



TOPIC 1 STOICHIOMETRIC RELATIONSHIPS

(IBDP syllabus Topic 1)

- 1.1 Introduction to the particulate nature of matter and chemical change
 - *Essential Idea: Physical and Chemical properties depends on the ways in which different atoms combine*
- 1.2 The mole concept
 - *Essential Idea: The mole make it possible to correlate the number of particles with the mass that can be measured.*
- 1.3 Reacting masses and volumes
 - *Essential Idea: Mole ratios in chemical equations can be used to calculate reacting ratios by mass and gas volume.*

(IBDP syllabus Topic 9)

- 9.1 Introduction to Oxidation and Reduction
 - *Essential Idea: Redox reactions play a key role in many chemical and biochemical processes.*

1.1 Introduction to the particulate nature of matter and chemical change

Essential idea: Physical and chemical properties depend on the ways in which different atoms combine.

✂ Nature of Science:

- Making quantitative measurements with replicates to ensure reliability—definite and multiple proportions.

Understandings:

- Atoms of different elements combine in fixed ratios to form compounds, which have different properties from their component elements.
- Mixtures contain more than one element and/or compound that are not chemically bonded together and so retain their individual properties.
- Mixtures are either homogeneous or heterogeneous.

Applications and skills:

- Deduction of chemical equations when reactants and products are specified.
- Application of the state symbols (s), (l), (g) and (aq) in equations.
- Explanation of observable changes in physical properties and temperature during changes of state.

Guidance:

- Balancing of equations should include a variety of types of reactions.
- Names of the changes of state—melting, freezing, vaporization (evaporation and boiling), condensation, sublimation and deposition—should be covered.
- The term “latent heat” is not required.
- Names and symbols of elements are in the data booklet in section 5.

1.2 The mole concept

Essential idea: The mole makes it possible to correlate the number of particles with the mass that can be measured.

✂ Nature of Science:

- Concepts—the concept of the mole developed from the related concept of “equivalent mass” in the early 19th century.

Understandings:

- The mole is a fixed number of particles and refers to the amount, n , of substance.
- Masses of atoms are compared on a scale relative to ^{12}C and are expressed as relative atomic mass (A_r) and relative formula/molecular mass (M_r).
- Molar mass (M) has the units g mol^{-1} .
- The empirical formula and molecular formula of a compound give the simplest ratio and the actual number of atoms present in a molecule respectively.

Applications and skills:

- Calculation of the molar masses of atoms, ions, molecules and formula units.
- Solution of problems involving the relationships between the number of particles, the amount of substance in moles and the mass in grams.
- Interconversion of the percentage composition by mass and the empirical formula.
- Determination of the molecular formula of a compound from its empirical formula and molar mass.
- Obtaining and using experimental data for deriving empirical formulas from reactions involving mass changes.

Guidance:

- The value of the Avogadro's constant (L or N_A) is given in the data booklet in section 2 and will be given for paper 1 questions.
- The generally used unit of molar mass (g mol^{-1}) is a derived SI unit.

1.3 Reacting masses and volumes

Essential idea: Mole ratios in chemical equations can be used to calculate reacting ratios by mass and gas volume.

✂ Nature of Science:

- Making careful observations and obtaining evidence for scientific theories—Avogadro's initial hypothesis.

Understandings:

- Reactants can be either limiting or excess.
- The experimental yield can be different from the theoretical yield.
- Avogadro's law enables the mole ratio of reacting gases to be determined from volumes of the gases.
- The molar volume of an ideal gas is a constant at specified temperature and pressure.
- The molar concentration of a solution is determined by the amount of solute and the volume of solution.
- A standard solution is one of known concentration.

Applications and skills:

- Solution of problems relating to reacting quantities, limiting and excess reactants, theoretical, experimental and percentage yields.
- Calculation of reacting volumes of gases using Avogadro's law.
- Solution of problems and analysis of graphs involving the relationship between temperature, pressure and volume for a fixed mass of an ideal gas.
- Solution of problems relating to the ideal gas equation.
- Explanation of the deviation of real gases from ideal behaviour at low temperature and high pressure.
- Obtaining and using experimental values to calculate the molar mass of a gas from the ideal gas equation.
- Solution of problems involving molar concentration, amount of solute and volume of solution.
- Use of the experimental method of titration to calculate the concentration of a solution by reference to a standard solution.

Guidance:

- Values for the molar volume of an ideal gas are given in the data booklet in section 2.
- The ideal gas equation, $PV = nRT$, and the value of the gas constant (R) are given in the data booklet in sections 1 and 2.
- Units of concentration to include: g dm^{-3} , mol dm^{-3} and parts per million (ppm).
- The use of square brackets to denote molar concentration is required.

9.1 Introduction to redox and redox titration (IB Syllabus Topic 9)

Essential idea: Redox (reduction–oxidation) reactions play a key role in many chemical and biochemical processes.

Understandings:

- Oxidation and reduction can be considered in terms of oxygen gain/hydrogen loss, electron transfer or change in oxidation number.
- An oxidizing agent is reduced and a reducing agent is oxidized.

Applications and skills:

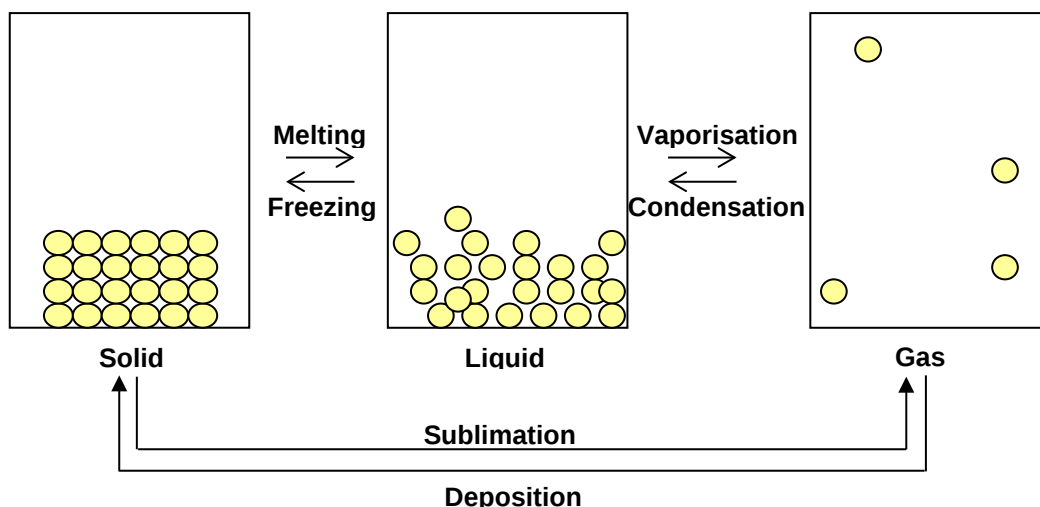
- Deduction of the oxidation states of an atom in an ion or a compound.
- Identification of the species oxidized and reduced and the oxidizing and reducing agents, in redox reactions.
- Deduction of redox reactions using half–equations in acidic or neutral solutions.
- Solution of a range of redox titration problems.

Guidance:

- Oxidation number and oxidation state are often used interchangeably, though IUPAC does formally distinguish between the two terms. Oxidation numbers are represented by Roman numerals according to IUPAC.
- Oxidation states should be represented with the sign given before the number, eg +2 not 2+.
- The oxidation state of hydrogen in metal hydrides (–1) and oxygen in peroxides (–1) should be covered.

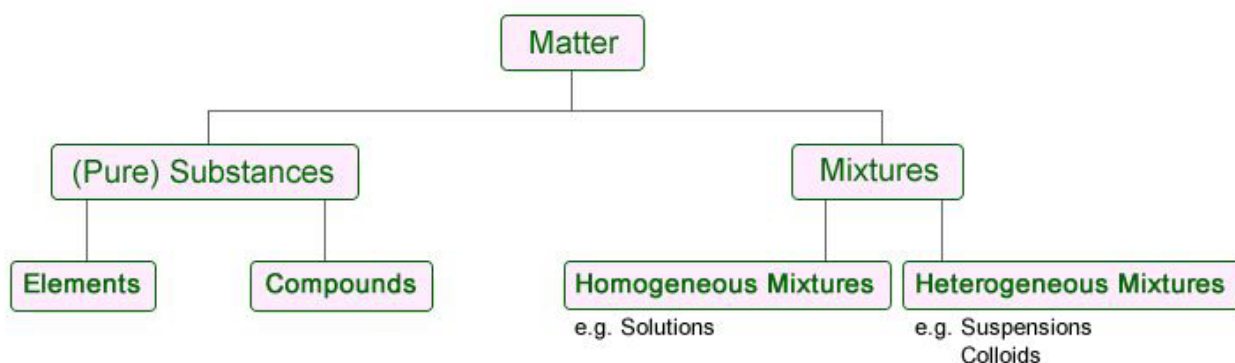
1.1 Introduction to the particulate nature of matter and chemical change

States of matter & Changes of state



Solids	Liquids	Gases
• Particles are close together. • Particles have lower energy than in the other two states. • Particles can only rotate and vibrate about fixed positions. • Strong forces of attraction between particles.	• Particles are slightly further apart than in solids. • Particles have larger amounts of energy than those in the solid state. • Particles can move about quite freely around one other while in close proximity. • Moderate forces of attraction between particles. (Some of the strong forces of attraction in the solid state have been broken.)	• Particles are far apart from one another. • Particles have much more energy than the other two states. • Particles can move rapidly, randomly and haphazardly into any space available. • Very little forces of attraction between the particles.
<u>Consequences</u>		
– definite shape – definite volume – incompressible – high density	– indefinite shape – definite volume – negligible compressibility – moderate to high density	– indefinite shape (occupy whole container) – indefinite volume (affected by temperature and pressure) – highly compressible – low density

Elements, compounds & mixtures



Source: <http://www.ivy-rose.co.uk/Chemistry/>

Elements consist of only one type of atoms.

Compounds consist of atoms of two or more different elements bounded together chemically in a fixed ratio.

Mixture is a combination of two or more substances and can be separated by physical methods.

Homogeneous mixture consists of two or more substances that are evenly distributed throughout the mixture, resulting in the mixture having a uniform composition and properties. E.g. vinegar is a homogeneous mixture of ethanoic acid and water.

Heterogeneous mixture consists of two or more substances that are not evenly distributed throughout the mixture, resulting in the mixture having a non-uniform composition and varying properties. E.g. oil and water.

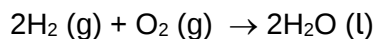
Theory of knowledge:

- Lavoisier's discovery of oxygen, which overturned the phlogiston theory of combustion, is an example of a paradigm shift. How does scientific knowledge progress?
- Chemical equations are the "language" of chemistry. How does the use of universal languages help and hinder the pursuit of knowledge?

Chemical Equations

Writing chemical equations is essential to Chemistry and requires a full understanding of the language of equations.

Consider the following balanced equation:



Qualitatively, a thermochemical equation states the names of the reactants and products (and gives their physical states).

Quantitatively, it expresses

1. the **relative number of molecules** of the reactants and products.

2 molecules of hydrogen react with 1 molecules of oxygen to form 2 molecules of water.

2. the **relative numbers of moles (amounts)** of reactants and products.

2 moles of hydrogen molecules react with 1 mole of oxygen molecules to form 2 moles of water molecules.

3. the **relative masses** of reactants and products.

4.04 g of molecular hydrogen reacts with 32.00 g of molecular oxygen to form 36.04 g of water.

4. the **relative volumes** of reactants and products.

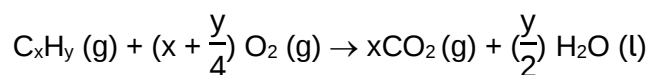
2 volumes of hydrogen react with 1 volume of oxygen to form liquid water.

Simple equations are balanced by a process of trial and error. However, it is helpful to balance the formula which contains the maximum number of elements first. You may be asked to balance equations in IB examinations, in Paper 1.

It should also be noted that some reactions do *not* occur, even though balanced equations can be written, for example, $\text{Cu} (\text{s}) + 2\text{HCl} (\text{aq}) \rightarrow \text{CuCl}_2 (\text{aq}) + \text{H}_2 (\text{g})$. Hence, the activity series (Oxidation and Reduction) should be consulted before equations for displacement reactions are written.

Equations that involve electron transfer (redox reactions) are sometimes difficult to balance by inspection. When you notice that the oxidation numbers for an element are not identical on both sides of the equation, you have a redox equation. You can sometimes balance such equations by inspection if the equation is simple but there is an approach for balancing redox equations that relies on balancing the changes in oxidation number. This will be discussed later in Topic 9.1.

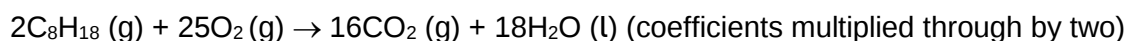
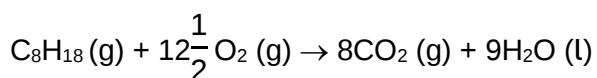
Hydrocarbons require oxygen to combust, and they form water and carbon dioxide as products. So a general formula might look something like this:



where x is the number of carbons in the hydrocarbon and y is the number of hydrogens.

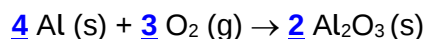
In writing equations describing the combustion of hydrocarbons, it is possible to have a fraction for the oxygen and sometimes essential if the enthalpy change of combustion (see energetics) is described. To remove the fractions, multiply each compound's coefficient by two (or whatever the denominator is in oxygen's coefficient, but it will rarely be anything but two because the number of hydrogens, y , will almost always be even).

For example, the complete combustion of octane (petrol)



Try balancing the following chemical equations:

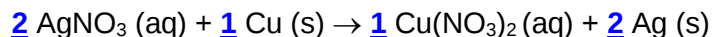
1. **Synthesis** of aluminum oxide



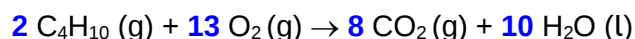
2. **Decomposition** of calcium carbonate



3. **Displacement** reaction of silver nitrate with copper



4. **Combustion** of butane

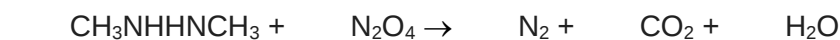


Do you know?

The process of refrigeration involves a condensation–evaporation cycle that requires the use of volatile liquids. Methylpropane (isobutane), an isomer of butane, is now widely used as a refrigerant. It is used as a replacement to chlorofluorocarbons (CFCs) that were traditionally used. CFCs cause the depletion of the ozone layer and are now banned in many countries.

