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PEARSON BACCALAUREATE

Chemistry

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Supporting every learner across the IB continuum

essentials

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Topic 1: Stoichiometric relationships

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.

Understanding: Atoms of different elements combine in fixed ratios to form compounds, which have different properties from their component elements.

- **Elements**:
  - cannot be changed into simpler substances by chemical reactions
  - are identified by their name and **chemical symbol**, e.g.
    helium has the symbol He
    carbon has the symbol C
  - are organized in the **periodic table** based on their **atomic number**, chemical properties, and the number of **valence electrons**.

There are over 100 chemical elements, and about 90 of these occur naturally.

Hints for success: Section 5 in the IB data booklet alphabetically lists the elements and their chemical symbols.

- **Atoms**:
  - are the simplest unit of an element that can exist on its own
  - are regarded as the building blocks of matter as all substances are made up of atoms of one or more element.

The atoms of one element are all the same but are different to atoms of other elements.

- **Compounds**:
  - are substances that contain two or more elements
  - are made when the atoms of different elements **bond**
  - have fixed ratios of the **component** elements
  - are described by **chemical formulas** that use the symbols of the elements in the compound, e.g. glucose has the chemical formula $C_6H_{12}O_6$, so a unit of glucose contains 6 carbon atoms, 12 hydrogen atoms and 6 oxygen atoms
  - have different chemical and physical properties from the elements they are made from, e.g. sodium chloride (NaCl) is made from sodium (Na) and chlorine (Cl_2):

    $2Na + Cl_2 \rightarrow 2NaCl$

Subject vocabulary

physical properties a property of a substance that can be measured without it changing into another substance. Melting points, boiling points, appearance, and density are examples of physical properties

chemical properties a property of a substance that becomes evident when it reacts and changes into another substance. Acidity, reactivity with water and enthalpies of reactions are examples of chemical properties

element a substance that cannot be broken down into a simpler substance by chemical means

chemical symbol a one-or two-letter representation of an element's name

periodic table a table that organizes the elements by increasing atomic number and the number of valence electrons

atomic number defined as the number of protons in the nucleus. It has the symbol *Z*

valence electrons the electrons that are in the outermost level of an atom

atom the smallest unit of an element that can exist on its own

compound a pure substance that is made up of one or more elements that are present in a fixed ratio

bond (as a verb) be held together by strong attractive forces

chemical formula a shorthand representation of a compound. It uses element symbols and subscripts to show how many atoms of each element are in the compound

General vocabulary

component one part of the whole

	Na	Cl_2	NaCl
Appearance	Silver metal	Green gas	White solid
Chemical reactivity	Very reactive	Very reactive	Not reactive
Physical properties	Low melting point Conducts electricity	Low boiling point Does not conduct electricity	High melting point Solid does not conduct electricity

Skill: Deduction of chemical equations when reactants and products are specified.

- **Chemical equations**:
  - use chemical formulas to describe a **chemical reaction**
  - show **reactants** changing to **products**
  - must be **balanced**, i.e. both sides of the equation must have the same number of each atom, e.g.

$CH_4 + 2O_2$	→	$CO_2 + 2H_2O$
Reactants		*Products*
1 carbon atom		1 carbon atom
4 hydrogen atoms		2 × 2 = 4 hydrogen atoms
2 × 2 = 4 oxygen atoms		2 + 2 = 4 oxygen atoms

- **Stoichiometric coefficients**:
  - are the numbers in front of the reactants and products in a balanced equation
  - give the relative amounts of each element or compound that react and the relative amounts of each element or compound that are formed.

Worked example

Deduce the chemical equation that represents the reaction between ethanol (C_2H_5OH) and oxygen (O_2) to give carbon dioxide (CO_2) and water (H_2O).

Solution

Start the chemical equation by writing down the reactants and products in the reaction with an arrow between them.

$C_2H_5OH + O_2 \rightarrow CO_2 + H_2O$

The number of carbon atoms can be balanced by putting a 2 in front of the CO_2 and the number of hydrogen atoms can be balanced by putting a 3 in front of the H_2O.

$C_2H_5OH + O_2 \rightarrow 2CO_2 + 3H_2O$

The right side now contains seven oxygen atoms and the left side contains three oxygen atoms. The oxygen atoms can be balanced by putting a three in front of the O_2 to give seven oxygen atoms on both sides.

$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$

Skill: Application of the state symbols (s), (l), (g), and (aq) in equations.

- **States of matter**:
  - are the different states in which substances can exist, depending on temperature and pressure: **solid** (s), **liquid** (l), or **gas** (g)

Subject vocabulary

chemical equation uses chemical formulas to show what happens in a chemical reaction

chemical reaction a process in which one set of substances is turned into another set of substances

reactants the substances that are turned into other substances in a chemical reaction. Reactants appear on the left of the arrow in a chemical equation

products the substances that are made from other substances in a chemical reaction. Products appear on the right of the arrow in a chemical equation

balanced equation a chemical equation in which the same number of atoms of each element are present on the reactant and product sides of the equation

stoichiometric coefficients the numbers that are written in front of the chemical formulas in a balanced equation

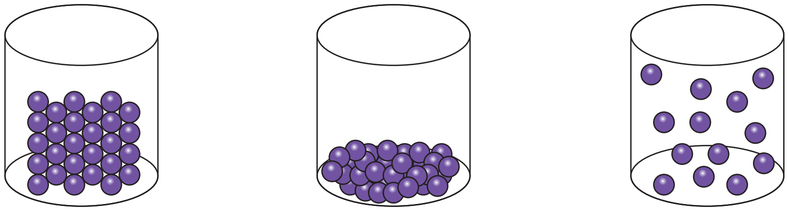
states of matter the different ways that substances can exist. Solids, liquids, and gases are the three states of matter that are most common

solid a state of matter in which the substance particles are held in fixed positions. A solid has a fixed shape and fixed volume

liquid a state of matter in which the substance particles are able to move. A liquid does not have a fixed shape but it does have a fixed volume

gas a state of matter in which the substance particles are able to move independently and are spread out. A gas does not have a fixed shape or fixed volume

- include **aqueous solutions** (aq), which are made when a substance is dissolved in water.



solid	liquid	gas
particles close together	particles more spaced	particles spread out
particles cannot move	particles can move	particles move freely
fixed shape	no fixed shape	no fixed shape
fixed volume	fixed volume	no fixed volume

increasing temperature

→

increasing kinetic energy of particles

Figure 1.1 *Representation of the arrangement of the particles of the same substance in the solid, liquid, and gas states.*

Worked example

Lithium (Li) reacts with water (H_2O) at room temperature and pressure to give lithium hydroxide (LiOH) and hydrogen (H_2). Write a balanced equation for this reaction that includes state symbols.

Solution

The balanced equation is $2Li + 2H_2O \rightarrow 2LiOH + H_2$.

At room temperature and pressure lithium is a solid, water is a liquid, and hydrogen is a gas. Lithium hydroxide is soluble in water so it will dissolve and be in an aqueous solution.

Including state symbols the balanced equation is
$2Li(s) + 2H_2O(l) \rightarrow 2LiOH(aq) + H_2(g)$.

Skill: Explanation of observable changes in physical properties and temperature during changes of state.

- Substances can change **reversibly** between different states of matter if they are heated or cooled.

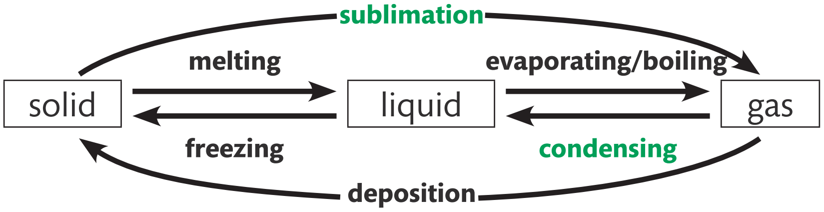


Figure 1.2 *The reversible changes that happen between different states of matter.*

- **Vaporization**:
  - is the change from liquid to gas
  - is called **evaporation** when the change happens at the surface of the liquid at temperatures below the boiling point of the liquid
  - is called **boiling** when the change happens throughout the liquid at temperatures at or above the boiling point.

Subject vocabulary

aqueous solution a solution that is formed by dissolving a substance in water

sublimation the change of state that occurs when a solid changes directly into a gas

condensing the change of state that occurs when a gas changes into a liquid

vaporization the change of state that occurs when a liquid changes into a gas. There are two types of vaporization: boiling and evaporation

evaporation the change of state that occurs when a liquid changes into a gas at a temperature below the boiling point. Evaporation occurs at the surface of the liquid

boiling the change of state that occurs when a liquid changes into a gas when it has been heated to the boiling point. Boiling occurs throughout the liquid

General vocabulary

reversibly changes that happen in one direction can be reversed and the opposite changes happen in the other direction

Skill: Explanation of observable changes in physical properties and temperature during changes of state.

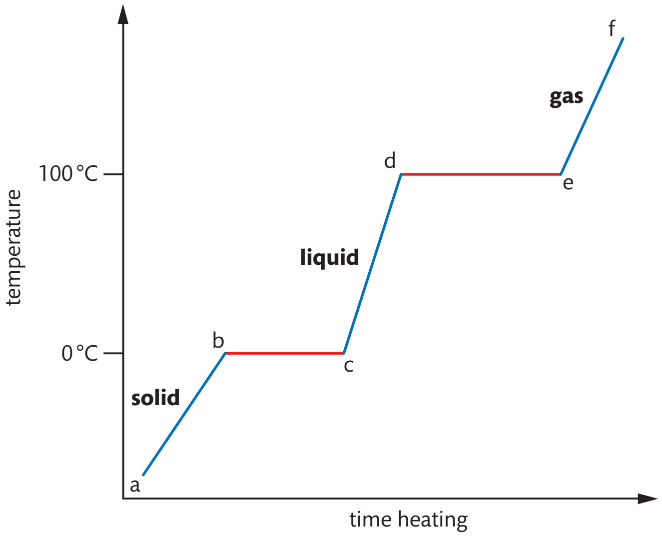


Figure 1.3 *Temperature changes that occur when solid water is heated.*

Worked example

Explain the changes that are occurring in the graph shown in Figure 1.3.

Solution

As the solid water (ice) is heated the temperature increases as the average kinetic energy of the water particles increases.

When the temperature reaches 0 °C at b in Figure 1.3, the temperature remains constant even though extra heat is being added. Instead of increasing the kinetic energy of the water particles the heat is overcoming the attractive forces between the water molecules in the solid ice.

When all the attractive forces between the solid water molecules have been overcome the solid water particles are able to move. The solid has melted and become a liquid.

Further heating of the liquid water (from c) increases the kinetic energy of the liquid water particles and increases the temperature.

When the temperature reaches 100 °C (at d) it remains constant even though extra heat is being added. Instead of increasing the kinetic energy of the water particles the heat is overcoming the attractive forces between the molecules in the liquid.

When all the attractive forces between the liquid water molecules have been overcome the liquid water particles are able to move independently. The liquid has boiled and become a gas.

Understanding: Mixtures contain more than one element and/or compound that are not chemically bonded together and so **retain** their individual properties.

- A **mixture** is a combination of two or more substances that are not chemically bonded.

  For example, air is a mixture that contains different gases: nitrogen (N_2), oxygen (O_2), carbon dioxide (CO_2), and water (H_2O).

Synonym

retain .... keep

Subject vocabulary

mixture a combination of two or more substances that are not chemically bonded to each other

- Because they are not chemically bonded, substances in a gaseous mixture have the same chemical and physical properties as the pure substances.

  For example, nitrogen (N_2) in an air mixture condenses at the same temperature as pure nitrogen gas.

Understanding: Mixtures are either homogeneous or heterogeneous.

Homogeneous mixture	Heterogeneous mixture
Components: ● are in the same state ● are spread evenly through the mixture ● cannot be individually identified	Components: ● are not in the same state ● are not spread evenly through the mixture ● can be individually identified
Examples: ● air (gases are evenly mixed) ● sugar dissolved in water (solid dissolves evenly through liquid)	Examples: ● oil and water (two layers observed) ● sand mixed with water (solid sits at bottom of liquid)

Subject vocabulary

homogeneous mixture a mixture in which all of the substances are present in the same state and are spread equally through the mixture

heterogeneous mixture a mixture in which the substances are present in different states and are not spread equally through the mixture

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.

Understanding: The mole is a fixed number of particles and refers to the amount, *n*, of substance.

- When carrying out chemical reactions it is necessary to know the amount of each reactant as well as the amount of each product formed. The typical units of amount we use to describe everyday items such as dozens, hundreds, thousands, etc., are not large enough to describe the number of atoms that are present in typical chemical reactions.
- The **mole**:
  - is the unit of amount (n) that is used in chemistry
  - has the symbol mol
  - is defined as the amount of substance that contains the same number of particles as there are atoms in exactly 12 g of **carbon-12** (^{12}C).

Understanding: 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).

- Carbon-12 (^{12}C):
  - is used as a standard and the masses of other substances are measured relative to the mass of carbon-12
  - has a mass of 12 atomic units.
- **Relative atomic mass**:
  - has the symbol A_r
  - does not have units because it is a ratio
  - $A_r = \dfrac{\text{mass of one atom of the element}}{\frac{1}{12}\text{ mass of carbon-12 atom}}$

Hints for success: The relative atomic masses for all the elements are given in section 6 of the IB data booklet.

- **Relative molecular mass** and **relative formula mass** both have the symbol M_r. They do not have units as they are ratios.
- Relative molecular mass is the relative mass of a **molecule** (the smallest unit of a **covalent compound**):
  - $M_r = \dfrac{\text{mass of one molecule}}{\frac{1}{12}\text{ mass of carbon-12 atom}}$
- Relative formula mass is the relative mass based on the formula of an **ionic compound**:
  - $M_r = \dfrac{\text{mass of ionic formula}}{\frac{1}{12}\text{ mass of carbon-12 atom}}$

Subject vocabulary

mole a unit of amount equal to the number of atoms in exactly 12 g of carbon-12. It has the symbol mol

carbon-12 the most common isotope of carbon; it has six protons and six neutrons in the nucleus

relative atomic mass the mass of an atom of an element relative to the mass of an atom of carbon-12. The relative atomic mass has the symbol A_r and it has no units

relative molecular mass the mass of one unit of a covalent compound expressed relative to the mass of an atom of carbon-12. It has the symbol M_r and it has no units

relative formula mass the mass of one unit of an ionic compound expressed relative to the mass of an atom of carbon-12. It has the symbol M_r and it has no units

molecule the smallest unit of a covalent compound

covalent compound a compound that is formed by covalent bonding between the atoms of different elements

ionic compound a compound that is formed by ionic bonding between the atoms of different elements

Understanding: Molar mass (M) has the units $\mathrm{g\,mol^{-1}}$.

Subject vocabulary

atomic mass the mass of one mole of the atoms of an element. It has the symbol M and has the units $\mathrm{g\,mol^{-1}}$

molar mass the mass of one mole of a substance. It has the symbol M and has the units $\mathrm{g\,mol^{-1}}$

Avogadro's number the number of particles in one mole of a substance, which is 6.02×10^{23}. Avogadro's number is given the symbol N_A or L and has units of $\mathrm{mol^{-1}}$

- **Atomic mass**:
  - is the molar mass of single atoms of an element
  - has the symbol M
  - has the same value as the relative atomic mass
  - has units of $\mathrm{g\,mol^{-1}}$.

For example, the relative atomic mass of chlorine is 35.45 and the atomic mass of chlorine is $35.45\,\mathrm{g\,mol^{-1}}$.

- **Molar mass**:
  - has the symbol M
  - is the mass of a substance in grams that contains one mole of the substance
  - has the units $\mathrm{g\,mol^{-1}}$
  - is equal to the sum of the atomic masses of the atoms in the substance.

Skill: Calculation of the molar masses of atoms, ions, and molecules, and of formula mass.

The molar mass of any compound is calculated by adding the atomic masses of all the elements present in the compound, e.g.

$$\begin{aligned} M(\mathrm{CuSO_4}) &= M(\mathrm{Cu}) + M(\mathrm{S}) + 4 \times M(\mathrm{O}) \\ &= 63.55\,\mathrm{g\,mol^{-1}} + 32.07\,\mathrm{g\,mol^{-1}} + 4 \times 16.00\,\mathrm{g\,mol^{-1}} \\ &= 159.62\,\mathrm{g\,mol^{-1}} \end{aligned}$$

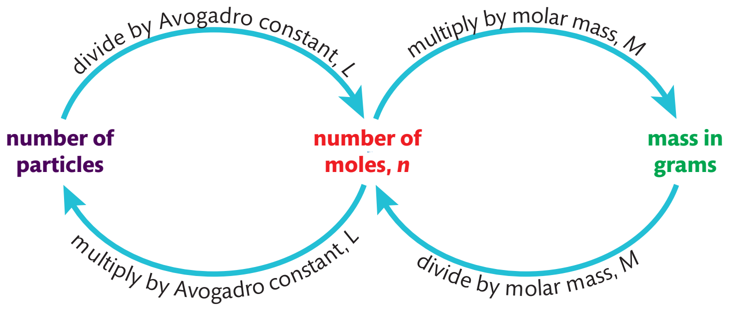
One mole of $\mathrm{CuSO_4}$ has a mass of 159.62 g.

Skill: Solution of problems involving the relationships between the number of particles, the amount of substance in moles, and the mass in grams.

- **Avogadro's number**:
  - is defined as the number of atoms in 12 g of carbon-12
  - has the symbol L (or N_A)
  - has the value $6.02 \times 10^{23}\,\mathrm{mol^{-1}}$.

There are 6.02×10^{23} chemical units in one mole of a substance.

- The number of particles and the number of moles present in a sample of a substance are related by Avogadro's number, L.
- The mass (m) and number of moles (n) of a substance are related by the molar mass (M).



number of particles = nL

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

Figure 1.4 *Summary of the central role of the number of moles, n, in converting between the number of particles and the mass in grams.*

Worked example

A spoonful of sugar, $C_6H_{12}O_6$, contains 2.55 g of sugar. How many moles of sugar are present? What is the number of sugar molecules present?

Solution

$$M(C_6H_{12}O_6) = 6 \times M(C) + 12 \times M(H) + 6 \times M(O)$$
$$= 6 \times 12.01\,\text{g mol}^{-1} + 12 \times 1.01\,\text{g mol}^{-1} + 6 \times 16.00\,\text{g mol}^{-1}$$
$$= 180.18\,\text{g mol}^{-1}$$

Number of moles of sugar molecules: $n = \frac{m}{M} = \frac{2.55\,\text{g}}{180.18\,\text{g mol}^{-1}} = 0.0142\,\text{mol}$

Number of sugar molecules = $nL = 0.0142\,\text{mol} \times 6.02 \times 10^{23}\,\text{mol}^{-1} = 8.52 \times 10^{21}$

Understanding: The empirical formula and molecular formula of a compound give the simplest ratio and the actual number of atoms present in a molecule respectively.

- The **empirical formula** is the *simplest ratio* of the atoms present in the compound.

  For example, H_2O and C_3H_8 are empirical formulas as they cannot be expressed as simpler ratios.
- The formulas for ionic compounds are *always* empirical formulas.

  For example, NaCl, Li_2O, and Mg_3N_2 are all examples of ionic compounds, and it can be seen that their chemical formulas are empirical formulas.
- A **molecular formula**:
  - gives the *exact* number of atoms of each element present in a molecule
  - is not always the same as the empirical formula for the compound
  - must be a whole-number multiplier of the empirical formula.

	Propane	Glucose
Molecular formula	C_3H_8	$C_6H_{12}O_6$
Empirical formula	C_3H_8	CH_2O
Multiplier	1	6 ($C_6H_{12}O_6 = 6 \times CH_2O$)

Subject vocabulary

empirical formula the chemical formula of a substance given as the simplest ratio

molecular formula the chemical formula of a molecule

percentage composition the mass of each element in a compound given as a percentage of the total mass

Skill: Interconversion of the percentage composition by mass and the empirical formula.

- **Percentage composition** gives the percentage by mass of each element in a compound, e.g.

  $M(CO) = 12.01 + 16.00 = 28.01$

  $\%(C) = \frac{12.01}{28.01} \times 100 = 42.88\%$ $\quad \%(O) = \frac{16.00}{28.01} \times 100 = 57.12\%$

The percentage composition of CO is 42.88% C and 57.12% O.

- The empirical formula of a compound can be determined from the percentage composition.

Worked example

Determine the empirical formula of a compound that is 38.76% by mass Ca, 19.97% P, and 41.27% O.

Solution

	Ca	**P**	**O**
Step 1: Write the mass of each element in 100 g of the compound.	38.76 g	19.97 g	41.27 g
Step 2: Divide by the atomic mass to give the number of moles of each element.	÷ 40.08 g mol^{-1} = 0.9671 mol	÷ 30.97 g mol^{-1} = 0.6448 mol	÷ 16.00 g mol^{-1} = 2.579 mol
Step 3: Divide by the smallest value to give the relative ratios of each element.	÷ 0.6448 mol = 1.500	÷ 0.6448 mol = 1.000	÷ 0.6448 mol = 4.000
Step 4: Convert to the simplest whole number ratio.	3	2	8

The empirical formula of the compound is $Ca_3(PO_4)_2$.

Skill: Obtaining and using experimental data for deriving empirical formulas from reactions involving mass changes.

- The empirical formula of the product in a reaction can be determined from the masses of reactants and products. This also requires knowledge of what elements are present in the product.

Worked example

In an experiment a sample of magnesium metal was heated in a crucible using a Bunsen burner. The product of the reaction was a grey powder known to be magnesium oxide.

The masses that were recorded in the experiment are given below. Use these masses to determine the empirical formula of magnesium oxide.

Mass of crucible: 25.623 g Mass of crucible and magnesium: 25.714 g

Mass of crucible and grey powder (magnesium oxide): 25.773 g

Solution

Step 1: Calculate the mass of magnesium that is present in the product.

mass of magnesium = mass of crucible and magnesium – mass of crucible

= 25.714 g – 25.623 g

= 0.091 g

Step 2: Calculate the mass of magnesium oxide formed in the experiment.

mass of magnesium oxide = mass of crucible and grey powder – mass of crucible

= 25.773 g – 25.623 g

= 0.150 g

Step 3: Calculate the mass of oxygen in the magnesium oxide.

mass of oxygen = mass of magnesium oxide – mass of magnesium

$$= 0.150\,\text{g} - 0.091\,\text{g}$$

$$= 0.059\,\text{g}$$

Step 4: Determine the empirical formula from the mass of magnesium and oxygen in the product.

	Mg	**O**
Step 1: Write the mass of each element.	0.091 g	0.059 g
Step 2: Divide by the atomic mass to give the number of moles of each element.	$\div$ 24.31 g mol^{-1} = 3.7×10^{-3} mol	$\div$ 16.00 g mol^{-1} = 3.7×10^{-3} mol
Step 3: Divide by the smallest value to give the relative ratios of each element.	$\div$ 3.7×10^{-3} mol = 1.0	$\div$ 3.7×10^{-3} mol = 1.0
Step 4: Convert to the simplest whole number ratio.	1	1

The empirical formula of the product is MgO.

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.

Understanding: Reactants can be either limiting or excess.

- Consider the reaction of hydrogen (H_2) with chlorine (Cl_2) to give hydrogen chloride (HCl):

  $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

  - The stoichiometric coefficients are the molar ratios of products and reactants:
  - 1 mole of H_2 will react with 1 mole of Cl_2 to form 2 moles of HCl.
  - If 1.5 moles of H_2 were reacted with 1.0 moles of Cl_2 then it would not be possible to change all of the reactants into HCl product. There would be too much H_2 (it is in excess) and not enough Cl_2 (it is limiting).
- The **limiting reactant**:
  - is the reactant that is present in too small an amount to allow complete reaction
  - limits the amount of product that is formed
  - is completely used up in the reaction.
- The **excess reactant**:
  - is the reactant that is present in too large an amount
  - is still present after the reaction is finished.

Subject vocabulary

limiting reactant the reacting substance that is competely used up in a chemical reaction and determines the amount of products formed

excess reactant the reacting substance that is present in an excess and is not competely used up in the reaction

Skill: Solution of problems relating to reacting quantities, limiting and excess reactants, theoretical, experimental, and percentage yields.

Worked example

The rocket fuel hydrazine (N_2H_4) can be formed from ammonia (NH_3) and chlorine (Cl_2) as shown in the following balanced equation:

$4NH_3(g) + Cl_2(g) \rightarrow N_2H_4(g) + 2NH_4Cl(s)$

If 12.0 g of NH_3 reacts with 25.0 g of Cl_2 what is the mass of N_2H_4 that is produced?

Solution

(i) Determine the number of moles of each reactant present:

$$n(NH_3) = \frac{m}{M} = \frac{12.0\,g}{(14.01 + 3 \times 1.01)\,g\,mol^{-1}} = 0.704\,mol$$

$$n(Cl_2) = \frac{m}{M} = \frac{25.0\,g}{(2 \times 35.45)\,g\,mol^{-1}} = 0.353\,mol$$

(ii) Based on the molar ratios determine which reactant is the limiting reactant.

The molar ratio of Cl_2:NH_3 in the balanced equation is 1:4.

This means that 0.353 mol of Cl_2 needs 4 × 0.353 = 1.41 mol of NH_3.

As there are only 0.704 mol of NH_3 present, NH_3 is the limiting reactant.

(iii) Calculate the amount of product that can be made from the limiting reactant.

The molar ratio of the limiting reactant, NH_3, to the product, N_2H_4, is 4:1.

$$n(N_2H_4) = \frac{n(NH_3)}{4} = \frac{0.704\,\text{mol}}{4} = 0.176\,\text{mol}$$

$$\begin{aligned}\text{mass}(N_2H_4) &= nM \\ &= 0.176\,\text{mol} \times (2 \times 14.01 + 4 \times 1.01)\,\text{g mol}^{-1} \\ &= 5.64\,\text{g}\end{aligned}$$

Understanding: The experimental yield can be different from the theoretical yield.

- The **theoretical yield**:
  - is the amount of a product *expected to be made* in a reaction
  - is calculated from the amount of the limiting reactant.
- The **experimental yield**:
  - is the mass of product that is *actually made* in the reaction
  - is often less than the theoretical yield because of factors such as incomplete reaction, loss of product, and presence of impurities.
- The **percentage yield** of a reaction compares the experimental yield with the theoretical yield:

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\%$$

Skill: Solution of problems relating to theoretical, experimental, and percentage yield.

Worked example

In the example given above for the reaction of 12.0 g of ammonia (NH_3) with 25.0 g chlorine (Cl_2) the theoretical yield of hydrazine (N_2H_4) product was 5.64 g.

The experimental yield was 4.68 g. What was the percentage yield of the reaction?

Solution

$$\text{percentage yield} = \frac{\text{experimental yield}}{\text{theoretical yield}} \times 100\% = \frac{4.68\,\text{g}}{5.64\,\text{g}} \times 100\% = 83.0\%$$

Understanding: Avogadro's law enables the mole ratio of reacting gases to be determined from volumes of the gases.

- **Avogadro's law**:
  - states that a fixed volume of all gases at the same temperature and pressure will contain the same number of particles, e.g.
    1.0 dm^3 of hydrogen (H_2) gas at 298 K and 100 kPa has the same number of particles as 1.0 dm^3 of ammonia gas (NH_3) at 298 K and 100 kPa
  - shows that volume is proportional to number of moles ($V \propto n$) for any gas at a constant temperature and pressure
  - allows calculations involving limiting reactants to be based on volumes rather than moles when the reactants and products are *gases*.

Subject vocabulary

theoretical yield the mass of product that would be formed if all of the limiting reactant is changed into products

experimental yield the mass of product that is obtained when the reaction is carried out experimentally

percentage yield the experimental yield expressed as a percentage of the theoretical yield

Avogadro's law the same volume of any gas at the same temperature and pressure will contain the same number of gas particles

Skill: Calculation of reacting volumes of gases using Avogadro's law.

Worked example

60.0 cm^3 of carbon disulfide (CS_2) reacts with 210.0 cm^3 of oxygen (O_2) at a constant temperature and pressure to form carbon dioxide (CO_2) and sulfur dioxide (SO_2) according to the equation below:

$$CS_2(g) + 3O_2(g) \rightarrow CO_2(g) + 2SO_2(g)$$

What is the volume of $SO_2(g)$ that can be formed in the reaction?

Solution

Because $V \propto n$, we can apply the stoichiometric coefficients to the *volumes* of the reacting gases just as we did with reacting moles in previous questions.

(i) 60.0 cm^3 of $CS_2(g)$ will require $3 \times 60.0\,cm^3 = 180.0\,cm^3$ of $O_2(g)$ to react completely.

(ii) As 210.0 cm^3 of $O_2(g)$ is present:

$O_2(g)$ is the excess reactant and $CS_2(g)$ is the limiting reactant.

(iii) As $CS_2(g)$ is the limiting reactant:

$V(SO_2) = 2 \times V(CS_2) = 2 \times 60.0\,cm^3 = 120.0\,cm^3$

Ideal gases and real gases

- Gases can be described as **ideal gases** or **real gases** depending on how the particles in the gas interact with each other.

Subject vocabulary

ideal gas a gas that obeys the ideal gas equation under all conditions

real gas a gas that does not obey the ideal gas equation under all conditions

Synonym

significant ..... large, meaningful

Ideal gases	Real gases
Particles *do not* interact with each other	Particles *do* interact with each other
Volume of gas particles is negligible compared with volume of container	Volume of gas particles is **significant** compared with volume of container
No attractive forces exist between gas particles	Attractive forces do exist between gas particles
Occur at low pressure and high temperature	Occur at high pressure and low temperature

Skill: Explanation of the deviation of real gases from ideal behaviour at low temperature and high pressure.

- Gases deviate from ideal behaviour and become real gases at high pressure and low temperature.
  - At high pressure there is a large number of gas particles present and the volume they occupy is significant compared with the volume of the container.

    This means the gas particles will be closer together and there is a high probability they will interact (collide) with each other.
  - At low temperature the gas particles have low kinetic energies.

    This means they will be moving more slowly and will interact more because they are more strongly affected by the attractive forces that exist between them.

Understanding: The molar volume of an ideal gas is a constant at specified temperature and pressure.

- **Molar volume**:
  - is the volume occupied by one mole of an ideal gas
  - has the symbol V_m
  - is constant at a specified temperature and pressure
  - is equal to 22.7 $dm^3\,mol^{-1}$ at standard temperature and pressure (STP).

Hints for success: The molar volume of an ideal gas at STP is given in section 2 of the IB data booklet.

- Standard temperature and pressure is 0 °C (273 K) and 100 kPa.
- The moles of gas in a given volume can be calculated using the molar volume:

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

Worked example

In the problem given above the volume of $SO_2(g)$ formed in the reaction was 120.0 cm^3. If this reaction was **conducted** at STP how many moles of SO_2 were formed?

Solution

(i) Convert the volume of $SO_2(g)$ from cm^3 to dm^3:

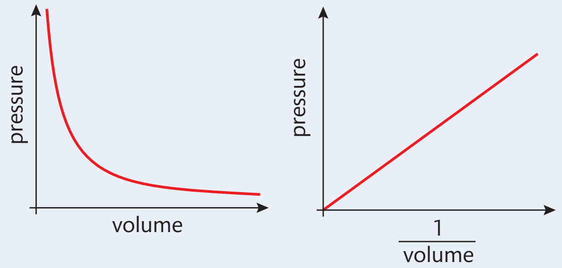
$$120.0\,cm^3 = \left(\frac{120.0}{1000}\right)dm^3 = 0.1200\,dm^3$$

(ii) Calculate the number of moles of $SO_2(g)$:

$$n = \frac{V}{V_m} = \frac{0.1200\,dm^3}{22.7\,dm^3\,mol^{-1}} = 0.00529\,mol$$

Skill: Solution of problems and analysis of graphs involving the relationship between temperature, pressure, and volume for a fixed mass of an ideal gas.

- **Gas laws** show the relationships between temperature, pressure, and volume for a fixed mass (or amount) of an ideal gas.

Gas law	Conditions	Graph
$P \propto \frac{1}{V}$	Constant temperature	 Plotting P against $\frac{1}{V}$ gives a straight line that passes through (0, 0)

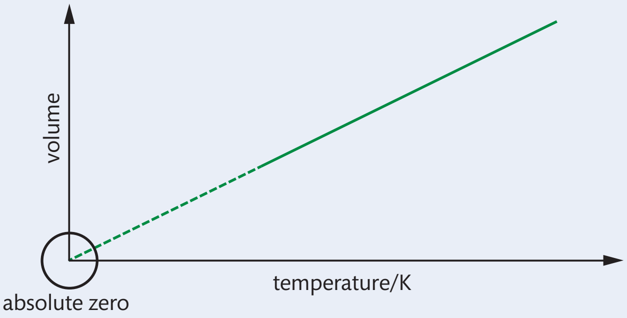
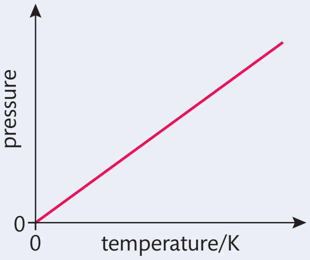
Subject vocabulary

molar volume the volume occupied by one mole of a gas. It has the symbol V_m

gas laws equations that define how the properties of gases such as temperature, pressure, volume, and amount are related

Synonym

conducted ..... undertook

Gas law	Conditions	Graph
$V \propto T$	Constant temperature	 Plotting V against T *in kelvin* gives a straight line that passes through (0, 0).
$P \propto T$	Constant volume	 Plotting P against T *in kelvin* gives a straight line that passes through (0, 0).

Subject vocabulary

ideal gas equation the equation that describes the relationship between the pressure, volume, temperature, and amount of an ideal gas; $PV = nRT$

universal gas constant a physical constant used in many chemical and physical equations. It has the symbol R and has a value of $8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$

Skill: Solution of problems relating to the ideal gas equation.

- The **ideal gas equation**:
  - is made by combining the individual gas laws
  - relates the pressure, volume, temperature, and amount of an *ideal gas* using the **universal gas constant**, R ($R = 8.31\,\mathrm{J\,K^{-1}\,mol^{-1}}$)
  - is $PV = nRT$
  - requires SI units to be used for each gas property.

Hints for success: The ideal gas equation is given in section 1 of the IB data booklet.

Property	SI unit	Common conversions
Pressure (P)	Pa	1 kPa = 1000 Pa
Volume (V)	m^3	$1\,dm^3 = 1 \times 10^{-3}\,m^3$ $1\,cm^3 = 1 \times 10^{-6}\,m^3$
Temperature (T)	K	K = 273 + °C

Worked example

An airbag in a car that is fully inflated with nitrogen (N_2) has a volume of $100.0\,dm^3$. Determine the number of moles of N_2 that are present in a fully inflated airbag at 20.0 °C and 101.3 kPa.

Solution

Pressure must be converted to Pa: $101.3\,kPa = 101.3 \times 10^3\,Pa$

Temperature must be converted to K: $20\,°C = (20 + 273)\,K = 293\,K$

Volume must be converted to m^3: $100.0\,dm^3 = 100.0 \times 10^{-3}\,m^3$

$PV = nRT$

$$n = \frac{pV}{RT} = \frac{101.3 \times 10^3\,Pa \times 100.0 \times 10^{-3}\,m^3}{8.31\,J\,K^{-1}\,mol^{-1} \times 293\,K} = 4.16\,mol$$

Skill: Obtaining and using experimental values to calculate the molar mass of a gas from the ideal gas equation.

- The ideal gas equation is $pV = nRT$.

  n can be substituted using $n = \frac{m}{M}$.

This gives the equation $PV = \frac{mRT}{M}$, which relates the molar mass of an ideal gas (M) to its temperature, pressure, volume, and mass.

Worked example

A 0.413 g sample of black silver oxide (Ag_2O) was heated in a closed boiling tube. At the end of the reaction 0.385 g of metallic silver (Ag) remained. A colourless gas was collected that had a volume of $21.3\,cm^3$ at 25 °C and 101.3 kPa.

Determine the molar mass of the gas that was produced in the reaction.

Solution

The volume of the gas must be converted to m^3: $21.3\,cm^3 = 21.3 \times 10^{-6}\,m^3$

The temperature of the gas must be converted to K: 25 + 273 = 298 K

mass (gas) = mass of Ag_2O – mass of Ag metal = 0.413 g – 0.385 g = 0.028 g

$$M = \frac{mRT}{PV} = \frac{0.028\,g \times 8.31\,J\,K^{-1}\,mol^{-1} \times 298\,K}{101\,300\,Pa \times 21.3 \times 10^{-6}\,m^3} = 32\,g\,mol^{-1}$$

(The molar mass of $32\,g\,mol^{-1}$ is consistent with O_2 being the colourless gas produced in the reaction.)

Understanding: The molar concentration of a solution is determined by the amount of solute and the volume of solution.

- A **solution** is created by dissolving a **solute** into a **solvent**.
- Adding more solvent to a solution:
  - **dilutes** the solution
  - makes the solution less concentrated (i.e. there is less solute relative to the volume of solution).
- The concentration of a solution (C) relates the amount of solute to the amount of solvent and can be measured in different ways.

Measure of concentration (C)	Relevant equation
$g\,dm^{-3}$	$C = \frac{\text{mass of solute in g}}{\text{volume of solution in dm}^3}$
ppm (parts per million)	$C = \frac{\text{mass of solute}}{\text{mass of solution}} \times 10^6$

Subject vocabulary

solution a homogeneous mixture formed by dissolving a solute (or solutes) into a solvent

solute the substance that is dissolved into a solvent to form a solution. The solute is present in a smaller amount than the solvent

solvent the substance that a solute dissolves in to form a solution. The solvent is present in a larger amount than the solute

dilutes increases the volume of solution relative to the amount of solute and decreases the concentration of the solution

Measure of concentration (C)	Relevant equation
mol dm^{-3}	$C = \dfrac{\text{moles of solute}}{\text{volume of solution in dm}^3}$

Subject vocabulary

molar concentration the number of moles of solute in a solution relative to the volume of solution measured in dm^3. It has the symbol C and units mol dm^{-3}

- **Molar concentration**:
  - relates the moles of solute to the volume of solution
  - is given by the equation $C = \dfrac{n}{V}$
  - has units of mol dm^{-3}
  - can be represented using square brackets, [ ], e.g. [NaCl] = 0.50 mol dm^{-3} means *the molar concentration of an NaCl solution is 0.50 mol dm^{-3}*

Skill: Solution of problems involving molar concentration, amount of solute, and volume of solution.

Worked example

Determine the molar concentration of a glucose solution ($C_6H_{12}O_6$) that is made by dissolving 3.56 g of glucose in water and making up to a total volume of 250.00 cm^3.

Solution

(i) Calculate the molar mass of glucose and then the moles of glucose that are dissolved.

$$M(C_6H_{12}O_6) = 6 \times M(\text{C}) + 12 \times M(\text{H}) + 6 \times M(\text{O})$$

$$= (6 \times 12.01 + 12 \times 1.01 + 6 \times 16.00)\ \text{g mol}^{-1}$$

$$= 180.18\ \text{g mol}^{-1}$$

$$n(C_6H_{12}O_6) = \frac{m}{M} = \frac{3.56\ \text{g}}{180.18\ \text{g mol}^{-1}} = 0.0198\ \text{mol}$$

(ii) Convert the volume into dm^3.

$$250.00\ \text{cm}^3 = 0.25000\ \text{dm}^3$$

(iii) Calculate the molar concentration.

$$C = \frac{n}{V} = \frac{0.0198\ \text{mol}}{0.25000\ \text{dm}^3} = 0.0792\ \text{mol dm}^{-3}$$

Worked example

25.00 cm^3 of a 0.750 mol dm^{-3} glucose solution is diluted to 175.00 cm^3. What is the concentration of the diluted solution in mol dm^{-3}?

Solution

Original solution: $n = C_1V_1$ Diluted solution: $n = C_2V_2$

Because n is the same in the two solutions: $C_1V_1 = C_2V_2$

$$C_1V_1 = C_2V_2$$

$$C_2 = \frac{C_1V_1}{V_2} = \frac{0.750\ \text{mol dm}^{-3} \times 25.00\ \text{cm}^3}{175.00\ \text{cm}^3} = 0.107\ \text{mol dm}^{-3}$$

Understanding: A standard solution is one of known concentration.

- **Standard solutions**:
    - are solutions that have a known concentration
    - are made by dissolving a known mass (or moles) of solute in a solvent and making a precise volume of solution.
- When a standard solution cannot be directly prepared, or the concentration of a solution is unknown, it is still possible to **standardize** the solution and determine its concentration by reacting it with a standard solution.

Skill: Use of the experimental method of titration to calculate the concentration of a solution by reference to a standard solution.

- A **titration** is an experimental technique used to calculate the concentration of a solution by reacting it with a standard solution.
- To perform a titration it is necessary to know:
    - the balanced equation for the titration reaction
    - the **equivalence point** where **stoichiometric equivalents** of the two reactants have been combined
    - the exact volume of unknown solution that is reacted
    - the exact volume of the standard solution that is needed to react with the solution of unknown concentration.

Worked example

25.00 cm^3 of an unknown solution of aqueous oxalic acid ($H_2C_2O_4$) was titrated against a standard solution of 0.1000 mol dm^{-3} aqueous potassium hydroxide (KOH). The end-point of the reaction was observed after the addition of 19.68 cm^3 of KOH(aq).

$$H_2C_2O_4(aq) + 2KOH(aq) \rightarrow K_2C_2O_4(aq) + 2H_2O(l)$$

Use this information to determine the concentration of the oxalic acid solution.

Solution

(i) Calculate the moles of the KOH standard used in the titration.

$$V(\text{KOH}) = 19.68\,\text{cm}^3 = 19.68 \times 10^{-3}\,\text{dm}^3$$

$$n(\text{KOH}) = CV = 0.1000\,\text{mol dm}^{-3} \times 19.68 \times 10^{-3}\,\text{dm}^3 = 1.968 \times 10^{-3}\,\text{mol}$$

(ii) Calculate the number of moles of $H_2C_2O_4$ using the molar ratio of $H_2C_2O_4$:KOH in the balanced equation.

$$n(H_2C_2O_4) = \frac{1}{2}n(\text{KOH}) = \frac{1}{2} \times 1.968 \times 10^{-3}\,\text{mol} = 9.840 \times 10^{-4}\,\text{mol}$$

(iii) Calculate the concentration of $H_2C_2O_4$(aq) from the volume that was used in the titration.

$$V(H_2C_2O_4) = 25.00\,\text{cm}^3 = 25.00 \times 10^{-3}\,\text{dm}^3$$

$$C = \frac{n}{V} = \frac{9.840 \times 10^{-4}\,\text{mol}}{25.00 \times 10^{-3}\,\text{dm}^3} = 0.03936\,\text{mol dm}^{-3}$$

Subject vocabulary

standard solution a solution that has a known concentration

standardize to determine the concentration of a solution

titration a technique used to determine the concentration of a solution by reacting it with another solution of known concentration

equivalence point the point in a titration where the exact volume of the standard solution needed to completely react with the unknown solution has been added

stoichiometric equivalent reactants are present in the exact amounts required to react completely based on the stoichiometric coefficients in the chemical equation

Topic 2: Atomic structure

2.1 The nuclear atom

General vocabulary

minute extremely small

dense having a relatively large mass contained in a small volume

negligible so small that its contribution to the overall total is minimal

concentrated gathered together in a small region

Subject vocabulary

proton a positively charged particle found in the nucleus of an atom

neutron a neutral particle found in the nucleus of an atom

electron a negatively charged particle that occupies the space outside the nucleus in an atom

sub-atomic particles particles that are smaller than an atom and combine to make up an atom

nucleus the dense positively charged core of an atom. Almost all of the mass of an atom is contained in the nucleus

nucleons particles found in the nucleus of an atom. Protons and neutrons are both nucleons

relative mass the mass of an object or particle expressed as a ratio of the mass of another object or particle. Relative masses have no units

atomic number defined as the number of protons in the nucleus. It has the symbol *Z*

mass number defined as the number of protons and neutrons in the nucleus. It has the symbol *A*

Essential idea:

The mass of an atom is concentrated in its **minute**, positively charged nucleus.

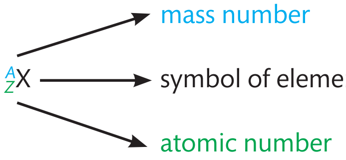
Understanding: Atoms contain a positively charged **dense** nucleus composed of protons and neutrons (nucleons).

Understanding: Negatively charged electrons occupy the space outside the nucleus.

- **Protons**, **neutrons**, and **electrons** are the three **sub-atomic particles** that make up an atom.
- Protons and neutrons are found in the dense **nucleus** of the atom and are known as **nucleons**.
- Protons are positively charged and neutrons have no charge (they are neutral) so the nucleus is positively charged.
- Electrons are negatively charged and occupy the space in the atom that is outside the nucleus.
- Protons and neutrons have the same **relative mass**.
- The mass of an electron is only 0.0005 that of a proton or neutron. This mass is **negligible** compared to the mass of protons and neutrons in the nucleus. The mass of an atom is **concentrated** in the nucleus.

Particle	Relative mass	Relative charge
proton	1	+1
electron	0.0005	–1
neutron	1	0

Skill: Using the nuclear symbol notation $^{A}_{Z}X$ to deduce the number of protons, neutrons, and electrons in atoms and ions.

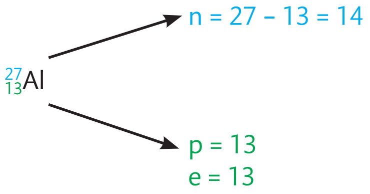


- The **atomic number** of an atom is given the symbol *Z* and is equal to the number of protons in the atom.
- The **mass number** of an atom is given the symbol *A* and is equal to the total number of protons and neutrons in the atom.
- *X* represents the symbol of the element.
- An atom contains the same number of protons and electrons. This means the atomic number is equal to the number of protons and to the number of electrons in an atom:

  number of protons = number of electrons = *Z*

- The mass number is equal to the number of protons plus the number of neutrons. The number of neutrons can be found by subtracting the atomic number from the mass number:

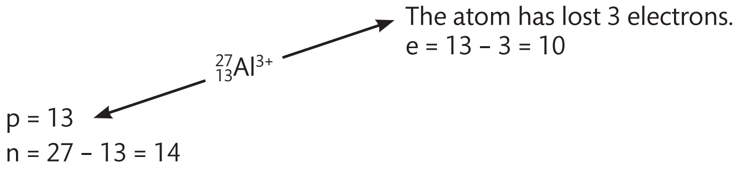
  number of neutrons = $A - Z$

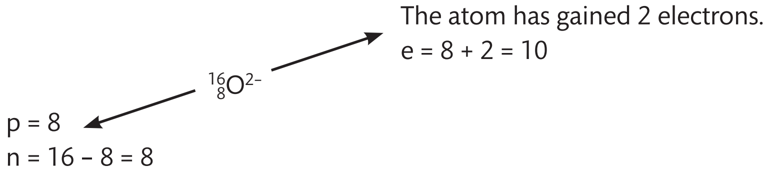


- An atom does not have an overall charge because it contains the same number of positively charged protons and negatively charged electrons.
- An **ion** is a charged species formed when an atom gains or loses electrons. An ion has a charge because the number of electrons is different from the number of protons.

  An **anion** (negative ion) is formed when an atom gains electrons. A **cation** (positive ion) is formed when an atom loses electrons.

  The total charge of the ion depends on the number of electrons that are gained or lost. The identity and total charge of any ion can be represented using element symbols:
  - O^{2-} is the oxide ion formed when an oxygen atom *gains* two electrons
  - Al^{3+} is the aluminium ion formed when an aluminium atom *loses* three electrons
- The number of protons and neutrons in an ion is the same as the numbers of protons and neutrons in the atom the ion was made from.
- The number of electrons can be calculated from the atomic number Z and the overall charge on the ion.





