume of gases. About a hundred years after, in the late 18th century, the hot air balloon flights of the Montgolfier brothers stimulated scientists to study the behaviour of gases. Two of these scientists were French: Joseph Gay-Lussac (1778–1850) and Jacques Charles (1746–1823). They were particularly interested in the variation of the volumes of gases with temperature. Jacques Charles put his theories to the test and in 1783 made the first ascent in a hydrogen balloon. Meanwhile the Italian scientist Amedeo Avogadro (1776–1856) proposed the law that equal volumes of all gases, at the same temperature and pressure, contain the same number of molecules.

These scientists discovered the **gas laws** that show how the volume, V, of a sample of gas depends on three things:

- the temperature, T
- the pressure, p
- the amount of gas in moles, n.

Real and ideal gases

Scientists have the concept of an '**ideal gas**' which obeys the gas laws perfectly. In practice, real gases do not obey the laws under all conditions. Under laboratory conditions, however, there are gases which are close to behaving like an ideal gas. These are the gases which, at room temperature, are well above their boiling points, such as helium, nitrogen, oxygen and hydrogen.

Chemists generally find that the gas laws predict the behaviour of real gases accurately enough to make them a useful practical guide, but it is important to bear in mind that gases such as ammonia, butane, sulfur dioxide and carbon dioxide can show marked deviations from ideal behaviour. These are the gases which boil only a little below room temperature and can be liquefied just by raising the pressure.

The ideal gas equation

The behaviour of an ideal gas can be summed up by combining the gas laws into a single equation called the ideal gas equation:

$pV = nRT$

This equation sums up all the gas laws.

When **SI units** are used, the **pressure** is measured in pascals, Pa, the **volume** in cubic metres, m^3, and the temperature in **kelvin**, K. R, in the ideal gas equation, is the gas constant. R has the value $8.31 \, J \, mol^{-1} \, K^{-1}$ if all quantities are in SI units.

Key terms

The **gas laws** describe the behaviour of gases and are summarised by the ideal gas equation.

Ideal gases are gases which obey the ideal gas equation. In practice, real gases deviate to at least some extent from ideal behaviour.

SI units are the internationally agreed units for measurement in science.

Pressure is defined as force per unit area. The SI unit of pressure is the pascal (Pa) which is a pressure of one newton per square metre ($1 \, N \, m^{-2}$). The pascal is a very small unit and so pressures are often quoted at kilopascals (kPa). Atmospheric pressure is measure in bar: 1 bar = $100\,000 \, Pa = 100 \, kPa$.

www.youtube.com/megalecture

Key terms

Volume is the amount of space taken up by a sample. The SI unit of volume is the cubic metre (m^3). Chemists generally measure volumes in cubic decimetres (dm^3) or cubic centimetres (cm^3): 1 dm = 10 cm and so $1\,dm^3$ = 10 cm × 10 cm × 10 cm = $1000\,cm^3$; $1\,dm^3$ is the same volume as a litre; 1 m = 10 dm so $1\,m^3$ = $10^3\,dm^3$ = $10^6\,cm^3$.

The **kelvin** is the SI unit of temperature on the absolute, or Kelvin, temperature scale. On this scale, absolute zero is 0 K, water freezes at 273 K and boils at 373 K.

Test yourself

7 What are the values of these temperatures on the Kelvin scale?

    a) boiling temperature of nitrogen, $-196\,°C$

    b) boiling temperature of butane, $-0.5\,°C$

    c) melting temperature of sucrose, $186\,°C$

    d) melting temperature of iron, $1540\,°C$

8 According to the ideal gas equation what is the relationship between:

    a) the volume of a gas and its temperature if the pressure and the amount of the gas are constant

    b) the pressure and the volume of a gas if the temperature and the amount of the gas are constant

    c) the volume and the amount of gas if the pressure and the temperature are constant?

The molar volume of gases

The ideal gas equation shows that at a fixed temperature and fixed pressure, the volume of a gas depends only on the amount of gas in moles; the type or the formula of the gas does not matter. This is only strictly true for ideal gases but is nevertheless useful when dealing with real gases.

Substituting in the ideal gas equation makes it possible to calculate the volume of one mole of gas under any conditions. This shows that the volume of one mole of any gas occupies about $24\,dm^3$ ($24\,000\,cm^3$) at a typical room temperature of around $16\,°C$ (298 K) and at atmospheric pressure (100 kPa). This volume of one mole of gas is called the **molar volume** under the stated conditions.

So, 1 mole of oxygen (O_2) and 1 mole of carbon dioxide (CO_2) each occupy $24\,dm^3$ at room temperature. Therefore 2 moles of O_2 occupy $48\,dm^3$ and 0.5 moles of O_2 occupy $12\,dm^3$ at room temperature. Notice from these simple calculations that:

volume of gas/cm^3 = amount of gas/mol × molar volume/$cm^3\,mol^{-1}$

So, under laboratory conditions at room temperature:

volume of gas/cm^3 = amount of gas/mol × $24\,000$/$cm^3\,mol^{-1}$

Key terms

The **molar volume** of a gas is the volume of 1 mole of the gas under stated conditions. At room temperature and atmospheric pressure, the molar volume of all gases is $24\,dm^3\,mol^{-1}$.

Test yourself

9 What is the amount, in moles, of gas at room temperature and pressure in:

    a) $240\,000\,cm^3$ chlorine

    b) $48\,cm^3$ hydrogen

    c) $3\,dm^3$ ammonia?

10 What are the volumes in cm^3 of the following amounts of gas at room temperature and pressure:

    a) 2 mol nitrogen

    b) 0.0002 mol neon

    c) 0.125 mol carbon dioxide?

Activity

Core practical: Measuring the molar volume of a gas

The syringe shown in Figure 5.4 is used in an experiment to measure the molar volume of several gases. The procedure is outlined in steps A – I. Sample results are given in Table 5.2.
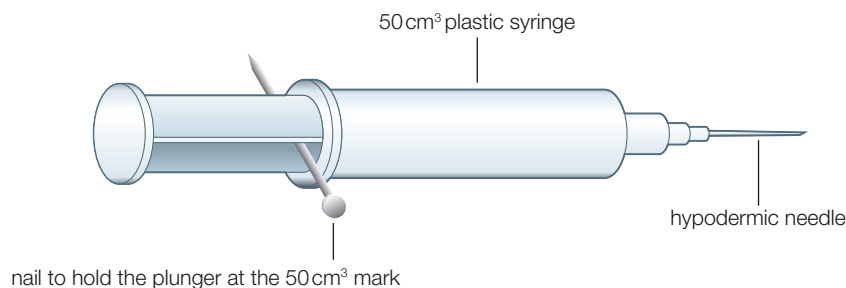
50 cm³ plastic syringe

hypodermic needle

nail to hold the plunger at the 50 cm³ mark

Figure 5.4 Plastic syringe with nail to lock the plunger at the 50 cm³ mark

A Remove the nail and needle. Fill the syringe to the 50 cm³ mark. Block the nozzle by pushing the needle into a small rubber bung. Check that the plunger returns to the 50 cm³ mark after pushing in the plunger by 10 cm³ and releasing, and after pulling out the plunger by 10 cm³ and releasing.

B Push in the plunger to empty the syringe. Block the nozzle of the needle with the rubber bung.

C Pull out the plunger and lock it at the 50 cm³ mark with the nail.

D Measure and record the mass of the syringe, stopper and nail using a three-place balance.

E Remove the rubber stopper from the needle and the nail from the plunger. Push in the plunger completely.

F Insert the needle, through a self-sealing cap, into a plastic bag containing one of the gases. Draw 50 cm³ gas into the syringe.

G Seal the gas by sticking the needle into the rubber bung again and use the nail to lock the syringe.

H Measure and record the mass of the syringe, bung and nail.

I Flush out the gas and repeat the procedure with another gas.

Table 5.2 Results recorded at room temperature and pressure.

	Mass/g
syringe + bung + nail (step D)	142.213
syringe + bung + nail + carbon dioxide	142.302
syringe + bung + nail + methane	142.247
syringe + bung + nail + butane	142.322

1 Explain the purpose of step A.

2 What was in the syringe at the end of step C, and why is it necessary to lock the plunger with the nail at the end of this step.

3 Why is the syringe weighed in step B with the plunger pulled out, rather than weighing the empty syringe with the plunger pushed in?

4 How might a bag be filled with a dry sample of carbon dioxide if the gas is not available from a cylinder? Why must the gas be dry?

5 Use the results in Table 5.2 to determine the molar volumes of the three gases.

6 Why is it necessary to use a three-place balance to measure the masses?

7 What are the main sources of measurement uncertainty in this experiment?

8 How might the procedure be modified to reduce the measurement uncertainty in the results.

www.youtube.com/megalecture

5.4 Calculations from equations

An equation is more than a useful shorthand for describing what happens during a reaction. In industry, in medicine and anywhere that chemists make products from reactants, it is vitally important to know the amounts of reactants that are needed for a chemical process and the amount of product that can be obtained. Chemists can calculate these amounts using equations.

Calculating the masses of reactants and products

There are four key steps in solving problems using equations.

Step 1: Write the balanced equation for the reaction.

Step 2: Write down the amounts in moles of the relevant reactants and products in the equation.

Step 3: Convert these amounts in moles of the relevant reactants and products to masses.

Step 4: Scale the masses to the quantities required.

Example

What mass of iron can be obtained from 1.0 kg of iron(III) oxide (iron ore)?

Notes on the method

Only do the calculation for the substances in the equation that affect the answer. In this instance, the CO and CO_2 can be ignored.