Exercise 1

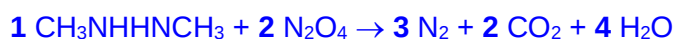
1. When the equation



is balanced, the sum of all the coefficients (simplest whole number) is

- A. 10
- B. 11
- C. 12
- D. 13

Answer: C

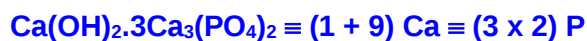


Hence, $1 + 2 + 3 + 2 + 4 = 12$

2. In a particular apatite ore in which $\text{Ca}(\text{OH})_2$ is associated with calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, an analysis shows that calcium and phosphorus are present in a mole ratio of 5:3. Which one of the following formulas agrees with this information?

- A. $\text{Ca}(\text{OH})_2 \cdot 2\text{Ca}_3(\text{PO}_4)_2$
- B. $\text{Ca}(\text{OH})_2 \cdot 3\text{Ca}_3(\text{PO}_4)_2$
- C. $(\text{Ca}(\text{OH})_2)_2 \cdot \text{Ca}_3(\text{PO}_4)_2$
- D. $(\text{Ca}(\text{OH})_2)_3 \cdot \text{Ca}_3(\text{PO}_4)_2$

Answer: B

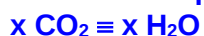


3. When a given hydrocarbon is converted completely to carbon dioxide and water, equal numbers of moles of CO_2 and H_2O are produced. The hydrocarbon could be

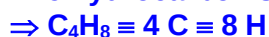
- A. C_2H_2
- B. C_2H_6
- C. C_3H_8
- D. C_4H_8

Answer: D

If there are equal number of moles of CO_2 and H_2O ,



The hydrocarbon should contain x moles of C atom and $2x$ moles of H atom



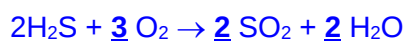
4. Hydrogen sulfide, H_2S , reacts with oxygen to form sulfur dioxide and water as shown below:



What is the whole number coefficient for oxygen when this equation is balanced?

- A. 1
- B. 2
- C. 3
- D. 6

Answer: C



5. The formula for samarium(III) chloride is SmCl_3 . What is the formula for samarium(III) sulfate?

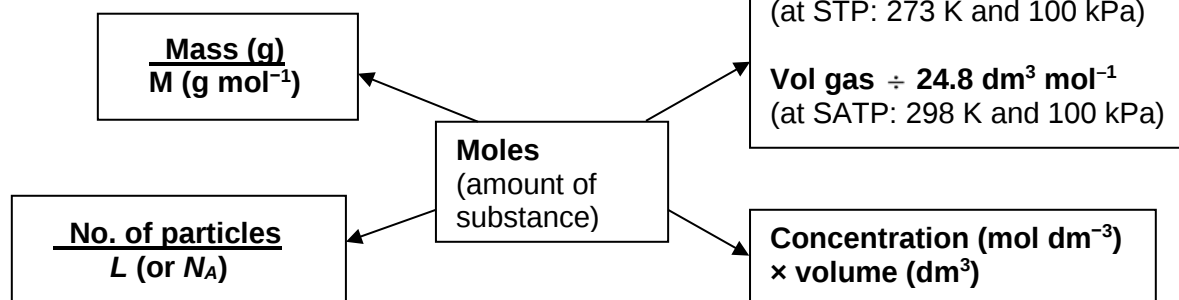
- A. Sm_3SO_4
- B. $\text{Sm}_3(\text{SO}_4)_2$
- C. $\text{Sm}(\text{SO}_4)_3$
- D. $\text{Sm}_2(\text{SO}_4)_3$

Answer: D

Samarium has a charge of +3, sulfate has a charge of -2.

1.2 The mole concept

The mole & related definitions



Avogadro's constant (L or N_A) is defined as the number of constituent particles (usually atoms or molecules) per mole of a given substance. It has a value of $6.02 \times 10^{23} \text{ mol}^{-1}$.

M refers to the **molar mass**. It is the mass of substance in grams that contains one mole of particles. It has units of grams per mole, g mol^{-1} , and the same numerical value as A_r or M_r .

A_r refers to **relative atomic mass**. It is defined as the weighted average of the atomic masses of its isotopes and their relative abundance compared to $\frac{1}{12}$ of (the mass of) of ^{12}C .

Note that A_r has **no units**.

M_r refers to **relative molecular mass**. It is defined as the **weighted average mass of a molecule** compared to $\frac{1}{12}$ of (the mass of) one atom of ^{12}C . (*Important definition in IB*).

Note that M_r has **no units** as well.

$$M_r = \frac{\text{average mass of a molecule}}{\text{mass of } \frac{1}{12} \text{ of one atom of } ^{12}\text{C}}$$

To calculate the mass of one molecule (or one atom) in grams, perform the following steps:

1. calculate the molar mass of the substance
2. divide by Avogadro's constant

Worked example 1

Calculate the mass of a single atom of nitrogen.

Answer:

$$\text{Mass of a single nitrogen atom} = \frac{14.01 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 2.33 \times 10^{-23} \text{ g}$$

Worked example 2

Calculate the mass (in grams) of a single molecule of hydrogen fluoride, HF.

Answer:

$$\text{Mass of a single HF molecule} = \frac{(1.01 + 19.00) \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} = 3.32 \times 10^{-23} \text{ g}$$

Exercise 2

1. Complete the following table

Amount of Substance / mol	Mass / g	No. of particles (in terms of L or N_A)
1 mole of iron, Fe	55.85	<u>L</u> atoms
1 mole of nitrogen molecules, N_2	28.02	<u>2L</u> atoms or <u>L</u> molecules
1 mole of methane, CH_4	16.05	<u>5L</u> atoms or <u>L</u> molecules
1 mole of magnesium nitrate, $Mg(NO_3)_2$	148.33	<u>L</u> formula units of $Mg(NO_3)_2$ <u>L</u> ions of Mg^{2+} , <u>2L</u> ions of NO_3^- Total: <u>3L</u> ions

2. What is the amount (mol) of ozone molecules that can be formed from 1.8×10^{22} oxygen atoms?

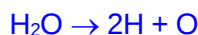


$$\text{Amount of oxygen atoms} = \frac{1.8 \times 10^{22}}{6.02 \times 10^{23}} = 2.99 \times 10^{-2} \text{ mol}$$

$$\text{Amount of ozone molecules} = (2.99 \times 10^{-2}) \times \frac{1}{3} = \underline{\underline{9.97 \times 10^{-3} \text{ mol}}}$$

3. How many atoms are there in:

(a) 18 g of water,



$$\text{Amount of water molecules} = \frac{18}{16.00 + (1.01 \times 2)} = 0.999 \text{ mol}$$

$$\text{Number of atoms} = (3 \times 0.999) \times (6.02 \times 10^{23}) = \underline{\underline{1.80 \times 10^{24} \text{ atoms}}}$$

(b) 8 g of sulfur trioxide?



$$\text{Amount of sulfur trioxide molecules} = \frac{8}{32.07 + (16.00 \times 3)} = 0.0999 \text{ mol}$$

$$\text{Number of atoms} = (4 \times 0.0999) \times (6.02 \times 10^{23}) = \underline{\underline{2.41 \times 10^{23} \text{ atoms}}}$$

Stoichiometric calculations may involve density. (refer to Question 4 of Exercise 3)

Density is the mass per unit volume.

Density = $\frac{\text{mass}}{\text{volume}}$. The SI unit of density is kilograms per cubic metre (kg/m^3 or kg m^{-3}). The unit is quite large and chemists often express density in g/cm^3 , where mass is expressed in grams and volume is expressed in cubic centimetres.

Exercise 3

1. A mole of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, refers to

- A. one $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ molecule
- B. 6.02×10^{23} g of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$
- C. 6.02×10^{23} g of carbon atoms
- D. 6.02×10^{23} of $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ molecules

Answer: D

$$1 \text{ mol of } \text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ molecules} = 1 \times (6.02 \times 10^{23}) \text{ } \text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ molecules}$$

2. Determine the mass (in grams) of an atom of gold-198.

$$\text{Amount of gold-198 atoms} = \frac{1}{6.02 \times 10^{23}} = 1.66 \times 10^{-24} \text{ mol}$$

$$\text{Mass of an atom of gold-198 atom} = (1.66 \times 10^{-24}) \times 198 = \underline{\underline{3.29 \times 10^{-22} \text{ g}}}$$

3. An accurate value for the molar mass of water is $18.01528 \text{ g mol}^{-1}$. Calculate the mass of one molecule of water in kilograms. Take $L = 6.022 \times 10^{23} \text{ mol}^{-1}$

$$\text{Amount of water molecules} = \frac{1}{6.022 \times 10^{23}} = 1.66 \times 10^{-24} \text{ mol}$$

$$\text{Mass of one mole of water in kg} = (1.66 \times 10^{-24}) \times 18.01528 = 2.99 \times 10^{-23} \text{ g} = \underline{\underline{2.99 \times 10^{-26} \text{ kg}}}$$

4. If the density of mercury is 13.534 g cm^{-3} and you have 62.5 cm^3 of mercury, how many grams, moles, and atoms of mercury do you have? (Mercury has a molar mass of $200.659 \text{ g mol}^{-1}$).

Mass of mercury present = $13.534 \times 62.5 = 845.875 \text{ g} = \underline{846 \text{ g}}$

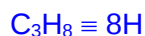
Amount of mercury = $\frac{845.875}{200.659} = \underline{4.22 \text{ mol}}$

Number of mercury atoms = $4.22 \times (6.02 \times 10^{23}) = \underline{2.54 \times 10^{24} \text{ atoms}}$

5. The number of hydrogen atoms required to prepare 0.88 g of propane, C_3H_8 , is (relative atomic mass of carbon, $A_r(\text{C}) = 12.01$; $A_r(\text{H}) = 1.01$).

- A. 9.6×10^{22}
- B. 8.0×10^{22}
- C. 4.8×10^{22}
- D. 1.2×10^{22}

Answer: A



Amount of H atoms required = $8 \times \frac{0.88}{(12.01 \times 3) + (1.01 \times 8)} = 0.160 \text{ mol}$

Number of H atoms required = $0.160 \times (6.02 \times 10^{23}) = 9.6 \times 10^{22} \text{ atoms}$

6. All of the following statements are consistent with the concept of a mole of substance except
- A. one mole of sodium contains 6.02×10^{23} sodium atoms.
 - B. one mole of carbon-12 atoms has a mass of twelve grams.
 - C. one mole of chlorine gas contains 6.02×10^{23} chlorine molecules.
 - D. one mole of sodium chloride contains 6.02×10^{23} ions.

Answer: D



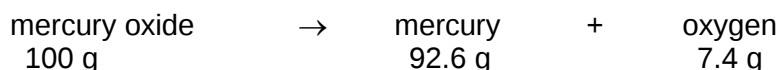
1 mole of sodium chloride gives 2 moles of ions in total.

Hence, number of ions = $2 \times (6.02 \times 10^{23}) = 1.20 \times 10^{24} \text{ ions}$

Enrichment reading: The Three Laws

Law of conservation of mass

During any chemical change, the total mass of the products remains equal to the total mass of the reactants, for example, when mercury oxide is heated the sum of the masses of mercury and oxygen was found to be equal to the mass of mercury oxide.



Law of constant composition

A chemical compound always contains the same elements in the same proportion by mass. This is the law of constant composition and it implies that in a compound the elements are present in fixed ratios by mass.

Law of multiple proportions

The law of multiple proportions, also known as Dalton's law, was based on English chemist John Dalton's observations of the reactions of atmospheric gases. It states that when elements form compounds, the proportions of the elements in those chemical compounds can be expressed in small whole number ratios. For example, the reaction of the elements carbon and oxygen can yield both carbon monoxide (CO) and carbon dioxide (CO₂). In CO₂, the ratio of the amount of oxygen compared to the amount of carbon is a fixed ratio of 1:2, a ratio of simple whole numbers. In CO, the ratio is 1:1.

Empirical & molecular formula determination

An empirical formula shows the kinds of atoms and their relative numbers in a substance in the smallest possible whole number ratios.

The molecular formula is the chemical formula that indicates the actual number of atoms of each element in one molecule of the substance.

Worked example 1

A sample of a compound has the following mass composition: sodium 9.20 g; sulfur 12.8 g; oxygen 9.60 g. Determine the empirical formula.

Answer:

Step 1: Write down the mass of each element.

Step 2: Write down the relative atomic mass of each element.

Step 3: Divide each mass by its relative atomic mass to obtain the amounts (number of moles).

Step 4: Divide each number by the smallest number of moles (in this case it is 0.399)

Step 5: Multiply each number by an appropriate integer to obtain whole numbers (in this case multiply by two).

	Sodium (Na)	Sulfur (S)	Oxygen (O)
Number of moles	$\frac{9.20}{22.99} = 0.400 \text{ mol}$	$\frac{12.8}{32.06} = 0.399 \text{ mol}$	$\frac{9.60}{16.00} = 0.600 \text{ mol}$
Divide by the smallest number	$\frac{0.400}{0.399} \approx 1$	$\frac{0.399}{0.399} = 1$	$\frac{0.600}{0.399} \approx 1.50$
Simplest mole ratio**	$1 \times 2 = 2$	$1 \times 2 = 2$	$1.5 \times 2 = 3$

**Note that the final step is not always necessary.

The empirical formula of the compound is $\text{Na}_2\text{S}_2\text{O}_3$

Worked example 2

Glucose has the empirical formula CH_2O and a relative molecular mass of 180. Find the molecular formula of glucose.

Answer:

Relative molecular mass of the empirical formula, $\text{CH}_2\text{O} = 12 + 2(1) + 16 = 30$

Relative molecular mass = $n \times$ relative molecular mass of the empirical formula

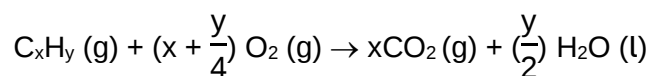
$$\text{i.e. } n = \frac{\text{relative molecular mass}}{\text{relative mass of the empirical formula}} = \frac{180}{30} = 6$$

The molecular formula of glucose is $6 \times \text{CH}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6$.