Subject vocabulary

ion a charged species formed when an atom (or molecule) gains or loses an electron or electrons

anion a negatively charged ion formed when an atom (or molecule) gains an electron or electrons

cation a positively charged ion formed when an atom (or molecule) loses an electron or electrons

isotopes atoms of the same element that have different numbers of neutrons and different mass numbers

isotopic composition the number and abundances of naturally occurring isotopes for an element

Understanding: The mass spectrometer is used to determine the relative atomic mass of an element from its isotopic composition.

- All atoms of an element have the same numbers of protons (and electrons) but they may have different numbers of neutrons.
- Atoms of the same element with different numbers of neutrons are called **isotopes**. The **isotopic composition** of an element is the number of isotopes and the **abundance** of each.
- Because isotopes of an atom have different numbers of neutrons they have different mass numbers and different relative atomic masses.

General vocabulary

abundance the amount that is present

Skill: Calculations involving non-integer relative atomic masses and abundance of isotopes from given data, including mass spectra.

- The **relative atomic mass** of an element depends on the atomic masses of the isotopes of that element and the **relative abundance** of each isotope.
- The number of isotopes of an element and the relative abundance of each isotope can be measured using a **mass spectrometer**. In the **mass spectrum** of an element a line is observed corresponding to the mass of each isotope present. The height of each line is **proportional** to the relative abundance of that isotope.

Worked example

Deduce the relative atomic mass of the element rubidium from the data given in Figure 2.1.

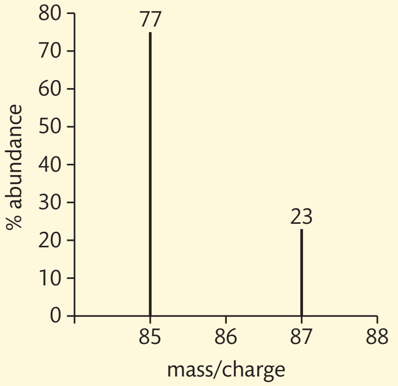


Figure 2.1 *Mass spectrum for rubidium.*

Solution

Consider a sample of 100 atoms.

total mass of 100 atoms = $(85 \times 77) + (87 \times 23) = 8546$

relative atomic mass = average mass of atom

$$= \frac{\text{total mass}}{\text{number of atoms}} = \frac{8546}{100} = 85.46$$

- The atomic mass of a particular isotope can be calculated from the relative atomic mass of an element if the atomic masses of all other isotopes are known.

Worked example

Boron exists in two isotopic forms, ^{10}B and ^{11}B. ^{10}B is used as a control for nuclear reactors. Use your periodic table to find the abundances of the two isotopes.

Solution

Consider a sample of 100 atoms.

Let x atoms be ^{10}B atoms. The remaining atoms are ^{11}B.

number of ^{11}B atoms $= 100 - x$

total mass of 100 atoms $= x \times 10 + (100 - x) \times 11 = 10x + 1100 - 11x = 1100 - x$

$$\text{average mass} = \frac{\text{total mass}}{\text{number of atoms}} = \frac{1100 - x}{100}$$

From the periodic table, the relative atomic mass of boron = 10.81.

$$10.81 = \frac{1100 - x}{100}$$

$$1081 = 1100 - x$$

$$x = 1100 - 1081 = 19$$

The abundances are ^{10}B = 19% and ^{11}B = 81%

Subject vocabulary

relative atomic mass the weighted average mass of the isotopes of an element relative to one-twelfth of an atom of carbon-12. It has the symbol A_r

relative abundance the number of atoms of one isotope of an element expressed as a ratio or percentage of the total number of atoms of all isotopes of that element

mass spectrometer an instrument that determines the masses and abundances of different chemical species present in a sample

mass spectrum a graphical representation of the results obtained by a mass spectrometer. Vertical lines occur at the mass of each ion present and the height of the line represents the abundance of that ion

General vocabulary

proportional related in size to

2.2 Electron configuration

Essential idea:

The electron configuration of an atom can be deduced from its atomic number.

Understanding: Emission spectra are produced when photons are emitted from atoms as excited electrons return to a lower energy level.

- **Excited electrons**:
  - are in high energy levels that are far from the nucleus
  - **emit** **photons** (light energy) when they move to lower energy levels that are closer to the nucleus.
- **Emission spectra**:
  - contain different wavelengths (colours) of light
  - are produced when excited electrons move to lower energy levels.

Skill: Description of the relationship between colour, wavelength, frequency, and energy across the electromagnetic spectrum.

- The **electromagnetic spectrum**:
  - contains all types of **electromagnetic radiation**
  - is divided into different **regions**: infrared, visible, ultraviolet, etc.
- Electromagnetic radiation:
  - behaves as a wave
  - travels at the speed of light, c
  - has energy.

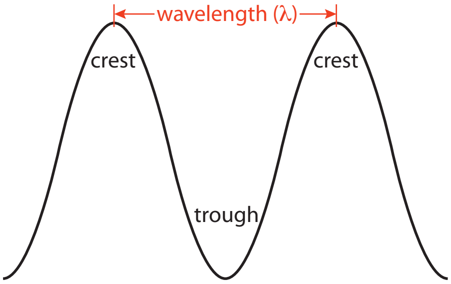


Figure 2.2 *Snapshot of a wave at a given instant. The distance between successive crests or peaks is called the wavelength (λ).*

- **Wavelength**, λ:
  - is the distance between successive crests of electromagnetic radiation
  - has units of metres, m (or other units of distance such as nm, cm).
- **Frequency**, ν:
  - is the number of peaks of electromagnetic radiation that pass through a point in a second
  - has units of s^{-1} (Hz)
  - is related to wavelength by the equation $c = \nu\lambda$.

Subject vocabulary

excited electrons electrons that are in high energy levels far from the nucleus

photons particles of light (electromagnetic radiation)

emission spectra the wavelengths (or frequencies) of light emitted by atoms or compounds that contain excited electrons

electromagnetic spectrum the range of different frequencies or wavelengths of electromagnetic radiation

electromagnetic radiation a form of energy that consists of perpendicular oscillating electric and magnetic fields that travel as waves

wavelength the distance between two successive peaks in a wave

frequency the number of wave peaks that pass through a given point in one second

Synonyms

emit	give out
regions	particular parts

- The energy of electromagnetic radiation:
  - increases as frequency *increases*
  - increases as wavelength *decreases*.
- The colour of visible light depends on its wavelength (and frequency), e.g.
  - light with λ = 680 nm is red
  - light with λ = 450 nm is blue.

Skill: Distinction between a continuous spectrum and a line spectrum.

Continuous spectrum	Line spectrum
Contains all colours (wavelengths) Looks like a rainbow 	Contains specific colours (wavelengths) Looks like a series of coloured lines 

Understanding: The line emission spectrum of hydrogen provides evidence for the existence of electrons in discrete energy levels, which converge at higher levels.

- The emission spectrum of hydrogen is a line spectrum.

Figure 2.3 *The visible emission spectrum of hydrogen.*

- Because **specific** wavelengths of light are emitted, this is **evidence** that electrons can only exist in **discrete energy levels**. (If the energy levels were not discrete and all energy levels were possible, then a continuous emission spectrum would be observed.)
- The lines observed in the emission spectrum of hydrogen **converge** (become closer) in energy as the energy increases (see Figure 2.4). This can only happen if the energy levels converge at higher energy and the energy difference between them becomes smaller.
- The **energy level diagram** (Figure 2.4) or the hydrogen atom shows the discrete energy levels and how they converge at higher energy levels.

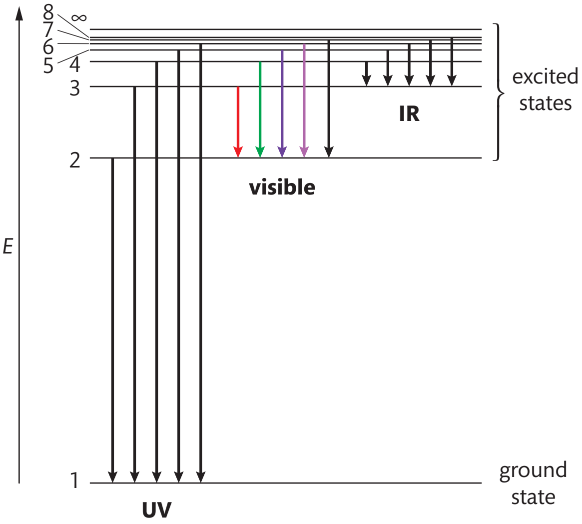


Figure 2.4 *Energy level diagram for the hydrogen atom showing the different emission series.*

Synonym

specific	clearly defined

General vocabulary

evidence	proof

Subject vocabulary

discrete energy levels	energy levels that are clearly separated in energy and do not overlap are discrete
converge	become closer
energy level diagram	a diagram that shows the energy levels available to an electron in an atom

- The energy levels are represented by **integer numbers**, *n*. The larger the value of *n* the further the electron is from the nucleus.
  - $n = 1$ is the lowest energy level. It is also called the **ground state**.
  - $n > 1$ are higher energy levels. They are called **excited states**.
  - $n = \infty$ represents **ionization**. The electron is in an energy level where it is so far from the nucleus it has been removed and the atom has been ionized.

Skill: Description of the emission spectrum of the hydrogen atom, including the relationships between the lines and energy transitions to the first, second, and third energy levels.

- The emission spectrum of the hydrogen atom:
  - is generated when excited electrons move from high energy levels to lower energy levels
  - has a series of lines that converge
  - depends on the energy level that the emissions occur to.

Level that emission occurs to	Energy of radiation emitted by series	Region of electromagnetic spectrum
$n = 1$	very high	ultraviolet (UV)
$n = 2$	high	visible
$n = 3$	low	infrared (IR)

Understanding: The main energy level or shell is given an integer number, *n*, and can hold a maximum number of electrons, $2n^2$.

- The different energy levels of an atom have a different maximum number of electrons. The maximum number of electrons in any energy level *n* is equal to $2n^2$.

Energy level (*n*)	Maximum number of electrons ($2n^2$)
1	2
2	8
3	18
4	32

Understanding: A more detailed model of the atom describes the division of the main energy level into s, p, d, and f sub-levels of successively higher energies.

- The different energy levels of an atom contain different **sub-levels**:
  - the first energy level ($n = 1$) contains an s sub-level only
  - the second energy level ($n = 2$) contains s and p sub-levels
  - the third energy level ($n = 3$) contains s, p, and d sub-levels
  - the fourth energy level ($n = 4$) contains s, p, d, and f sub-levels.

General vocabulary

integer numbers whole numbers

Subject vocabulary

ground state the lowest energy state of an atom or molecule

excited states energy levels of an atom or a molecule that are higher in energy than the ground state

ionization the process in which an atom or molecule loses an electron and becomes a positive ion

sub-levels different energy levels that exist within a main energy level

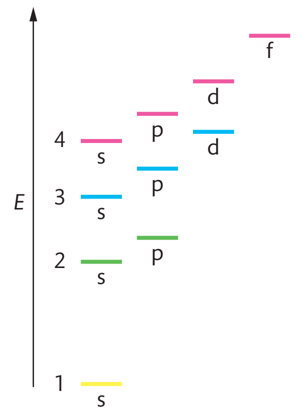


Figure 2.5 *The relative energies of the energy levels and sub-levels in an atom.*

Understanding: Sub-levels contain a fixed number of orbitals, regions of space where there is a high probability of finding an electron.

- An **orbital**:
  - is a region of space where there is a high probability of finding an electron
  - represents a solution to the **Schrödinger wave equation**
  - can contain one electron or two electrons.

Subject vocabulary

orbital a region of space where there is a high probability of finding an electron

Schrödinger wave equation an equation that describes the behaviour of electrons as three-dimensional waves moving around the nucleus of an atom

Skill: Recognition of the shape of an s atomic orbital, and the p_x, p_y, and p_z atomic orbitals.

- The different sub-levels contain different types and numbers of orbitals.

Level	Sub-level	Maximum number of electrons in sub-level	Maximum number of electrons in level
$n = 1$	1s	2	2
$n = 2$	2s	2	8
	2p	6	
$n = 3$	3s	2	18
	3p	6	
	3d	10	
$n = 4$	4s	2	32
	4p	6	
	4d	10	
	4f	14	

- The s orbital is shaped like a sphere. The higher the energy level the larger the diameter of the s orbital.

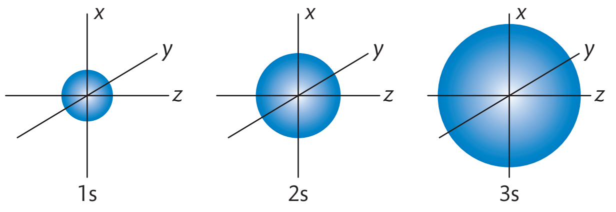


Figure 2.6 *The relative sizes of the 1s, 2s, and 3s orbitals.*

- In each p sub-level there are three p orbitals that are shaped like dumb-bells. All three have the same shape but they have different **orientations** and are at 90° to each other.

General vocabulary

orientations directions in space that objects are facing or aligned on

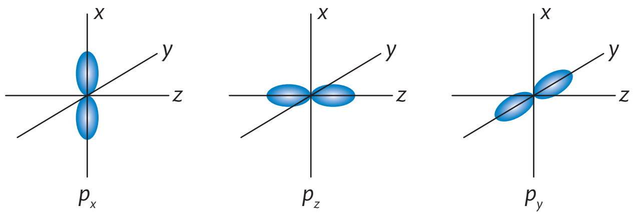


Figure 2.7 *The three p orbitals that are in a p sub-level: p_x, p_z, and p_y.*

- The higher the energy level the bigger the size of the p orbitals in that level: 3p orbitals are bigger in size than 2p orbitals.
- In a d sub-level there are five d orbitals. In a f sub-level there are seven f orbitals.

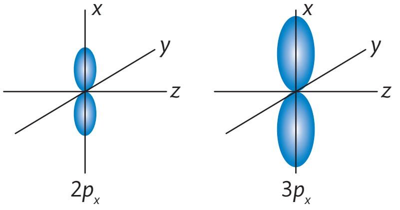


Figure 2.8 *The relative sizes of* $2p_x$ *and* $3p_x$ *orbitals.*

Understanding: Each orbital has a defined energy state for a given electronic configuration and chemical environment and can hold two electrons of opposite spin.

Skill: Application of the Aufbau principle, Hund's rule, and the Pauli exclusion principle to find electronic configurations for atoms and ions up to $Z = 36$.

- The **Aufbau principle** states that electrons will occupy the lowest energy orbital available first before filling successively higher energy orbitals.

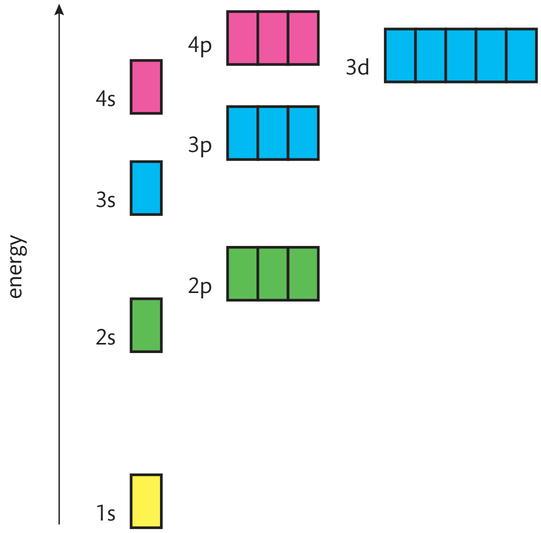
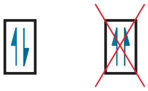


Figure 2.9 *The relative energies of the atomic orbitals up to the 4p sub-level. Each box represents an orbital.*

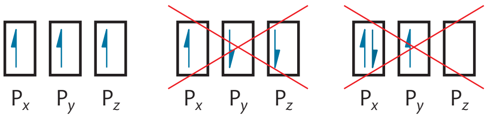
- Electrons have a property called **spin**. There are two possible spin states an electron can have: 'spin up' or 'spin down'. Arrows are used to represent electrons with different spins.

↓ means "spin down" ↑ means "spin up"

- The **Pauli exclusion principle** states that if two electrons occupy the same orbital they must have different spins.



- **Hund's rule** states that when more than one orbital is available in a sub-level, electrons will occupy different orbitals and they will have the same spin.



Subject vocabulary

Aufbau principle 'Aufbau' means 'building up' in German. Electrons will occupy the lowest energy level available. Only after the lowest energy level is filled will the next highest energy level be occupied

electron spin a quantum mechanical property of electrons

Pauli exclusion principle two electrons occupying the same orbital must have different spins

Hund's rule if more than one orbital in a sub-level is available, electrons occupy different orbitals with the same spins

Subject vocabulary

electron configuration a description of which orbitals are occupied in an atom

condensed electron configurations electron configurations that use noble gas configurations as a core

- The **electron configuration**:
  - tells us how electrons are distributed in an atom
  - lists sub-levels in order of increasing energy
  - shows the number of electrons in each sub-level using **superscripts**, e.g. the electron configuration of nitrogen is $1s^2\ 2s^2\ 2p^3$ which means that nitrogen has 2 electrons in the 1s sub-level, 2 electrons in the 2s sub-level, and 3 electrons in the 2p sub-level.

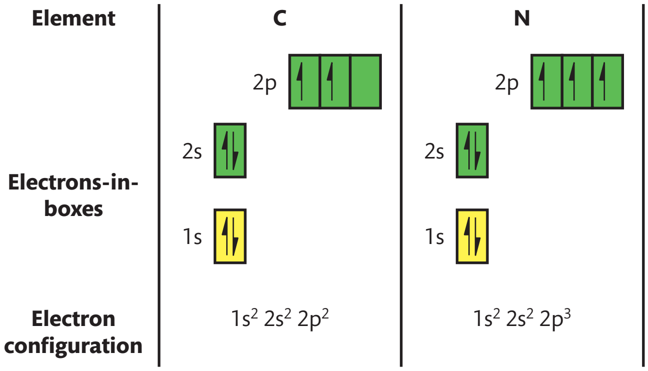


Figure 2.10 *Both carbon and nitrogen obey Hund's rule as the electrons in the 2p sub-level are in different orbitals and have the same spin.*

- The order of filling the sub-levels is shown in Figure 2.11.

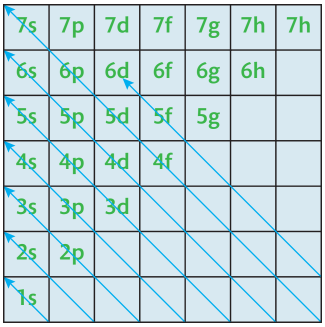


Figure 2.11 *Following the arrows gives the order of filling the sub-levels. Start at the bottom left arrow and write down the sub-levels it passes through. After reaching the head of one arrow, move to the tail of the next arrow to the right. This gives the order 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s.*

- Vanadium, $Z = 23$, has 23 electrons. It has the electron configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^3$. (Note that the superscripts add up to 23.)
- **Condensed electron configurations** use noble gas electron configurations as a core. The condensed electron configuration of vanadium is:

Vanadium has: V: [Ar] $4s^2\ 3d^3$

the same electron configuration as Ar ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$)

followed by $4s^2\ 3d^3$

- For elements containing 4s and 3d electrons the order can be switched when writing the electron configuration. The electron configuration of vanadium can be written as [Ar] $3d^3\ 4s^2$ or [Ar] $4s^2\ 3d^3$.
- Two important exceptions to the Aufbau principle are the electron configurations of chromium and copper.

	Cr	Cu
Aufbau prediction	[Ar] $3d^4\ 4s^2$	[Ar] $3d^9\ 4s^2$
Actual configuration	[Ar] $3d^5\ 4s^1$	[Ar] $3d^{10}\ 4s^1$

Topic 3: Periodicity

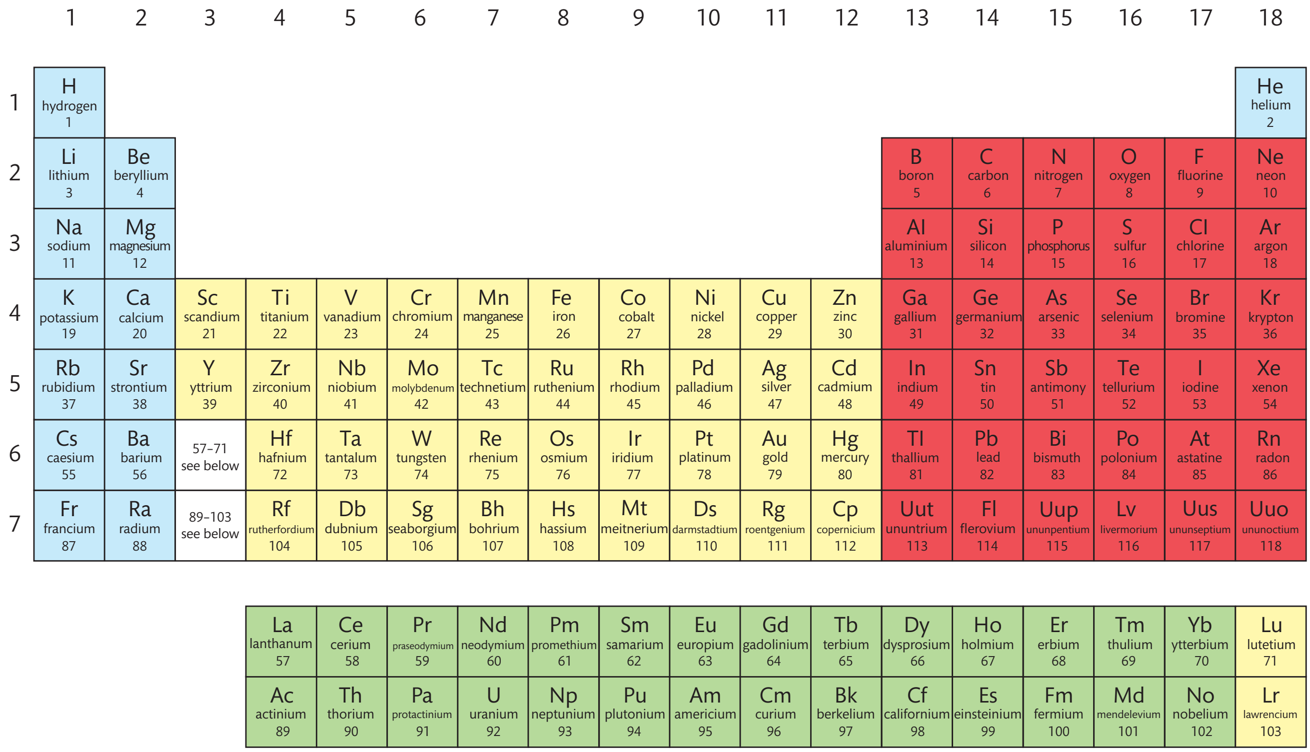
3.1 Periodic table

Essential idea:

The arrangement of elements in the periodic table helps to predict their electron configuration.

Understanding: The periodic table is arranged into four blocks associated with the four sub-levels: s, p, d, and f.

- In Chapter 2 we saw that the electrons in an atom occupy distinct energy levels. Within the main energy levels there can be different sub-levels corresponding to the different types of orbitals: s, p, d, and f orbitals.
- The periodic table arranges the elements by increasing atomic number. It can be broken into 'blocks' of elements based on which sub-levels are occupied by the outer electrons in the atoms of that element.



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H hydrogen 1																	He helium 2
2	Li lithium 3	Be beryllium 4											B boron 5	C carbon 6	N nitrogen 7	O oxygen 8	F fluorine 9	Ne neon 10
3	Na sodium 11	Mg magnesium 12											Al aluminium 13	Si silicon 14	P phosphorus 15	S sulfur 16	Cl chlorine 17	Ar argon 18
4	K potassium 19	Ca calcium 20	Sc scandium 21	Ti titanium 22	V vanadium 23	Cr chromium 24	Mn manganese 25	Fe iron 26	Co cobalt 27	Ni nickel 28	Cu copper 29	Zn zinc 30	Ga gallium 31	Ge germanium 32	As arsenic 33	Se selenium 34	Br bromine 35	Kr krypton 36
5	Rb rubidium 37	Sr strontium 38	Y yttrium 39	Zr zirconium 40	Nb niobium 41	Mo molybdenum 42	Tc technetium 43	Ru ruthenium 44	Rh rhodium 45	Pd palladium 46	Ag silver 47	Cd cadmium 48	In indium 49	Sn tin 50	Sb antimony 51	Te tellurium 52	I iodine 53	Xe xenon 54
6	Cs caesium 55	Ba barium 56	57–71 see below	Hf hafnium 72	Ta tantalum 73	W tungsten 74	Re rhenium 75	Os osmium 76	Ir iridium 77	Pt platinum 78	Au gold 79	Hg mercury 80	Tl thallium 81	Pb lead 82	Bi bismuth 83	Po polonium 84	At astatine 85	Rn radon 86
7	Fr francium 87	Ra radium 88	89–103 see below	Rf rutherfordium 104	Db dubnium 105	Sg seaborgium 106	Bh bohrium 107	Hs hassium 108	Mt meitnerium 109	Ds darmstadtium 110	Rg roentgenium 111	Cp copernicium 112	Uut ununtrium 113	Fl flerovium 114	Uup ununpentium 115	Lv livermorium 116	Uus ununseptium 117	Uuo ununoctium 118

La lanthanum 57	Ce cerium 58	Pr praseodymium 59	Nd neodymium 60	Pm promethium 61	Sm samarium 62	Eu europium 63	Gd gadolinium 64	Tb terbium 65	Dy dysprosium 66	Ho holmium 67	Er erbium 68	Tm thulium 69	Yb ytterbium 70	Lu lutetium 71
Ac actinium 89	Th thorium 90	Pa protactinium 91	U uranium 92	Np neptunium 93	Pu plutonium 94	Am americium 95	Cm curium 96	Bk berkelium 97	Cf californium 98	Es einsteinium 99	Fm fermium 100	Md mendelevium 101	No nobelium 102	Lr lawrencium 103

Figure 3.1 *The periodic table split into s, p, d, and f blocks.*

- **s block** (blue): contains the elements whose outer electrons occupy an s sub-level
- **p block** (red): contains the elements whose outer electrons occupy a p sub-level
- **d block** (yellow): contains the elements whose outer electrons occupy a d sub-level
- **f block** (green): contains the elements whose outer electrons occupy f orbitals.

The elements in the f block are known as **lanthanoids** (first row of the f block) and **actinoids** (second row of the f block).

Subject vocabulary

lanthanoids elements in the first row of the f block of the periodic table

actinoids elements in the second row of the f block of the periodic table

Understanding: The periodic table consists of groups (vertical columns) and periods (horizontal rows).

Understanding: The period number (n) is the outer energy level that is occupied by electrons.

- **Periods**:
  - are horizontal rows in the periodic table
  - contain elements with **valence electrons** in the same **principal energy level**
  - are numbered from period 1, which is the top row, to period 7, which is the bottom row.
- The **period number** corresponds to the outer energy level of an element. Elements in the first row ($n = 1$) have outer electrons in the first energy level. Elements in the fourth row ($n = 4$) have outer electrons in the fourth energy level.
- **Groups**:
  - are vertical columns in the periodic table
  - contain elements that have the same number of valence electrons and have similar chemical reactivities
  - contain elements whose outer electrons occupy the same type of sub-level
  - are numbered from group 1 on the left of the periodic table through to group 18 on the right.
- The elements in group 1 are very **reactive** and are known as the **alkali metals**. Alkali metals have one valence electron that is in the s sub-level, ns^1.
- The elements in group 17 are very reactive and are known as the **halogens**. Halogens have seven valence electrons and the five outermost electrons are in the p sub-level, np^5.
- The elements in group 18 are **unreactive** and are known as the **noble gases**. Noble gases have complete valence shells and the six outermost electrons are in the p sub-level, np^6.

Subject vocabulary

periods horizontal rows of elements in the periodic table

valence electrons the electrons that are in the outermost level of an atom

principal energy level the highest energy level occupied by electrons in an atom

period number the number of the outermost energy level occupied by electrons, equivalent to the row in the periodic table where the element appears

groups vertical columns of elements in the periodic table

reactive can easily undergo chemical reactions

alkali metals the elements that are in group 1 of the periodic table

halogens the elements that are in group 17 of the periodic table

unreactive does not easily undergo chemical reaction

noble gases the elements that are in group 18 of the periodic table

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Understanding: The number of the principal energy level and the number of valence electrons in an atom can be deduced from its position in the periodic table.

Skill: Deduction of the electron configuration of an atom from the element's position in the periodic table, and vice versa.

Worked example

Use the position of the element silicon (Si) in the periodic table to determine: (i) the number of valence electrons in a silicon atom, (ii) the outer energy level of a silicon atom, and (iii) the electron configuration of silicon.

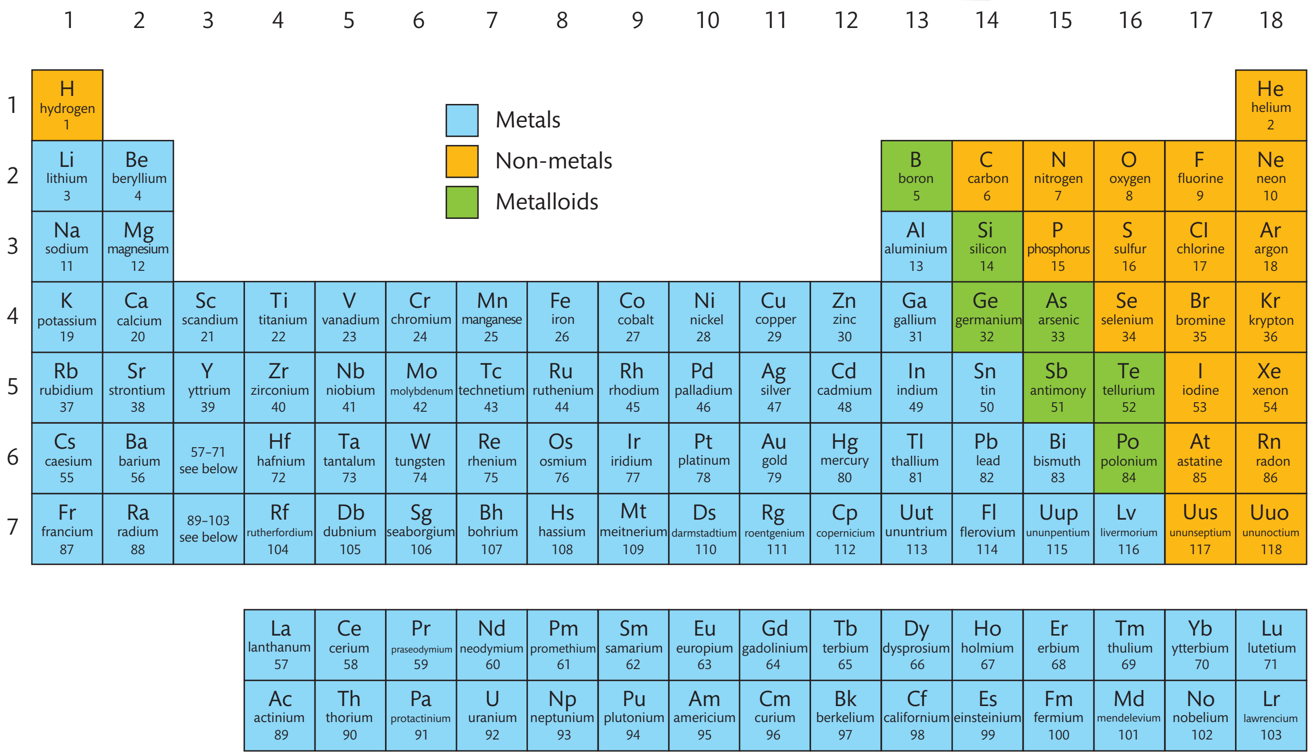
Solution

(i) Silicon is in group 14 so it has four valence electrons.

(ii) Silicon is in period 3 so the third energy level is the outer energy level.

(iii) The electron configuration of silicon is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ (or $[Ne]\ 3s^2\ 3p^2$)

Understanding: The periodic table shows the position of metals, non-metals, and metalloids.



🟦 Metals
🟨 Non-metals
🟩 Metalloids

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	🟨 H hydrogen 1																	🟨 He helium 2
2	🟦 Li lithium 3	🟦 Be beryllium 4											🟩 B boron 5	🟨 C carbon 6	🟨 N nitrogen 7	🟨 O oxygen 8	🟨 F fluorine 9	🟨 Ne neon 10
3	🟦 Na sodium 11	🟦 Mg magnesium 12											🟦 Al aluminium 13	🟩 Si silicon 14	🟨 P phosphorus 15	🟨 S sulfur 16	🟨 Cl chlorine 17	🟨 Ar argon 18
4	🟦 K potassium 19	🟦 Ca calcium 20	🟦 Sc scandium 21	🟦 Ti titanium 22	🟦 V vanadium 23	🟦 Cr chromium 24	🟦 Mn manganese 25	🟦 Fe iron 26	🟦 Co cobalt 27	🟦 Ni nickel 28	🟦 Cu copper 29	🟦 Zn zinc 30	🟦 Ga gallium 31	🟩 Ge germanium 32	🟩 As arsenic 33	🟨 Se selenium 34	🟨 Br bromine 35	🟨 Kr krypton 36
5	🟦 Rb rubidium 37	🟦 Sr strontium 38	🟦 Y yttrium 39	🟦 Zr zirconium 40	🟦 Nb niobium 41	🟦 Mo molybdenum 42	🟦 Tc technetium 43	🟦 Ru ruthenium 44	🟦 Rh rhodium 45	🟦 Pd palladium 46	🟦 Ag silver 47	🟦 Cd cadmium 48	🟦 In indium 49	🟦 Sn tin 50	🟩 Sb antimony 51	🟩 Te tellurium 52	🟨 I iodine 53	🟨 Xe xenon 54
6	🟦 Cs caesium 55	🟦 Ba barium 56	🟦 57–71 see below	🟦 Hf hafnium 72	🟦 Ta tantalum 73	🟦 W tungsten 74	🟦 Re rhenium 75	🟦 Os osmium 76	🟦 Ir iridium 77	🟦 Pt platinum 78	🟦 Au gold 79	🟦 Hg mercury 80	🟦 Tl thallium 81	🟦 Pb lead 82	🟦 Bi bismuth 83	🟩 Po polonium 84	🟨 At astatine 85	🟨 Rn radon 86
7	🟦 Fr francium 87	🟦 Ra radium 88	🟦 89–103 see below	🟦 Rf rutherfordium 104	🟦 Db dubnium 105	🟦 Sg seaborgium 106	🟦 Bh bohrium 107	🟦 Hs hassium 108	🟦 Mt meitnerium 109	🟦 Ds darmstadtium 110	🟦 Rg roentgenium 111	🟦 Cp copernicium 112	🟦 Uut ununtrium 113	🟦 Fl flerovium 114	🟦 Uup ununpentium 115	🟦 Lv livermorium 116	🟨 Uus ununseptium 117	🟨 Uuo ununoctium 118

🟦 La lanthanum 57	🟦 Ce cerium 58	🟦 Pr praseodymium 59	🟦 Nd neodymium 60	🟦 Pm promethium 61	🟦 Sm samarium 62	🟦 Eu europium 63	🟦 Gd gadolinium 64	🟦 Tb terbium 65	🟦 Dy dysprosium 66	🟦 Ho holmium 67	🟦 Er erbium 68	🟦 Tm thulium 69	🟦 Yb ytterbium 70	🟦 Lu lutetium 71
🟦 Ac actinium 89	🟦 Th thorium 90	🟦 Pa protactinium 91	🟦 U uranium 92	🟦 Np neptunium 93	🟦 Pu plutonium 94	🟦 Am americium 95	🟦 Cm curium 96	🟦 Bk berkelium 97	🟦 Cf californium 98	🟦 Es einsteinium 99	🟦 Fm fermium 100	🟦 Md mendelevium 101	🟦 No nobelium 102	🟦 Lr lawrencium 103

Figure 3.2 *The periodic table split into metals, non-metals, and metalloids.*

- The periodic table can also be broken into families of elements based on their general properties and reactivity.
  - **Metals** (blue) are elements that lose electrons and form positive ions.
  - **Non-metals** (yellow) are elements that gain electrons and form negative ions.
  - **Metalloids** (green) are elements that have properties of metals and non-metals.

Subject vocabulary

metals elements that tend to lose electrons and form positive ions

non-metals elements that tend to gain electrons and form negative ions

metalloids elements that have the properties of metals and non-metals

3.2 Periodic trends

Essential idea:

Elements show trends in their physical and chemical properties across periods and down groups.

Understanding: Vertical and horizontal trends in the periodic table exist for atomic radius, ionic radius, ionization energy, electron affinity, and electronegativity.

- **Periodicity** refers to trends in the physical and chemical properties of elements based on their positions in the periodic table. These trends:
  - increase or decrease along a row (period)
  - increase or decrease down a column (group)
  - can be explained by how the **effective nuclear charge** changes for elements in the period or group.
- **Nuclear charge**:
  - is a measure of the attraction that an electron has to the nucleus of an atom when it is not affected by other electrons
  - depends on the number of protons in the nucleus.
- Effective nuclear charge:
  - is a measure of the overall attraction an electron has to the nucleus of an atom when it also experiences repulsions and **shielding** due to other electrons
  - is less than the nuclear charge because repulsions and shielding effects decrease the overall attraction the electron has to the nucleus
  - decreases down a group because more inner energy levels are occupied and this increases the shielding of the outer electrons
  - increases across a period, because the extra attraction to the nucleus that results when protons are added is greater than the extra repulsion that occurs when electrons are added to the same energy level.
- **Atomic radius**:
  - is the distance from the centre of the nucleus to the outermost electrons of an atom
  - cannot be measured directly
  - is defined as half the distance between two nuclei of the element that are bonded together in a compound
  - is determined experimentally
  - decreases as effective nuclear charge increases because the outer electrons are attracted more and are held closer to the nucleus.

Subject vocabulary

periodicity patterns in physical and chemical properties observed in the periodic table

effective nuclear charge the overall attraction that the electrons have to the nucleus after the effect of the nuclear charge is reduced by the repulsions by other electrons

nuclear charge the total charge exerted by the nucleus of an atom. It depends on the number of protons in the nucleus

shielding the blocking effect that electrons in inner energy levels have on valence electrons. Shielding prevents the valence electrons from experiencing the full nuclear charge

atomic radius half the distance between the nuclei of two bonded atoms of an element

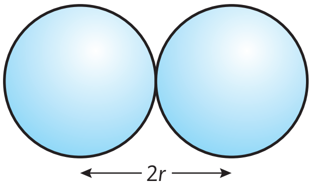


Figure 3.3 *The atomic radius r is measured as half the distance between neighbouring nuclei.*

- Atomic radius:
  - increases down a group because the outer electrons are in energy levels that are further out from the nucleus.

Element	Period	No. of occupied principal energy levels	Atomic radius/10^{-12} m
Li	2	2	152
Na	3	3	186
K	4	4	231
Rb	5	5	244
Cs	6	6	262

  - decreases across a period because the effective nuclear charge increases. A greater effective nuclear charge means that the outer electrons are held closer to the nucleus.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Atomic radius/10^{-12} m	186	160	143	117	110	104	99	–

Hints for success: Atomic radius values are given in section 9 of the IB data booklet.

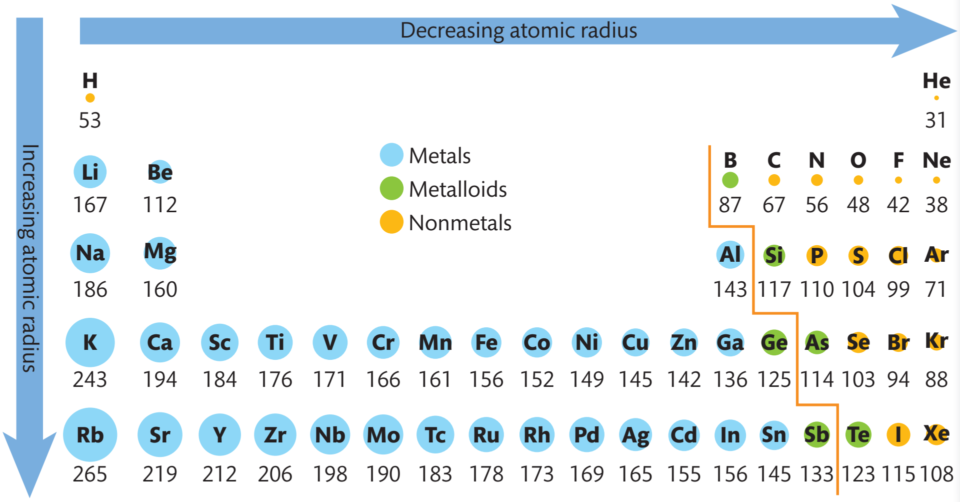


Figure 3.4 *A visual comparison of the atomic radii of the elements.*

- **Ionic radius**:
  - is the distance from the centre of the nucleus to the outermost electrons of an ion
  - cannot be measured directly
  - is determined experimentally from the distances between the nuclei of ions in an ionic solid
  - decreases as effective nuclear charge increases because the outer electrons are attracted more and are held closer to the nucleus.

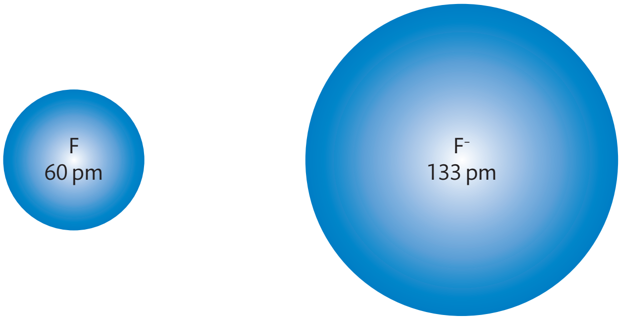
Subject vocabulary

ionic radius distance from the nucleus of an ion to the outer electrons

Hints for success: Ionic radius values are given in section 9 of the IB data booklet.

- Ionic radius is larger than the atomic radius for *anions*

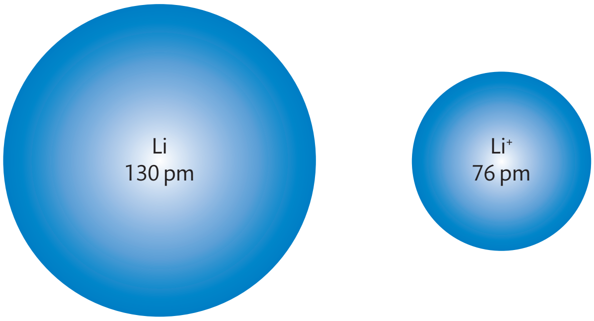
  Adding extra electrons increases electron repulsions and decreases the effective nuclear charge, e.g. the ionic radius of F^- is larger than the atomic radius of F:



1 picometre (pm) = 1×10^{-12} m

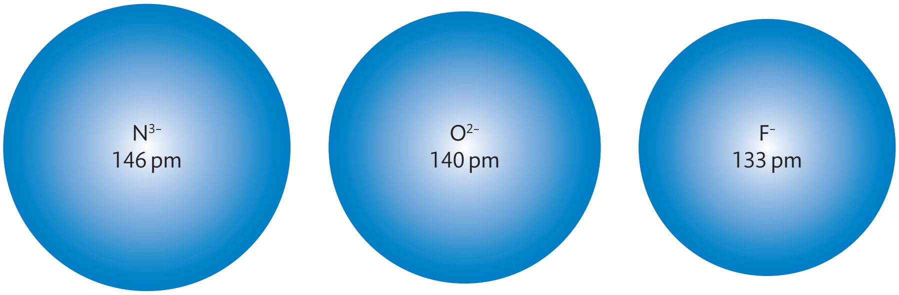
- Ionic radius is smaller than the atomic radius for *cations*

  Removing electrons decreases the electron repulsions and increases the effective nuclear charge, e.g. the ionic radius of Li^+ is smaller than the atomic radius of Li:



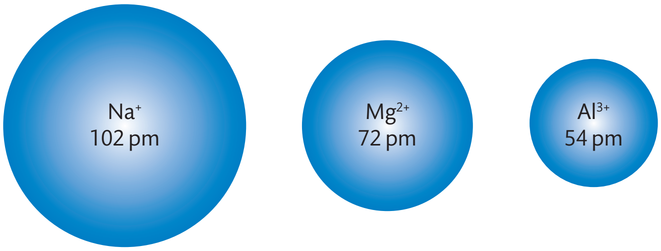
- Ionic radius decreases across a period for anions

  The greater the charge on the anion the more electrons that have been added, which increases the electron repulsions and decreases the effective nuclear charge, e.g. ionic radius of N^{3-} > ionic radius of O^{2-} > ionic radius of F^-:



- Ionic radius decreases across a period for cations

  The greater the charge on the cation the more electrons that have been removed, which decreases the electron repulsions and increases the effective nuclear charge, e.g. ionic radius of Na^+ > ionic radius of Mg^{2+} > ionic radius of Al^{3+}:



- Ionic radius increases down a group for both cations and anions because the outer electrons occupy energy levels that are further from the nucleus.

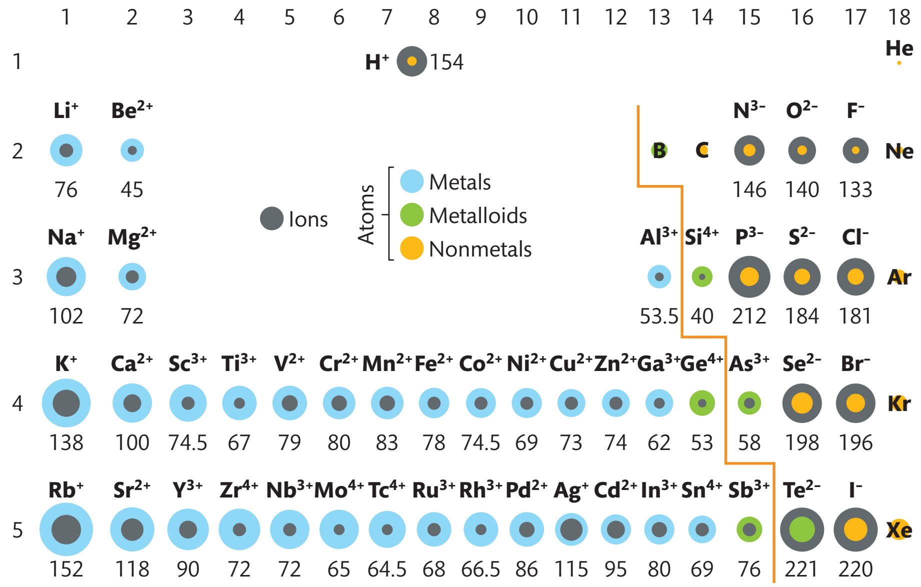


Figure 3.5 *A visual comparison of the atomic and ionic radii of the elements.*

- **Ionization energy**:
  - is the energy required to remove one mole of electrons from one mole of atoms in the gaseous state:

    $M(g) \rightarrow M^+(g) + e^-$
  - decreases down a period because the electrons are in energy levels further from the nucleus and take less energy to remove
  - increases across a group because the effective nuclear charge increases and this means more energy is needed to remove electrons.

Hints for success: First ionization energy values are given in section 8 of the IB data booklet.

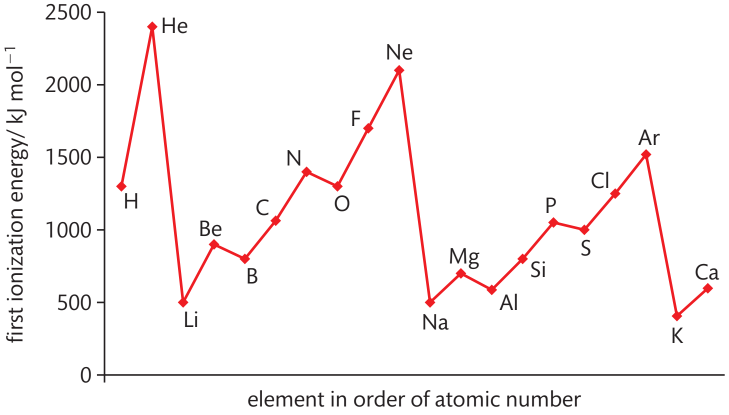


Figure 3.6 *First ionization energies of the first 20 elements.*

Subject vocabulary

ionization energy is the energy required to remove one mole of electrons from one mole of atoms in the gaseous state

Exceptions to the general trends for ionization energy

- A decrease in first ionization energy occurs between beryllium and boron.

