QUANTITATIVE CHEMISTRY

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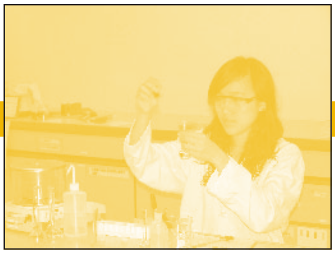


SOME FUNDAMENTAL CONCEPTS

Chemistry is a science that deals with the composition, structure and reactions of matter. It is involved with looking at the properties of materials and interpreting these in terms of models on a sub-microscopic scale. Investigations form an important part of any study of chemistry. This involves making observations, and using these in the solution of problems. A typical investigation requires choosing a problem, working out a way of attempting to solve it, and then describing both the method, the results and the manner in which these are interpreted. Namely, "a scientist chooses, imagines, does and describes". Along with many other syllabuses, practical investigations are a requirement of IB Chemistry.

Matter occupies space and has mass. It can be subdivided into **mixtures** and **pure substances**. Mixtures consist of a number of different substances, not chemically combined together. Thus the ratio of these components is not constant from one sample of mixture to another. The different components of a mixture often have different **physical properties** (such as melting point and density) and **chemical properties** (such as flammability and acidity). The properties of the mixture are similar to those of the components (e.g. a match burns in both air and pure oxygen), though they will vary with its exact composition. The fact that the different components of the mixture have different physical properties means that the mixture can be separated by physical means, for example by dissolving one component whilst the other remains as a solid. A pure substance cannot be separated in this way because its physical properties are constant throughout all samples of that substance. Similarly all samples of a pure substance have identical chemical properties, for example pure water from any source freezes at 0 ^{o}C.

Pure substances may be further subdivided into **elements** and **compounds**. The difference between these is that an element cannot be split up into simpler substances by chemical means, whilst a compound can be changed into these more basic components.

The interpretation on a sub-microscopic scale is that all substances are made up of very tiny particles called **atoms**. Atoms are the smallest particles present in an element which can take part in a chemical change and they cannot be split by ordinary chemical means.

An **element** is a substance that only contains one type of atom, so it cannot be converted into anything simpler by chemical means. (note; 'type' does not imply that all atoms of an element are identical. Some elements are composed of a mixture of closely related atoms called **isotopes** (refer to Section 2.1). All elements have distinct names and symbols. Atoms can join together by **chemical bonds** to form compounds. Compounds are therefore made up of particles (of the same type), but these particles are made up of different types of atoms chemically bonded together. This means that in a **compound**, the constituent elements will be present in fixed proportions such as H_2O (water), H_2SO_4 (sulfuric acid), CO_2 carbon dioxide) and NH_3 (ammonia). The only way to separate a compound into its component elements is by a chemical change that breaks some bonds and forms new ones, resulting in new substances. The physical and chemical properties of a compound are usually totally unrelated to those of its component elements. For example a match will not burn in water even though it is a compound of oxygen.

If a substance contains different types of particles, then it is a mixture. These concepts in terms of particles are illustrated in Figure 101. Copper, water and air provide good examples of an element, a compound and a mixture respectively.

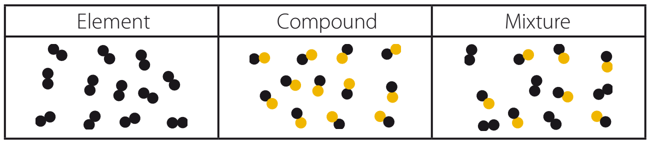


Figure 101 The particles in an element, a compound and a mixture

The term **molecule** refers to a small group of atoms joined together by covalent bonds (refer to Section 4.2). If the atoms are of the same kind, then it is a molecule of an element, if different it is a molecule of a compound. Most elements that are gases are **diatomic** (composed of molecules containing two atoms). Examples are hydrogen gas (H_2), nitrogen gas (N_2) and oxygen gas (O_2). The halogens (F_2, Cl_2, Br_2 and I_2) are also diatomic in all physical states. The noble gases (He, Ne, Ar, Kr, Xe and Rn) however are **monatomic** (i.e. exist as single atoms).

The properties of a typical element, compound and mixture are shown in Figure 102.

The Types of Atoms

There are 92 kinds of atoms, and hence 92 chemical elements, that occur naturally and about another seventeen that have been produced artificially. Only about thirty of these elements are usually encountered in school chemistry and most of this would deal with about half of these, shown in bold type in Figure 103. Each element is given a **symbol** that is used to write the formulas of the compounds that it forms. The significance of the **atomic number** and **relative atomic mass** of the elements will be explained in Sections 2.1 and 1.3).

Figure 103 shows the common elements and some of their characteristics.

- Parts of the names where there are common spelling difficulties have been underlined.
- You should know the symbols for the elements, especially those in **bold** type. Most of them are closely related to the name of the element (e.g. chlorine is Cl). Elements that were known in early times have symbols that relate to their Latin names (e.g. Ag, silver, comes from *Argentium*).
- Note that the first letter is always an upper case letter and the second one a lower case, so that, for example Co (cobalt) and CO (carbon monoxide) refer to very different substances.

Substance	Proportions	Properties	Separation
Element Copper - a pure element	Contains only one type of atom.	These will depend on the forces between the atoms of the element.	Cannot be converted to a simpler substance by chemical means.
Compound Water - a compound of oxygen and hydrogen	Always contains two hydrogen atoms for every oxygen atom.	Totally different from its elements, e.g. water is a liquid, but hydrogen and oxygen are gases.	Requires a chemical change, e.g. reacting with sodium will produce hydrogen gas.
Mixture Air - a mixture of nitrogen, oxygen, argon, carbon dioxide etc.	The proportions of the gases in air, especially carbon dioxide and water vapour, can vary.	Similar to its constituents, e.g. supports combustion like oxygen.	Can be carried out by physical means, e.g. by the fractional distillation of liquid air.

Figure 102 The properties of a typical element, compound and mixture

Element	Symbol	Atomic Number	Relative Atomic Mass
Hydrogen	**H**	**1**	**1.01**
Helium	He	2	4.00
Lithium	Li	3	6.94
Beryllium	Be	4	9.01
Boron	B	5	10.81
Carbon	**C**	**6**	**12.01**
Nitrogen	**N**	**7**	**14.01**
Oxygen	**O**	**8**	**16.00**
Fluorine	F	9	19.00
Neon	Ne	10	20.18
Sodium	**Na**	**11**	**22.99**
Magnesium	**Mg**	**12**	**24.31**
Aluminium	**Al**	**13**	**26.98**
Silicon	Si	14	28.09
Phosphorus	**P**	**15**	**30.97**
Sulfur	**S**	**16**	**32.06**
Chlorine	**Cl**	**17**	**35.45**
Argon	Ar	18	39.95
Potassium	**K**	**19**	**39.10**
Calcium	**Ca**	**20**	**40.08**
Chromium	Cr	24	52.00
Manganese	Mn	25	54.94
Iron	**Fe**	**26**	**55.85**
Cobalt	Co	27	58.93
Nickel	Ni	28	58.71
Copper	**Cu**	**29**	**63.55**
Zinc	**Zn**	**30**	**65.37**
Bromine	Br	35	79.90
Silver	Ag	47	107.87
Iodine	I	53	126.90
Barium	Ba	56	137.34
Lead	**Pb**	**82**	**207.19**

Figure 103 The common elements

TOK Numbers in Chemistry

Try to imagine what it must have been like to have been an alchemist about 500 years ago. Apart from trying experiments out for yourself, you might be able to read in some books (if you had enough money to buy them - they were very expensive in those days) experiments other people had done, but there was probably little order to it. There was no theoretical paradigm underpinning observations, no framework within which to relate substances other than superficial groupings such as substances that change colour when heated, substances that burn, substances that dissolve.

This all changed with John Dalton's atomic theory, propounded in the early 19th century, which is the basis of modern chemistry:

- Elements are made of tiny particles called atoms
- All atoms of a given element are identical.
- The atoms of a given element are different from those of any other element .
- Atoms of one element can combine with atoms of other elements to form compounds. A given compound always has the same relative numbers of the different types of atoms.
- Atoms cannot be created, divided into smaller particles, nor destroyed in the chemical process. A chemical reaction simply changes the way atoms are grouped together.

The second point might need slight amendment to take account of isotopes, but apart from that this is more or less what we take for granted nowadays. Even though we now take it for granted, it was not universally accepted until late in the 19th century - a common feature of any paradigm change.

So where did atomic theory come from? Did Dalton just dream up these rules? Far from it, his atomic theory was the crowning achievement of quantitative chemistry, pioneered notably by Antoine Lavoisier, during the preceding half century. These scientists for the first time started to systematically record the masses of the reactants and products during their reactions. Having numbers allowed people to use mathematics in their application of deductive logic to discover patterns in their results. The patterns discovered led scientists to postulate about the existence of atoms (an idea that goes back to the ancient Greeks) and to propose that these had

Exercise

1. A grey solid when heated vapourised to form pure white crystals on the cooler parts of the test tube leaving a black solid as the residue. It is likely that the original solid was

   A an element.
   B a metal.
   C a pure compound.
   D a mixture.

2. Which one of the following is a chemical property rather than a physical property?

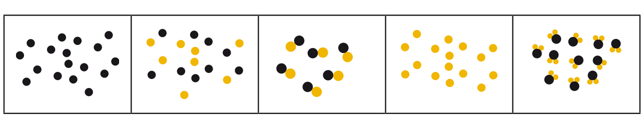
   A Boiling point
   B Density
   C Flammability
   D Hardness

3. Which one of the following is a physical change rather than a chemical change?

   A Combustion
   B Distillation
   C Decomposition
   D Neutralisation

4. State whether the sketches below represent elements, compounds or mixtures.

A B C D E



5. State whether the following refer to an element, a compound or a mixture:

   (a) Easily separated into two substances by distillation.
   (b) Its components are always present in the same proportions.
   (c) Its properties are similar to those of its components.
   (d) Cannot be broken down by chemical means.
   (e) Very different properties to its components.

1.1 THE MOLE CONCEPT AND AVOGADRO'S CONSTANT

1.1.1 Apply the mole concept to substances.

1.1.2 Determine the number of particles and the amount of substance (in moles).

Atoms and **molecules** are inconceivably minute, with equally small masses. The masses of all atoms are not however the same and it is often convenient to be able to weigh out amounts of substances that contain the same number of atoms or molecules. The same amount of any substance will therefore contain the same number of particles and we measure the **amount of substance** in **moles**. It is for this reason that the **mole concept** is important.

Amount of substance, *n* (the number of moles), is a quantity that is proportional to the number of particles in a sample of substance: its units are moles (mol). A mole of a substance contains 6.02×10^{23} particles of the substance (this very large number is expressed in scientific notation; for further explanation of scientific notation refer to Appendix 1A). This is the same number of particles as there are atoms in exactly 12 g of the C-12 ($^{12}_{6}C$) isotope.

Since a mole of carbon atoms weighs 12 g, an atom of carbon (C) weighs only: 1.995×10^{-23} g atom^{-1}.

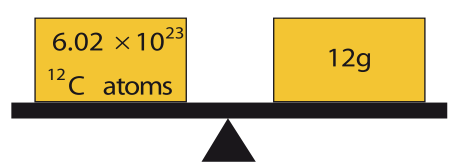


Figure 105 Avogadro's number

The value 6.02×10^{23} mol^{-1} is called the Avogadro's Constant (L or N_A). The particles may be atoms, molecules, ions, formula units, etc., but should be specified. For example, 1 mol of carbon contains 6.02×10^{23} carbon (C) atoms (and weighs 12 g), where as 1 mol of water, H_2O, contains 6.02×10^{23} H_2O molecules or $3 \times 6.02 \times 10^{23}$ atoms since each water molecule contains a total of 3 atoms.

$$\text{Number of moles} = \frac{\text{Number of particles}}{6.02 \times 10^{23}}$$

This can be written as $n = \frac{N}{6.02 \times 10^{23}}$ or $N = n \times 6.02 \times 10^{23}$.

A sample of water that contains 3.01×10^{25} water molecules therefore contains $\frac{3.01 \times 10^{25}}{6.02 \times 10^{23}} = 50$ moles of water molecules.

This is very similar to saying that 36 oranges is equivalent to 3 dozen oranges ($\frac{36}{12} = 3$).

The formula may be rearranged to calculate the number of particles. For example 0.020 moles of carbon dioxide will contain $0.020 \times 6.02 \times 10^{23} = 1.2 \times 10^{22}$ molecules of CO_2.

This number of molecules of carbon dioxide will contain 1.2×10^{22} atoms of carbon but 2.4×10^{22} (i.e. $2 \times 1.2 \times 10^{22}$) atoms of oxygen, because each molecule contains one atom of carbon, but two atoms of oxygen and the total number of atoms is 3.6×10^{22} (i.e. $3 \times 1.2 \times 10^{22}$). Note, therefore, how important it is to state what particles are being referred to.

TOK The scale of chemistry

'Chemistry deals with enormous differences in scale. The magnitude of Avogadro's constant is beyond the scale of our everyday experience'.

Dealing with very large and very small scales is almost impossible for the human brain - maybe it would disconcert our egos to be continually aware that we are infinitesimal dots living on an infinitesimal dot! So how can we try to come to terms with the enormous and minute numbers we meet in science? One approach is to try to apply the scale to things we are familiar with. For example if sand were made up of cubic grains 1/10th mm on each side, then what length of a beach 60 m deep and 1 km wide would 1 mole (i.e. 6×10^{23}) of these form? The answer is about 10,000 km of it!!! Coming from the other end, suppose the population of the whole world (let's say 4000 million people) were turned into atoms of gold (quite big, heavy atoms) our combined mass would be about one-millionth of a microgram, too small for any balance to detect (our grains of sand above would weigh about 2 μg) and we would form a cube with a side of about $^1/_{50}$ μm, a factor of ten below the theoretical range of the best optical microscope. Hence we would not be able to detect ourselves! Fortunately we have mathematics to rely on, so we do not have to depend on being able to imagine these scales!

Exercise 1.1

(Take the value of Avogadro's constant as 6.02×10^{23} mol^{-1}.)

1. Calculate how many atoms are there in 5 moles of sulfur atoms.

   A 1.20×10^{23}
   B 6.02×10^{23}
   C 6.02×10^{115}
   D 3.01×10^{24}

2. Which one of the following is not the same number as the rest?

   A The number of molecules in 4 moles of CO_2.
   B The number of hydrogen atoms in 2 moles of H_2O.
   C The number of chloride ions in 4 moles of $CaCl_2$.
   D The number of hydrogen atoms in 1 mole of C_3H_8.

3. The number of atoms present in 0.10 mol of ethene (C_2H_4) is:

   A 3.61×10^{22}
   B 6.02×10^{22}
   C 3.61×10^{23}
   D 6.02×10^{23}

4. One mole of water contains

   A 6.02×10^{23} atoms of hydrogen.
   B 2.01×10^{23} atoms of oxygen.
   C 6.02×10^{23} atoms in total.
   D 6.02×10^{23} molecules of water.

5. The number of atoms present in 36 molecules of glucose ($C_6H_{12}O_6$) is

   A 24
   B 36
   C 24×36
   D $24 \times 36 \times 6.02 \times 10^{23}$

6. The mass of one atom of carbon -12 is:

   A 1 g.
   B 12 g.
   C $12 \times 6.02 \times 10^{23}$ g.
   D $12 / 6.02 \times 10^{23}$ g.

7. A sample of phosphoric(V) acid H_3PO_4 contains 1.2×10^{23} molecules.

   (a) Calculate how many moles of phosphoric(V) acid is this.
   (b) Calculate how many atoms of phosphorus will there be.
   (c) Calculate how many atoms of hydrogen will it contain.

8. (a) Calculate how many molecules are there in 6 moles of hydrogen sulfide (H_2S).

   (b) The formula of gold(III) chloride is $AuCl_3$. Calculate how many chloride ions are there in 0.30 moles of gold(III) chloride.

1.2 FORMULAS

1.2.1 Define the terms relative atomic mass (A_r) and relative molecular mass (M_r).

1.2.2 Calculate the mass of one mole of a species from its formula.

The atomic mass, A, of an element indicates how heavy an atom of that element is compared to an atom of another element where a standard, the carbon-12 isotope ($^{12}_{6}C$), is assigned a value of exactly 12 g mol^{-1}. Atomic mass therefore has units of g mol^{-1}, hence A(C) = 12.01 g mol^{-1} and A(Cl) = 35.45 g mol^{-1}. **Formula mass** is the sum of the atomic masses of the atoms in the compound formula (so it also has units of g mol^{-1}), and usually refers to ionic compounds. Similarly **molecular mass** is the sum of the atomic masses of all the atoms in one molecule (again expressed in units of g mol^{-1}).

The relative atomic mass, A_r, is the ratio of the average mass per atom of an element to $^1/_{12}$ of the mass of an atom of the C-12 isotope. A_r therefore has no units. Thus, A_r(C) = 12.01 and A_r(Cl) = 35.45. This scale is approximately equal to a scale on which a hydrogen atom has a relative atomic mass of 1. Relative atomic masses are shown on the **periodic table** and those of the common elements are given in Figure 103. Most are approximately whole numbers, but some are not because these elements exist as mixtures of **isotopes** (refer to Section 2.1). With **elements**, especially the common gaseous elements, it is very important to differentiate between the relative atomic mass and the **relative molecular mass**. Thus nitrogen, for example, has a relative atomic mass of 14.01, but a relative molecular mass of 28.02 because it exists as diatomic molecules (N_2). The relative molecular mass, M_r, similarly indicates how heavy a molecule is compared to the C-12 isotope and, like the concept of relative atomic mass, is defined as the ratio of the average mass of a molecule of the substance to $^1/_{12}$ of the mass of an atom of the C-12 ($^{12}_{6}C$) isotope, so M_r also has no units.