In Step 2, you obtain the numbers of moles from the numbers in front of the formulae for the substances. The number is '1' if there is no number in front of the formula.

Look up the relative atomic masses of the elements in the Periodic Table so that you can work out the molar masses.

The proportions are the same whether the mass of iron oxide is 1.0 g or 1.0 kg (1000 g).

Answer

Step 1: $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$

Step 2: $1 \, mol \, Fe_2O_3 \rightarrow 2 \, mol \, Fe$
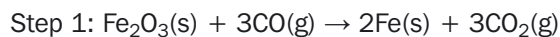
Step 3: $M(Fe_2O_3) = (2 \times 55.8 \, g \, mol^{-1}) + (3 \times 16.0 \, g \, mol^{-1})$

$$= 111.6 + 48.0 = 159.6 \, g \, mol^{-1}$$

So, $159.6 \, g \, Fe_2O_3 \rightarrow 2 \times 55.8 \, g \, Fe = 111.6 \, g \, Fe$

Step 4: $159.6 \, g \, Fe_2O_3 \rightarrow 111.6 \, g \, Fe$

$$1.0 \, g \, Fe_2O_3 \rightarrow \frac{111.6}{159.6} \, g \, Fe$$

$= 0.70 \, g \, Fe$ (giving the answer to two significant figures)

Similarly, 1.0 kg of iron(III) oxide produces 0.70 kg of iron.

---

www.youtube.com/megalecture

Test yourself

11 What mass of calcium oxide, CaO, forms when 25 g calcium carbonate, $CaCO_3$, decomposes on heating?

12 What mass of sulfur combines with 8.0 g copper to form copper(I) sulfide, Cu_2S?

13 What mass of sulfur is needed to produce 1 kg of sulfuric acid, H_2SO_4?

Measuring the volumes of gases in reactions

The apparatus in Figure 5.5 can be used to measure the reacting volumes of dry ammonia gas (NH_3) and dry hydrogen chloride gas (HCl).
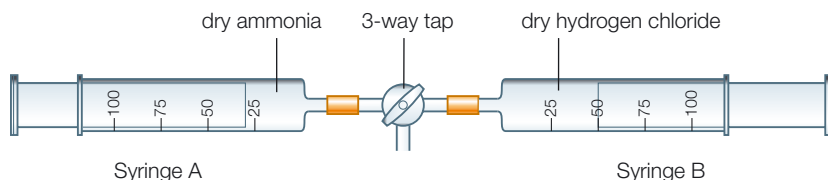

Figure 5.5 Measuring the reacting volumes of ammonia and hydrogen chloride.

When 30 cm³ of ammonia gas and 50 cm³ of hydrogen chloride gas are mixed, ammonium chloride (NH_4Cl) forms as a white solid. The volume of this solid is insignificant compared to the volume of the gases. The volume of gas remaining is 20 cm³, which turns out to be excess hydrogen chloride.

So,

30 cm³ of NH_3 reacts with 30 cm³ of HCl

1 cm³ of NH_3 reacts with 1 cm³ of HCl

and 24 dm³ of NH_3 reacts with 24 dm³ of HCl.

This shows that 1 mol of NH_3 reacts with 1 mol of HCl.

Notice that the ratio of the reacting volumes of these gases is the same as the ratio of the reacting amounts in moles shown in the equation for the reaction. This is always the case when gases react.

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$
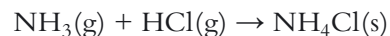
1 mol   1 mol
1 volume 1 volume

Gas volume calculations

Gas volume calculations are straightforward when all the relevant substances are gases. In these cases, the ratio of the gas volumes in the reaction is the same as the ratio of the numbers of moles in the equation. This is the case because the volume of a gas, under given conditions of temperature and pressure, depends only on the amount of the gas and not on the type of gas.

www.youtube.com/megalecture

Tip

Remember that you cannot ignore the volume of water in a gas volume calculation if the temperature is above 100 °C and the water is in the gas state.

Example

What volume of oxygen reacts with 60 cm³ methane and what volume of carbon dioxide is produced if all volumes are measured at the same temperature and pressure?

Notes on the method

Write the balanced equation.

Note that below 100 °C the water formed condenses to an insignificant volume of liquid.

Apply the rule that the ratios of gas volumes are the same as the ratio of the amounts in moles if measured under the same conditions of temperature and pressure.

Answer

The equation for the reaction is:

$$CH_4(g) \ + \ 2O_2(g) \ \rightarrow \ CO_2(g) + 2H_2O(l)$$

1mol　　　2mol　　　1mol

1 volume　2 volumes　1 volume

So, 60 cm³ methane reacts with 120 cm³ oxygen to produce 60 cm³ carbon dioxide.

The other approach to gas volume calculations also is based on the fact that the volume of a gas, under given conditions, depends only on the amount of gas in moles. The molar volume of a gas can be used to convert the amounts of gases shown in equations to volumes.

Example

What volume of hydrogen is produced under laboratory conditions when 0.024 g magnesium reacts with excess hydrochloric acid (Figure 5.6).

Notes on the method

Start by writing the equation for the reaction.

Convert the mass of magnesium to an amount in moles.

Use the equation to determine the amount of gas formed, in moles.

Multiply the amount of gas in moles by the molar volume under the conditions of the expreiment. The molar volume is 24 000 cm³ at room temperature and pressure.
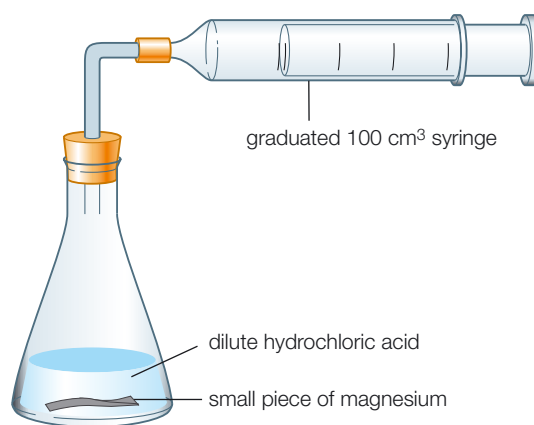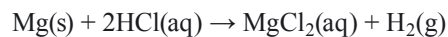

graduated 100 cm³ syringe

dilute hydrochloric acid

small piece of magnesium

Figure 5.6 Apparatus for measuring the volume of gas formed when a metal reacts with an acid.

www.youtube.com/megalecture

Answer

The equation for the reaction is:

$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

The amount of magnesium = $0.024\,g \div 24\,g\,mol^{-1} = 0.001\,mol$

From the equation, 1 mol magnesium produces 1 mol hydrogen.

Volume of hydrogen = $0.001\,mol \times 24\,000\,cm^3\,mol^{-1} = 24\,cm^3$

Test yourself

14 Assuming that all gas volumes are measured under the same conditions of temperature and pressure, what volume of:

  a) nitrogen forms when $2\,dm^3$ ammonia gas, NH_3, decomposes into its elements

  b) oxygen is needed to react with $50\,cm^3$ ethane, C_2H_6, when it burns, and what volume of carbon dioxide forms?

15 a) Copy and balance this equation for the complete combustion of propane (Calor gas).

  $C_3H_8(g) + \underline{\quad}O_2(g) \rightarrow \underline{\quad}CO_2(g) + \underline{\quad}H_2O(g)$
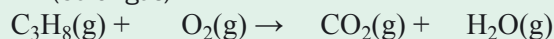
  b) What volume of oxygen reacts with $200\,cm^3$ of propane and what volume of carbon dioxide is produced? (Assume that all volumes are measured at room temperature and pressure.)

  c) What is the mass of the carbon dioxide produced?

16 What volume of gas forms at room temperature and pressure when:

  a) $0.654\,g$ of zinc reacts with excess dilute hydrochloric acid

  b) $2.022\,g$ of potassium nitrate, KNO_3, decomposes on heating to potassium nitrite, KNO_2, and oxygen?

5.5 Amounts in solutions

The **concentration** of a solution shows how much solute is dissolved in a certain volume of solution. It can be measured in grams per cubic decimetre ($g\,dm^{-3}$) but in chemistry it is more useful to measure concentrations in moles per cubic decimetre ($mol\,dm^{-3}$). For example, a solution of sodium hydroxide containing $1.0\,mol\,dm^{-3}$ has one mole of sodium hydroxide ($40\,g$ of $NaOH$) in $1\,dm^3$ ($1000\,cm^3$) of solution.

Key terms

$Concentration/g\,dm^{-3} = \dfrac{mass\ of\ solute/g}{volume\ of\ solution/dm^3}$

$Concentration/mol\,dm^{-3} = \dfrac{amount\ of\ solute/mol}{volume\ of\ solution/dm^3}$

www.youtube.com/megalecture

Tip

Concentrations are measured in moles per dm^3 of solution – not per dm^3 of water used to make up the solution. This is because there are small volume changes when solutes dissolve in water.

Example

A car battery contains $2350\,g$ of sulfuric acid (H_2SO_4) in $6.0\,dm^3$ of the battery liquid. What is the concentration of sulfuric acid in

a) $g\,dm^{-3}$
b) $mol\,dm^{-3}$?

Notes on the method

Divide the mass in grams of solute by the volume in dm^3 to find the concentration in $g\,dm^{-3}$.

Divide the mass of solute by its molar mass to find its amount in moles.

Divide the amount in moles of solute by the volume in dm^3 to find the concentration in $mol\,dm^{-3}$.