  The electron configurations of beryllium and boron are:

  Be: $1s^2\ 2s^2$ B: $1s^2\ 2s^2\ 2p^1$

  An electron in a 2p orbital:

  - is shielded more than an electron in a 2s orbital
  - experiences a weaker attraction to the nucleus than an electron in a 2s orbital
  - is easier to remove from the atom than an electron in a 2s orbital.

  Boron has a lower first ionization energy than beryllium because the 2p electron in boron is easier to remove than the 2s electrons in beryllium.

- A similar decrease in first ionization energy occurs between magnesium and aluminium.

  The electron configurations of magnesium and aluminium are:

  Mg: $1s^2\ 2s^2\ 2p^6\ 3s^2$ Al: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

  Aluminium has a lower ionization energy than magnesium because the 3p electron in aluminium is easier to remove than the 3s electrons in magnesium.

- A decrease in ionization energy occurs between nitrogen and oxygen.

  The electron configurations of nitrogen and oxygen are:

  N: $1s^2\ 2s^2\ 2p^3$ O: $1s^2\ 2s^2\ 2p^4$

  In oxygen two electrons occupy the same p orbital. Electrons that are paired in the same p orbital:

  - repel each other more than unpaired electrons
  - experience a weaker attraction to the nucleus than unpaired electrons
  - are easier to remove from the atom than unpaired electrons.

  Oxygen has a lower first ionization energy than nitrogen because the paired 2p electrons in oxygen are easier to remove than the unpaired 2p electrons in nitrogen.

- A similar decrease in first ionization energy occurs between phosphorus and sulfur.

  The electron configurations of phosphorus and sulfur are:

  P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$ S: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$

  Sulfur has a lower first ionization energy than phosphorus because one of the paired 3p electron in sulfur is easier to remove than the unpaired 3p electrons in phosphorus.

Hints for success: Electron affinity values are given in section 8 of the IB data booklet.

Subject vocabulary

electron affinity the energy change that occurs when one mole of electrons is added to one mole of atoms in the gaseous state

- **Electron affinity**:
  - is the energy change that occurs when one mole of electrons is added to one mole of neutral atoms in the gaseous state:
    $X(g) + e^- \rightarrow X^-(g)$
  - is negative for most atoms, which means that energy is released when the electron is added to the atom
  - increases as the measured values become more negative
  - cannot be measured for group 18 elements as they do not form negative ions
  - increases across a period because the effective nuclear charge of the atom increases.

    This means that an electron being added to the atom will also experience a greater attraction to the nucleus across the period. This makes it easier to add the electron and the electron affinity is greater (has a more negative value).

Hints for success: Electronegativity values are given in section 8 of the IB data booklet.

- **Electronegativity**:
    - is the ability of an atom to attract the shared pair of electrons in a **covalent bond**
    - is measured relative to fluorine, which is the most electronegative element and has an electronegativity value of 4.0
    - cannot be measured for group 18 elements as they do not form covalent bonds
    - decreases down a group because the shared pair of electrons are in energy levels that are further out from the nucleus.

      This means that the shared electrons experience more shielding and will be less attracted to the nucleus of the atom.
    - increases across a period because the effective nuclear charge of the atom increases.

      The shared pair of electrons will be more attracted to the nucleus of the atom.

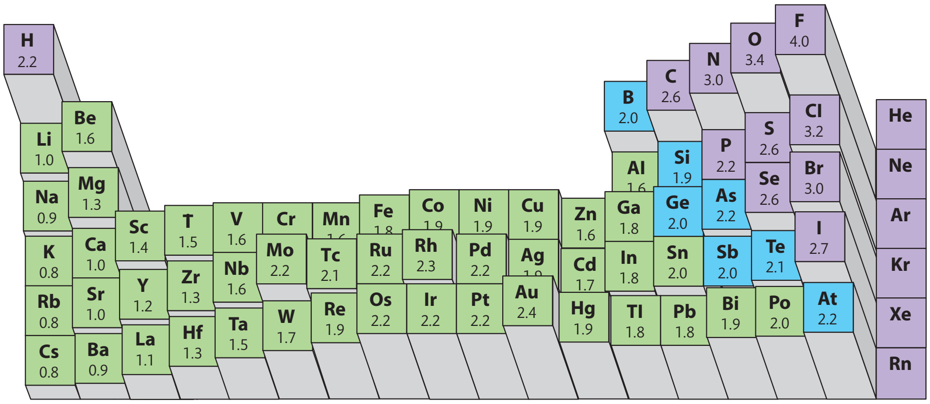


Figure 3.7 *3D representation of the electronegativity values in section 8 of the IB data booklet.*

Skill: Discussion of the similarities and differences in the properties of elements in the same group, with reference to alkali metals (group 1) and halogens (group 17).

Alkali metals (group 1 elements):

- are very reactive
- have to be stored under oil or in sealed tubes to prevent reaction with oxygen and water in the air
- have very low ionization energies, which means they easily react to form 1+ ions
- increase in reactivity down the group.

  Because caesium has the lowest ionization energy it is the most reactive alkali metal. Lithium is the least reactive alkali metal because it has the highest ionization energy.
- react with water to give hydroxide salts (MOH) and hydrogen gas (H_2):

  General reaction: $2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$ (M = any alkali metal)

  Specific example: $2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g)$

Subject vocabulary

electronegativity the ability of an atom to attract the shared electrons in a covalent bond

covalent bond a chemical bond that occurs when two atoms share pairs of electrons

- react with halogens (group 17 elements) to give halide salts (MX):

  General reaction: $2M(s) + X_2(s,l,g) \rightarrow 2MX(s)$ (M = any alkali metal, X = any halogen)

  Specific example: $2K(s) + Br_2(l) \rightarrow 2KBr(s)$

Halogens (group 17 elements):

- exist in their elemental form as diatomic molecules, X_2
- fluorine (F_2) and chlorine (Cl_2) are yellow-green gases, bromine (Br_2) is a brown liquid, and iodine (I_2) is a purple solid
- are reactive
- have high electron affinities and easily gain electrons to form 1– ions
- decrease in reactivity down the group from fluorine.

  Fluorine has the largest electron affinity and is the most reactive halogen. Iodine has the smallest electron affinity and is the least reactive.
- react with alkali metals (M) to give halide salts (see above)
- undergo **displacement reactions**: a more electronegative halogen will displace the halide ion of a less electronegative halogen.

  General reaction: $X_2(aq) + 2Y^-(s) + \rightarrow 2X^-(aq) + Y_2(aq)$

  (X = more electronegative halogen, Y = less electronegative halogen)

  Specific examples:

  $Cl_2(aq) + 2I^-(s) + \rightarrow 2Cl^-(aq) + I_2(aq)$

  $Br_2(aq) + 2Cl^-(s) + \rightarrow$ **no reaction** as Cl is more electronegative than Br.

Subject vocabulary

displacement reaction a reaction in which a more reactive element replaces a less reactive element in a compound

Understanding: Trends in metallic and non-metallic behaviour are due to the trends above.

- Figure 3.2 (page 31) shows how the periodic table can be divided into metals, non-metals, and metalloids. Across a period the characteristics of the elements progress from being metals to metalloids to non-metals.
- Metals (blue):
  - are elements with low ionization energies and low electronegativities
  - are found on the left and at the bottom of the periodic table
  - easily lose electrons to form positive ions because of their low ionization energies
  - have low electronegativities, and their valence electrons are not held to a single atom so can move from atom to atom throughout the metal solid, which means that metals have a high conductivity.
- Non-metals (yellow):
  - are elements with high ionization energies, high electronegativities, and high electron affinities
  - are found at the top right of the periodic table
  - easily gain electrons to form negative ions because of their high electron affinities
  - do not conduct electricity because their valence electrons are held in covalent bonds.

- Metalloids (green):
  - are elements that have properties of metals and non-metals
  - are found between the metals and non-metals in the periodic table
  - are usually more similar to metals in their physical properties and more similar to non-metals in their chemical reactivity.

Skill: Prediction and explanation of the metallic and non-metallic behaviour of an element based on its position in the periodic table.

Worked example

On the basis of their positions in the periodic table predict and explain whether barium and sulfur will behave as metals or non-metals.

Solution

Barium is found in group 2 so it behaves as a metal. It has a low ionization energy and forms positive ions when it reacts with non-metals. As barium is a metal it is malleable and conducts electricity.

Sulfur is in group 16 and is in the upper right of the periodic table so it behaves as a non-metal. It has a high electron affinity so accepts electrons to form negative ions when reacted with metals. Because it is a non-metal sulfur does not conduct electricity.

Understanding: Oxides change from basic through amphoteric to acidic across a period.

- The properties of the elements change across a period from metallic through metalloid to non-metallic. This is evident in the acid–base properties of the **oxides** of elements.
- Metallic oxides:
  - are compounds that contain metals and oxygen, e.g. magnesium oxide (MgO) and sodium oxide (Na_2O)
  - are ionic compounds because the large electronegativity difference between the metal and oxygen results in an ionic bond
  - dissolve in water to form **basic solutions** (solutions that contain an excess of OH^-), e.g. lithium oxide (Li_2O) dissolves in water to give lithium hydroxide (LiOH):

    $Li_2O(s) + H_2O(l) \rightarrow 2LiOH(aq)$
- Non-metallic oxides:
  - are compounds that contain non-metals and oxygen, e.g. carbon dioxide (CO_2) and sulfur trioxide (SO_3)
  - are covalent compounds because the small electronegativity difference between the non-metal and oxygen results in a covalent bond
  - dissolve in water to form **acidic solutions** (solutions that contain an excess of H^+), e.g. carbon dioxide (CO_2) dissolves in water to give carbonic acid, H_2CO_3:

    $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$

Subject vocabulary

oxides compounds that contain only oxygen and one other element

basic solutions solutions that contain an excess of OH^- ions. Basic solutions have a pH > 7

acidic solutions solutions that contain an excess of H^+ ions. Acidic solutions have a pH < 7

Subject vocabulary

amphoteric can behave as an acid or a base

- Metalloid oxides:
  - are **amphoteric**, which means that they can act as acids or bases, e.g. aluminium oxide (Al_2O_3) acts as a base when it reacts with hydrochloric acid:

    $Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

    and acts as an acid when it reacts with sodium hydroxide:

    $Al_2O_3(s) + 3H_2O(l) + 2OH^-(aq) \rightarrow 2Al(OH)_4^-(aq)$

Skill: Construction of equations to explain the pH changes for reactions of Na_2O, MgO, P_4O_{10}, and the oxides of nitrogen and sulfur with water.

- Sodium oxide (Na_2O) is an ionic oxide so it dissolves in water to give a basic solution of sodium hydroxide, NaOH. The pH is greater than 7.

  $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$
- Magnesium oxide (MgO) is an ionic oxide so it dissolves in water to give a basic solution of magnesium oxide. The pH is greater than 7.

  $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$
- Phosphorus(V) oxide (P_4O_{10}) is a covalent oxide so it dissolves in water to give an acidic solution of phosphorus(V) acid. The pH is less than 7.

  $P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ (phosphorus(V) acid or phosphoric acid)
- The most common nitrogen oxide is nitrogen dioxide (NO_2). It is a covalent oxide and dissolves in water to give an acidic solution containing nitrogen(III) acid (nitrous acid) and nitrogen(V) acid (nitric acid). The pH is less than 7.

  $$2NO_2(g) + H_2O(l) \rightarrow \underset{\text{nitrogen(III) acid}}{HNO_2(aq)} + \underset{\text{nitrogen(V) acid}}{HNO_3(aq)}$$
- The sulfur oxides are sulfur dioxide (SO_2) and sulfur trioxide (SO_3). They are both covalent oxides and dissolve in water to give acidic solutions. The pH is less than 7.

  $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$ (sulfur(IV) acid or sulfurous acid)

  $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$ (sulfur(VI) acid or sulfuric acid)

Topic 4: Chemical bonding and structure

4.1 Ionic bonding and structure

Essential idea:

Ionic compounds consist of ions held together in lattice structures by ionic bonds.

Understanding: Positive ions (cations) form by metals losing valence electrons.

Understanding: Negative ions (anions) form by non-metals gaining electrons.

- Non-metals have a high electronegativity and metals have a low electronegativity. The large **electronegativity difference** between metals and non-metals results in metal atoms transferring valence electrons to non-metal atoms.

  Metals have low ionization energies so they easily lose valence electrons to become positive ions (cations), e.g. $Na \rightarrow Na^+ + e^-$

  Non-metals have high electron affinities so they easily gain electrons to form negative ions (anions), e.g. $Cl + e^- \rightarrow Cl^-$

Subject vocabulary

electronegativity difference the difference in electronegativity between two atoms

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Understanding: The number of electrons lost or gained is determined by the electron configuration of the atom.

- It is possible to predict the charge of the ion that an atom will form based on its position in the periodic table.

  Metals will lose the electrons that are in their valence shell and form cations. The positive charge on a cation is equal to the number of valence electrons lost by the metal atom, e.g. Mg is in group 2 and has two valence electrons. Mg loses two electrons to form the Mg^{2+} ion.

  Non-metals will gain the number of electrons needed to fill the valence shell. The negative charge on an anion is equal to the number of valence electrons gained by the non-metal atom, e.g. O is in group 16 and it needs two electrons to fill the valence shell. O gains two electrons to form the O^{2-} ion.

Group	Example	Number of valence electrons	Electrons lost or gained	Number of electrons transferred	Charge on ion formed	Type of element
1	sodium	1	lost	1	1+	metal
2	calcium	2	lost	2	2+	metal
13	aluminium	3	lost	3	3+	metal
14	carbon	4	–	–	–	non-metal
15	phosphorus	5	gained	3	3–	non-metal
16	oxygen	6	gained	2	2–	non-metal
17	bromine	7	gained	1	1–	non-metal

- Group 14 atoms tend not to form ions. It takes too much energy to fill the valence shell by gaining four electrons and forming a 4– anion. It also takes too much energy to remove the four electrons and form a 4+ cation.

Understanding: The ionic bond is due to electrostatic attraction between oppositely charged ions.

- Cations and anions are oppositely charged and there is a strong **electrostatic attraction** between them. An **ionic bond** is the strong electrostatic attraction that exists between oppositely charged ions (cations and anions).

Subject vocabulary

electrostatic attraction the force that attracts a positively charged species to a negatively charged species

ionic bond a chemical bond that is caused by the electrostatic attraction between positive and negative ions

ionic lattice the three-dimensional structure of an ionic compound

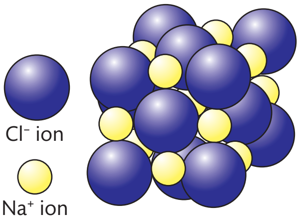


Figure 4.1 *The NaCl lattice is built up from oppositely charged sodium and chloride ions.*

Understanding: Under normal conditions, ionic compounds are usually solids with lattice structures.

- Normal conditions are the temperatures and pressures we normally encounter. Normal temperature and pressure is defined as 20 °C and 1 atm (101.3 kPa).
- In an ionic solid the positive ions are surrounded by negative ions and the negative ions are surrounded by positive ions. This results in a three-dimensional structure known as an **ionic lattice**.

Skill: Deduction of the formula and name of an ionic compound from its component ions, including polyatomic ions.

- When writing the formula of an ionic compound the cation is always put before the anion.
- When an ionic compound is formed the total positive charge of the cations must equal the total negative charge of the anions.
- When naming an ionic compound:
  - the name of the cation is always put before the before the name of the anion
  - the cation keeps the name of the metal it is made from, e.g. Li^+ is the lithium ion
  - the anion starts with the name of the non-metal but ends with '-ide', e.g. S^{2-} is the sulfide ion, H^- is the hydride ion.

Ionic compound	Formula	Positive ion	Negative ion
sodium chloride	$NaCl$	Na^+ (total charge = 1+)	Cl^- (total charge = 1–)
magnesium oxide	MgO	Mg^{2+} (total charge = 2+)	O^{2-} (total charge = 2–)
magnesium chloride	$MgCl_2$	Mg^{2+} (total charge = 2+)	2 × Cl^- (total charge = 2–)
sodium oxide	Na_2O	2 × Na^+ (total charge = 2+)	O^{2-} (total charge = 2–)
aluminium oxide	Al_2O_3	2 × Al^{3+} (total charge = 6+)	3 × O^{2-} (total charge = 6–)

- **Polyatomic ions** are ions that contain two or more atoms. The names of common polyatomic ions, along with their charges and chemical formulas, are provided in table below.

Subject vocabulary

polyatomic ions ions that contain more than one atom

Hints for success: It is necessary to memorize the names, formulas, and charges of these polyatomic ions as they are not provided in the IB data booklet.

Polyatomic ion	Formula of ion	Example of compound with polyatomic ion	Formula of compound
nitrate	NO_3^-	barium nitrate	$Ba(NO_3)_2$
hydroxide	OH^-	magnesium hydroxide	$Mg(OH)_2$
carbonate	CO_3^{2-}	calcium carbonate	$CaCO_3$
hydrogen carbonate	HCO_3^-	sodium hydrogen carbonate	$NaHCO_3$
sulfate	SO_4^{2-}	potassium sulfate	K_2SO_4
phosphate	PO_4^{3-}	calcium phosphate	$Ca_3(PO_4)_2$
ammonium	NH_4^+	ammonium chloride	NH_4Cl

Skill: Explanation of the physical properties of ionic compounds (volatility, electrical conductivity, and solubility) in terms of their structure.

- **Volatility** refers to how easily a substance can be converted into a gas.
  - Substances with a high volatility have low boiling points and are easily converted into gases.
- **Ionic compounds**:
  - contain strong ionic bonds that require a large amount of energy to break
  - have high boiling points
  - have low volatilities.
- **Solubility** refers to how easily a substance dissolves in a solvent to form a solution.
  - Substances with a high solubility easily dissolve in a solvent and form concentrated solutions
  - Ionic compounds:
    - contain ions that attract the **dipoles** in polar solvents
    - are most soluble in highly **polar** solvents such as water.
  - Most ionic compounds are soluble in water. The polar water molecules are attracted to the charged ions in the ionic compound. When enough water molecules surround the ions at the outside of the ionic lattice the ions become **hydrated** and break away from the solid and it dissolves.

Subject vocabulary

volatility	a measure of how easily a substance can be converted to a gas
ionic compound	a chemical compound that is formed by ionic bonding
solubility	a measure of how easily a substance can be dissolved into a solvent (usually water)
dipole	two regions of opposite charges (or partial charges) separated by a distance
polar	containing partial charges separated by a distance
hydrated	surrounded by water molecules

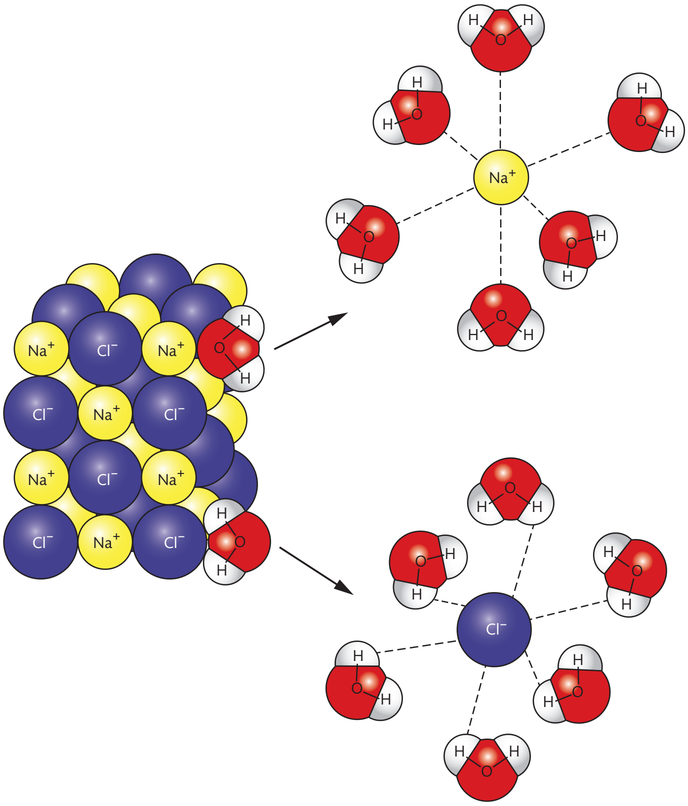


Figure 4.2 *Dissolving NaCl in water involves the attraction of the polar water molecules to the oppositely charged ions in the NaCl lattice and the hydration of the separated ions.*

- **Electrical conductivity** refers to the ability of a substance to **transport** charge. Substances have a high electrical conductivity if they contain charged particles (electrons or ions) that are able to move.
- Ionic compounds:
  - have a low electrical conductivity in the solid state because the ions are in fixed positions and cannot move
  - have a high electrical conductivity when they are **molten liquids** because the ions are able to move
  - dissolve in water to form solutions that have a high electrical conductivity because the ions are able to move.

Subject vocabulary

electrical conductivity the ability of a substance to transport charge

molten liquids liquids made by heating substances above their melting point

Synonym

transport .... movement

Essential idea:

Covalent compounds form by the sharing of electrons.

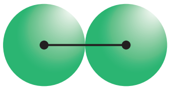
Understanding: A covalent bond is formed by the electrostatic attraction between a shared pair of electrons and the positively charged nuclei.

- A **covalent bond**:
  - forms when two non-metal atoms share a pair of electrons
  - is the strong electrostatic attraction between the shared pair of electrons and the positively charged nuclei of both atoms.

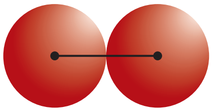
Understanding: Single, double, and triple covalent bonds involve one, two, and three shared pairs of electrons, respectively.

Understanding: Bond length decreases and bond strength increases as the number of shared electrons increases.

- Single covalent bonds:
  - are formed when two atoms share *one* pair of electrons
  - are represented by a single line between the two atoms, e.g. C–C represents a single bond between two carbon atoms.
- **Double covalent bonds**:
  - are formed when two atoms share *two* pairs of electrons
  - are represented by a double line between the two atoms, e.g. C=C represents a double bond between two carbon atoms.
- **Triple covalent bonds**:
  - are formed when two atoms share *three* pairs of electrons
  - are represented by a triple line between the two atoms, e.g. C≡C represents a triple bond between two carbon atoms.
- **Bond length**:
  - is defined as the distance between the nuclei of two covalently bonded atoms
  - is longer when bonds are formed from bigger atoms, e.g. Cl_2 contains smaller atoms than Br_2 and has a shorter bond length.



Cl_2 bond length 199 pm



Br_2 bond length 228 pm

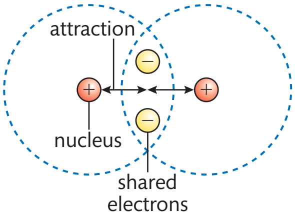


Figure 4.3 *In a covalent bond the shared electrons are attracted to the nuclei of both atoms.*

Subject vocabulary	
covalent bond	a chemical bond that is formed by the electrostatic attraction between a shared pair of electrons and the nuclei of two atoms
double bond	a covalent bond that is formed by the sharing of two pairs of electrons
triple bond	a covalent bond that is formed by the sharing of three pairs of electrons
bond length	the distance between the centres of the two nuclei in a covalent bond

  - decreases as the number of shared electrons increases. With more shared electrons there is a greater attraction between the shared electrons and the nuclei. This results in the two nuclei being held closer together and a shorter bond length.

    single bonds > double bonds > triple bonds

    longest → *shortest*

e.g. C–C	>	C=C	>	C≡C
154 pm		134 pm		120 pm

- Bond strength:
  - is a measure of how much energy is needed to break a covalent bond and separate the two atoms
  - is also known as **bond enthalpy**
  - increases as the number of shared electrons increases.

Subject vocabulary

bond enthalpy the energy required to break one mole of a particular bond in the gaseous state

non-polar covalent bond a covalent bond in which the electron pair is equally shared between the two nuclei

polar covalent bond a covalent bond in which the electron pair is not equally shared between the two nuclei

Hints for success: Bond enthalpies are given in section 11 of the IB data booklet.

With more shared electrons there is a greater attraction between the shared electrons and the nuclei. This results in more energy being needed to break the bond and separate the atoms.

single bonds < double bonds < triple bonds

weakest → *strongest*

e.g. C–C	>	C=C	>	C≡C
$346\ \text{kJ mol}^{-1}$		$614\ \text{kJ mol}^{-1}$		$839\ \text{kJ mol}^{-1}$

Understanding: Bond polarity results from the difference in electronegativities of the bonded atoms.

- Bond polarity:
  - is a measure of how electrons in a covalent bond are shared between the two atoms
  - depends on the difference in electronegativities of the two bonded atoms.
- **Non-polar covalent bonds**:
  - are bonds in which the electrons are shared equally between the two atoms
  - are formed when the two bonded atoms have the same electronegativity; e.g. H–H, O=O, and N≡N are all non-polar covalent bonds.
- **Polar covalent bonds**:
  - are bonds in which the electrons are *not* shared equally between the two atoms
  - are formed between atoms with different electronegativities; e.g. H–Cl, C=O, and C≡N are all polar covalent bonds
  - have a partial negative charge ($\delta-$) on the atom with the higher electronegativity because it exerts a greater attraction on the shared electrons

  - have a partial positive charge (δ+) on the atom with the lower electronegativity because it exerts a smaller attraction on the shared electrons.
  - H–Cl is a polar covalent bond:
    - the electronegativity values are H = 2.2 and Cl = 3.2, and the electronegativity difference is 1.0
    - chlorine is more electronegative and will have a partial negative charge
    - hydrogen will have a partial positive charge.
- A dipole:
  - is two regions of opposite charge (or partial charge) separated by a distance
  - is created by a polar covalent bond
  - can be represented using the symbol $+\!\!\longrightarrow$ (the arrow points towards the more electronegative atom)
- Polar covalent bonds can be represented in different ways:
  - using partial charge symbols

    $\overset{\delta+}{\text{H}} - \overset{\delta-}{\text{Cl}}$

  - using vectors (the vector points towards the more electronegative atom)

    $\text{H} \rightarrow \text{Cl}$

  - using dipole symbols.

    $\overset{+\!\!\longrightarrow}{\text{H} - \text{Cl}}$

Skill: Deduction of the polar nature of a covalent bond from electronegativity values.

Worked example

Rank the polarities of the H–Cl, H–F, H–N, and H–O bonds in order of least polar to most polar.

Solution

The polarities for each bond can be determined from the electronegativity values of the atoms in the bond. The most polar bond has the biggest electronegativity difference between the atoms.

H–Cl: electronegativity difference = 3.2 – 2.2 = 1.0

H–F: electronegativity difference = 4.0 – 2.2 = 1.8

H–N: electronegativity difference = 3.0 – 2.2 = 0.8

H–O: electronegativity difference = 3.4 – 2.2 = 1.2

The ranking of the bonds from least polar to most polar is
H–N < H–Cl < H–O < H–F

Hints for success: Electronegativity values are given in section 8 of the IB data booklet.

4.3 Covalent structures

Essential idea:

Lewis (electron dot) structures show the electron domains in the valence shell and are used to predict molecular shape.

General vocabulary

tendency observed pattern of behaviour

Subject vocabulary

octet rule atoms in covalent compounds will have eight electrons in their valence shell

Lewis structure a representation of a molecule that shows the bonds and lone pairs in the valence shell of the atoms in the molecule. It uses lines or pairs of crosses (or dots) to represent electron pairs

Understanding: The 'octet' rule refers to the **tendency** of atoms to gain a valence shell with a total of 8 electrons.

- For many atoms a stable electron configuration is achieved when they have *eight* electrons in the valence shell, and this is the basis of the **octet rule**.
- The octet rule does not apply to hydrogen and helium atoms as they can only have a maximum of two electrons in their valence shell.

Understanding: Lewis (electron dot) structures show all the valence electrons in a covalently bonded species.

- A **Lewis structure** is a simple method for showing how valence electrons are distributed in a molecule. Electrons are arranged in pairs represented by dots or crosses or as a single line. The electron pairs can be bonding (shared between two atoms) or non-bonding (belonging to one atom).
- Lewis structures of polyatomic ions must be drawn inside square brackets with the overall charge on the ion shown at the top right (see example for CN^- below).

Steps to follow in drawing a Lewis structure.

1. Calculate the total number of valence electrons in the molecule by multiplying the number of valence electrons of each element by the number of atoms of the element in the formula and totalling these.
2. Draw the skeletal structure of the molecule to show how the atoms are linked to each other.
3. Use a pair of crosses, a pair of dots, or a single line to show one electron pair and put a pair in each bond between atoms.
4. Add more electron pairs to complete the octets (8 electrons) around the atoms (other than hydrogen, which must have 2 electrons).
5. If there are not enough electrons to complete the octets, form double bonds and if necessary triple bonds.
6. Check that the total number of electrons in your finished structure is equal to your calculation in the first step.

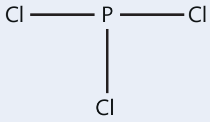
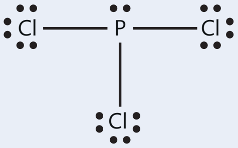
Skill: Deduction of Lewis (electron dot) structure of molecules and ions showing all valence electrons for up to four electron pairs on each atom.

Worked example

Deduce the Lewis (electron dot) structures for PCl_3 and CN^-.

Solution

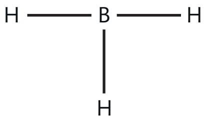
Following the steps in the flow chart above:

	PCl_3	CN^-
Step 1: Total valence electrons	5 + (3 × 7) = 26	4 + 5 + 1 = 10
Steps 2 and 3: Skeletal structure with bonds shown as lines		
Steps 4 and 5: Complete octets around each atom using double or triple bonds if necessary		
Add brackets and charge to structures of charged species		
Step 6: Check the total number of electrons drawn in the structure is correct	26 electrons	10 electrons

Understanding: Some atoms, like Be and B, might form stable compounds with incomplete octets of electrons.

- An **incomplete octet**:
  - happens when an atom has fewer than eight electrons in its valence shell
  - can occur with stable compounds that have boron (B) or beryllium (Be) as the central atom, e.g.

    BH_3 total valence electrons = 3 + 3 × 1 = 6 so the Lewis structure is:

    The central boron atom only has six electrons so it has an incomplete octet.

Understanding: Resonance structures occur when there is more than one possible position for a double bond in a molecule.

- **Resonance structures**:
  - can be drawn for some molecules that contain double bonds
  - have the double bond (or double bonds) in different positions, e.g. ozone (O_3) has two possible Lewis structures. Each Lewis structure contains one single and one double bond but they are in different positions.

    The individual Lewis structures are known as resonance structures. A double-headed arrow is drawn between the Lewis structures to show they are resonance structures.

Subject vocabulary

incomplete octet an atom that has fewer than eight electrons in its valence shell has an incomplete octet

resonance structures the possible Lewis structures that can be drawn for some compounds containing a double bond

Skill: Deduction of resonance structures; examples include but are not limited to C_6H_6, CO_3^{2-}, and O_3.

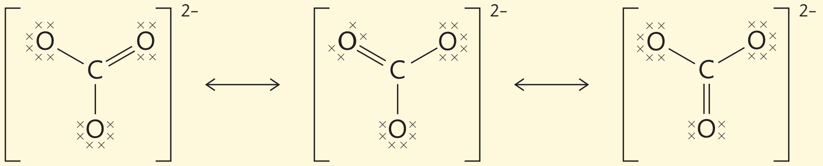
Worked example

Draw the resonance structures for the carbonate ion CO_3^{2-}.

Solution

Count the number of valence electrons: 4 + (6 × 3) + 2 = 24

Draw the Lewis structure, noting that there are three possible positions for the double bond. This means there will be three resonance structures, as follows:

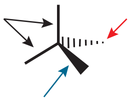


Understanding: Shapes of species are determined by the repulsion of electron pairs according to VSEPR theory.

- The shape of a species (molecule or polyatomic ion):
  - is the **molecular geometry** (three-dimensional shape)
  - can be determined from the Lewis structure of the molecule or polyatomic ion using **VSEPR theory**.
- Valence Shell Electron Pair Repulsion (VSEPR) theory is based on the simple idea that **electron domains** in the valence shell of an atom will repel each other and move as far away from each other as possible.
- An electron domain:
  - is one or more electron pairs that are in the same region of an atom's valence shell
  - includes single bonds, double bonds, triple bonds, and non-bonded pairs of electrons (**lone pairs**).
- The **electron domain geometry**:
  - is the three-dimensional arrangement of the electron domains around the central atom
  - depends on the number of electron domains around the central atom
  - has specific angles between the electron domains
- Three-dimensional shapes are drawn using wedges to signify bonds coming in or out of the plane of the paper, e.g. a tetrahedral shape is drawn in three dimensions as:

normal lines represent a bond in the plane of the page

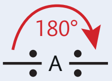
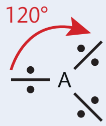
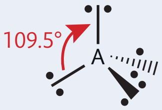
a dashed wedge represents a bond going back into the page



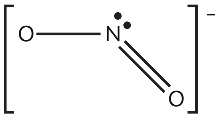
a solid wedge represents a bond coming out of the page

Subject vocabulary

molecular geometry	the three-dimensional shape of a molecule
VSEPR theory	Valence Shell Electron Pair Repulsion theory
electron domain	a region around an atom that contains electron pairs
lone pairs	non-bonding pairs of electrons that belong to one atom
electron domain geometry	the three-dimensional shape taken by the electron domains around a central atom

Number of electron domains	Angle between electron domains	Electron domain geometry	Diagram of electron domain geometry
2	180°	linear	
3	120°	trigonal planar	
4	109.5	tetrahedral	

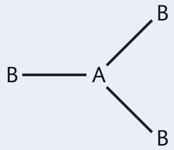
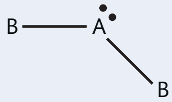
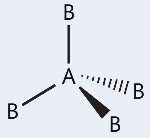
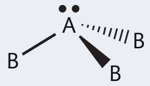
- The shape (molecular geometry):
  - is based on the electron domain geometry
  - depends on the number of bonded electron domains, e.g. NO_2^-,
    - the electron domain geometry is trigonal planar
    - the shape defined by the bonded atoms (O–N–O) is a V-shape.



- Bond angles:
  - are the angles formed by three atoms in a molecule or polyatomic ion
  - depend on the electron domain geometry and the repulsions exerted by the different electron domains that are on the central atom.
- Multiple bonds and non-bonded pairs (lone pairs) exert a greater repulsion than single bonds and this affects the bond angles.
  - Non-bonded pairs (lone pairs) will repel more because they are closer to the atom than the bonded pair in single bonds
  - Multiple bonds (double and triple bonds) will repel more because they contain more electrons than a single bond.

The shapes that are formed from different electron geometries are given in the table below.

'A' represents the central atom and 'B' represents the atoms that are bonded to the central atom.

Electron domain geometry	Number of electron domains	Number of bonded pairs	Shape (molecular geometry)	Drawing of shape	Bond angles (B–A–B)
trigonal planar	3	3	trigonal planar		120°
		2	V-shaped (bent)		≈117°
tetrahedral	4	4	tetrahedral		109.5°
		3	trigonal pyramidal		≈107°
		2	V-shaped (bent)		≈105°

Skill: The use of VSEPR theory to predict the electron domain geometry and the molecular geometry for species with two, three, and four electron domains.

Skill: Prediction of bond angles from molecular geometry and the presence of non-bonding pairs of electrons.

The steps used to determine the shape (molecular geometry) of a molecule or polyatomic ion and the relevant bond angles in the molecule or polyatomic ion are:

Step 1: Draw the Lewis structure following the steps on page 48.

Step 2: Count the total number of electron domains on the central ion.

Step 3: Determine the electron domain geometry as follows:

- two electron domains → linear
- three electron domains → trigonal planar
- four electron domains → tetrahedral

Step 4: Count the number of bonded electron domains.

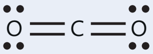
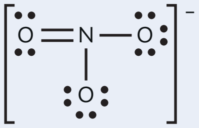
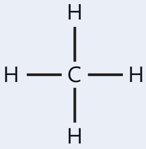
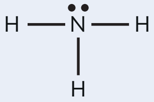
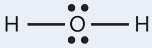
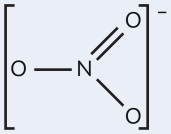
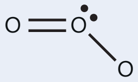
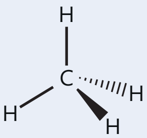
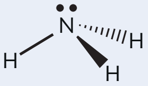
Step 5: Determine the molecular geometry from the electron domain geometry and the number of bonding electron domains.

Step 6: If non-bonding pairs are on the central atom adjust the bond angles to account for the extra repulsion of non-bonding pairs.

Worked example

Determine the molecular geometries of CO_2, NO_3^-, O_3, CH_4, NH_3, and H_2O.
Determine the bond angles for each molecule or ion.

Hints for success: Lewis structures (Step 1) *must* show all valence electrons. Drawings of the shape (Step 4) do not require all valence electrons to be shown but the non-bonding pairs on the central atom should be included. (Drawing all of the electron pairs on the central atom shows the electron domain geometry used to determine the molecular geometry.)

	CO_2	NO_3^-	O_3	CH_4	NH_3	H_2O
Step 1: Lewis Structure						
Step 2: Number of electron domains	2	3	3	4	4	4
Step 3: Electron domain geometry	linear	trigonal planar	trigonal planar	tetrahedral	tetrahedral	tetrahedral
Step 4: Number of bonded electron domains	2	3	2	4	3	2
Step 5: Molecular geometry (shape)	linear 	trigonal planar 	V-shaped (bent) 	tetrahedral 	trigonal pyramidal 	V-shaped (bent) 
Step 6: Bond angles	180°	120°	≈117°	109.5°	≈107°	≈105°

Skill: Prediction of molecular polarity from bond polarity and molecular geometry.

- As we saw earlier a polar covalent bond is formed when there is an electronegativity difference between the two bonded atoms. Molecules can also be polar or non-polar.
- **Polar molecules** contain an **overall dipole** and must contain polar bonds.
- **Non-polar molecules** do not contain an overall dipole. This happens when:
  - the molecule has no polar bonds
  - the molecule has polar bonds but the dipoles cancel.
- The steps used to determine whether a molecule is polar or non-polar are:

  Step 1: Determine if the molecule contains polar bonds.
  - If there are no polar bonds then the molecule is non-polar.
  - If there are polar bonds then move on to step 2.

  Step 2: Determine the shape (molecular geometry) of the molecule following the steps on page 52.

Subject vocabulary

polar molecules molecules that contain an overall dipole

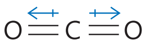
overall dipole the dipole on a molecule that is made by the summing of individual dipoles from any polar bonds in the molecule

non-polar molecules molecules that do not contain a net dipole

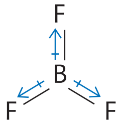
Step 3: Draw the dipoles for each polar bond in the molecule and determine if they cancel.

- If the dipoles cancel then the molecule will be non-polar.
- If the dipoles do not cancel there is an overall dipole and the molecule will be polar.

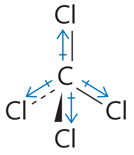
- Dipoles cancel when:
  - the molecule has a regular geometry (linear, trigonal planar, or tetrahedral) *and*
  - the bonds all have the same polarity.



CO_2

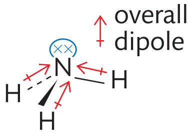


BF_3

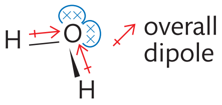


CCl_4

- Dipoles do not cancel when:
  - the molecule has a geometry that is not regular (V-shaped or trigonal pyramidal)



NH_3



H_2O

  - the molecule has a regular geometry but the bonds have different polarities.

Figure 4.4 *Equal and opposite pulls cancel each other out.*

Figure 4.5 *When the pulls are not equal and opposite there is a net pull.*

Understanding: Carbon and silicon form giant covalent/ network covalent structures.

- **Network covalent structures**:
  - are also called giant covalent structures
  - occur when every atom in the structure is covalently bonded to two or more atoms
  - contain a repeating structure
  - have no fixed size
  - can contain carbon or silicon, e.g. silicon dioxide (SiO_2):
    - forms a covalent network structure
    - has each silicon atom covalently bonded to four oxygen atoms
    - has each oxygen atom bonded to two silicon atoms
    - has an Si:O ratio of 1:2 so SiO_2 is the empirical formula.

Subject vocabulary

network covalent structures covalent compounds in which all of the atoms are linked by covalent bonds

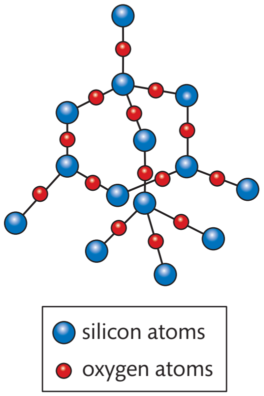


Figure 4.6 *The structure of quartz SiO_2.*

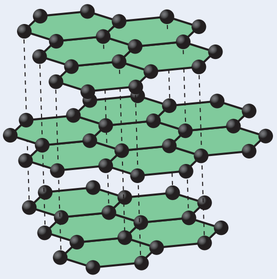
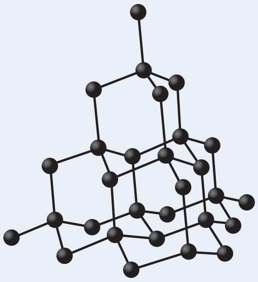
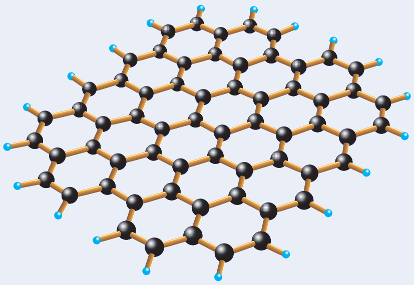
- Silicon dioxide is also commonly known as silica or quartz. Like most network solids it is insoluble in water and has a high melting point. There are no delocalized electrons in silicon dioxide so it does not conduct electricity.
- **Allotropes** are different forms of an element that can exist in the same state, e.g. oxygen (O_2) and ozone (O_3) are allotropes as they are both forms of oxygen that exist as gases.
- Carbon has four allotropes that can exist as solids: graphite, diamond, graphene, and fullerene (C_{60}). Graphite, diamond, and graphene are network solids as all the carbon atoms in these substances are covalently bonded to two or more other carbon atoms.

Subject vocabulary

allotropes different forms of an element that can exist in the same state

Skill: Explanation of the properties of giant covalent compounds in terms of their structures.

- The structural features and physical properties of the different giant covalent compounds formed by carbon are outlined in the table below.

Graphite	Diamond	Graphene
		
Structural features		
Each C atom is bonded to three other atoms 120° bond angles Forms sheets of repeating hexagons The sheets are held together by London dispersion forces Has delocalized valence electrons on each sheet	Each C atom bonded to four other atoms 109.5° bond angles Forms repeating tetrahedral units Has no delocalized electrons because all of the valence electrons are in covalent bonds	Each C atom bonded to three other atoms 120° bond angles Forms a single sheet of repeating hexagons Has delocalized valence electrons on the sheet
Physical properties		
Is a good electrical conductor because the delocalized electrons can move Is a good lubricant because the sheets can slide over each other Has a very high melting point because C–C bonds must be broken before it melts	Is a poor electrical conductor because there are no delocalized electrons that can move Is very hard as all the atoms are held in fixed positions Has a very high melting point because C–C bonds must be broken before it melts	Is a good electrical conductor because the delocalized electrons can move Is very flexible because the sheet is only one atom thick Is very strong because all of the atoms are bonded together Has a very high melting point because C–C bonds must be broken before it melts

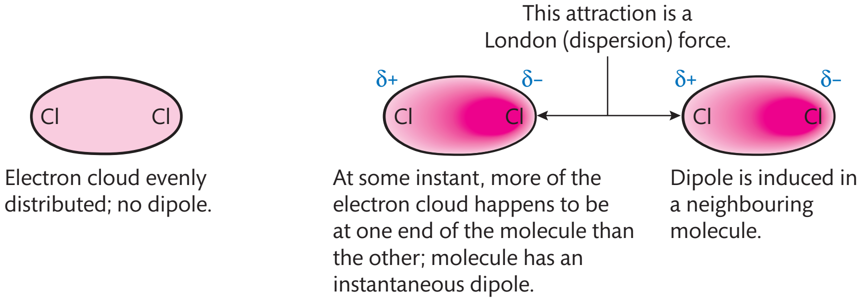
4.4 Intermolecular forces

Essential idea:

The physical properties of molecular substances result from different types of forces between their molecules.

Understanding: Intermolecular forces include London (dispersion) forces, dipole–dipole forces, and hydrogen bonding.

- **Intermolecular forces**:
    - are electrostatic attractions that exist *between* molecules
    - have three main types: **London (dispersion) forces**, **dipole–dipole forces**, and **hydrogen bonding**.
- London (dispersion) forces:
    - can be called London forces or dispersion forces
    - occur between all molecules
    - are the only intermolecular forces that occur between non-polar molecules
    - are the electrostatic attraction between an **instantaneous dipole** and an **induced dipole**
    - are stronger between molecules that have a large number of electrons because there is a higher probability that an instantaneous dipole will form.



This attraction is a London (dispersion) force.

Electron cloud evenly distributed; no dipole.

At some instant, more of the electron cloud happens to be at one end of the molecule than the other; molecule has an instantaneous dipole.

Dipole is induced in a neighbouring molecule.

Figure 4.7 *London forces in* Cl_2 *are the attraction between an instantaneous dipole on one molecule and an induced dipole on another molecule.*

London forces are weak forces so most molecules that have only London forces have low melting and boiling points.

Element	M_r	Boiling point / °C	State at room temperature
F_2	38	−188	gas
Cl_2	71	−34	gas
Br_2	160	59	liquid
I_2	254	185	solid

boiling point increases with increasing number of electrons

Alkane	M_r	Boiling point / °C
CH_4	16	−164
C_2H_6	30	−89
C_3H_8	44	−42
C_4H_{10}	58	−0.5

boiling point increases with increasing number of electrons

Subject vocabulary

intermolecular forces attractive forces that exist between molecules

London (dispersion) forces the electrostatic attraction between instantaneous dipoles on one molecule and induced dipoles on another molecule

dipole–dipole forces the electrostatic attraction between permanent dipoles on two molecules

hydrogen bonding a strong intermolecular force that occurs between molecules containing a hydrogen atom bonded to a highly electronegative atom

instantaneous dipole a dipole that only exists for a brief time on a molecule

induced dipole a dipole that forms on a molecule when its electrons are attracted or repelled by a dipole on another molecule

- **Dipole–dipole forces:**
    - exist between polar molecules that each contain a **permanent dipole**
    - are the electrostatic attraction between the permanent dipole on one molecule and the permanent dipole on another molecule

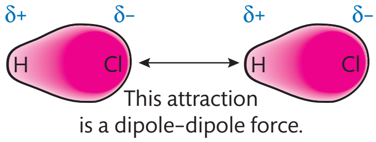
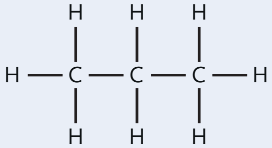
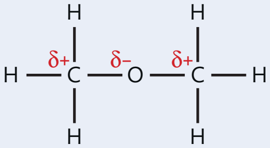


Figure 4.8 *Dipole–dipole forces in HCl are the attraction between the permanent dipoles of two molecules.*

Subject vocabulary

permanent dipole a dipole that is always present on a polar molecule

- increase in strength with the size of the overall dipole in the molecule
- are stronger than London forces for molecules of similar size. Compounds with dipole–dipole forces will have higher melting points and higher boiling points.

	C_3H_8	CH_3OCH_3
Molar mass (g mol⁻¹)	44	46
Structure		
Intermolecular forces	London forces	London forces and dipole–dipole forces
Boiling point (K)	229	249

- **Hydrogen bonding:**
    - occurs for molecules that have a hydrogen atom covalently bonded to a highly electronegative atom (nitrogen, oxygen, or fluorine)
    - is the electrostatic attraction between:
        - a hydrogen atom bonded to a highly electronegative atom in one molecule *and*
        - a lone pair of electrons on a highly electronegative atom in another molecule
    - is the strongest intermolecular force.