Molar mass, M, is the mass of one mole of any substance such as atoms, molecules, ions, etc., where the carbon-12 ($^{12}_{6}C$) isotope is assigned a value of exactly 12 g mol^{-1} and is a particularly useful term as it applies to any entity. The molar mass should be accompanied by the formula of the particles. Consider chlorine, where ambiguity is possible because the molar mass of chlorine atoms (Cl) is 35.45 g mol^{-1}, but the molar mass of chlorine molecules (Cl_2) is 70.90 g mol^{-1}. The molar mass, *M*, of a compound is determined by adding the atomic masses of all the elements in the compound.

Thus $M(CO_2)$ = 12.01 + (2 × 16.00) = 44.01 g mol^{-1} of CO_2 and the molar mass of sulfuric acid (H_2SO_4) is: (2 × 1.01) + 32.06 + (4 × 16.00) = 98.08 g mol^{-1} of H_2SO_4.

If a substance contains water of crystallisation, then this must be included in the molar mass, for example the molar mass of sodium sulfate heptahydrate crystals ($Na_2SO_4.7H_2O$) is: (2 × 22.99) + 32.06 + (4 × 16.00) + (7 × 18.02) = 268.18 g mol^{-1} of $Na_2SO_4.7H_2O$.

If the mass of a substance and its formula are given, the amount of substance,

$$n = \frac{\text{Mass (g)}}{\text{Molar Mass (g mol}^{-1})} \qquad n = \frac{m}{M}$$

You can calculate any one quantity given the other two. Thus the mass, m = n (mol) × M (g mol^{-1}) (m=n . M), and M (g mol^{-1}) = m (g) / n (mol) $(M = \frac{m}{n})$

Exercise 1.2

1. The molar mass of iron(III) sulfate $Fe_2(SO_4)_3$ will be

   A 191.76 g mol^{-1}
   B 207.76 g mol^{-1}
   C 344.03 g mol^{-1}
   D 399.88 g mol^{-1}

2. A certain substance has a molar mass (to 2 significant figures) of 28 g mol^{-1}. Which of the following is not a possible formula?

   A CH_2O
   B Si
   C C_2H_4
   D CO

3. Calculate the molar mass of the following substances (correct to 1 decimal place).

   (a) HI
   (b) $NaClO_3$
   (c) $(NH_4)_2HPO_4$
   (d) $(CO_2H)_2.2H_2O$
   (e) Chromium(III) oxide
   (f) Iodine trichloride

Moles and Mass

1.2.3 Solve problems involving the relationship between the amount of substance in moles, mass and molar mass.

It follows from the above that the mass of one mole of any substance will be equal to its molar mass in grams. If one mole of fluorine atoms has a mass of 19 g, then 76 g of fluorine atoms will contain four moles of fluorine atoms, hence the amount of substance may be calculated from its molar mass using the formula

Amount of substance,

$$n = \frac{\text{Mass (g)}}{\text{Molar Mass (g mol}^{-1})} \qquad n = \frac{m}{M}$$

4.904 g of sulfuric acid will therefore contain:

$$\frac{m}{M} = \frac{4.904\text{ g}}{98.08\text{ g mol}^{-1}}$$
$$= 0.05000 \text{ moles of sulfuric acid}$$

[**Note** - It is important to pay attention to significant figures in calculations. A short description of the scientific notation and significant figures is given later in the chapter.]

The equation may be rearranged to calculate the molar mass from the mass and the amount of substance, or to find the mass from the amount and the molar mass. For example the mass of 3.00 moles of carbon dioxide is

$$n \times M = 3.00 \text{ mol} \times 44.01 \text{ g mol}^{-1}$$
$$= 132 \text{ g of carbon dioxide}$$

Similarly if 0.200 moles of a substance has a mass of 27.8 g, then its molar mass (M) will be

$$M = \frac{m}{n} = \frac{27.8\text{ g}}{0.200\text{ mol}} = 139 \text{ g mol}^{-1}$$

Knowing the mass of a given number of atoms or molecules means that the mass of one atom or molecule can be calculated. For example as the molar mass of the hydrogen atom is 1.01 g mol^{-1}, 6.02×10^{23} atoms of hydrogen have a mass of 1.01 g, hence the mass of a single atom is:

$$\frac{1.01\text{ g mol}^{-1}}{6.02 \times 10^{23}\text{ atoms mol}^{-1}}$$
$$= 1.68 \times 10^{-24} \text{ g atom}^{-1}$$

Similarly the mass of one molecule of glucose ($C_6H_{12}O_6$, M = 180.18 g mol^{-1}) is:

$$\frac{180.18\text{ g mol}^{-1}}{6.02 \times 10^{23}\text{ molecules mol}^{-1}}$$
$$= 2.99 \times 10^{-22} \text{ g molecule}^{-1}$$

Exercise 1.2.3

1. Determine the mass of 0.700 moles of Li_2SO_4 taking its molar mass as exactly 110 g mol^{-1}.

   A 15.4 g
   B 77 g
   C 110 g
   D 157 g

2. 0.200 moles of a substance has a mass of 27.0 g. Determine the molar mass of the substance.

   A 13.5 g mol^{-1}
   B 27 g mol^{-1}
   C 54 g mol^{-1}
   D 135 g mol^{-1}

3. One drop of water weighs 0.040 g. Calculate how many molecules are there in one drop, taking the molar mass of water as exactly 18 g þmol^{-1}.

   A 1.3×10^{21}
   B 2.4×10^{22}
   C 3.3×10^{22}
   D 3.9×10^{22}

4. Determine the mass (in g) of one molecule of sulfuric acid (H_2SO_4).

   A 98.08
   B $98.08 \div (6.02 \times 10^{23})$
   C $98.08 \div 7$
   D $98.08 \div (7 \times 6.02 \times 10^{23})$

5. A polymer molecule has a mass of 2.5×10^{-20} g. Determine the molar mass of the polymer.

   A 1.4×10^{4} g mol^{-1}
   B 2.4×10^{43} g mol^{-1}
   C 6.7×10^{-5} g mol^{-1}
   D 4.2×10^{-44} g mol^{-1}

6. Calculate (correct to 3 significant figures) the mass of

   (a) 3.00 moles of ammonia.
   (b) ¼ mole of Li_2O.
   (c) 0.0500 moles of aluminium nitrate.
   (d) 3.01×10^{23} molecules of PCl_3.
   (e) 2.60×10^{22} molecules of dinitrogen monoxide.

7. Calculate how many moles are there in

   (a) 28.1 g of silicon.
   (b) 303 g of KNO_3.
   (c) 4000 g of nickel sulfate.
   (d) 87.3 g of methane.

8. a) 0.30 moles of a substance has a mass of 45 g. Determine its molar mass.

   b) 3.01×10^{25} molecules of a gas has a mass of 6.40 kg. Determine its molar mass.

9. Some types of freon are used as the propellant in spray cans of paint, hair spray, and other consumer products. However, the use of freons is being curtailed, because there is some suspicion that they may cause environmental damage. If there are 25.00 g of the freon CCl_2F_2 in a spray can, calculate how many molecules are you releasing to the air when you empty the can.

10. Vitamin C, ascorbic acid, has the formula $C_6H_8O_6$.

   a) The recommended daily dose of vitamin C is 60.0 milligrams. Calculate how many moles are you consuming if you ingest 60 milligrams of the vitamin.
   b) A typical tablet contains 1.00 g of vitamin C. Calculate how many moles of vitamin C does this represents.
   c) When you consume 1.00 g of vitamin C, calculate how many oxygen atoms are you eating.

1.2.4 Distinguish between the terms empirical formula and molecular formula.

1.2.5 Determine the empirical formula from the percentage composition or from other experimental data.

1.2.6 Determine the molecular formula when given the empirical formula and experimental data.

PERCENTAGE COMPOSITION AND EMPIRICAL FORMULA

Knowing the formula of a substance and the molar masses of the elements, then the percentage composition may be found by calculating the proportion by mass of each element and converting it to a percentage. For example the molar mass of carbon dioxide is

$$12.01 + (2 \times 16.00) = 44.01 \text{ g mol}^{-1}$$

Oxygen constitutes 32.00 g mol^{-1} of this (2×16.00), so that the percentage of oxygen by mass in carbon dioxide is:

$$\frac{32.00}{44.01} \times 100 = 72.71\% \text{ oxygen by mass.}$$

The empirical formula, sometimes called the simplest formula, of a compound indicates:

- the elements present in the compound
- the simplest whole number ratio of these elements

It may be found by dividing the coefficients in the molecular formula by their highest common factor, for example the molecular formula of glucose is $C_6H_{12}O_6$, so its empirical formula is CH_2O.

If the mass of the elements in a compound is found by experiment (empirical means "by experiment"), then the amount of each element may be found using its molar mass and the formula:

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

Example 1

2.476 g of an oxide of copper is found to contain 2.199 g of copper. Determine its empirical formula.

Solution

The oxide therefore contains 0.277 g (2.476g – 2.199g) of oxygen. The amount of each element can therefore be calculated using the molar masses (O = 16.00 g mol^{-1}; Cu = 63.55 g mol^{-1}).

$$\text{Amount of oxygen} = \frac{0.277\ \text{g}}{16.00\ \text{g mol}^{-1}} = 0.01731\ \text{mol}$$

$$\text{Amount of copper} = \frac{2.199\ \text{g}}{63.55\ \text{g mol}^{-1}} = 0.03460\ \text{mol}$$

The whole number ratio of oxygen to copper may be found by dividing through by the smaller number

Ratio of O : Cu = 0.01731: 0.3460 = 1: 1.999 (dividing by 0.01731)

The simplest whole number ratio of oxygen to copper is therefore 1: 2, so that the empirical formula is Cu_2O.

In some cases this does not give whole numbers and then multiplying by a small integer will be necessary. For example a ratio of Fe:O of 1:1⅓ gives a whole number ratio of 3:4 when multiplied by 3. Percentage composition data can be used in a similar way.

Example 2

Determine the empirical formula of a compound of phosphorus and oxygen that contains 43.64% phosphorus by mass.

Solution

In 100 g, there are 43.64 g of phosphorus and 56.36 g (i.e. 100 – 43.64 g) of oxygen.

$$\text{Amount of phosphorus} = \frac{43.64\ \text{g}}{30.97\ \text{g mol}^{-1}} = 1.409\ \text{mol}$$

$$\text{Amount of oxygen} = \frac{56.36\ \text{g}}{16.00\ \text{g mol}^{-1}} = 3.523\ \text{mol}$$

The whole number ratio of phosphorus to oxygen may be found by dividing through by the smaller number:

Ratio of P : O = 1.409 : 3.523
= 1 : 2.5 (dividing by 1.409)
= 2 : 5 (multiplying by 2)

In this case it is necessary to multiply by a small integer, in this case 2, in order to produce a whole number ratio. The empirical formula is, therefore, P_2O_5.

Similar techniques may also be applied to calculate the amount of water of crystallisation in hydrated salts, by calculating the ratio of the amount of water to the amount of anhydrous salt.

In summary:

- Calculate the amount (in moles) of each element (or component).
- Find the simplest whole number ratio between these amounts.

CORE

EXPERIMENTAL METHODS

Empirical formulas can often be found by direct determination, for example converting a weighed sample of one element to the compound and then weighing the compound to find the mass of the second element that combined with the first (see exercise 1.5, Q 13). Another method is to decompose a weighed sample of a compound containing only two elements, so that only one element remains and then finding the mass of that element. This second method is similar to the one that is usually used to determine the formula of a hydrated salt (see exercise 1.5, Q 14). There are also many other methods for determining percentage composition data, too numerous to mention.

The percentage composition of organic compounds is usually found by burning a known mass of the compound in excess oxygen, then finding the masses of both carbon dioxide (all the carbon is converted to carbon dioxide) and water (all the hydrogen is converted to water) formed. The mass of oxygen can be found by subtracting the mass of these two elements from the initial mass, assuming that this is the only other element present.

Example 1

2.80 g of an organic compound, containing only carbon and hydrogen forms 8.80 g of carbon dioxide and 3.60 g of water when it undergoes complete combustion. Determine its empirical formula.

Solution

Amount of CO_2 = amount of C

$$\text{Amount of C} = \frac{m}{M} = \frac{8.80\text{ g}}{44.0\text{ g mol}^{-1}} = 0.200\text{ mol}$$

Amount of H_2O = ½ amount of H

$$\text{Amount of } H_2O = \frac{m}{M} = \frac{3.60\text{ g}}{18.0\text{ g mol}^{-1}} = 0.200\text{ mol}$$

Therefore amount of H = 2 × 0.200
= 0.400 mol

Ratio C : H = 0.200 : 0.400 = 1 : 2;
Therefore the empirical formula is CH_2.

Example 2

Consider vitamin C, a compound that contains carbon, hydrogen and oxygen only. On combustion of 1.00 g vitamin C, 1.50 g CO_2 and 0.408 g H_2O are produced. Determine the empirical formula of vitamin C.

Solution

All the carbon in the CO_2 came from the vitamin C. The mass of carbon in 1.50 g CO_2 can be easily calculated.

$$\text{Amount of } CO_2 = \frac{m}{M} = \frac{1.50\text{ g}}{44.0\text{ g mol}^{-1}} = 0.03408\text{ mol}$$

Since each CO_2 contains 1 C

$$\begin{aligned} m_C &= n_C \times A(\text{C}) \\ &= 0.0340(8)\text{ mol} \times 12.01\text{ g mol}^{-1} \\ &= 0.409\text{ g C} \end{aligned}$$

1.50 g CO_2 contains 0.409 g of C
all of which came from vitamin C.

Similarly, all the H in the H_2O is from the vitamin C:

18.02 g H_2O contains 2.02 g H
∴ 0.408 g H_2O contains $0.408\text{ g} \times \frac{2.02}{18.02}$
= 0.0457 g of hydrogen

The rest must therefore be oxygen:
∴ Mass of oxygen = (1.00 – 0.409 – 0.0457) g
= 0.54(5) g

Once the proportion by mass of the elements is known, the mole ratios can be calculated:

	C	H	O
m (g):	0.409	0.0457	0.54(5)
A_r:	12.01	1.01	16.00
n (mol):	0.0341	0.0452	0.0341
divide by smallest number:			
	1.00	1.33	1.00
	1 :	1⅓ :	1
	3 :	4 :	3

Therefore the empirical formula of vitamin C is $C_3H_4O_3$

MOLECULAR FORMULA

The molecular formula of a compound indicates:

- the elements present in the compound
- the actual number of atoms of these elements in one molecule

Hence the molar mass can be calculated from the molecular formula, as can the percentage composition by mass and the empirical formula. Note that the molecular formula of a compound is a multiple of its empirical formula, e.g., for butane, its molecular formula is C_4H_{10} and its empirical formula is C_2H_5. Other examples are shown in Figure 106. It therefore follows the relative molecular divided by the relative empirical mass is a whole number.

n.b.The relative empirical mass is the sum of the relative atomic masses of the atoms in the empirical (simplest) formula.

The relative molecular mass, M_r, for a compound can be determined experimentally using mass spectrometry (refer to Section 2.2), or from physical properties such as the density of the substance in the gas phase (refer to Section 1.4) making it possible to determine the molecular formula of the compound provided the empirical formula is known.

It can be seen from Figure 106 that ethyne and benzene both have the same empirical formula (CH), but the relative molar mass of ethyne is ≈ 26, whereas that of benzene is ≈ 78, so the molecular formula of ethyne must be C_2H_2 (2 × CH) whereas that of benzene is C_6H_6 .

In the case of the compound with the empirical formula P_2O_5, the molecular formula could actually be P_2O_5 or it could be P_4O_{10}, P_6O_{15}, P_8O_{20} etc. The relative empirical mass of P_2O_5 is 141.94 .

In order to know which molecular formula is correct, it is necessary to have information about the approximate molar mass of the substance. The molar mass of this oxide of phosphorus is found to be ≈ 280 g mol^{-1}. It must therefore contain two P_2O_5 units, hence the molecular formula is P_4O_{10}.

Compound	Percentage composition	Empirical Formula	M_r	Molecular Formula
Ethane	%H = 6 × $^{1.01}/_{30.08}$ = 20.1%; %C = 2 × $^{12.01}/_{30.08}$ = 79.9%	CH_3	30.08	C_2H_6
Hexene	%H = 12 × $^{1.01}/_{84.18}$ = 14.4%; %C = 6 × $^{12.01}/_{84.18}$ = 85.6%	CH_2	84.18	C_6H_{12}
Benzene	%H = 6 × $^{1.01}/_{78.12}$ = 7.8%; %C = 6 × $^{12.01}/_{78.12}$ = 92.2%	CH	78.12	C_6H_6
Ethyne	%H = 2 × $^{1.01}/_{26.04}$ = 7.8%; %C = 2 × $^{12.01}/_{26.04}$ = 92.2%	CH	26.04	C_2H_2

Figure 106 The percentage composition and empirical formulas of some hydrocarbons

Example 1

A hydrocarbon contains 92.24% by mass of carbon and its M_r = 78.1. Determine its molecular formula.

Solution

	C	H
m (g):	92.24	(100-92.24) = 7.76
M_r:	12.01	1.01
n (mol):	1 :	1

Simplest formula is CH, and its relative empirical mass = 12.01 + 1.01 = 13.02

Since M_r = 78.1; molecular formula is C_6H_6.

CORE

Example 2

The percentage of carbon, hydrogen and nitrogen in an unknown compound is found to be 23.30%, 4.85% and 40.78% respectively. Calculate the empirical formula of the compound.

Solution

Since % ≠ 100, the rest must be oxygen. ∴ % oxygen = (100 – 23.30 – 4.85 – 40.78) = 31.07% O

Assume 100 g sample, then percentages become masses in grams:

	C	H	N	O
m (g):	23.30	4.85	40.78	31.07
A_r:	12.01	1.01	14.00	16.00
$n = m/A_r$ (mol):				
	1.940	4.80	2.913	1.942
divide by smallest n				
	1	2.5	1.5	1
	2	5	3	2

∴ The empirical formula is $C_2H_5N_3O_2$

Exercise 1.2.4

1. Determine the percentage by mass of silver in silver sulfide (Ag_2S).

   A 33.3%
   B 66.7%
   C 77.1%
   D 87.1%

2. Of the following, the only empirical formula is

   A N_2F_2
   B N_2F_4
   C HNF_2
   D H_2N_2

3. A compound of nitrogen and fluorine contains 42% by mass of nitrogen. If the molar mass of the compound is about 66 g mol^{-1}, determine its molecular formula.