Answer

a)   Concentration of the acid/$g\,dm^{-3}$ = $\dfrac{\text{mass of solute/g}}{\text{volume of solution/dm}^3}$

$$= \frac{2350\,g}{6.0\,dm^3}$$

$$= 392\,g\,dm^{-3}$$

b) $M(H_2SO_4) = 98.1\,g\,mol^{-1}$

So, amount of H_2SO_4 in the battery $= \dfrac{2350\,g}{98.1\,g\,mol^{-1}}$

$$= 24.0\,mol$$

Concentration $= \dfrac{\text{amount of solute/mol}}{\text{volume of solution/dm}^3}$

$$= 24.0\,mol / 6.0\,dm^3$$

$$= 4.0\,mol\,dm^{-3}$$

When ionic compounds dissolve, the ions separate in the solution.

For example:

$$CaCl_2(s) \xrightarrow{aq} Ca^{2+}(aq) + 2Cl^-(aq)$$
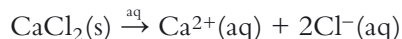
So, if the concentration of $CaCl_2$ is $0.1\,mol\,dm^{-3}$, then the concentration of Ca^{2+} is also $0.1\,mol\,dm^{-3}$, but the concentration of Cl^- is $0.2\,mol\,dm^{-3}$.

www.youtube.com/megalecture

Test yourself

17 What is the concentration, in $mol\,dm^{-3}$, of a solution containing:

a) 4.25 g silver nitrate, $AgNO_3$, in 500 cm^3 solution

b) 4.0 g sodium hydroxide, NaOH, in 250 cm^3 of solution

c) 20.75 g potassium iodide, KI, in 200 cm^3 of solution?

18 What mass of solute is present in:

a) 50 cm^3 of 2.0 $mol\,dm^{-3}$ sulfuric acid

b) 100 cm^3 of 0.010 $mol\,dm^{-3}$ potassium manganate(VII), $KMnO_4$

c) 250 cm^3 of 0.20 $mol\,dm^{-3}$ sodium carbonate, Na_2CO_3?

5.6 Solutions for quantitative analysis

Quantitative analysis involves techniques which answer the question 'How much?' In many laboratories, quantitative analysis is based on instrumental techniques such as chromatography and spectroscopy (see Topic 7).

Accurate chemical analysis generally involves preparing a solution of an unknown sample. It may then be necessary to dilute the solution before analysing it by **titration** or by some instrumental method. Titrations are an important procedure for checking and calibrating instrumental methods. In a titration, the analyst finds the volume of the sample solution that reacts with a certain volume of a reference solution with an accurately known concentration. Titrations are widely used because they are quick, convenient, accurate and easy to automate.

Key terms

A **titration** is a volumetric analysis technique for finding the concentrations of solutions and for investigating the amounts of chemicals involved in reactions.

Test yourself

19 Why might the results of the following examples of quantitative analysis be important and why must the results be reliable:

a) the concentration of sugars in urine

b) the concentration of alcohol in blood

c) the percentage by mass of haematite (iron ore) in a rock sample

d) the concentration of nitrogen oxides in the air?

Many laboratories have automatic instruments for carrying out titrations (Figure 5.7), but the principle is exactly the same as in titrations where the volumes are measured with a traditional burette and pipette. Volumetric titrations with the kinds of glassware used in school and college laboratories are widely used in the food, pharmaceutical and other industries.
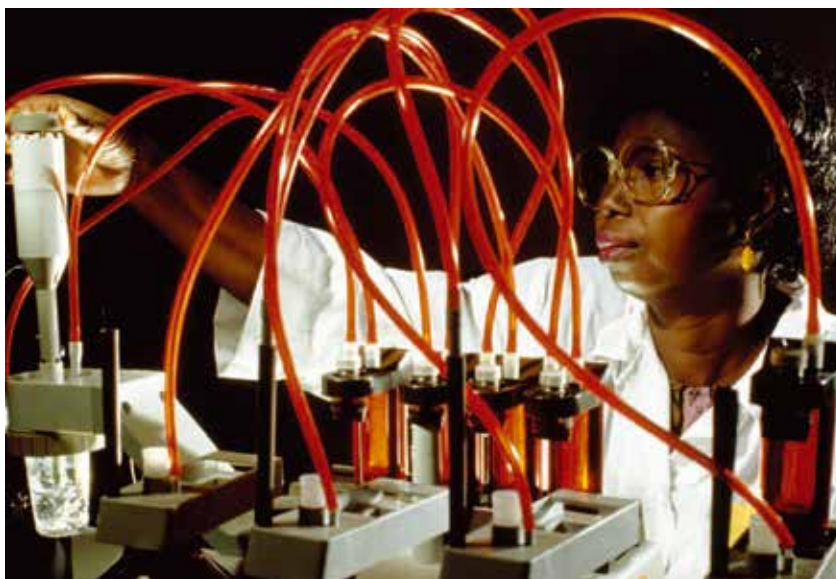
Figure 5.7 A scientist in Nigeria adjusting an automatic titration device. This is being used to check that a pharmaceutical product contains the right amount of folic acid.

Pipettes, burettes and graduated flasks make it possible to measure out volumes of solutions very precisely during a titration. There are correct techniques for using all this glassware which must be followed carefully for accurate results.

Standard solutions

Any titration involves two solutions. Typically, a measured volume of one solution is run into a flask from a pipette. Then the second solution is added bit by bit from a burette until the colour change of an indicator, or the change in a signal from an instrument, shows that the reaction is complete. The procedure only gives accurate results if the reaction between the two solutions is rapid and proceeds exactly as described by the chemical equation. So long as these conditions apply, titrations can be used to study acid–base and other types of reactions.

Standard solutions make volumetric analysis possible. The direct way of preparing a standard solution is to dissolve a known mass of a chemical in water and then to make the volume of solution up to a definite volume in a graduated flask.

This method for preparing a standard solution is only appropriate with a chemical that:

● is very pure
● does not gain or lose mass when in the air
● has a relatively high molar mass so that weighing errors are minimised.

Chemicals that meet these criteria are called **primary standards**. A titration with a primary standard can be used to measure the concentration of a solution to be analysed.

Key terms

A **standard solution** is a solution with an accurately known concentration.

A **primary standard** is a chemical which can be weighed out accurately to make up a standard solution.

Test yourself

20 Suggest a reason why sodium hydroxide cannot be used as a primary standard.

21 Suggest a reason why anhydrous sodium carbonate can be used as a primary standard but hydrated sodium carbonate cannot.

www.youtube.com/megalecture

Activity

Core practical: Preparation of a standard solution from a solid acid

A standard solution of a solid acid was prepared in a graduated flask using the procedure illustrated in Figure 5.8. The acid used was a potassium salt of benzene-1,2-dicarboxylic acid. The traditional name for the salt is potassium hydrogenphthalate which is often referred to as KHP.
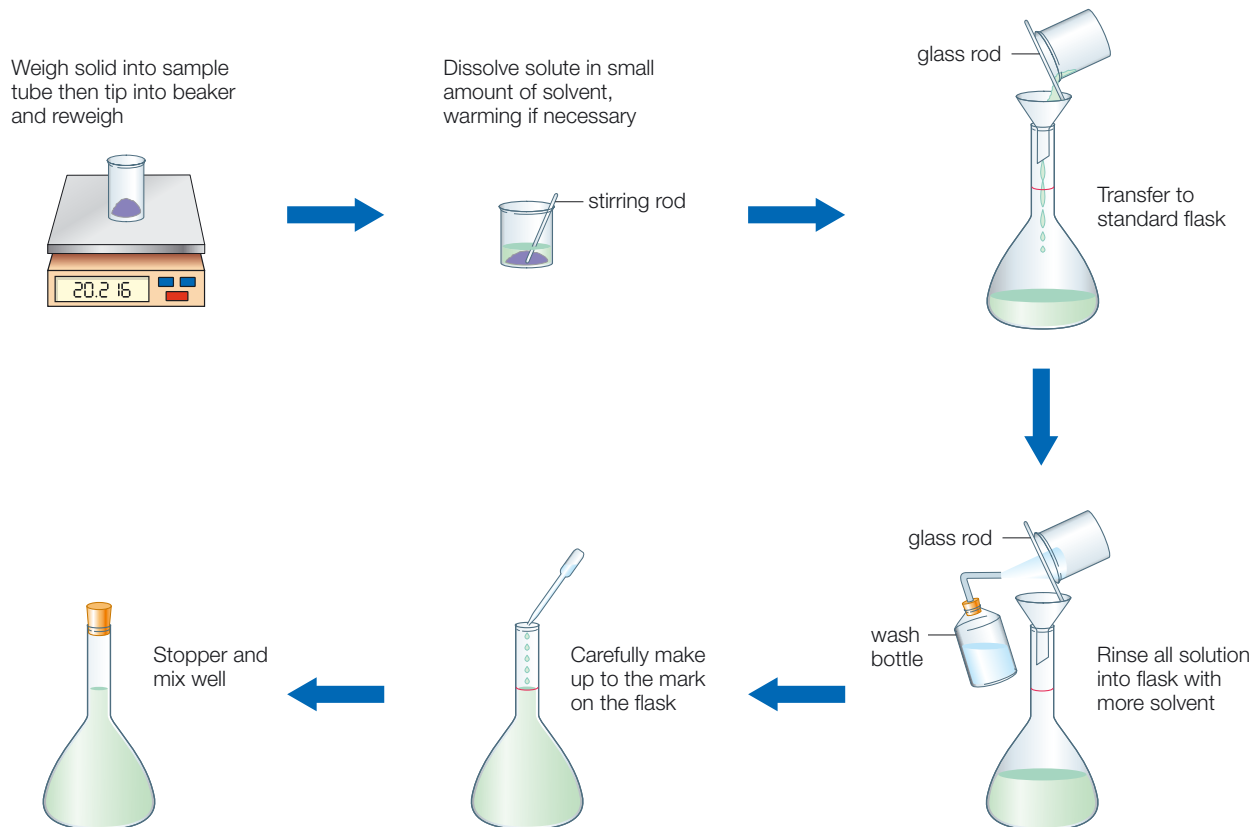
Weigh solid into sample tube then tip into beaker and reweigh

Dissolve solute in small amount of solvent, warming if necessary

stirring rod

glass rod

Transfer to standard flask

glass rod

wash bottle

Rinse all solution into flask with more solvent

Carefully make up to the mark on the flask

Stopper and mix well

Figure 5.8 Using a standard flask to prepare a solution with a specified concentration.