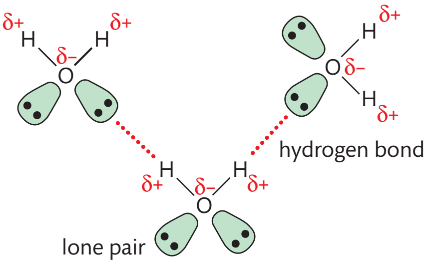


Figure 4.9 *Hydrogen bonding between water molecules.*

Water is an example of a substance in which hydrogen bonding occurs between the molecules.

The highly electronegative oxygen atom pulls electron density away from the hydrogen atom. This means:

- there is very little electron density around the nucleus of the hydrogen atom
- the hydrogen nucleus will strongly attract lone pairs of electrons on the oxygen atoms of neighbouring water molecules.

Hints for success: Do not confuse hydrogen bonds with covalent bonds. Hydrogen bonds are very strong intermolecular forces. Hydrogen bonds are not covalent bonds.

Understanding: The relative strengths of these forces are London (dispersion) forces < dipole–dipole forces < hydrogen bonds.

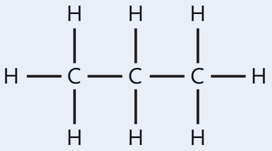
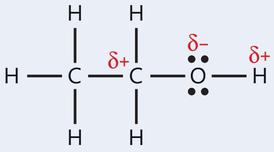
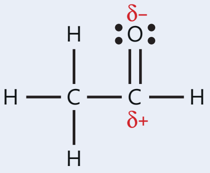
- When comparing molecules of similar sizes the relative strengths of intermolecular forces increase in the order:

  London forces < dipole–dipole forces < hydrogen bonding

Skill: Deduction of the types of intermolecular forces present in substances, based on their structure and chemical formula.

Worked example

Determine the strongest intermolecular forces present in the following compounds: $CH_3CH_2CH_3$, CH_3CH_2OH, and CH_3CHO.

Compound	Lewis structure (showing dipoles)	Key features	Strongest intermolecular forces present
$CH_3CH_2CH_3$		Non-polar molecule	London (dispersion) forces
CH_3CH_2OH		Polar molecule Hydrogen atom covalently bonded to highly electronegative oxygen atom	Hydrogen bonding
CH_3CHO		Polar molecule	Dipole–dipole forces

Skill: Explanation of the physical properties of covalent compounds (volatility, electrical conductivity, and solubility) in terms of their structure and intermolecular forces.

- The structure and physical properties of covalent network structures were discussed in the table on page 55.
- The physical properties of small covalent compounds can be explained on the basis of their intermolecular forces.

Volatility

- Small covalent compounds have a high volatility because the intermolecular forces between them are weak and this means they have low boiling points.
- Compounds that can form hydrogen bonds have higher boiling points and are less volatile than molecules with London (dispersion) forces and dipole–dipole forces. This is because hydrogen bonding is stronger than London (dispersion) forces and dipole–dipole forces.

	CH_4	CHF_3	NH_3	HF	H_2O
Strongest intermolecular forces present	London forces	dipole–dipole forces	hydrogen bonding	hydrogen bonding	hydrogen bonding
Boiling point (K)	112	191	240	293	373
Volatility	**highest** ←				**lowest**

- The boiling point of water is much higher than the boiling points of other small molecules that can form hydrogen bonds (NH_3 and HF). This is because each water molecule can form *more* hydrogen bonds to neighbouring molecules.

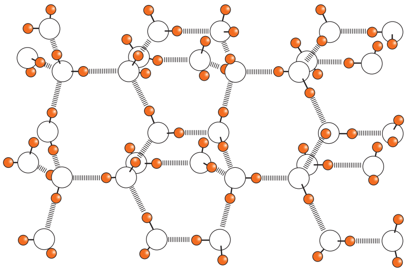


Figure 4.10 *The hydrogen bonding in solid water (ice). Each water molecule is hydrogen bonded to four other water molecules.*

Electrical conductivity

- Covalent molecules:
  - do not contain ions or delocalized electrons
  - have no charged species that are able to move
  - are not able to conduct electricity.

Solubility

- Solutes will dissolve in solvents that have similar bonding or intermolecular forces.

  This is described by the simple phrase 'like dissolves like'.
- The solubility of solutes in different solvents is summarized in the table below. Note that these are general trends and may not apply to all combinations of solutes and solvents.

	Non-polar solute (London forces)	**Polar solute (dipole–dipole)**	**Polar solute (H-bonding)**
Non-polar solvent (London forces), e.g. hexane, C_6H_{14}	soluble	not soluble	not soluble
Polar solvent (dipole–dipole), e.g. propanone, CH_3COCH_3	not soluble	soluble	soluble
Polar solvent (hydrogen bonding), e.g. water, H_2O	not soluble	soluble	very soluble

- Water is a polar solvent that can form hydrogen bonds. The solutes that have the highest solubility in water will be polar molecules that can also form hydrogen bonds, e.g. ethanol (CH_3CH_2OH).
- Non-polar compounds have a low solubility in water; e.g. hexane (C_6H_{14}) is a non-polar liquid and it does not dissolve in water. Two layers are observed when hexane is added to water.
- Hexane is a non-polar solvent. The solutes that have the highest solubility in hexane will be non-polar molecules; e.g. Cl_2, Br_2, and I_2 are all non-polar solutes and dissolve in non-polar solvents such as hexane.

4.5 Metallic bonding

Essential idea:

Metallic bonds involve a lattice of cations with delocalized electrons.

Understanding: A metallic bond is the electrostatic attraction between a lattice of positive ions and delocalized electrons.

- Metallic bonding:
  - occurs between metal atoms that have low electronegativities
  - is the electrostatic attraction between metal cations (positive ions) and delocalized electrons
  - can be explained by the **electron-sea model**.
- The electron-sea model:
  - There is a weak attraction between the nucleus of the metal atom and its valence electrons.
  - The valence electrons on one metal atom are attracted to the nuclei of other nearby metal atoms and they can move from one atom to another.
  - This means that the metal atoms lose their valence electrons and become cations that are arranged in a three-dimensional lattice structure.
  - The valence electrons are then present as an electron sea that is delocalized over the lattice of metal cations.

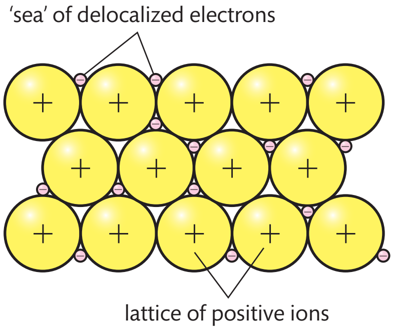


Figure 4.11 *The electron-sea model of metallic bonding.*

Subject vocabulary

electron-sea model a model that describes metallic bonding as the attraction between a lattice of cations and a sea of delocalized valence electrons

molten liquids liquids made by heating substances above their melting point

malleability the ability to be shaped under pressure

Skill: Explanation of electrical conductivity and malleability in metals.

Electrical conductivity

- Metals have a high electrical conductivity because the delocalized valence electrons are free to move throughout the metal lattice.
- Metals have a high electrical conductivity in the solid state and as **molten liquids**.

Malleability

- **Malleability** refers to the ability of a substance to be shaped under pressure. Most metals are very malleable.
- Metals are malleable because:
  - the metal cations in the lattice move to new positions when pressure is applied
  - a new shape is created
  - the delocalized electrons can still move freely through the new lattice shape
  - the metallic bonding is not affected by the new shape.

Understanding: The strength of a metallic bond depends on the charge of the ions and the radius of the metal ion.

- The strength of a metallic bond:
  - depends on the force of attraction between the sea of delocalized electrons and the metal cations
  - increases with a larger number of delocalized electrons in the electron sea
  - increases with a larger charge on the metal cation
  - increases with a smaller radius of the metal cation
  - affects the melting point of the metal: the stronger the metallic bond the higher the melting point of the metal.

Skill: Explanation of trends in melting points of metals.

Worked example

Sodium and magnesium are two metals in the third period. Explain why the melting point of magnesium (650 °C) is higher than the melting point of sodium (98 °C).

Solution

Magnesium has a higher melting point than sodium so magnesium must have stronger metallic bonding than sodium.

Magnesium forms Mg^{2+} ions and has twice as many delocalized electrons per cation than sodium, which forms Na^+ ions.

The attraction between the Mg^{2+} ions and the larger sea of delocalized electrons in magnesium will be greater than the attraction between the Na^+ ions and the electron sea in sodium.

Worked example

Explain why sodium (98 °C) has a higher melting point than potassium (63 °C) and rubidium (39 °C).

Solution

Sodium, potassium, and rubidium are all group 1 metals. The melting points decrease going down the group so the strength of metallic bonding must also decrease going down the group.

This is because the radius of the cations increases going down the group and the **charge density** of the cations decreases. (The same 1+ charge is spread over a larger volume with larger cations.)

The electron sea is more strongly attracted to cations with a larger charge density so the metallic bond strength and melting points decrease down the group.

Subject vocabulary

charge density a measure of the amount of charge that is contained within a volume

Subject vocabulary

alloys mixtures that are held together by metallic bonding. Usually an alloy is a mixture of two or more metals. Some alloys involve a metal mixed with a small amount of a non-metal

corrosion a natural process in which a metal reacts with oxygen in the air to form its oxide

General vocabulary

enhanced improved

Understanding: Alloys usually contain more than one metal and have enhanced properties.

- **Alloys**:
  - are typically made from adding one metal to another
  - are held together by metallic bonding between the different metals
  - have **enhanced** properties compared with the metals they are made from, e.g. alloys are often stronger than the metals they are made from.
- Common alloys include brass (copper and zinc), bronze (copper and tin), and pewter (tin, antimony, and copper).

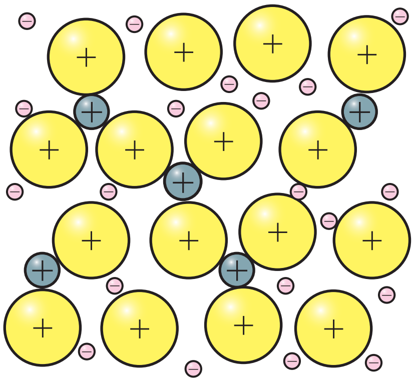


Figure 4.12 *Alloys consist of different metal ions and a sea of delocalized electrons. The smaller ions are able to fit in the spaces between the larger ions in the lattice structure.*

Skill: Explanation of the properties of alloys in terms of non-directional bonding.

- The different packing of the two metal cations in an alloy means that alloys have different properties from those of the parent metals they are made from:
  - alloys are often more chemically stable and resistant to **corrosion**
  - alloys are often stronger (i.e. harder to **deform**) than the parent metals because they are less malleable. (Because the cations have different sizes it is harder for the layers of cations in an alloy to slide past each other and form a new shape when pressure is applied.)
- The properties of alloys can be modified by:
  - mixing more than two metals
  - changing the relative amounts of the metals that are mixed
  - changing the size (atomic radius) of the metal added to make the alloy.

Synonym

deform .... distort

Topic 5: Energetics/thermochemistry

5.1 Measuring energy changes

Essential idea:

The enthalpy changes from chemical reactions can be calculated from their effect on the temperature of their surroundings.

Understanding: Heat is a form of energy.

- **Energy** is a measure of the ability to do **work**. The unit of energy is the joule (J).
- **Heat** is the transfer of energy that results from a temperature difference between two objects. When two objects are touching heat will flow from the object with the higher temperature to the object with the lower temperature.

Understanding: Temperature is a measure of the average kinetic energy of the particles.

- **Temperature** is a measure of the average kinetic energy of the particles in that substance. The average kinetic energy of the particles in a substance is **proportional** to temperature measured in **kelvin**.

Covered in a previous chapter: To convert from degrees Celsius (°C) to kelvin (K): K = °C + 273

- **Absolute zero** occurs at 0 K. At this temperature all movement stops so the average kinetic energy of particles is zero.

Understanding: Total energy is **conserved** in chemical reactions.

- Energy cannot be created or destroyed but it can be changed into different forms of energy and transferred between objects.
- **Chemical energy** is the energy that is stored in the chemical bonds and interparticle forces that are present in substances. When chemical reactions occur there will be a change in energy as products have different bonds (and different chemical energies) than reactants.

Understanding: Chemical reactions that involve transfer of heat between the system and the surroundings are described as endothermic or exothermic.

- In chemical reactions the **system** is regarded as the reaction mixture. The **surroundings** are everything that is outside the system.

  An **open system** is able to exchange energy and matter with the surroundings.

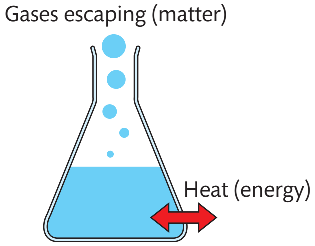


Figure 5.1 *An open system: gases (matter) can escape and transfer of energy as heat can occur.*

Subject vocabulary

energy	the ability to do work. Energy can be converted into different forms and transferred between objects. Energy cannot be created or destroyed
work	the ability to move an object against an opposing force
heat	the transfer of energy between two objects that have different temperatures
temperature	a measure of the average kinetic energy of particles
kelvin scale	a scale used to measure temperature. The units are called kelvin and have the symbol K
absolute zero	the temperature that represents zero on the kelvin scale (0 K). At absolute zero all movement stops and the average kinetic energy is zero
chemical energy	energy that is stored in chemical bonds and interparticle forces
system	the part of the universe being studied
surroundings	everything that is outside of the system
open system	can exchange mass and energy with the surroundings

General vocabulary

proportional	related in size to

Synonym

conserved ..... saved/retained , left unchanged

Subject vocabulary

closed system can exchange energy but not mass with the surroundings

exothermic reaction a reaction that gives off heat

endothermic reaction a reaction that takes in heat

specific heat capacity the amount of heat needed to raise the temperature of 1 g of a substance by 1 kelvin. Units are $J\,g^{-1}\,K^{-1}$

enthalpy (*H*) the heat that is contained in a system

enthalpy change (ΔH) the change in enthalpy that occurs due to a chemical reaction or process. It is equal to the amount of heat energy released or absorbed at constant pressure

A **closed system** is only able to exchange energy with the surroundings.

- An **exothermic reaction** transfers heat energy from the system to the surroundings. The temperature of the surroundings will increase.
- An **endothermic reaction** transfers heat energy from the surroundings to the system. The temperature of the surroundings will decrease.
- The **specific heat capacity** of a substance (*c*):
  - is the amount of energy needed to raise the temperature of one gram of the substance by one kelvin
  - has units $J\,g^{-1}\,K^{-1}$
- The change in heat (*q*) that occurs in a substance is related to:
  - the mass of the substance (*m*) in grams
  - the specific heat capacity (*c*) of the substance
  - the temperature change observed (ΔT) in kelvin.

The equation used to calculate the change in heat (*q*) is: $q = mc\Delta T$.

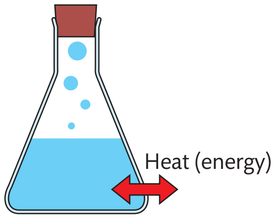


Figure 5.2 *A closed system: gases cannot escape but transfer of energy as heat can occur.*

Skill: Calculation of the heat change when the temperature of a pure substance is changed using $q = mc\Delta T$.

Worked example

Determine the amount of heat gained when a 3.50 kg aluminium bar is heated from 298.0 K to 357.3 K. The specific heat capacity of aluminium is $0.900\,J\,g^{-1}\,K^{-1}$.

Solution

$m = 3.50\,kg = 3500\,g$ $\Delta T = 357.3\,K - 298.0\,K = 59.3\,K$

$q = mc\Delta T = 3500\,g \times 0.900\,J\,g^{-1}\,K^{-1} \times 59.3\,K = 187\,000\,J = 187\,kJ$

Understanding: The enthalpy change (ΔH) for chemical reactions is indicated in $kJ\,mol^{-1}$.

- The **enthalpy (*H*)** of a system is the heat contained in the system. Enthalpy cannot be measured directly but the **enthalpy change (ΔH)** that occurs during chemical reactions can be measured. At constant pressure the enthalpy change (ΔH) is equal to the heat that is lost or gained by the system (*q*):

  $\Delta H = q$

  $\Delta H = H(\text{products}) - H(\text{reactants})$

  The sign of ΔH depends on whether the reaction is exothermic or endothermic.

Hints for success: The value of an enthalpy change always has a positive sign or a negative sign to show if it is endothermic or exothermic.

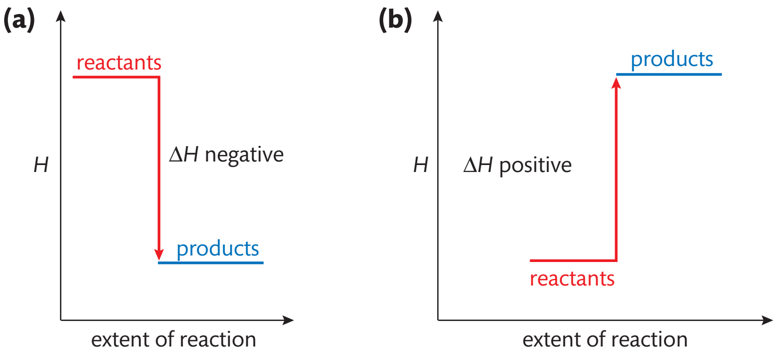


Figure 5.3 ***(a)*** *An exothermic reaction. The enthalpy of the products is less than the enthalpy of the reactants.* ***(b)*** *An endothermic reaction. The enthalpy of the products is greater than the enthalpy of the reactants.*

- The enthalpy change (ΔH) for a chemical reaction depends on the conditions under which it is measured. This means that enthalpy changes should be compared using a standard set of conditions.
- **Standard enthalpy changes ($\Delta H^{\ominus}$)** are measured using:
  - a pressure of 100 kPa (100 000 Pa)
  - a concentration of 1 mol dm^{-3} for all solutions
  - all reactants in their **standard states** (the states that the reactants normally exist in at 100 kPa)
  - no defined temperature but 298 K (25 °C) is commonly used.
- Enthalpy changes (ΔH) are calculated for *one mole* of substance so the units are kJ mol^{-1} (kJ per mole).

Skill: A calorimetry experiment for an enthalpy of reaction should be covered and the results evaluated.

- The **enthalpy of reaction ($\Delta H^{\ominus}_{\text{reaction}}$)** is the enthalpy change that occurs when one mole of a substance is reacted under standard conditions.
- A **calorimeter** is an instrument used to measure the heat changes that occur during a reaction. The enthalpy of reaction can then be calculated from these measurements.

  An insulated coffee cup can be used as a calorimeter to measure heat changes that occur in solution during a reaction.

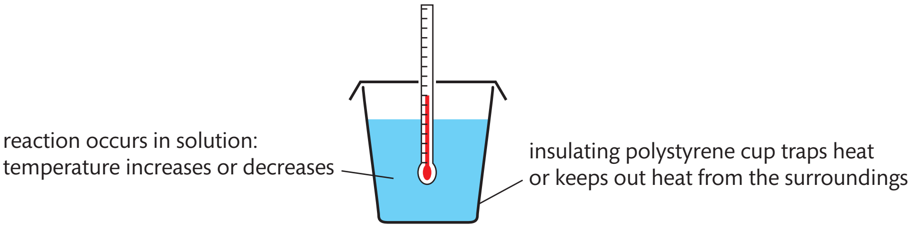


Figure 5.4 *A simple calorimeter. The polystyrene is a very good thermal insulator with a low heat capacity.*

Worked example

50.0 cm^3 of 1.00 mol dm^{-3} copper(II) sulfate solution was placed in a polystyrene coffee cup and excess zinc powder was added to the solution. The temperature change (ΔT) that occurred due to the reaction was 48.2 K.

Use these results to calculate the enthalpy change for the reaction (ΔH_r) in kJ mol^{-1}:

$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$

Solution

Assumptions:

(i) heat capacity (c) of solution = heat capacity of water = 4.18 J g^{-1} K^{-1}

(ii) density of solution = density of water = 1.00 g cm^{-3} (so 50.0 cm^3 has a mass of 50.0 g)

$$\Delta H_r = \frac{q}{n(Cu^{2+})}$$

$$q = mc\Delta T = 50.0\,\text{g} \times 4.18\,\text{J g}^{-1}\,\text{K}^{-1} \times 48.2\,\text{K} = 10.1\,\text{kJ}$$

$$n(\text{Cu}^{2+}) = CV = 1.00\,\text{mol dm}^{-3} \times \frac{50.0}{1000}\text{dm}^3 = 0.0500\,\text{mol}$$

$$\Delta H_r = \frac{q}{n(Cu^{2+})} = \frac{-10.1\,kJ}{0.0500\,mol} = -202\,\text{kJ mol}^{-1}$$

ΔH is negative as the reaction released heat and is exothermic.

Subject vocabulary

standard enthalpy changes the heat that is given off or taken in by reactions that occur under standard conditions

standard states the state in which an element or compound exists under standard conditions

enthalpy of reaction ($\Delta H^{\ominus}_{\text{reaction}}$) the enthalpy change that occurs when one mole of a substance is reacted under standard conditions

calorimeter an instrument that measures the heat changes that occur during a reaction

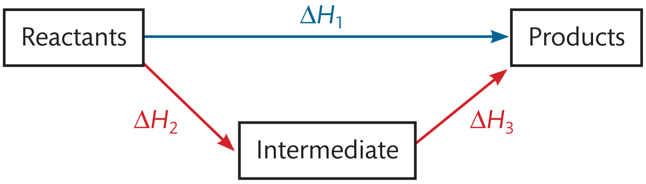
5.2 Hess's Law

Essential idea:

In chemical transformations energy can be neither created nor destroyed (the first law of thermodynamics).

Understanding: The enthalpy change for a reaction that is carried out in a series of steps is equal to the sum of the enthalpy changes for the individual steps.

- **Hess's Law** states that enthalpy change is independent of the reaction pathway.



Applying Hess's Law: $\Delta H_1 = \Delta H_2 + \Delta H_3$

(the two reaction pathways have the same overall reaction so have the same overall enthalpy change)

Subject vocabulary

Hess's Law enthalpy change is independent of pathway

standard enthalpy of formation ($\Delta H_f^{\ominus}$) the enthalpy change that occurs when one mole of a substance is formed from its elements in their standard states and under standard conditions

Skill: Application of Hess's Law to calculate enthalpy changes.

Worked example

Figure 5.5 illustrates the enthalpy changes occurring for a set of reactions:

Use this information to determine the enthalpy change for:

(i) P → S

(ii) Q → S

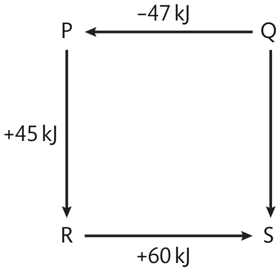


Figure 5.5 *illustrates the enthalpy changes occurring for a set of reactions.*

Solution

(i) $\Delta H(\mathrm{P} \rightarrow \mathrm{S}) = \Delta H(\mathrm{P} \rightarrow \mathrm{R}) + \Delta H(\mathrm{R} \rightarrow \mathrm{S}) = +45\text{ kJ} + 60\text{ kJ} = +105\text{ kJ}$

(ii) $\Delta H(\mathrm{P} \rightarrow \mathrm{S}) = \Delta H(\mathrm{P} \rightarrow \mathrm{Q}) + \Delta H(\mathrm{Q} \rightarrow \mathrm{S})$

$+105\text{ kJ} = -(-47\text{ kJ}) + \Delta H(\mathrm{Q} \rightarrow \mathrm{S})$

$+105\text{ kJ} = +47\text{ kJ} + \Delta H(\mathrm{Q} \rightarrow \mathrm{S})$

$\Delta H(\mathrm{Q} \rightarrow \mathrm{S}) = +58\text{ kJ}$

Hints for success: Enthalpy values are added when following the direction of arrows in an enthalpy cycle and subtracted when going against an arrow.

Standard enthalpies of formation

- The **standard enthalpy of formation ($\Delta H_f^{\ominus}$)** is the enthalpy change when one mole of a substance is formed from its elements in their standard states and under standard conditions, e.g. the standard enthalpies of formation for water (H_2O) and ethanol (C_2H_5OH) are the enthalpy changes that occur for the reactions:

  $\Delta H_f^{\ominus}(H_2O)$: $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$

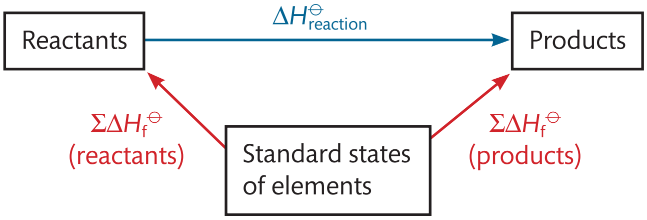
  $\Delta H_f^{\ominus}(C_2H_5OH)$: $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \rightarrow C_2H_5OH\,(l)$

  $\Delta H_f^{\ominus}$ of all *elements* in their standard states is zero, e.g. $\Delta H_f^{\ominus}(O_2) = 0$.

Hints for success: Standard enthalpies of formation are given in section 12 of the IB data booklet.

- Hess's Law allows us to use enthalpies of formation to calculate the standard enthalpy change of a reaction ($\Delta H^{\ominus}_{\text{reaction}}$)

$\Delta H^{\ominus}_{\text{reaction}} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})$



Applying Hess's Law:

$\Delta H^{\ominus}_{\text{reaction}} = \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})$

Skill: Calculation of Δ*H* for reactions using $\Delta H_f^{\ominus}$ data.

Worked example

Use the standard enthalpy of formation data provided to determine the standard enthalpy change for the reaction of hydrazine (N_2H_4) and hydrogen (H_2) to form ammonia (NH_3):

$N_2H_4(g) + H_2(g) \rightarrow 2NH_3(g)$

$\Delta H_f^{\ominus}(N_2H_4) = +95\ \text{kJ mol}^{-1}$ $\quad\quad$ $\Delta H_f^{\ominus}(NH_3) = -46\ \text{kJ mol}^{-1}$

$$\begin{aligned}\Delta H^{\ominus}_{\text{reaction}} &= \Sigma\Delta H_f^{\ominus}(\text{products}) - \Sigma\Delta H_f^{\ominus}(\text{reactants})\\ &= 2 \times \Delta H_f^{\ominus}(NH_3) - [\Delta H_f^{\ominus}(N_2H_4) + \Delta H_f^{\ominus}(H_2)]\\ &= 2 \times -46\ \text{kJ mol}^{-1} - [+95 + 0]\ \text{kJ mol}^{-1}\\ &= -187\ \text{kJ mol}^{-1}\end{aligned}$$

Hints for success: The $\Delta H_f^{\ominus}$ values for a compound must be multiplied by the coefficient of that compound.

Skill: Determination of the enthalpy change of a reaction that is the sum of multiple reactions with known enthalpy changes.

Worked example

Determine the standard enthalpy change ($\Delta H^{\ominus}$) for the reaction:

$C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g)$

Using the information:

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$ $\quad$ $\Delta H^{\ominus} = -394\ \text{kJ}$ $\quad$ (Reaction 1)

$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g)$ $\quad$ $\Delta H^{\ominus} = -283\ \text{kJ}$ $\quad$ (Reaction 2)

Solution

We can rearrange the two equations provided to give the overall equation of the reaction required. The enthalpy change for the reaction can then be determined using Hess's Law.

Reaction 1:	$C(\text{graphite}) + \cancel{O_2(g)}\ \frac{1}{2}O_2(g)$	$\rightarrow \cancel{CO_2(g)}$	$\Delta H^{\ominus} = -394\ \text{kJ}$
Reverse reaction 2:	$\cancel{CO_2(g)}$	$\rightarrow CO(g) + \cancel{\frac{1}{2}O_2(g)}$	$\Delta H^{\ominus} = +283\ \text{kJ}$
Overall equation:	$\mathbf{C(\text{graphite}) + \frac{1}{2}O_2(g)}$	$\mathbf{\rightarrow CO(g)}$	$\mathbf{\Delta H^{\ominus} = -111\ \text{kJ}}$

Hints for success: Reversing a reaction means that +Δ*H* becomes –Δ*H*.

5.3 Bond enthalpies

Essential idea:

Energy is absorbed when bonds are broken and is released when bonds are formed.

Understanding: Bond forming releases energy and bond breaking requires energy.

Understanding: Average bond enthalpy is the energy needed to break one mole of a bond in a gaseous molecule averaged over similar compounds.

- Energy is needed to break chemical bonds so bond breaking is an endothermic process.

  Energy is released when making chemical bonds so bond forming is an endothermic process.

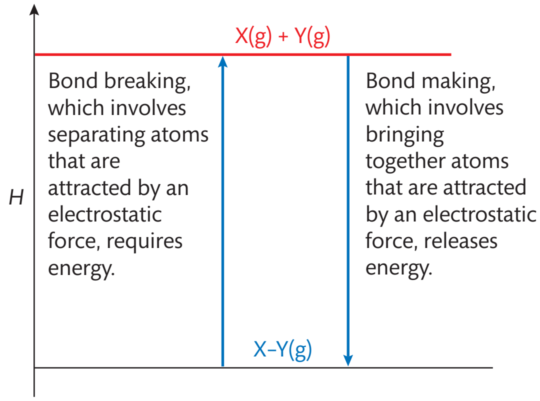


Figure 5.6 *The energy changes that occur when bonds are broken and bonds are formed.*

- The enthalpy change for a reaction is equal to the difference between the energy required to break bonds in the reactants and the energy released when bonds are formed in the products.

  $\Delta H_{\text{reaction}} = \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})$
- The **bond enthalpy** is the energy required to break one mole of a particular covalent bond in *gaseous* molecules.

  Section 11 of the IB data booklet gives *average* bond enthalpies for various covalent bonds. These are average values because the enthalpy measured for a particular bond in various molecules will be affected by the other bonds that are present in the molecule, e.g. the bond enthalpy for the C–H bonds in methane (CH_4) will not be the same as the bond enthalpy for the C–H bonds in chloromethane (CH_3Cl).

  Because the tabulated values are average bond enthalpies they can only be used to *estimate* the enthalpy change of a reaction.

  The tabulated bond enthalpies give the best estimates for gas reactions as they do not account for the intermolecular forces present in solids and liquids.

Subject vocabulary

bond enthalpy the energy required to break one mole of a particular bond in the gaseous state

Skill: Calculation of the enthalpy changes from known bond enthalpy values and comparison of these to experimentally measured values.

Worked example

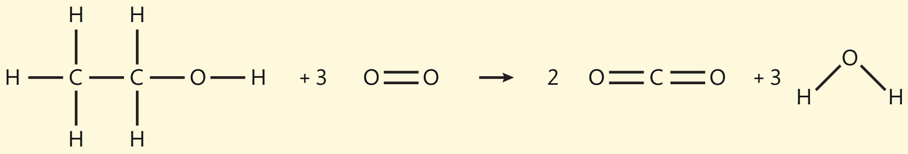
Use bond enthalpies to determine the change of enthalpy ($\Delta H_{\text{reaction}}$) that occurs for the combustion reaction of ethanol (CH_3CH_2OH) with oxygen (O_2) to give carbon dioxide (CO_2) and water (H_2O):

$CH_3CH_2OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

Compare your answer to the value of −1367 kJ mol⁻¹ obtained experimentally and explain any differences between the two values.

Solution

To answer this question it is necessary to first draw the structures of the reactants and products. This makes it easier to visualize the bonds that are being broken in the reactants and the bonds being formed in the products.



Bonds broken		**Bonds formed**	
Bond	**Bond enthalpy /kJ mol^{-1}**	**Bond**	**Bond enthalpy /kJ mol^{-1}**
5 C–H	5 × 414	4 C=O	4 × 804
C–O	358	6 O–H	6 × 463
C–C	346		
O–H	463		
3 O=O	3 × 498		
ΣE(bonds broken)	**4731 kJ mol^{-1}**	ΣE(bonds formed)	**5994 kJ mol^{-1}**

$$\begin{aligned}\Delta H_{\text{reaction}} &= \Sigma E(\text{bonds broken}) - \Sigma E(\text{bonds formed})\\ &= 4731\ \text{kJ mol}^{-1} - 5994\ \text{kJ mol}^{-1}\\ &= -1263\ \text{kJ mol}^{-1}\end{aligned}$$

The enthalpy change calculated for the reaction using the bond enthalpies from section 11 of the IB data booklet is −1263 kJ mol^{-1}.

The value obtained experimentally for the reaction (given in the question) is −1367 kJ mol^{-1}.

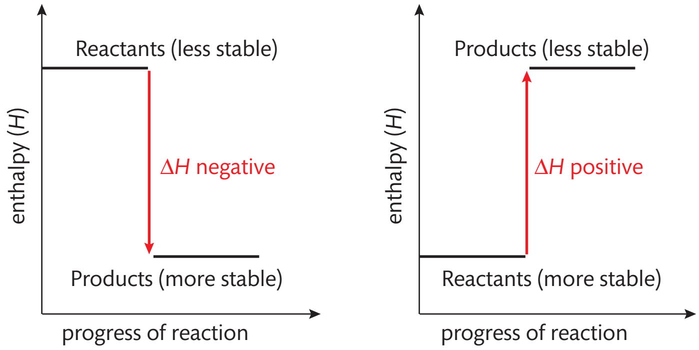
Possible reasons for the difference:

- bond enthalpies are measured for *gases* but the reaction involves liquids
- bond enthalpies are *averaged* values and will not be the exact values for the bonds in the reactants and products of this reaction.

Skill: Sketching and evaluation of potential energy profiles in determining whether reactants or products are more stable and if the reaction is exothermic or endothermic.

- Products are more stable than reactants if they have a lower enthalpy than the reactants. This happens for exothermic reactions (ΔH is negative).
- For endothermic reactions (ΔH is positive) reactants are more stable than products.

Figure 5.7 *The relative stability of reactants and products in exothermic and endothermic reactions.*

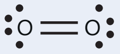
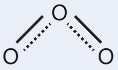


Exothermic reaction
Energy released in bond making > energy used in bond breaking

Endothermic reaction
Energy released in bond making < energy used in bond breaking

Skill: Discussion of the bond strength in ozone relative to oxygen and its importance to the atmosphere.

The combination of oxygen (O_2) and ozone (O_3) in the atmosphere absorbs most harmful ultraviolet (UV) radiation. Because O_2 contains stronger bonds it absorbs UV radiation of a shorter wavelength (higher energy) than the UV radiation absorbed by O_3.

	Oxygen O_2	**Ozone O_3**
		
Bond order	2	1.5
Bond enthalpy	498 kJ mol^{-1}	364 kJ mol^{-1}
Dissociated by UV light	<242 nm	<330 nm

Ozone levels in the atmosphere have been depleted because of chemicals released by human activity. This has serious health consequences because the harmful UV wavelengths that would normally be absorbed by ozone are more likely to reach the Earth's surface.

Topic 6: Chemical kinetics

6.1 Collision theory and rates of reaction

Essential idea:

The greater the probability that molecules will collide with sufficient energy and proper orientation, the higher the **rate** of reaction.

Synonym

rate .... speed

Understanding: Species react as a result of collisions of sufficient energy and proper orientation.

- All particles in a substance move **randomly** because of the **kinetic energy** they have. The random motion results in the particles colliding with each other, and chemical reactions can happen as a result of these collisions.
- Only some collisions will result in the reaction happening. For products to form, the reactant particles must:
  (i) collide with enough energy
  (ii) collide with the correct **orientation**.

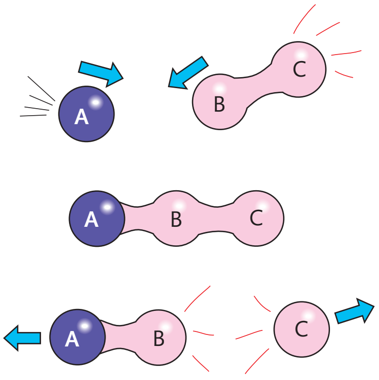


Figure 6.1 *Particles react by colliding.*

General vocabulary

randomly without a pattern

orientation the direction that an object is moving in relative to another object

Subject vocabulary

kinetic energy the energy that an object has due to its motion

Maxwell–Boltzmann distribution the range of kinetic energies that a sample of particles has at a given temperature

Skill: Description of the kinetic theory in terms of the movement of particles whose average kinetic energy is proportional to temperature in kelvin.

- The temperature, in kelvin (K), of a substance is a measure of the average kinetic energy of the particles in the substance. As temperature increases:
  - the average kinetic energy of the particles increases
  - particles collide more frequently
  - particles collide with greater energy.
- Because temperature is a measure of *average* kinetic energy there will be a range of kinetic energies at a given temperature. Some particles will move faster and have a higher kinetic energy than the average. Other particles will move slower and have a lower kinetic energy than the average. The range of kinetic energies that particles have at a given temperature is called the **Maxwell–Boltzmann distribution**.

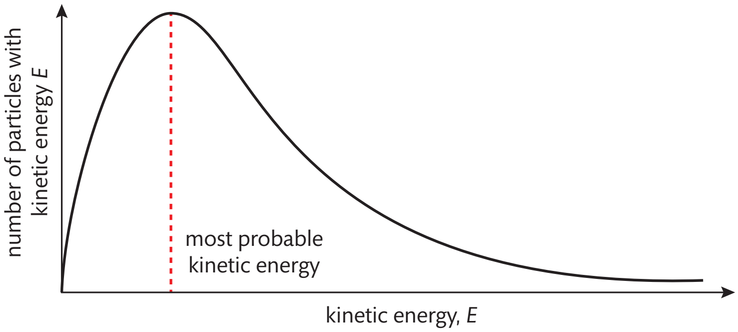


Figure 6.2 *The Maxwell–Boltzmann distribution curve.*

- The area below the curve in Figure 6.2 represents the total number of particles that are in the sample. The peak of the distribution represents the most probable kinetic energy.

Understanding: Activation energy (E_a) is the minimum energy that colliding molecules need in order to have successful collisions leading to a reaction.

- The energy of a collision depends on the kinetic energy of the particles involved. The minimum amount of kinetic energy that the particles must have before a collision will lead to a reaction is known as the **activation energy (E_a)**. Different chemical reactions have different activation energies.

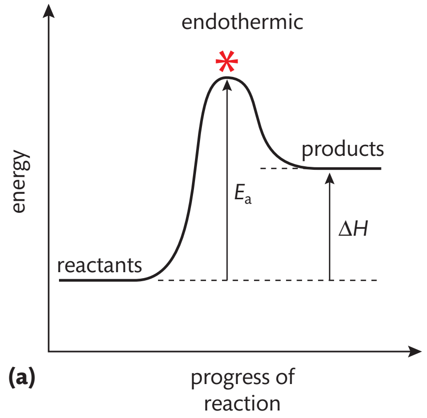


Figure 6.3 *Energy path of a reaction with the activation energy for* ***(a)*** *endothermic and* ***(b)*** *exothermic reactions.*
** represents the transition state.*

- If the reactants collide with enough energy to reach the **transition state** then the reaction can continue on and form products.
- The activation energy for a reaction can be included in the Maxwell–Boltzmann distribution to show the proportion of particles that have enough kinetic energy to react:

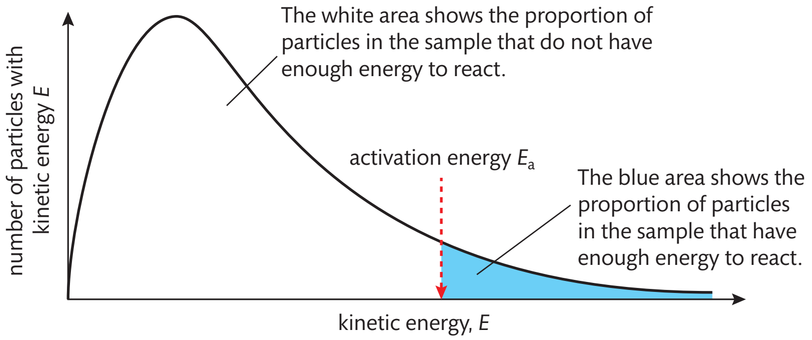


Figure 6.4 *Maxwell–Boltzmann distribution showing how the activation energy, E_a, distinguishes between particles that have greater or lesser values of kinetic energy.*

Understanding: The rate of reaction is expressed as the change in concentration of a particular reactant/product per unit time.

- In chemistry we are interested in the **rate of reaction**, which is a measure of how fast a reaction happens and reactants are changed into products.
- A **rate** is a measure of how quickly something changes over time and always has units of 'per time', e.g. per second (s^{-1}) or per minute (min^{-1}).
- The rate of reaction is determined by measuring how the concentration of products increases over time or by measuring how the concentration of reactants decreases over time.

$$\text{rate of reaction} = \frac{\Delta[\text{products}]}{\Delta t} = -\frac{\Delta[\text{reactants}]}{\Delta t}$$

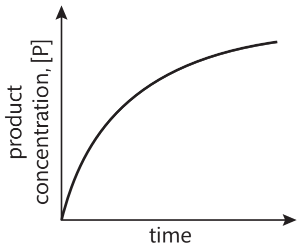


Figure 6.5 *Concentration of product against time.*

Subject vocabulary

activation energy (E_a) the minimum amount of energy needed for a reaction to occur

transition state a high energy state that must be reached before a reaction can happen

rate of reaction how fast a reaction happens (how quickly reactants are changed into products)

General vocabulary

rate a measure of how quickly a change occurs over time

- The negative sign in front of $\frac{\Delta[\text{reactants}]}{\Delta t}$ is because rates of reaction must be positive values. The concentration of reactants is decreasing so Δ[reactants] will be a negative value. Note that adding the negative sign converts this to a positive value.
- Because a rate of reaction is measured as a change in concentration over time the units for a rate of reaction will be equal to the units of concentration over units of time, $\frac{\text{mol dm}^{-3}}{\text{s}}$ or $\text{mol dm}^{-3}\,\text{s}^{-1}$.

Skill: Analysis of graphical and numerical data from rate experiments.

- If the concentration of reactants is measured for a reaction and then plotted against time the graph shows a curve.

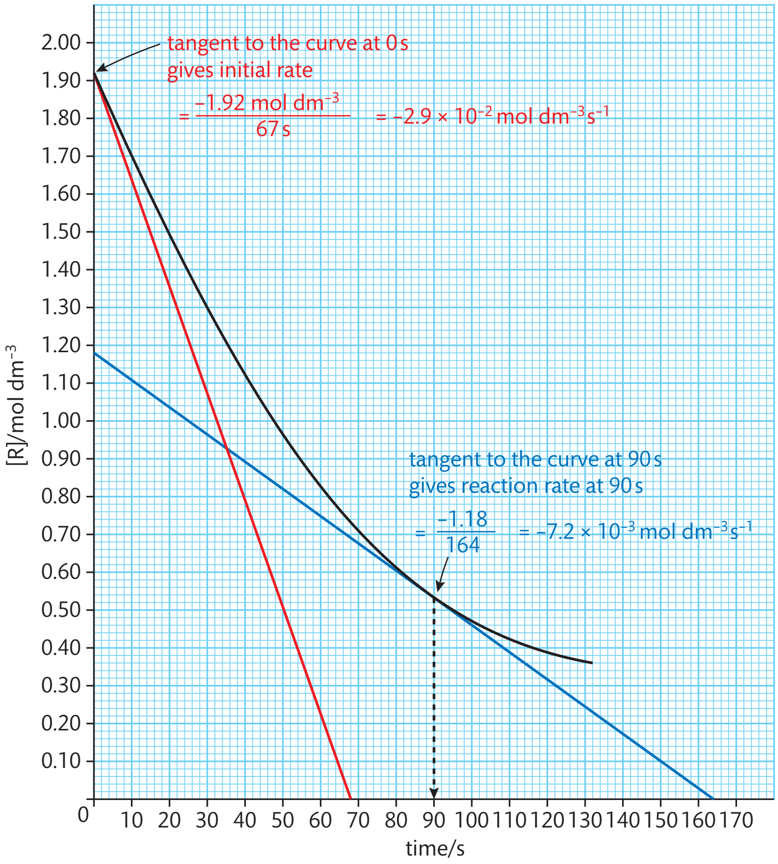


Figure 6.6 *Measuring the gradient of the tangent to the curve at two different times during a reaction. The rate decreases as the reaction proceeds.*

- The curve shows that the rate of reaction is fastest at the start of the reaction and decreases as the reaction proceeds.
- The **gradient** of the curve at any given point gives the rate of reaction at that time. The gradient of a curve is obtained from the tangent to the curve at that point. In Figure 6.6 this is shown using the blue tangent line at *t* = 90 s:

$$\text{rate of reaction (90 s)} = -\frac{\Delta[\text{reactants}]}{\Delta t} = -(-7.2 \times 10^{-3}\,\text{mol dm}^{-3}\,\text{s}^{-1})$$
$$= 7.2 \times 10^{-3}\,\text{mol dm}^{-3}\,\text{s}^{-1}$$

- When the rate is obtained at *t* = 0 this is the **initial rate of reaction**. In Figure 6.6 this is shown using the red tangent line:

$$\text{initial rate of reaction (0 s)} = -\frac{\Delta[\text{reactants}]}{\Delta t} = -(-2.9 \times 10^{-3}\,\text{mol dm}^{-3}\,\text{s}^{-1})$$
$$= 2.9 \times 10^{-3}\,\text{mol dm}^{-3}\,\text{s}^{-1}$$

General vocabulary

gradient the slope (or steepness) of a line

Subject vocabulary

initial rate of reaction the rate of reaction that occurs at the start of the reaction (when *t* = 0)

Understanding: Concentration changes in a reaction can be followed indirectly by monitoring changes in mass, volume, and colour.

- It is often difficult to directly measure concentration changes during a reaction. Instead a property that depends on concentration is continuously measured. The rate of reaction can then be calculated from the rate of change for the property measured.

  Suitable changes that can be measured include change in volume, change in mass, change in **absorption**, change in conductivity, and change in pH.

Synonym

absorption .... taking in

Measuring the change in volume of a gas

If the products of the reaction include a gas then the gas can be collected and the volume of gas produced by the reaction is recorded over time, e.g.

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

$Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l) + CO_2(g)$

The reaction rate is obtained from a graph of the volume of gas collected against time (Figure 6.7).

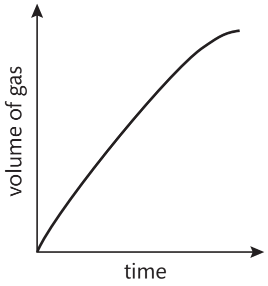


Figure 6.7 *Volume of gas against time.*

Measuring the change in mass of a reaction

If the reaction produces a gas we can also measure the change in mass that occurs when the gas escapes the reaction mixture.

The reaction rate is obtained from a graph of the mass of the reaction mixture against time (Figure 6.8).

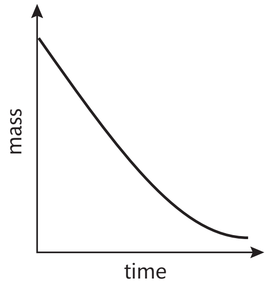


Figure 6.8 *Mass against time.*

Hints for success: This method is not suitable for gases with low molar masses (e.g. H_2) as the change in mass that occurs may be too small to measure accurately.

Measuring the change in colour during a reaction

If the reaction involves a change in colour it is possible to measure the change in **absorbance** of the solution using a **spectrophotometer**.

Subject vocabulary

absorption the amount of light taken in when it passes through a liquid

absorbance a measure of the amount of light absorbed by coloured solutions

spectrophotometer an instrument that measures the absorbance of light

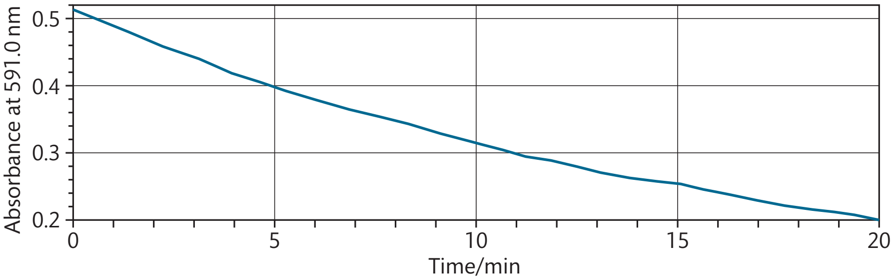


Figure 6.9 *Absorbance against time.*

The reaction rate is obtained from a graph of absorbance against time (Figure 6.9).