   A NF
   B N_2F_2
   C NF_2
   D N_2F

4. An organic compound which has the empirical formula CHO has a relative molecular mass of 232. Its molecular formula is:

   A CHO
   B $C_2H_2O_2$
   C $C_4H_4O_4$
   D $C_8H_8O_8$

5. 3.40 g of anhydrous calcium sulfate (M = 136 g mol^{-1}) is formed when 4.30 g of hydrated calcium sulfate is heated to constant mass. Calculate how many moles of water of crystallisation are combined with each mole of calcium sulfate.

   A 1
   B 2
   C 3
   D 4

6. 2.40 g of element Z combines exactly with 1.60 g of oxygen to form a compound with the formula ZO_2. Determine the relative atomic mass of Z.

   A 24.0
   B 32.0
   C 48.0
   D 64.0

7. Of the following, the only empirical formula is

   A $C_{12}H_{22}O_{11}$
   B $C_6H_{12}O_6$
   C C_6H_6
   D C_2H_4

8. A certain compound has a molar mass of about 56 g mol^{-1}. All the following are possible empirical formulas for this compound except

   A CH_2
   B CH_2O
   C C_3H_4O
   D CH_2N

9. The empirical formula of a compound with the molecular formula $C_6H_{12}O_3$ is

   A $C_6H_{12}O_3$
   B $C_3H_6O_2$
   C C_2H_3O
   D C_2H_4O

10. What percentage of 'chrome alum' [$KCr(SO_4)_2{\bullet}12H_2O$; M = 499.4 g mol^{-1}] is water.

   A $\frac{18.01}{499.4} \times 100$
   B $\frac{12 \times 18.01}{499.4} \times 100$
   C $\frac{18.01}{499.4 - 18.01} \times 100$
   D $\frac{12 \times 18.01}{499.4 - (12 \times 18.01)} \times 100$

11. What percentage by mass of sodium thiosulfate pentahydrate ($Na_2S_2O_3{\bullet}5H_2O$) is water.

12. a) 2.0 g of an oxide of iron contains approximately 0.60 g oxygen and 1.4 g iron. Determine the empirical formula of the oxide.

    b) A compound of silicon and fluorine contains about 73% fluorine by mass. Determine its empirical formula.

    c) A compound of carbon, hydrogen and oxygen only, with a molar mass of ≈90 g mol^{-1} contains 26.6% carbon and 2.2% hydrogen by mass. Determine its molecular formula.

13. 1.000 g of tin metal burns in air to give 1.270 g of tin oxide. Determine the empirical formula of the oxide.

14. A 1.39 g sample of hydrated copper(II) sulfate ($CuSO_4{\bullet}xH_2O$) is heated until all the water of hydration is driven off. The anhydrous salt has a mass of 0.89 g. Determine the formula of the hydrate.

15. The red colour of blood is due to haemoglobin. It contains 0.335% by mass of iron. Four atoms of iron are present in each molecule of haemoglobin. If the molar mass of iron is 55.84 g mol^{-1}, estimate the molar mass of haemoglobin.

16. A 200.0 mg sample of a compound containing potassium, chromium, and oxygen was analyzed and found to contain 70.8 mg chromium and 53.2 mg potassium. Calculate the empirical formula of the sample.

17. The molecular formula of the insecticide DDT is $C_{14}H_9Cl_5$. Calculate the molar mass of the compound and the percent by mass of each element.

18. The percentages of carbon, hydrogen, and oxygen in vitamin C are determined by burning a sample of vitamin C weighing 1.000 g. The masses of CO_2 and H_2O formed are 1.500 g and 0.408 g, respectively.

    a) Calculate the masses and amounts of carbon and hydrogen in the sample.
    b) Determine the amount of oxygen in the sample.
    c) From the above data, determine the empirical formula of vitamin C.

19. The percentages by mass of carbon, hydrogen and nitrogen in an unknown compound are found to be 23.30%, 4.85%, and 40.78%, respectively. (Why do these not add up to 100%?). Determine the empirical formula of the compound. If the molar mass of the compound is 206 g mol^{-1}, determine its molecular formula.

20. Efflorescence is the process by which some hydrated salts lose water of crystallisation when exposed to the air. 'Washing soda' ($Na_2CO_3{\bullet}10H_2O$) is converted to the monohydrate ($Na_2CO_3{\bullet}H_2O$) when exposed to the air. Determine the percentage loss in mass of the crystals.

CORE

1.3 CHEMICAL EQUATIONS

1.3.1 Deduce chemical equations when all reactants and products are given.

1.3.2 Identify the mole ratio of any two species in a chemical equation.

1.3.3 Apply the state symbols (s), (l), (g) and (aq).

Chemical Formulas

Chemical formulas are a shorthand notation for elements, ions and compounds. They show the ratio of the number of atoms of each element present and, in the case of molecules or ions held together by covalent bonds, it gives the actual number of atoms of each element present in the molecule or ion. For example, the formula for magnesium chloride, which is ionically bonded, is $MgCl_2$. This tells us that in magnesium chloride there are twice as many chloride ions as there are magnesium ions. The formulas of ionic compounds can be deduced from the electrical charges of the ions involved (refer to Section 4.1).The formula for glucose, which is a molecular covalent compound, is $C_6H_{12}O_6$. This tells us that a molecule of glucose contains six carbon atoms, twelve hydrogen atoms and six oxygen atoms. The formulas of covalent compounds have to be memorised or deduced from their names.

The carbonate ion, which is a covalently bonded ion, has the formula CO_3^{2-}. This tells us that the carbonate ion consists of a carbon atom bonded to three oxygen atoms, that has also gained two electrons (hence the charge). Brackets are used to show that the subscript affects a group of atoms, for example the formula of magnesium nitrate is $Mg(NO_3)_2$, showing that there are two nitrate ions (NO_3^-) for every magnesium ion (Mg^{2+}). Sometimes brackets are also used to indicate the structure of the compound, for example urea is usually written as $(NH_2)_2CO$ rather than CN_2H_4O, to show that it consists of a carbon joined to two $-NH_2$ groups and an oxygen. The ending of the names of ions often indicate their composition. For example the ending *–ide* usually indicates just the element with an appropriate negative charge (e.g. sulfide is S^{2-}). The ending *-ate* usually indicates the the ion contains the element and oxygen atoms (e.g. sulfate is SO_4^{2-}). The ending *–ite*, also indicates an ion containing oxygen, but less oxygen than the *–ate* (e.g. sulfite is SO_3^{2-}).

Sometimes compounds are hydrated, that is they contain water molecules chemically bonded into the structure of the crystals. This is known as water of crystallisation or hydration and it is indicated by the formula for water following the formula of the substance and separated from it by a dot. For example in hydrated sodium sulfate crystals seven molecules of water of crystallisation are present for every sulfate ion and every two sodium ions, so its formula is written as $Na_2SO_4 \cdot 7H_2O$. When the crystals are heated this water is frequently given off to leave the anhydrous salt (Na_2SO_4). Similarly blue hydrated copper(II) sulfate crystals ($CuSO_4{\cdot}5H_2O$) forms white anhydrous copper(II) sulfate ($CuSO_4$) when strongly heated.

Exercise 1.3

1. The formula of the cadmium ion is Cd^{2+} and that of the benzoate ion is $C_6H_5COO^-$. Determine the formula of cadmium benzoate.

   A $Cd(C_6H_5COO)_2$
   B CdC_6H_5COO
   C $Cd_2(C_6H_5COO)_2$
   D $Cd_2C_6H_5COO$

2. An ore contains calcium hydroxide, $Ca(OH)_2$ in association with calcium phosphate, $Ca_3(PO_4)_2$. Analysis shows that calcium and phosphorus are present in a mole ratio of 5:3. Which of the following best represents the composition of the ore?

   A $Ca(OH_2) \cdot Ca_3(PO_4)_2$
   B $Ca(OH)_2 \cdot 2\ Ca_3(PO_4)_2$
   C $Ca(OH)_2 \cdot 3\ Ca_3(PO_4)_2$
   D $Ca(OH)_2 \cdot 4\ Ca_3(PO_4)_2$

3. If the formula of praseodymium oxide is PrO_2, Determine the formula of praseodymium sulfate.

   A Pr_2SO_4
   B $PrSO_4$
   C $Pr_2(SO_4)_3$
   D $Pr(SO_4)_2$

4. Write the formulas of the following common compounds:

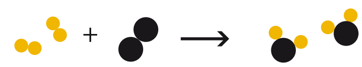
   a) Sulfuric acid
   b) Sodium hydroxide
   c) Nitric acid
   d) Ammonia
   e) Hydrochloric acid
   f) Ethanoic acid
   g) Copper (II) sulfate
   h) Carbon monoxide
   i) Sulfur dioxide
   j) Sodium hydrogencarbonate

5. Write the formulas of the following substances:

   a) Sodium chloride
   b) Copper (II) sulfide
   c) Zinc sulfate
   d) Aluminium oxide
   e) Magnesium nitrate
   f) Calcium phosphate
   g) Hydroiodic acid
   h) Ammonium carbonate
   i) Methane
   j) Phosphorus pentachloride

CHEMICAL EQUATIONS

A **chemical equation** is a record of what happens in a chemical reaction.



$$2\,H_2 + O_2 \longrightarrow 2\,H_2O$$

It shows the formulas (molecular formulas or formula units) of all the reactants (on the left hand side) and all the products (on the right hand side). It also gives the number of each species that are required for complete reaction. The example shows the reaction of hydrogen and oxygen to produce water.

Note that all of the elements that are gases and take part in chemical reactions (i.e. not the noble gases) are diatomic. Hence hydrogen gas is H_2 not H and chlorine gas is Cl_2 not Cl. The two non-gaseous halogens are also diatomic and so bromine is alwayswritten as Br_2 and iodine as I_2.

The first stage in producing an equation is to write a word equation for the reaction. The reaction of calcium carbonate with hydrochloric acid, for example, which

TOK When are symbols necessary in aiding understanding and when are they redundant?

How often when reading a news article do we say to ourselves "Why is that relevant?"; for example why do we need to know that the woman who appeared in court for shop-theft was age 37, or even that it was a woman come to that? (Though the English language, having "he" and "she", but no gender neutral equivalent would make this difficult - what about other languages?) If pressed a journalist would probably talk about "human interest". The same thing however arises in science - how much information does the person reading or work require; what is relevant and what irrelevant. In the case of state symbols then certainly it is relevant if the focus is thermochemistry because changes of state (like ice melting) involve heat changes. They are also probably useful when considering equilibrium (which side of the equation has most moles of gas?) or kinetics (water in the gas phase is much more "dilute" than as a liquid) and in electrolysis (molten and aqueous sodium chloride give different products). If the focus is purely stoichiometric however then the information may be redundant, for example

$$C_6H_6 + 3\,H_2 \longrightarrow C_6H_{12}$$

one mole of benzene, whether it is in the liquid or gas phase, will still react with three moles of hydrogen (pretty safe to assume this is a gas!). Probably the best policy is to consider that you really do not know what use an equation may be put to, and so include state symbols just to be on the safe side (as we have in this book), but whether it adds human interest to these equations is another matter!

produces calcium chloride, carbon dioxide and water can be represented as

Calcium carbonate + Hydrochloric acid $\longrightarrow$
Calcium chloride + Carbon dioxide + Water

The next stage is to replace the names of the compounds with their formulas, so that this equation becomes:

$$CaCO_3 + HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

Finally, because matter cannot be created or destroyed (at least in chemical reactions) and the charge of the products must be equal to that of the reactants, the equation must be balanced with respect to both number of atoms of each element and the charge by placing coefficients, also called stoichiometric coefficients, in front of some of the formulas. These multiply the number of atoms of the elements in the formula by that factor and represent the number of moles of the species required. In the example above, there are two chlorines on the right hand side, but only one on the left hand side. Similarly the hydrogen atoms do not balance. This can be corrected by putting a '2' in front of the hydrochloric acid, so the final balanced equation is

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + CO_2 + H_2O$$

This means that one formula unit of calcium carbonate will just react completely with two formula units of hydrochloric acid to produce one formula unit of calcium chloride, one molecule of carbon dioxide and one molecule of water. Scaling this up means that one mole of calcium carbonate reacts with two moles of hydrochloric acid to produce one mole of calcium chloride, one mole of carbon dioxide and one mole of water. The amounts of substances in a balanced equation are known as the stoichiometry of the reaction, hence these equations are sometimes referred to as stoichiometric equations. One corollary of balancing chemical equations is that as a result mass is conserved.

Note that the formulas of compounds can never be changed, so balancing the equation by altering the subscripts, for example changing calcium chloride to $CaCl_3$ or water to H_3O, is incorrect.

It is sometimes helpful to show the physical state of the substances involved and this can be done by a suffix, known as a state symbol placed after the formula. The state symbols used are; (s) - solid, (l) - liquid, (g) - gas and (aq) - aqueous solution. State symbols should be used as a matter of course as it gives more information about a reaction and in some cases, such as when studying thermochemistry, their use is vital. Adding these, the equation for the reaction between calcium carbonate and hydrochloric acid becomes

$$CaCO_3\,(s) + 2\ HCl\,(aq) \longrightarrow CaCl_2\,(aq) + CO_2\,(g) + H_2O\,(l)$$

It is often better to write the equation for a reaction occurring in aqueous solution as an **ionic equation**. This is particularly true for precipitation reactions, acid-base reactions and redox reactions. An example would be the reaction between aqueous lead nitrate and aqueous sodium chloride to precipitate lead chloride and leave a solution of sodium nitrate.

$$Pb(NO_3)_2\,(aq) + 2\ NaCl(aq) \longrightarrow PbCl_2\,(s) + 2\ NaNO_3\,(aq)$$

When soluble ionic compounds, as well as strong acids and bases, dissolve in water they totally dissociate into their component ions and so the equation above would be more correctly written as:

$$Pb^{2+}\,(aq) + 2\ NO_3^-\,(aq) + 2\ Na^+\,(aq) + 2\ Cl^-\,(aq) \longrightarrow PbCl_2\,(s) + 2\ Na^+\,(aq) + 2\ NO_3^-\,(aq)$$

This shows that the reaction actually involves just the lead ions and chloride ions. The hydrated nitrate ions and sodium ions are present in both the reactants and products and so do not take part in the reaction. They are known as **spectator ions**. The spectator ions can therefore be cancelled from both sides so that the net ionic equation becomes:

$$Pb^{2+}(aq) + 2\ Cl^-(aq) \longrightarrow PbCl_2\,(s)$$

Ionic equations are far more general than normal equations. This ionic equation, for example, states that any soluble lead compound will react with any soluble chloride to form a precipitate of lead chloride. For example the reaction

$$Pb(CH_3COO)_2\,(aq) + MgCl_2\,(aq) \longrightarrow PbCl_2\,(s) + Mg(CH_3COO)_2\,(aq)$$

would have exactly the same ionic equation:

$$Pb^{2+}\,(aq) + 2\ Cl^-\,(aq) \longrightarrow PbCl_2\,(s)$$

In order to know which salts are soluble there are certain simple rules that it is useful to remember:

Always soluble – salts of Na^+, K^+, NH_4^+ and NO_3^-

Usually soluble - salts of Cl^- and SO_4^{2-}, but $AgCl$, $PbCl_2$, $PbSO_4$ and $BaSO_4$ are insoluble

Usually insoluble - salts of OH^-, O^{2-}, CO_3^{2-} and PO_4^{3-}, but Na^+, K^+, NH_4^+ salts soluble

Common slightly soluble substances – $Ca(OH)_2$ and $Ca\ SO_4$

CORE

Exercise 1.3.1

1. Which one of the following equations best represents the reaction between iron and hydrochloric acid?

   A $Fe + HCl \longrightarrow FeCl + H$
   B $Fe + HCl \longrightarrow FeCl + H_2$
   C $Fe + 2\ HCl \longrightarrow FeCl_2 + H_2$
   D $Fe + 2\ HCl \longrightarrow FeCl_2 + 2\ H$

2. What numerical value of Q is required to balance the equation below?

   $2\ H_2S + Q\ O_2 \longrightarrow 2\ SO_2 + 2\ H_2O$

   A 2
   B 3
   C 4
   D 6

3. The equation for the reaction of sodium sulfate with barium nitrate to form a precipitate of barium sulfate is

   $Ba(NO_3)_2 + Na_2SO_4 \longrightarrow BaSO_4 + 2\ NaNO_3$

   Which one of the following is the correct ionic equation for this reaction?

   A $Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4$
   B $Na^+ + NO_3^- \longrightarrow NaNO_3$
   C $Ba^{2+} + Na_2SO_4 \longrightarrow BaSO_4 + 2\ Na^+$
   D $Ba(NO_3)_2 + SO_4^{2-} \longrightarrow BaSO_4 + 2\ NO_3^-$

4. Insert coefficients, to balance the following equations.

   (a) $CaO + HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O$
   (b) $NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$
   (c) $HCl + ZnCO_3 \longrightarrow ZnCl_2 + H_2O + CO_2$
   (d) $SO_2 + Mg \longrightarrow S + MgO$
   (e) $Fe_3O_4 + H_2 \longrightarrow Fe + H_2O$
   (f) $K + C_2H_5OH \longrightarrow KC_2H_5O + H_2$
   (g) $Fe(OH)_3 \longrightarrow Fe_2O_3 + H_2O$
   (h) $CH_3CO_2H + O_2 \longrightarrow CO_2 + H_2O$
   (i) $Pb(NO_3)_2 \longrightarrow PbO + NO_2 + O_2$
   (j) $NaMnO_4 + HCl \longrightarrow NaCl + MnCl_2 + Cl_2 + H_2O$

5. Write balanced equations for the following reactions.

   (a) Copper(II) carbonate forming copper (II) oxide and carbon dioxide.
   (b) Nickel oxide reacting with sulfuric acid to form nickel sulfate and water.
   (c) Iron and bromine reacting to give iron(III) bromide.
   (d) Lead(IV) oxide and carbon monoxide forming lead metal and carbon dioxide.
   (e) Iron(II) chloride reacting with chlorine to form iron(III) chloride.
   (f) Ethanol burning in air to form carbon dioxide and water.
   (g) Silver reacting with nitric acid to form silver nitrate, nitrogen dioxide and water.
   (h) Manganese(IV) oxide reacting with hydrochloric acid to form manganese(II) chloride, chlorine and water.
   (i) Sulfur dioxide reacting with hydrogen sulfide to form sulfur and water.
   (j) Ammonia reacting with oxygen to form nitrogen monoxide and water.