Molecular formula = $n \times$ empirical formula

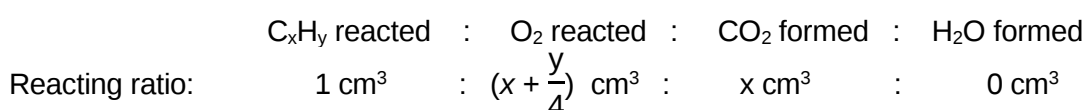
Determination of molecular formula from combustion data

All hydrocarbons generally burn in oxygen according to the equation:



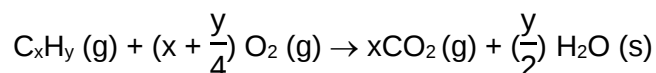
Under SATP or at STP, the **water product is a liquid**. Hence the **volume of water is negligible compared with the volumes of the C_xH_y , O_2 and CO_2 gases** in the equation.

From Avogadro's Law, **equal volumes** of gases, under the same conditions of temperature and pressure, contain **equal numbers** of molecules. Hence, the reacting molar ratio is equal to the reacting ratio by volume:



Worked example 1

20 cm³ of a gaseous hydrocarbon was mixed with 150 cm³ of oxygen. The mixture was sparked so that the hydrocarbon was completely burnt. The gaseous products had a total volume of 130 cm³. When this product was passed over soda lime, the volume of the product decreased to 90 cm³. All volume measurements were made at STP. Deduce the molecular formula of the hydrocarbon.



Initially:	20	150	0	–
------------	----	-----	---	---

After reaction:	0	90	(130 – 90)	–
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Volume of CO_2 produced = $130 - 90 = 40 \text{ cm}^3$

Volume of O_2 reacted with hydrocarbon = $150 - 90 = 60 \text{ cm}^3$

Using Avogadro's Law, volume ratios can be treated as mole ratios

Considering $\text{C}_x\text{H}_y : \text{CO}_2$ we have, $\frac{1}{x} = \frac{20}{40} = \frac{1}{2} \Rightarrow \underline{x = 2}$

Considering $\text{C}_x\text{H}_y : \text{O}_2$ we have, $\frac{1}{x + \frac{y}{4}} = \frac{20}{60} = \frac{1}{3}$

$2 + \frac{y}{4} = 3 \Rightarrow \underline{y = 4}$

Molecular formula is: C_2H_4

Exercise 4

1. A liquid **L** contains 62.1 % carbon, 10.3 % hydrogen and 27.6 % oxygen by mass. When 0.125 g of **L** was evaporated in a syringe at STP, 24.10 cm³ of vapour was produced. Determine (a) the empirical formula and (b) the molecular formula of **L**.

	Carbon (C)	Hydrogen (H)	Oxygen (O)
Number of moles	$\frac{62.1}{12.01} = 5.17 \text{ mol}$	$\frac{10.3}{1.01} = 10.2 \text{ mol}$	$\frac{27.6}{16.00} = 1.73 \text{ mol}$
Divide by the smallest number	$\frac{5.17}{1.73} \approx 3$	$\frac{10.2}{1.73} \approx 6$	$\frac{1.73}{1.73} = 1$

Empirical formula is: **C₃H₆O**

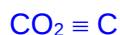
$$\text{Amount of vapour L present} = \frac{\frac{24.10}{1000}}{22.7} = 1.06 \times 10^{-3} \text{ mol}$$

$$\text{Relative molecular mass} = \frac{0.125}{1.06 \times 10^{-3}} = 117.74$$

$$n = \frac{\text{relative molecular mass}}{\text{relative mass of the empirical formula}} = \frac{117.74}{(12.01 \times 3) + (1.01 \times 6) + 16.00} = 2$$

Molecular formula is: **C₆H₁₂O₂**

2. (a) Crocetin consists of the elements carbon, hydrogen and oxygen. Determine the empirical formula of crocetin, if 1.00 g of crocetin forms 2.68 g of carbon dioxide and 0.665 g of water when it undergoes complete combustion.



$$\text{Amount of C atoms present} = \frac{2.68}{12.01 + (16.00 \times 2)} = 6.09 \times 10^{-2} \text{ mol}$$

$$\text{Mass of C atoms present} = (6.09 \times 10^{-2}) \times 12.01 = 0.731 \text{ g}$$



$$\text{Amount of H atoms present} = 2 \times \frac{0.665}{(1.01 \times 2) + 16.00} = 7.38 \times 10^{-2} \text{ mol}$$

$$\text{Mass of H atoms present} = (7.38 \times 10^{-2}) \times 1.01 = 7.45 \times 10^{-2} \text{ g}$$

$$\text{Mass of O atoms present} = 1.00 - 0.731 - (7.45 \times 10^{-2}) = 0.195 \text{ g}$$

$$\text{Amount of O atoms present} = \frac{0.195}{16.00} = 1.22 \times 10^{-2} \text{ mol}$$

	Carbon (C)	Hydrogen (H)	Oxygen (O)
Number of moles	6.09×10^{-2}	7.38×10^{-2}	1.22×10^{-2}
Divide by the smallest number	$\frac{0.0609}{0.0122} \approx 5$	$\frac{0.0738}{0.0122} \approx 6$	$\frac{0.0122}{0.0122} = 1$

Empirical formula is: **C₅H₆O**

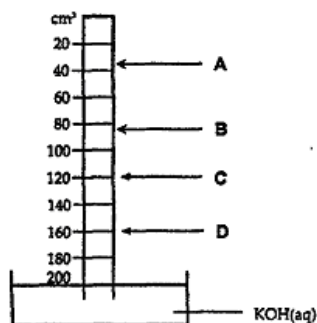
- (b) Determine the molecular formula of crocetin given that 0.300 mol of crocetin has a mass of 98.50 g.

$$\text{Relative molecular mass} = \frac{98.50}{0.300} = 328.33$$

$$n = \frac{\text{relative molecular mass}}{\text{relative mass of the empirical formula}} = \frac{328.33}{(12.01 \times 5) + (1.01 \times 6) + 16.00} = 4$$

Molecular formula is: **C₂₀H₂₄O₄**

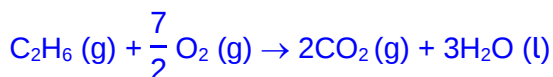
3. A tube was filled with a mixture 10 cm³ of methane (CH₄), 30 cm³ of ethane (C₂H₆) and 160 cm³ of oxygen at room temperature. The open end of the tube was placed in a beaker of KOH (aq) as shown. The gas mixture was sparked. What would the final level of the liquid be in the tube after it cooled to room temperature?



KOH will absorb all the acidic CO₂ gas produced.



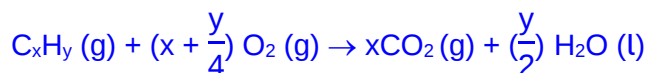
Volume of oxygen gas required = $2 \times 10 = 20 \text{ cm}^3$



Volume of oxygen gas required = $\frac{7}{2} \times 30 = 105 \text{ cm}^3$

Volume of oxygen gas remaining = $160 - 20 - 105 = \mathbf{35 \text{ cm}^3}$ (**Level A**)

4. 20 cm³ of a gaseous hydrocarbon was burnt in 100 cm³ of oxygen. Upon complete combustion, the gas remaining occupied 70 cm³. After passing this gaseous mixture through soda lime, 10 cm³ of gas remained. All volumes were measured at SATP. Determine the molecular formula of the hydrocarbon.



Initially: **20** **100** **0** –

After reaction: **0** **10** **(70 – 10)** –

Volume of CO₂ produced = **70 – 10 = 60 cm³**

Volume of O₂ reacted with hydrocarbon = **100 – 10 = 90 cm³**

Using Avogadro's Law, volume ratios can be treated as mole ratios

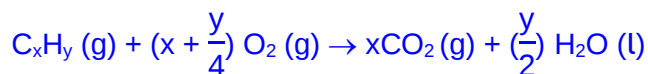
Considering C_xH_y : CO₂ we have, $\frac{1}{x} = \frac{20}{60} = \frac{1}{3} \Rightarrow \mathbf{x = 3}$

Considering C_xH_y : O₂ we have, $\frac{1}{x + \frac{y}{4}} = \frac{20}{90} = \frac{1}{4.5}$

$3 + \frac{y}{4} = 4.5 \Rightarrow \mathbf{y = 6}$

Molecular formula is: **C₃H₆**

5. 10 cm³ of a hydrocarbon, C_xH_y were exploded with an excess of oxygen. A contraction of 25 cm³ occurred. On treating the products with aqueous NaOH, a further contraction in volume of 40 cm³ occurred. Deduce the values of x and y. (All volumes measured at SATP)



Volume of CO₂ produced = **40 cm³**

Initial volume of gases due to C_xH_y (g) and excess O₂ (g)

⇒ Initial volume of gases due to C_xH_y (g) + reacted O₂ (g) + unreacted O₂ (g)

Final volume of gases due to CO₂ (g) + unreacted O₂ (g)

Initial volume – final volume

= (C_xH_y (g) + reacted O₂ (g) + unreacted O₂ (g)) – (CO₂ (g) + unreacted O₂ (g))

= C_xH_y (g) + reacted O₂ (g) – CO₂ (g)

C_xH_y (g) + reacted O₂ (g) – CO₂ (g) = 25 cm³

10 + reacted O₂ (g) – 40 = 25

Reacted O₂ (g) = 55 cm³

Using Avogadro's Law, volume ratios can be treated as mole ratios

Considering C_xH_y : CO₂ we have, $\frac{1}{x} = \frac{10}{40} = \frac{1}{4} \Rightarrow \underline{\underline{x = 4}}$

Considering C_xH_y : O₂ we have, $\frac{1}{x + \frac{y}{4}} = \frac{10}{55} = \frac{1}{5.5}$

$4 + \frac{y}{4} = 5.5 \Rightarrow \underline{\underline{y = 6}}$

Molecular formula is: **C₄H₆**

Theory of knowledge:

- The magnitude of Avogadro's constant is beyond the scale of our everyday experience. How does our everyday experience limit our intuition?

1.3 Reacting masses and volumes

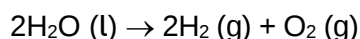
A) Problems involving a mass–mass relationship

Write down the balanced equation to represent the chemical reaction. Convert mass into moles, then use the coefficients in the balanced equation to obtain the moles of the required substance. Convert back into mass.

Worked example 1

Calculate the mass of oxygen (in kg) that can be obtained from completely decomposing 1802 g of water.

Answer:



$$\text{Amount of water} = \frac{1802 \text{ g}}{18.02 \text{ g mol}^{-1}} = 100 \text{ mol}$$

$$\text{Amount of oxygen} = \frac{100}{2} = 50 \text{ mol}$$

$$\text{Mass of oxygen} = 50 \text{ mol} \times 32.00 = 1600 \text{ g} = 1.6 \text{ kg}$$

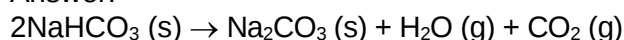
B) Problems involving a mass–volume relationship

Write down the balanced equation to represent the chemical reaction. Convert mass into moles, then use the coefficients in the balanced equation to obtain the moles of the required substance. Convert back into volume of gas using the molar gas volume.

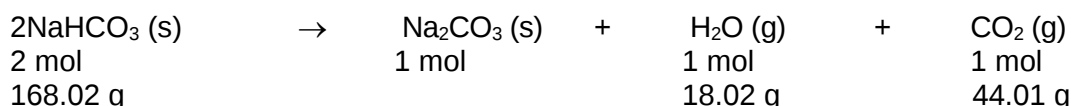
Worked example 2

A 2.000 g sample containing Na_2CO_3 and NaHCO_3 loses 0.248 g when heated to 300°C (the temperature at which NaHCO_3 decomposes to Na_2CO_3 , CO_2 and H_2O). What is the percentage of Na_2CO_3 in the sample?

Answer:



Since steam and carbon dioxide escape during this reaction, the loss of mass must correspond to the mass of water and carbon dioxide.



$$\frac{0.248}{62.03} \times 168.02 = 0.672 \text{ g of NaHCO}_3$$

$$\text{Mass of Na}_2\text{CO}_3 = 2.000 \text{ g} - 0.672 \text{ g} = 1.328 \text{ g}$$

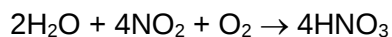
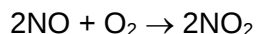
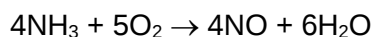
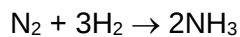
$$\text{Percentage of Na}_2\text{CO}_3 = \frac{1.328}{2.000} \times 100 = 66.4 \%$$

C) Consecutive reactions

Determining the mass of a product (from consecutive reactions), where the product of a reaction is the reactant of a subsequent reaction.

Worked example 3

Calculate the mass of nitric acid that can be produced from 5.60 grams of nitrogen gas.



Answer:

The coefficients in the equation indicate that: 1 mol of N_2 produces 2 mol of NH_3 ; 4 mol of NH_3 produces 4 mol of NO ; 2 mol of NO produces 2 mol of NO_2 and 4 mol of NO_2 produces 4 mol of HNO_3 . So overall, 1 mol of N_2 produces 2 mol HNO_3 .

$$\text{Amount of nitrogen, N}_2 = \frac{5.60 \text{ g}}{28.02 \text{ g mol}^{-1}} = 0.200 \text{ mol}$$

$$\text{Amount of nitric acid produced} = 2 \times 0.200 \text{ mol} = 0.400 \text{ mol}$$

$$\text{Hence, mass of nitric acid produced} = 0.400 \text{ mol} \times 63.02 \text{ g mol}^{-1} = 25.2 \text{ g}$$

Theory of knowledge:

- Assigning numbers to the masses of the chemical elements has allowed chemistry to develop into a physical science. Why is mathematics so effective in describing the natural world?

Stoichiometry: Excess reagent, limiting reagent, theoretical, actual & percentage yield

The quantity of product calculated to form when all of the **limiting reagent** is consumed is called the **theoretical yield**.

The amount of product actually obtained, called the **actual yield** (or experimental yield), is always less than the theoretical yield. This is because part of the reactants may not react or they may react in a different way from the desired reaction (side reactions).

For example, when magnesium is burnt in air, some of the magnesium reacts with nitrogen to form magnesium nitride. In addition, it is not always possible to recover all the products from the reaction mixture. The reaction may also be reversible, for example, the formation of ethyl ethanoate from the reaction between ethanol and ethanoic acid (Topic 7, Equilibrium).