1 The formula of KHP is $KHC_8H_4O_4$. What mass of KHP is needed to prepare a 0.10 mol dm^{-3} solution in a 250 cm^3 graduated flask?

2 Suggest a reason why KHP is a better primary standard to use than the oxalic acid ($H_2C_2O_4.2H_2O$) which is also available as a pure solid.

3 **a)** Why is the solution poured down a glass rod as the liquids are transferred from the beaker to the graduated flask?
   b) What other steps must be taken to ensure that every drop of the solution is transferred to the graduated flask?

4 After transferring the solution from the beaker, the graduated flask is filled with water to within about 1 cm of the graduation mark. The contents are then mixed well before finally adding water dropwise until the meniscus just rests on the mark. What are the reasons for following this procedure?

5 Calculate the concentration of the standard solution made by the procedure in Figure 5.8 when the readings from the balance when weighing out the solid are as follows and the volume of the graduated flask is 250.0 cm^3:

Mass of weighing bottle plus sample of KHP = 20.216 g

Mass of weighing bottle after tipping KHP into the beaker = 14.855 g

www.youtube.com/megalecture

Diluting a solution quantitatively

Quantitative dilution is an important procedure in analysis. Two common reasons for carrying out dilutions are:

- to make a solution with the concentration needed for a particular experiment from a standard solution
- to dilute an unknown sample for analysis to give a concentration suitable for titration.

The procedure for dilution is to take a measured volume of the more concentrated solution with a pipette (or burette) and run it into a graduated flask. The flask is then carefully filled to the mark with pure water.

The key to calculating the volumes to use when diluting a solution is to remember that the amount, in moles, of the chemical dissolved in the diluted solution is equal to the amount, in moles, of the chemical taken from the concentrated solution. If c is the concentration in $mol\,dm^{-3}$ and V is the volume in dm^3, then we can write the following expressions.

The amount, in moles, of the chemical taken from the concentrated solution $= c_A V_A$

The amount, in moles, of the same chemical in the diluted solution $= c_B V_B$

These two amounts are the same, so $c_A V_A = c_B V_B$

Example

An analyst requires a $0.10\,mol\,dm^{-3}$ solution of sodium hydroxide, NaOH(aq). The analyst has a $250\,cm^3$ graduated flask and a supply of $0.50\,mol\,dm^{-3}$ sodium hydroxide solution. What volume of the concentrated solution should be measured into the graduated flask?

Notes on the method

Use the relationship $c_A V_A = c_B V_B$

This can be rearranged to show that: $V_A = \dfrac{c_B V_B}{c_A}$

Answer

$c_A = 0.50\,mol\,dm^{-3}$ $\qquad\qquad c_B = 0.10\,mol\,dm^{-3}$

$V_A =$ to be calculated $\qquad\quad V_B = 250\,cm^3 = 0.25\,dm^3$

$V_A = \dfrac{c_B V_B}{c_A} = \dfrac{0.10\,mol\,dm^{-3} \times 0.25\,dm^3}{0.50\,mol\,dm^{-3}}$

$\qquad\qquad = 0.050\,dm^3 = 50.0\,cm^3$

Pipetting $50.0\,cm^3$ of the concentrated solution into the $250\,cm^3$ graduated flask and making up to the mark with pure water gives the required dilution after thorough mixing.

www.youtube.com/megalecture

Test yourself

22 How would you prepare:

  a) a $0.05\,mol\,dm^{-3}$ solution of $HCl(aq)$ given a $1000\,cm^3$ graduated flask and a $1.00\,mol\,dm^{-3}$ solution of the acid

  b) a $0.01\,mol\,dm^{-3}$ solution of $NaOH(aq)$ given a $500\,cm^3$ graduated flask and a $0.50\,mol\,dm^{-3}$ solution of the alkali?

23 What is the concentration of the solution produced when making up to the mark with pure water and mixing:

  a) $10.0\,cm^3$ of a $0.01\,mol\,dm^{-3}$ solution of $AgNO_3(aq)$ in a $100\,cm^3$ graduated flask

  b) $50.0\,cm^3$ of a $2.00\,mol\,dm^{-3}$ solution of nitric acid in a $250\,cm^3$ graduated flask?

5.7 Titration principles

A titration involves two solutions. A measured volume of one solution is run into a flask. The second solution is then added bit by bit from a burette until the reaction is complete (Figure 5.9).
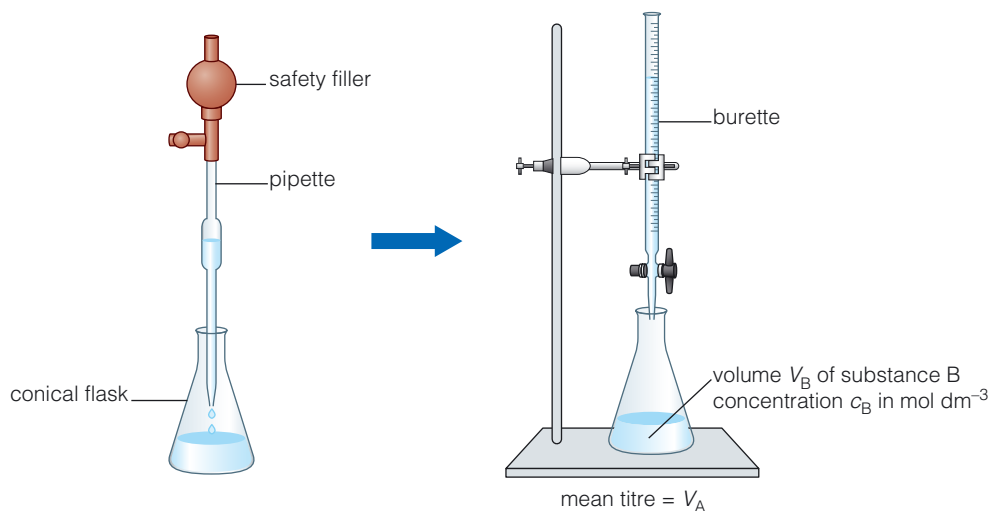

Figure 5.9 The apparatus used for a titration based on a reaction between two chemicals in solution, A and B.

Some titrations are used to investigate reactions. In these experiments the concentrations of both solutions are known and the aim is to determine the equation for the reaction.

More often, titrations are used to measure the concentration of an unknown solution knowing the equation for the reaction and using a second solution of known concentration.

In general, n_A moles of A react with n_B moles of B.
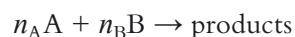
$$n_A A + n_B B \rightarrow products$$

The concentration of solution B in the flask is c_B and the concentration of solution A in the burette is c_A. Both are measured in $mol\,dm^{-3}$. The analyst uses a pipette to run a volume V_B of solution B into the flask. Then solution A is added from the burette until an indicator shows that the reaction is complete. This is the **end-point** of the titration.

In a well planned titration the colour change observed at the end-point corresponds exactly with the point when the amount in moles of the reactant added from a burette is just enough to react exactly with all of the measured amount of chemical in the flask as shown by the balanced equation. This is the **equivalence point**.

At the end-point, the volume added is the titre, V_A. The analyst should repeat the titration enough times to achieve consistent results.

Titration calculations

In the laboratory, volumes of solutions are normally measured in cm^3, but they should be converted to dm^3 in calculations so that they are consistent with the units used for concentrations.

The amount, in moles, of B in the flask at the start $= c_B \times V_B$

The amount, in moles, of A added from the burette $= c_A \times V_A$

The ratio of these amounts must be the same as the ratio of the reacting amounts n_A and n_B. This means that:

$$\frac{c_A \times V_A}{c_B \times V_B} = \frac{n_A}{n_B}$$

In any titration, all but one of the values in this relationship are known. The one unknown is calculated from the results, so this formula can be used to analyse titration results. It is generally better, however, to work out the results step by step as shown in the worked examples in this chapter.

Analysing solutions

In titrations designed to analyse solutions, the equation for the reaction is given so that the ratio n_A/n_B is known. The concentration of one of the solutions is also known. The volumes V_A and V_B are measured during the titration. Substituting all the known quantities in the titration formula allows the concentration of the unknown solution to be calculated.

Investigating reactions

In titrations to investigate reactions, the problem is to determine the ratio n_A/n_B. The concentrations c_A and c_B are known and the volumes V_A and V_B are measured during the titration. So the ratio n_A/n_B can be calculated from the formula.

5.8 Acid–base titrations

Coloured indicators can be used to detect the end-points of acid–base reactions. These are chemicals which change colour as the pH varies. Typically, an indicator completes its colour change over a range of about two pH units as shown in Table 5.3. In any acid–base titration there is a sudden change of pH at the end-point. The chosen indicator must therefore complete its colour change within the range of pH values spanned at the end-point.

whatsapp: +92 323 509 4443, email: megalecture@gmail.com

Some acids and alkalis are fully ionised in solution. These are **strong acids** and strong alkalis. For a titration of a strong acid with a strong alkali, the pH jumps from around pH3 to pH10 at the end-point. Most common indicators change colour sharply within this range.