CORE

1.4 MASS AND GASEOUS VOLUME RELATIONSHIPS IN CHEMICAL REACTIONS

1.4.1 Calculate theoretical yields from chemical equations.

1.4.2 Determine the limiting reactant and the reactant in excess when quantities of reacting substances are given.

1.4.3 Solve problems involving theoretical, experimental and percentage yield.

Reacting masses

Stoichiometry is the study of quantitative (i.e., numerical) aspects of chemical equations. A balanced equation gives the amount in moles of each substance in the reaction, making it possible to calculate the masses of reactants or products in the reaction. In chemical reactions matter cannot be created or destroyed, so that the total mass of the products is equal to the total mass of the reactants. If a gas is given off or absorbed, then the mass of the solids and liquids will appear to change, but if the gas is taken into account, mass is conserved.

Chemical equations give the amounts of substances related by a chemical reaction. Consider the reaction of methane with oxygen:

$$CH_{4\,(g)} + 2\,O_{2\,(g)} \longrightarrow CO_{2\,(g)} + 2\,H_2O_{(l)}$$

One mole of methane (i.e. 16 g) will react with two moles of oxygen molecules (i.e. 64 g) to form one mole of carbon dioxide (i.e. 44 g) and two moles of water (i.e. 36 g). The total mass is 80 g on both sides of the equation, in accordance with the principle of conservation of mass, but the equation allows us to predict that burning 16 g of methane will consume 64 g (= 2 × 32) of oxygen. What if only 4 g of methane is burnt? This is $^4/_{16} = {}^1/_4$ of the amount of methane, so it will consume ¼ of the amount of oxygen, i.e. 16 g.

If the molar masses are known, the masses of substances related in a chemical equation may be calculated by applying the formula $n = \frac{m}{M}$

These calculations are best thought of as being carried out in three stages as illustrated in the examples below:

Example 1

Consider that you had 10.00 g of sodium hydroxide. What mass of hydrated sodium sulfate crystals ($Na_2SO_4{\bullet}7H_2O$) could be produced by reaction with excess sulfuric acid?

Solution

<u>Stage One</u> - Calculate the amount of the substance whose mass is given.

$$\text{Amount of NaOH} = \frac{m}{M} = \frac{10.00\text{ g}}{40.00\text{ g mol}^{-1}}$$

$$= 0.2500\text{ mol}$$

<u>Stage Two</u> - Use the balanced equation to calculate the amount of the required substance.

$$2\,NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O$$

2 mol 1 mol

$$\therefore \text{ mol } Na_2SO_4 = \tfrac{1}{2}\text{ mol NaOH}$$

0.2500 mol NaOH

$$\therefore\ \tfrac{1}{2} \times 0.2500\text{ mol } Na_2SO_4$$

$$= 0.1250\text{ mol}$$

<u>Stage Three</u> - Calculate the mass of the required substance from the amount of it.

Mass of hydrated sodium sulfate

$$= n \times M$$
$$= 0.1250\text{ mol} \times 268.18\text{ g mol}^{-1}$$
$$= 33.52\text{ g}$$

(N.B. the molar mass of the hydrated salt must be used)

The procedure is exactly the same irrespective of whether the calculation starts with the mass of reactant and calculates the mass of product, or calculates the mass of reactant required to give a certain mass of product, as illustrated by a second example.

Example 2

What mass of sodium hydrogencarbonate must be heated to give 8.80 g of carbon dioxide?

Solution

Stage One

$$\text{Amount of } CO_2 = \frac{8.80 \text{ g}}{44.01 \text{ g mol}^{-1}}$$

$$= 0.200 \text{ mol}$$

Stage Two

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + CO_2 + H_2O$$

2 mol | 1 mol

$2 \times 0.200 = 0.400$ mol | 0.200 mol

Stage Three

$$\text{Mass of } NaHCO_3 = 0.400 \text{ mol} \times 84.01 \text{ g mol}^{-1}$$

$$= 33.6 \text{ g}$$

Example 3

Calculate the mass of O_2 required for the combustion of 0.250 mol propane gas, $C_3H_{8\,(g)}$.

Solution

Stage One

Aleady completed;
we are given the moles of propane (0.250)

Stage Two

$$C_3H_8\,(g) \quad + \quad 5\,O_2\,(g) \longrightarrow 3\,CO_2\,(g) + 4\,H_2O\,(l)$$

1 mol C_3H_8 | 5 mol O_2

0.250 mol C_3H_8 | $0.25 \times 5 = 1.25$ mol O_2

Stage Three

$$\text{Mass of } O_2 \text{ required} = 1.25 \text{ mol} \times 32.0 \text{ g mol}^{-1}$$

$$= 40.0 \text{ g}$$

In summary

- Calculate the amount of the substance whose mass is given.
- Use the balanced equation to calculate the amount of the required substance.
- Calculate the mass of the required substance from the amount of it.

Exercise 1.4

1. When butane is burnt in excess air, the following reaction takes place

$$2\,C_4H_{10\,(g)} + 13\,O_{2\,(g)} \longrightarrow 8\,CO_{2\,(g)} + 10\,H_2O_{(l)}$$

Calculate how many moles of oxygen are required to react with five moles of butane.

A 6.5
B 13
C 32.5
D 65

2. When magnesium is added to aqueous silver nitrate, the following reaction takes place

$$Mg_{(s)} + 2\,AgNO_{3\,(aq)} \longrightarrow 2\,Ag_{(s)} + Mg(NO_3)_{2\,(aq)}$$

What mass of silver is formed when 2.43 g of magnesium is added to an excess of aqueous silver nitrate.

A 107.9 g
B 21.6 g
C 10.8 g
D 5.4 g

3. When heated potassium chlorate(V) decomposes to form potassium chloride and oxygen. The unbalanced equation is:

$$KClO_{3\,(s)} \longrightarrow KCl_{\,(s)} + O_{2\,(g)}$$

(a) Balance the equation.
(b) Calculate how many moles of $KClO_3$ are needed to produce 0.60 moles of oxygen.
(c) What mass of $KClO_3$ is needed to produce 0.0200 moles of KCl?

4. What mass of copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) can be produced by reacting 12.00 g of copper(II) oxide with an excess of sulfuric acid?

5. Pure compound A contains 63.3% manganese and 36.7% oxygen by mass. Upon heating compound A, oxygen is evolved and pure compound B is formed which contains 72.0% manganese and 28.0% oxygen by mass.

   (a) Determine the empirical formula for compounds A and B.
   (b) Write a balanced equation which represents the reaction that took place.
   (c) Calculate how many grams of oxygen would be evolved when 2.876 g of A is heated to form pure B.

Limiting reagents

The quantities of reactants related in the section above are the precise amounts, or stoichiometric amounts, required to just react with each other. More commonly there will be an excess of all of the reagents except one, so that all of this last reagent will be consumed. This reagent is known as the **limiting reagent** because it is the amount of this that limits the quantity of product formed. It may be identified by calculating the amount of each reagent present and then dividing by the relevant coefficient from the equation. The reagent corresponding to the smallest number is the limiting reagent.

Example

Consider the reaction:

$$H_2O_{2\,(aq)} + 2KI_{(aq)} + H_2SO_{4\,(aq)} \longrightarrow I_{2\,(s)} + K_2SO_{4\,(aq)} + 2H_2O_{(l)}$$

What mass of iodine is produced when 100.00 g of KI is added to a solution containing 12.00 g of H_2O_2 and 50.00 g H_2SO_4?

Solution

The mole ratio from the equation is

$$\begin{array}{ccccc} H_2O_2 & : & KI & : & H_2SO_4 \\ 1 & : & 2 & : & 1 \end{array}$$

The actual mole ratio of reagents present is

$$\begin{array}{rccccc} & \frac{12.00}{34.02} & & \frac{100.00}{166.00} & & \frac{50.00}{98.08} \\ = & 0.3527 & : & 0.6024 & : & 0.5098 \\ = & 1 & : & 1.708 & : & 1.445 \end{array}$$

Ratio divided by coefficient

$$= \quad 1 \quad : \quad 0.854 \quad : \quad 1.445$$

It can be seen that even though there is the greatest mass of potassium iodide, it is still the limiting reagent, owing to its large molar mass and the 2:1 mole ratio. The maximum yield of iodine will therefore be ½ × 0.6024 = 0.3012 moles. This is the theoretical yield, which can, if required, be converted into a mass:

$$\begin{aligned} \text{Theoretical yield} &= n \times M \\ &= 0.3012 \text{ mol} \times 253.8 \text{ g mol}^{-1} \\ &= 76.44 \text{ g} \end{aligned}$$

There is an excess of both hydrogen peroxide and sulfuric acid. The amounts in excess can be calculated:

0.6024 moles of potassium iodide will react with:

½ × 0.6024 = 0.3012 moles of both H_2O_2 and H_2SO_4 (both a 2:1 mole ratio).

Mass of H_2O_2 reacting = 0.3012 mol × 34.02 g mol^{-1} = 10.24 g,

$$\begin{aligned} \text{Mass of } H_2SO_4 \text{ reacting} &= 0.3012 \times 98.08 \\ &= 29.54 \text{ g,} \end{aligned}$$

therefore mass in excess $= 50.00 - 29.54$
$= 20.46$ g

In practice the theoretical yield based on the balanced chemical equation is never achieved owing to impurities in reagents, side reactions and other sources of experimental error. Supposing 62.37 g of iodine was eventually produced, the **percentage yield** can be calculated as follows:

$$\text{Percentage yield} = \frac{62.37}{76.44} \times 100 = 81.59\%.$$

Exercise 1.4.1

1. Consider the reaction:

$$2\ Al\ (s) + 3\ I_2\ (s) \longrightarrow 2\ AlI_3\ (s)$$

Determine the limiting reagent and the theoretical yield of the product from:

(a) 1.20 mol aluminium and 2.40 mol iodine.
(b) 1.20 g aluminium and 2.40 g iodine.
(c) Calculate how many grams of aluminium are left over in part b.

2. Freon-12 (used as coolant in refrigerators), is formed as follows:

$$3\ CCl_4\ (l) + 2\ SbF_3\ (s) \longrightarrow 3\ CCl_2F_2\ (g) + 2\ SbCl_3\ (s)$$

150 g tetrachloromethane is combined with 100 g antimony(III) fluoride to give Freon-12 (CCl_2F_2).

(a) Identify the limiting and excess reagents.
(b) Calculate how many grams of Freon-12 can be formed.
(c) How much of the excess reagent is left over?

3. Aspirin is made by adding acetic anhydride to an aqueous solution of salicylic acid. The equation for the reaction is:

$$2\ C_7H_6O_3\ (aq) + C_4H_6O_3\ (l) \longrightarrow 2C_9H_8O_4\ (aq) + H_2O\ (l)$$

salicylic acid + acetic anhydride ⟶ aspirin + water

If 1.00 kg of salicylic acid is used with 2.00 kg of acetic anhydride, determine:

(a) the limiting reagent.
(b) the theoretical yield.
(c) If 1.12 kg aspirin is produced experimentally, determine the percentage yield.

AVOGADRO'S HYPOTHESIS AND THE MOLE CONCEPT APPLIED TO GASES

1.4.4 Apply Avogadro's law to calculate reacting volumes of gases.

1.4.5 Apply the concept of molar volume at standard temperature and pressure in calculations.

1.4.6 Solve problems involving the relationship between temperature, pressure and volume for a fixed mass of an ideal gas.

1.4.7 Solve problems relating to the ideal gas equation, PV=nRT.

1.4.8 Analyse graphs relating to the ideal gas equation.

At constant temperature and pressure it is found that a given volume of any gas always contains the same number of particles (i.e. molecules except in the case of the noble gases) at the same temperature and pressure. In other words, equal amounts of gases at the same temperature and pressure occupy the same volume! This is known as **Avogadro's hypothesis**. It means that in reactions involving gases the volumes of reactants and products, when measured at the same temperature and pressure, are in the same ratio as their coefficients in a balanced equation. For example when carbon monoxide reacts with oxygen to form carbon dioxide, the volume of oxygen required is only half the volume of carbon monoxide consumed and carbon dioxide formed:

$$2\ CO_{(g)} + O_{2\ (g)} \longrightarrow 2\ CO_{2\ (g)}$$

2 vol　1 vol　2 vol

This may be used to carry out calculations about the volume of gaseous product and the volume of any excess reagent:

Example 1

10 cm^3 of ethyne is reacted with 50 cm^3 of hydrogen to produce ethane according to the equation:

$$C_2H_{2\,(g)} + 2\,H_{2\,(g)} \longrightarrow C_2H_{6\,(g)}$$

Calculate the total volume and composition of the remaining gas mixture, assuming that temperature and pressure remain constant.

Solution

Ratio of volume of reactants to products is in the ratio of the coefficients:

$$C_2H_{2\,(g)} + 2\,H_{2\,(g)} \longrightarrow C_2H_{6\,(g)}$$

1 vol	2 vol	1 vol
10 cm^3	20 cm^3	10 cm^3

Hence it can be seen that the hydrogen is in excess:

Volume of remaining hydrogen = 50 cm^3 - 20 cm^3 = 30 cm^3

The total volume of the gas mixture that remains is 40 cm^3, comprising of 10 cm^3 ethane and 30 cm^3 hydrogen.

If the temperature and pressure are specified, then the volume of any gas that contains one mole may be calculated. This is known as the **molar volume**. At standard temperature and pressure (abbreviated to stp; i.e. 1 atm = 101.3 kPa and 0 °C = 273 K) this volume is 22.4 dm^3. [Note: 1 dm^3 = 1 dm × 1 dm × 1 dm = 10 cm × 10 cm × 10 cm = 1000 cm^3 = 1 litre (L)] This is called the molar gas volume, V_m, and contains 6.02×10^{23} molecules for a molecular gas (or 6.02×10^{23} atoms for noble gases). V_m is the same for all gases (under ideal conditions; see Ideal Gas Equation).

The concept of molar volume allows one to solve a variety of problems in which gases are involved in terms of the mole concept. For example the amount of gas can be calculated from the volume of the gas under these conditions using the formula:

$$\text{Amount of gas} = \frac{\text{Volume of gas}}{\text{Molar volume}}$$

This may be abbreviated to:

$$n = \frac{V_{stp}}{22.4}$$

where V_{stp} is the volume of gas in dm^3 at 273 K and 101.3 kPa.

Example 2

Calculate how many moles of oxygen molecules are there in 5.00 dm^3 of oxygen at s.t.p..

Solution

$$n = \frac{V_{stp}}{22.4} = \frac{5.00}{22.4} = 0.223 \text{ mol}$$

This equation may also be rearranged to calculate the volume of gas under these conditions, knowing the amount of gas. The relationship between the amount of gas and its volume can then be used in calculations in the same way as the relationship between mass and molar mass.

Example 3

What mass of sodium hydrogencarbonate must be heated to generate 10.0 dm^3 of carbon dioxide, measured at standard temperature and pressure?

Solution

Stage One *- Calculate the amount of the substance for which data is given.*

$$n = \frac{V_{stp}}{22.4} = \frac{10.00 \text{ dm}^3}{22.4 \text{ mol dm}^{-3}} = 0.446 \text{ mol}$$

Stage Two *- Use the balanced equation to calculate the amount of the required substance.*

$$2\,NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2$$

2 moles 1 mole

$2 \times 0.446 = 0.892$ moles   0.446 moles

Stage Three *- Calculate the result for the required substance from the number of moles.*

Mass of sodium hydrogencarbonate

$= n \times M$

$= 0.892 \text{ mol} \times 84.0 \text{ g mol}^{-1}$

$= 74.9$ g.

Example 4

What volume of air (assumed to contain 20% oxygen by volume), measured at s.t.p., is required for the complete combustion of 1.000 kg of gasoline, assuming that this is totally composed of octane (C_8H_{18})?

Solution

Stage One *- Calculate the amount of the substance for which data is given.*

$$n = \frac{m}{M_r} = \frac{1000}{114.2} = 8.76 \text{ mol}$$

Stage Two *- Use the balanced equation to calculate the amount of the required substance.*

$$2\,C_8H_{18} + 25\,O_2 \longrightarrow 16\,CO_2 + 18\,H_2O$$

2 moles   25 mole

8.76 $\frac{1}{2} \times 25 \times 8.76$

$= 109.5$ moles

Stage Three *- Calculate the result for the required substance from the number of moles.*

Volume of oxygen $= n \times 22.4$

$= 109.5 \times 22.4$

$= 2543 \text{ dm}^3$

Volume of air $= 2543 \times {}^{100}/_{20}$

$= 12260 \text{ dm}^3$

Exercise 1.4.2

1. According to the equation below, what volume of nitrogen dioxide would you expect to be formed from 20 cm^3 of nitrogen monoxide, assuming that the volumes are measured at the same temperature and pressure?

$$2\,NO\,(g) + O_2\,(g) \longrightarrow 2\,NO_2\,(g)$$

A 10 cm^3
B 15 cm^3
C 20 cm^3
D 30 cm^3

2. Four identical flasks are filled with hydrogen, oxygen, carbon dioxide and chlorine at the same temperature and pressure. The flask with the greatest mass will be the one containing

A hydrogen.
B oxygen.
C carbon dioxide.
D chlorine.