To calculate the **percentage yield**, a comparison is made between the theoretical and actual yield:

$$\text{Percentage yield} = \frac{\text{Experimental yield}}{\text{Theoretical yield}} \times 100\%$$

Worked example 1

Calculate the volume of hydrogen gas evolved at SATP when 0.623 g of calcium reacts with 27.30 cm³ of 1.25 mol dm⁻³ hydrochloric acid.

Equation: $\text{Ca (s)} + 2\text{HCl (aq)} \rightarrow \text{CaCl}_2 \text{ (aq)} + \text{H}_2 \text{ (g)}$

$$\text{Amount of Ca present} = \frac{0.623}{40.08} = 0.0155 \text{ mol}$$

$$\text{Amount of HCl present} = \frac{27.30}{1000} \times 1.25 = 0.0341 \text{ mol}$$

$$\text{Reacting ratio} = \begin{array}{ccc} \text{Ca} & : & \text{HCl} \\ 1 & : & 2 \end{array}$$

0.0155 mol of Ca react with 0.0310 mol of HCl, thus HCl is present in excess and the limiting reagent is Ca.

Therefore,

$$\text{Amount of hydrogen gas evolved} = 0.0155 \text{ mol}$$

$$\text{Volume of hydrogen gas evolved at SATP} = 0.0155 \times 24.8 = \underline{0.384 \text{ dm}^3}$$

Exercise 5

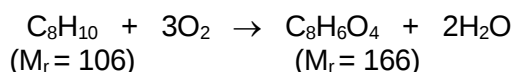
1. The foul smell that skunks spray is due to a number of thiols, one of which is methanethiol, CH_3SH . A 10 cm^3 sample of methanethiol was exploded with 60 cm^3 of oxygen. What would be the final volume of the resultant mixture of gases when cooled to room temperature?



Initial / cm^3	10	60	0	0	–
Change / cm^3	–10	–30	+10	+10	–
Final / cm^3	0	30	10	10	–

$$\text{Final volume} = 30 + 10 + 10 = \underline{50\text{ cm}^3}$$

2. Terephthalic acid, $\text{C}_8\text{H}_6\text{O}_4$ is a raw material used for the production of the polyester, terylene. It is made commercially by the oxidation of 1,4-dimethylbenzene, C_8H_{10} .



- (a) If 25.0 g of 1,4-dimethylbenzene (limiting reagent) is used, calculate the theoretical yield of terephthalic acid.

$$\text{Amount of C}_8\text{H}_{10} \text{ used} = \frac{25.0}{106} = 0.236\text{ mol}$$

$$\text{Amount of C}_8\text{H}_6\text{O}_4 \text{ produced} = 0.236\text{ mol}$$

$$\text{Theoretical yield of C}_8\text{H}_6\text{O}_4 = 0.236 \times 166 = \underline{39.2\text{ g}}$$

- (b) If 28.5 g of terephthalic acid is obtained from an experiment, what is the percentage yield in that experiment?

$$\begin{aligned} \text{Percentage yield} &= \frac{\text{Experimental yield}}{\text{Theoretical yield}} \times 100\% \\ &= \frac{28.5}{39.2} \times 100\% \\ &= \underline{72.7\%} \end{aligned}$$

Concentrations

When using a solution of a substance, it is important to know how much of the substance is dissolved in a volume of solvent, so as to reproduce solutions of the same **concentration**.

$$\text{Solute} + \text{Solvent} = \text{Solution}$$

- Units of concentration to include: mol dm^{-3} , g dm^{-3} and parts per million (ppm).

The **molar concentration** or **molarity (M)** is concentration expressed in mol dm^{-3} . It is often denoted by the use of square brackets, [].

To convert molarity to concentration in g dm^{-3} ,

$$\text{Concentration (g dm}^{-3}\text{)} = \text{Molarity} \times \text{Molar mass}$$

Parts per million

One ppm is the number of milligrams of solute per kg of solution, since $1 \text{ mg} = 10^{-3} \text{ g}$ and $1 \text{ kg} = 10^3 \text{ g}$.

Assuming the density of water is 1.00 g cm^{-3} , 1 litre (dm^3) of solution = 1 kg and hence, **$1 \text{ mg dm}^{-3} = 1 \text{ ppm}$** . This is approximately true for dilute aqueous solutions.

Parts per million concentrations are essentially mass ratios (solute to solution) $\times 1 \text{ million}$ (10^6).

To convert concentrations in mg dm^{-3} (or ppm in dilute solution) to molarity (mol dm^{-3}), divide concentrations in g dm^{-3} by the molar mass of the analyte (chemical under analysis) to get the corresponding number of moles per dm^3 .

Eg. Calculate the molarity of a 6.2 mg dm^{-3} solution of O_2 .

Solutions

A solution with a known concentration is called a **standard solution**.

A **primary standard** is usually made up of a substance that has **high purity and stability**. This is because it allows the substance to be accurately weighed, such that an **accurately known concentration** can be used reliably for the calibration of other standards. It is prepared using a volumetric flask, where solvent is added to a high purity sample until the solvent reaches the calibrated mark on the flask.

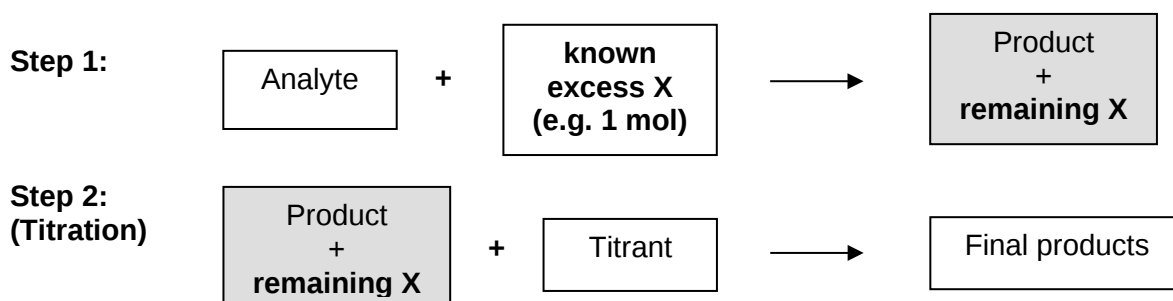
Examples of primary standards include ethanedioic acid, butanedioic acid, sodium hydrogencarbonate and anhydrous sodium carbonate. Sodium hydroxide is not a good primary standard because it absorbs atmospheric CO_2 . For redox titrations, sodium ethanedioate, potassium iodate(V) and potassium dichromate are usually used. Sodium thiosulfate is not a suitable primary standard because of its water of crystallisation.

Titration

Titration is a commonly used quantitative method to determine the unknown concentration of a solution. The **titrant**, which is usually placed in the burette, is a standard solution added to react with the **analyte** of an unknown concentration. The **end point** marks the end (completion) of the titration (reaction), usually indicated by a colour change. This is ideally the same volume required as at the **equivalence point**, which denotes the exact amount of titrant needed to react with the fixed amount of analyte.

However, not all substances can be quantitatively determined by direct titration method. **Back titration** is an indirect titration method usually employed when a compound is an insoluble solid (e.g. CaCO_3 in toothpaste or eggshell) in which the end-point is difficult to detect or reaction is too slow. Similarly, compounds which contain impurities that may interfere with direct titration or contain volatile substances (ammonia, iodine etc) that may result in inaccuracy due to loss of substance during titration will require the use of back titration.

Back Titration



If the amount of titrant used is 0.2 mol, amount of remaining **X** = 0.2 mol (if the mole ratio is 1:1)

So, amount of **X** reacted with analyte = known excess of **X** – remaining **X**
(e.g. 1.0 mol – 0.2 mol = 0.8 mol)

Therefore, amount of analyte = 0.8 mol (if the mole ratio is 1:1)



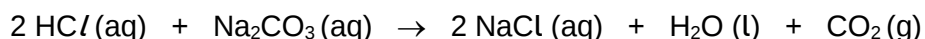
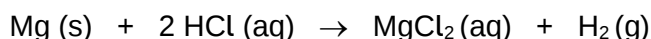
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view a video
on how a
standard
solution is
made*



*Scan me to
view a video
on how a
titration is
conducted*

Worked example 1

In an experiment, 2.500 g of impure magnesium ribbon was put into a beaker of 500 cm³ of 1.0 mol dm⁻³ HCl (**excess**). There was immediate effervescence and the reaction stopped after some time. The final product was a colourless solution. The solution was then titrated with aqueous sodium carbonate (0.500 mol dm⁻³). It was found that 20.0 cm³ of the solution required exactly 12.80 cm³ of sodium carbonate solution for complete neutralisation. The equations for the reactions are shown below. Calculate the percentage purity of the magnesium ribbon.



Amount of Na₂CO₃ titrated = (12.80 × 10⁻³) × 0.500 mol dm⁻³ = 0.00640 mol

Amount of HCl titrated in 20.0 cm³ = 0.00640 mol × 2 = 0.0128 mol

Amount of HCl titrated in 500 cm³ = $\left(\frac{500}{20}\right) \times 0.0128 \text{ mol} = 0.320 \text{ mol}$

Amount of HCl added initially = (500 × 10⁻³) × 1.0 mol dm⁻³ = 0.500 mol

Amount of HCl reacted with Mg ribbon = 0.500 mol – 0.320 mol = 0.180 mol

Amount of magnesium ribbon reacted = $\frac{0.180 \text{ mol}}{2} = 0.090 \text{ mol}$

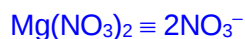
Mass of magnesium in impure ribbon = 0.090 mol × 24.31 g mol⁻¹ = 2.1879 g

Percentage purity = $\left(\frac{2.1879}{2.500}\right) \times 100 \% = 87.5 \%$

Exercise 6

1. A 1.285 g sample of magnesium nitrate is dissolved in water and the total volume of solution is made up to 250.0 cm³. How many moles of nitrate ions does 10 cm³ of the solution contain?

$$\text{Amount of Mg(NO}_3)_2 \text{ dissolved} = \frac{1.285}{(24.31 + 2 \times (14.01 + 16.00 \times 3))} = 8.66 \times 10^{-3} \text{ mol}$$

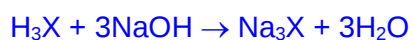
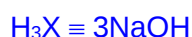


$$\text{Amount of NO}_3^- \text{ present} = 2 \times (8.66 \times 10^{-3}) = 1.73 \times 10^{-2} \text{ mol}$$

$$\text{Amount of NO}_3^- \text{ present in 10 cm}^3 \text{ of the solution} = \frac{10}{250.0} \times (1.73 \times 10^{-2}) = \underline{\underline{6.93 \times 10^{-4} \text{ mol}}}$$

2. 2.800 g of an acid (H₃X) were dissolved in water to make 250 cm³. A 25.0 cm³ portion of this solution was neutralised by 28.60 cm³ of 0.300 mol dm⁻³ sodium hydroxide solution. Calculate the relative molecular mass of the acid. [Hint: H₃X is a tribasic acid]

Since H₃X is a tribasic acid, one mole of H₃X reacts with three moles of NaOH



$$\text{Amount of NaOH reacted} = \frac{28.60}{1000} \times 0.300 = 8.58 \times 10^{-3} \text{ mol}$$

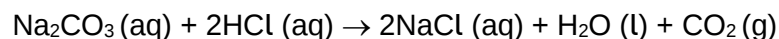
$$\text{Amount of H}_3\text{X in 25.0 cm}^3 = \frac{8.58 \times 10^{-3}}{3} = 2.86 \times 10^{-3} \text{ mol}$$

$$\text{Amount of H}_3\text{X in 250 cm}^3 = \frac{250}{25.0} \times (2.86 \times 10^{-3}) = 2.86 \times 10^{-2} \text{ mol}$$

$$\text{Relative molecular mass of acid} = \frac{2.800}{2.86 \times 10^{-2}} = \underline{\underline{97.90}}$$

3. Hydrated sodium carbonate has the formula $\text{Na}_2\text{CO}_3 \cdot n\text{H}_2\text{O}$. An experiment was conducted to determine n , the number of water of crystallization in hydrated sodium carbonate.

50.000 g of hydrated sodium carbonate was dissolved in 250.0 cm^3 of water. 20.0 cm^3 of this solution reacts completely with 27.90 cm^3 of 1.00 mol dm^{-3} dilute hydrochloric acid. The equation for this reaction is shown below. Calculate the value of n .



$$\text{Amount of HCl reacted} = \frac{27.90}{1000} \times 1.00 = 2.79 \times 10^{-2} \text{ mol}$$

$$\text{Amount of Na}_2\text{CO}_3 \cdot n\text{H}_2\text{O} \text{ in } 20.0 \text{ cm}^3 = \frac{2.79 \times 10^{-2}}{2} = 1.40 \times 10^{-2} \text{ mol}$$

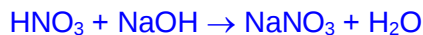
$$\text{Amount of Na}_2\text{CO}_3 \cdot n\text{H}_2\text{O} \text{ in } 250 \text{ cm}^3 = \frac{250}{20.0} \times (1.40 \times 10^{-2}) = 0.175 \text{ mol}$$

$$\text{Relative molecular mass of Na}_2\text{CO}_3 \cdot n\text{H}_2\text{O} = \frac{50.000}{0.175} = 285.71$$

$$n = \frac{285.71 - (22.99 \times 2) - 12.01 - (16.00 \times 3)}{(1.01 \times 2) + 16.00} \approx \underline{10} \text{ (nearest integer)}$$

4. A sample of 6.500 g impure calcium oxide is dissolved completely in 250.0 cm³ of 1.00 mol dm⁻³ dilute nitric acid. The resulting mixture is then titrated with sodium hydroxide solution of concentration 0.500 mol dm⁻³. 20.0 cm³ of this resulting mixture requires 14.10 cm³ of sodium hydroxide solution for complete neutralisation.

(a) How many moles of unreacted nitric acid were left in the resulting mixture?



$$\text{Amount of NaOH reacted} = \frac{14.10}{1000} \times 0.500 = 7.05 \times 10^{-3} \text{ mol}$$

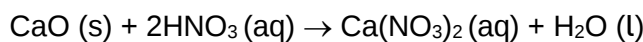
$$\text{Amount of HNO}_3 \text{ present in } 20.0 \text{ cm}^3 = 7.05 \times 10^{-3} \text{ mol}$$

$$\begin{aligned} \text{Amount of unreacted HNO}_3 \text{ present in } 250.0 \text{ cm}^3 \\ &= \frac{250.0}{20.0} \times (7.05 \times 10^{-3}) \\ &= \underline{\underline{8.81 \times 10^{-2} \text{ mol}}} \end{aligned}$$

(b) How many moles of nitric acid were originally present in the solution?

$$\text{Amount of HNO}_3 \text{ originally present} = \frac{250.0}{1000} \times 1.00 = \underline{\underline{0.250 \text{ mol}}}$$

(c) Calcium oxide reacts with dilute nitric acid as shown in the equation below.