Skill: Explanation of the effects of temperature, pressure/concentration, and particle size on rate of reaction.

The rate of a reaction will increase with any factor that increases the frequency of successful collisions.

Effect of temperature

The rate of reaction increases when temperature is increased. At a higher temperature the particles have a greater average kinetic energy and this increases the rate of reaction because:

- the particles collide at a higher frequency
- a higher **proportion** of the collisions have enough kinetic energy to overcome the activation energy.

General vocabulary

proportion an amount expressed relative to the total

Skill: Construction of Maxwell–Boltzmann energy distribution curves to account for the probability of successful collisions and factors affecting these, including the effect of a catalyst.

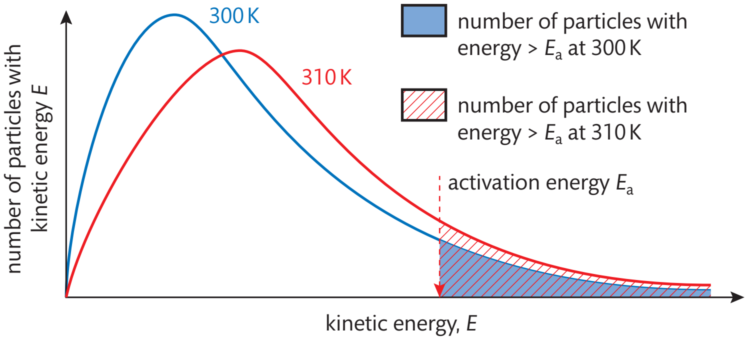


Figure 6.10 *Maxwell–Boltzmann distribution curves for a sample of gas at two different temperatures, showing the higher proportion of particles with kinetic energy greater than the activation energy at the higher temperature.*

- In Figure 6.10 the Maxwell–Boltzmann distributions of the same sample of particles are shown for 300 K and 310 K. The total area under the two curves is the same as they represent the same number of particles.
- At higher temperatures:
  - the distribution is wider because a greater range of kinetic energies is possible
  - the peak of the curve moves to the right as the most probable kinetic energy occurs at a higher kinetic energy
  - the peak of the curve is lower.

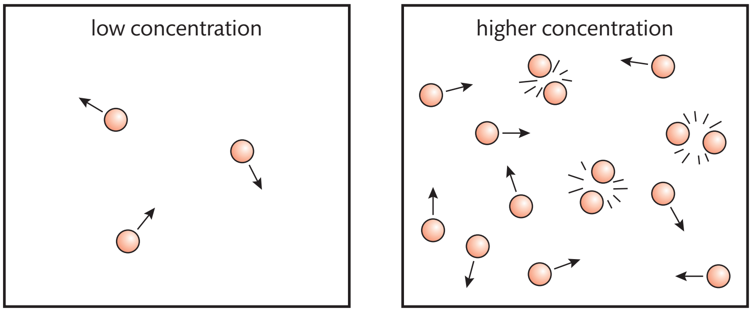
Hints for success: When asked to draw two Maxwell–Boltzmann distributions at different temperatures make sure they both start at the origin (0, 0). The distribution at higher temperature should be wider and lower, with the peak occurring at a greater kinetic energy.

- The shaded areas to the right of the activation energy in Figure 6.10 represent the proportion of particles at each temperature that have sufficient kinetic energy to overcome the activation energy. At the higher temperature a larger proportion of particles have enough kinetic energy to react so the rate of reaction will increase with an increase in temperature.

Effect of concentration and pressure on rate of reaction

- Increasing the concentration of solutions:
  - means that there are more reactant particles within the same volume
  - results in collisions happening at a higher frequency
  - results in the rate of reaction increasing.

Figure 6.11 *Effect of concentration on collision frequency.*



When particles are closer together they have a greater chance of reacting.

- Increasing the pressure of gases:
  - means that there are more reactant particles within the same volume (i.e. the concentration has increased)
  - results in collisions between gas particles happening at a higher frequency
  - results in the rate of reaction increasing.

Effect of particle size on rate of reaction

- Particle size affects the rates of reactions that involve solids.
- Reactions of solids:
  - involve collisions that happen at the *surface* of the solid
  - will have a faster rate if the solid has a bigger **surface area**
  - will have a faster rate for the same mass of a solid if it is broken into many small pieces (or particles) because this increases the surface area.

    For example when a large piece of coal is crushed into a **powder** it has a much larger surface area. The coal powder will react much faster than the large piece of coal.

General vocabulary

surface area	the total area of the surface of a solid
powder	a solid made up of very small particles

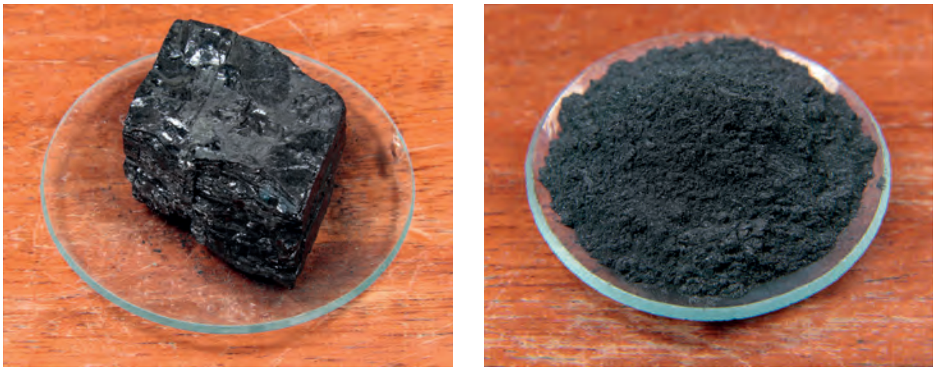


Figure 6.12 *The powdered coal (right) has the same mass as the lump of coal (left), but it has a larger surface area and will react faster.*

Understanding: By decreasing E_a, a catalyst increases the rate of a chemical reaction, without being permanently chemically changed.

- A **catalyst** is a substance that increases the rate of a reaction but is not permanently chemically changed by the reaction. Most catalysts provide an alternative reaction pathway with a lower activation energy (E_a).

Subject vocabulary

catalyst	a substance that speeds up a reaction but is unchanged at the end of the reaction

Skill: Sketching and explanation of energy profiles with and without catalysts.

An energy diagram can be drawn that shows the effect of a catalyst on activation energies. When a catalyst is added the energies of the reactants and products do not change so the reaction has the same enthalpy change (Δ*H*).

The activation energy that occurs between the reactants and products is lower for the catalysed reaction than for the uncatalysed reaction.

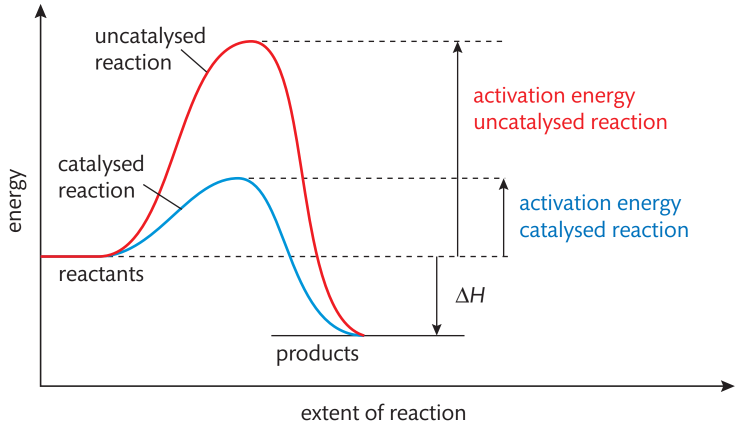


Figure 6.13 *Effect of a catalyst on lowering the activation energy of a reaction.*

When the activation energy is lowered a greater proportion of reactant particles have enough kinetic energy to overcome the activation energy so the rate of reaction increases. This can be illustrated by a Maxwell–Boltzmann distribution that shows the activation energies for the catalysed and uncatalysed reactions.

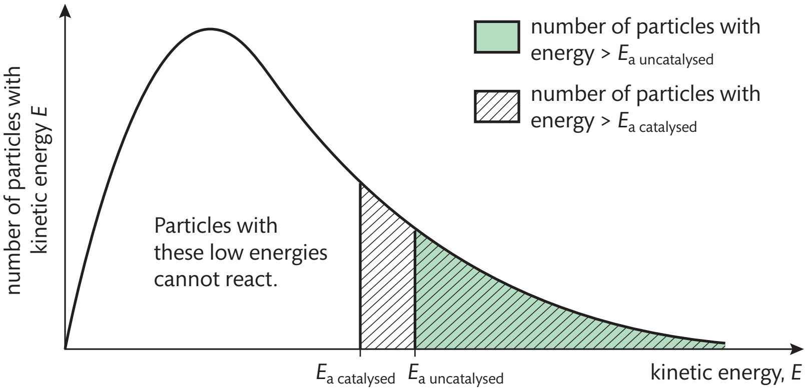


Figure 6.14 *Effect of catalyst on increasing the proportion of particles able to react.*

Topic 7: Equilibrium

7.1 Equilibrium

Essential idea:

Many reactions are reversible. These reactions will reach a state of equilibrium when the rates of the **forward reaction** and **reverse reaction** are equal. The position of equilibrium can be controlled by changing the conditions.

Subject vocabulary

forward reaction reaction that proceeds from left to right as written; reactants are converted into products

reverse reaction reaction that proceeds from right to left as written; products are converted into reactants

equilibrium a state in which forward and reverse reactions are occurring at the same rate in a closed system. There is no overall change in the concentrations of reactants and products

dissociation a reaction in which a molecule is split into smaller molecules, atoms, or ions

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Understanding: A state of equilibrium is reached in a closed system when the rates of the forward and reverse reactions are equal.

- In a reaction, reactants are changed into products in the forward reaction.
- In some reactions, the reverse (or backward) reaction also occurs, where products are changed into reactants.

$$\text{reactants} \underset{\text{backward reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} \text{products}$$

- A reaction is said to be at **equilibrium** when the rate of the forward reaction is equal to the rate of the reverse reaction. At equilibrium the concentrations of reactants and products remain constant.

Example of equilibrium in a physical system:

- Liquid bromine changes into vapour in a closed system. A closed system, for example a sealed container, does not allow exchange of matter with the surroundings. At equilibrium the amount of liquid bromine and bromine vapour in the container remain constant.

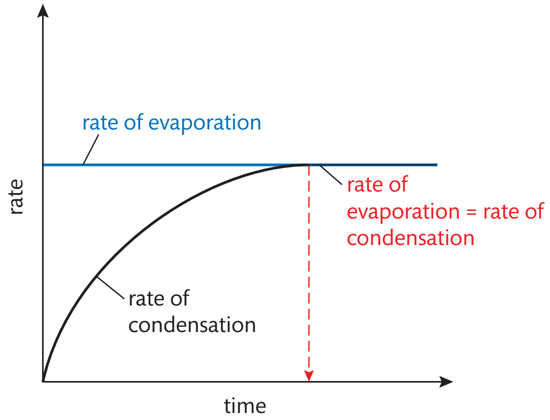


Figure 7.1 *The rates of evaporation and condensation as liquid–vapour equilibrium is established in a closed system. The rate of evaporation is constant, while the rate of condensation increases with increasing concentration of vapour. Equilibrium is established when the two rates are equal.*

Example of equilibrium in a chemical system:

- The **dissociation** of hydrogen iodide, HI, into hydrogen, H_2, and iodine, I_2.

$$\begin{array}{ccccc} 2HI(g) & \rightleftharpoons & H_2(g) & + & I_2(g) \\ \text{colourless gas} & & \text{colourless gas} & & \text{purple gas} \end{array}$$

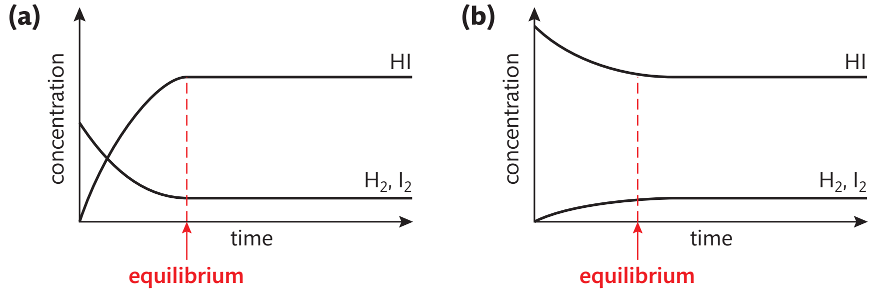


Figure 7.2 *Equilibrium is reached when the concentrations of reactants and products become constant. Note the same equilibrium mixture is reached starting from* ***(a)*** *a mixture of H_2 and I_2 or* ***(b)*** *pure HI.*

Skill: The characteristics of chemical and physical systems in a state of equilibrium.

Like the examples above, all reactions at equilibrium have the following characteristics:

	Feature of equilibrium state	Explanation
1	Equilibrium is **dynamic**	The reaction has not stopped but both forward and backward reactions are still occurring at the same rate.
2	Equilibrium is achieved in a closed system	A closed system has no exchange of matter with the surroundings, so equilibrium is achieved where both reactants and products can react and recombine with each other.
3	The concentrations of reactants and products remain constant at equilibrium	They are being produced and destroyed at an equal rate.
4	At equilibrium there is no change in macroscopic properties	Macroscopic properties are **observable** properties such as colour and density. These do not change as they depend on the concentrations of the **components** of the mixture.
5	Equilibrium can be reached from either direction	The same equilibrium mixture will result under the same conditions, no matter whether the reaction is started with all reactants, all products, or a mixture of both.

Understanding: The equilibrium law describes how the equilibrium constant (K_c) can be determined for a particular chemical reaction.

- At equilibrium, the reaction mixture may consist mainly of reactants, mainly of products, or a mixture of reactants and products. The proportion of reactants and products in the mixture is referred to as the **equilibrium position**.
- If the equilibrium mixture has a high proportion of products, the equilibrium position is said to lie to the right. This means that the forward reaction has been favoured and the reaction has gone almost to completion.
- If the equilibrium mixture has a high proportion of reactants, the equilibrium position is said to lie to the left. This means that the reverse reaction has been favoured and the forward reaction has not happened to a great extent.

General vocabulary

dynamic proceeding in the forward and backward directions at the same time

observable that can be detected by sight, sound, smell etc.

Synonym

components .. parts

Subject vocabulary

equilibrium position the proportion of reactants and products in a reaction mixture that is at equilibrium

General vocabulary

quantify make a numerical measurement of a quantity

numerator the number or numbers above the line in a fraction

denominator the number or numbers below the line in a fraction

magnitude the relative size of a measurement, how large it is

- We can **quantify** the equilibrium position using the equilibrium expression. The equilibrium law states that for a reaction:

  $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

  when the concentrations of all reactants and products are measured in the equilibrium mixture, the relationship:

  $$\frac{[\text{C}]^c\,[\text{D}]^d}{[\text{A}]^a\,[\text{B}]^b}$$

  gives a constant K_c, known as the equilibrium constant. K_c has a constant value for a particular reaction at a fixed temperature.
- The concentration used in the equilibrium expression must be the *equilibrium* concentration of reactant or product.
- The equilibrium constant expression has the concentrations of products in the **numerator** and the concentrations of reactants in the **denominator**.
- Each concentration is raised to the power of its coefficient in the balanced equation. (Where it is equal to one it does not have to be given.)
- Where there is more than one reactant or product the terms are multiplied together.

Skill: Deduction of the equilibrium constant expression (K_c) from an equation for a homogeneous reaction.

Worked example

Write the equilibrium expression for the following reactions.

(i) $2\text{H}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{H}_2\text{O(g)}$

(ii) $\text{Cu}^{2+}\text{(aq)} + 4\text{NH}_3\text{(aq)} \rightleftharpoons [\text{Cu(NH}_3)_4]^{2+}\text{(aq)}$

Solution

(i) $$K_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2[\text{O}_2]}$$

(ii) $$K_c = \frac{[[\text{Cu(NH}_3)_4]^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$

Understanding: The magnitude of the equilibrium constant indicates the extent of a reaction at equilibrium and is temperature dependent.

- We can deduce information about the equilibrium position from the **magnitude** of the equilibrium constant, $K_{c.}$
- In the equilibrium expression, the concentrations of products are put in the numerator and the concentrations of reactants are put in the denominator. This means that a high value of K_c indicates a reaction in which reactants have mostly been converted into products. A low value of K_c indicates a reaction in which a small proportion of reactants have been converted into products.

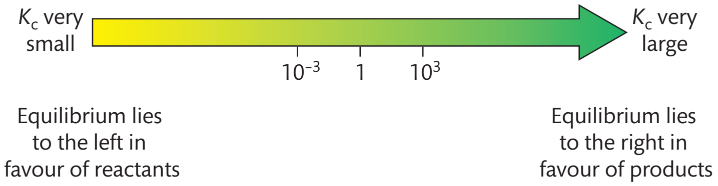


Figure 7.3 *The larger the value of K_c, the further the equilibrium mixture lies to the right.*

- Remember that the value of K_c changes with the temperature of the reaction, so the temperature must always be stated with any data value for K_c.

Skill: Determination of the relationship between different equilibrium constants (K_c) for the same reaction (at the same temperature) when represented by equations written in different ways.

The equilibrium expression for a particular reaction is based on the stoichiometric equation and depends on two factors:

1. which components are defined as reactants (left side) and which are defined as products (right side)

   If the reaction is written the other way round, it is said to be the **inverse** reaction, for example for the reaction

   $aA + bB \rightleftharpoons cC + dD$

   the inverse reaction will be

   $cC + dD \rightleftharpoons aA + bB$

2. the coefficients for the reactants and products, because these give the power of the concentration terms in the equilibrium expression.

General vocabulary

inverse the reverse or the opposite of something els

The effect on the equilibrium expression of changing either of these factors is summarized in the table below.

	Effect on equilibrium expression	Effect on K_c
inverse the reaction	inverts the expression	$\frac{1}{K_c}$ or K_c^{-1}
doubling the reaction coefficients	squares the expression	K_c^2
tripling the reaction coefficients	cubes the expression	K_c^3
halving the reaction coefficients	square roots the expression	$\sqrt{K_c}$
adding together two reactions	multiplies the two expressions	$K_c^{i} \times K_c^{ii}$

Understanding: The reaction quotient (Q) measures the relative amount of products and reactants present during a reaction at a particular point in time. Q is the equilibrium expression with non-equilibrium concentrations.

- The value of K_c can be calculated only by substituting the *equilibrium concentrations* of all reactants and products into the equilibrium expression. If the concentrations of reactants and products at *any time* in the reaction are put into the equilibrium expression, then a different value known as the reaction quotient, Q, can be calculated.

- Note that Q (unlike K_c) does not have a fixed value, but depends on the point during the reaction when the concentrations are measured.
- As the reaction **proceeds** towards equilibrium, the value of Q changes in the direction of K_c.
- We can use the reaction quotient, Q, to predict the direction in which the reaction will proceed towards equilibrium. This is summarized in the table below.

Relative value of Q and K_c	Direction in which reaction will proceed towards equilibrium
$Q = K_c$	Reaction is at equilibrium, no net reaction occurs
$Q < K_c$	Reaction proceeds to the right in favour of products
$Q > K_c$	Reaction proceeds to the left in favour of reactants

General vocabulary

proceeds moves in a particular direction

qualitatively without using numerical data

Understanding: The position of the equilibrium changes with changes in concentration, pressure, and temperature.

- The equilibrium position (the relative concentrations of reactants and products) is dependent on the reaction conditions and it changes when concentration, pressure (if it involves gases), and temperature change.
- Under different conditions, an equilibrium may shift to the left in favour of reactants or shift to the right in favour of products.
- Note that the value of the equilibrium constant, K_c, does *not* change with changes in any conditions except temperature.

Skill: Use of Le Châtelier's principle to predict the qualitative effects of changes of temperature, pressure, and concentration on the position of equilibrium and on the value of the equilibrium constant.

Le Châtelier's principle states that: *a system at equilibrium when subjected to a change will respond in such a way as to minimize the effect of the change*. This means that the system responds in the opposite way to the change applied.

Le Châtelier's principle enables us to describe **qualitatively** how a reaction at equilibrium will respond to any change.

Subject vocabulary

Le Châtelier's principle a system at equilibrium when subjected to a change will respond in such a way as to minimize the effect of the change

Changes in concentration

- If the concentration of a reactant is increased, the system responds by decreasing the concentration of the reactant, so the forward reaction is favoured. This causes the equilibrium position to shift to the right.
- If the concentration of a reactant is decreased, the system responds by increasing the concentration of the reactant, so the reverse reaction is favoured. This causes the equilibrium position to shift to the left.
- Similar predictions can be made for changes in the concentration of a product.

  Example: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
  - If we increase the concentration of $N_2(g)$, we favour the forward reaction so the equilibrium shifts to the right.
  - If we decrease the concentration of $NH_3(g)$, we favour the forward reaction so the equilibrium shifts to the right.
  - If we decrease the concentration of $H_2(g)$, we favour the reverse reaction so the equilibrium shifts to the left.

Note that although the equilibrium position shifts in these cases, the value of K_c does not change.

Changes in pressure

- If the pressure is increased in a reaction that involves a change in the number of gas molecules, the system responds to decrease the pressure. This means it favours the reaction that produces the smaller number of gas molecules.

  Example: $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

  reactants : product

  3 molecules of gas : 1 molecule of gas

  - If we increase the pressure, we favour the forward reaction so the equilibrium shifts to the right.
  - If we decrease the pressure, we favour the reverse reaction so the equilibrium shifts to the left.

Note again that although the equilibrium position shifts in these cases, the value of K_c does not change.

Changes in temperature

- The direction in which a reaction at equilibrium shifts in response to a change in temperature depends on whether the forward or reverse reaction is endothermic ($+\Delta H$) or exothermic ($-\Delta H$).
- Remember that the enthalpy changes of the forward and reverse reactions are equal and opposite to each other.
- If the temperature is increased, the system responds to decrease the temperature by favouring the endothermic reaction. If the temperature is decreased, the system responds to increase the temperature by favouring the exothermic reaction.

  Example: $2NO_2(g) \rightleftharpoons N_2O_4(g) \quad \Delta H = -57\,\text{kJ mol}^{-1}$

  - Because ΔH is negative, the forward reaction is exothermic and the reverse reaction is endothermic.
  - If we increase the temperature, we favour the reverse endothermic reaction so the equilibrium shifts to the left.
  - If we decrease the temperature, we favour the forward exothermic reaction so the equilibrium shifts to the right.

Temperature is the only condition that also changes the value of K_c. An increase in temperature increases the value of K_c for an endothermic reaction and decreases the value of K_c for an exothermic reaction.

Understanding: A catalyst has no effect on the position of equilibrium or the equilibrium constant.

Catalysts increase the rate of both the forward and reverse reactions by providing an alternative reaction pathway that has a lower activation energy.

The effect of catalysts on increasing the rate of reaction is the same for both the forward and reverse reactions.

Catalysts have no effect on the position of equilibrium or on the value of K_c.

Catalysts speed up the time taken to reach equilibrium, but do not increase the equilibrium **yield** of a reaction.

Subject vocabulary

yield amount of product obtained

The responses of a system at equilibrium to applied changes are summarized in the table below.

Changing condition	**Prediction from Le Châtelier's principle**	**Effect on equilibrium position**	**Effect on equilibrium constant, K_c**
Concentration	An increase in the concentration of one of the components of the equilibrium mixture shifts the position of equilibrium to the opposite side to reduce the concentration of this component	Changes	No change
Pressure	An increase in pressure favours the side of the equilibrium that has the smaller number of gas molecules	Changes if the reaction involves a change in the number of gas molecules	No change
Temperature	An increase in temperature shifts the equilibrium in the endothermic direction	Changes	Changes
Catalyst	A catalyst has equal effect on both the forward and reverse reactions, so does not cause a change in the equilibrium position	No change	No change

Topic 8: Acids and bases

8.1 Theories of acids and bases

Essential idea:

Many reactions involve the transfer of a proton from an acid to a base.

Understanding: A Brønsted–Lowry acid is a proton/H^+ donor and a Brønsted–Lowry base is a proton/H^+ acceptor.

In acid–base chemistry the terms H^+ and proton are both used to describe the hydrogen ion.

The Brønsted–Lowry theory of acids and bases is based on the transfer of a proton (H^+) between two chemical compounds:

- a **Brønsted–Lowry acid** *donates* the proton
- a **Brønsted–Lowry base** *accepts* the proton.

Subject vocabulary

Brønsted–Lowry acid a substance that is a proton (H^+) donor

Brønsted–Lowry base a substance that is a proton (H^+) acceptor

amphiprotic able to act as a Brønsted–Lowry acid and a Brønsted–Lowry base

conjugate base the base that is formed when a compound acts as a Brønsted–Lowry acid

Skill: **Deduction of the Brønsted–Lowry acid and base in a chemical reaction.**

Worked example

In the following reaction determine which reactant is the Brønsted–Lowry acid and which is the Brønsted–Lowry base.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Solution

In the forward reaction:

- $NH_3(aq)$ is the Brønsted–Lowry base because it accepts a proton (and becomes NH_4^+)
- $H_2O(l)$ is the Brønsted–Lowry acid because it donates a proton (and becomes OH^-).

Understanding: Amphiprotic species can act as both Brønsted–Lowry acids and bases.

Amphiprotic species are compounds that:

- can accept a proton and act as a Brønsted–Lowry acid *and*
- can donate a proton and act as a Brønsted–Lowry base.

Example: HCO_3^- is an amphiprotic species:

- Acting as an acid: $HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$
- Acting as a base: $HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$

Understanding: A pair of species differing by a single proton is called a conjugate acid–base pair.

A Brønsted–Lowry acid **donates** a proton to form a **conjugate base**, which is a species that can act as a base in the reverse reaction.

Synonym

donates .... gives or provides

Synonym

accepts .... takes

Subject vocabulary

conjugate acid the acid that is formed when a compound acts as a Brønsted–Lowry base

conjugate acid–base pair two species with chemical formulas that differ by H^+

A Brønsted–Lowry base **accepts** a proton to form a **conjugate acid**, which is a species that can act as an acid in the reverse reaction.

$$\underset{\text{acid}}{HA(aq)} + \underset{\text{base}}{B(aq)} \rightleftharpoons \underset{\text{conjugate base}}{A^-(aq)} + \underset{\text{conjugate acid}}{BH^+(aq)}$$

Conjugate acid–base pairs have chemical formulas that differ by H^+.

In the reaction above the two conjugate acid–base pairs are: HA/A^- and B/BH^+.

Skill: Deduction of the conjugate acid or conjugate base in a chemical reaction.

Worked example

Deduce the conjugate acid and conjugate base, as well as the conjugate acid–base pairs, for the following acid–base reaction:

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Solution

NH_4^+ is the conjugate acid because it donates a proton in the reverse reaction.

OH^- is the conjugate base because it accepts a proton in the reverse reaction.

The two conjugate acid–base pairs are NH_3/NH_4^+ and H_2O/OH^-.

$$\underset{\text{base}}{NH_3(aq)} + \underset{\text{acid}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{NH_4^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

8.2 Properties of acids and bases

Essential idea:

The characterization of an acid depends on empirical evidence such as the production of gases in reactions with metals, the colour changes of indicators, or the release of heat in reactions with metal oxides and hydroxides.

Understanding: Most acids have observable characteristic chemical reactions with reactive metals, metal oxides, metal hydroxides, hydrogen carbonates, and carbonates.

- The reaction of acids with reactive metals:

  acid + metal → salt + hydrogen gas

Examples: $H_2SO_4(aq) + Fe(s) \rightarrow FeSO_4(aq) + H_2(g)$

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

- The reaction of acids with metal oxides:

  acid + metal oxide → salt + water

Examples: $2HCl(aq) + MgO(s) \rightarrow MgCl_2(aq) + H_2O(l)$

$2HNO_3(aq) + CuO(s) \rightarrow Cu(NO_3)_2(aq) + H_2O(l)$

- The reaction of acids with hydrogen carbonates and carbonates:

  acid + carbonate → salt + carbon dioxide + water
  (or hydrogen carbonate)

Examples: $2HCl(aq) + K_2CO_3(s) \rightarrow 2KCl(aq) + CO_2(g) + H_2O(l)$

$H_2SO_4(aq) + MgCO_3(s) \rightarrow MgSO_4(aq) + CO_2(g) + H_2O(l)$

$HNO_3(aq) + KHCO_3(s) \rightarrow KNO_3(aq) + CO_2(g) + H_2O(l)$

$CH_3COOH(aq) + NaHCO_3(s) \rightarrow NaCH_3COO(aq) + CO_2(g) + H_2O(l)$

Skill: Balancing chemical equations for the reactions of acids.

Worked example

Write balanced equations for the following reactions:

1 Aluminium metal (Al) with sulfuric acid (H_2SO_4).

2 Sodium oxide (Na_2O) with hydrochloric acid (HCl).

3 Calcium carbonate ($CaCO_3$) with nitric acid (HNO_3).

Solution

1 Aluminium metal (Al) with sulfuric acid (H_2SO_4).

This is a reaction between a metal and an acid:

acid + metal → salt + hydrogen gas

$3H_2SO_4(aq) + 2Al(s) \rightarrow Al_2(SO_4)_3\,(aq) + 3H_2(g)$

2 Sodium oxide (Na_2O) with hydrochloric acid (HCl).

This is a reaction between a metal oxide and an acid:

acid + metal oxide → salt + water

$2HCl(aq) + Na_2O(s) \rightarrow 2NaCl(aq) + H_2O(l)$

3 Calcium carbonate ($CaCO_3$) with nitric acid (HNO_3).

This is a reaction between a carbonate and an acid:

acid + carbonate → salt + carbon dioxide + water

$2HNO_3(aq) + CaCO_3(s) \rightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$

Understanding: Salt and water are produced in exothermic neutralization reactions.

A **neutralization reaction**:

- occurs between an acid and a base
- forms a salt and water as products
- is highly exothermic and generates heat.

acid + base → salt + water

Examples: $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$ ΔH –ve

$H_2SO_4(aq) + 2KOH(aq) \rightarrow K_2SO_4(aq) + 2H_2O(l)$ ΔH –ve

Subject vocabulary

neutralization reaction a reaction between an acid and a base

Skill: Identification of the acid and base needed to make different salts.

The formula of a salt can be used to identify the acid and base that reacted to make the salt:

- the negative ion comes from the acid
- the positive ion comes from the base.

Salt	Negative ion in salt	Acid source	Positive ion in salt	Base source
$LiCl$	Cl^-	HCl	Li^+	$LiOH$
$NaNO_3$	NO_3^-	HNO_3	Na^+	$NaOH$
K_2SO_4	SO_4^{2-}	H_2SO_4	K^+	KOH
$Ba(CH_3COO)_2$	CH_3COO^-	CH_3COOH	Ba^{2+}	$Ba(OH)_2$
$(NH_4)_2CO_3$	CO_3^{2-}	H_2CO_3	NH_4^+	NH_3
Na_3PO_4	PO_4^{3-}	H_3PO_4	Na^+	$NaOH$

Worked example

Deduce the acids and bases that react to make the following salts.

(i) K_3PO_4

(ii) NH_4NO_3

(iii) $LiCH_3COO$

Solution

(i) K_3PO_4: K^+ comes from the base KOH. PO_4^{3-} comes from the acid H_3PO_4.

(ii) NH_4NO_3: NH_4^+ comes from the base NH_3. NO_3^- comes from the acid HNO_3.

(iii) $LiCH_3COO$: Li^+ comes from the base LiOH. CH_3COO^- comes from the acid CH_3COOH.

Skill: Candidates should have experience of acid-base titrations with different indicators.

An **acid-base titration** is a technique that determines the exact concentration of an acid or base solution. For example, a base solution of unknown concentration can be titrated against a standard acid solution, as shown in Figure 8.1.

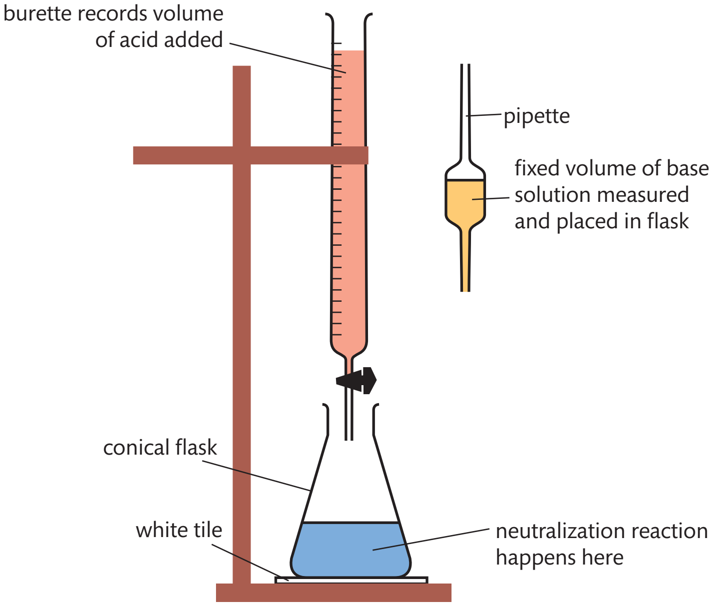


Figure 8.1 *The titration of a base of unknown concentration with a standard acid solution.*

Hints for success: Figure 8.1 shows an acid-base titration in which acid is added from the burette to a base in the conical flask. Acid-base titrations can also add base from the burette to acid in the conical flask.

The **equivalence point**:

- is reached when stoichiometrically equivalent amounts of acid and base have been combined in a titration
- can be detected using an **indicator** that changes colour when neutralization has happened.

Subject vocabulary

acid-base titration a technique used to determine the unknown concentration of an acid (or base) solution through reaction with a base (or acid) solution of known concentration

equivalence point the point in a titration at which the exact volume of the standard solution needed to completely react with the unknown solution has been added

indicator a substance that has different colours at different pH values

8.3 The pH scale

Essential idea:

The pH scale is an artificial scale used to distinguish between acidic, neutral, and basic/alkaline solutions.

Understanding: pH = $-\log[H^+(aq)]$ and $[H^+] = 10^{-pH}$.

The pH scale uses logarithms to convert the concentration of H^+ ions to numbers that are easier to compare:

$pH = -\log_{10}[H^+(aq)]$ and $[H^+] = 10^{-pH}$

pH and $[H^+]$ have an **inverse relationship**: This means that pH decreases as $[H^+]$ increases.

General vocabulary

inverse relationship a relationship in which the value of one quantity increases as the value of another decreases

Worked example

An aqueous solution of hydrochloric acid (HCl) has a hydrogen ion concentration of 5.5×10^{-3} mol dm^{-3}. What is the pH of this solution?

$pH = -\log_{10}[H^+(aq)] = -\log(5.5 \times 10^{-3}) = 2.26$

An aqueous solution of nitric acid (HNO_3) has a pH of 4.78. What is the hydrogen ion concentration of this solution?

$[H^+] = 10^{-pH} = 10^{-4.78} = 1.7 \times 10^{-5}$ mol dm^{-3}

Hints for success: When calculating log values the final answer should have the same number of decimal places as the number of significant figures in the initial value. 5.5×10^{-3} has 2 significant figures, therefore the answer of $\log(5.5 \times 10^{-3})$ should have 2 decimal places.

Understanding: A change of one pH unit represents a 10-fold change in the hydrogen ion concentration $[H^+]$.

In logarithmic scales a difference of one unit represents a change of a factor of 10.

pH	$[H^+]$/mol dm^{-3}	Change in pH	Change in $[H^+]$
3	1.0×10^{-3}	↑ decreases by 1	↑ increases by 10
4	1.0×10^{-4}	↓ increases by 1	↓ decreases by 10
5	1.0×10^{-5}		

Understanding: pH values distinguish between acidic, neutral, and alkaline solutions.

Understanding: The ionic product constant, $K_w = [H^+][OH^-] = 10^{-14}$ at 298 K.

The pH value tells us if a solution is **acidic**, **neutral**, or **basic** (**alkaline**) at 25 °C.

The concentrations of H^+ ions and OH^- ions in aqueous solution are related by the **ionic product of water** (K_w):

- $K_w = [H^+][OH^-]$
- At 298 K, $K_w = 1.00 \times 10^{-14}$
- This relationship shows that there is an inverse relationship between $[H^+]$ and $[OH^-]$, i.e. $[H^+]$ increases as $[OH^-]$ decreases.

Subject vocabulary

acidic	has a pH < 7 at 25 °C
neutral	has a pH = 7 at 25 °C
basic	has a pH > 7 at 25 °C
alkaline	has a pH > 7 at 25 °C
ionic product of water	a constant that relates the equilibrium concentrations of H^+ ions and OH^- ions in aqueous solutions at a specific temperature

		at 298 K
Acidic solutions are defined as those in which	$[H^+] > [OH^-]$	$pH < 7$
Neutral solutions are defined as those in which	$[H^+] = [OH^-]$	$pH = 7$
Alkaline solutions are defined as those in which	$[H^+] < [OH^-]$	$pH > 7$

Skill: Solving problems involving pH, $[H^+]$ and $[OH^-]$.

Worked example

A sample of blood at 298 K has $[H^+] = 4.60 \times 10^{-8}$ mol dm^{-3}.

Calculate the concentration of OH^- and state whether the blood is acidic, neutral, or basic.

Solution

At 298 K, $K_w = 1.00 \times 10^{-14} = [H^+][OH^-]$

$$[OH]^- = \frac{1.00 \times 10^{-14}}{4.60 \times 10^{-8}} = 2.17 \times 10^{-7} \text{ mol dm}^{-3}$$

As $[OH^-] > [H^+]$ the solution is basic.

Worked example

An alkaline solution of sodium hydroxide (NaOH) has a pH of 10.45. What is the concentration of hydrogen ions (H^+) and hydroxide ions (OH^-) in this solution?

$[H^+] = 10^{-pH} = 10^{-10.45} = 3.5 \times 10^{-11}$ mol dm^{-3}

$K_w = [H^+][OH^-]$

$$[OH^-] = \frac{K_W}{[H^+]} = \frac{1.00 \times 10^{-14}}{3.5 \times 10^{-11}} = 2.9 \times 10^{-4} \text{ mol dm}^{-3}$$

Skill: Students should be familiar with the use of a pH meter and universal indicator.

An **indicator** is a substance that can change colour depending on the pH of the solution. **Litmus** is a common indicator that is red in acidic solutions and blue in basic solutions.

Universal indicator gives a **progression** of colours as the pH changes from strongly acidic (pH = 0) through to strongly basic (pH = 14). The pH can be estimated by comparing the colour of the solution to a colour chart that gives the indicator colour for different pH values.

Subject vocabulary

indicator	a substance that has different colours at different pH values
litmus	an indicator that is blue in basic solutions (pH >7) and red in acidic solutions (pH < 7)
universal indicator	an indicator that is a series of different colours at different pH values

General vocabulary

progression	a gradual change

Figure 8.2 *The pH scale and universal indicator. The tubes contain universal indicator added to solutions of pH 0–14 from left to right.*

Subject vocabulary

pH meter an instrument that measures pH

electrode an electrical conductor that provides a surface where current can enter or leave an electrolyte solution

A **pH meter**:

- is a precise way to measure the pH of solutions
- has a special **electrode** that accurately measures the concentration of H^+ ions
- needs to be calibrated each time it is used by checking the pH of standard solutions with known pH values
- must be corrected for the temperature because pH depends on temperature.

8.4 Strong and weak acids and bases

Essential idea:

The pH depends on the concentration of the solution. The strength of acids or bases depends on the extent to which they dissociate in aqueous solution.

Understanding: Strong and weak acids and bases differ in the extent of ionization.

- Acids and bases **dissociate** (ionize) in aqueous solution:
  - acids dissociate to give H^+ ions
  - bases dissociate to give OH^- ions.

Acids are defined as **weak acids** or **strong acids**.

Weak acids *do not dissociate fully* and there is an equilibrium reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$$

Strong acids *dissociate fully* and there is no equilibrium reaction:

$$HA(aq) + H_2O(l) \rightarrow A^-(aq) + H_3O^+(aq)$$

Note that H_3O^+ is written as a product, not H^+. This is because the H^+ that dissociates from the acid bonds to an H_2O molecule and really exists as H_3O^+ in aqueous solutions.

Bases are defined as **weak bases** or **strong bases**.

Weak bases *do not dissociate fully* and there is an equilibrium reaction:

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

Strong bases *dissociate fully* and there is no equilibrium reaction:

$$B(aq) + H_2O(l) \rightarrow BH^+(aq) + OH^-(aq)$$

	Acid		Base	
common examples of **strong** forms	HCl	hydrochloric acid	LiOH	lithium hydroxide
	HNO_3	nitric acid	NaOH	sodium hydroxide
	H_2SO_4	sulfuric acid	KOH	potassium hydroxide
			$Ba(OH)_2$	barium hydroxide
some examples of **weak** forms	CH_3COOH and other organic acids	ethanoic acid	NH_3	ammonia
	H_2CO_3	carbonic acid	$C_2H_5NH_2$	ethylamine
	H_3PO_4	phosphoric acid	and other amines	

Subject vocabulary

dissociate break up to form ions

weak acids acids that partially dissociate in aqueous solution

strong acids acids that fully dissociate in aqueous solution

weak bases bases that partially dissociate in aqueous solution

strong bases bases that fully dissociate in aqueous solution

Understanding: Strong acids and bases of equal concentrations have higher conductivities than weak acids and bases.

The conductivity of a solution depends on the concentration of ions that are in the solution. A strong acid, because it dissociates fully, has a higher concentration of H^+ ions in solution than a weak acid of the same concentration. This means that the strong acid will have a higher conductivity than the weak acid.

Subject vocabulary

conductivity ability to conduct an electrical current

proton donor a substance that acts as a Brønsted–Lowry acid and donates H^+ to a base

Skill: Distinction between strong and weak acids in terms of the rates of their reactions with metals, metal oxides, metal hydroxides, metal hydrogen carbonates and metal carbonates. Strong and weak acids and bases also differ in their electrical conductivities for solutions of equal concentrations.

- The rate of reaction of an acid will depend upon the $[H^+]$ present in the solution. Because strong acids dissociate fully their solutions have a larger $[H^+]$ in solution and will react faster than weak acids of the same concentration.
- The rate of reaction of a base will depend upon the $[OH^-]$ present in the solution. Because strong bases dissociate fully their solutions have a larger $[OH^-]$ and will react faster than weak bases of the same concentration.

Acid ($1.0\,mol\,dm^{-3}$)	**Strong/ weak**	**Dissociate**	**$[H^+]$**	**Relative conductivity**	**Relative rate of reaction with other compounds**
Hydrochloric acid (HCl)	strong	fully	higher	higher	faster
Ethanoic acid (CH_3COOH)	weak	partially	lower	lower	slower
Base ($1.0\,mol\,dm^{-3}$)	**Strong/ weak**	**Dissociate**	**$[OH^-]$**	**Relative conductivity**	**Relative rate of reaction**
Sodium hydroxide (NaOH)	strong	fully	higher	higher	faster
Ammonia (NH_3)	weak	partially	lower	lower	slower

Understanding: A strong acid is a good proton donor and has a weak conjugate base.

A strong acid is a good proton donor so there is no reverse reaction in the dissociation reaction of a strong acid. This means that the conjugate base of a strong acid is unlikely to accept protons.

Example: $\underset{\text{acid}}{HCl(aq)} + H_2O(l) \rightarrow \underset{\text{conjugate base}}{Cl^-(aq)} + H_3O^+(aq)$

HCl is a strong acid and its conjugate base, Cl^-, does not act as a base.

Understanding: A strong base is a good proton acceptor and has a weak conjugate acid.

A strong base is a good **proton acceptor** so there is no reverse reaction in the dissociation of a strong base. This means that the conjugate acid of a strong base is unlikely to donate protons.

Subject vocabulary

proton acceptor a substance that acts as a Brønsted–Lowry base and accepts H^+ from an acid

Essential idea:

Increased industrialization has led to greater production of nitrogen and sulfur oxides, leading to acid rain, which is damaging our environment. These problems can be reduced through collaboration with national and intergovernmental organizations.

Understanding: Rain is naturally acidic because of dissolved CO_2 and has a pH of 5.6. Acid deposition has a lower pH, usually below 5.0.

Rain:

- dissolves carbon dioxide, $CO_2(g)$, to form carbonic acid, $H_2CO_3(aq)$
- is naturally acidic
- has a pH of 5.6.

Acid deposition:

- occurs when rainwater dissolves covalent oxides such as SO_2, SO_3, and NO_2
- contains stronger acids than normal rain
- is more acidic than normal rain
- has a pH that is usually less than 5.0.

Subject vocabulary

acid deposition the formation of acidic solutions that happens when acidic substances dissolve in atmospheric or surface water

---

Understanding: Acid deposition is formed when nitrogen or sulfur oxides dissolve in water to form HNO_3, HNO_2, H_2SO_4, and H_2SO_3.

Understanding: Sources of the oxides of sulfur and nitrogen and the effects of acid deposition should be covered.

Skill: Balancing the equations that describe the combustion of sulfur and nitrogen to their oxides and the subsequent formation of H_2SO_3, H_2SO_4, HNO_2, and HNO_3.

The main source of nitrogen acids is nitrogen monoxide (NO), which is formed when nitrogen (N_2) and oxygen (O_2) react in engines because of the high temperatures:

- $N_2(g) + O_2(g) \rightarrow 2NO(g)$

Nitrogen dioxide (NO_2) can be formed from NO or N_2:

- $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$
- $N_2(g) + 2O_2(g) \rightarrow 2NO_2(g)$

Nitrogen dioxide dissolves in water to give nitrous acid (HNO_2) and nitric acid (HNO_3):

- $2NO_2(g) + H_2O(l) \rightarrow HNO_2(aq) + HNO_3(aq)$

The main source of sulfur acids is sulfur dioxide (SO_2), which is formed from the sulfur released when coal or heavy oils are burned as fuels:

- $S(s) + O_2(g) \rightarrow SO_2(g)$

Sulfur trioxide (SO_3) can be formed from SO_2:

- $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

Sulfur dioxide dissolves in water to give sulfurous acid (H_2SO_3). Sulfur trioxide dissolves in water to give sulfuric acid:

- $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
- $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$

Skill: Deduction of acid deposition equations for acid deposition with reactive metals and carbonates.

Marble and limestone are two building materials that contain calcium carbonate ($CaCO_3$). Calcium carbonate reacts with acid so acid deposition will slowly dissolve the surface of buildings and statues made of marble or limestone:

- $CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + CO_2(g) + H_2O(l)$
- $CaCO_3(s) + 2HNO_3(aq) \rightarrow Ca(NO_3)_2(aq) + CO_2(g) + H_2O(l)$

The corrosion of iron and steel is accelerated by acid deposition:

- $Fe(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + H_2(g)$
- $Fe(s) + 2HNO_3(aq) \rightarrow Fe(NO_3)_2(aq) + H_2(g)$

Skill: Distinction between the pre-combustion and post-combustion methods of reducing sulfur oxides emissions.

Sulfur oxide emissions can be reduced by **pre-combustion** and **post-combustion** methods.