Other acids are only slightly ionised in solution. These are **weak acids**. During a titration of a weak acid with a strong alkali, the jump is from about pH6 to pH10. So the indicator must be chosen with care so that it changes colour in this range.

Table 3.5 Some common indicators and the pH range over which they change colour.

Indicator	Colour change low pH–high pH	pH range over which the colour change occurs
Methyl orange	Red–yellow	3.2−4.2
Methyl red	Yellow–red	4.8−6.0
Bromothymol blue	Yellow–blue	6.0−7.6
Phenolphthalein	Colourless–red	8.2−10.0

Key terms

A **strong acid** is one that is fully ionised when it dissolves in water. Hydrochloric acid is an example of a strong acid.

A **weak acid** is one that is only slightly ionised when it dissolves in water. Ethanoic acid is an example of a weak acid.

Tip

You will learn more about indicators and why they change colour over different pH ranges later in your advanced chemistry course.

Example

Calcium hydroxide is an alkali that is only slightly soluble in water. Its solubility, at a given temperature, can be determined by titration of a saturated solution of the alkali with a standard solution of hydrochloric acid as shown in Figure 5.10. Work out the solubility of $Ca(OH)_2$ in moles per dm^3, and in grams per dm^3, given that the volume V_A of acid added from the burette at the end point was $23.50\,cm^3$.
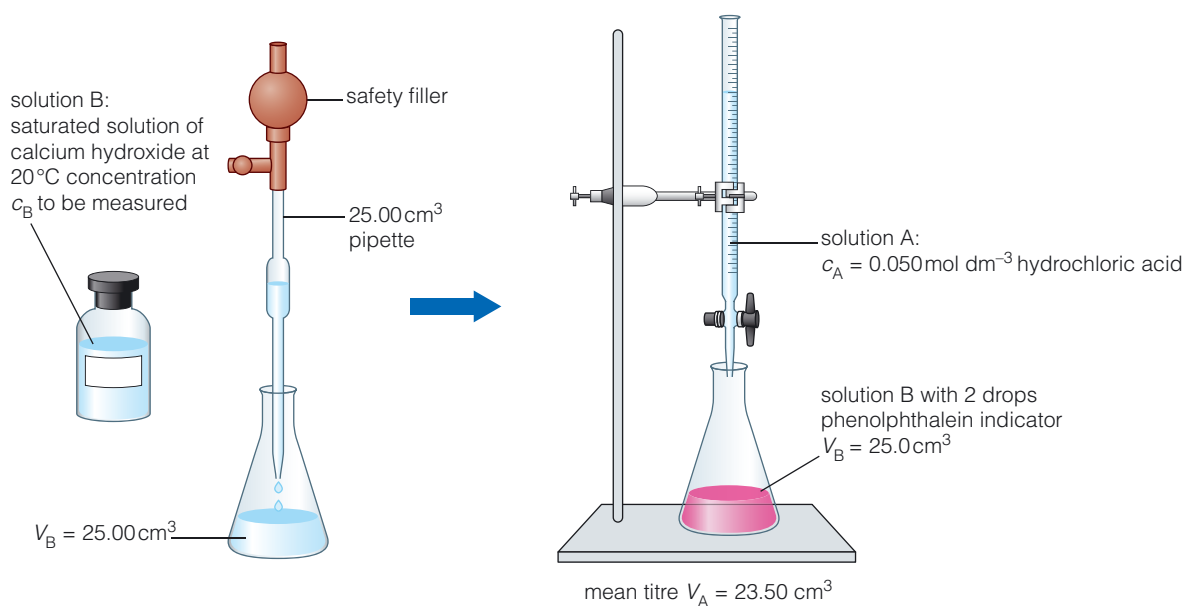

Figure 5.10 A titration to determine the solubility of calcium hydroxide.

www.youtube.com/megalecture

Notes on the method

Both the volume and concentration of the acid are known so the first step is to work out the amount in moles of acid added from the burette.

Next look at the balanced equation to see how much $Ca(OH)_2$ this amount of acid reacts with.
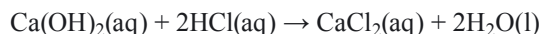
Finally work out the concentration of calcium hydroxide in the saturated solution.

Answer

Step 1: Work out the amount of acid added from the burette.

The concentration of the acid, c_A $= 0.050\,mol\,dm^{-3}$

Amount of HCl(aq) added from the burette $= \dfrac{23.50\,dm^3}{1000} \times 0.050\,mol\,dm^{-3}$
$= 0.001175\,mol$

Step 2: Use the equation for the titration reaction to find the amount of alkali in the flask.

$$Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$$

So 1 mol of the alkali reacts with 2 mol of the acid.

Hence the amount of calcium hydroxide in the flask $= 0.5 \times 0.001175\,mol$
$= 0.0005875\,mol$

Step 3: Work out the concentration of the saturated solution.

The $0.0005875\,mol$ of alkali is dissolved in $25.0\,cm^3$ of saturated solution.

So the concentration of saturated calcium hydroxide solution
$= 0.0005875\,mol \div 0.025\,dm^3$
$= 0.0235\,mol\,dm^{-3}$

The molar mass of calcium hydroxide is $74.1\,g\,mol^{-1}$.

So the concentration of saturated calcium hydroxide solution

$= 0.0235\,mol\,dm^{-3} \times 74.1\,g\,mol^{-1}$
$= 1.74\,g\,dm^{-3}$

Test yourself

24 Suggest why methyl orange is distinctly orange when the pH is 3.7.

25 A $25.0\,cm^3$ sample of nitric acid was neutralised by $18.0\,cm^3$ of $0.15\,mol\,dm^{-3}$ sodium hydroxide solution. Calculate the concentration of the nitric acid.

26 A $2.65\,g$ sample of anhydrous sodium carbonate was dissolved in water and the solution made up to $250\,cm^3$. In a titration, $25.0\,cm^3$ of this solution was added to a flask and the end-point was reached after adding $22.5\,cm^3$ of hydrochloric acid. Calculate the concentration of the hydrochloric acid.

27 A $41.0\,g$ sample of the acid H_3PO_3 was dissolved in water and the volume of solution was made up to $1\,dm^3$. $20.0\,cm^3$ of this solution was required to react with $25.0\,cm^3$ of $0.80\,mol\,dm^{-3}$ sodium hydroxide solution. What is the equation for the reaction?

www.youtube.com/megalecture

5.9 Evaluating results

Accuracy of data is determined by how close a measured quantity is to the correct value. In chemical analysis the correct value is often not known and so chemists need to estimate the measurement uncertainty.

Every time an analyst carries out a titration, there is some uncertainty in the result. It is important to be able to assess measurement uncertainty (Figure 5.11). Key decisions are based on the results of chemical analysis in healthcare, in the food industry, in law enforcement and in many other areas of life. It is important that the people making these decisions understand the extent to which they can rely on the data from analysis.
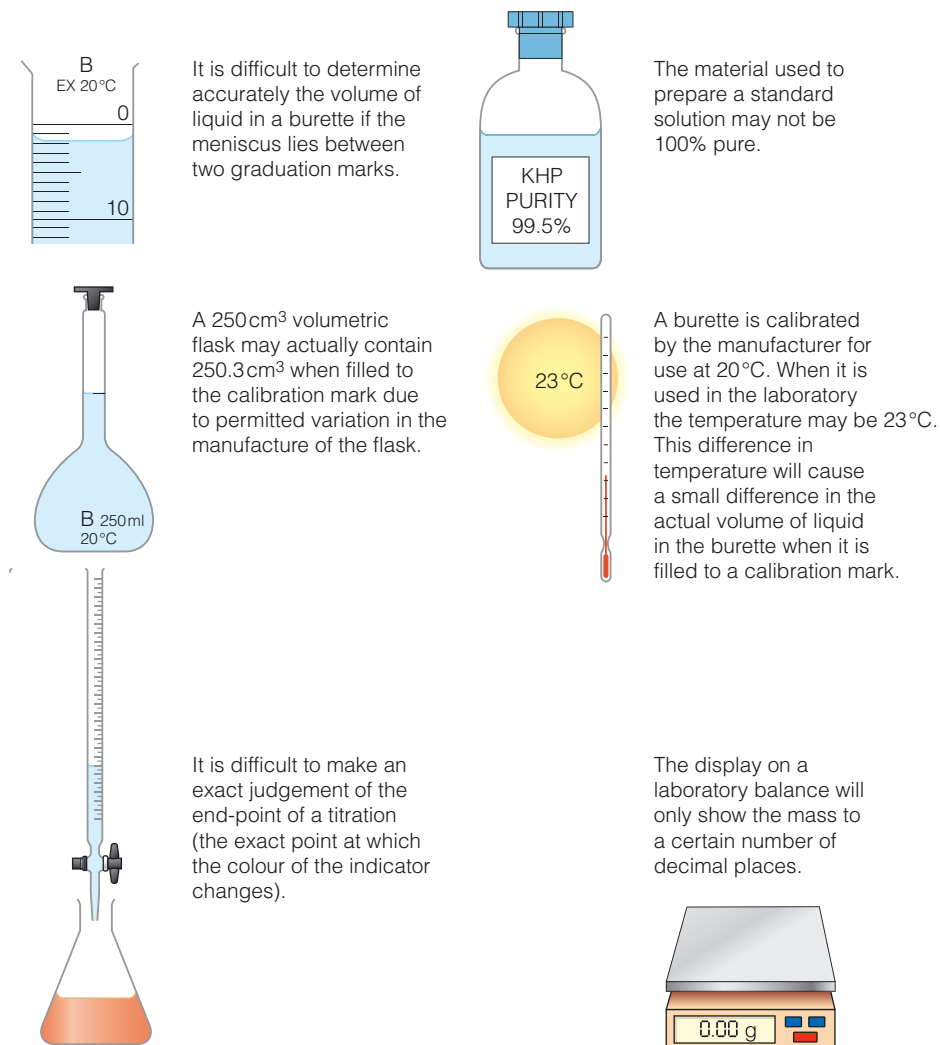
It is difficult to determine accurately the volume of liquid in a burette if the meniscus lies between two graduation marks.