Calculate the number moles of calcium oxide present in the sample.

$$\text{Amount of HNO}_3 \text{ reacted with CaO} = 0.250 - (8.81 \times 10^{-2}) = 0.162 \text{ mol}$$

$$\text{Amount of CaO present in sample} = \frac{0.162}{2} = \underline{\underline{8.09 \times 10^{-2} \text{ mol}}}$$

(d) Calculate the percentage purity of calcium oxide in the sample.

$$\text{Mass of pure CaO present in sample} = (8.09 \times 10^{-2}) \times (40.08 + 16.00) = 4.54 \text{ g}$$

$$\text{Percentage purity} = \left(\frac{4.54}{6.500} \right) \times 100 \% = \underline{\underline{69.8 \%}}$$

Dilution of concentrated solutions

For example, a purchased standard solution of potassium hydroxide, KOH has a concentration of 1.0 mol dm^{-3} . How would you prepare 100 cm^3 of a 0.1 mol dm^{-3} KOH solution to perform a titration with an acid?

The required concentration is $\frac{1}{10}$ th of the original KOH solution.

To make 1 dm^3 (1000 cm^3) of the diluted solution you will take 100 cm^3 of the original KOH solution and mix with 900 cm^3 of water.

The total volume is 1 dm^3 with only $\frac{1}{10}$ th original potassium hydroxide in this diluted solution, so the concentration is $\frac{1}{10}$ th, 0.1 mol dm^{-3} .

To make only 100 cm^3 of the diluted solution you will dilute 10 cm^3 by mixing it with 90 cm^3 of water.

Acids are supplied as concentrated acids. The solutions required in the laboratory are prepared by diluting the concentrated acids with water. **When a concentrated solution is diluted by adding water, the number of moles of solute in the solution remains unchanged on dilution.**

Hence, the following relationship holds during dilution:

$M_1 \times V_1 = M_2 \times V_2$, where M_1 represents the initial molar concentration, M_2 represents the molar concentration after dilution, V_1 represents the initial volume and V_2 represents the volume after dilution. This is an alternative approach to calculating how the solution is to be diluted.

Worked example 1

Calculate the volume to which 25.0 cm^3 of 5.00 mol dm^{-3} hydrobromic acid (HBr) must be diluted to produce a concentration of 1.50 mol dm^{-3} .

Answer:

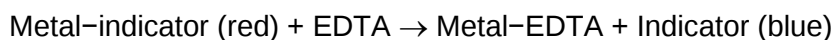
$$M_1 \times V_1 = M_2 \times V_2$$

$$5.00 \text{ mol dm}^{-3} \times 25.0 \text{ cm}^3 = 1.5 \text{ mol dm}^{-3} \times V_2$$

$$V_2 = 25.0 \times \frac{5.0}{1.5} = 83.3 \text{ cm}^3$$

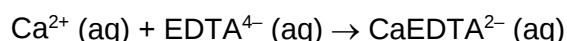
Enrichment reading: complexometric titrations

The complexes formed by a number of metal ions with the substance EDTA are very stable, and this method can be used to find the concentration of metal ions by titration. The end point in the titration is shown by an indicator, e.g. Eriochrome black, which forms a coloured complex with the metal ion. Complexometric titrations can be used to determine the hardness of water and the amount of magnesium salts in pharmaceutical preparations.



Example:

Hardness in a sample of tap water is caused by the presence of calcium ions.



100 cm³ of tap water are measured into a conical flask. An alkaline buffer and suitable complexometric indicator are added and the solution is titrated against 0.100 mol dm⁻³ EDTA solution. The volume of EDTA required is 22.00 cm³. Calculate the concentration of calcium ions. (Answer = 2.20×10^{-2} mol dm⁻³).

Gases

Assumptions of Kinetic-Molecular Theory

1. Gases are made up of very small particles, separated by large distances. Most of the volume occupied by a gas is empty space.
2. The gas particles do not attract each other at all (or there are negligible forces of attraction between gas particles).
3. The gas particles are in a state of continual and random motion.
4. If collisions occur between the gas particles, they are perfectly elastic i.e. no loss of kinetic energy during collisions.
5. The absolute temperature of gas is proportional to the average kinetic energy of the gas particles.

Under standard temperature and pressure, an **ideal gas** obeys the above assumptions.

Avogadro's law

- **Equal volumes** of all gases at the **same temperature and pressure** contain **equal numbers of moles** irrespective of the type of gases.
 - At 273 K and 100 kPa (STP), all gases will have identical volumes of $22.7 \text{ dm}^3 \text{ mol}^{-1}$.
 - At 298 K and 100 kPa (**SATP**), all gases will have identical volumes of **$24.8 \text{ dm}^3 \text{ mol}^{-1}$** .
- The **volume occupied by one mole of any gas** at a particular temperature and pressure is called the **molar volume**.

Comparison between a real gas and an ideal gas

Very often, scientists make predictions by assuming that the gases are ideal. This simplistic assumption allows scientists to make very good estimations of measurements such as pressure, volume, temperature, density, molar mass and relative molecular mass.

The molecules of an ideal gas are assumed to be volume-less points with no attractive or repulsive forces operating between the particles (atoms or molecules). It is a hypothetical state but gases (especially the noble gases) approach ideal behaviour under certain conditions.

	Real Gas	Ideal Gas
1.	Each particle has a definite volume and hence, occupies space. So the volume of the gas is the volume of the particles and the spaces between them.	The particles have a negligible volume compared to volume of its container. Hence, the volume of the gas is the volume of the space between the particles.
2.	Attractive forces are present between the particles.	There are negligible attractive forces operating between the particles.
3.	Collisions between the particles are non-elastic , and hence, there is <u>loss of kinetic energy</u> from the particles after collision.	Collisions between the particles are elastic , and hence, there is <u>no loss of kinetic energy</u> from the particles after collision.

Hence,

- real gases can be compressed into liquids but theory predicts that ideal gases cannot,
- only ideal gases obey the equation: $pV = nRT$, and
- a gas behaves like an ideal gas at **high temperatures** and **low pressures**.

Exercise 7

1. Why do gases behave as ideal gases at high temperatures and low pressures?

At low pressures the molecules (or atoms) are, on average, far apart. This means that the intermolecular (or interatomic) forces of attraction are relatively weak / negligible, so they move around independently (like the molecules in an ideal gas). The size of the molecules is also negligible in comparison with the actual volume of the gas.

At high temperatures, the attractive forces between the molecules become insignificant. The average kinetic energy of the molecules is much greater than the intermolecular forces of attraction.

2. Comment on the statement: "The particles in an ideal gas possess the same kinetic energy."

No, there is a range of kinetic energies in an ideal gas (at constant temperature) which is described by the Maxwell Boltzmann distribution. Constant elastic collisions rapidly change *individual* kinetic energies, but in a large sample of gas particles the distribution of kinetic energies remains constant. The *average* kinetic energy of the gas particles remains constant.

3. If 2.0 moles of N_2 occupy 75 dm³ at a given temperature and pressure what will the volume be for a mixture of 2.0 moles of N_2 and 2.0 moles of O_2 at the same temperature?

- A. 38 dm³
- B. 75 dm³
- C. 150 dm³
- D. 300 dm³

Answer: C

According to Avogadro's Law, equal volumes of all gases at the same temperature and pressure contain equal numbers of moles irrespective of the type of gases.

New total number of moles of gases present = 2.0 + 2.0 = 4.0 mol

Hence, new volume for the mixture = $\frac{4.0}{2.0} \times 75 = \underline{150 \text{ dm}^3}$

4. In which gas sample do molecules have the greatest average kinetic energy?

- A. H_2 at 100 K
- B. CH_4 at 273 K
- C. H_2O at 373 K
- D. CH_3OH at 353 K

Answer: C

The absolute temperature of gas is proportional to the average kinetic energy of the gas particles.

5. 1 mole of hydrogen, 2 moles of oxygen and 3 moles of carbon dioxide are placed in a closed container at 298 K. What is the ratio of average kinetic energies of each gas under these conditions?
- A. 1 : 2 : 3
B. 3 : 2 : 1
C. 1 : 1 : 1
D. 1 : 2 : 1

Answer: C

The absolute temperature of gas is proportional to the average kinetic energy of the gas particles. Since all the gases are at the same absolute temperature, they will have the same average kinetic energies.

Enrichment reading: Average kinetic energy of gases

The following expression can be derived for the kinetic energy, KE, of a gas particle:

$$KE = \frac{3}{2}RT,$$

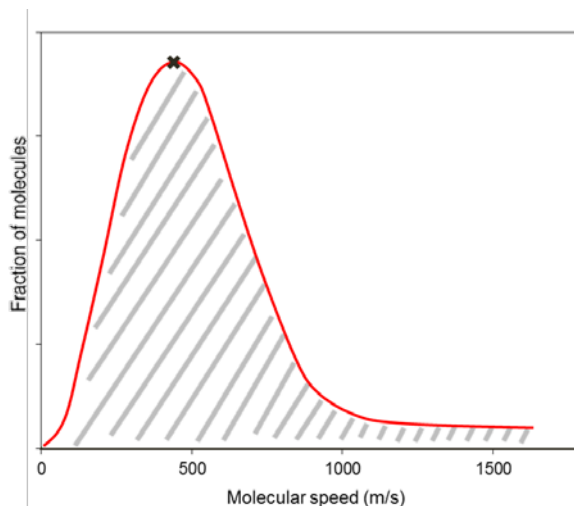
where R is the gas constant and T is the temperature in Kelvins. The expression shows that KE is directly proportional to the absolute temperature.

Note: At any given temperature, all gases have the same **average** kinetic energy.

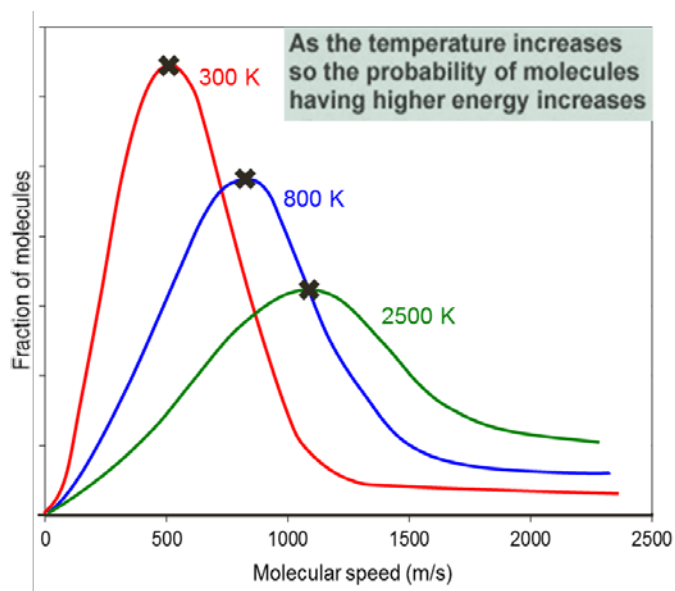
The Maxwell-Boltzmann Speed Distribution

- Although the molecules in a sample of gas have the same average kinetic energy, they move at various speeds due to collisional changes, i.e. they exhibit a distribution of speeds; some move fast, others relatively slowly. Collisions change individual molecular speed but the distribution of speeds remains the same.
- At the same temperature, molecules or atoms of lighter gases move, on average, faster than heavier gases.

- The graph shows the distribution of speeds for a gas, i.e. the fraction of the sample of gas molecules that have a given speed is shown by the height of the curve above the speed axis. There are no molecules exactly at rest.



- At higher temperatures, a greater fraction of the molecules are moving at higher speeds. This is important for activated chemical processes.



The Ideal Gas Equation

The behaviour of an ideal gas can be described by the ideal gas equation. The ideal gas equation allows you to convert from volumes of gases to amounts (in moles) at any particular temperature and pressure.

$$PV = nRT$$

P = pressure in pascal or N m^{-2} ($1 \text{ atm} = 1.00 \times 10^5 \text{ Pa}$)

V = volume in m^3 ($1 \text{ m}^3 = 1000 \text{ dm}^3 = 1\,000\,000 \text{ cm}^3$)

n = amount of gas (mol)

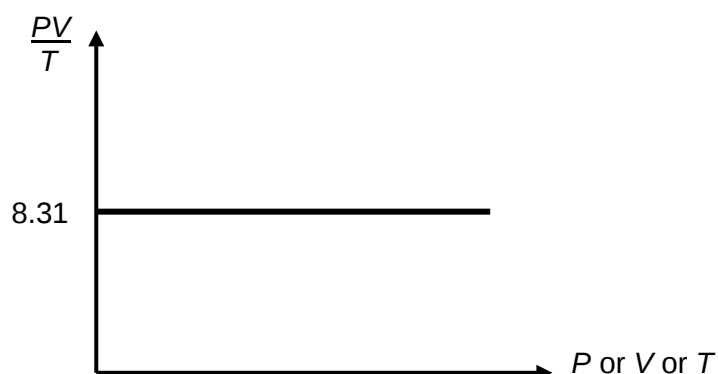
T = thermodynamic or absolute temperature in kelvin ($\text{K} = ^\circ\text{C} + 273$)

R = gas constant = $8.31 \text{ J K}^{-1} \text{ mol}^{-1}$

Therefore, for **1 mole** of ideal gas,

$$\frac{pV}{T} = R = 8.31 \text{ (constant)}.$$

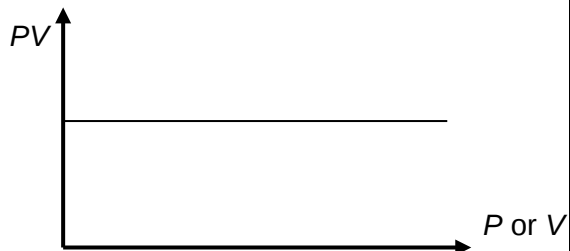
A graph of $\frac{pV}{T}$ against P or V or T can be plotted.