Pre-combustion methods:

- remove sulfur from coal and oil before they are burned
  - remove sulfur from crushed coal by washing with water
  - remove sulfur from oil by reacting with H_2 in the presence of catalysts to make hydrogen sulfide (H_2S):

    $H_2(g) + S(s) \rightarrow H_2S(g)$

Post-combustion methods:

- remove sulfur dioxide from exhaust gases after the coal or oil is burned
  - react SO_2 with calcium oxide (CaO) or calcium carbonate ($CaCO_3$) to form calcium sulfite:

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

    $SO_2(g) + CaCO_3(s) \rightarrow CaSO_3(s) + CO_2(g)$
  - the $CaSO_3$ is then reacted with oxygen to form calcium sulfate:

    $2CaSO_3(s) + O_2(g) \rightarrow 2CaSO_4(s)$

Subject vocabulary

pre-combustion occuring before the combustion reaction of a substance

post-combustion occuring after the combustion reaction of a substance

Topic 9: Redox processes

9.1 Oxidation and reduction

Essential idea:

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

Understanding: Oxidation and reduction can be considered in terms of oxygen gain/hydrogen loss, electron transfer, or change in oxidation number.

The definition that covers all types of redox (**reduction**–**oxidation**) reactions is based on the transfer of electrons. Specific types of redox reactions involve the gain or loss of hydrogen and oxygen atoms.

Oxidation occurs when:	Reduction occurs when:
a species loses electrons	a species gains electrons
a species loses hydrogen atoms	a species gains hydrogen atoms
a species gains oxygen atoms	a species loses oxygen atoms
the oxidation state of an atom increases	the oxidation state of an atom decreases

Subject vocabulary

reduction the gain of electrons by a chemical species

oxidation the loss of electrons by a chemical species

oxidizing agent a substance that oxidizes another substance and is reduced itself

reducing agent a substance that reduces another substance and is oxidized itself

oxidation state a measure of how many electrons an atom has gained or lost when forming a compound

Understanding: An oxidizing agent is reduced and a reducing agent is oxidized.

When a redox reaction occurs one reactant is the **oxidizing agent** and another reactant is the **reducing agent**.

Oxidizing agent:	Reducing agent:
gains electrons	loses electrons
oxidizes another reactant	reduces another reactant
is reduced during the reaction	is oxidized during the reaction

Skill: Deduction of the oxidation states of an atom in an ion or compound.

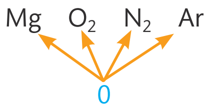
An **oxidation state** is a measure of how many electrons an atom has gained or lost after it bonds with other elements to form compounds. The number of electrons in the bonded atom is compared to the number of electrons in an unbonded atom of that element.

Oxidation states must be represented with + or – signs. A positive oxidation state means the atom has lost electrons. A negative oxidation state means the atom has gained electrons, for example:

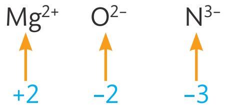
- An oxidation state of +2 means the atom has lost two electrons.
- An oxidation state of –3 means the atom has gained three electrons.

The oxidation state of an atom is determined using the following rules:

1 Atoms in the free (uncombined) element have an oxidation state of zero: for example,



2 In simple ions, the oxidation state is the same as the charge on the ion: for example,



3 The oxidation states of all the atoms in a neutral (uncharged) compound must add up to zero:
for example, in H_2SO_4 the sum of oxidation states = 0.

4 The oxidation states of all the atoms in a polyatomic ion must add up to the charge on the ion:
for example, in SO_4^{2-} the sum of oxidation states = −2.

5 The usual oxidation state for an element is the same as the charge on its most common ion:
for example, group 1 elements have oxidation state = +1, H is usually +1, O is usually −2.

6 Most main group non-metals, the elements at the bottom of group 14, and transition elements have oxidation states that vary in different compounds – depending on the conditions and other elements present. So for N, P, S, Sn, Pb, and all transition elements, the oxidation state of the element in a particular species needs to be determined on a case-by-case basis.

Element	Usual oxidation state	Exceptions	Explanation
Li, Na, K	+1		
Mg, Ca	+2		
F	−1		there are no exceptions because F is the most electronegative element
O	−2	peroxides such as H_2O_2, where it is −1; OF_2, where it is +2	each H can only give one electron in the peroxide; F is more electronegative so O loses electrons in OF_2
H	+1	metal hydrides such as NaH, where it is −1	H is more electronegative than Na and so gains an electron from Na
Cl	−1	when it is combined with O or F	Cl is less electronegative than O and F, and so loses an electron to these elements

Worked example

Assign oxidation states to all the elements in (a) H_2SO_4 and (b) SO_3^{2-}.

Solution

(a) We can assign H and O as follows:

$$\underset{+1}{\underset{\uparrow}{H}}_2S\underset{-2}{\underset{\uparrow}{O}}_4$$

Note that the oxidation states apply to each atom and that here the sum of all the oxidation states must be zero as H_2SO_4 is electrically neutral.

Therefore, $2(+1) + S + 4(-2) = 0 \Rightarrow S = +6$

(b) Here we start by assigning O:

$$S\underset{-2}{\underset{\uparrow}{O}}_3^{2-}$$

Note that here the oxidation states must add up to −2, the charge on the ion.

Therefore, $S + 3(-2) = -2 \Rightarrow S = +4$

Understanding: Variable oxidation numbers exist for transition metals and for most main-group non-metals.

Transition metals and most main-group non-metals have **variable** oxidation states because they can gain or lose different numbers of electrons. First-row transition metals can lose 4s and one or more 3d electrons.

General vocabulary

variable with more than one possible value

Example: Vanadium can have oxidation states of +2 to +5, depending on the compound or ion it forms.

Vanadium ion or compound	Oxidation state of vanadium	Electrons lost
V^{2+}	+2	Two 4s
V^{3+}	+3	Two 4s and one 3d
VO_2	+4	Two 4s and two 3d
V_2O_5	+5	Two 4s and three 3d

Main group non-metals can have positive or negative oxidation states depending on the electronegativity values of the atoms they bond with.

For a non-metal:

- the maximum positive oxidation state is equal to the number of valence electrons
- the maximum negative oxidation state is equal to the number of electrons needed to fill the valence shell.

  Example: sulfur and compounds.

Sulfur compound	Oxidation state of sulfur	
H_2S	−2	Maximum negative oxidation state
S	0	
SCl_2	+2	↓
SO_2	+4	Maximum positive oxidation state
H_2SO_4	+6	

Skill: Deduction of the name of a transition metal compound from a given formula, applying oxidation numbers represented by Roman numerals.

For transition metal complex ions the oxidation state of the metal ion can be determined using the charges on the ligands and the overall charge.

Worked example

Assign oxidation states to the metal ion in (a) $[Co(NH_3)_6]^{3+}$ and (b) $[CuCl_4]^{2-}$.

Solution

(a) NH_3 is a neutral ligand, so the charge on the complex is the same as the charge on the metal ion ∴ Co = +3

(b) Cl has a 1− charge ∴ (charge on Cu) + (4 × 1−) = 2−

∴ Cu = +2

The oxidation state of the transition metal ion is included in the name of the complex ion.

Worked example

Deduce the names of the following compounds using oxidation numbers.

(a) V_2O_5 **(b)** $Ni(OH)_2$ **(c)** $TiCl_4$

Solution

1 First deduce the oxidation state:

(a) V_2O_5 V is +5

(b) $Ni(OH)_2$ Ni is +2

(c) $TiCl_4$ Ti is +4

2 Then the corresponding Roman numeral is inserted after the name of the element. There is no space between the name and the number, and the number is placed in brackets.

(a) vanadium(V) oxide

(b) nickel(II) hydroxide

(c) titanium(IV) chloride

Skill: Identification of the species oxidized and reduced and the oxidizing and reducing agents, in redox reactions.

A redox equation can be divided into two **half-equations** showing which species gain electrons (are reduced) or lose electrons (are oxidized).

Subject vocabulary

half-equation an equation that shows the changes that happen in a redox reaction due to either oxidation only or reduction only

Subject vocabulary

oxidation half-equation a half-equation that shows only the chemical changes that happen in a redox reaction due to oxidation

reduction half-equation a half-equation that shows only the chemical changes that happen in a redox reaction due to reduction

- The **oxidation half-equation** shows the reducing agent being oxidized to its product(s).
- The **reduction half-equation** shows the oxidizing agent being reduced to its product(s).

Each half-equation must show the number of electrons being gained or lost.

Worked example

Deduce the two half-equations for the following reaction

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Solution

Assign oxidation states so we can see what is being oxidized and what is reduced.

$$\begin{array}{ccccccc} Zn(s) & + & Cu^{2+}(aq) & \rightarrow & Zn^{2+}(aq) & + & Cu(s) \\ 0 & & +2 & & +2 & & 0 \end{array}$$

Here we can see that Zn is being oxidized and Cu^{2+} is being reduced.

oxidation: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ electrons are lost

reduction: $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ electrons are gained

Note there must be equal numbers of electrons in the two half-equations, so that when they are added together the electrons cancel out.

Skill: Deduction of redox reactions using half-equations in acidic or neutral solutions.

Redox equations that contain hydrogen and oxygen can be balanced using the following steps:

1. Assign oxidation states to determine which atoms are being oxidized and which are being reduced.
2. Write half-equations for oxidation and reduction as follows:
    - **(a)** balance the atoms other than H and O
    - **(b)** balance each half-equation for O by adding H_2O as needed
    - **(c)** balance each half-equation for H by adding H^+ as needed
    - **(d)** balance each half-equation for charge by adding electrons to the sides with the more positive charge
    - **(e)** check that each half-equation is balanced for atoms and for charge.
3. Equalize the number of electrons in the two half-equations by multiplying each appropriately.
4. Add the two half-equations together, cancelling out anything that is the same on both sides.

Worked example

Balance the redox equation that occurs in acidic solution when sulfurous acid (H_2SO_3) is titrated against potassium dichromate ($K_2Cr_2O_7$):

$$Cr_2O_7^{2-}(aq) + H_2SO_3(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$$

Solution

Step 1: Assign oxidation states	$Cr_2O_7^{2-}(aq) + H_2SO_3(aq) \rightarrow Cr^{3+}(aq) + SO_4^{2-}(aq)$ +6 −2 +1 +4 −2 +3 +6 −2	
Step 2: Write half-equations	Oxidation $H_2SO_3(aq) \rightarrow SO_4^{2-}(aq)$	Reduction $Cr_2O_7^{2-}(aq) \rightarrow Cr^{3+}(aq)$
(a) Balance atoms other than H and O	$H_2SO_3(aq) \rightarrow SO_4^{2-}(aq)$	$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq)$
(b) Balance for O by adding H_2O	$H_2SO_3(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq)$	$Cr_2O_7^{2-}(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
(c) Balance for H by adding H^+	$H_2SO_3(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq)$	$Cr_2O_7^{2-}(aq) + 14H^+(aq) \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
(d) Balance charge by adding electrons	$H_2SO_3(aq) + H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Step 3: Multiply half-equations so they both have same number of electrons	$3H_2SO_3(aq) + 3H_2O(l) \rightarrow 3SO_4^{2-}(aq) + 12H^+(aq) + 6e^-$	$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$
Step 4: Add half-equations together and cancel anything on both sides	$3H_2SO_3(aq) + \cancel{3H_2O(l)} + Cr_2O_7^{2-}(aq) + \cancel{14}\,2H^+(aq) + \cancel{6e^-} \rightarrow 3SO_4^{2-}(aq) + \cancel{12H^+(aq)} + \cancel{6e^-} + 2Cr^{3+}(aq) + \cancel{7}\,4H_2O(l)$ $3H_2SO_3(aq) + Cr_2O_7^{2-}(aq) + 2H^+ \rightarrow 3SO_4^{2-}(aq) + 2Cr^{3+}(aq) + 4H_2O(l)$	

Hints for success: Balanced oxidation half-equations will have electrons on the product side. Balanced reduction half-equations will have electrons on the reactant side.

Skill: Solution of a range of redox titration problems.

A **redox titration** determines the concentration of an unknown solution by titrating it against a standard solution. A colour change associated with the redox reaction shows when the equivalence point has been reached.

Subject vocabulary

redox titration a technique used to determine the unknown concentration of a solution through a redox reaction with another solution of known concentration

Worked example

All the iron in a 2.000 g tablet was dissolved in an acidic solution and converted to Fe^{2+}. This was then titrated with $KMnO_4$. The titration required 27.50 cm^3 of 0.100 mol dm^{-3} $KMnO_4$. Calculate the total mass of iron in the tablet and its percentage by mass. Describe what would be observed during the reaction, and how the equivalence point can be detected.

Solution

First we need the balanced equation for the reaction, which is solved by the half-equation method described earlier.

oxidation: $Fe^{2+} \rightarrow Fe^{3+} + e^-$

reduction: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

overall: $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$

Next we need to know the amounts of reactants used to reach equivalence. We start with $KMnO_4$ as we know both its concentration and its volume.

$$n = cV$$

$$n(MnO_4^-) = 0.100\,\text{mol dm}^{-3} \times \frac{27.50}{1000}\,\text{dm}^3 = 0.00275\,\text{mol } MnO_4^-$$

From the equation for the reaction we know the reacting ratio:

$$MnO_4^- : Fe^{2+} = 1 : 5$$

$$\therefore \text{ mol } Fe^{2+} = 0.00275\,\text{mol } MnO_4^- \times 5 = 0.01375\,\text{mol}$$

$$M(\text{Fe}) = 55.85\,\text{g mol}^{-1}$$

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

$$\therefore\ m(\text{Fe}) = 0.01375\,\text{mol} \times 55.85\,\text{g mol}^{-1} = 0.7679\,\text{g}$$

$$\%\ \text{Fe in tablet} = \frac{0.768\,\text{g}}{2.000\,\text{g}} \times 100 = 38.39\%$$

$$\therefore\ \text{Fe in tablet} = 0.768\ \text{g},\ 38.4\%$$

MnO_4^- in the burette is purple, but forms a nearly colourless solution in the flask as it reacts to form Mn^{2+}. But when the reducing agent Fe^{2+} in the flask has been used up at equivalence, MnO_4^- ions will not react and the purple colour will persist.

Understanding: The activity series ranks metals according to the ease with which they undergo oxidation.

Metals are **ranked** in the **activity series** according to how easily they lose electrons and are oxidized:

Mg strongest reducing agent; it is the easiest metal to oxidize
Al
Zn
Fe
Pb
Cu
Ag weakest reducing agent; it is the hardest metal to oxidize

General vocabulary

ranked placed in order

Subject vocabulary

activity series a series that lists metals by their strength as reducing agents

Hints for success: An activity series containing more metals is given in section 25 of the IB data booklet.

Skill: Deduction of the feasibility of a redox reaction from the activity series or reaction data.

The activity series can be used to predict whether or not a redox reaction that involves a metal can happen.

Worked example

Refer to the activity series given on page 104 to predict whether the following reactions will occur:

(a) $ZnCl_2(aq) + 2Ag(s) \rightarrow 2AgCl(s) + Zn(s)$

(b) $2FeCl_3(aq) + 3Mg(s) \rightarrow 3MgCl_2(aq) + 2Fe(s)$

Solution

(a) This reaction would involve Ag reducing Zn^{2+} in $ZnCl_2$. But Ag is a weaker reducing agent than Zn, so this will not occur.

(b) This reaction involves Mg reducing Fe^{3+} in $FeCl_3$. Mg is a stronger reducing agent than Fe, so this will occur.

Understanding: The Winkler Method can be used to measure biochemical oxygen demand (BOD), used as a measure of the degree of pollution in a water sample.

Biochemical oxygen demand (BOD) is the quantity of oxygen needed to break down organic matter in a sample of water over a 5-day period at a set temperature.

A high BOD means that high levels of bacteria or algae are present in the water and this will result in a low level of **dissolved oxygen**.

The **Winkler Method** uses a series of three redox reactions to determine the concentration of dissolved oxygen in a water sample.

1 Dissolved oxygen reacts with Mn^{2+} ions in basic conditions to form MnO_2:

$$2Mn^{2+}(aq) + O_2(aq) + 4OH^-(aq) \rightarrow 2MnO_2(s) + 2H_2O(l)$$

2 MnO_2 reacts with I^- in acidic conditions to form I_2 and Mn^{2+}:

$$MnO_2(s) + 2I^-(aq) + 4H^+(aq) \rightarrow Mn^{2+}(aq) + I_2(aq) + 2H_2O(l)$$

3 I_2 is titrated with $S_2O_3^{2-}$ to give I^- and $S_4O_6^{2-}$:

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

The moles of dissolved oxygen in the original solution can be calculated from the moles of $S_2O_3^{2-}$ used in the final reaction:

$$n(S_2O_3^{2-}) = 4n(O_2)$$

Subject vocabulary

dissolved oxygen	oxygen gas (O_2) that is dissolved in water
Winkler Method	a method that uses redox reactions to determine the concentration of dissolved oxygen in aqueous solutions

Skill: Application of the Winkler Method to calculate BOD.

Worked example

A 500 cm^3 sample of water was collected and tested for dissolved oxygen by the addition of $MnSO_4$ in basic solution, followed by the addition of acidified KI. It was found that 12.50 cm^3 of 0.0500 $mol\,dm^{-3}$ $Na_2S_2O_3(aq)$ was required to react with the iodine produced. Calculate the dissolved oxygen content of the water in $g\,dm^{-3}$, using the equations given above.

Solution

Start with calculating the amount of $S_2O_3^{2-}$, as we are given both its volume and its concentration.

$n = cV$

$n(S_2O_3^{2-}) = 0.0500\,\text{mol dm}^{-3} \times \frac{12.50}{1000}\,\text{dm}^3 = 6.25 \times 10^{-4}\,\text{mol}$

From the reacting ratio in step 3, $S_2O_3^{2-} : I_2 = 2 : 1$

$\therefore n(I_2) = 0.5 \times 6.25 \times 10^{-4} = 3.125 \times 10^{-4}\,\text{mol}$

From the reacting ratio in step 2, $I_2 : MnO_2 = 1 : 1$

$\therefore n(MnO_2) = 3.125 \times 10^{-4}\,\text{mol}$

From the reacting ratio in step 1, $MnO_2 : O_2(g) = 2 : 1$

$\therefore n(O_2) = 0.5 \times 3.125 \times 10^{-4}\,\text{mol} = 1.5625 \times 10^{-4}\,\text{mol}$

(We could also go directly from a ratio of $O_2 : S_2O_3^{2-} = 1 : 4$)

Finally express the amount of $O_2(g)$ as g dm^{-3}

$m(O_2) = n \times M = 1.5625 \times 10^{-4}\,\text{mol} \times 32.00\,\text{g mol}^{-1} = 5.000 \times 10^{-3}\,\text{g in } 500\,\text{cm}^3$

$\therefore$ dissolved oxygen $= 0.0100\,\text{g dm}^{-3}$

9.2 Electrochemical cells

Essential idea:

Voltaic cells convert chemical energy to electrical energy and **electrolytic cells** convert electrical energy to chemical energy.

Subject vocabulary

voltaic cells devices that convert chemical energy to electrical energy

electrolytic cells devices that convert electrical energy to chemical energy

spontaneous happening by itself

non-spontaneous not happening by itself

electrochemical cells devices that convert chemical energy to electrical energy or electrical energy to chemical energy

half-cell the component of a voltaic cell where either oxidation or reduction occurs

anode the electrode (or half-cell) where oxidation occurs

cathode the electrode (or half-cell) where reduction occurs

salt bridge a device that connects the anode and cathode in a voltaic cell. It contains a concentrated solution of an unreactive salt and allows ions to flow into the two half-cells

Understanding: Voltaic cells convert energy from **spontaneous**, exothermic chemical processes to electrical energy.

Understanding: Electrolytic cells convert electrical energy to chemical energy, by bringing about **non-spontaneous** processes.

Voltaic cells and electrolytic cells are different types of **electrochemical cells**.

Electrochemical cells

Voltaic cell	**Electrolytic cell**
Uses spontaneous redox reactions to make electricity	Uses electricity to make non-spontaneous redox reactions happen
Converts chemical energy into electrical energy	Converts electrical energy into chemical energy

Understanding: Oxidation occurs at the anode (negative electrode) and reduction occurs at the cathode (positive electrode) in a voltaic cell.

A voltaic cell contains two **half-cells**:

- **anode**: where oxidation occurs, the negative electrode
- **cathode**: where reduction occurs, the positive electrode.

Simple half-cells contain a metal strip in a salt solution that contains the ions of that metal.

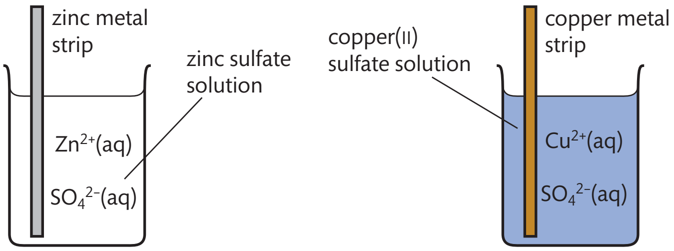


Figure 9.1 *Copper and zinc half-cells.*

Skill: Distinction between electron and ion flow in a voltaic cell.

Two half-cells can be combined to create a voltaic cell (see Figure 9.2) using:

- a wire connecting the two electrodes, which allows electrons to flow from the anode to the cathode
- a **salt bridge** connecting the two half-cells, which contains a concentrated salt solution and allows ions to flow into the half-cells.

The salt bridge is needed to balance the change in charge that happens in the half-cells because of the redox reactions.

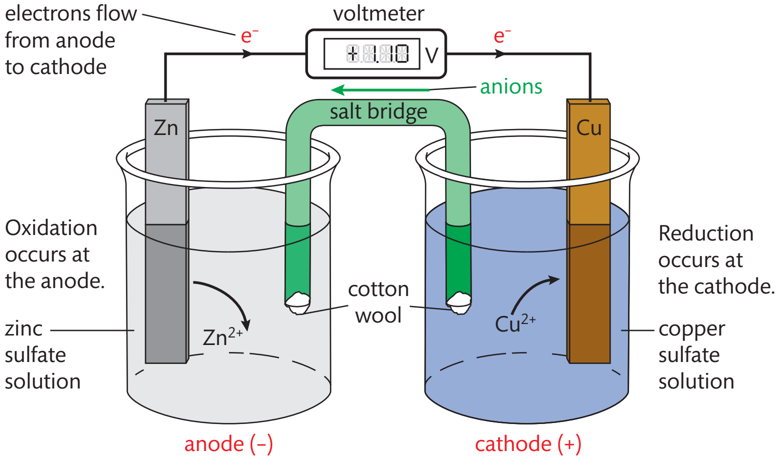
- Anions flow from the salt bridge into the anode.
- Cations flow from the salt bridge into the cathode.

The voltage difference that exists between two half-cells can be measured using a voltmeter.

Skill: Construction and annotation of a voltaic cell.

Skill: Performance of laboratory experiments involving a typical voltaic cell using two metal/metal-ion half-cells.

Connecting a copper half-cell and a zinc half-cell creates a voltaic cell. The zinc half-cell will be the anode because zinc is a more reactive metal than copper.



$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Net reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

Figure 9.2 *A copper–zinc voltaic cell.*

The **cell diagram convention** is a simple representation of a voltaic cell. The copper–zinc voltaic cell drawn above is represented as:

salt bridge phase boundary

$Zn(s)\,|\,Zn^{2+}(aq)\,||\,Cu^{2+}(aq)\,|\,Cu(s)$

anode cathode

oxidation reduction

$Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

The key features of a cell diagram representation are:

- The anode is normally shown on the left and cathode on the right.
- A double vertical line represents the salt bridge between the anode and cathode.
- Single vertical lines represent **phase boundaries** and show that the half-cell contains different phases, for example, a solid metal and an aqueous solution.
- Aqueous solutions in each half-cell are shown next to the salt bridge.
- **Spectator ions** are not oxidized or reduced in the reactions so are not included in the representation.

Subject vocabulary

cell diagram convention a method for representing the components of a voltaic cell

phase boundary a boundary that exists between components of a cell that are in different phases, e.g. a metal electrode and a salt solution in a voltaic half-cell

spectator ions ions that are present in solution but do not participate in any reactions

Skill: Explanation of how a redox reaction is used to produce electricity in a voltaic cell.

When all of the components of a voltaic cell are present:

- a **closed circuit** is created
- electrons generated by oxidation at the anode flow through the external wire and are used in reduction at the cathode
- the flow of electrons from anode to cathode produces an electric current (electricity).

Understanding: Oxidation occurs at the anode (positive electrode) and reduction occurs at the cathode (negative electrode) in an electrolytic cell.

An electrolytic cell contains:

- an anode: where oxidation occurs, the positive electrode
- a cathode: where reduction occurs, the negative electrode
- a **battery** or DC **power source** that forces electrons to flow from the anode to the cathode
- an **electrolyte solution**, which allows ions to flow and balance the changes in charge that happen at the electrodes because of the redox reactions.

Hints for success: In all electrochemical cells oxidation occurs at the anode and reduction at the cathode. However, the charge on the cathode and the charge on the anode are different in voltaic and electrolytic cells.

Skill: Construction and annotation of an electrolytic cell.

An electrolytic cell does not require two half-cells.

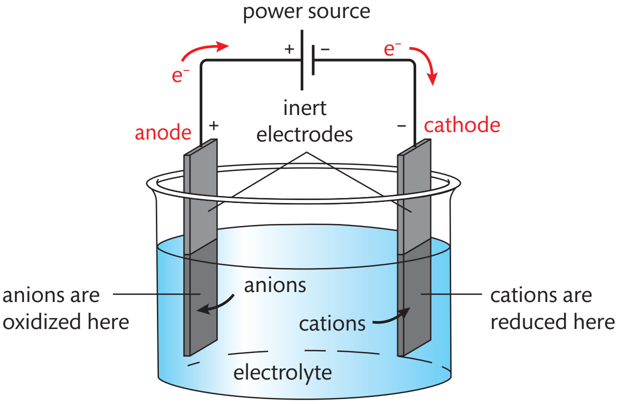


Figure 9.3 *Components of an electrolytic cell.*

The electrodes in an electrolytic cell are usually made of inert materials such as graphite or platinum. These materials can conduct electricity but are not oxidized or reduced themselves.

Subject vocabulary

closed circuit a circuit through which current can flow without being interrupted

battery a device that converts stored chemical energy into electrical energy

power source an electronic device that is a source of electrical energy

electrolyte solution a solution that contains ions and is able to conduct charge

DC stands for direct current

Skill: Explanation of how current is conducted in an electrolytic cell.

Skill: Distinction between electron and ion flow in an electrolytic cell.

When all the components of an electrolytic cell are present:

- a closed circuit is created
- the flow of electrons is controlled by the power source: electrons flow from the anode to the cathode
- cations (M^+) in the electrolyte flow to the cathode and are reduced
- anions (A^-) in the electrolyte flow to the anode and are oxidized
- reduction occurs at the negative cathode: $M^+ + e^- \rightarrow M$
- oxidation occurs at the positive anode: $A^- \rightarrow A + e^-$

Reactive metals such as sodium, aluminium, lithium, and magnesium naturally exist as positive ions in ionic compounds, e.g. NaCl and Al_2O_3.

The pure metals are obtained by electrolysis of their **molten** salts, e.g. sodium is obtained from the electrolysis of molten NaCl.

Subject vocabulary

molten melted (of a liquid that is formed only at high temperatures)

discharged changed by the electrolysis reaction (by losing its charge)

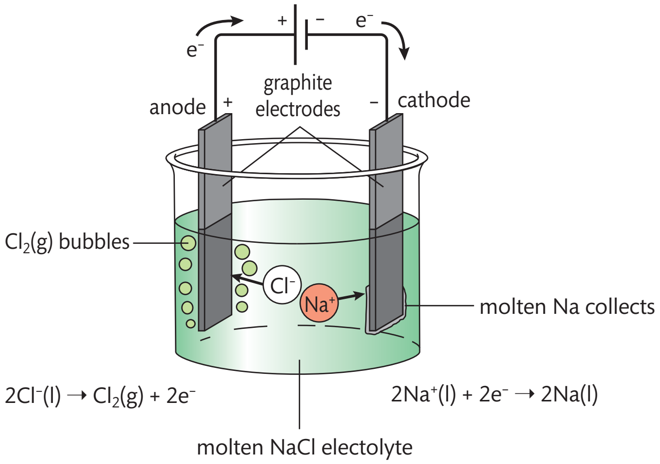


Figure 9.4 *Electrolysis of molten sodium chloride. Chloride ions are oxidized at the anode and sodium ions are reduced at the cathode. The overall equation is* $2NaCl(l) \rightarrow 2Na(l) + Cl_2(g)$.

Skill: Deduction of the products of the electrolysis of a molten salt.

In the electrolysis of a molten salt, e.g. NaCl(l)

- the cation is **discharged** to its metal: $M^+ + e^- \rightarrow M$
  - Example: $Na^+(l) + e^- \rightarrow Na(l)$
- The anion is discharged to its natural product: $A^- \rightarrow A + e^-$
  - Example: $2Cl^-(l) \rightarrow Cl_2(g) + 2e^-$

Hints for success: The electrolysis products may not be in the same states as they would be at 25 °C because of the high temperatures needed to make molten salts.

Salt	Cation	Anion	Product of cation reduction	Product of anion oxidation
NaCl	Na^+	Cl^-	Na	Cl_2
Al_2O_3	Al^{3+}	O^{2-}	Al	O_2
$MgCl_2$	Mg^{2+}	Cl^-	Mg	Cl_2

Topic 10: Organic chemistry

10.1 Fundamentals of organic chemistry

Essential idea:

Organic chemistry focuses on the chemistry of compounds containing carbon.

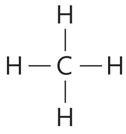
Understanding: A homologous series is a series of compounds of the same family, with the same general formula, which differ from each other by a common structural unit.

The **successive** members of a **homologous series**:

- belong to the same family of compounds (have the same **functional group**)
- differ by a common structural unit, $-CH_2-$ group (the common structural unit)
- have the same general formula
- have similar **chemical properties**
- show a gradual change in their **physical properties**.

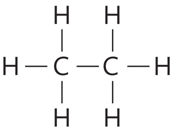
Example: Alkanes are a family of compounds made up of C and H atoms and only contain C–C single bonds:

CH_4



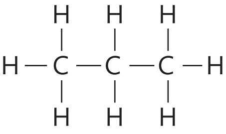
methane

C_2H_6



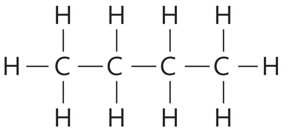
ethane

C_3H_8



propane

C_4H_{10}

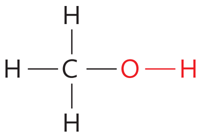


butane

The general formula for the alkane family is C_nH_{2n+2}

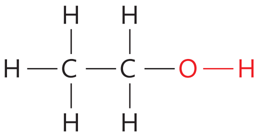
Example: Alcohols are a family of compounds that contain an $-OH$ functional group:

CH_3OH



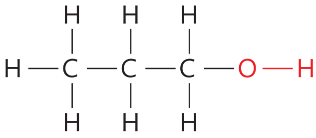
methanol

C_2H_5OH



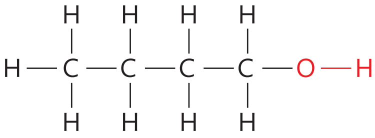
ethanol

C_3H_7OH



propanol

C_4H_9OH



butanol

The general formula for the alcohol family is $C_nH_{2n+1}OH$

Skill: Explanation of the trends in boiling points of members of a homologous series.

The boiling points for compounds in a homologous series increase with the length of the carbon chain. This **trend** happens because London dispersion forces become stronger as the size of the molecule increases.

General vocabulary

successive occuring one after each other in a series

Subject vocabulary

homologous series a family of organic compounds in which the chemical formula of successive members differs by CH_2

functional group a group of atoms that is present in a family of compounds. The functional group gives each member of the family the characteristic chemical properties of that family of compounds

chemical properties a property of a substance that becomes evident when it reacts and changes into another substance. Reactivity with water is an example of a chemical property

physical properties a property of a substance that can be measured without it changing into another substance. Melting points, boiling points, appearance, and density are examples of physical properties

Synonyms

trend .... pattern

Alkane		Boiling point / °C
methane	CH_4	−164
ethane	C_2H_6	−89
propane	C_3H_8	−42
butane	C_4H_{10}	−0.5
pentane	C_5H_{12}	36
hexane	C_6H_{14}	69
heptane	C_7H_{16}	98
octane	C_8H_{18}	125

gases at room temperature

liquids at room temperature

increasing boiling point

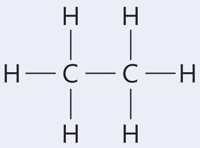
Understanding: Structural formulas can be represented in full and condensed format.

Understanding: Structural isomers are compounds with the same molecular formula but different arrangements of atoms.

An organic compound can be represented using an empirical formula, molecular formula, or **structural formula**.

A **full structure** shows all of the atoms and bonds in a molecule. A **condensed structure** places atoms in groups and does not show bonds.

Skill: Distinction between empirical, molecular, and structural formulas.

Ethane			
Empirical formula	**Molecular formula**	**Full structural formula**	**Condensed structural formula**
CH_3	C_2H_6		CH_3CH_3

Structural isomers are compounds that have the same molecular formula but have different arrangements of the atoms.

The **IUPAC** rules for naming straight-chain and branched-chain isomers are:

- **Rule 1:** Identify the longest chain in the compound. This gives the **stem** of the name.

Number of carbon atoms in longest chain	Stem in IUPAC name	Example of compound
1	meth-	CH_4, methane
2	eth-	C_2H_6, ethane
3	prop-	C_3H_8, propane

Subject vocabulary

structural formula a representation of a molecule that shows how the atoms are arranged

full structure a drawing of a molecule that shows all atoms and bonds

condensed structure a drawing of a molecule that groups atoms but does not show bonds

structural isomers compounds that have the same molecular formula but a different arrangement of atoms

IUPAC International Union of Pure and Applied Chemistry

General vocabulary

stem the root or base from which something larger is made

Number of carbon atoms in longest chain	Stem in IUPAC name	Example of compound
4	but-	C_4H_{10}, butane
5	pent-	C_5H_{12}, pentane
6	hex-	C_6H_{14}, hexane

- **Rule 2:** Identify the functional group. This usually gives the **suffix** of the name.

See the table on pages 114 and 115 for the different functional groups and their suffixes.

- **Rule 3:** Identify the **substituent** groups. These give the **prefix** of the name.

A number is given before the prefix for a substituent group to show where it occurs on the longest chain. If a substituent occurs more than once the prefix is modified to show this: e.g. dimethyl (two methyl substituents), trichloro (three chloro substituents).

General vocabulary

suffix an ending added to a word

substituent something that has replaced something else. In organic compounds substituents have usually replaced a hydrogen atom

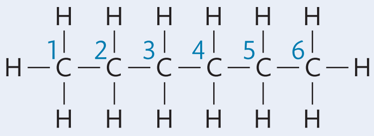
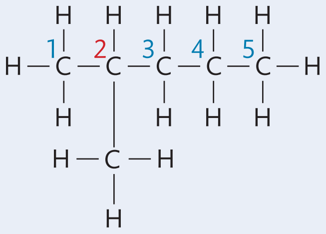
prefix a beginning added to a word

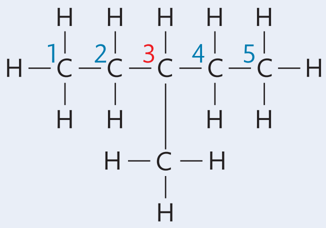
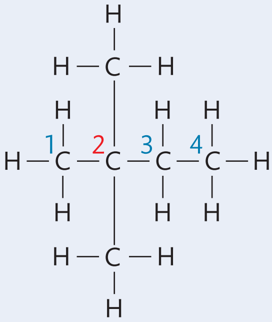
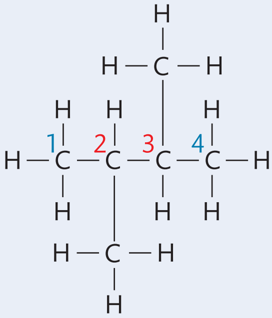
Hints for success: The numbering of the longest chain must start at the end that gives the lowest numbers for the substituents.

Number of carbons in alkyl side chain	Prefix in IUPAC name	Other substituent groups	Prefix in IUPAC name
1 ($-CH_3$)	methyl	–F	fluoro
2 ($-C_2H_5$)	ethyl	–Cl	chloro
3 ($-C_3H_7$)	propyl	–Br	bromo
4 ($-C_4H_9$)	butyl	–I	iodo
5 ($-C_5H_{11}$)	pentyl	$-NH_2$	amino

Skill: Application of IUPAC rules in the nomenclature of straight-chain and branched-chain isomers.

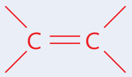
Draw and name the structural isomers of hexane (C_6H_{14}).

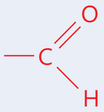
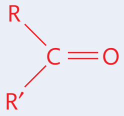
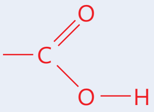
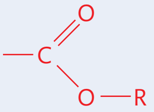
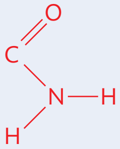
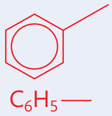
Full structure	Condensed structure	Name	Comments
 hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$ or $CH_3(CH_2)_4CH_3$	hexane	Longest chain has 6 carbon atoms No branches
 2-methylpentane	$CH_3CH(CH_3)CH_2CH_2CH_3$	2-methylpentane	Longest chain has 5 carbon atoms $-CH_3$ at position 2

Full structure	Condensed structure	Name	Comments
 3-methylpentane	$CH_3CH_2CH(CH_3)CH_2CH_3$	3-methylpentane	Longest chain has 5 carbon atoms $-CH_3$ at position 3
 2,2-dimethylbutane	$CH_3C(CH_3)_2CH_2CH_3$	2,2-dimethylbutane	Longest chain has 4 carbon atoms Two $-CH_3$ at position 2
 2,3-dimethylbutane	$CH_3CH(CH_3)CH(CH_3)CH_3$	2,3-dimethylbutane	Longest chain has 4 carbon atoms Two $-CH_3$ at positions 2 and 3

Understanding: Functional groups are the reactive parts of molecules.

Organic compounds are organized into classes (or families) based on their functional groups.

Class	Functional group	Name of functional group	Suffix in IUPAC name	Example of compound	General formula
alkane			-ane	C_2H_6, ethane	C_nH_{2n+2}
alkene		alkenyl	-ene	$H_2C{=}CH_2$, ethene	C_nH_{2n}
alkyne	$-C\equiv C-$	alkynyl	-yne	$HC\equiv CH$, ethyne	C_nH_{2n-2}
alcohol	$-OH$	hydroxyl	-anol	C_2H_5OH, ethanol	$C_nH_{2n+1}OH$

Class	Functional group	Name of functional group	Suffix in IUPAC name	Example of compound	General formula
ether	R—O—R′	ether	-oxyalkane	$H_3C-O-C_2H_5$, methoxyethane	R—O—R′
aldehyde		aldehyde (carbonyl)	-anal	C_2H_5CHO, propanal	R—CHO
ketone		carbonyl	-anone	CH_3COCH_3, propanone	R—CO—R′
carboxylic acid		carboxyl	-anoic acid	C_2H_5COOH, propanoic acid	$C_nH_{2n+1}COOH$
ester*		ester	-anoate	$C_2H_5COOCH_3$, methyl propanoate	R—COO—R′
amide		carboxyamide	-anamide	$C_2H_5CONH_2$, propanamide	
amine	$-NH_2$	amine	-anamine	$C_2H_5NH_2$, ethanamine	
nitrile	$-C\equiv N$	nitrile	-anenitrile	C_2H_5CN, propanenitrile	
arene		phenyl	-benzene	$C_6H_5CH_3$, methylbenzene	

*Esters form when the alkyl group of an alcohol replaces the hydrogen of a carboxylic acid in a condensation reaction:

$R\text{-}COOH + R'OH \rightarrow R\text{-}COO\text{-}R' + H_2O$

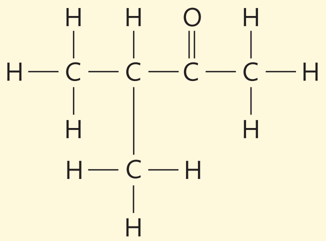
They are named in a similar way to salts, which form when a metal has replaced the hydrogen of a carboxylic acid. Salts take the stem of the name from the parent acid. For example, C_2H_5COONa is sodium propanoate. In esters, the alkyl group of the alcohol is the prefix, so $C_2H_5COOCH_3$ is methyl propanoate.

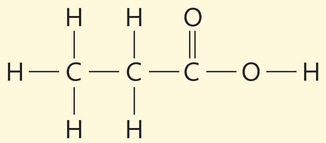
Skill: Identification of different classes: alkanes, alkenes, alkynes, halogenoalkanes, alcohols, ethers, aldehydes, ketones, esters, carboxylic acids, amines, amides, nitriles, and arenes.

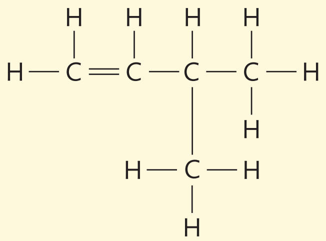
Skill: Identification of typical functional groups in molecules: e.g. phenyl, hydroxyl, carbonyl, carboxyl, carboxamide, aldehyde, ester, ether, amine, nitrile, alkyl, alkenyl, and alkynyl.

Worked example

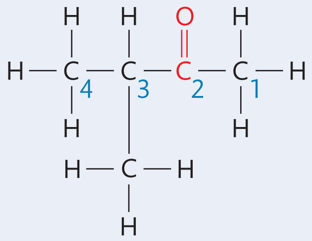
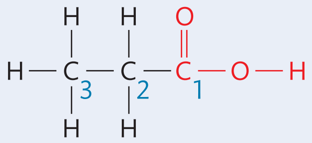
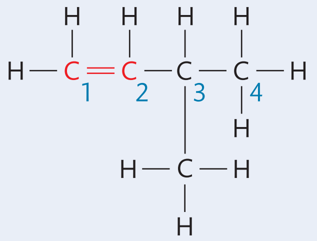
Identify the functional groups in the following compounds and name the class that they belong to. Determine the IUPAC name for each compound.



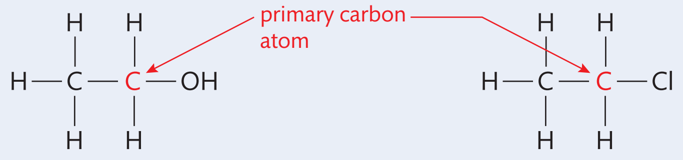


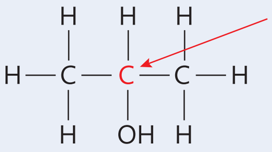
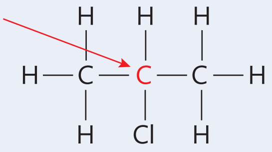
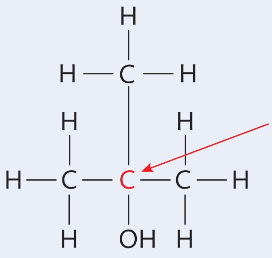
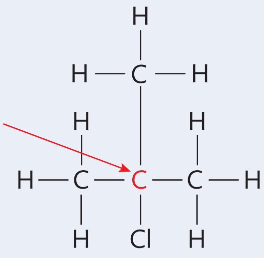


Solution

			
Functional group	carbonyl	carboxyl	alkenyl
Class (family)	ketone	carboxylic acid	alkene
	Naming compounds		
Step 1: Longest chain	4 carbons (but-)	3 carbons (prop-)	4 carbons (but-)
Step 2: Functional group	carbonyl at position 2 (ketone) -an-2-one	carboxyl (carboxylic acid) -anoic acid	alkenyl (after first position) -1-ene
Step 3: Side chains or substituents	–CH_3 at position 3	–	–CH_3 at position 3
IUPAC name	3-methylbutan-2-one	propanoic acid	3-methylbut-1-ene

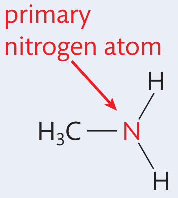
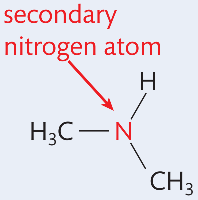
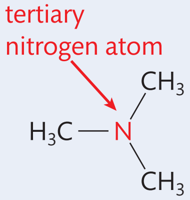
Skill: Identification of primary, secondary, and tertiary carbon atoms in halogenoalkanes and alcohols.

Type of compound	**Functional group attached to**	**Examples**	
		Alcohols	**Halogenoalkanes**
Primary alcohol or primary halogenoalkane	**Primary carbon** (bonded to one alkyl chain)	 ethanol, C_2H_5OH	chloroethane, C_2H_5Cl

Type of compound	Functional group attached to	Examples	
		Alcohols	Halogenoalkanes
Secondary alcohol or secondary halogenoalkane	**Secondary carbon** (bonded to two alkyl chains)	 propan-2-ol, $CH_3CH(OH)CH_3$	 2-chloroethane, $CH_3CHClCH_3$
Tertiary alcohol or tertiary halogenoalkane	**Tertiary carbon** (bonded to three alkyl chains)	 2-methylpropan-2-ol $C(CH_3)_3OH$	 2-chloro-2-methylpropane $C(CH_3)_3Cl$

Methanol is also regarded as a primary alcohol even though the hydroxyl group is attached to a carbon that is not bonded to any alkyl chains.

Skill: Identification of primary, secondary and tertiary nitrogen atoms in amines.

Primary amine	Secondary amine	Tertiary amine
		
Amine group has a **primary nitrogen** that is bonded to one alkyl chain	Amine group has a **secondary nitrogen** that is bonded to two alkyl chains	Amine group has a **tertiary nitrogen** that is bonded to three alkyl chains

Subject vocabulary

primary carbon	a carbon atom that is bonded to one alkyl chain
secondary carbon	a carbon atom that is bonded to two alkyl chains
tertiary carbon	a carbon atom that is bonded to three alkyl chains
primary nitrogen	a nitrogen atom that is bonded to one alkyl chain
secondary nitrogen	a nitrogen atom that is bonded to two alkyl chains
tertiary nitrogen	a nitrogen atom that is bonded to three alkyl chains

Understanding: Saturated compounds contain single bonds only and unsaturated compounds contain double or triple bonds.

Subject vocabulary

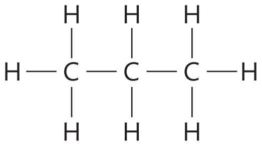
saturated only single bonds are present in the molecule (the molecule only contains sigma bonds)

unsaturated the molecule contains double or triple bonds (the molecule contains pi bonds)

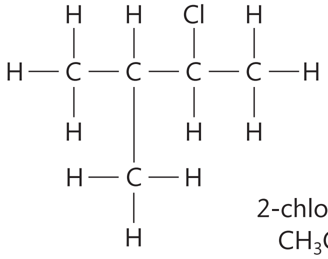
benzene an aromatic compound with the formula C_6H_6 and in which the carbon atoms are arranged in a hexagonal ring

aromatic contains delocalized pi bonds in a ring structure

Saturated compounds contain single bonds only, e.g.

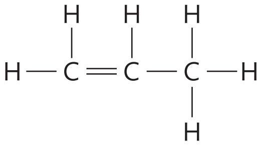


propane
C_3H_8

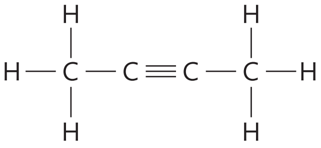


2-chloro-3-methylbutane
$CH_3CHClCH(CH_3)CH_3$

Unsaturated compounds contain double or triple bonds, e.g.



propene
C_3H_6



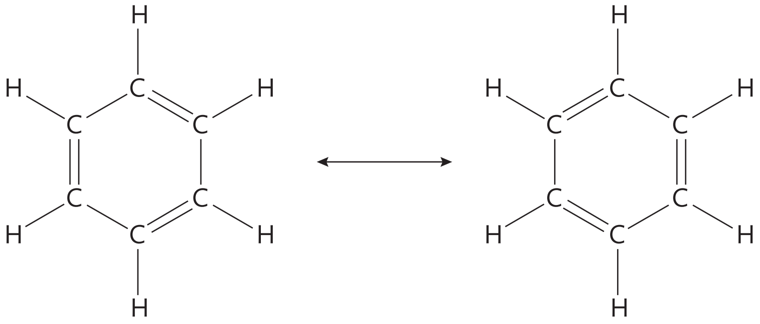
but-2-yne
C_4H_6

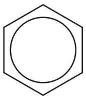
Hints for success: A compound is unsaturated if it contains multiple bonds.