The material used to prepare a standard solution may not be 100% pure.

KHP PURITY 99.5%

A 250 cm^3 volumetric flask may actually contain 250.3 cm^3 when filled to the calibration mark due to permitted variation in the manufacture of the flask.

23 °C

A burette is calibrated by the manufacturer for use at 20 °C. When it is used in the laboratory the temperature may be 23 °C. This difference in temperature will cause a small difference in the actual volume of liquid in the burette when it is filled to a calibration mark.

It is difficult to make an exact judgement of the end-point of a titration (the exact point at which the colour of the indicator changes).

The display on a laboratory balance will only show the mass to a certain number of decimal places.

0.00 g

Figure 5.11 Sources of uncertainty in volumetric analysis.

Random errors in titrations

Every time an analyst carries out a titration, there are small differences in the results. This is not because the analyst has made mistakes but because there are factors that are impossible to control. Unavoidable random errors arise in judging when the bottom of the meniscus is level with the graduation on a pipette, in judging the colour change at the end–point and when taking the reading from a burette scale. If these random errors are small then the results are all close together – in other words, they are **precise** (Figure 5.12). The precision of a set of results can be judged from the range in a number of repeated titrations.

www.youtube.com/megalecture

# Systematic errors in titrations

Systematic errors mean that the results differ from the true value by the same amount each time. The measurement is always too high or too low, so it is **biased** in one way or the other (Figure 5.12). One source of systematic error is the tolerance allowed in the manufacture of graduated glassware. The tolerance for grade B 250 cm³ graduated flasks is ± 0.3 cm³. This means that when an analyst chooses to use a particular flask, the volume of solution may be as little as 249.7 cm³ or as much as 250.3 cm³ when it is filled correctly to the graduation mark. This introduces a systematic error when using this same flask to make up solutions for a series of titrations.

Similar tolerances are allowed for pipettes and burettes: for a class B 25 cm³ pipette the tolerance is ± 0.06 cm³, while for a class B 50 cm³ burette the tolerance is ± 0.1 cm³.

Systematic errors can be allowed for by calibrating the measuring instruments. It is possible to calibrate pipettes and burettes by using them to measure out pure water and then weighing the water with an accurate balance.

A darts player is practising throwing darts at a board. The aim is to get all the darts close together near the centre of the board. The results of some of the attempts are shown below.
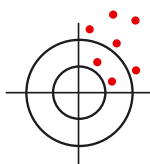
1st attempt: The shots are quite widely scattered and some have not even hit the board. The shots show *poor precision* as they are quite widely scattered. There is also a *bias* in where the shots have landed – they are grouped in the top right-hand corner, not near the centre of the board.

bias

2nd attempt: The *precision* has improved as the shots are now more closely grouped. However, there is still a *bias*, as the group of shots is offset from the centre of the board.
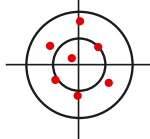
3rd attempt: The player has improved to *reduce* the *bias* – all the shots are now on the board and scattered round the centre. Unfortunately the *precision* is *poor* as the shots are quite widely scattered.

Some time later: The shots are *precise* and *unbiased* – they are all grouped close together in the centre of the board.

Figure 5.12 Throwing darts at the bullseye of a dartboard illustrates the notions of precision and bias. Reliable players throw precisely and without bias so that their darts hit the centre of the board accurately.

Tip

See Sections 5.9 and 11.10 to find out how to estimate measurement errors and calculate overall measurement uncertainties.

Test yourself

28 Identify examples of random and systematic error when:

   a) using a pipette

   b) using a burette

   c) making up a standard solution in a graduated flask.

Activity

Core practical: Finding the concentration of a solution of hydrochloric acid

A student carried out a titration to determine the concentration of a solution of hydrochloric acid. He used the apparatus shown in Figure 5.13 and followed the instructions numbered A–F. The results are shown in the table below the instructions.
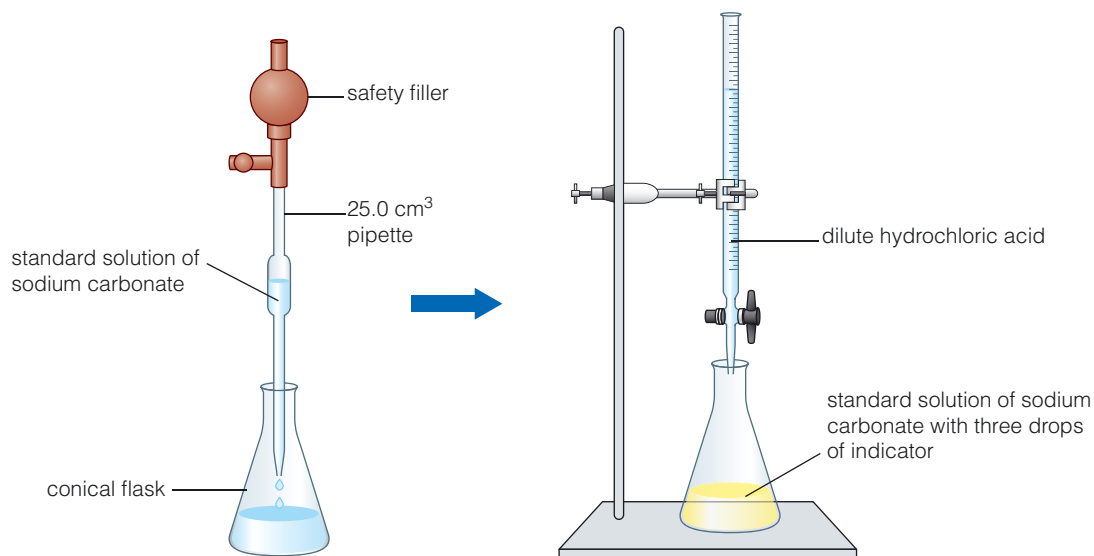

Figure 5.13

Instructions

A Wash out the pipette, burette and conical flask with pure (deionised or distilled) water.

B Rinse the burette with a little of the solution of hydrochloric acid, then fill the burette remembering to run out some of the solution through the tap.

C Rinse the 25.0 cm³ pipette with the standard solution of sodium carbonate. Fill the pipette to the mark and run out the measured alkali into a clean conical flask allowing the pipette to drain adequately.

D Add three drops of methyl orange indicator.

E Carry out one rough and then accurate titrations to give two titres that are within 0.10 cm³ of each other. In the accurate titrations the colour change at the end-point should be caused by adding one drop of acid.

F Each time record the initial and final burette readings. Take the burette readings to the nearest half-scale division.

Results

Burette: Solution of hydrochloric acid to be standardised

Pipette: Standard solution of sodium carbonate

Indicator: Methyl orange

1 Explain briefly the reasons for carrying out each of the steps A–F.

2 Describe what the student should do to 'allow the pipette to drain adequately' in Step C.

3 The standard solution of sodium carbonate was prepared with 2.920 g anhydrous Na_2CO_3 in a 500 cm³ graduated flask. Calculate the concentration of the sodium carbonate solution.

4 How should the student read the burette in order to justify recording results to the nearest 0.05 cm³?

5 Use the titration results in Table 5.4 to calculate the concentration of the dilute hydrochloric acid.

6 The glassware used for the titration was all grade B apparatus. Estimate the total uncertainty in your calculated result (see Sections 5.9 and 11.10).

Table 5.4 Titration results

	Rough	Accurate 1	Accurate 2	Accurate 3
Final burette reading	28.0	24.00	25.70	26.50
Initial burette reading	5.0	1.55	3.30	4.15
Titre/cm³	23.0	22.45	22.40	22.35

www.youtube.com/megalecture

5.10 Yields and atom economies

If there are no losses during a chemical reaction, the starting reactants are converted to the required products. Often, some reactants are added in excess to ensure that the most valuable reactant is converted to as much product as possible. Then the reactant that is not in excess is the substance that limits the maximum yield that is possible.

Converting all of the **limiting reagent** to the desired product gives a 100% **yield**. But few reactions are so efficient and many give low yields. There are various reasons why yields are not 100%:

- the reactants may not be totally pure
- some of the product may be lost during transfer of the chemicals from one container to another, when the product is separated and purified
- there may be side reactions in which the reactants form different products
- some of the reactants may not react because the reaction is so slow (Chapter 9) or because it comes to equilibrium (Chapter 10).

Key terms

Yield calculations are used to assess the efficiency of a chemical process. The actual yield is the mass of product obtained from a reaction. The theoretical yield is the mass of product obtained if the reaction goes according to the equation.

The percentage yield = $\dfrac{\text{actual yield}}{\text{theoretical yield}} \times 100$

A **limiting reactant** is a substance which is present in an amount which limits the theoretical yield.

Example

A modern gas-fuelled lime kiln produces 500 kg of calcium oxide, CaO (quicklime), from 1000 kg of crushed calcium carbonate, $CaCO_3$(limestone).

What is the percentage yield of calcium oxide?

Notes on the method

Start by writing the balanced equation for the reaction.