THE IDEAL GAS LAW

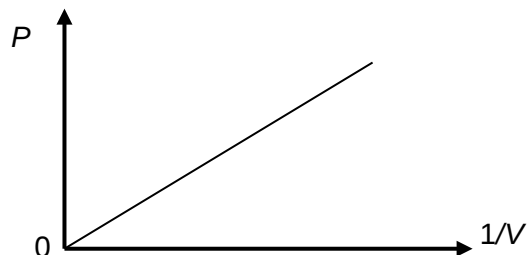
If **temperature is constant**, then

$$PV = nRT = \text{constant}$$



If **temperature is constant**, then

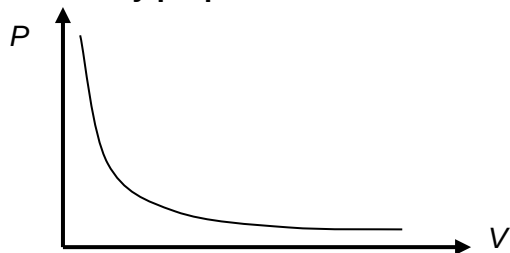
$$P = \frac{nRT}{V} = \frac{\text{constant}}{V}, \text{ so } P \propto \frac{1}{V}$$



If **temperature is constant**, then

$$P = \frac{nRT}{V} = \frac{\text{constant}}{V}, \text{ so}$$

P is **inversely proportional** to V .



In general, if **temperature is constant**,

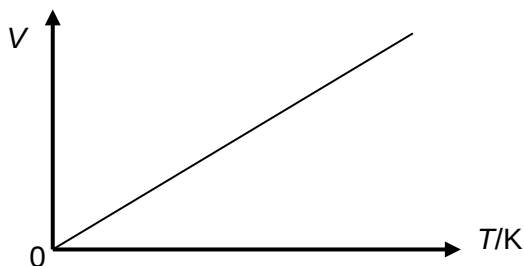
$PV = \text{constant}$ therefore,

$$P_1V_1 = P_2V_2 = \text{constant}$$

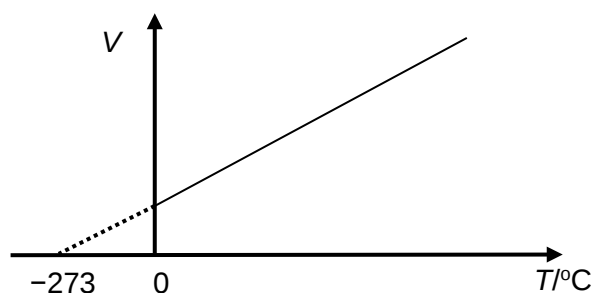
where subscripts 1 and 2 refer to two gaseous systems at the same temperature and containing the same number of moles of particles.

If **pressure is constant**, then

$$V = \frac{nRT}{P} = \frac{\text{constant}}{P} \times T, \text{ so } V \propto T$$



OR



In general, if **pressure is constant**, $\frac{V}{T} = \text{constant}$, therefore,

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} = \text{constant}$$

where subscripts 1 and 2 refer to two gaseous systems at the same pressure and containing the same number of moles of particles.

Exercise 8

1. At 338 K, pure PCl_5 gas present in a flask has a pressure of 25.5 kPa. At 480 K, this is completely dissociated into PCl_3 (g) and Cl_2 (g). Write a balanced equation for the reaction taking place in the flask. What is the pressure in the flask at 480 K?



Since pressure is directly proportional to absolute temperature,

$$\text{At 480 K, pressure of } \text{PCl}_5 (\text{g}) \text{ before dissociation} = \frac{480}{338} \times 25.5 = 36.2 \text{ kPa}$$

Since pressure is directly proportional to number of moles of gaseous particles,

$$\text{Pressure in the flask after complete dissociation} = 36.2 \times 2 = \underline{\underline{72.4 \text{ kPa}}}$$

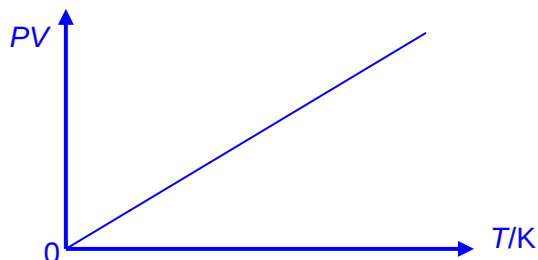
2. For a fixed amount of gas, show graphically how PV varies with T .

$$PV = nRT$$

For a fixed amount of gas: $n = \text{constant}$, $R = \text{constant}$

$$\text{Hence, } PV = kT$$

Graph will follow the shape of $y = mx$, where y -axis is PV and x -axis is T



Applications based on Ideal gas equation

The ideal gas equation can be applied for the following:

- (i) to determine the **relative molecular mass**, M_r of compounds in gaseous state.
- (ii) to determine the **density**, ρ of a gas.

(i) Determination of relative molecular mass (M_r) of compounds in the gaseous state

By noting down the mass (m) of the gas, the pressure (P), temperature (T) and volume (V) that the gas is subjected to and using this new form of Ideal Gas Equation shown below, we can find the relative molecular mass of the compound in its gaseous state.

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

(ii) Determination of density (ρ) of compounds in the gaseous state

If we know the relative molecular mass (M_r), pressure (p) and temperature (T) of the gas, we can also use this alternate form of the Ideal Gas Equation to find the density (ρ) of the compound in its gaseous state.

$$\rho = \frac{PM_r}{RT}$$

In reality, gases sometimes do not behave ideally. Real gases only behave similar to ideal gases when they are subjected to:

- **Low Pressure**
- **High Temperature**

At **high pressure or low temperature**, the assumptions would not be obeyed by these real gases.

An ideal gas is a gas, which obeys the Ideal Gas Equation and obeys the assumptions under all conditions.



***Scan me to view
a video on
experimental
determination of
relative
molecular mass
of gases***

Exercise 9

1. Chloroethene is a chemical used to make the polymer PVC. A sample of the gas containing 3.93 mol has a volume of 98.4 dm³ at 24 °C. What is the pressure of the gas?

$$PV = nRT$$

$$P = \frac{nRT}{V} = \frac{3.93 \times 8.31 \times (24 + 273)}{\frac{98.4}{1000}} = \underline{\underline{98.6 \text{ kPa}}}$$

2. In an experiment, 0.271 g of a liquid gave a volume of 30.2 cm³ on vaporisation at 15 °C and 96.9 kPa. What is the relative molecular mass of the liquid?

$$PV = nRT$$

$$PV = \frac{m}{M_r} RT$$

$$M_r = \frac{mRT}{PV} = \frac{0.271 \times 8.31 \times (15 + 273)}{(96.9 \times 1000) \times \frac{30.2}{1000000}} = \underline{\underline{222.32}}$$

3. What is the volume of 1 mole of methane gas at:
(a) 25 °C and 100 kPa?

The condition stated is identical to standard ambient temperature and pressure (SATP). Therefore, volume of 1 mole of methane gas = **24.8 dm³**

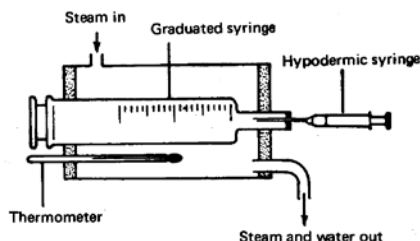
- (b) 0 °C and 100 kPa?

The condition stated is identical to standard temperature and pressure (STP). Therefore, volume of 1 mole of methane gas = **22.7 dm³**

Will 1 mole of hydrogen gas occupy a similar volume at the same condition above? Explain.

Yes. One mole of any gas (assuming it is behaving ideally) will occupy a similar volume under the same conditions. This is because the particles of an ideal gas do not interact with each other and have negligible volume (i.e. most of the volume occupied by a gas is empty space).

4. 0.12 g of a liquid hydrocarbon was injected into the graduated syringe as shown below:



The results are shown below:

Initial volume of air in graduated syringe = 10.00 cm³

Final volume of air and vapour in syringe = 53.25 cm³

Temperature of experiment = 100 °C

Atmospheric pressure = 100 kPa

- (a) Calculate the relative molecular mass of the hydrocarbon.

$$M_r = \frac{mRT}{PV} = \frac{0.12 \times 8.31 \times (100 + 273)}{(100 \times 1000) \times \left(\frac{53.25 - 10.00}{1000000}\right)} = \underline{86.00}$$

- (b) Would this method be suitable for liquids which boil above 80 °C?

No. Temperature is too close to boiling point of water. The vapour may not be completely vapourised.

- (c) What are the main sources of error in this experiment?

The calculation is based on the ideal gas law and assumes ideal behaviour.

The gas will be at relatively high pressure and low temperature and will not be approaching ideal behaviour. Molecular attractive forces and the actual volume occupied by the gas molecules may be significant.

The temperature and pressure are not measured with the same sensitivity as the volume readings.

Not all the liquid may be vaporised and the volume of gas measured is then less than the true value.

Some liquid can evaporate and be lost from the syringe nozzle, so the amount of liquid is reduced. (This will make the actual mass smaller than you think which increases the value of the molar mass – change numbers in a calculation to verify this).

- (d) What are the limitations of this method as a means of determining relative molecular masses?

Some molecular liquids may decompose at temperatures near their boiling point.

It only works with liquids that are highly volatile, i.e., those which evaporate easily and have low boiling points. It works less well for gases that deviate from ideal behaviour due to strong intermolecular forces of attraction.

Note that another instrument that can determine the molar mass of compounds is the **mass spectrometer**. Operation of this instrument is available in the chapter on atomic structure.

Enrichment reading: Dalton's law of partial pressure

Dalton's Law of partial pressures states that at constant temperature the total pressure exerted by a mixture of ideal gases in a fixed volume is equal to the sum of the individual pressures which each gas will exert if it alone occupies the same total volume. The partial pressure of a gas is the pressure it will exert if it is the only gas in the container.

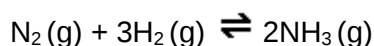
For a mixture of gases 1, 2, 3 ..., $p_{\text{tot}} = p_1 + p_2 + p_3 \dots$ where p_{tot} is the total pressure of all gases and p_1, p_2 etc. represents the partial pressures. The partial pressure ratio is the same as the percentage by volume ratio and the same as the mole ratio of gases in the mixture.

This means for a component gas **z**:

$$p_z = p_{\text{tot}} \times \frac{z \text{ mol}}{\text{total mol}} = p_{\text{tot}} \times \text{mole fraction of } z$$

Example 1

In the manufacture of ammonia, a mixture of nitrogen and hydrogen gases in a 1 : 3 ratio is passed over an iron/iron oxide catalyst at moderate temperature and pressure.



What are the partial pressures of nitrogen and hydrogen if the total pressure of the gases is 200 atm at the start of the reaction?

Answer:

The 1 : 3 N_2 : H_2 ratio means that nitrogen forms $\frac{1}{4}$ of the mixture, therefore

$$p_{\text{N}_2} = \frac{1}{4} \times 200 = 50 \text{ atm and}$$

$$p_{\text{H}_2} = p_{\text{tot}} - p_{\text{N}_2} = 150 \text{ atm (or from } \frac{3}{4} \times 200)$$

✂ Nature of Science: Collaboration

The progress of science depends on interactions within the scientific community — that is, the community of people and organizations that generate scientific ideas, test those ideas, publish scientific journals, organize conferences, train scientists, distribute research funds, etc. This scientific community provides the cumulative knowledge base that allows science to build on itself. It is also responsible for the further testing and scrutiny of ideas and for performing checks and balances on the work of community members.

In addition, much scientific research is collaborative, with different people bringing their specialized knowledge to bear on different aspects of the problem. For example, the three gas laws, Charles's law, Boyle's law, and Gay-Lussac's law, are combined in one law called the combined gas law.

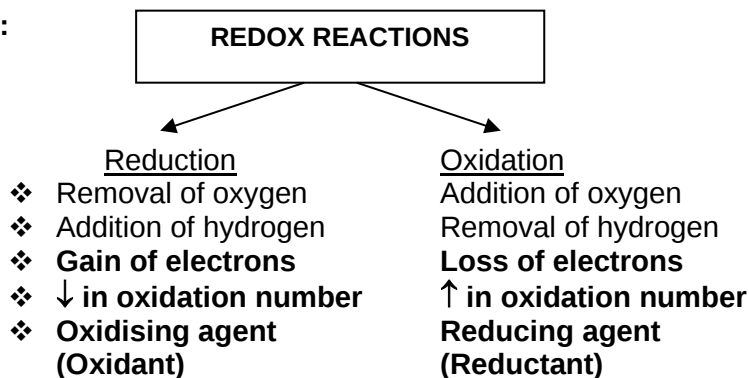
The addition of Avogadro's law to the combined gas law yields the ideal gas law.

Source: http://undsci.berkeley.edu/article/0_0_0/whatisscience_07

9.1 Introduction to oxidation and reduction (IB Syllabus Topic 9)

Redox reactions are **electron transfer** reactions where **reduction** and **oxidation** occur simultaneously.

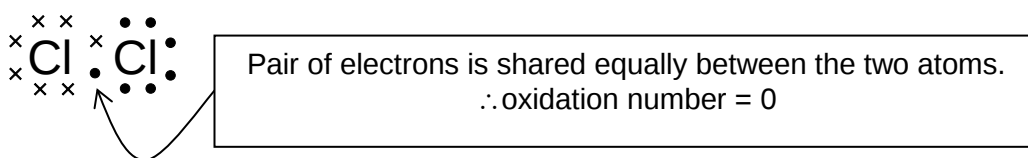
Definition:



Important rules for assigning oxidation number to elements and compounds.

1. Elements

The oxidation number of atoms in an element is **zero**. For example, O₂, S₈ and Mg.



2. Ions and Ionic compounds

(a) The oxidation number of a single ion is equal to the **charge** on the ion.

<u>Ion</u>	<u>Oxidation number</u>	<u>Ion</u>	<u>Oxidation number</u>
Na ⁺	+1	Cl ⁻	-1
Mg ²⁺	+2	O ²⁻	-2
Al ³⁺	+3	N ³⁻	-3

(b) In a polyatomic ion, the **sum of the oxidation number** of all the atoms is **equal to ionic charge**. For example, in SO₄²⁻,

The oxidation number of O is **-2** and the net charge of ion is **2-**.
Let the oxidation number of S be x.

$$\begin{aligned} x + 4(-2) &= -2 \\ x &= \mathbf{+6} \end{aligned}$$

(c) The **Roman numeral** in the naming of ionic compounds indicates the oxidation number of the atom. For example, iron(II) and chromate(VI) ions.