3. Calculate how many moles of hydrogen molecules are there in 560 cm^3 of hydrogen gas measured at s.t.p..

A 0.0250
B 0.050
C 25.0
D 50.0

4. What volume would 3.20 g of sulfur dioxide ocupy at s.t.p.?

A 0.56 dm^3
B 1.12 dm^3
C 2.24 dm^3
D 4.48 dm^3

5. Potassium nitrate ($M = 101 \text{ g mol}^{-1}$) decomposes on heating as shown by the equation below. What mass of the solid must be heated to produce 10.0 dm^3 of oxygen gas, measured at s.t.p.?

$$2\,KNO_3\,(s) \longrightarrow 2\,KNO_2\,(s) + O_2\,(g)$$

A $101 \times \frac{22.4}{10.0}$ g

B $101 \times \frac{10.0}{22.4}$ g

C $\frac{1}{2} \times 101 \times \frac{10.0}{22.4}$ g

D $2 \times 101 \times \frac{10.0}{22.4}$ g

CORE

CORE

6. A mixture of 20 cm^3 hydrogen and 40 cm^3 oxygen is exploded in a strong container. After cooling to the original temperature and pressure (at which water is a liquid) what gas, if any, will remain in the container?

7. To three significant figures, calculate how many methane molecules are there in 4.48 dm^3 of the gas at standard temperature and pressure?

8. If 3.00 dm^3 of an unknown gas at standard temperature and pressure has a mass of 6.27 g, Determine the molar mass of the gas.

9. Determine the density of ammonia, in g dm^{-3}, at s.t.p..

10. Sulfur dioxide, present in flue gases from the combustion of coal, is often absorbed by injecting powdered limestone into the flame, when the following reactions occur:

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

$$CaO\ (s) + SO_2\ (g) \longrightarrow CaSO_3\ (s)$$

What volume of sulfur dioxide, measured at s.t.p., can be absorbed by using 1 tonne (1.00×10^6 g) of limestone in this way?

The Ideal gas equation

An '**ideal gas**' is one in which the particles have negligible volume, there are no attractive forces between the particles and the kinetic energy of the particles is directly proportional to the absolute temperature. For many real gases this approximation holds good at low pressures and high temperatures, but it tends to break down at low temperatures and high pressures (when the separation of molecules is reduced), especially for molecules with strong intermolecular forces, such as hydrogen bonding (e.g. ammonia). In an ideal gas the pressure and volume of the gas are related to the amount and temperature of the gas by the Ideal Gas Equation:

$$P.V = n.R.T$$

R is known as the Ideal Gas Constant and its numerical value will depend on the units used to measure pressure, P, and volume, V and n (n.b. Temperature, T must be expressed in Kelvin -not degrees Celsius). If P is in kPa, n is in moles, and V is in dm^3, then R has a value of 8.314 J K^{-1} mol^{-1}.

The ideal gas equation may be used to find any one of the terms, provided that the others are known or remain constant. For example we can calculate the volume occupied by 1 mole of a gas (so n=1) at 20.0° C (so T = 293.0 K, note that this conversion to Kelvin is vital!) and normal atmospheric pressure (101.3 kPa):

Hence the volume of a gas under known conditions may be used to calculate the amount of a gas. Similarly if the volume of a known mass of gas (or the density of the gas) is measured at a particular temperature and pressure, then the ideal gas equation may be used, along with the formula $n = \frac{m}{M}$, to calculate the molar mass of the gas.

Example

3.376 g of a gas occupies 2.368 dm^3 at 17.6° C and a pressure of 96.73 kPa, determine its molar mass.

Solution

(note: temperature is in K)

$$n = \frac{PV}{RT} = \frac{96.73 \times 2.368}{8.314 \times 290.6} = 0.09481$$

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

$$= \frac{3.376}{0.09481}$$

$$= 35.61 \text{ g mol}^{-1}$$

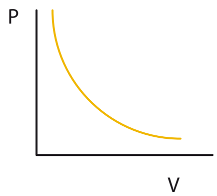
This technique may also be used to determine the molar mass of a volatile liquid by making the measurements at a temperature above the boiling point of the liquid.

The effect of conditions on the volume of a fixed mass of ideal gas

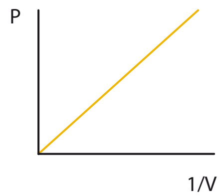
In order to convert the volume, pressure and temperature of a given amount of ideal gas (so n and R are both constant) from one set of conditions (1) to another set of conditions (2), when the third variable remains constant, the ideal gas equation simplifies to:

Boyle-Mariotte Law $P_1V_1 = P_2V_2$

(at constant n and T)

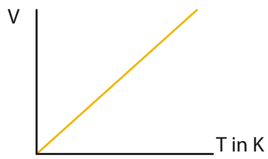


or

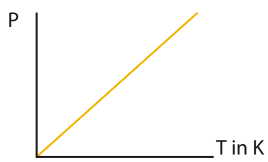


Charles' Law $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

(at constant n and P)



Pressure (Gay Lussac's) Law $\frac{P_1}{T_1} = \frac{P_2}{T_2}$ (at constant n and V)



These may be combined into the expression:

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

In this and the preceding equations, T must be expressed in Kelvin, but P and V may be expressed in any units provided the same units are used consistently throughout the calculation.

Example

A syringe contains 50 cm^3 of gas at 1.0 atm pressure and 20 °C. What would the volume be if the gas were heated to 100 °C, whilst at the same time compressing

Solution

it to 5 atm?

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

$$\therefore \frac{1.0 \times 50}{293} = \frac{5.0 \times V_2}{373}$$

$$V_2 = 50 \times \frac{1.0}{5.0} \times \frac{373}{292} = 13 \text{ cm}^3$$

Exercise 1.4.3

1) A sealed flask contains 250 cm^3 of gas at 35°C and atmospheric pressure. The flask is then heated to 350°C. The pressure of the gas will increase by a factor of about

A 2
B 10
C 250
D 585

2) The pressure on 600 cm^3 of gas is increased from 100 kPa to 300 kPa at constant temperature. What will the new volume of gas be?

A 200 cm^3
B 300 cm^3
C 1200 cm^3
D 1800 cm^3

3) 1 dm^3 of gas in a container at -73°C is allowed to expand to 1.5 dm^3, what must the temperature be increased to so that the pressure remains constant?

A −36°C
B 0°C
C 27°C
D 73°C

4) 4.00 dm^3 of air at 0°C and a pressure of 2.00 atmospheres, is heated to 273°C and the pressure increased to 8 atmospheres. What will the new volume of the gas be?

A 1.00 dm^3
B 2.00 dm^3
C 8.00 dm^3
D 32.00 dm^3

5) A 2.00 dm^3 of a gas at a pressure of 1000 kPa is allowed to expand at constant temperature until the pressure decreases to 300 kPa. What will the new volume of the gas be?

A 3.00 dm^3
B 3.33 dm^3
C 6.00 dm^3
D 6.66 dm^3

6) What volume is occupied by 0.0200 g of oxygen gas at 27 °C and a pressure of 107 kPa?

A 0.466 dm^3
B 0.029 dm^3
C 0.015 dm^3
D 0.002 dm^3

7) In a particular experiment aluminium was reacted with dilute hydrochloric acid according to the equation:

$$2\ Al\ (s) + 6\ HCl\ (aq) \longrightarrow 2\ AlCl_3\ (aq) + 3\ H_2\ (g)$$

355 cm^3 of hydrogen was collected at 25.0 °C a pressure of 100.0 kPa.

a) Calculate how many moles of hydrogen were collected.
b) If 0.300 g of aluminium was used with excess acid, determine the percentage yield of hydrogen.

8) A steel cylinder contains 32 dm^3 of hydrogen at 4×10^5 Pa and 39 °C. Calculate

a) The volume that the hydrogen would occupy at s.t.p. (0 °C and 101.3 kPa)
b) The mass of hydrogen in the cylinder.

9) The following readings were taken during the determination of the molar mass of a gas by direct weighing. If the experiment was carried out at 23 °C and 97.7 kPa, calculate the molar mass of the gas.

Mass of evacuated flask 183.257 g
Mass of flask and gas 187.942 g
Mass of flask filled with water 987.560 g

10) Two 5 dm^3 flasks are connected by by a narrow tube of negligible volume. Initially the two flasks are both at 27 °C and contain a total of 2 moles of an ideal gas. One flask is heated to a uniform temperature of 127 °C while the other is kept at 27 °C. Assuming their volume does not alter, calculate the number of moles of gas in each flask of the gas and the final pressure.

1.5 SOLUTIONS

1.5.1 Distinguish between the terms solute, solvent, solution and concentration ($g\ dm^{-3}$ and $mol\ dm^{-3}$).

1.5.2 Solve problems involving concentration, amount of solute and volume of solution.

Sometimes when a substance is mixed with a liquid, it disperses into sub-microscopic particles (i.e. atoms, molecules or ions) to produce a homogenous mixture of two or more substances - this is known as a **solution**. The liquid, present in excess, in which the dispersion occurs is known as the **solvent** and the substance dissolved in it, which can be a solid, a liquid or a gas, is known as the **solute**. A **solution** is different from a **suspension** (fine particles of solid in a liquid) because it is transparent, does not settle out and cannot be separated by filtration.

The **solubility** of a substance is the quantity of that substance that will dissolve to form a certain volume of solution in that solvent (water is assumed unless another solvent is stated). The units vary from source to source (the quantity may be in moles or grams, and this may be in 100 cm^3 or in 1 dm^3), so this is always worth checking. It is important to also note that solubility varies with temperature. With solids it usually (though not always) increases with temperature, for gases it decreases with temperature. If a certain volume of solution contains a small amount of dissolved solid it is said to be dilute and if it contains a large amount of solute it is said to be concentrated. Care must be taken not to replace these with the terms weak and strong, as these have a very different meaning in chemistry (refer to Section 8.3). A **saturated solution** is one in which no more solute will dissolve at that temperature, and excess solute is present. Sometimes, temporarily, the concentration of a solute (or its component ions) can exceed its solubility and in this case the solution is referred to as a **supersaturated solution**. This can occur if the temperature of a solution is changed, or more commonly, if the substance is produced in a chemical reaction. In this case the excess solid will eventually separate from the solution as a **precipitate**.

CONCENTRATION

The **concentration** (c) is the amount of substance (n) contained within a given volume (V) of solution. In chemistry this is given as the number of moles of the substance in one cubic decimetre (dm^3; note that this volume is equivalent to 1 litre). Concentration can therefore be calculated using the formula:

$$\text{Concentration (of solution)} = \frac{\text{Amount of solute}}{\text{Solution volume in dm}^3}$$

This can be written as: $c = \frac{n}{V}$

Example 1

Calculate the concentration of the solution formed when 4.00 moles of glucose are dissolved in 5.00 dm^3 of water.

Solution

$$c = \frac{n}{V}$$

$$c = \frac{4.00\text{ mol}}{5.00\text{ dm}^3}$$

$$= 0.800\text{ mol dm}^{-3}$$

Although the preferred unit for concentration is mol dm^{-3}, because 1 dm^3 is equal to 1 litre (L), concentration may also be quoted as mol/L, mol/dm^3, mol L^{-1}, or even just 'M'. 2 M sulfuric acid is therefore sulfuric acid with a concentration of 2 moles per litre. International convention however recommends that this use of 'M', and the use of the term 'molarity' instead of concentration, be discontinued as M is the notation commonly used for molar mass.

Because we frequently refer to the concentrations of species in chemistry, the convention has arisen that square brackets around a symbol means 'the concentration of', so that [NaCl] = 0.5 mol dm^{-3} means the concentration of sodium chloride is 0.5 mol dm^{-3}.

The concentration of the solution formed by dissolving a given mass of a substance may be found by substituting in the concentration formula above, having first calculated the amount of the substance using the formula $n = \frac{m}{M}$.

Example 2

If 2.00 g of sodium hydroxide is dissolved in 200 cm^3 of water, determine the concentration of the resulting solution.

Solution

$$\text{Amount of NaOH} = \frac{2.00\text{ g}}{40.0\text{ g mol}^{-1}}$$

$$= 0.0500\text{ mol}$$

$$[\text{NaOH}] = \frac{0.0500\text{ mol}}{0.200\text{ dm}^3}$$

$$= 0.250\text{ mol dm}^{-3}$$

Note that the 200 cm^3 of water has to be converted to 0.200 dm^3 before it can be substituted in the equation. Similarly this process can be modified to calculate the amount (and hence the mass) of solute present, or the volume of the solution required.

Example 3

What mass of hydrated copper (II) sulfate crystals ($CuSO_4{\bullet}5H_2O$) is present in 17.3 cm^3 of a 0.279 mol dm^{-3} solution of copper (II) sulfate?

Solution

$$\text{Amount of CuSO}_4\text{ (n)} = c \times V$$
$$= 0.279\text{ mol dm}^{-3} \times 0.0173\text{ dm}^3$$
$$= 0.00483\text{ mol}$$

$$\text{Mass of CuSO}_4{\bullet}5\text{H}_2\text{O} = n \times M$$
$$= 0.00483\text{ mol} \times 249.7\text{ g mol}^{-1}$$
$$= 1.21\text{ g}$$

Soluble ionic compounds split up into their component ions when dissolved in water. The concentrations of the individual ions will depend on how many of these ions are produced when the substance dissolves. In a 2 mol dm^{-3} solution of aluminium sulfate, for example, the concentration of the aluminium ions is 4 mol dm^{-3} and that of the sulfate ions is 6 mol dm^{-3}, as illustrated by the equation below

$$\underset{\text{1 mole}}{Al_2(SO_4)_3\text{ (aq)}} \longrightarrow \underset{\text{2 moles}}{2\ Al^{3+}\text{ (aq)}} + \underset{\text{3 moles}}{3\ SO_4^{2-}\text{ (aq)}}$$

2 mol dm^{-3}	4 mol dm^{-3}	6 mol dm^{-3}

A concentrated solution may have solvent added to produce a more dilute one; since the amount of solute remains the same on dilution, then increasing the volume decreases its concentration. Because the amount of solute before and after dilution is constant: ($n_b = n_a$) and $n = cV$, the concentrations and volumes before and after dilution are related by the expression:

$$n = c_1 \times V_1 = c_2 \times V_2$$

where c_1 and V_1 are the initial concentration and volume and c_2 and V_2 the final concentration and volume. Note that c and V can be in any units provided that the same units are used on both sides of the equation.

Example 4

Calculate the volume to which 20.0 cm^3 of 7.63 mol dm^{-3} hydrochloric acid must be diluted to produce a solution with a concentration of exactly 5.00 mol dm^{-3}.

$$c_1 \times V_1 = c_2 \times V_2$$

Solution

Substituting:

$$7.63 \times 20.0 = 5.00 \times V_2$$

Hence:

$$V_2 = 20.0 \times \frac{7.63}{5.00}$$

$$= 30.5 \text{ cm}^3$$

Therefore the 20.0 cm^3 of the original acid must be diluted to 30.5 cm^3. Assuming that there is no volume change on dilution 30.5 cm^3 - 20.0 cm^3 = 10.5 cm^3 of water must be added.

Exercise 1.5

1. Calculate how many moles of hydrochloric acid are present in 0.80 dm^3 of a solution with a concentration of 0.40 mol dm^{-3}.

   A 0.32
   B 0.5
   C 0.8
   D 2

2. Sodium phosphate has the formula Na_3PO_4. Determine the concentration of sodium ions in a 0.6 mol dm^{-3} solution of sodium phosphate?

   A 0.2 mol dm^{-3}
   B 0.3 mol dm^{-3}
   C 0.6 mol dm^{-3}
   D 1.8 mol dm^{-3}

3. What volume of a 0.5 mol dm^{-3} solution of sodium hydroxide can be prepared from 2 g of the solid?

   A 0.05 litres
   B 0.1 litres
   C 0.4 litres
   D 0.5 litres

4. What are the concentrations of the solutions produced by dissolving

   a) 3.0 moles of nitric acid in 4.0 dm^3 of solution?
   b) 2.81 g of KOH in 2.00 dm^3 of solution?
   c) 5.00 g of magnesium sulfate heptahydrate in 250 cm^3 of solution?

5. Calculate how many moles are there in the following:

   a) 7.0 dm^3 of sulfuric acid of concentration 0.30 mol dm^{-3}.
   b) 50 cm^3 of a 0.040 mol dm^{-3} solution of lithium chloride.
   c) 15.0 cm^3 of a solution made by dissolving 5.80 g of zinc chloride in 2.50 dm^3 of solution.

6. What volume of solution could you produce in the following cases?

   a) 1 mol dm^{-3} copper(II) chloride from 0.4 moles of the solid.

b) 0.0200 mol dm^{-3} $NaNO_3$ starting from 5.00 g of the solid.

c) 0.50 mol dm^{-3} sulfuric acid starting with 20 cm^3 of a concentrated 18 mol dm^{-3} solution.

7. How would you prepare 500 cm^3 of a 0.100 mol dm^{-3} NaCl solution?

8. How would you prepare 1.2 dm^3 of a 0.40 mol dm^{-3} solution of hydrochloric acid starting from a 2.0 mol dm^{-3} solution?

9. 500 cm^3 of 0.500 mol dm^{-3} NaCl is added to 500 cm^3 of 1.00 mol dm^{-3} Na_2CO_3 solution. Calculate the final concentration of Na^+ ions in solution.

10. When hydrochloric acid is added to aqueous lead (II) nitrate, solid lead (II) chloride is precipitated. If 10 cm^3 of 2 mol dm^{-3} hydrochloric acid is added to 40 cm^3 of 0.5 mol dm^{-3} aqueous lead nitrate, determine the concentration in the final solution of

a) nitrate ions
b) chloride ions
c) hydrogen ions
d) lead (II) ions.

TITRATION CALCULATIONS

Titration is a technique which involves measuring the volume of one solution which just reacts completely with another solution.