Understanding: Benzene is an aromatic, unsaturated hydrocarbon.

Benzene:

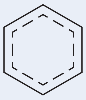
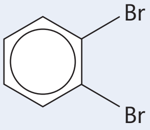
- has the formula C_6H_6
- is unsaturated because it contains double bonds
- has two resonance structures:



- is **aromatic** (the three double bonds in the ring are delocalized)
- has the shorthand representation: 

Each point represents a carbon atom. Hydrogen atoms are not shown. The circle represents the three delocalized double bonds.

Skill: Discussion of the structure of benzene using physical and chemical evidence.

Property	Observation / evidence	Explanation
(a) Bond lengths	All carbon–carbon bond lengths in benzene are equal and have a bond length between single and double bonds.	Each bond contains a share of three delocalized double bonds. X-ray bond length data: alkane single bond C—C 0.154 nm alkene double bond C═C 0.134 nm benzene  0.139 nm
(b) $\Delta H_{\text{hydrogenation}}$ for the reaction $C_6H_6 + 3H_2 \rightarrow C_6H_{12}$	Theoretical value based on adding H_2 across three localized C═C double bonds = −362 kJ mol^{-1} Experimental value for benzene = −210 kJ mol^{-1} Benzene is more stable than predicted from three localized C═C bonds by approx. 152 kJ mol^{-1}	Delocalization minimizes the repulsion between electrons and so gives benzene a more stable structure, lowering its internal energy by 152 kJ mol^{-1}.
(c) Type of reactivity	Benzene does not undergo addition reactions and is more likely to undergo substitution reactions.	Addition reactions are not favoured as they would involve disrupting the entire cloud of delocalized electrons. Benzene can instead undergo substitution reactions that preserve the stable ring structure.
(d) Isomers	Only one isomer exists of compounds such as 1,2-dibromobenzene.	As benzene is a symmetrical molecule with no alternating single and double bonds, all adjacent positions in the ring are equal. For example 1,2-dibromobenzene, $C_6H_4Br_2$ 

10.2 Functional group chemistry

Essential idea:

Structure, bonding, and chemical reactions involving functional group interconversions are **key strands** in organic chemistry.

Understanding: Alkanes have low reactivity and undergo free-radical substitution reactions.

Alkanes are saturated **hydrocarbons** with the general formula C_nH_{2n+2}.

Alkanes have a low reactivity because they contain C–C and C–H bonds which:

- are strong bonds and are hard to break
- are non-polar bonds and do not attract reactive species such as electrophiles and nucleophiles.

Two reactions of alkanes that do occur are:

- **combustion** with oxygen (alkanes are good fuels)
- **free-radical substitution** with halogens.

Skill: Writing equations for the complete and incomplete combustion of hydrocarbons.

Complete combustion of alkanes occurs when there is an excess of oxygen. The products are carbon dioxide and water, e.g.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

$2C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

Incomplete combustion of alkanes occurs when oxygen is limiting. The products are carbon monoxide and water, e.g.

$2C_3H_8(g) + 7O_2(g) \rightarrow 6CO(g) + 8H_2O(g)$

$2C_8H_{18}(l) + 17O_2(g) \rightarrow 16CO(g) + 18H_2O(g)$

Skill: Explanation of the reaction of methane and ethane with halogens in terms of a free-radical substitution mechanism involving photochemical homolytic fission.

Free radicals are species that contain an unpaired electron and they are highly reactive.

Homolytic fission is when a covalent bond breaks and each atom gets one electron:

$A–B \rightarrow A\bullet + B\bullet$ (A• and B• are free radicals)

Photochemical homolytic fission happens when the molecule absorbs light energy and this causes the bond to break.

The free-radical substitution mechanism has three steps:

Step 1 **Initiation**: free radicals are made from homoloytic fission and **initiate** the reaction.

Step 2 **Propagation**: the free radicals made in Step 1 **propagate** (continue reacting) to create new free radicals.

Step 3 **Termination**: the free radicals combine to form a covalent bond and the reaction **terminates**.

Synonyms

key strands .... important features

initiate .... start

propagate ..... continue

terminate ...... end

Subject vocabulary

alkanes hydrocarbons that only contain single bonds. They have the general formula C_nH_{2n+2}

hydrocarbons compounds that contain only carbon and hydrogen atoms

combustion the reaction of a substance with oxygen

free-radical substitution a substitution reaction in which a bonded atom is replaced by a free radical

complete combustion the combustion reaction of a substance that happens when excess oxygen is available

incomplete combustion the combustion reaction of a substance that happens when limited amounts of oxygen is available

free radicals species that contain an upaired electron

homolytic fission the breaking of a covalent bond to form two free radicals

photochemical chemical changes that happen after light energy is absorbed by compounds

initiation the first step in the free-radical mechanism, where free radicals are formed

propagation the steps in the free-radical mechanism where free radicals react to form new free radicals

termination the last step in the free-radical mechanism, where two radicals combine and end the reaction

	Free-radical substitution of methane (CH_4) with Cl_2	**Free-radical substitution of ethane (CH_3CH_3) with Br_2**
Step 1: Initiation	$Cl_2 \xrightarrow{\text{UV light}} 2Cl\bullet$	$Br_2 \xrightarrow{\text{UV light}} 2Br\bullet$
Step 2: Propagation	$Cl\bullet + CH_4 \rightarrow CH_3\bullet + H\text{–}Cl$	$Br\bullet + CH_3CH_3 \rightarrow CH_3CH_2\bullet + H\text{–}Br$
Step 3: Termination	$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl$	$CH_3CH_2\bullet + Br\bullet \rightarrow CH_3CH_2Br$
Overall equation	$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	$CH_3CH_3 + Br_2 \rightarrow CH_3CH_2Br + HBr$

Hints for success: Cl_2 and Br_2 are good initiators as they have weak bonds that are easily broken by UV light.

Understanding: Alkenes are more reactive than alkanes and undergo addition reactions. Bromine water can be used to distinguish between alkenes and alkanes.

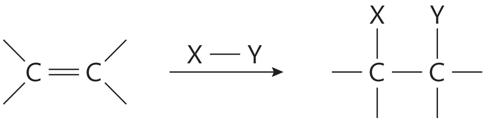
Alkenes are unsaturated hydrocarbons that have the general formula C_nH_{2n} and contain a double bond. Alkenes are more reactive than alkanes because they contain a double bond.

Subject vocabulary

alkenes hydrocarbons that contain one or more double bonds

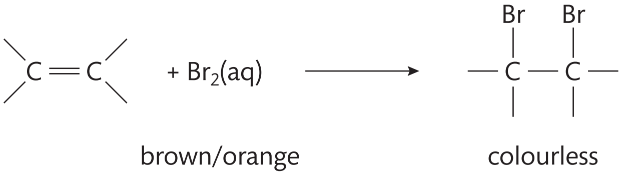
addition reaction a reaction of alkenes that forms saturated products

Alkenes can undergo **addition reactions**: the double bond between two carbon atoms breaks and two single bonds are formed.



The overall result is that the reactant X–Y has been added to the unsaturated alkene to form a saturated product.

The addition reaction between Br_2(aq) (bromine water) and an alkene provides an easy way to test for alkenes. If an alkene is present the solution will change colour from brown/orange to colourless.



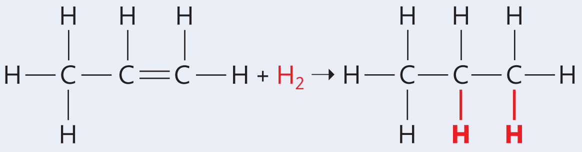
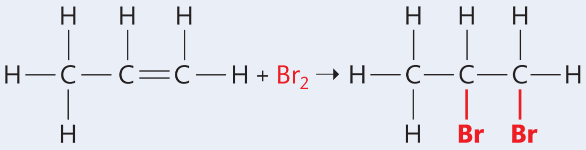
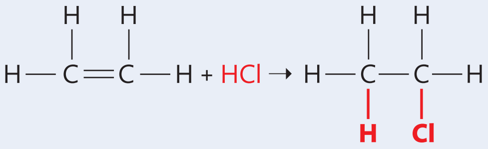
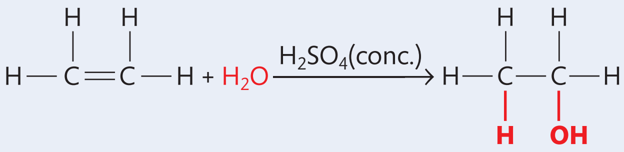
Subject vocabulary

symmetrical alkene an alkene that has the same groups on the two carbons that make the double bond

hydrogenation the addition reaction of alkenes with H_2

hydration the addition reaction of alkenes with H_2O

Skill: Writing equations for the reactions of alkenes with hydrogen and halogens and of symmetrical alkenes with hydrogen halides and water.

Addition reactant	Organic product	Comments
H_2	alkane	Needs a nickel catalyst and high temperature (150 °C) Called a **hydrogenation** reaction
	Example:  $CH_3CHCH_2 + H_2 \xrightarrow[150\,°C]{\text{Ni catalyst}} CH_3CH_2CH_3$ propene propane	
Cl_2, Br_2, I_2	dihalogenoalkane	Reaction with $Br_2(aq)$ tests for alkenes (or alkynes)
	Example:  $CH_3CHCH_2 + Br_2 \longrightarrow CH_3CHBrCH_2Br$ propene 1,2-dibromopropane	
HCl, HBr, HI	halogenoalkane	Reactivity is in order: HI > HBr > HCl (weakest H–X bond reacts fastest)
	Example:  $CH_2CH_2 + HCl \longrightarrow CH_3CH_2Cl$ ethene chloroethane	
H_2O	alcohol	Needs concentrated sulfuric acid (H_2SO_4) catalyst Called a **hydration** reaction
	Example:  $CH_2CH_2 + H_2O \xrightarrow{H_2SO_4(conc.)} CH_3CH_2OH$ ethene ethanol	

Understanding: Alcohols undergo **esterification** (or condensation) reactions with acids and some undergo oxidation reactions.

Alcohols are saturated compounds that contain the –OH functional group and have the general formula $C_nH_{2n+1}OH$.

Three important reactions of alcohols are:

- combustion with oxygen (alcohols are good fuels)
- reactions with **carboxylic acids** to make **esters**
- oxidation with oxidizing agents such as potassium dichromate(VI) or potassium manganate(VII).

Skill: Writing equations for the complete combustion of alcohols.

Complete combustion of alcohols occurs when there is an excess of oxygen. The products are carbon dioxide and water.

Examples:

$$2C_3H_7OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(g)$$

$$C_6H_{13}OH\ (l) + 9O_2(g) \rightarrow 6CO_2(g) + 7H_2O(g)$$

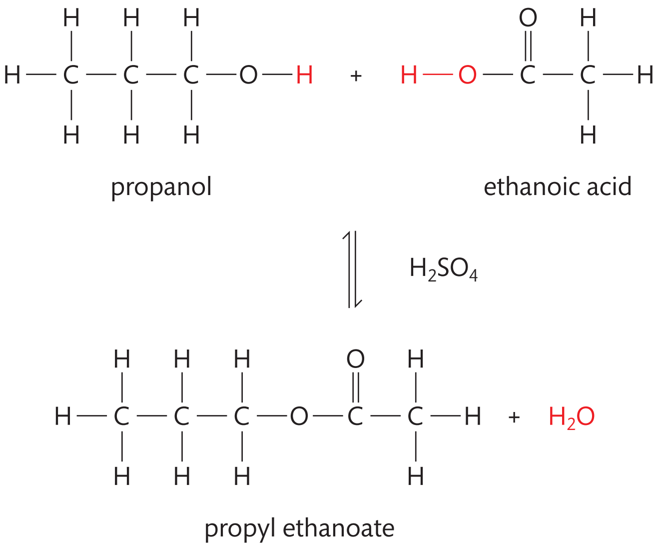
Skill: Writing the equation for the condensation reaction of an alcohol with a carboxylic acid, in the presence of a catalyst (e.g. concentrated sulfuric acid) to form an ester.

Esterification reactions:

- are condensation reactions
- occur between alcohols and carboxylic acids
- form esters and water as products
- are catalysed by concentrated sulfuric acid (H_2SO_4):

$$\text{alcohol} + \text{carboxylic acid} \overset{H_2SO_4}{\rightleftharpoons} \text{ester} + \text{water}$$

Example:



Subject vocabulary

esterification the reaction between an alcohol and a carboxylic acid to make an ester and water

alcohols a family of compounds that contain the –OH functional group

carboxylic acids a family of compounds that contain the –COOH functional group

esters a family of compounds that contain the –COO– functional group

condensation reaction a reaction that forms water as a product

Skill: Writing equations for the oxidation reactions of primary and secondary alcohols (using acidified potassium dichromate(VI) or potassium manganate(VII) as oxidizing agents). Explanation of distillation and reflux in the isolation of the aldehyde and carboxylic acid products.

Different oxidation reactions occur for primary, secondary, and tertiary alcohols.

The oxidizing agents normally used to oxidize alcohols are:

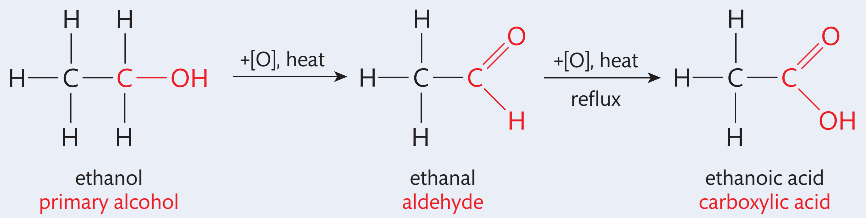
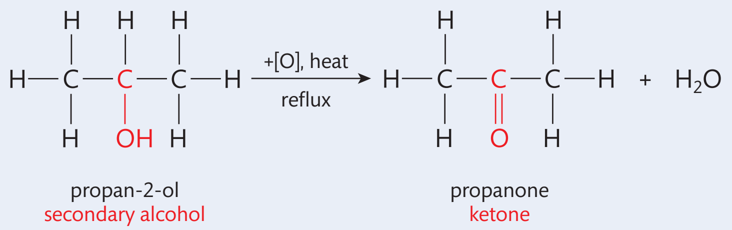
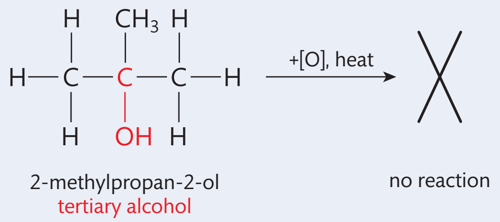
- acidified potassium dichromate(VI), $H^+(aq)/K_2Cr_2O_7(aq)$ (orange $Cr_2O_7^{2-}$ ion changes to green Cr^{3+} ion)
- acidified potassium manganate(VII), $H^+(aq)/KMnO_4(aq)$ (purple MnO_4^- ion changes to colourless Mn^{2+} ion).

Hints for success: [O] can be used to represent an oxidizing agent when writing an oxidation reaction.

Subject vocabulary

aldehyde a family of compounds that contain the –CHO functional group

ketone a family of compounds that contain the –CO– functional group

Alcohol	Oxidation products	Example
primary	**aldehyde** → carboxylic acid	
secondary	**ketone**	
tertiary	no reaction	

The oxidation of a primary alcohol has two possible products: an aldehyde or a carboxylic acid. These can be separated depending on the reaction conditions.

Figure 10.1 *Distillation apparatus is used to separate liquids with different boiling points. In the oxidation of primary alcohols, the aldehyde has a lower boiling point than the alcohol or the acid, and so is collected as a gas and passes into the condensing tube, which is surrounded by cold flowing water. The gas condenses back into a liquid, which is collected in the beaker at the bottom. This prevents further oxidation of the aldehyde to the carboxylic acid.*

- The aldehyde has a lower boiling point than the primary alcohol. **Distillation** can be used to remove the aldehyde as it is formed.
- The carboxylic acid is formed if the reaction is in **reflux**. The initial aldehyde product stays in the reaction mixture and is converted to the carboxylic acid.

Understanding: Halogenoalkanes are more reactive than alkanes. They can undergo (nucleophilic) substitution reactions. A nucleophile is an electron-rich species containing a lone pair that it donates to an electron-deficient carbon.

Halogenoalkanes are saturated compounds that have the general formula $C_nH_{2n+1}X$, where X = F, Cl, Br, or I.

The polar C–X bond makes halogenoalkanes more reactive than alkanes.

Nucleophilic substitution reactions involve the halogen atom in a halogenoalkane being replaced by a **nucleophile**.

A nucleophile:

- is an electron-rich species that contains a lone pair of electrons, e.g. OH^-, CN^-
- can donate its lone pair to an **electron-deficient carbon** to form a coordinate bond. (The nucleophile can act as a Lewis base; see Chapter 18.)

Skill: Writing the equation for the substitution reactions of halogenoalkanes with aqueous sodium hydroxide.

Halogenoalkanes react with aqueous hydroxide ions (OH^-) in a nucleophilic substitution reaction to form alcohols, e.g.

$$CH_3Cl + NaOH \rightarrow CH_3OH + NaCl$$

chloromethane methanol

$$C_3H_7Br + NaOH \rightarrow C_3H_7OH + NaBr$$

1-bromopropane propan-1-ol

Understanding: Addition polymers consist of a wide range of monomers and form the basis of the plastics industry.

The plastics industry is based on making new polymers (plastics) that have properties that make them suitable for various applications.

Small molecules called **monomers** are reacted together to make very large molecules known as **polymers**. The properties of the polymers will depend on the monomers that they are made from.

Addition polymerization reactions:

- occur between individual alkene molecules (monomers)
- create molecules with very long carbon chains (**addition polymers**).

Subject vocabulary

distillation a process in which a mixture is separated into components by heating the mixture and selectively boiling off and condensing the components into a separate container

reflux a process in which a reaction mixture is kept at the boiling point of the solvent by condensing the solvent that boils off and returning it to the reaction mixture

halogenoalkanes alkanes in which a hydrogen atom has been replaced by a halogen atom

nucleophilic substitution reactions substitution reactions in which a nucleophile replaces a leaving group

nucleophile an electron-rich species that can act as a Lewis base and donate an electron pair to form a coordinate bond

electron-deficient carbon a carbon that has a partial positive charge

monomers individual molecules that can combine to form polymers

polymers very large molecules made up of repeating units

addition polymers polymers that are formed by addition reactions of alkenes

Skill: Outline of the addition polymerization of alkenes.

In addition polymerization reactions the double bond in the monomer alkene breaks to make two single bonds in the polymer. The single bonds that form link one monomer to another to create the long polymer chain:

n(monomer) addition polymer

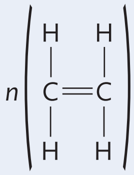
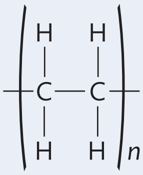
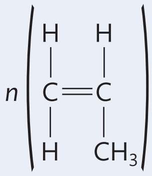
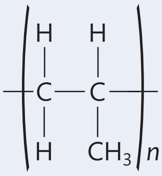
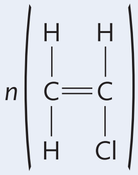
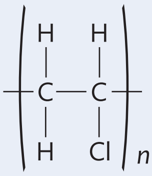
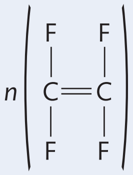
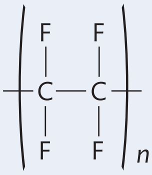
Hints for success: The brackets contain the repeating unit of the polymer. The polymer is a chain of these repeating units linked to each other.

n represents the number of monomers used in the reaction and is the number of **repeating units** which are linked together in the polymer.

Subject vocabulary

repeating units a group of atoms that come from a monomer and link repeatedly to form the polymer chain

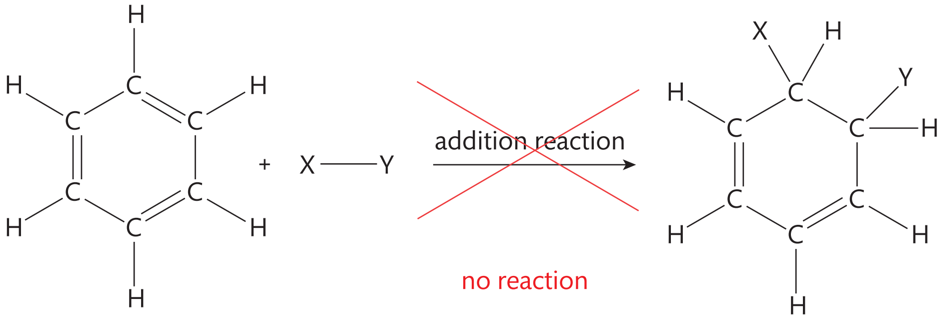
Skill: Relationship of the structure of the monomer to the polymer and repeating unit.

Monomer	Polymer	Uses
 ethene	 polyethene	Most common plastic: used in plastic bags, bottles, films.
 propene	 polypropene	Second most common plastic: used in clothing, ropes, machine parts.
 chloroethene (vinyl chloride)	 polychloroethene (polyvinyl chloride, PVC)	Third most common plastic: used in pipes, plastic cards, inflatable toys.
 tetrafluoroethene	 polytetrafluoroethene, PTFE (Teflon)	Used in non-stick cookware, waterproof and breathable clothing, medical plastics.

Understanding: Benzene does not readily undergo addition reactions but does undergo electrophilic substitution reactions.

The benzene ring is stabilized by the three delocalized double bonds in the ring.

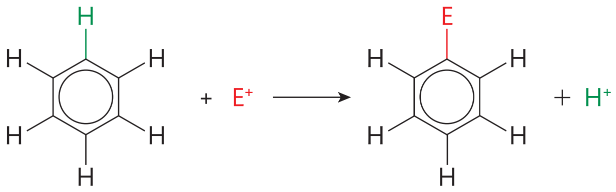
If benzene undergoes an addition reaction the product has two double bonds that are localized. This means the product is less stable than benzene so addition reactions of benzene are unlikely to happen.

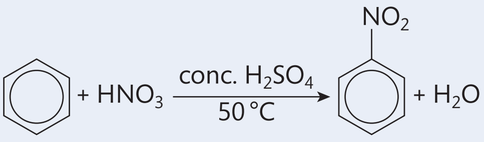
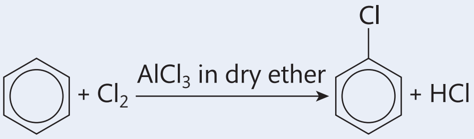


Electrophiles:

- are electron-poor species
- have a positive charge or a partial positive charge
- are attracted to the electron-rich benzene ring.

Benzene can undergo **electrophilic substitution reactions**, in which an electrophile (E^+) replaces a hydrogen atom:



Reaction (electrophile)	Comments	Reaction
nitration (NO_2^+)	NO_2^+ is made from nitric acid using sulfuric acid catalyst	 nitrobenzene
chlorination (Cl^+)	Cl^+ is made from chlorine (Cl_2) using $AlCl_3$ catalyst	 chlorobenzene

Subject vocabulary

electrophiles electron-poor species that can act as Lewis acids and accept electron pairs to form coordinate bonds

electrophilic substitution reactions substitution reactions in which an electrophile replaces a hydrogen atom

Topic 11: Measurement and data processing

11.1 Uncertainties and errors in measurement and results

Essential idea:

All measurement has a limit of precision and accuracy, and this must be taken into account when evaluating experimental results.

Understanding: Qualitative data include all non-numerical information obtained from observation not from measurement.

- **Qualitative data**:
  - are obtained by making **observations**
  - are **descriptive**
  - are **non-numerical**.
- Examples of qualitative data:
  - observing that the colour of a solution is blue
  - observing that gas bubbles are given off during a reaction
  - observing that a beaker gets hot during a reaction.

Subject vocabulary

qualitative data data that are obtained by making observations

quantitative data data that are obtained by making measurements

random errors errors that are associated with measurements and are a result of natural variability due to the procedure or instrument used to make the measurement

General vocabulary

observation watching an object or process and recording any changes that occur

descriptive using words to describe how something appears or how it changes

non-numerical without numbers

measurements assigning numbers or values to physical properties

numerical including numbers

Understanding: Quantitative data are obtained from measurements and are always associated with random errors/uncertainties, determined by the apparatus, and by human limitations such as reaction times.

- **Quantitative data**:
  - are obtained by making **measurements**
  - are **numerical**
  - have **random errors** (uncertainty) associated with the measurement.
- Examples of quantitative data:
  - the mass of a NaCl sample weighed with an analytical balance
  - the volume of a NaOH solution measured with a measuring cylinder
  - the pH of a solution measured with a pH meter.

Skill: Record uncertainties in all measurements as a range (±) to an appropriate precision

Measurements and uncertainties must have the same number of decimal places.

Type of measurement

Digital

The uncertainty is equal to the smallest scale division

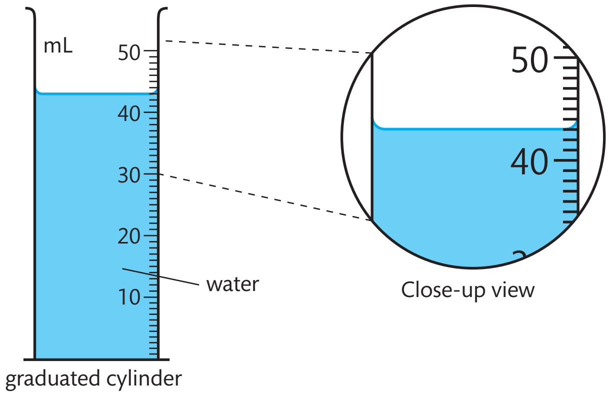
smallest division: 0.01 g

uncertainty: ± 0.01 g

mass of beaker and solution: 100.00 ± 0.01 g

Analogue (using a scale)

The uncertainty is equal to half the smallest scale division



smallest division: 1 cm^3

uncertainty: ± 0.5 cm^3

volume of solution: 43.0 ± 0.5 cm^3

Understanding: Repeat trials and measurements will reduce random errors but not systematic errors.

Skill: Distinction between random errors and systematic errors.

Random errors	Systematic errors
Associated with all measurements Depend on the precision of the instrument Reduced by repeat measurements Equally likely to be in both directions (too high or too low)	Due to poor experimental design, inaccurate instruments, human error Not reduced by repeat measurements Likely to be in a single direction (e.g. too low)

Understanding: Propagation of random errors in data processing shows the impact of the uncertainties on the final result.

- Uncertainty can be expressed as absolute uncertainty, relative uncertainty, or percentage uncertainty.

Subject vocabulary

systematic errors errors that result from inaccuracy or bias in the procedure or instrument used to make the measurement

absolute uncertainty the uncertainty that is associated with a measured or calculated value

relative uncertainty the absolute uncertainty expressed as a ratio of the measured or calculated value

percentage uncertainty the absolute uncertainty expressed as a percentage of the measured or calculated value

Absolute uncertainty	Relative uncertainty	Percentage uncertainty
The uncertainty that is associated with a measured or calculated value Absolute uncertainties have the same units as the measured or calculated value	The absolute uncertainty expressed as a *ratio* of the measured or calculated value: relative uncertainty = $\frac{\text{uncertainty}}{\text{value}}$ Relative uncertainties have no units	The absolute uncertainty expressed as a *percentage* of the measured or calculated value: percentage uncertainty = $\frac{\text{uncertainty}}{\text{value}} \times 100$
Volume of solution = 37.5 ± 0.5 cm^3		
Absolute uncertainty: ±0.5 cm^3	Relative uncertainty: $\frac{0.5\,\text{cm}^3}{37.5\,\text{cm}^3} = \pm 0.013$	Percentage uncertainty: $\frac{0.5\,\text{cm}^3}{37.5\,\text{cm}^3} \times 100 = \pm 1.3\%$

Skill: Propagation of uncertainties in processed data, including the use of percentage uncertainties.

Many calculations (processed data) involve more than one measurement. This means that the uncertainty in the calculated value depends on the uncertainties of *all* the measured values.

The final uncertainty is found by the **propagation of uncertainties**.

Subject vocabulary

propagation of uncertainties a mathematical process for determining the uncertainty in a calculated value from the uncertainties in all the measurements used in the calculation

Addition/subtraction

The final uncertainty is found by adding the *absolute uncertainties*.

Example: Calculating the volume of solution delivered from a burette.

Final volume:	22.45 ± 0.05 cm^3
Initial volume:	0.20 ± 0.05 cm^3
Volume added:	22.25 ± 0.10 cm^3

Multiplication/division

The final uncertainty is found by adding the *percentage uncertainties* then converting the answer to an absolute uncertainty.

Example: Calculating the density (ρ) of a liquid.

Mass (m): 26.05 ± 0.01 g   Volume (V): 25.00 ± 0.04 cm^3

$$\rho = \frac{m}{V} = \frac{26.05\,\text{g}}{25.00\,\text{cm}^3} = 1.042\,\text{g}\,\text{cm}^{-3}$$

percentage uncertainty in ρ =

percentage uncertainty in m + percentage uncertainty in V

$$= \frac{0.01\,\text{g}}{26.05\,\text{g}} \times 100\% + \frac{0.04\,\text{cm}^3}{25.00\,\text{cm}^3} \times 100\%$$

$$= 0.20\%$$

The percentage uncertainty in the final result must be converted to an absolute uncertainty.

$$\text{absolute uncertainty in } \rho = \frac{\text{percentage uncertainty}}{100} \times \text{value of density}$$

$$= \frac{0.20}{100} \times 1.042\,\mathrm{g\,cm^{-3}} = 0.002\,\mathrm{g\,cm^{-3}}$$

The density of the liquid is $\underbrace{1.042 \pm 0.002\,\mathrm{g\,cm^{-3}}}$

Note that the value and the uncertainty have the same number of decimal places.

Hints for success: A calculated absolute uncertainty has only one *significant figure*. If necessary the calculated value is adjusted so it has the same number of *decimal places* as the calculated uncertainty.

Understanding: Experimental design and procedure usually lead to systematic errors in measurement, which cause a deviation in a particular direction.

Skill: Estimation of whether a particular source of error is likely to have a major or minor effect on the final result.

- A student conducts an experiment to determine the enthalpy of solution (ΔH_{sol}) of sodium hydroxide (NaOH) by dissolving a sample of NaOH in a known volume of water and measuring the temperature change. The experiment is conducted in a polystyrene coffee cup.

$$\Delta H_{sol} = \frac{q}{n} \qquad q = mc\Delta T \qquad n(\mathrm{NaOH}) = \frac{m}{M}$$

Measurement	Instrument	Value	Uncertainty	Percentage uncertainty
Mass of NaOH	Digital balance	1.115 g	±0.001 g	0.09%
Volume of water	Measuring cylinder	100.0 $\mathrm{cm^3}$	±0.5 $\mathrm{cm^3}$	0.5%
Initial temperature (T_i)	Digital thermometer	22.3 °C	±0.1 °C	
Final temperature (T_f)		24.8 °C		
Change in temperature (ΔT)	($= T_f - T_i$)	2.5 °C	±0.2 °C	8%

From the table above, the percentage uncertainties show that:

- the uncertainty in the measured mass (0.09%) will have a very small effect on the final propagated uncertainty
- the uncertainty in the measured volume (0.5%) will have a small effect on the final propagated uncertainty
- the uncertainty in the measured temperature change (8%) will have the largest effect on the final propagated uncertainty.

Skill: Discussion of systematic errors in all experimental work, their impact on the results, and how they can be reduced.

If the experimental value does not agree with the known value then a systematic error is present.

For example, the known value for ΔH_{sol}(NaOH) is −44.5 kJ mol^{-1}. The experimental value for ΔH_{sol}(NaOH) calculated using the results above is −37 ± 3 kJ mol^{-1}:

$-44.5\text{ kJ mol}^{-1} \neq -37 \pm 3\text{ kJ mol}^{-1}\ (-34\text{ kJ mol}^{-1} \Leftrightarrow -40\text{ kJ mol}^{-1})$

This means a systematic error is present as the difference between experimental and known values cannot be explained by the propagated random uncertainties.

Skill: Discussion of ways to reduce uncertainties in an experiment.

- Random errors can be reduced by:
  - conducting repeated trials
  - using more precise equipment and instruments.

  In the above example for determining ΔH_{sol}(NaOH) the biggest experimental uncertainty was in the measurement of ΔT. Using a digital thermometer that measures temperature to two decimal places (±0.01 °C) would reduce the random uncertainty in ΔT and the uncertainty in the final result.
- Systematic errors can be reduced by improving the procedure or equipment used in the experiment.

  In the above example for determining ΔH_{sol} a systematic error was present. The experimental value was less than the known value. This indicates that the experiment was not measuring all of the heat released by the reaction.

  The most likely source of this systematic error is heat loss to the surroundings from the poorly insulated coffee cup.

  The experiment could be improved by using an insulated vacuum flask instead of the coffee cup as this would reduce the amount of heat loss to the surroundings.

Skill: Calculation of percentage error when the experimental result can be compared with a theoretical or accepted result.

$$\text{percentage error} = \frac{\text{accepted value} - \text{experimental value}}{\text{accepted value}} \times 100\%$$

Example: The experiment to determine ΔH_{sol}(NaOH):

$$\text{percentage error} = \frac{-44.5\text{ kJ mol}^{-1} - (-37\text{ kJ mol}^{-1})}{-44.5\text{ kJ mol}^{-1}} \times 100\% = 17\%$$

Skill: Distinction between accuracy and precision in evaluating results.

Two students perform three trials of the experiment to determine ΔH_{sol}(NaOH).

	Student A	Student B
Trial 1	−37.2 kJ mol^{-1}	−43.6 kJ mol^{-1}
Trial 2	−38.1 kJ mol^{-1}	−48.2 kJ mol^{-1}
Trial 3	−37.6 kJ mol^{-1}	−40.2 kJ mol^{-1}

The results obtained by student B are closer to the accepted value of −44.5 kJ mol^{-1}. This means that student B's results are more **accurate**.

The results obtained by student A have a smaller range. This means that student A's results are more **precise**.

Subject vocabulary

accurate the measured value is similar to the known exact value

precise repeated measurements give similar results

11.2 Graphical techniques

Essential idea:

Graphs are a visual representation of trends in data.

Understanding: Graphical techniques are an effective means of communicating the effect of an independent variable on a dependent variable, and can lead to determination of physical quantities.

- **Independent variable**: the variable that is changed to determine the effect on the dependent variable.
- **Dependent variable**: the variable that is measured to determine the effect of changing the independent variable.
- Drawing a graph with the independent variable on the *x*-axis and the dependent variable on the *y*-axis shows the relationship between the two variables.

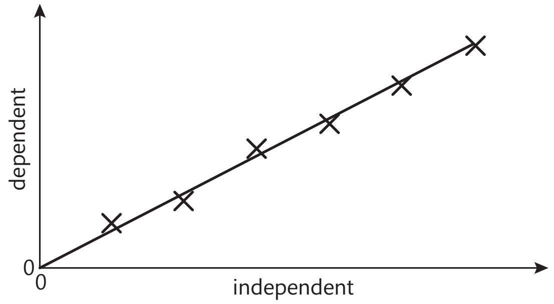


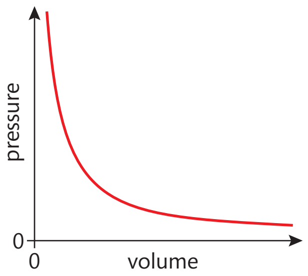
Figure 11.1 *A straight-line graph that passes through the origin shows that the dependent variable is proportional to the independent variable.*

Skill: Interpretation of graphs in terms of the relationships of dependent and independent variables.

The ideal gas equation $PV = nRT$ can be rearranged to $P = nRT\frac{1}{V}$

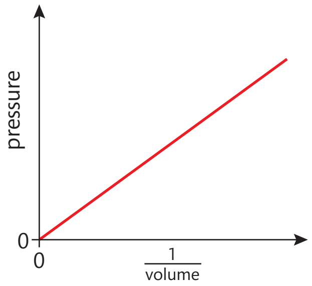
$$PV = nRT$$

Graphing pressure (P) against volume (V) shows that the two variables are inversely proportional.



$$P = nRT\frac{1}{V}$$

Plotting pressure (P) against $\frac{1}{\text{volume }(V)}$ produces a straight line with gradient = nRT.



Subject vocabulary

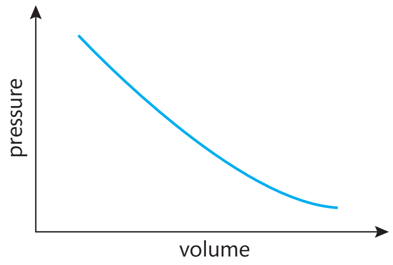
independent variable a variable (property) that can be changed or modified to see how it changes another variable

dependent variable the variable (property) that is measured to see how it is affected by changes in the independent variable

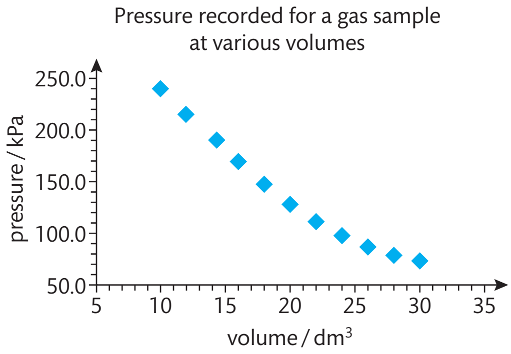
Understanding: Sketched graphs have labelled but unscaled axes, and are used to show qualitative trends, such as variables that are proportional or inversely proportional.

Understanding: Drawn graphs have labelled and scaled axes, and are used in quantitative measurements.

Sketched graphs



Drawn graphs



- Sketch does not have a title
- Axes have titles
- No scale on axes
- No units on axes
- Trend line or curve is shown
- Points are not plotted

- Graph has a title
- Axes have titles
- Axes are scaled
- Axis titles include units
- Points are plotted on the graph

Skill: Drawing graphs of experimental results including the correct choice of axes and scale.

Skill: Production and interpretation of best-fit lines or curves through data points, including an assessment of when it can and cannot be considered as a linear function.

Skill: Calculation of quantities from graphs by measuring slope (gradient) and intercept, including appropriate units.

The pressure of a sample of air was measured for various volumes at a constant room temperature (20.0 °C) using a gas syringe and a pressure sensor.

A graph of pressure against volume shows that pressure decreases as volume increases.

The relationship does not appear to be linear.

Volume/cm^3	Pressure/kPa	1/volume/cm^{-3}
10.0	0.26	0.10
9.0	0.25	0.11
8.0	0.29	0.13
7.0	0.35	0.14
6.0	0.44	0.17
5.0	0.48	0.20
4.0	0.63	0.25
3.0	0.83	0.33
2.0	1.19	0.50

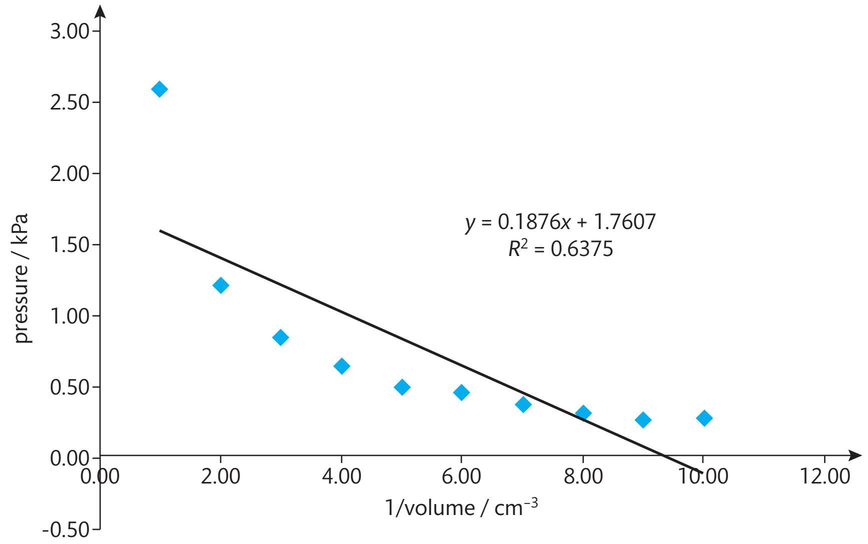


Figure 11.2 *Pressure measured for a sample of air at different volumes.*

A graph of pressure against $\left(\frac{1}{\text{volume}}\right)$ shows that pressure increases as $\left(\frac{1}{\text{volume}}\right)$ increases.

The relationship does appear to be linear.

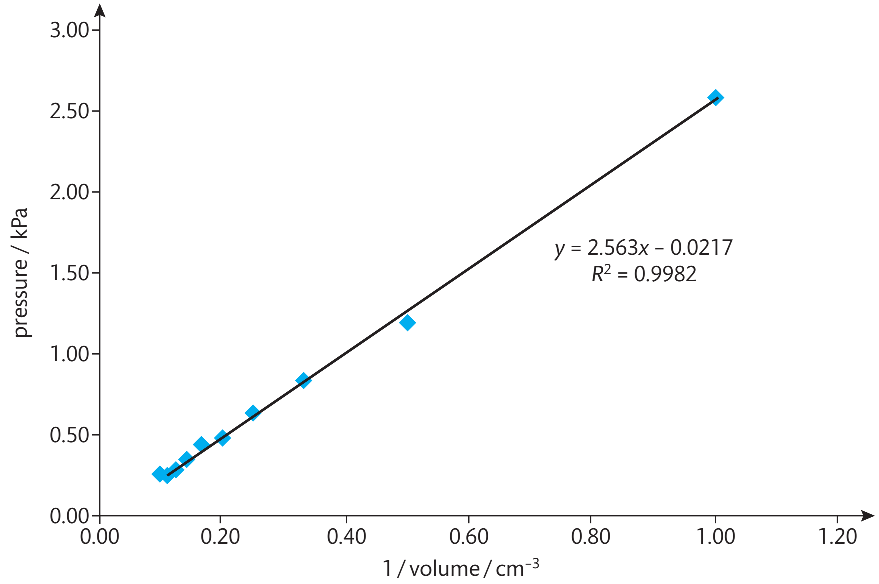


Figure 11.3 *Pressure plotted against* $\frac{1}{\textit{volume}}$ *for a sample of air at different volumes.*

The coefficient of determination (r^2 or R^2):

- can be calculated using a graphing calculator or appropriate software
- indicates if the relationship is linear.

1: perfectly linear

Value of R^2 $\uparrow$ **Relationship between variables**

0: no relationship

Using software analysis the value of R^2 was obtained for the two graphs.

Graph	**R^2 value**	**Relationship indicated by R^2**
Pressure against volume	0.6375	Moderate linear relationship
Pressure against $\left(\frac{1}{\text{volume}}\right)$	0.9982	Very strong linear relationship

The values of R^2 confirm that a linear relationship exists between pressure and $\left(\frac{1}{\text{volume}}\right)$.

The equation for the line of best fit for pressure against $\left(\frac{1}{\text{volume}}\right)$ was determined using software analysis and is shown on the graph:

$y = 2.563x - 0.0217$

The gradient and y intercept of the line can be determined from this equation (the equation of a line is $y = mx + c$, where m is the gradient and c is the y intercept):

- gradient for pressure against $\left(\frac{1}{\text{volume}}\right) = 2.563\ \text{kPa cm}^3$
- y intercept for pressure against $\left(\frac{1}{\text{volume}}\right) = -0.0217\ \text{kPa}$

Hints for success: The units for the gradient of a line = $\frac{\text{units of variable on } y\text{-axis}}{\text{units of variable on } x\text{-axis}}$

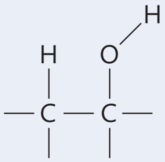
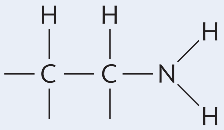
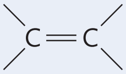
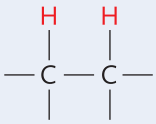
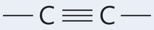
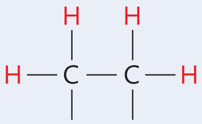
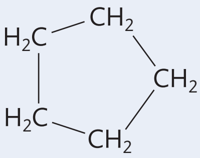
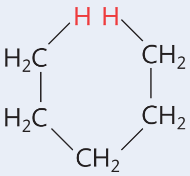
11.3 Spectroscopic identification of organic compounds

Essential idea:

Analytical techniques can be used to determine the structure of a compound, analyse the composition of a substance, or determine the purity of a compound. Spectroscopic techniques are used in the structural identification of organic and inorganic compounds.

Understanding: The degree of unsaturation or index of hydrogen deficiency (IHD) can be used to determine from a molecular formula the number of rings or multiple bonds in a molecule.

- The **index of hydrogen deficiency** (IHD):
  - measures the degree of **unsaturation** in an organic compound
  - shows how many H_2 molecules are needed to **saturate** the compound
  - provides clues to the structure of an unknown compound.

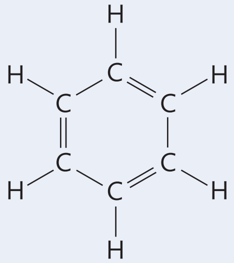
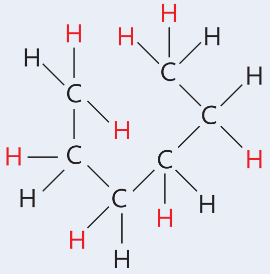
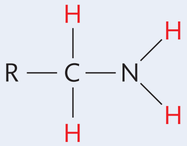
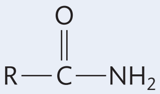
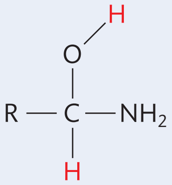
Saturated compounds			**IHD**
alkanes, alcohols, halogenoalkanes, amines, ethers	For example, 		0
Unsaturated compounds	**Structure**	**Structure if saturated**	**IHD**
alkene			1
alkyne			2
cycloalkanes (e.g. cyclopentane)			1

Subject vocabulary

index of hydrogen deficiency a measure of how many H_2 molecules have to be added to a compound to make it saturated and non-cyclic

unsaturation multiple bonds or rings

saturate create a non-cyclic compound that has only single bonds

Unsaturated compounds	**Structure**	**Structure if saturated**	**IHD**
arenes			4
nitriles	$R-C\equiv N$		2
aldehydes, ketones, carboxylic acids, amides	For example,  $R-\overset{\overset{\large O}{\|}}{C}-NH_2$		1

Skill: Determination of the IHD from a molecular formula.

Determine the IHD for the following compounds: C_3H_8O, C_3H_6O, $C_3H_4O_2$.

	C_3H_8O	C_3H_6O	$C_3H_6O_2$
Formula if saturated ($C_nH_{2n+2}X$)	C_3H_8O	C_3H_8O	$C_3H_8O_2$
IHD	0	1	1

Understanding: Mass spectrometry (MS), proton nuclear magnetic resonance (^1H NMR) spectroscopy, and infrared (IR) spectroscopy are techniques that can be used to help identify compounds and to determine their structure.

- **Mass spectrometry** is a technique that converts molecules into ions and then determines the mass of the ions.
- The **parent ion**, or **molecular ion** (M^+), is formed when the molecule (M) loses one electron:

  $M \rightarrow M^+ + e^-$

  If the molecular ion breaks into smaller ions then a **fragmentation pattern** is obtained. The mass spectrum will have a peak for every ion that has been formed, e.g. the mass spectrum of ethanol, C_2H_5OH, shows a fragmentation pattern as the $C_2H_5OH^+$ parent ion breaks into smaller ions.