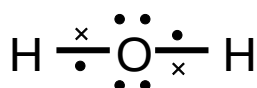
3. Covalent compounds

The oxidation numbers of the atoms are obtained by assuming the bonds are 'ionic' i.e.: the **more electronegative atom** (the atom with greater attraction for electron pairs in covalent bonds) is given the **negative** oxidation number and *vice versa*.

Useful rules:

	Oxidation number
Group 1 metals	+1
Group 2 metals	+2
Group 13 metals	+3
Hydrogen	+1 (−1 in metal hydrides eg NaH [Na ⁺ H [−]])
Oxygen	−2 (−1 in peroxides eg H ₂ O ₂)
Fluorine	−1

For example, in H₂O,



Oxidation state of H = **+1**
(Hydrogen "loses" 1 electron each to oxygen)

Oxidation state of O = **−2**
(Oxygen "attracts" two electrons from both hydrogens)

$$\Sigma(\text{oxidation states}) = 2(+1) + (-2) = 0$$

Exercise 10

What is the oxidation number of the elements in the following species?

1. chlorine in the perchlorate anion (ClO₄[−]),

Let the oxidation number of Cl be x .

$$x + 4(-2) = -1 \Rightarrow x = \underline{+7}$$

2. manganese in MnO₄[−],

Let the oxidation number of Mn be x .

$$x + 4(-2) = -1 \Rightarrow x = \underline{+7}$$

3. chromium in Cr₂O₇^{2−},

Let the oxidation number of Cr be x .

$$2x + 7(-2) = -2 \Rightarrow x = \underline{+6}$$

4. oxygen in OF₂,

Let the oxidation number of O be x .

$$x + 2(-1) = 0 \Rightarrow x = \underline{+2} \text{ (Note that F is more electronegative than O and should take a negative oxidation number)}$$

5. iodine in ICl?

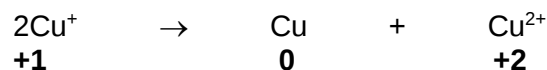
Let the oxidation number of I be x .

$$x + (-1) = 0 \Rightarrow x = \underline{+1} \text{ (Note that Cl is more electronegative than I and should take a negative oxidation number)}$$

Disproportionation reactions

Disproportionation reaction is a redox reaction whereby **an element undergoes both oxidation and reduction simultaneously**. The oxidation state of that element increases and decreases at the same time.

Worked example 1

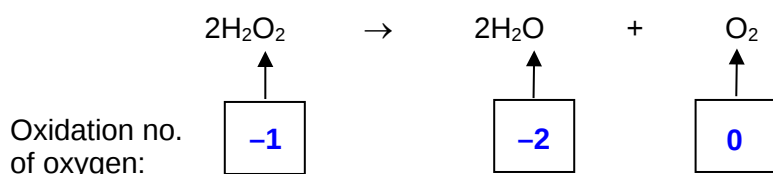


Oxidation: $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$ (+1 $\rightarrow$ +2)

Reduction: $\text{Cu}^+ \rightarrow \text{Cu}$ (+1 $\rightarrow$ 0)

Copper(I) ion is not stable and **disproportionates** spontaneously to form **copper atoms** and **copper(II) ions**.

Worked example 2



The oxidation number of **oxygen** changes from -1 in H_2O_2 to -2 in H_2O and 0 in O_2 . H_2O_2 has undergone disproportionation as it undergoes reduction to H_2O and oxidation to O_2 .

Redox equations

Common Oxidising and Reducing Agents

Oxidising Agents	Reduced to
MnO_4^- (aq) manganate(VII) purple	Mn^{2+} (aq) (under acidic conditions) manganese(II) ion pale pink / colourless
MnO_4^- (aq) manganate(VII) purple	MnO_2 (s)(under neutral/ alkaline conditions) manganese dioxide brown ppt
$\text{Cr}_2\text{O}_7^{2-}$ (aq) (acidic) dichromate(VI) orange	Cr^{3+} (aq) chromium(III) green
IO_3^- (aq) iodate(V) colourless	I_2 (aq) iodine brown
I_2 (aq) iodine brown	I^- (aq) iodide colourless
Fe^{3+} (aq) iron(III) pale yellow	Fe^{2+} (aq) iron(II) pale green
H_2O_2 (aq) hydrogen peroxide colourless	H_2O (l) water colourless
NO_2^- (aq) nitrite colourless	NO (g) Nitrogen monoxide (colourless) NO can be easily oxidised to NO_2 (brown gas)

Reducing Agents	Oxidised to
$\text{C}_2\text{O}_4^{2-}$ (aq) ethanedioate	CO_2 (g) carbon dioxide gas
$\text{S}_2\text{O}_3^{2-}$ (aq) thiosulfate	$\text{S}_4\text{O}_6^{2-}$ (aq) tetrathionate
H_2O_2 (aq) hydrogen peroxide	O_2 (g) oxygen gas
NO_2^- (aq) nitrite	NO_3^- (aq) nitrate (V)
I^- (aq) iodide (colourless)	I_2 (aq) iodine (brown)
Fe^{2+} (aq) iron(II) (light green)	Fe^{3+} (aq) iron(III) (pale yellow)

Note:

H_2O_2 and NO_2^- are both oxidising and reducing agents.

Whether it is acting as an oxidising or a reducing agent would depend on the conditions of the reaction (i.e. the identity of other reacting species).

The following are some important redox half-equations that you will encounter in your practicals:

Reduction reactions	Oxidation reactions
$\text{MnO}_4^- + 8 \text{H}^+ + 5 \text{e}^- \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O}$	$\text{C}_2\text{O}_4^{2-} \rightarrow 2 \text{CO}_2 + 2 \text{e}^-$
$\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O}$	$2 \text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2 \text{e}^-$
$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}$	$\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^-$
$\text{I}_2 + 2 \text{e}^- \rightarrow 2 \text{I}^-$	$2 \text{I}^- \rightarrow \text{I}_2 + 2 \text{e}^-$
$\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$	$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$

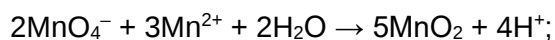
Potassium manganate(VII)

Potassium manganate(VII) is not a primary standard. It is difficult to obtain the substance perfectly pure and completely free from manganese dioxide. Moreover, ordinary distilled water is likely to contain reducing substances (traces of organic matter, etc.) which will react with the potassium manganate(VII) to form manganese(IV) oxide.

The presence of the latter is a problem because it catalyses the auto-decomposition of the manganate(VII) solution on standing. The decomposition:



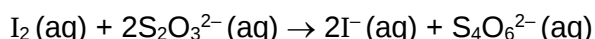
is catalysed by solid manganese dioxide. Manganate(VII) is inherently unstable in the presence of manganese(II) ions:



This reaction is slow in acid solution, but is very rapid in neutral solution.

Sodium thiosulfate

Sodium thiosulfate is used to estimate iodine by a redox titration. Sodium thiosulfate is a reducing agent and it is able to reduce iodine to iodide ions:



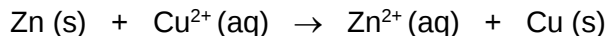
When sodium thiosulfate is added to an aqueous solution of iodine the brown colour of the iodine fades. Near the end-point, a few drops of starch solution is added. A blue/black colour is produced due to the formation of a blue-black starch-iodine complex. With continued addition of sodium thiosulfate, the blue/black colour eventually disappears at the end point because all the iodine has reacted.



Balancing redox equation

Half equations method

Generally all equations are balanced with respect to the number of atoms (mass balance) as well as charges, e.g. the ionic equation for the displacement of copper(II) ions by zinc metal:



Charges on both sides of the equations are 2+.

In balancing redox reactions like:



It would be difficult to balance both the charges and atoms on both sides of the equation just by observation. The following method can be used to balance redox reactions.

General rules:

1. Identify the species undergoing oxidation and reduction by checking oxidation numbers.
2. Write an unbalanced half-equation for oxidation and reduction.
3. Balance all elements other than H and O first.
4. Balance oxygen by adding H_2O .
5. For **acidic** conditions, balance hydrogen by adding H^+ .
6. Balance the charges by adding electrons to the side with excess positive charge.
7. Balance the overall equation by adding the two half-equations such that the number of electrons is the same.

Worked example 1

Balance the redox reaction between acidified potassium manganate(VII) and iron(II) sulfate using the half-equation method.

Answer:



Balanced equation:

Discussion:

If a solution of iron(II) sulfate is **titrated** with acidified potassium manganate(VII), what is:

(i) the indicator required?

No

(ii) the end point colour change?

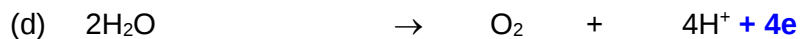
Pale green (or colourless if the concentration of Fe^{2+} is low)
to orange (due to yellow colour of Fe^{3+} and pale pink colour of Mn^{2+})



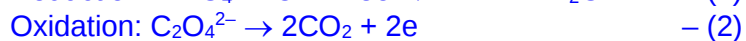
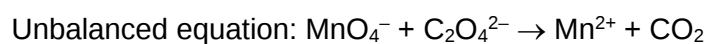
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a video on
redox titration
between Fe^{2+}
and MnO_4^-

Exercise 11

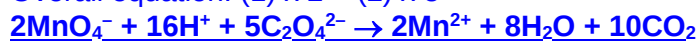
1. Fill in the number of electrons needed to balance the following half equations:



2. Balance the redox reaction between acidified potassium manganate(VII) and ethanedioic acid $(\text{COOH})_2$ using the half-equation method.



Overall equation: (1) $\times 2$ + (2) $\times 5$



Exercise 12

1. What are the oxidation numbers of

(a) iodine in KIO_3 ,

Let the oxidation number of I be x .

$$x + (+1) + 3(-2) = 0 \Rightarrow x = \underline{+5}$$

(b) iodine in KIO ,

Let the oxidation number of I be x .

$$x + (+1) + (-2) = 0 \Rightarrow x = \underline{+1}$$

(c) sulfur in Na_2SO_3 ,

Let the oxidation number of S be x .

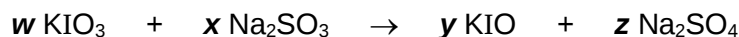
$$x + 2(+1) + 3(-2) = 0 \Rightarrow x = \underline{+4}$$

(d) sulfur in Na_2SO_4 ?

Let the oxidation number of S be x .

$$x + 2(+1) + 4(-2) = 0 \Rightarrow x = \underline{+6}$$

(e) With the help of your answers above, balance the following equation:



Oxidation number of iodine decreased from +5 in KIO_3 to +1 in KIO . Hence, 4 electrons were gained when KIO_3 was reduced to KIO .

Oxidation number of sulfur increased from +4 in Na_2SO_3 to +6 in Na_2SO_4 . Hence, 2 electrons were lost when Na_2SO_3 was oxidised to Na_2SO_4 .

For a redox reaction, number of electrons gained = number of electrons lost.

Hence, 1 mole of KIO_3 reacts with 2 moles Na_2SO_3 of to form 1 mole of KIO and 2 moles of Na_2SO_4 .

$$\underline{w = 1, x = 2, y = 1, z = 2}$$

2. Determine the coefficient **a to e** in the equation below using the oxidation number method:



Oxidation number of nitrogen decreased from +5 in HNO_3 to +2 in NO. Hence, 3 electrons were gained when HNO_3 was reduced to NO.

Oxidation number of sulfur increased from -2 in H_2S to 0 in S. Hence, 2 electrons were lost when H_2S was oxidised to S.

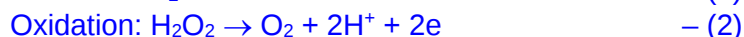
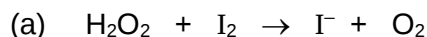
For a redox reaction, number of electrons gained = number of electrons lost.

Hence, 2 moles of HNO_3 reacts with 3 moles H_2S of to form 2 moles of NO and 3 moles of S.

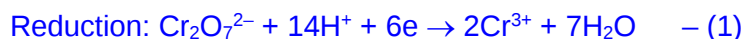
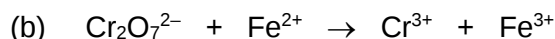


$$\mathbf{a = 2, b = 3, c = 3, d = 4, e = 2}$$

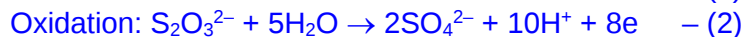
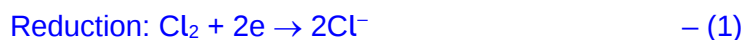
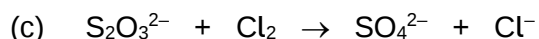
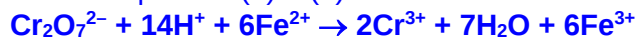
3. Balance the following redox equations under acidic conditions:



Overall equation: (1) + (2)



Overall equation: (1) + (2) x 6



Overall equation: (1) x 4 + (2)



Redox titration

Calculations for redox titrations are identical to that of acid–base titrations. Completion of a redox reaction may be shown by complete consumption of a reactant, for example, when a reducing agent is added to an acidified solution of manganate(VII) ions. The appearance of excess reagent (the first permanent colour when manganate(VII) ions is added to an acidified solution of a reducing agent) marks the end point of titration.

Worked example 1

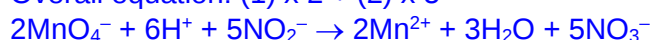
Sodium nitrite, NaNO_2 is used as a preservative in meat products such as frankfurters. In an acidic solution, nitrite ions are converted to nitrous acid, HNO_2 , which reacts with the manganate(VII) ions. A 1.00 g sample of a water-soluble solid containing NaNO_2 was dissolved in dilute H_2SO_4 and titrated with $0.0100 \text{ mol dm}^{-3}$ aqueous KMnO_4 solution. In the reaction, NO_2^- is oxidised to NO_3^- . The titration required 12.15 cm^3 of the KMnO_4 solution. Calculate the percentage by mass of NaNO_2 in the 1.00 g sample.