Usually one of the solutions will have an accurately known concentration and this will be used to find the concentration of the other solution. The solution of accurately known concentration is called a **standard solution**. Its concentration can be checked by titrating it against a solution of a **primary standard**, which is prepared by dissolving a precisely known mass of pure solute to make an accurately known volume of solution, using a **volumetric flask**.

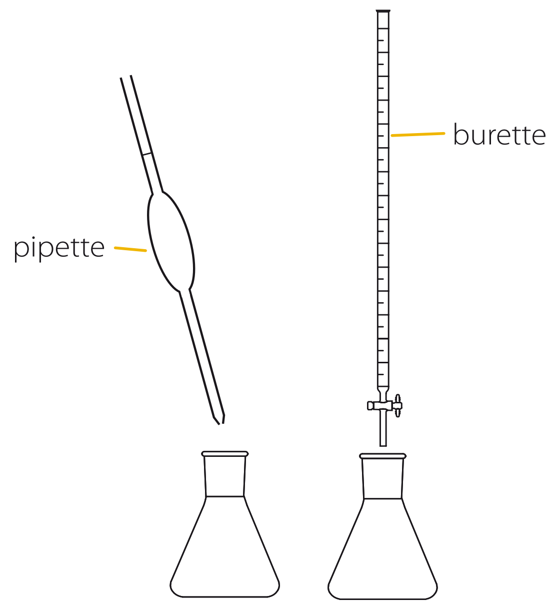


Figure 107 Pipette and burette

A primary standard must:

- be available in very pure form
- have a relatively high molar mass
- be stable as both the solid and in solution
- be readily soluble in water
- react completely in a known manner

Sodium carbonate and potassium hydrogenphthalate are commonly used as primary standards for acid-base titrations. Although acid-base titrations are the most common, the technique is not restricted to these. Redox, precipitation and compleximetric titrations are also frequently encountered.

An accurately known volume of one of the solutions will be measured out into a conical flask with a **pipette** (**pipet**), which is designed to deliver exactly the same volume each time it is used. An **indicator** will usually be added and the second solution run in from a **burette** (**buret**), until the indicator just changes colour. The burette is fitted with a tap and is calibrated so as to accurately measure a variable volume of solution. The volume of the second solution required, called the **titre**, can be found by subtracting the initial burette reading from the final one.

The amount of solute can be calculated from the volume of the solution of known concentration. The amount of the unknown may then be found using the balanced equation. Finally the concentration of the unknown may be calculated from this and the volume of the second solution used. The three stages involved are closely analogous to those used in reacting mass calculations.

Example 1

It is found that 10.00 cm^3 of 0.2000 mol dm^{-3} aqueous sodium carbonate requires 25.00 cm^3 of hydrochloric acid to just neutralise it. Determine the concentration of the hydrochloric acid.

Solution

Stage One *- Calculate the amount in the solution of known concentration*

Amount of sodium carbonate = $c \times V$
$= 0.200 \text{ mol dm}^{-3} \times 0.0100 \text{ dm}^{-3}$
$= 0.00200$ mol

Stage Two *- Use a balanced equation to calculate the amount of the unknown*

$$Na_2CO_3 + 2\,HCl \longrightarrow 2\,NaCl + CO_2 + H_2O$$

Na_2CO_3	$2\,HCl$
1 mol	2 mol
0.00200 mol	2 × 0.00200
	= 0.00400 mol

Stage Three *- Calculate the concentration of the unknown solution*

$$[HCl] = \frac{n}{V} = \frac{0.00400 \text{ mol}}{0.02500 \text{ dm}^3} = 0.160 \text{ mol dm}^{-3}$$

Example 2

If the volume of NaOH solution required to neutralize 1.325 g hydrated ethanedioic acid ($H_2C_2O_4{\bullet}2H_2O$) is 27.52 cm^3, calculate the concentration of the sodium hydroxide solution.

Solution

Stage One

$M_r = (2.02+24.02+64.00+4.04+32.00)$
$= 126.08$

$$\text{Amount of ethanedioic acid} = \frac{1.325}{126.08} = 0.010509 \text{ mol}$$

Stage Two

Since ethanedioic acid is diprotic, the balanced chemical equation for the neutralization reaction is:

$$H_2C_2O_4 + 2\,NaOH \longrightarrow Na_2C_2O_4 + 2\,H_2O$$

$H_2C_2O_4$	$2\,NaOH$
1	2
0.010509 mol	2 × 0.010509 mol
	= 0.021018 mol

Stage Three

27.52 cm^3 = 0.02752 dm^3,

Hence

$$[NaOH] = \frac{0.021018}{0.02750} = 0.07638 \text{ mol dm}^{-3}$$

Note the conversion of volume to dm^3 and correct rounding to 4 significant figures at the end of the calculation.

Example 3

A titration technique can also be used to investigate the stoichiometry of an equation by finding out the amounts of the various reagents that react together.

It is found that 10.0 cm^3 of iodine solution of concentration 0.131 mol dm^{-3}, just reacts completely with 20.4 cm^3 of aqueous sodium thiosulfate of concentration 0.128 mol dm^{-3}. Calculate the stoichiometry of the reaction between iodine and the thiosulfate ion.

Calculate the amounts of each of the reagents involved

Solution

Amount of iodine = c × V
= 0.131 mol dm^{-3} × 0.01 dm^3
= 1.31 × 10^{-3} mol

(n.b. 10 cm^3 = 0.01 dm^3)

Amount of thiosulfate = c × V
= 0.128 mol dm^{-3} × 0.0204 dm^3
= 2.61 × 10^{-3} mol

Then calculate the ratio of these:

Ratio of moles I_2 : moles $S_2O_3^{2-}$ = 1.31 × 10^{-3} : 2.61 × 10^{-3}
= 1 : 2

Exercise 1.5.1

1. Sulfuric acid from an automobile battery reacts with sodium hydroxide according to the equation.

$$2\,NaOH\,(aq) + H_2SO_4\,(aq) \longrightarrow Na_2SO_4\,(aq) + 2\,H_2O\,(l)$$

It is found that 10 cm^3 of the acid is just neutralised by 32 cm^3 of 2.0 mol dm^{-3} aqueous sodium hydroxide. Determine the concentration of the battery acid.

A 0.63 mol dm^{-3}
B 1.6 mol dm^{-3}
C 3.2 mol dm^{-3}
D 6.4 mol dm^{-3}

2. The amount of copper(II) ions present in a solution may be estimated by adding excess iodide ions and then titrating the iodine formed with aqueous thiosulfate ions. The equations involved are:

$$2\,Cu^{2+}(aq) + 4\,I^-\,(aq) \longrightarrow 2\,CuI\,(s) + I_2\,(aq)$$

$$2\,S_2O_3^{2-}\,(aq) + I_2\,(aq) \longrightarrow S_4O_6^{2-}\,(aq) + 2\,I^-\,(aq)$$

Calculate how many moles of thiosulfate will be required for each mole of copper (II) ions.

A 1
B 2
C 4
D 8

3. Which one of the following is not an important property for a primary standard?

A Purity
B Stability as a solid
C Stability in solution
D Bright colour

4. 20 cm^3 of hydrochloric acid was just neutralised by 25.0 cm^3 of a solution of potassium hydroxide of concentration 0.500 mol dm^{-3}.

(a) Calculate how many moles of potassium hydroxide were used in the reaction.
(b) Calculate how many moles of hydrochloric acid this reacted with.
(c) What was the concentration of the hydrochloric acid?

5. 25.0 cm^3 of saturated calcium hydroxide solution (limewater) required 7.50 cm^3 of 0.0500 mol dm^{-3} nitric acid to just neutralise it.

(a) Calculate how many moles of nitric acid were used.
(b) Calculate how many moles of calcium hydroxide did this react with.
(c) Determine the concentration of the calcium hydroxide in grams per litre.

6. A 0.245 g sample of a mixture of calcium chloride and sodium nitrate is dissolved in water to give 50.0 cm^3 of solution. This solution is titrated with 0.106 mol dm^{-3} aqueous silver nitrate which reacts with the chloride ions present to form insoluble silver chloride. The end point is reached after 37.7 cm^3 of the silver nitrate solution has been added.

(a) Write a balanced chemical equation for the reaction, including state symbols.
(b) Calculate the amount of silver nitrate used in the titration.
(c) Calculate the amount of calcium chloride present in the solution.
(d) Calculate the percentage by mass of calcium chloride in the original mixture.

7. The number of moles of water of crystallisation (x) present in hydrated ammonium iron(II) sulfate, $Fe(NH_4)_2(SO_4)_2{\cdot}xH_2O$, can be determined by oxidising the iron(II) ions with aqueous potassium permanganate in acidified solution. The ionic equation for the reaction is

$$MnO_4^- (aq) + 5\ Fe^{2+} (aq) + 8\ H^+ (aq) \longrightarrow Mn^{2+} (aq) + 5\ Fe^{3+} (aq) + 4\ H_2O\ (l)$$

It is found that when 0.980 g of the compound is dissolved in 25.0 cm^3 of water and titrated with 0.0300 mol dm^{-3} aqueous permanganate, 16.7 cm^3 are required for complete reaction.

(a) Calculate the amount of potassium permanganate used in the titration.
(b) Calculate the amount of iron(II) ions present in the solution.
(c) Given that the molar mass of $Fe(NH_4)_2(SO_4)_2$ is 284 g mol^{-1}, calculate the mass of anhydrous solid that must have been present.
(d) Calculate the mass of water present in the crystals and hence the value of *x*.

8. Concentrated hydrochloric acid has a density of 1.15 g cm^{-3} and contains 30.0% by mass hydrogen chloride.

(a) Determine the concentration of the hydrochloric acid.
(b) What volume of this must be diluted to 5.00 dm^3 to give a solution of concentration 0.200 mol dm^{-3}.

9. 0.130 g of a sample of impure iron was dissolved in excess dilute sulfuric acid to form iron(II) sulfate. This was then titrated with a 0.0137 mol dm^{-3} solution of dichromate ions ($Cr_2O_7^{2-}$) and was found to be just sufficient to reduce 27.3 cm^3 of the solution to chromium(III) ions (Cr^{3+}).

(a) Write a balanced ionic equation for the titration reaction.
(b) Calculate the amount of dichromate ion used in the reaction.
(c) Calculate the amount of iron(II) ions present in the solution.
(d) Calculate the percentage purity (by mass) of the iron.

10. 1.552 g of a pure carboxylic acid (Y—COOH) is titrated against 0.4822 mol dm^{-3} aqueous sodium hydroxide and 26.35 cm^3 are found to be required for complete neutralisation. Calculate the molar mass of the acid and hence deduce its probable formula.

Back titration

Sometimes reactions occur too slowly for a titration to be employed. This, for example, is usually the case when insoluble solid reagents are used. Back titration is usually employed for quantitative work with substances of this kind. In this technique the sample (say an insoluble base) is reacted with a known excess of one reagent (in this case a known volume of a standard solution of acid). When the reaction with the sample is complete a titration is then carried out (in the example with an alkali of known concentration), to determine how much of the reagent in excess remains unreacted. By knowing the initial amount of the reagent and the amount remaining as excess, then the amount that has reacted with the sample can be calculated. This is clarified by Figure 108.

Amount of standard acid - known from volume and concentration	
Amount of acid reacting with the sample - unknown	Amount of acid reacting with the standard alkali used in the titration - known from volume and concentration

Figure 108 Illustration of the principle of back titration

The total (known) amount of acid must be the sum of the amount that reacted with the alkali (known) and the amount that reacted with the sample (unknown) so the latter can be calculated.

Back titration can be used to determine the percentage by mass of one substance in an impure mixture. For example a sample of calcium hydroxide, a base, containing non-basic impurities can be reacted with excess hydrochloric acid. The excess amount of hydrochloric acid can then be determined by titrating with aqueous sodium hydroxide of known concentration. If the total amount of acid is known and the excess determined, the difference gives the amount that reacted with calcium hydroxide. Thus the mass of calcium hydroxide and its percentage in the mixture can be calculated by 'back titration'. This is illustrated in the example below.

Example

0.5214 g of impure calcium hydroxide was dissolved in 50.00 cm^3 of 0.2500 mol dm^{-3} hydrochloric acid. When the reaction was complete, 33.64 cm^3 of 0.1108 mol dm^{-3} aqueous sodium hydroxide was required to just neutralise the excess acid. Assuming that the impurities do not react, what percentage of the sample was calcium hydroxide?

Solution

Amount of alkali in titration

$= c \times V$

$= 0.1108 \text{ mol dm}^{-3} \times 0.03364 \text{ dm}^3$

$= 0.003727 \text{ mol}$

$$HCl\ (aq) + NaOH\ (aq) \longrightarrow NaCl\ (aq) + H_2O\ (l)$$

1: 1 reaction therefore 0.003727 moles of HCl react with the NaOH added.

Amount of acid used initially

$= c \times V$

$= 0.2500 \text{ mol dm}^{-3} \times 0.05000 \text{ dm}^3$

$= 0.01250 \text{ mol}$

Amount of acid reacting with calcium hydroxide

$= 0.01250 \text{ mol} - 0.003727 \text{ mol}$

$= 0.008773 \text{ mol}$

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

2:1 ratio therefore 0.004386 $\left(= \frac{1}{2} \times 0.008773 \right)$ moles of calcium hydroxide react with the hydrochloric acid.

Mass of $Ca(OH)_2 = n \times M$

$= 0.004386 \text{ mol} \times 74.10 \text{ g mol}^{-1}$

$= 0.3250 \text{ g}$

$$\text{Percent by mass of } Ca(OH)_2 = 100 \times \frac{0.3250}{0.5214}$$

$$= 62.34\%$$

The same technique can be used to determine the percentage of calcium carbonate (a base) in egg shell or a sample of impure limestone.

Exercise 1.5.2

1. Aspirin is a sparingly soluble monobasic acid. 1.0 g of impure aspirin ($C_9H_8O_4$) was added to 10 cm^3 of 1.0 mol dm^{-3} aqueous sodium hydroxide. The excess base was then titrated with 0.20 mol dm^{-3} hydrochloric acid and 25 cm^3 were needed to neutralise the excess alkali.

   a) Calculate how many moles of hydrochloric acid were used.
   b) Calculate how many moles of sodium hydroxide were taken initially.
   c) Calculate how many moles of aspirin were present in the tablet.
   d) What mass of aspirin does this correspond to?
   e) What was the percentage purity of the aspirin?

2. A 20.0 g block of impure marble was dissolved in 250 cm^3 of 2.00 mol dm^{-3} nitric acid. When the block completely dissolved, 25.0 cm^3 of the solution was titrated with 1.00 mol dm^{-3} aqueous sodium hydroxide and 17.0 cm^3 were required for neutralisation. What percent by mass of the marble was calcium carbonate. What assumptions did you make in calculating this?

3. 0.600g of a metal M was dissolved in 200 cm^3 of 0.500 mol dm^{-3} hydrochloric acid. 25.0 cm^3 of 2.00 mol dm^{-3} aqueous sodium hydroxide were required to neutralise the excess acid. Calculate the molar mass of the metal assuming that the formula of its chloride is:

   a) MCl
   b) MCl_2
   c) MCl_3

   Which do you consider to be the more likely value? Why?

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APPENDIX

1A Scientific Notation

Scientific notation is a method of expressing large or small numbers as factors of the powers of 10. One can use exponents of 10 to make the expression of scientific measurements more compact, easier to understand, and simpler to manipulate (0.0000000013 m compared with 1.3×10^{-9} m and 7500000 g compared to 7.5×10^{6} g — note: these may also be found as $1.3 \bullet 10^{-9}$ m and $7.5 \bullet 10^{6}$ g where the point represents multiplication).

To express numbers in scientific notation, one should use the form: $a \times 10^{b}$ where a is a real number between 1 and 10 (but not equal to 10), and b is a positive or negative integer.

This form works for 7500000, a large number as follows:

1. Set a equal to 7.5, which is a real number between 1 and 10.

2. To find b, count the places to the right of the decimal point in a to the original decimal point. There are 6 places to the right (+6) from the decimal point in a to the original decimal point, so $b = 6$. The number is expressed as 7.5×10^{6}.

For a large number, the exponent of 10 (b) will be a POSITIVE integer equal to the number of decimal places to the RIGHT from the decimal point in a to the original decimal point.

For 0.0000000013, a small number:

1. *Set a* = 1.3, which is a real number between 1 and 10.

2. To find b, count the places to the left of the decimal point in a, finishing up at the original decimal point. There are 9 places from the left (–9) of the decimal point, so b = –9. This is expressed as 1.3×10^{-9}.

For a small number, the exponent of 10 will be a NEGATIVE integer equal to the number of decimal places to the LEFT from the decimal point in a to the original decimal point.

Manipulating numbers in this form is also easier, especially multiplying and dividing. In multiplying the first part of the numbers (the 'a' s) are multiplied, the exponents are added and then the decimal place adjusted.

Example 1

Calculate the number of oxygen molecules in 5.00×10^{-8} moles of oxygen.

Solution

$$\begin{aligned} N &= n \times 6.02 \times 10^{23} \\ &= 5 \times 10^{-8} \times 6.02 \times 10^{23} \\ &= (5 \times 6.02) \times 10^{(-8+23)} \\ &= 30.1 \times 10^{15} \\ &= 3.01 \times 10^{16} \end{aligned}$$

Similarly, in dividing numbers, the first part of the numbers (the 'a' s) are divided, the exponents subtracted and then the decimal place adjusted.

Example 2

Calculate the mass of a protein molecule that has a molar mass of 1.76×10^{4} g mol^{-1}.