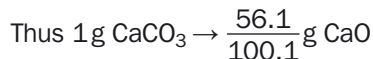Use the method for calculating reactant and product masses in Section 1.3.

Answer

The equation for the reaction involved is:

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

From the equation, 1 mole $CaCO_3 \rightarrow$ 1 mole CaO

$[40.1 + 12 + (3 \times 16)]\,g\,CaCO_3 \rightarrow (40.1 + 16)\,g\,CaO$

So 100.1 g $CaCO_3 \rightarrow$ 56.1 g CaO

Thus 1 g $CaCO_3 \rightarrow \dfrac{56.1}{100.1}$ g CaO

Theoretical yield from 1000 kg $CaCO_3 = \dfrac{56.1}{100.1} \times 1000$ kg CaO

$= 560$ kg

The actual yield of CaO $= 500$ kg CaO

Percentage yield $= \dfrac{500\,\text{kg}}{560\,\text{kg}} \times 100 = 89\%$

www.youtube.com/megalecture

Atom economy

The yield in a laboratory or industrial process focuses on the desired product. But many atoms in the reactants do not end up in the desired product. This can lead to a huge waste of material. For example, when calcium carbonate (limestone) is decomposed to produce calcium oxide (quicklime), part of the calcium carbonate is lost as carbon dioxide in the atmosphere.

The waste in many reactions has led scientists and industrialists to use the term **atom economy** in calculating the overall efficiency of a chemical process (Figure 5.14). The atom economy of a reaction is the molar mass of the desired product expressed as a percentage of the sum of the molar masses of all the products as shown in the equation for the reaction.

$$\text{atom economy} = \frac{\text{molar mass of the desired product}}{\text{sum of the molar masses of all the products}} \times 100\%$$

Key terms

Atom economy is a measure of how efficiently a chemical reaction converts the atoms in its reactants to atoms in the product. The atom economy for a reaction is calculated from the balanced equation to show the percentage of the mass of the atoms in the reactants that is converted to the desired product.
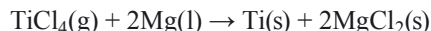

Figure 5.14 The production of ibuprofen is an excellent example of atom economy. Ibuprofen is an important medicine which reduces swelling and pain. In the 1960s, Boots made ibuprofen in five steps with an atom economy of only 40%. When the patent expired, another company developed a new process requiring just two steps with an atom economy of 100%.

> ### Example
>
> Titanium is manufactured by heating titanium(IV) chloride with magnesium. The equation for the reaction is:
>
> $$TiCl_4(g) + 2Mg(l) \rightarrow Ti(s) + 2MgCl_2(s)$$
>
> What is the atom economy of this process?
>
> ### Answer
> Molar mass of all products = $M(Ti) + 2M(MgCl_2)$
>
> = $47.9\,g\,mol^{-1} + 190.6\,g\,mol^{-1} = 238.5\,g\,mol^{-1}$
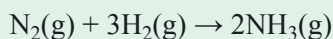>
> Molar mass of desired product = $47.9\,g\,mol^{-1}$
>
> Therefore: atom economy = $47.9 \div 238.5 \times 100\% = 20.1\%$

Almost 80% of the reactants are 'wasted' in the manufacture of titanium by the process described above because magnesium and chlorine atoms are lost as magnesium chloride. If society is to use raw materials as efficiently as possible, chemists must look for high atom economies as well as high percentage yields, particularly in industrial processes.
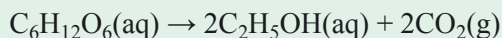
> ### Test yourself
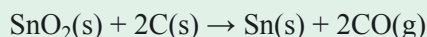>
> **31** Calculate the atom economy for:
>   **a)** the conversion of nitrogen (N_2) to ammonia (NH_3) in the Haber process:
> $$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$
>   **b)** the fermentation of glucose ($C_6H_{12}O_6$) to ethanol (C_2H_5OH)
> $$C_6H_{12}O_6(aq) \rightarrow 2C_2H_5OH(aq) + 2CO_2(g)$$
>   **c)** the manufacture of tin (Sn) from tinstone (SnO_2)
> $$SnO_2(s) + 2C(s) \rightarrow Sn(s) + 2CO(g)$$

5.11 Tests and observations in inorganic chemistry

Formulae and equations are not only used to solve quantitative problems. They are also important in qualitative analysis.

Qualitative analysis answers the question 'What is it?' In advanced chemistry courses, this question is often answered by careful observation of the changes during test tube experiments and flame tests. These changes include gases bubbling off, different smells, precipitates forming, solids dissolving, temperatures changing or new colours appearing.

The skill is knowing what to look for. Some visible changes are much more significant than others and a capable analyst can spot the important changes and know what they mean. Good chemists have a 'feel' for the way in which chemicals behave and recognise characteristic patterns of behaviour. With experience they know what to look for when making observations.

Success also depends on good techniques when mixing chemicals, heating mixtures and testing for gases.

In inorganic chemistry most observations can be explained in terms of a number of types of reaction (see also Chapter 3 and Section 4.1).

Ionic precipitation reactions

This type of reaction can be used to test for negative ions (anions). Adding a solution of silver nitrate to a halide produces a precipitate that can be used to distinguish chlorides, bromides and iodides. Adding a soluble barium salt (nitrate or chloride) to a solution of a sulfate produces a white precipitate of insoluble barium sulfate.

Acid–base reactions

Acids and alkalis are commonly used in chemical tests. Dilute hydrochloric acid is a convenient strong acid. Sodium hydroxide solution is often chosen as a strong base.

Adding dilute hydrochloric acid to a carbonate, for example, adds hydrogen ions to the carbonate ions, CO_3^{2-}, turning them into carbonic acid molecules, H_2CO_3, which immediately decomposes into carbon dioxide and water.

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow H_2CO_3(aq) \rightarrow H_2O(l) + CO_2(g)$$

Testing with limewater can then identify the gas given off, confirming that the compound tested is a carbonate.

Redox reactions

Common oxidising agents used in inorganic tests include chlorine, bromine and acidic solutions of iron(III) ions, manganate(VII) ions or dichromate(VI) ions.

Some reagents change colour when oxidised, which makes them useful for detecting oxidising agents. In particular, a colourless solution of iodide ions turns to a yellow–brown colour when oxidised. This can be a very sensitive test if starch is present because starch gives an intense blue–black colour with low concentrations of iodine. This is the basis of using starch–iodide paper to test for chlorine and other oxidising gases. The oxidation of iodide ions by chlorine or bromine is a redox reaction in which one halogen displaces another (Section 4.10).

Common inorganic reducing agents are metals (in the presence of acid or alkali), sulfur dioxide and iron(II) ions.

Some reagents change colour when reduced. In particular, dichromate(VI) ions in acid change from orange to green. This is the basis of a test for sulfur dioxide gas.

www.youtube.com/megalecture

Test yourself

32 For each of the following tests, identify the type of chemical reaction taking place, name the products and write a balanced equation for the reaction:

a) testing for iodide ions with silver nitrate solution

b) adding dilute hydrochloric acid to magnesium carbonate

c) testing for sulfate ions with barium chloride

d) strongly heating a sample of potassium nitrate

e) using concentrated ammonia solution to detect hydrogen chloride

f) adding chlorine to a solution of potassium bromide.

Activity

Core practical: Analysis of inorganic unknowns

A series of tests was carried out on two unknown inorganic salts labelled X and Y. The tests and observations were recorded as in Table 5.5.

Table 5.5 Tests and observations on two inorganic unknowns

Test	Observations with compound X	Observations with compound Y
1 Carry out a flame test on the salt	Lilac coloured flame	Lilac coloured flame
2 Heat a sample of the salt first gently and then more strongly. Identify any gases evolved.	Melts to a colourless liquid. It gives off a colourless gas that relights a glowing splint. On strong heating the gas is tinged with purple. In time the liquid turns red.	Melts to a clear liquid but no gas is given off. In time the hot liquid turns red. There are slight traces of a purple vapour. Molten Y resembles the liquid formed on decomposing X.
3 Allow the residue from test 2 to cool, then add a few drops of concentrated sulfuric acid. Warm gently and then more strongly. Identify any gases evolved.	On cooling, the liquid crystallises to a colourless (white) solid. The cold crystals react immediately with concentrated sulfuric acid. There are traces of a fuming, acidic gas. There is a smell of bad eggs. On warming a purple vapour can be seen.	On cooling, the liquid crystallises to a colourless (white) solid. The solid reacts with concentrated sulfuric acid in the same way as the residue after heating X.
4 Make separate aqueous solutions of X and Y. Mix the two solutions and then add dilute sulfuric acid.	Both X and Y dissolve in water. The solutions are colourless. There is no change at first when the solutions are mixed. On adding dilute sulfuric acid the solutions turn dark brown. Specks of a grey solid separate from the solution.	