Step 1

Determine the reacting ratio between NO_2^- and MnO_4^- by balancing the redox equation:



Overall equation: $(1) \times 2 + (2) \times 5$



Step 2

$$\text{Amount of } \text{KMnO}_4 = \frac{12.15}{1000} \times 0.0100 = 1.22 \times 10^{-4} \text{ mol}$$

From the reacting ratio above,

$$\text{Amount of } \text{NO}_2^- = \frac{5}{2} \times (1.22 \times 10^{-4}) = 3.04 \times 10^{-4} \text{ mol}$$

$$\text{Mass of } \text{NaNO}_2 = (3.04 \times 10^{-4}) \times (22.99 + 14.01 + 16.00 \times 2) = 0.0210 \text{ g}$$

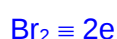
$$\% \text{ mass of } \text{NaNO}_2 = \left(\frac{0.0210}{1.00} \right) \times 100 \% = \underline{\underline{2.10 \%}}$$

Exercise 13

1. Sodium thiosulfate is a reducing agent commonly used to react with Br_2 . 0.050 mol of bromine reacted with 25.0 cm³ of 0.50 mol dm⁻³ of sodium thiosulfate solution. The oxidation state of S in $\text{S}_2\text{O}_3^{2-}$ is +2. Calculate the oxidation state of sulfur in the reaction product.

$$\text{Amount of } \text{S}_2\text{O}_3^{2-} = \frac{25.0}{1000} \times 0.50 = 1.25 \times 10^{-2} \text{ mol}$$

$$\text{Amount of } \text{Br}_2 \text{ reacted} = 0.050 \text{ mol}$$

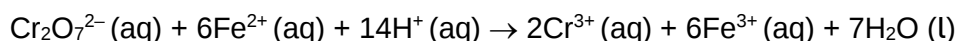


$$\text{Hence, } 4\text{Br}_2 \equiv \text{S}_2\text{O}_3^{2-} \equiv 8\text{e}^-$$

1 mole of $\text{S}_2\text{O}_3^{2-}$ loses 8 moles of electrons.

$$\text{Oxidation state of sulfur in the reaction product} = (+2) - (-4) = \underline{+6}$$

2. Hydrated iron(II) sulfate has the formula $\text{FeSO}_4 \cdot x\text{H}_2\text{O}$. An experiment was conducted to determine x, the number of moles of water of crystallization in hydrated iron(II) sulfate. 101.2 g of hydrated iron(II) sulfate was dissolved in 500 cm³ of water. 20.0 cm³ of this solution reacts completely with 24.00 cm³ of 0.100 mol dm⁻³ dichromate(VI) solution. Calculate the value of x. The equation for the reaction is shown below.



$$\text{Amount of } \text{Cr}_2\text{O}_7^{2-} \text{ reacted} = \frac{24.00}{1000} \times 0.100 = 2.40 \times 10^{-3} \text{ mol}$$

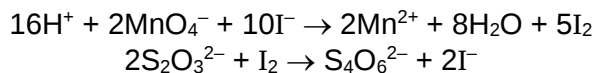
$$\text{Amount of } \text{Fe}^{2+} \text{ reacted in } 20.0 \text{ cm}^3 = (2.40 \times 10^{-3}) \times 6 = 1.44 \times 10^{-2} \text{ mol}$$

$$\text{Amount of } \text{Fe}^{2+} \text{ present in } 500 \text{ cm}^3 = \frac{500}{20} \times (1.44 \times 10^{-2}) = 0.360 \text{ mol}$$

$$\text{Relative molecular mass of } \text{FeSO}_4 \cdot x\text{H}_2\text{O} = \frac{101.2}{0.360} = 281.11$$

$$n = \frac{288.11 - 55.85 - 32.07 - (16.00 \times 4)}{(1.01 \times 2) + 16.00} \approx \underline{7} \text{ (nearest integer)}$$

3. Potassium manganate(VII), KMnO_4 , oxidises potassium iodide, KI , to liberate iodine, I_2 . The iodine liberated can be titrated with aqueous sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$. From the results obtained, the concentration of potassium manganate(VII) solution can be calculated. The equations for the reactions are shown below.



In the experiment, the iodine liberated from 25.0 cm^3 of potassium manganate(VII) requires 26.20 cm^3 of $0.500 \text{ mol dm}^{-3}$ sodium thiosulfate for complete reaction. Using the equations and the titration results, calculate the concentration of the potassium manganate(VII) solution.

$$\text{Amount of } \text{S}_2\text{O}_3^{2-} = \frac{26.20}{1000} \times 0.500 = 1.31 \times 10^{-2} \text{ mol}$$

$$\text{Amount of } \text{I}_2 = \frac{1}{2} \times (1.31 \times 10^{-2}) = 6.55 \times 10^{-3} \text{ mol}$$

$$\text{Amount of } \text{MnO}_4^- = \frac{2}{5} \times (6.55 \times 10^{-3}) = 2.62 \times 10^{-3} \text{ mol}$$

$$\text{Concentration of } \text{KMnO}_4 = \frac{2.62 \times 10^{-3}}{\frac{25.0}{1000}} = \underline{\underline{0.105 \text{ mol dm}^{-3}}}$$

Winkler Method

Environmental application of redox chemistry: Biochemical Oxygen Demand and Winkler Method

Biochemical Oxygen Demand (BOD)

Biochemical Oxygen Demand (BOD), units of ppm (parts per million) refers to the amount of oxygen that would be consumed if all the organic matters were oxidized in a sample of water at a particular temperature over a period of 5 days.

The first step in measuring BOD is to obtain 2 samples of equal volumes of water from the area to be tested and dilute each specimen with a known volume of distilled water which has been thoroughly shaken to ensure oxygen saturation. After this, Winkler method is used to determine the concentration of dissolved oxygen of the first sample. The second sample is then sealed and placed in darkness and tested 5 days later. BOD is then calculated by subtracting the concentration of dissolved oxygen in the second sample from the first sample, which gives the concentration of oxygen consumed by the oxidation of organic matter in the sample.

The range of possible readings can vary considerably:

Example source	BOD (ppm)
Pure water	Less than 1
Untreated	350
Effluent from a brewery	500
Water from an abattoir	3000

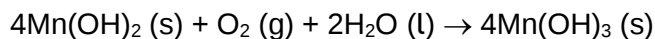
Aquatic life can only survive in fresh water because of the oxygen dissolved in it. Hence it is important to monitor the dissolved oxygen concentration. If this is less than 5 mg dm^{-3} then most species of fish cannot survive. The solubility of oxygen in water is temperature dependent. At 273 K (0°C) the solubility is 14.6 mg dm^{-3} (14.6 ppm) and 7.6 mg dm^{-3} (7.6 ppm) at 293 K (20°C). Solubility of oxygen in water decreases with increasing temperature. It was observed that a high level of dissolved oxygen is a good indication of a low level of pollution.



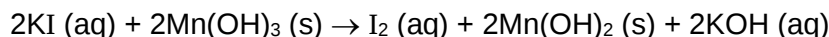
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Winkler
Method*

Winkler Method

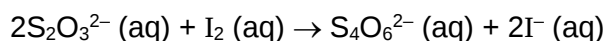
One of the most accurate methods for measuring dissolved oxygen concentrations in water is the Winkler method, which is based on a series of redox reactions. Under alkaline conditions manganese(II) ions are rapidly oxidized to manganese(III) by dissolved oxygen, producing a pale brown precipitate of manganese(III) hydroxide, Mn(OH)_3 .



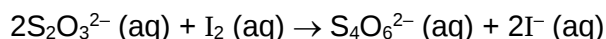
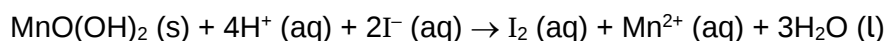
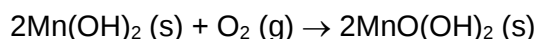
A sample of river or stream water is shaken with excess alkaline manganese(II) ions, and the resulting pale brown precipitate is then reacted with an excess of potassium iodide, which it oxidises to iodine.



The amount of iodine is then determined by titration with sodium thiosulfate of known concentration. Starch is used to show the end point.



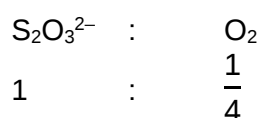
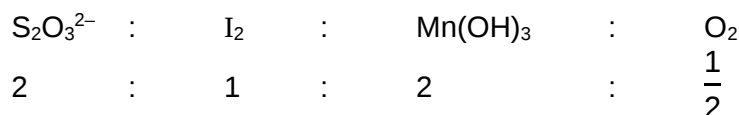
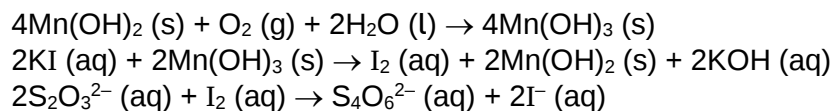
The Winkler method can also be carried out under acidic conditions, according to the following equations:



Worked example 1

Using the Winkler method, it was found that a 25.0 cm³ of a sample of river water at 293 K required 25.0 cm³ of 0.00100 mol dm⁻³ sodium thiosulfate solution to react with the iodine produced.

- (a) Calculate the concentration of dissolved oxygen in parts per million, ppm. (ppm is defined as mg dm⁻³)



$$\text{Amount of S}_2\text{O}_3^{2-} = \frac{25.0}{1000} \times 0.00100 = 2.50 \times 10^{-5} \text{ mol}$$

$$\text{Amount of O}_2 = \frac{1}{4} \times (2.50 \times 10^{-5}) = 6.25 \times 10^{-6} \text{ mol}$$

$$\text{Mass of dissolved O}_2 = 6.25 \times 10^{-6} \times 32.00 = 0.200 \text{ mg in } 25.0 \text{ cm}^3 \text{ of water.}$$

Hence, concentration of dissolved O₂ = 8.00 mg dm⁻³ (or ppm).

- (b) Hence deduce the BOD (in ppm) of the water sample, assuming the maximum solubility of oxygen in water is 9.00 ppm at 293 K.

$$\text{Oxygen used to oxidise organic matter, BOD} = 9.00 - 8.00 = 1.00 \text{ ppm}$$

(This BOD value shows excellent water quality, refer to table above and compare with BOD value of other water sources)

Summary of Stoichiometric Relationships

1.1 Introduction to the particulate nature of matter and chemical change (IB syllabus Topic 1)

- The study of quantitative relationship between chemical formulas and chemical equations is known as stoichiometry.
- A balanced chemical equation shows equal numbers of atoms of each element on each side of the equation. Equations are balanced by placing coefficient in front of the chemical formulas.

1.2 The mole concept

- The mole (mol) is a chemist's measure of the amount of substance.
- One mole (1 mol) of a chemical species contains the same number of particles as the atoms in 12 g of carbon-12.
- The Avogadro constant (L or N_A) has the value $6.02 \times 10^{23} \text{ mol}^{-1}$.
- The relative atomic mass of an element, A_r , gives the ratio of the mass of the atom to the mass of one atom of carbon-12 (taken exactly as 12 units). A_r has no units. The relative molecular mass, M_r , is defined in a similar way.
- The molar mass is the mass of one mole of an entity. It has units of grams per mol (g mol^{-1}).

$$\text{Hence, amount of a substance (mol)} = \frac{\text{mass of substance (g)}}{\text{molar mass (g mol}^{-1}\text{)}}.$$

- The empirical formula is the simplest whole number (integer) ratio of the atoms in a compound. Empirical formulas can be determined from the masses of the atoms present in the compound.
- The molecular formula is the actual formula of a compound. It is a multiple of the empirical formula.

1.3 Reacting masses and volumes

- A limiting reactant is completely used up in a reaction. When it is used up, the reaction stops, which limits the quantities of products formed.
- The theoretical yield of a reaction is the quantity of products calculated to form when all of the limiting reactant reacts. The actual yield is always less than the theoretical yield. The percentage yield gives the ratio of the actual yield to the theoretical yields.
- The concentration of a solution is measured in g dm^{-3} or mol dm^{-3} . A 1 mol dm^{-3} solution contains one mole (of solute) in one dm^3 of solution.
- Solutions of known concentrations can be formed by weighing out the solute and dissolving it in a known volume or by the dilution of concentrated solution (a stock solution). Adding solvent to the solution (the process of dilution) decreases the concentration of the solute without changing the number of moles in the solution.

$$M_1 \times V_1 = M_2 \times V_2$$

- Titrations can be used to determine concentrations, percentage purity and formulas.
- A typical acid-base reaction involves the neutralization reaction between hydrogen and hydroxide ions: $\text{H}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{H}_2\text{O} (\text{l})$.
- Other titrations include various redox titrations (including iodine) and precipitation titrations (including silver nitrate).
- Precipitation reactions are those in which an insoluble product called a precipitate is formed.

- One mole of a gas occupies 22.7 dm³ at standard temperature and pressure (273 K and 100 kPa).
- Avogadro's law states that equal volumes of all gases, under the same conditions of temperature and pressure, contain the same number of molecules.
- The molar mass of a gas can be found by weighing a known volume of gas. The molar mass of a volatile liquid (low b.p.) can be found by converting a weighed amount of it into a vapour (a gas near its b.p.) and measuring its volume.
- The molecules in a gas are in a state of constant random motion.
- In an ideal gas, there are no intermolecular or interatomic forces of attraction and therefore no tendency to liquefy.
- An ideal gas is a hypothetical state of matter, in which the gas particles can be pictured as a collection of tiny, hard inelastic spheres in constant motion.
- The zero on the absolute or thermodynamic temperature scale is the temperature at which the volume of an ideal gas is zero. Absolute zero is approximately -273°C.
- The ideal gas law is $pV = nRT$, where n is the amount of gas and R is the gas constant.
- Real gases do not obey the ideal gas law exactly.
- At high pressures and low temperatures, intermolecular forces start operating strongly between molecules of gas as they come close to each other.
- Gas pressure is due to the collisions of the atoms or molecules against the walls of the container.
- The Maxwell-Boltzmann distribution of molecular speeds shows that most molecules have kinetic energies near the average (root mean square), with some molecules having kinetic energies significantly greater and smaller than average.

9.1 Introduction to redox and redox titration (IB syllabus Topic 9)

- Oxidation is the gain of oxygen, the loss of hydrogen, the loss of electrons or an increase in oxidation number. Reduction is the converse.
- An element has an oxidation number of zero.
- An ion of an element has an oxidation number equal to its charge.
- A change in oxidation number of one unit represents the transfer of one electron from one atom to another.
- The oxidation state of an element is written using a Roman number.
- Redox reactions can be represented by two half equations: one for oxidation and one for reduction.
- The equation for a redox reaction is obtained by combining the half-equations for the oxidising agent and the reducing agent.

Reference

1. Bylikin, S.; Horner, G.; Murphy, B.; Tarcy, D.: Oxford IB Diploma Programme 2014 Edition Chemistry Course Companion; Oxford University Press: Oxford, 2014.