Solution

$$\begin{aligned} m &= \frac{M}{6.02 \times 10^{23}} \\ &= \frac{1.76 \times 10^{4}}{6.02 \times 10^{23}} \\ &= \left(\frac{1.76}{6.02}\right) \times 10^{(4-23)} \\ &= 0.292 \times 10^{-19} \\ &= 2.92 \times 10^{-20}\,\text{g} \end{aligned}$$

Exercise 1.5.2

1. Which one of the following numbers is in correct scientific notation?

    A 862×10^5
    B 0.26×10^5
    C 4.73×10^5
    D $2.93 \times 10^{5.2}$

2. The number 57230.357 is best shown in scientific notation as

    A 5.7230357×10^{-4}
    B 57230357×10^{-3}
    C 5.7230357×10^4
    D 5.7230357×10^8

3. 2.872×10^{-4} is best written as a normal number in the form

    A 0.0002872
    B 28720
    C −42.872
    D −28720

4. Write the following in scientific notation:

    a) 437600
    b) 0.00000023
    c) 415000000
    d) 0.0372
    e) 476.8
    f) 3.26

5. Write the following as normal numbers:

    a) 8.2×10^5
    b) 6.29×10^{-3}
    c) 2.7138×10^{11}
    d) 2×10^{-7}
    e) 4.2×10^1
    f) 5.89×10^{-1}

1B Significant figures

The accuracy of a measurement depends on the quality of the instrument one uses for measuring and on the carefulness of the measurement. When a measurement is reported, the number of significant figures, can be used to represent one's own precision and that of the instrument. So significant figures should show the limits of accuracy and where the uncertainty begins. Section 11.1 discusses this subject in much more detail.

Measuring with an ordinary meter stick, you might report the length of an object as 1.4 m, which means you measured it as being longer than 1.35 m, but shorter than 1.45 m. The measurement 1.4 has *two* significant figures. If you had a better ruler, or were more careful, you might have reported the length as 1.42 m, which means that you measured the object as being longer than 1.415 m, but shorter than 1.425 m. The measurement 1.42 has *three* significant figures.

The last digit in a significant figure is uncertain because it reflects the limit of accuracy.

Significant zeros

You may have to decide whether zeros are significant in three different situations.

1. *If the zeros precede the first non-zero digit, they are not significant*. Such zeros merely locate the decimal point; i.e., they define the magnitude of the measurement. For example, 0.00014 m has two significant figures, and 0.01 has one significant figure.

2. *If the zeros are between non-zero digits, they are significant*. For example, 103307 kg has six significant figures while 0.04403 has four significant figures.

3. *If the zeros follow non-zero digits, there is ambiguity if no decimal point is given*. If a volume is given as 300 cm^3, you have no way of telling if the final two zeros are significant. But if the volume is given as 300. cm^3, you know that it has three significant figures; and if it is given as 300.0 cm^3, it has four significant figures.

Note: You can avoid ambiguity by expressing your measurements in scientific notation. Then if you record your final zeros in *a*, they are significant. So, if you report '300 cm^3' as 3×10^2 cm^3, it has only one significant figure; 3.0×10^2 cm^3 has two significant figures; and 3.00×10^2 has three significant figures. A number such as 20700 in which the last two zeros are not significant is probably better written as 2.07×10^4, to avoid ambiguity.

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Using significant figures in calculations

For multiplication and division, a result can only be as accurate as the factor with the least number of significant figures that goes into its calculation.

Note: Integers or whole numbers and constants do not alter your calculation of significant figures. For example, the volume of a sphere is $v = {}^4/_3\pi r^3$. The 4 and 3 are exact whole numbers, while the constant pi can be reported to any desired degree of accuracy (3.14159...). The result for the volume will depend only on the accuracy of the measurement for the radius r.

Rounding off

The rounding off rules are simple: If the digit following the last reportable digit is:

- 4 or less, you drop it
- 5 or more, you increase the last reportable digit by one

For addition and subtraction, the answer should contain no more digits to the right of the decimal point than any individual quantity i.e. use the <u>least number of decimal places</u>.

For multiplication and division, use the <u>least number of significant figures</u>.

Note: You may wonder just when to round off. The answer is, round off when it's most convenient. With calculators and computers, it's as easy to carry six or seven digits as it is to carry three or four. <u>So, for economy and accuracy, do your rounding off at the last step of a calculation</u>.

Exercise 1.16

1. The number of significant figures in 0.0003701 is

   A 3
   B 4
   C 7
   D 8

2. A calculator display shows the result of a calculation to be 57230.357. If it is to be reported to 4 significant figures, it would be best recorded as

   A 5723
   B 57230
   C 5.723×10^{-4}
   D 5.723×10^{4}

3. If a sample of a metal has a mass of 26.385 g and a volume of 5.82 cm^3, its density is best recorded as

   A 4.5 g cm^{-3}
   B 4.53 g cm^{-3}
   C 4.534 g cm^{-3}
   D 4.5335 g cm^{-3}

4. A bottle of mass 58.32 g contains 0.373 kg of water and a crystal of mass 3000.6 mg. To how many significant figures should the total mass be recorded?

   A 2
   B 3
   C 4
   D 5

5. Give the results of the following calculations to the appropriate degree of accuracy.

   (a) 0.037×0.763

   (b) $200.1257 \div 7.2$

   (c) $3.76 \times 10^5 - 276$

   (d) $0.00137 + 3.762 \times 10^{-4}$

   (e) $3 \times 10^8 \times 7.268$

FURTHER WORKED EXAMPLES

There are only four formulas used in these worked examples, though these formulas may be rearranged or combined together depending on what is required and the data available. These four formulas are:

$$\text{Number of moles} = \frac{\text{Number of particles}}{6.02 \times 10^{23}}$$

$$n = \frac{N}{6.02 \times 10^{23}}$$

$$\text{Number of moles} = \frac{\text{Mass of substance}}{\text{Molar mass of substance}}$$

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

$$\text{Number of moles of gas} = \frac{\text{Volume of gas}}{\text{Molar volume at same T \& P}}$$

$$n = \frac{V}{V_m}$$

Pressure × Volume = R × Moles of gas × Absolute temperature

$$P.v = n.R.T$$

$$\text{Concentration of solution} = \frac{\text{Moles of solute}}{\text{Volume in dm}^3}$$

$$n = \frac{n}{V}$$

1. Finding the amount of substance from the number of particles.

Determine the amount of substance in 2.408×10^{21} molecules of ammonia.

SOLUTION

Required - n Known - N (2.408×10^{21} particles)

Therefore use:

$$n = \frac{N}{6.02 \times 10^{23}}$$

Substituting:

$$n = \frac{N}{6.02 \times 10^{23}}$$

$$= \frac{2.408 \times 10^{21}}{6.02 \times 10^{23}}$$

= 0.004 moles of ammonia.

2. Finding number of particles from the amount of substance.

Calculate how many molecules are there in 15.0 moles of water.

SOLUTION

Required - N Known - n (15.0 moles)

Therefore use:

$$n = \frac{N}{6.02 \times 10^{23}}$$

Substituting:

$$15.0 = \frac{N}{6.02 \times 10^{23}}$$

Rearranging:

$$N = 15.0 \times 6.02 \times 10^{23}$$

$= 9.03 \times 10^{24}$ molecules of water.

3. Finding the amount of substance from the mass and the molar mass

Determine the amount of substance in 12.00 g of barium sulfate.

(Ba = 137.34 g mol^{-1}, S = 32.06 g mol^{-1}, O = 16.00 g mol^{-1})

SOLUTION

Required - n Known - m (12 g) & M (from formula).

Therefore use:

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

Molar mass of $BaSO_4$ = 137.34 + 32.06 + (4 × 16.00) = 233.40 g mol^{-1}

Substituting:

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

$$= \frac{12.00}{233.40}$$

= 0.0514 moles of barium sulfate.

4. Finding mass from the amount of substance and molar mass.

Determine the mass of 0.500 moles of borax crystals, $Na_2B_4O_7{\cdot}10H_2O$

(Na = 22.99 g mol^{-1}, O = 16.00 g mol^{-1}, B = 10.81 g mol^{-1}, H = 1.01 g mol^{-1})

SOLUTION

Required - m Known - n (0.500 mole) & M (from formula)

Therefore use: $n = \frac{m}{M}$

Molar mass of $Na_2B_4O_7{\cdot}10H_2O$
$= (2 \times 22.99) + (4 \times 10.81) + (7 \times 16.00) + (10 \times 18.02)$
$= 381.42$ g mol^{-1}

Substituting:

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

$$0.500 = \frac{m}{381.42}$$

Rearranging

$$m = 0.500 \text{ mol} \times 381.42 \text{ g mol}^{-1}$$
$$= 191 \text{ g of borax crystals.}$$

5. Finding the molar mass from the mass and amount of substance

5.42 g of a substance is found to contain 0.0416 moles. Determine its molar mass.

SOLUTION

Required - M Known - n (0.0416 mol) & m (5.42 g)

Therefore use: $n = \frac{m}{M}$

Substituting:

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

$$0.416 \text{ mol} = \frac{5.42 \text{ g}}{M}$$

Rearranging:

$$M = \frac{5.42 \text{ g}}{0.0416 \text{ mol}}$$

$$= 130 \text{ g mol}^{-1}.$$

6. Finding the percentage composition

Gypsum is a naturally occuring form of calcium sulfate ($CaSO_4{\cdot}2H_2O$). What percentage by mass of gypsum is water?

(Ca = 40.08 g mol^{-1}; S = 32.06 g mol^{-1}; O = 16.00 g mol^{-1}; H = 1.01 g mol^{-1})

SOLUTION

Required - % H_2O
Known - molar masses of gypsum and water.

Molar mass of gypsum
$= 40.08 + 32.06 + (4 \times 16.00) + (2 \times 18.02)$
$= 172.18$ g mol^{-1}

Mass of water in this $= 2 \times 18.02$
$= 36.04$

$$\text{Percentage of water} = \frac{36.04}{172.16} \times 100$$

$$= 20.93 \text{ \%}$$

7. Finding the empirical formula from mass data

5.694 g of an oxide of cobalt yielded 4.046 g of the metal on reduction. What was the empirical formula of the oxide?

(Co = 58.93 g mol^{-1}; O = 16.00 g mol^{-1})

SOLUTION

Required - molar ratio of Co to O.
Known - the masses and molar masses of Co and O.

$$\text{Amount of cobalt in the oxide} = \frac{m}{M}$$
$$= \frac{4.046 \text{ g}}{58.93 \text{ g mol}^{-1}}$$
$$= 0.06866 \text{ moles.}$$

$$\text{Amount of oxygen in the oxide} = \frac{m}{M}$$
$$= \frac{5.694 \text{ g} - 4.046 \text{ g}}{16.00 \text{ g mol}^{-1}}$$
$$= 0.1030 \text{ moles}$$

$$\text{Ratio of cobalt to oxygen} = 0.06866 : 0.1030$$
$$= 1 : \frac{0.1030}{0.06866}$$
$$= 1 : 1.500$$
$$= 2 : 3$$

Therefore the empirical formula of the oxide is Co_2O_3.

8. Finding the empirical formula from percentage composition data

Treatment of metallic copper with excess of chlorine results in a yellow solid compound which contains 47.2% copper, and 52.8% chlorine. Determine the simplest formula of the compound.

(Cu = 63.55 g mol^{-1}; Cl = 35.45 g mol^{-1})

SOLUTION

Required - molar ratio of Cu to Cl.
Known - the percentages by mass and molar masses of Cu and Cl.

In 100.0 g of compound there are 47.2 g of copper and 52.8 g of chlorine.

$$\text{Amount of Cu} = \frac{m}{M} = \frac{47.2\text{ g}}{63.55\text{ g mol}^{-1}} = 0.7427\text{ mol}$$

$$\text{Amount of Cl} = \frac{m}{M} = \frac{52.8\text{ g}}{35.45\text{ g mol}^{-1}} = 1.489\text{ mol}$$

Ratio of amounts of Cu : Cl = 0.7427 : 1.489
= 1 : 2.005 = 1 : 2

The empirical formula is therefore $CuCl_2$.

9. Finding the empirical formula of a hydrate from percentage composition data.

When hydrated strontium hydroxide crystals are strongly heated, they decrease in mass by 54.2% to leave the anhydrous solid. Determine the formula of the hydrate.

(Sr = 87.62 g mol^{-1}; O = 16.00 g mol^{-1};
H = 1.01 g mol^{-1})

SOLUTION

Knowing that the strontium ion is Sr^{2+} (in Group 2 of the Periodic Table) and that the hydroxide ion is OH^-, the formula of strontium hydroxide can be calculated as $Sr(OH)_2$. (N.B. positive and negative charges must cancel.)

Required - molar ratio of to $H_2O : Sr(OH)_2$
Known - the molar masses and masses of these in 100 g of the hydrate.

$$\text{Amount of } H_2O = \frac{m}{M} = \frac{54.2\text{ g}}{18.02\text{ g mol}^{-1}} = 3.008\text{ mol}$$

$$\text{Amount of } Sr(OH)_2 = \frac{100\text{ g} - 54.2\text{ g}}{121.64\text{ g mol}^{-1}} = 0.3765\text{ mol}$$

Ratio of amounts of $H_2O : Sr(OH)_2$ = 3.008 : 0.3765
= 7.989 : 1

The formula of the hydrate must be $Sr(OH)_2{\cdot}8H_2O$.

10. The molecular formula from molar mass and combustion data.

Vitamin C, a compound of carbon hydrogen and oxygen only, is found in many fruits and vegetables. The percentages, by mass, of carbon, hydrogen, and oxygen in vitamin C are determined by burning a sample of vitamin C weighing 2.00 mg. The masses of carbon dioxide and water formed are 3.00 mg and 0.816 mg, respectively. By titration its molar mass is found to be about 180 g mol^{-1}. From these data, determine the molecular formula of vitamin C.

(O = 16.00 g mol^{-1}; C = 12.01 g mol^{-1}; H = 1.01 g mol^{-1}).

SOLUTION

Required - molar ratio of C, H and O.
Known - the molar masses and masses of CO_2 and H_2O formed by the combustion of 2.00 mg of the compound and the approximate molar mass.

Firstly calculate that amounts of CO_2 and H_2O:

$$\text{Amount of } CO_2 = \frac{3.00 \times 10^{-3}\text{ g}}{44.01\text{ g mol}^{-1}} = 6.816 \times 10^{-5}\text{ moles.}$$

$$\text{Amount of } H_2O = \frac{m}{M} = \frac{8.16 \times 10^{-4}\text{ g}}{18.02\text{ g mol}^{-1}} = 4.528 \times 10^{-5}\text{ moles.}$$

The amounts of C and H in the 2.00 mg of vitamin C must have been 6.816×10^{-5} and 9.056×10^{-5} (as it is H_2O) respectively.

Calculate the mass of oxygen in the sample by subtraction and hence the amount:

Mass of oxygen
$= 0.002 - (12.01 \times 6.816 \times 10^{-5}) - (1.01 \times 9.056 \times 10^{-5})$
$= 1.090 \times 10^{-3}$ g.

Amount of oxygen $= \frac{m}{M}$

$= \frac{1.090 \times 10^{-3}}{16.00}$

$= 6.812 \times 10^{-5}$ moles.

Ratio of amounts of C : H : O
= 6.816 : 9.056 : 6.812
= 1 : 1.33 : 1
= 3 : 4 : 3

The empirical formula of vitamin C must be $C_3H_4O_3$,

The molar mass of this would be approximately $(3 \times 12) + (4 \times 1) + (3 \times 16) = 88$

The observed molar mass is ≈180,
so it is composed of $\frac{188}{88} \approx 2$ of these units.

The molecular formula of vitamin C is therefore $2 \times (C_3H_4O_3) = C_6H_8O_6$.

11. Reacting mass calculations

When aqueous silver nitrate is added to an aqueous solution containing chromate ions, a brick-red precipitate of silver chromate (Ag_2CrO_4) forms. What mass of silver chromate could be obtained from a solution containing 5.00 g of silver nitrate?

(Ag = 107.87 g mol^{-1}; Cr = 52.00 g mol^{-1};
O = 16.00 g mol^{-1}; N = 14.01 g mol^{-1})

SOLUTION

Required: mass of silver chromate
Known: mass and molar mass of, hence the amount of $AgNO_3$.
equation, hence the amount of Ag_2CrO_4.
molar mass of Ag_2CrO_4, hence calculate the mass from the amount.

Amount of $AgNO_3 = \frac{m}{M}$

$= \frac{5.00}{169.88}$

= 0.02943 moles.

Equation:
$Na_2CrO_4 + 2\ AgNO_3 \longrightarrow Ag_2CrO_4 + 2\ NaNO_3$

2 moles	1 mole
0.02943 moles	0.01472 moles

Mass of $Ag_2CrO_4 = n \times M$
$= 0.01472 \times 331.74$
= 4.89 g.

12. The amount of reactant required.

When potassium nitrate is heated, it decomposes to potassium nitrite and oxygen. What mass of potassium nitrate must be heated to produce 10 g of oxygen?

(Potassium nitrite is KNO_2; K = 39.10 g mol^{-1};
O = 16.00 g mol^{-1}; N = 14.01 g mol^{-1})

SOLUTION

Required: mass of potassium nitrate.
Known: mass and molar mass of O_2, hence the amount of O_2.
equation, hence the amount of KNO_3.
molar mass of KNO_3, hence calculate the mass from the amount.

Amount of $O_2 = \frac{m}{M}$

$= \frac{10}{32.00}$

= 0.3215 moles.

Equation:
$2\ KNO_3 \longrightarrow 2\ KNO_2 + O_2$

2 moles	1 mole
0.3125 × 2 moles	0.3125 moles

Mass of $KNO_3 = n \times M$
$= 0.625 \times 101.11$
= 63.19 g.

13. Finding the molar mass of a gas from the mass of a sample under standard conditions.

10.4 g of a gas occupies a volume of 3.72 dm^3 at standard temperature and pressure. Determine the molar mass of the gas.

SOLUTION

Required: M
Known: m (10.4 g) and V (3.72 dm^3)

Therefore use $n = \frac{V}{V_m}$ to find n

and then use $n = \frac{m}{M}$ to find M.

$$\text{Moles of gas} = \frac{V}{22.4} = \frac{3.72}{22.4} = 0.166 \text{ moles}$$

$$\text{Molar mass} = \frac{m}{n} = \frac{10.4}{0.166} = 62.7 \text{ g mol}^{-1}.$$

14. Finding the volume of gas produced in a reaction.

When hydrogen peroxide is added to a manganese(IV) oxide catalyst it undergoes catalytic decomposition to water and oxygen. What volume of oxygen, measured at standard temperature and pressure, can be produced from a solution containing 17 g of hydrogen peroxide?