1 Describe in outline the procedure for carrying out a flame test on an unknown salt.

2 What precautions have to be taken to avoid contamination, and why are they necessary?

3 Describe in outline the procedure for the gas tests mentioned in Table 5.5.

4 What can be deduced from the results of the flame tests in Table 5.5?

5 Suggest explanations for the observations on heating X and Y, including equations for any reactions.

6 What can be deduced from the results of Test 3?

7 Explain the observations in Test 4 and write an equation for the reaction which took place on adding acid.

8 Describe two further tests that could be carried out to confirm the conclusions based on these observations. What are the expected results of these tests.

www.youtube.com/megalecture

Exam practice questions

1 Balance the following equations:

a) $Cu_2S(s) + O_2(g) \rightarrow CuO(s) + SO_2(g)$ *(1)*

b) $FeS(s) + O_2(g) + SiO_2(s) \rightarrow FeSiO_3(s) + SO_2(g)$ *(3)*

c) $Fe(NO_3)_3(s) \rightarrow Fe_2O_3(s) + NO_2(g) + O_2(g)$ *(3)*

2 a) How many molecules are present in 4.0 g of oxygen, O_2? (O = 16) *(3)*

b) How many ions are present in 9.4 g of potassium oxide, K_2O? (K = 39, O = 16) (Avogadro constant = 6.02×10^{23} mol^{-1}) *(3)*

3 One cubic decimetre of tap water was found to contain 0.112 mg of iron(III) ions (Fe^{3+}) and 12.40 mg of nitrate ions (NO_3^-).

a) What are these masses of Fe^{3+} and NO_3^- in grams? *(1)*

b) What are the amounts in moles of Fe^{3+} and NO_3^-? *(2)*

c) What are the numbers of Fe^{3+} and NO_3^- ions? *(2)*

4 a) What is the empirical formula of a substance X with this percentage composition: C = 42.87%, H = 2.36%, N = 16.67% and O = 38.10%? *(4)*

b) Mass spectrometry shows that the relative molecular mass of X is 168. What is the molecular formula of X? (2)

5 For each of the following equations, state the type of reaction which it represents.

a) $Ca(NO_3)_2(aq) + K_2CO_3(aq) \rightarrow CaCO_3(s) + 2KNO_3(aq)$

b) $Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$

c) $2Zn(NO_3)_2(s) \rightarrow 2ZnO(s) + 4NO_2(g) + O_2(g)$

d) $H_2SO_4(aq) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + 2H_2O(l)$ *(4)*

6 For each of the following tests, identify the type of chemical reaction taking place, name the products and write a balanced equation for the reaction:

a) testing for iodide ions with silver nitrate solution *(3)*

b) adding dilute hydrochloric acid to magnesium carbonate *(3)*

c) testing for sulfate ions with barium chloride *(3)*

d) heating a sample of zinc carbonate *(3)*

e) adding zinc metal to a solution of copper(II) sulfate. *(3)*

7 The concentration of cholesterol ($C_{27}H_{46}O$) in a patient's blood was found to be $6.0\,mmol\,dm^{-3}$.

    a) What is the concentration of cholesterol in $mol\,dm^{-3}$?
        $(1000\,mmol = 1\,mol)$ *(1)*

    b) Calculate the concentration of cholesterol in $g\,dm^{-3}$. *(2)*

    c) What is the mass of cholesterol in $10\,cm^3$ of the patient's blood? *(1)*

8 a) Ammonium sulfate was prepared by adding ammonia solution to $25\,cm^3$ of $2.0\,mol\,dm^{-3}$ sulfuric acid.

$$2NH_3(aq) + H_2SO_4(aq) \rightarrow (NH_4)_2SO_4(aq)$$

    i) What volume of $2.0\,mol\,dm^{-3}$ ammonia solution was needed to just neutralise the sulfuric acid? *(1)*

    ii) How can the solution be tested to check that enough ammonia had been added to neutralise all the acid without contaminating the solution? *(2)*

  b) Iron(II) sulfate, $FeSO_4$, was dissolved in the solution of ammonium sulfate solution to produce the double salt ammonium iron(II) sulfate hexahydrate, $(NH_4)_2SO_4.FeSO_4.6H_2O$.

    i) What mass of iron(II) sulfate was added to the ammonium sulfate solution? *(3)*

    ii) The double salt was crystallised from the solution. What mass of ammonium iron(II) sulfate hexahydrate was obtained if the percentage yield was 50%? ($H = 1, N = 14, Fe = 56, S = 32, O = 16$) *(4)*

9 a) A compound Z is a compound of carbon, hydrogen and oxygen only. Analysis of a sample of the compound shows that it is made up of 54.5% by mass of carbon and 9.1% by mass of hydrogen. Find the empirical formula of Z. *(4)*

  b) When $0.270\,g$ of Z is heated to $100\,°C$ it vaporises to produce $100\,cm_3$ gas at a pressure of $95.0\,kPa$. Determine the molar mass and molecular formula of Z. *(5)*

10 Excess calcium reacted vigorously with $25.0\,cm^3$ of $1.0\,mol\,dm^{-3}$ hydrochloric acid producing calcium chloride solution and hydrogen.

    a) Write a balanced equation, with state symbols, for the reaction. *(3)*

    b) Draw a labelled diagram showing how the hydrogen gas could be collected during the reaction. *(2)*

    c) Suggest a procedure for obtaining clean, dry crystals of hydrated calcium chloride, $CaCl_2.6H_2O$, from the solution formed. *(4)*

    d) What is the maximum possible yield of hydrated calcium chloride, $CaCl_2.6H_2O$, from the reaction? ($Ca = 40.0, Cl = 35.5, O = 16.0$) *(4)*

    e) Suggest two reasons why the actual yield of hydrated calcium chloride is much less than the mass calculated in part (d). *(2)*

5 Formulae, equations and amounts of substance

www.youtube.com/megalecture

11 A carbonate of metal M has the formula M_2CO_3. In a titration, a $0.245\,g$ sample of M_2CO_3 was found to neutralise $23.6\,cm^3$ of $0.150\,mol\,dm^{-3}$ hydrochloric acid. Follow these steps to identify the metal M.

    a) Write the equation for the reaction of M_2CO_3 with hydrochloric acid. *(1)*

    b) Calculate the amount, in moles, of hydrochloric acid needed to react with the sample of the metal carbonate. *(1)*

    c) Use the equation to calculate the amount, in moles, of M_2CO_3 in the sample. *(1)*

    d) Use your answer to part (c) and the mass of the sample to calculate the relative formula mass of M_2CO_3. *(2)*

    e) Calculate the relative atomic mass of metal M. *(1)*

    f) Identify the metal M. *(1)*

12 a) The reaction of ammonia, NH_3, with sodium chlorate(I), NaOCl produces the rocket fuel hydrazine, N_2H_4, together with sodium chloride and water. Determine the atom economy for the process. *(4)*

    b) Calculate the atom economies for each of these processes for making bromoethane:

        i) The reaction of ethane, C_2H_6 with bromine to form bromoethane, C_2H_5Br, and hydrogen bromide. *(4)*

        ii) The reaction of ethene, C_2H_4, with hydrogen bromide to make bromoethane, C_2H_5Br, as the only product. *(3)*

    c) Why do both yield and atom economy have to be considered when selecting a process for manufacturing a chemical product? *(6)*

13 a) An analyst investigates an impure sample of sodium sulfate. The impurities are unreactive. A $0.250\,g$ sample of the Na_2SO_4 is dissolved in water. Excess barium chloride is added to the solution to precipitate all the sulfate ions as barium sulfate, $BaSO_4$. The mass of the pure, dry, precipitated barium sulfate is $0.141\,g$. Calculate the percentage purity of the sample of sodium sulfate. *(5)*

    b) A $0.500\,g$ sample of steel consisting of iron alloyed with carbon and silicon gave off $191\,cm^3$ hydrogen gas when it reacted with excess hydrochloric acid. The gas volume was measured at room temperature and pressure. Calculate the percentage of iron in the steel.
(Fe = 55.8, molar volume of a gas at room temperature and pressure = $24\,dm^3\,mol^{-1}$) *(5)*

14 $1.576\,g$ of ethanedioic acid crystals, $(COOH)_2.nH_2O$, were dissolved in water and made up to $250\,cm^3$. In a titration, $25.0\,cm^3$ of the acid solution reacted exactly with $15.6\,cm^3$ of $0.160\,mol\,dm^{-3}$ sodium hydroxide solution. Show by calculation that this data confirms that n = 2 in the formula for the acid. *(8)*

www.youtube.com/megalecture

15 A sample of sodium carbonate crystals, $Na_2CO_3.10H_2O$, had lost part of its water of crystallisation on exposure to air. 2.696 g of the crystals were dissolved in water and made up to 250 cm³ in a graduated flask. In a series of titrations, 20.0 cm³ portions of the solution were titrated with 0.10 mol dm⁻³ hydrochloric acid giving the results shown in the table.

Titration number	1 (rough)	2	3
Final burette reading/cm³	22.00	23.00	22.15
Initial burette reading/cm³	1.00	2.35	1.60

Determine the percentage of loss of mass from the crystals from the titration results. *(10)*

16 Egg shells contain calcium carbonate. It is possible to determine the percentage of calcium carbonate in an egg shell by titration. Calcium carbonate reacts with acids but it is not possible to titrate this directly with an acid from a burette.

An analyst adds 40.00 cm³ of 1.200 mol dm⁻³ hydrochloric acid (an excess) to a 1.510 g sample of the crushed shell. When the reaction with calcium carbonate in the egg shell is complete, all the solution is transferred to a 250 cm³ graduated flask. Water is then added to the mark and the diluted solution is well mixed.

Next the analyst titrates separate 25.0 cm³ portions of the diluted solution with a 0.100 mol dm⁻³ solution of sodium hydroxide to determine the amount of acid that did not react with the egg shell. The mean titre was 24.30 cm³.

a) Give two reasons why titrating the calcium carbonate in an egg shell with hydrochloric acid from a burette is not possible. *(2)*

b) Use the data about the titration to calculate the amount of excess hydrochloric acid, in moles, left over after reaction with the egg shell. *(3)*

c) Hence calculate how much hydrochloric acid, in moles, reacted with calcium carbonate in the sample of egg shell. *(2)*

d) Use the results to calculate the percentage of calcium carbonate in the egg shell. *(5)*

e) The procedure used in this analysis is called a 'back titration'. Explain what you understand by this term. *(3)*

www.youtube.com/megalecture