SOLUTION

Required - V
Known - m (17 g) and M (34 g mol^{-1})

Therefore use $n = \frac{m}{M}$ to find $n(H_2O_2)$,

use balanced equation to find $n(O_2)$,

and then use $n = \frac{V}{V_m}$ to find V.

$$\text{Moles of } H_2O_2 = \frac{m}{M} = \frac{17}{34} = 0.5 \text{ moles.}$$

Balanced equation:

$$2\,H_2O_2 \longrightarrow 2\,H_2O + O_2$$

2 moles　　1 mole
0.5 moles　　0.25 moles

$$\text{Volume of oxygen} = n \times 22.4 = 0.25 \times 22.4 = 5.6 \text{ dm}^3.$$

15. Volume of .a known amount of gas under given conditions.

A lighter contains 0.217 mol of butane. What volume would this occupy if it were released on top of a mountain where the temperature was 5°C and the pressure was 92.0 kPa?

SOLUTION

Required: V
Known: n (0.217 mol),
T (5 °C = 278K) and
P (92.0 kPa)

$$V = \frac{n.R.T}{P}$$

$$V = \frac{0.217 \times 8.314 \times 278}{92.0} = 5.45 \text{ dm}^3$$

16. Calculating the pressure of a known gas under given conditions.

A test tube of volume 25 cm^3 sealed with a bung contains 0.1 cm^3 of water. It is heated to a temperature of 200°C, what pressure, in atmospheres, will the vapourised water create inside the test tube?

(O = 16.00 g mol^{-1}; H = 1.01 g mol^{-1}).

SOLUTION

Required: P
Known: V (25 cm^3 = 0.025 dm^3),
m (0.1 cm^3 will have a mass of 0.1 g) and
T (200 °C = 473K)

therefore use

$n = \frac{m}{M}$ followed by $P = \frac{n.R.T}{V}$

$$\text{amount of water} = \frac{0.1}{(2\times1.01)+16.00} = 0.005549 \text{ mol}$$

$$P = \frac{0.005549 \times 8.314 \times 473}{0.025} = 873 \text{ kPa}$$

$$= {}^{873}/_{101.3} = 8.62 \text{ atm}$$

17. Finding the number of molecules in a given volume of gas under specified conditions.

Calculate the number of molecules in a classroom that measures 5.00 m × 6.00 m with a height of 2.50 m on a day when the temperature in the room is 27.0 °C and the pressure is 100.0 kPa.

SOLUTION

Required: N
Known: V (5 × 6 × 2.5 m^3),
T (27 °C = 300 K),
P (100.0 kPa)

Therefore use $n = \frac{P.V}{R.T}$

followed by $N = n \times 6.02 \times 10^{23}$

$$n = \frac{100 \times [(6 \times 5 \times 2.5) \times 10^3]}{8.314 \times 300}$$

= 3007 mol

N = $3007 \times 6.02 \times 10^{23}$

= 1.81×10^{27} molecules

18. Finding the mass of a given volume of gas at specified conditions and how the conditions mutually affect each other.

A gas cylinder containing 50.0 dm^3 of hydrogen has a pressure of 70.0 atm at 20 °C.

a) What mass of hydrogen does it contain?

b) What volume of hydrogen would this produce at atmospheric pressure?

c) If the bursting pressure of the cylinder were 100 atm to what temperature would the cylinder have to be heated for it to explode?

SOLUTION

a) Required: m
Known: V (50.0 dm^3),
T (20 °C = 293 K),
P (70.0 atm = 7091 kPa)

Therefore use $n = \frac{P.V}{R.T}$

followed by m = n × M

$$n = \frac{7091 \times 50}{8.314 \times 293} = 146 \text{ mol}$$

m = 146 × 2
= 291 g of hydrogen

b) Required: V at 1.00 atm
Known: V (50.0 dm^3) at 70.0 atm

Therefore use $P_1 \times V_1 = P_2 \times V_2$

Substituting:
$70 \times 50 = 1 \times V_2$

Rearanging: $V_2 = 3500 \text{ dm}^3$

c) Required: T at which P = 100 atm
Known: P at (20 °C = 293 K)

Therefore use $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

$$\frac{100}{T_1} = \frac{70}{293} \quad \text{therefore} \quad T_1 = 293 \times \frac{100}{70}$$

= 419 K or 146 °C

19. Finding the concentration from the amount of substance and the volume.

Determine the concentration of the solution produced when 0.02 moles of magnesium sulfate is dissolved to give 40 cm^3 of solution.

SOLUTION

Required: c
Known: n (0.02 mole) and
V (0.04 dm^3).

Therefore use: $c = \frac{n}{V}$

Substituting $c = \frac{0.02}{0.040}$

= 0.5 mol dm^{-3}.

20. Volume from concentration and amount of substance

What volume of 0.200 mol dm^{-3} nitric acid contains 5.00×10^{-2} moles of the acid?

SOLUTION

Required: V
Known: n (5×10^{-2} moles) and
c (0.2 mol dm^{-3}).

Therefore use: $V = \frac{n}{c}$

Substituting $V = \frac{n}{c}$

$= \frac{5.00 \times 10^{-2}}{0.200}$ dm^3

$= 250$ cm^3

21. Concentration from mass and volume

What concentration is the solution formed when 2.00 g of solid potassium chloride is dissolved in 250 cm^3 of solution?

(K = 39.10 g mol^{-1}, Cl = 35.45 g mol^{-1}).

SOLUTION

Required: c
Known: m (2.00 g),
M (39.1 + 35.45g mol^{-1}) and
V (0.250 dm^3).

Therefore: first use $n = \frac{m}{M}$ to find n and then $c = \frac{n}{V}$.

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

$= \frac{2.00}{74.55}$

$= 0.02683$ moles.

$c = \frac{n}{V}$

$= \frac{0.02683}{0.250}$

$= 0.107$ mol dm^{-3}.

22. Mass from concentration and volume.

What mass of solid will remain when 2.0 dm^3 of a 0.40 mol dm^{-3} solution of sucrose ($C_{12}H_{22}O_{11}$) is evaporated to dryness?

(O = 16.00 g mol^{-1}; C = 12.01 g mol^{-1};
H = 1.01 g mol^{-1}).

SOLUTION

Required: m
Known: c (0.40 mol dm^3),
M (342.34 g mol^{-1}) and
V (2 dm^3).

Therefore: first use $n = c \times V$ to find n
and then $m = n \times M$

Substituting: $n = c \times V$
$=0.40$ mol dm^{-3} $\times$ 2.0 dm^3
$= 0.80$ moles.

$m = n \times M$
$= 0.80$ mol $\times$ 342.34 g mol^{-1}
$= 270$ g.

23. Calculating concentration from titration results.

It is found that 33.7 cm^3 of hydrochloric acid just neutralises 20 cm^3 of aqueous sodium carbonate with a concentration of 1.37 mol dm^{-3}. Determine the concentration of the acid.

SOLUTION

Required: c
Known: c_{alkali} (1.37 mol dm^{-3}),
V_{alkali} (0.02 dm^3),
V_{acid} (0.0337 dm^3)

Therefore:
first use $n = c_{alkali} \times V_{alkali}$ to find the amount of alkali used;
then use the balanced equation to calculate the amount of acid required.
finally use $c = \frac{n}{V_{acid}}$ to calculate the concentration of the acid.

Substituting: $n = c_{alkali} \times V_{alkali}$

$= 1.37$ mol dm^{-3} $\times$ 0.02 dm^3
$= 0.0274$ moles

Balanced equation:
$2\,HCl + Na_2CO_3 \longrightarrow 2\,NaCl + H_2O + CO_2$

2 moles	1 mole
0.0548	0.0274

Substituting: $c = \frac{n}{V_{acid}}$

$= \frac{0.0548}{0.0337}$

$= 1.63$ mol dm^{-3}.

24. A complex titration calculation to find the concentration of a reactant.

10.0 cm^3 of household bleach (active ingredient ClO^-) is diluted to a total volume of 250 cm^3. 20.0 cm^3 is then added to 1 g of potassium iodide (an excess) and the iodine produced is titrated with 0.0206 sodium thiosulfate. Using starch solution as an indicator the end point is found after 17.3 cm^3 has been added. The equations for the reactions taking place are:

$$2\,ClO^- (aq) + 2\,I^- (aq) + 2\,H^+ (aq) \longrightarrow 2\,Cl^- (aq) + I_2 (aq) + H_2O (l)$$

$$2\,S_2O_3^{2-} (aq) + I_2 (aq) \longrightarrow S_4O_6^{2-} (aq) + 2\,I^- (aq)$$

Calculate the concentration of the active ingredient in the bleach as the percentage of sodium chlorate(I) (i.e. mass of NaClO in 100 cm^3).

($Cl = 35.45\ g\ mol^{-1}$, $Na = 22.99\ g\ mol^{-1}$, $O = 16.00\ g\ mol^{-1}$)

SOLUTION

Required: *First of all, initial c_{NaClO}, then convert to mass of NaClO*

Known: $c_{S_2O_3}$ ($0.0206\ mol\ dm^{-3}$),
$V_{S_2O_3}$ ($17.3\ cm^3$) and
V_{NaClO} ($20.0 \times {}^{10}/_{250}\ cm^3$)

Therefore: use $n = c \times V$ successsively followed by $m = n \times M$

Moles $ClO^- = c_{NaClO} \times V_{NaClO}$

$= 2 \times$ moles I_2

$=$ moles $S_2O_3^{2-}$

$= c_{S_2O_3} \times V_{S_2O_3}$

$c_{NaClO} \times 0.020 \times {}^{10}/_{250}$

$= 0.0206 \times 0.0173$

$$c_{NaClO} = \frac{0.0206 \times 0.0173 \times 250}{0.020 \times 10}$$

$= 0.445\ mol\ dm^{-3}$

Mass of NaClO in 100 cm^3 $= c_{NaClO} \times {}^{100}/_{1000} \times M_{NaClO}$

Mass of NaClO in 100 cm^3
$= 0.445 \times 0.1 \times (22.99 + 35.45 + 16.00)$
$= 3.32$ g

Therefore the percent of active ingredient in the bleach is 3.32%.

25. Diluting an acid.

250 cm^3 of hydrochloric acid with a concentration of exactly $0.1\ mol\ dm^{-3}$ is to be prepared using hydrochloric acid with a concentration of $1.63\ mol\ dm^{-3}$. What volume of this must be diluted?

SOLUTION

Required: $V_{starting}$

Known: $c_{starting}$ ($1.63\ mol\ dm^{-3}$),
c_{final} ($0.1\ mol\ dm^{-3}$) and
V_{final} ($0.25\ dm^3$)

Therefore: first use $n = c_{final} \times V_{final}$ to find the amount required

then $V_{starting} = \dfrac{n}{c_{starting}}$

to calculate the volume of the acid required.

Substituting: $n = c_{final} \times V_{final}$
$= 0.1\ mol\ dm^{-3} \times 0.25 dm^3 = 0.025$ moles.

$$V_{starting} = \frac{n}{c_{starting}} = \frac{0.025}{1.63}$$

$= 0.0154\ dm^3$
$= 15.4\ cm^3$.

26. Finding the percentage of a component in a mixture by titration.

'Iron tablets', to prevent anaemia, often contain hydrated iron(II) sulfate ($FeSO_4{\bullet}7H_2O$). One such tablet weighing 1.863 g was crushed, dissolved in water and the solution made up to a total volume of 250 cm^3. When 10 cm^3 of this solution when added to 20 cm^3 of dilute sulfuric acid and titrated with aqueous $0.002\ mol\ dm^{-3}$ potassium pemanganate, was found on average to require 24.5 cm^3 to produce a permanent pink colouration. Given that the equation for the reaction between iron(II) ions and permanganate ions is

$$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

calculate the percentage of the tablet that was iron(II) sulfate.

($Fe = 55.85\ g\ mol^{-1}$; $S = 32.06\ g\ mol^{-1}$; $O = 16.00\ g\ mol^{-1}$)

SOLUTION

Required: the mass of iron(II) sulfate in the tablet, hence the percentage by mass.
Known: the volume of permanganate solution reacting with a fraction of the tablet.

Therefore: Find the amount of permanganate used.
Hence find the amount of iron reacting.
Hence find the amount of iron in total tablet.
Hence find the mass of the iron(II) sulfate and the percentage.

Amount of permanganate $= c \times V$
$= 0.002 \times 0.0245$
$= 4.90 \times 10^{-5}$ moles.

$$MnO_4^- + 5\,Fe^{2+} + 8\,H^+ \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$$

1 mole	5 moles
4.90×10^{-5}	$(5 \times 4.90 \times 10^{-5})$
	$= 2.45 \times 10^{-4}$

There are 2.45×10^{-4} moles of iron(II) in 10 cm^3 of solution, so in 250 cm^3 there are

$$2.45 \times 10^{-4} \times \frac{250}{10} = 6.125 \times 10^{-3} \text{ moles.}$$

Mass of iron(II) sulfate $= n \times M$
$= 6.125 \times 10^{-3} \times 278.05$
$= 1.703$ g.

$$\text{Percentage by mass of iron(II) sulfate} = \frac{1.703}{1.863} \times 100$$
$$= 91.4\%$$

27. Finding the concentration of the solution produced by a reaction.

1.86 g of lead carbonate is added to 50.0 cm^3 (an excess) of nitric acid. Determine the concentration of lead nitrate in the resulting solution.

(Pb = 207.19 g mol^{-1}; O = 16.00 g mol^{-1}; C = 12.01 g mol^{-1})

SOLUTION

Required: c
Known: m (1.86 g), M (283.2); V (0.050 dm^3)

Therefore: first use $n = \frac{m}{M}$ to find the amount of lead carbonate, then use the balanced equation to find the amount of lead nitrate, and finally use $c = \frac{n}{V}$ to find the concentration.

Substituting: $n = \frac{m}{M}$
$= \frac{1.86}{267.2}$
$= 0.006961$ moles.

$$PbCO_3 + 2\,HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + CO_2$$

1 mole	1 mole
0.006961	0.006961

$c = \frac{n}{V}$
$= \frac{0.006961}{0.050}$
$= 0.139$ mol dm^{-3}.

28. Calculating the limiting reagent.

1.34 g of magnesium are added to 120 cm^3 of a 0.200 mol dm^{-3} solution of silver nitrate. What mass of silver will be formed?

(Ag = 107.87 g mol^{-1}, Mg = 24.31 g mol^{-1})

SOLUTION

Required: m_{Ag}
Known: c_{Ag} (0.20 mol dm^{-3});
V_{Ag} (0.12 dm^3);
m_{Mg} (1.34 g)

Therefore: use $n = \frac{m}{M}$ to find the amount of Mg,
then use $n = c \times V$ to find the amount of Ag^+,
use a balanced equation to find the limiting reagent and the amount of Ag, and
finally calculate the mass using $m = n \times M$.

$n = \frac{m}{M}$
$= \frac{1.34}{24.31}$
$= 0.05512$ moles of magnesium.

$n = c \times V$
$= 0.200 \times 0.120$
$= 0.024$ moles of silver nitrate.

$$Mg + 2\,Ag^+ \longrightarrow 2\,Ag + Mg^{2+}$$

	Mg	Ag^+
In theory -	1	2
Actually -	0.05512	0.024

Magnesium is in excess as only 0.012 moles are required. The silver is the limiting reagent and therefore it controls the yield of the metal:

$$Mg + 2\,Ag^{+} \longrightarrow 2\,Ag + Mg^{2+}$$

	2	2
	0.024	0.024

$m = n \times M$
$= 0.024 \times 107.87$
$= 2.59$ g.

29. Calculating the number of molecules from the concentration

The concentration of gold in seawater is approximately 10^{-10} mol dm^{-3}. Calculate how many gold atoms will there be in the average drop (0.04 cm^3) of seawater.

SOLUTION

Required: N
Known - c (10^{-10} mol dm^{-3}) and V (4×10^{-5} dm^3)

Therefore: use $n = c \times V$ to find the amount of gold, then use $N = n \times 6.02 \times 10^{23}$ to find the number of gold atoms.

Substituting: $n = c \times V$
$= 10^{-10} \times 4 \times 10^{-5}$
$= 4 \times 10^{-15}$

$N = n \times 6.02 \times 10^{23}$
$= 4 \times 10^{-15} \times 6.02 \times 10^{23}$
$= 2.41 \times 10^{9}$

i.e. each drop has over 2 billion gold atoms in it!

30. Calculating molar mass by back titration.

2.04 g of an insoluble, dibasic organic acid were dissolved in 20.0 cm^3 of 2.00 mol dm^{-3} aqueous sodium hydroxide. The excess alkali required 17.6 cm^3 of 0.50 mol dm^{-3} hydrochloric acid to neutralise it. Determine the molar mass of the acid.

SOLUTION

Required: moles of acid in known mass and hence molar mass

Known: volumes and concentrations of excess alkali and neutralising acid

Therefore: find amount of excess alkali and neutralising acid,
use these to calculate the amount of the organic acid,

find the molar mass of the organic acid from the mass and amount

Amount of excess alkali $= c \times V$
$= 2.00 \times 0.020$
$= 0.040$ moles.

Amount of neutralising acid $= c \times V$
$= 0.50 \times 0.0176$
$= 0.0088$ moles.

Amount of alkali reacting with organic acid
$= 0.040 - 0.0088$
$= 0.0312$ moles

$$H_2A + 2\,NaOH \longrightarrow Na_2A + 2\,H_2O$$

1 moles	2 mole
0.0156	0.0312

Hence 0.0156 moles of the organic acid has a mass of 2.04 g

Molar mass of the organic acid $= \dfrac{m}{n}$

$= \dfrac{2.04}{0.0156}$

$= 131$