Subject vocabulary

mass spectrometry a technique that determines the masses and abundances of different chemical species present in a sample

parent ion (also known as a molecular ion) the ion that is formed when a molecule loses a single electron

molecular ion (also known as a parent ion) the ion that is formed when a molecule loses a single electron

fragmentation pattern the pattern of peaks that are observed in the mass spectrum of a molecule that breaks up to form smaller ions (fragments)

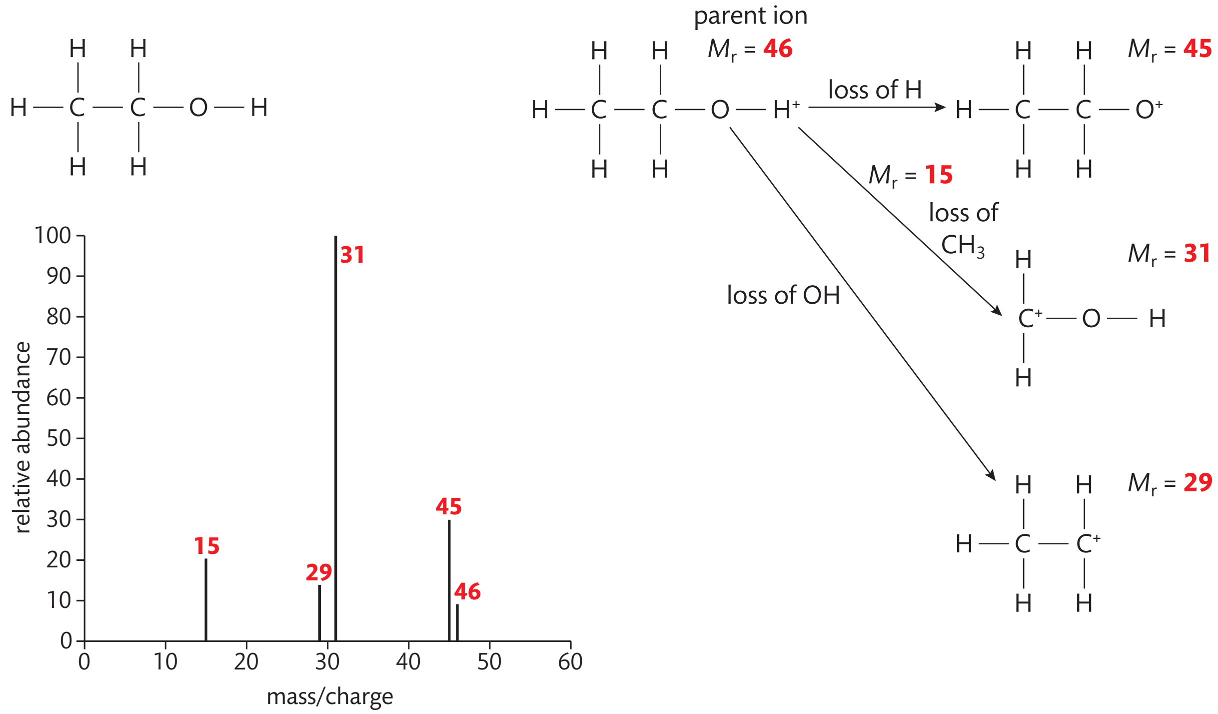


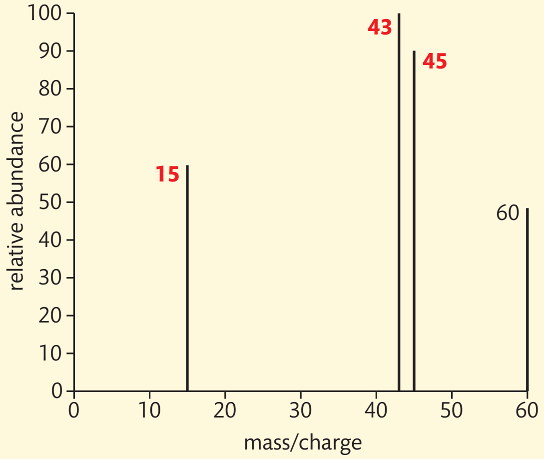
Figure 11.4 *The structure of ethanol and its mass spectrum. Possible fragmentation pattern produced when ethanol is bombarded with high-energy electrons.*

Hints for success: The masses of common fragment ions are given in section 28 of the IB data booklet.

Skill: Deduction of information about the structural features of a compound from MS.

Worked example

A molecule with an empirical formula CH_2O has the simplified mass spectrum below. Deduce the molecular formula and give a possible structure of the compound.



Solution

empirical formula = CH_2O; molecular formula = $C_nH_{2n}O_n$

We can see that the parent ion has a relative mass of 60.

$M_r = n(12.01) + 2n(1.01) + n(16.00) = 30.03n$

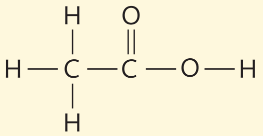
$$n = \frac{60}{30.03} = 2$$

molecular formula = $C_2H_4O_2$

From the spectrum we can identify the following peaks:

Peaks	Explanation
15 (60 – 45)	presence of CH_3^+ loss of COOH from molecule
43 (60 – 17)	presence of $C_2H_3O^+$ loss of OH from molecule
45 (60 – 15)	presence of $COOH^+$ loss of CH_3 from molecule

A structure consistent with this fragmentation pattern is:


$\mathrm{H{-}C(H)_2{-}C({=}O){-}O{-}H}$

- Different regions of the electromagnetic spectrum give different information about the structure of a molecule.

Region of electromagnetic spectrum	Technique	Physical changes and information obtained
Radio waves	NMR spectroscopy	Absorption of radio waves changes the **nuclear spin** of atoms The energy absorbed depends on the **chemical environment** of the atom
Infrared	IR spectroscopy	Absorption of IR radiation changes the **vibrational energy** of molecules The energy absorbed depends on the covalent bonds in the molecule

- The frequency of IR radiation is measured in **wavenumbers** (cm^{-1}):

$$\text{wavenumber } (cm^{-1}) = \frac{1}{\text{wavelength (cm)}}$$

Infrared spectroscopy is a technique that measures the frequencies of infrared radiation absorbed by covalent bonds in a molecule. The covalent bonds in the molecule can be identified by the frequencies of the absorption peaks in the IR spectrum, e.g. an absorption peak at 1600 cm^{-1} indicates that a C=O bond is in the molecule.

Hints for success: The absorption frequencies for common bonds are given in section 26 of the IB data booklet.

Subject vocabulary

nuclear spin a quantum mechanical property of a nucleus that can be modified by a magnetic field

chemical environment the environment of an atom in a molecule that is described by the number and identity of the neighbouring atoms

vibrational energy the kinetic energy associated with the vibrations (stretches and bends) in molecules

wavenumbers a unit of frequency; wavenumber = 1/cm = cm^{-1}

infrared spectroscopy a technique that measures the frequencies of infrared radiation absorbed by covalent bonds in a molecule

Skill: Deduction of information about the structural features of a compound from IR spectroscopy.

The IR spectra for two compounds, C_3H_6O and C_2H_6O, are given below. These spectra show how structural features (the covalent bonds present) can be identified from the absorptions in the spectra.

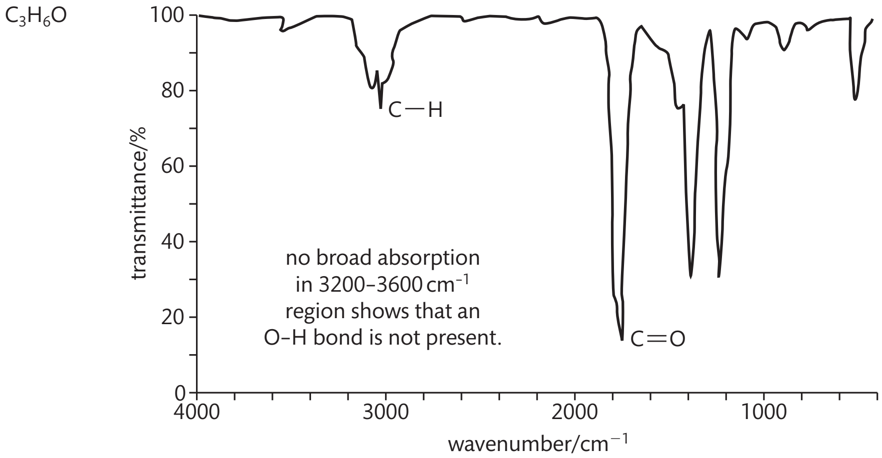


Figure 11.5 *The molecular structure and spectrum of propanone, a ketone.*

C_3H_6O could be a ketone or an aldehyde.

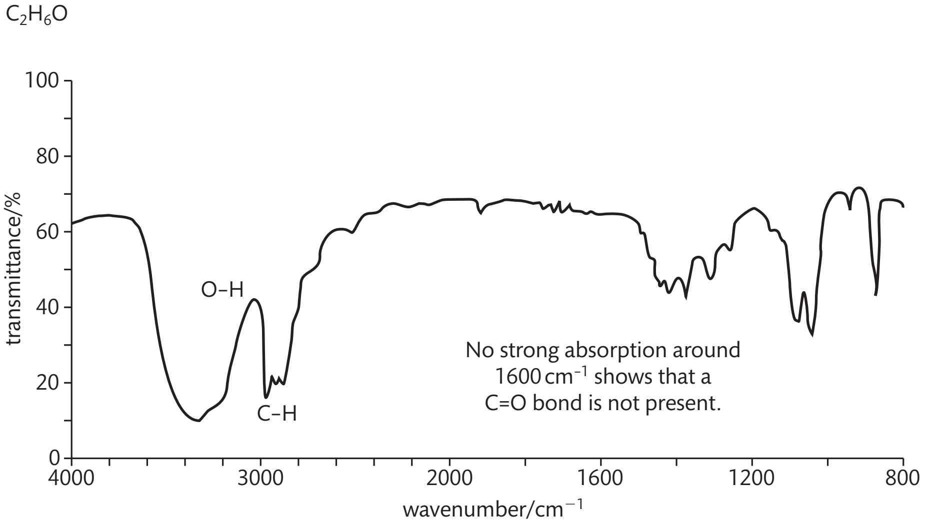


Figure 11.6 *The IR spectrum of ethanol.*

C_2H_6O is an alcohol.

Subject vocabulary

proton nuclear magnetic resonance spectroscopy a technique that measures the frequency of radio waves absorbed by hydrogen atoms in a molecule

chemical shift a unit of measurement in NMR spectroscopy that changes according to the chemical environment of the nuclei. It has units of parts per million (ppm)

integrated area the total area that is measured under a peak

- **Proton nuclear magnetic resonance spectroscopy** is a technique that measures the frequency of radio waves absorbed by hydrogen nuclei in a molecule. The frequencies that are absorbed provide information about the chemical environments of the hydrogen atoms in the molecule.

Important features of an ^{1}H NMR spectrum	
Number of peaks	The number of peaks is equal to the number of different *hydrogen* chemical environments
Chemical shifts	The **chemical shift**: - is the position of a peak in the ^{1}H NMR spectrum - has units of parts per million (ppm) - depends on the electronegativities of other atoms that are in the molecule (A large chemical shift occurs for hydrogen atoms close to highly electronegative atoms)
Integrated areas	The **integrated area** of a peak is proportional to the number of hydrogen atoms in the chemical environment

Hints for success: The chemical shifts for various hydrogen chemical environments are given in section 27 of the IB data booklet.

Skill: Deduction of information about the structural features of a compound from ^{1}H NMR spectroscopy.

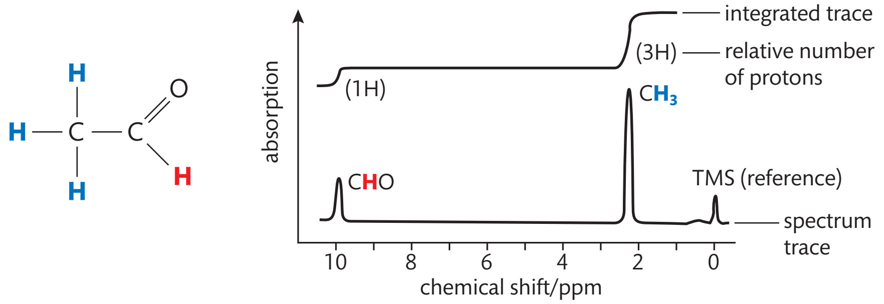
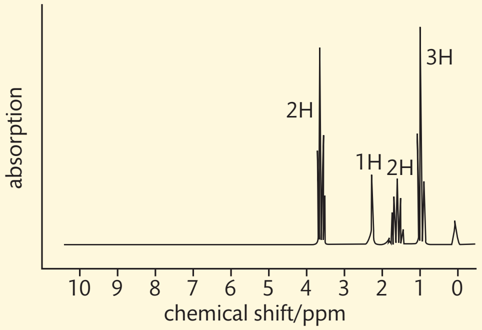


Figure 11.7 *The ^{1}H NMR spectrum of ethanal shows two peaks because the hydrogen atoms are in two different environments. The **integrated trace** indicates the relative number of hydrogen atoms in the two environments.*

Worked example

The NMR spectrum of a compound that has the molecular formula C_3H_8O is shown here.



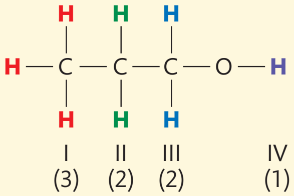
(a) Draw the full structural formulas and give the names of the three possible isomers of C_3H_8O.

(b) Identify the unknown compound from the number of peaks in the spectrum.

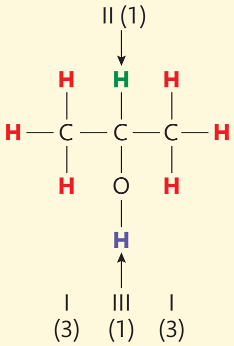
(c) Identify the group responsible for the signal at 0.9 ppm.

Solution

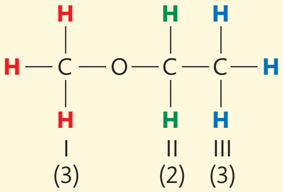
(a) The structures and names are:



propan-1-ol



propan-2-ol



methoxyethane

(b) For each structure, I–IV identifies the different environments of the H atoms in the molecule. 1–3 represents the number of atoms in each environment. There are four peaks in the spectrum. Propan-1-ol has four peaks with the correct areas.

(c) The peak at 0.9 ppm corresponds to the CH_3 group.

Topic 12: Atomic structure

12.1 Electrons in atoms

Subject vocabulary

quantized occurring with discrete or specific values; not continuous

transitions movement of an electron from one energy level to another

emission spectrum the frequencies of electromagnetic radiation observed when a high-energy species loses energy by emitting electromagnetic radiation

limit a final value

∞ the symbol for infinity

limit of convergence the final value that the emission frequencies converge to

ground state the lowest energy level of an atom or molecule

ionization energy the energy required to remove one mole of electrons from one mole of gaseous atoms in their lowest energy state

Essential idea:

The **quantized** nature of energy **transitions** is related to the energy states of electrons in atoms and molecules.

Understanding: In an **emission spectrum**, the limit of convergence at higher frequency corresponds to the first ionization energy.

- The energy levels in a hydrogen atom:
  - converge (get closer in energy) as the value of n increases.
  - reach a **limit** in energy when $n = \infty$.
- $n = \infty$ is the energy level:
  - where the electron is so far from the nucleus that it has been removed from the atom
  - where the hydrogen atom has been ionized: $H(g) \rightarrow H^+(g) + e^-$.
- The frequencies of emissions that occur from $n > 1 \rightarrow n = 1$:
  - get bigger as n increases, for example $n = 5 \rightarrow n = 1$ has a higher frequency than $n = 3 \rightarrow n = 1$
  - converge at higher frequency (because the energy levels are converging the frequency of the emissions between them must also converge)
  - reach a **limit of convergence**, which occurs for $n = \infty \rightarrow n = 1$ and is the emission with the highest frequency.

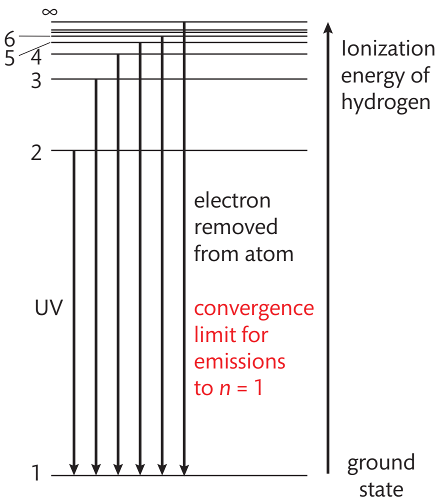


Figure 12.1 *The energy level diagram for the hydrogen atom.*

- The limit of convergence at $n = \infty \rightarrow n = 1$:
  - is from the energy level emission of an ionized hydrogen atom ($n = \infty$) to the lowest energy level (**ground state**) of a hydrogen atom
  - has the same energy as the **ionization energy** of hydrogen.
- The ionization energy of hydrogen:
  - is represented for a single hydrogen atom by $n = 1 \rightarrow n = \infty$ in Figure 12.1
  - is 2.18×10^{-18} J for a single hydrogen atom
  - is 1312 kJ mol^{-1} for one mole of hydrogen atoms.

  Because the ionization energy is very small for a single atom it is more practical to define ionization energy as the energy required to ionize one mole of atoms.

Skill: Solving problems using $E = h\nu$.

The energy of electromagnetic radiation, E:

- is related to its frequency, ν, by the equation $E = h\nu$
- is related to its wavelength, λ, by the equation $E = \frac{hc}{\lambda}$ (because $\nu = \frac{c}{\lambda}$)

Solving problems using these equations requires:

- energy, E, to have units of joules (J)
- frequency, ν, to have units of per second (s^{-1})
- wavelength, λ, to have units of metres (m).

Planck's constant, h, has units of joule seconds (J s).

Worked example

The frequency of the electromagnetic radiation emitted in the transition $n = 2 \rightarrow n = 1$ for the hydrogen atom is $24.66 \times 10^{14}\,s^{-1}$. What is the energy difference between the $n = 2$ and $n = 1$ energy levels of the hydrogen atom?

Solution

The energy difference between the $n = 2$ and $n = 1$ energy levels (ΔE) is equal to the energy of the electromagnetic radiation emitted:

$$\Delta E = E(\text{radiation}) = h\nu = 6.63 \times 10^{-34}\,\text{J s} \times 24.66 \times 10^{14}\,s^{-1} = 1.64 \times 10^{-18}\,\text{J}$$

The energy difference between the $n = 2$ and $n = 1$ energy levels is 1.64×10^{-18} J.

Skill: Calculation of the value of the first ionization energy from spectral data that give the wavelength or frequency of the convergence limit.

Worked example

The convergence limit for emissions from higher energy levels to the $n = 1$ level of the hydrogen atom occurs at a frequency of $3.29 \times 10^{15}\,s^{-1}$. Use this convergence limit to:

(i) determine the ionization energy of hydrogen in kJ mol^{-1}

(ii) determine the wavelength of electromagnetic radiation required to ionize a hydrogen atom.

Solution

(i) The convergence limit of $3.29 \times 10^{15}\,s^{-1}$:

- occurs for the transition $n = \infty \rightarrow n = 1$
- is related to the ionization energy of a hydrogen atom.

$$E = h\nu = 6.63 \times 10^{-34}\,\text{J s} \times 3.29 \times 10^{15}\,s^{-1} = 2.18 \times 10^{-18}\,\text{J}$$

This is the energy required to ionize a single hydrogen atom. However, ionization energy is the energy required to ionize *one mole* of atoms.

For one mole of atoms:

$$E = 2.18 \times 10^{-18}\,\text{J} \times 6.02 \times 10^{23}\,\text{mol}^{-1} = 1.31 \times 10^{6}\,\text{J mol}^{-1} = 1310\,\text{kJ mol}^{-1}\ (3\ \text{s.f.})$$

(ii) Frequency and wavelength are related by the equation $c = \nu\lambda$

$$\lambda = \frac{c}{\nu} = \frac{3.00 \times 10^{8}\,\text{m s}^{-1}}{3.29 \times 10^{15}\,s^{-1}} = 9.12 \times 10^{-8}\,\text{m}$$

Understanding: Trends in first ionization energy across periods account for the existence of main energy levels and sub-levels in atoms.

Subject vocabulary

first ionization energy the energy required to remove one mole of electrons from one mole of gaseous atoms in their lowest energy state

General vocabulary

evidence information that supports a theory or conclusion

discontinuities breaks or changes that occur in a trend

- The **first ionization energy** of any element is the energy required to remove one mole of electrons from one mole of atoms of that element in the gaseous state.
  $M(g) \rightarrow M^{+}(g) + e^{-}$
- A graph of first ionization energies of the elements:
  - shows repeating trends
  - provides **evidence** for the existence of energy levels and sub-levels in atoms.

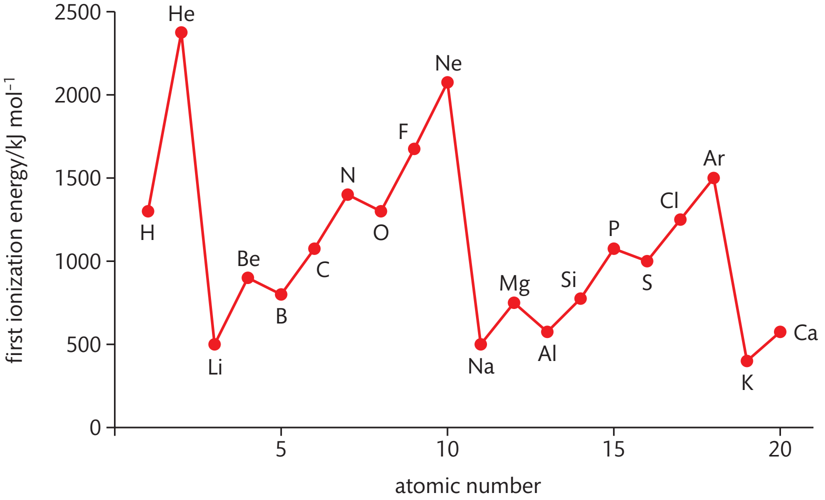


Figure 12.2 *The first ionization energies of the first 20 elements.*

Skill: Explanation of the trends and discontinuities in first ionization energy across a period.

In Figure 12.2:

- repeating trends provide evidence for energy levels
- repeating discontinuities provide evidence for sub-levels (s and p).

Evidence for energy levels	
Trend	**Explanation**
Ionization energy increases from: • hydrogen (Z = 1) to helium (Z = 2) • lithium (Z = 3) to neon (Z = 10) • sodium (Z = 11) to argon (Z = 18)	The ionization energy increases because each extra electron: • is added to the same energy level • experiences a greater effective nuclear charge • is harder to remove from the atom
Ionization energy decreases from: • helium (Z = 2) to lithium (Z = 3) • neon (Z = 10) to sodium (Z = 11) • argon (Z = 18) to potassium (Z = 19)	The ionization energy decreases because the extra electron: • is added to an energy level further from the nucleus • is shielded by electrons in inner energy levels • experiences a weaker effective nuclear charge • is easier to remove from the atom

Evidence for energy sub-levels (s and p sub-levels)	
Discontinuity	**Explanation**
Ionization energy decreases from: - beryllium ($1s^2\ 2s^2$) to boron ($1s^2\ 2s^2\ 2p^1$) - magnesium ($1s^2\ 2s^2\ 2p^6\ 3s^2$) to aluminium ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$)	The ionization energy decreases in both discontinuities because the extra electron is in a p orbital Electrons in p orbitals: - are shielded more than electrons in s orbitals - experience a weaker effective nuclear charge - are easier to remove from the atom
Ionization energy decreases from: - nitrogen ($1s^2\ 2s^2\ 2p^3$) to oxygen ($1s^2\ 2s^2\ 2p^4$) - phosphorus ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$) to sulfur ($1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$)	The ionization energy decreases in both discontinuities because the extra electron is in an occupied p orbital Electrons that are paired in p orbitals: - repel each other more - experience a weaker effective nuclear charge - are easier to remove from the atom

Understanding: **Successive** ionization energy data for an element give information that shows relations to electron configurations.

- When electrons are successively removed from an atom:
  - one electron is removed each time
  - the charge on the ion formed increases by one each time (the nth electron removed forms an n+ ion)
  - the energy required to remove the electron increases each time
  - the energy required to remove each electron depends on the electron configuration.

General vocabulary

successive following one after another

Ionization energy	Definition	Relevant equation
First ionization energy	The energy required to remove one mole of electrons from one mole of atoms in the gaseous state	$M(g) \rightarrow M^+(g) + e^-$
Second ionization energy	The energy required to remove one mole of electrons from one mole of 1+ ions in the gaseous state	$M^+(g) \rightarrow M^{2+}(g) + e^-$
Third ionization energy	The energy required to remove one mole of electrons from one mole of 2+ ions in the gaseous state	$M^{2+}(g) \rightarrow M^{3+}(g) + e^-$

- Similar definitions and equations are obtained for the fourth and higher ionization energies.

- When graphing the successive ionization energies of an element against the number of electrons removed the following trends are observed.

Trend	Explanation
The first ionization energy is the lowest	The electron being removed: ● is furthest from the nucleus ● experiences the greatest shielding ● is the easiest to remove
When electrons are removed from the *same energy level* there is a *gradual increase* in successive ionization energies	Removing electrons from the same energy level: ● reduces the repulsions between the electrons ● increases the effective nuclear charge ● makes it harder to remove successive electrons
When electrons are removed from an *energy level closer to the nucleus* there is a *large increase* between successive ionization energies	Electrons in an energy level closer to the nucleus: ● experience less shielding ● experience a greater effective nuclear charge ● are much harder to remove

These trends can be observed in Figure 12.3, which shows the successive ionization energies for aluminium.

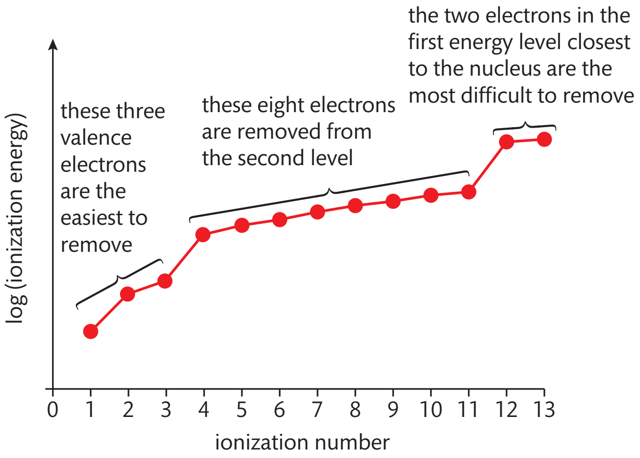


Figure 12.3 *Successive ionization energies for aluminium. Note the jumps between the 3rd and 4th and between the 11th and 12th ionization energies as electrons start to be removed from lower energy levels. The wide range in values is best presented on a log scale.*

Skill: Deduction of the group of an element from its successive ionization energy data.

Worked example

The graph of successive ionization energies against number of electrons removed is shown in Figure 12.4 for an unknown element. Not all ionization energies are shown but the element has $Z < 20$. Use this graph to determine the identity of the element.

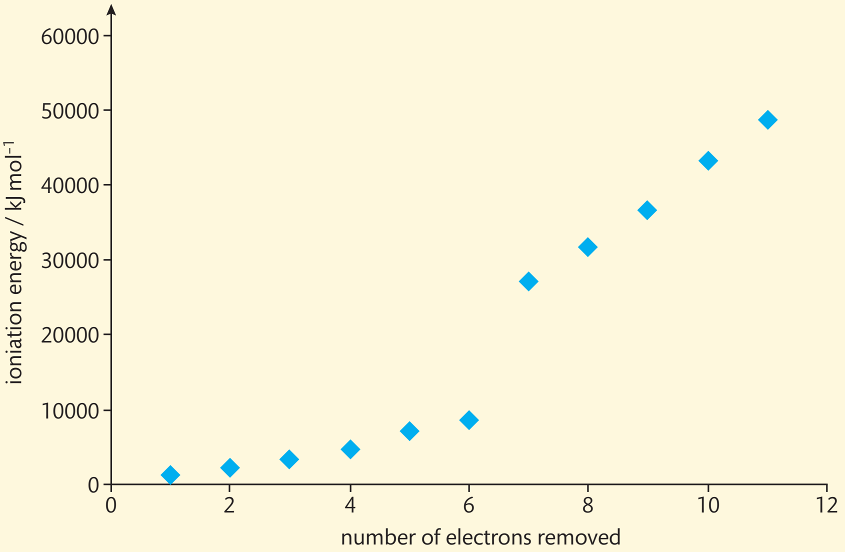


Figure 12.4 *The successive ionization energies of an unknown element.*

Solution

- A gradual increase in ionization energy occurs for the first six electrons removed. A large increase in ionization energy occurs for the seventh electron removed.
- This means the element has six electrons in its valence energy level and the seventh electron is removed from an energy level closer to the nucleus. The element must be from group 16.
- The unknown element cannot be oxygen. The graph shows that 11 electrons have been removed from the unknown element and oxygen only has eight electrons.
- The unknown element must be sulfur ($Z = 16$) as it is the only other group 16 element with $Z < 20$.

Topic 13: The periodic table: the transition metals

13.1 First-row d-block elements

Essential idea:

The transition elements have characteristic properties; these properties are related to their all having incomplete d sub-levels.

Subject vocabulary

oxidation state a measure of how many electrons an atom has gained or lost in forming a compound or ion

transition elements elements that have a partially filled d sub-level or can form ions with a partially filled d sub-level

ligands species that donate a lone pair of electrons to a transition metal ion and form a coordinate bond

complex ions ions that contain a transition metal bonded to ligands

Understanding: Transition elements have variable **oxidation states**, form complex ions with ligands, and display catalytic and magnetic properties.

- The **transition elements**:
  - are found in the d-block of the periodic table
  - are defined as elements that have partially filled d sub-levels or form ions with partially filled d sub-levels
  - can have more than one oxidation state
  - can covalently bond with **ligands** to form **complex ions**
  - are often used as catalysts (have catalytic properties)
  - show magnetism when placed in a magnetic field (have magnetic properties).

Understanding: Transition elements show an oxidation state of +2 when the s electrons are removed.

- The first-row transition elements (Sc → Zn):
  - can lose the 4s and 3d electrons when forming ions because the 4s and 3d are the two highest energy sub-levels and they have similar energies
  - can lose both 4s electrons to give the +2 oxidation state because the 4s energy sub-level is lower than the 3d sub-level for transition element ions
  - can lose 3d electrons to give higher oxidation states.

Oxidation states for first-row transition elements. States marked in blue are more common than those in black.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								+1	
+2	+2	+2	+2	+2	+2	+2	+2	+2	+2
+3	+3	+3	+3	+3	+3	+3	+3	+3	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5	+5	+5			
			+6	+6	+6				
				+7					

Skill: Explanation of the ability of transition metals to form variable oxidation states from successive ionization energies.

The common oxidation states of a transition element are related to its ionization energies.

For example, titanium ([Ar] $3d^2$ $4s^2$):

Electron removed	Ionization energy / kJ mol^{-1}	Electrons that are removed	Oxidation state formed
First	659	One 4s electron	+1
Second	1310	Two 4s electrons	+2
Third	2653	Two 4s electrons, one 3d electron	+3
Fourth	4175	Two 4s electrons, two 3d electrons	+4
Fifth	9581	Two 4s electrons, two 3d electrons, one 3p electron	+5

The +1 oxidation state of titanium is not common because:

- the second ionization energy of titanium is low
- it is easy for titanium in the +1 oxidation state to lose the second 4s electron and form the +2 oxidation state.

The +5 oxidation state of titanium is not common because:

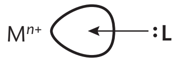
- the fifth ionization energy of titanium is very high because the fifth electron must be taken from a 3p subshell that is closer to the nucleus
- it is hard to remove the fifth electron and form the +5 oxidation state.

The common oxidation states of titanium are +2, +3, and +4.

Skill: Explanation of the nature of the coordinate bond within a complex ion.

Transition element ions:

- have empty d orbitals
- can act as Lewis bases and accept an electron pair from a ligand, which acts as a Lewis acid



M^{n+} = transition element ion; L = ligand

- form coordinate bonds (dative bonds) with ligands because the ligand donates both of the electrons that form the covalent bond
- form complex ions when they bond with one or more ligands.

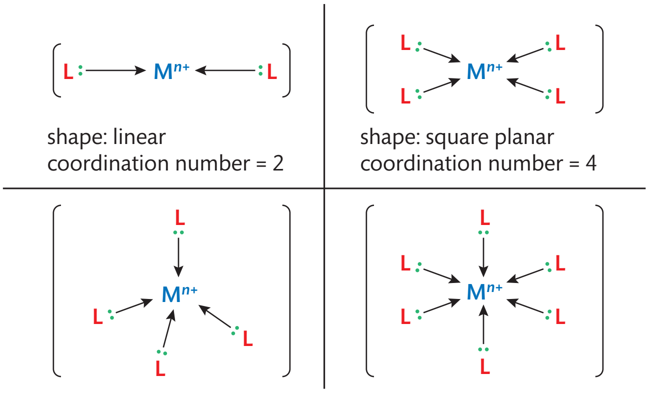
The **coordination number** of a complex ion is the number of ligands that are bonded to the transition element ion.

Different coordination numbers can give different shapes for the complex ions.

Subject vocabulary

coordinate bond (also known as a dative bond) a covalent bond in which one atom donates both of the electrons that are shared in the bond

coordination number the number of ligands that are bonded to the central transition metal in a complex ion



shape: linear
coordination number = 2

shape: square planar
coordination number = 4

shape: tetrahedral
coordination number = 4

shape: octahedral
coordination number = 6

Figure 13.1 *Shapes and coordination numbers of some complex ions.*

The chemical formulas of complex ions:

- are written inside square brackets
- have the transition element written first
- include all the ligands bonded to the central transition element ion.

Examples: $[Fe(OH_2)_6]^{2+}$, $[Cr(NH_3)_4Cl_2]^{3+}$, $[CuCl_4]^{2-}$

Skill: Deduction of the total charge [of a complex ion] given the formula of the ion and ligands present.

Ligands can be negatively charged ions or neutral species.

Hints for success: Common ligands and their charges are given in section 15 of the IB data booklet.

The total charge on a complex ion will depend on:

(i) the charge on the transition metal ion

(ii) the charge on the ligand(s)

(iii) the number of charged ligands bonded to the transition metal ion.

Worked example

Determine the formula and charge of the complex ion formed when a chromium(III) ion bonds to four water ligands and two chloride ligands.

Solution

(i) The chromium(III) ion has a charge of 3+.

(ii) From section 15 in the IB data booklet, H_2O is a neutral ligand and Cl^- has a charge of 1–.

(iii) There are two chloride ligands with a charge of 1–.

The total charge on the complex ion = 3+ + 2 × 1– = 1+

The formula of the complex is $[Cr(OH_2)_4Cl_2]^+$.

Skill: Explanation of the magnetic properties of transition metals in terms of unpaired electrons.

When placed in an external magnetic field compounds can show different magnetic properties known as **diamagnetism** and **paramagnetism**.

Diamaganetism occurs:

- when the applied magnetic field **induces** a weak magnetic field in the compound that is opposite in direction to the applied field
- for all transition metals and transition metal ions.

Paramagnetism occurs:

- when the applied magnetic field induces a magnetic field in the compound that is in the same direction as the applied field
- for transition metals and transition metal ions that have unpaired electrons.

Paramagnetism is stronger than diamagnetism so transition metals and transition metal ions with unpaired electrons will be paramagnetic.

Subject vocabulary

diamagnetism a magnetic property of substances that generate a magnetic field that is opposed to an applied magnetic field

paramagnetism a magnetic property of substances that generate a magnetic field that is aligned with an applied magnetic field

General vocabulary

induces causes to happen

Understanding: Zn is not considered to be a transition element as it does not form ions with incomplete d orbitals.

- Transition elements are defined as elements that have incomplete (partially filled) d sub-levels or can form ions that have incomplete d sub-levels.
- Zinc:
    - has the electron configuration [Kr] $3d^{10}$ $4s^{2}$
    - only forms the Zn^{2+} ion, which has the electron configuration [Kr] $3d^{10}$
    - is not a transition element because it has a complete d sub-level both when it is Zn metal and when it is the Zn^{2+} ion.

Essential idea:

All d orbitals have the same energy in an isolated atom, but they split into two sub-levels in a complex ion. The electric field of ligands may cause the d orbitals in complex ions to split so that the energy of an electron transition between them corresponds to a photon of visible light.

Understanding: The d sub-level splits into two sets of orbitals of different energy in a complex ion.

- A free transition metal ion, M^{n+}:
  - is not bonded to any ligands
  - has d orbitals that all have the same energy.
- In an octahedral complex ion, $[ML_6]^{n+}$:
  - the six ligands are bonded along the *x*-, *y*-, and *z*-axes
  - the electrons in the two d orbitals that are **aligned** on the *x*-, *y*-, and *z*-axes are repelled more by the lone pairs of electrons on the ligands
  - the energies of the two d orbitals aligned on the *x*-, *y*-, and *z*-axes increase
  - the energies of the three d orbitals not aligned on the *x*-, *y*-, and *z*-axes decrease
  - the d orbitals are split into two sets that have different energies.

Synonym

aligned .... lined up

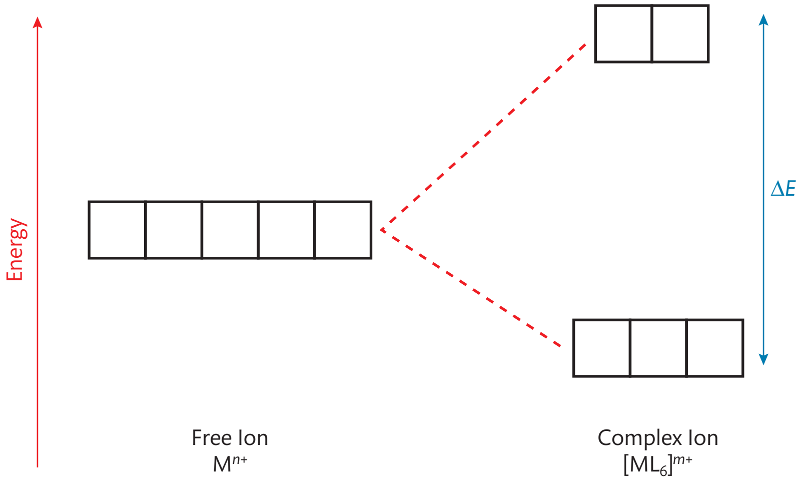


Figure 13.2 *The splitting of the energies of d orbitals in an octahedral complex.*

Understanding: Complexes of d-block elements are coloured, as light is absorbed when an electron is excited between the d orbitals.

Understanding: The colour absorbed is complementary to the colour observed.

- The **splitting energy** (ΔE):
  - is the energy difference between the two sets of d orbitals in a complex ion (see Figure 13.2)

Subject vocabulary

splitting energy the energy gap between the two sets of d orbitals in a transition element complex

  - is equal to the energy of electromagnetic radiation in the visible region of the electromagnetic spectrum.
- When a complex ion absorbs visible light:
  - an electron is promoted from the low-energy set of d orbitals to the high-energy set of d orbitals
  - the complex moves from the ground state to an excited state
  - it appears coloured because visible (coloured) light is absorbed
  - the colour that is observed depends on the size of the splitting energy and the frequency of the visible light that is absorbed
  - the colour that is observed is the **complementary colour** of the light that is absorbed.
- A colour wheel shows the relationship between the colour that is observed for a complex ion and the colour of light that is absorbed by the complex ion. The colour that is observed is on the opposite side of the wheel from the colour that is absorbed.

Hints for success: Section 17 in the IB data booklet provides a simple colour wheel that relates complementary colours.

Subject vocabulary

complementary colours colours that are opposite each other in the colour spectrum

Figure 13.3 *The colour wheel. There is a colour wheel in section 17 of the IB data booklet.*

- For example, the complex ion $[Ti(OH_2)_6]^{3+}$ is violet in colour because it absorbs green light.

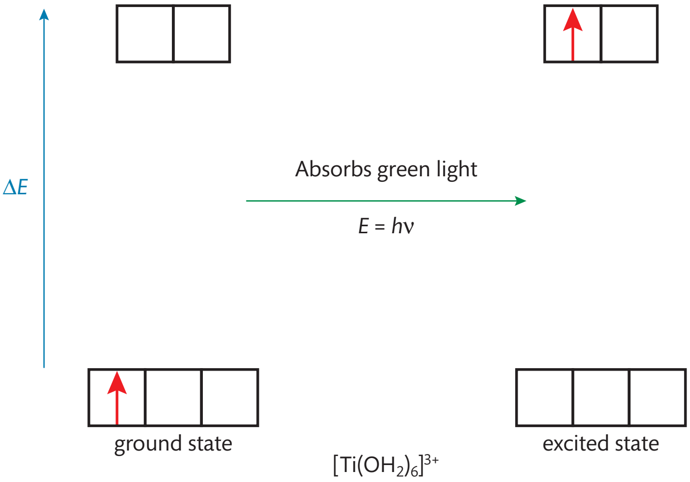


Figure 13.4 *When $[Ti(OH_2)_6]^{2+}$ absorbs green light the d electron moves from a low-energy d orbital (ground state) to a high-energy d orbital (excited state).*

Skill: Explanation of the effect of the identity of the metal ion, the oxidation number of the metal, and the identity of the ligand on the colour of transition metal ion complexes.

- The colour of light that is observed for any complex ion depends on the size of the splitting energy (ΔE) between the two sets of d orbitals in the complex.
- The size of the splitting energy depends on the strength of the attraction between the transition metal ion and the ligands. The greater the attraction:
  - the shorter the metal ion–ligand bond
  - the greater the repulsion between d electrons on the metal and the lone pairs of electrons on the ligands
  - the larger the splitting energy.

- The attraction between the metal ion and the ligands depends on:
    - the identity and nuclear charge of the transition metal ion
    - the oxidation state of the transition metal ion
    - the identity of the ligand and where it appears on the **spectrochemical series**.

Subject vocabulary

spectrochemical series a list of ligands that orders them according to the size of the splitting energy they produce when bonding to transition elements

Factor	Examples	Effect on splitting energy (ΔE)
Identity and nuclear charge of the transition metal ion	$[Cr(OH_2)_6]^{3+}$ $[Fe(OH_2)_6]^{3+}$	The Fe^{3+} ion ($Z = 26$) has a greater nuclear charge than the Cr^{3+} ion ($Z = 24$) Fe^{3+} exerts a greater attraction on the ligands and causes a bigger splitting energy $[Fe(OH_2)_6]^{3+}$ absorbs higher energy purple light and appears yellow-brown $[Cr(OH_2)_6]^{3+}$ absorbs lower energy red light and appears green
Oxidation state of the transition metal ion	$[Fe(OH_2)_6]^{2+}$ $[Fe(OH_2)_6]^{3+}$	Fe^{3+} has a greater charge than Fe^{2+} Fe^{3+} exerts a greater attraction on the ligands and causes a bigger splitting energy $[Fe(OH_2)_6]^{3+}$ absorbs higher energy purple light and appears yellow-brown $[Fe(OH_2)_6]^{2+}$ absorbs lower energy red light and appears pale green
Identity of the ligand and its position on the spectrochemical series	$[CrF_6]^{3-}$ $[Cr(NH_3)_6]^{3+}$	NH_3 is higher on the spectrochemical series for ligands than F^- NH_3 is more strongly attracted to the Cr^{3+} ion and causes a bigger splitting energy $[Cr(NH_3)_6]^{3+}$ absorbs higher energy purple light and appears yellow $[CrF_6]^{3-}$ absorbs lower energy green light and appears pink

Skill: Explanation of the effect of the identity of different ligands on the splitting of the d orbitals in transition metal complexes and colour observed using the spectrochemical series.

The spectrochemical series lists ligands in order of the splitting energies they generate when bonded to the same transition element ion. Section 15 in the IB data booklet gives the spectrochemical series for some common ligands:

$I^- < Br^- < S^{2-} < Cl^- < F^- < OH^- < H_2O < SCN^- < NH_3 < CN^- \approx CO$

Worked example

When aqueous ammonia (NH_3) is added to a solution of $[Cu(OH_2)_6]^{2+}$ a new complex ion is formed, $[Cu(NH_3)_4(OH_2)_2]^{2+}$, and the colour changes from pale blue-green to dark blue.

Explain the colour change that is observed using the spectrochemical series.

Solution

$[Cu(NH_3)_4(OH_2)_2]^{2+}$ has a bigger splitting energy than $[Cu(OH_2)_6]^{2+}$ because ammonia is higher on the spectrochemical series than water.

Because the splitting energy is bigger for $[Cu(NH_3)_4(OH_2)_2]^{2+}$ it will absorb visible light that is higher in energy than the visible light absorbed by $[Cu(OH_2)_6]^{2+}$.

The complementary colour observed for $[Cu(NH_3)_4(OH_2)_2]^{2+}$ will be different from the complementary colour observed for $[Cu(OH_2)_6]^{2+}$.

$[Cu(NH_3)_4(OH_2)_2]^{2+}$ is dark blue in colour because it absorbs higher energy yellow light.

$[Cu(OH_2)_6]^{2+}$ is pale blue-green in colour because it absorbs lower energy orange-red light.

Topic 14: Chemical bonding and structure

14.1 Further aspects of covalent bonding and structure

Essential idea:

Larger structures and more in-depth explanations of bonding systems often require more sophisticated concepts and theories of bonding.

Understanding: Covalent bonds result from the overlap of atomic orbitals. A sigma (σ) bond is formed by the direct head-on/end-to-end overlap of atomic orbitals, resulting in electron density concentrated between the nuclei of the bonding atoms. A pi (π) bond is formed by the sideways overlap of atomic orbitals, resulting in electron density above and below the plane of the nuclei of the bonding atoms.

- In topic 4 a simple model of covalent bonding was introduced. In that model a covalent bond was regarded as the sharing of a pair of electrons between two atoms.
- Covalent bonding can also be explained using a more **in-depth** model involving the linear combination of atomic orbitals. In this model a covalent bond:
  - is formed from the overlap of atomic orbitals on two atoms
  - involves a pair of electrons that move through both overlapping orbitals and are attracted to the nuclei of both atoms.
- There are two different types of covalent bonds: **sigma (σ) bonds** and **pi (π) bonds**.

Synonym

in-depth .... covered in more detail or involving a higher level of understanding

Subject vocabulary

sigma (σ) bonds covalent bonds formed by head-on overlap of atomic orbitals

pi (π) bonds covalent bonds formed by side-on overlap of atomic orbitals

Skill: Prediction of whether sigma (σ) or pi (π) bonds are formed from the linear combination of atomic orbitals.

Sigma bonds are formed from the *head-on overlap* of atomic orbitals. These orbitals can be:

- two s orbitals
- two p orbitals
- an s orbital on one atom and a p orbital on the other atom.

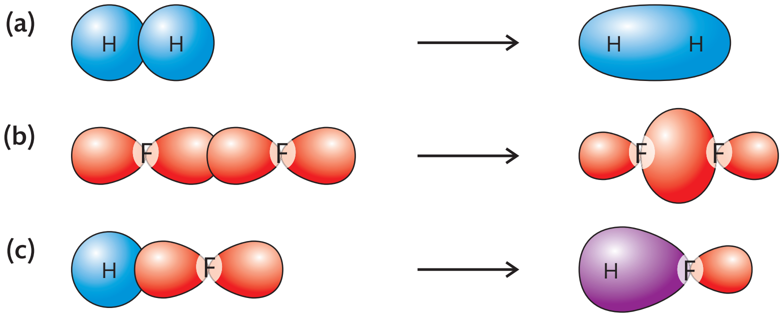


Figure 14.1 *Formation of sigma bond by overlap of* **(a)** *s orbitals, e.g.* $H + H \rightarrow H_2$*,* **(b)** *p orbitals end-on, e.g.* $F + F \rightarrow F_2$ *and* **(c)** *s and p orbitals, e.g.* $H + F \rightarrow HF$*. The symbol for the element denotes the position of the nucleus. In all cases, the electron density is greatest along the bond axis.*

Later in the chapter we will see that sigma bonds are also formed from the head-on overlap of hybrid orbitals.

In a sigma bond the **electron density** is found along the **inter-nuclear axis**.

Pi bonds are formed from the sideways overlap of p orbitals. In a pi bond the electrons in the bond are found above and below the inter-nuclear axis.

Subject vocabulary

electron density a measure of how likely it is to find an electron at a particular location

inter-nuclear axis a line joining the centres of two nuclei

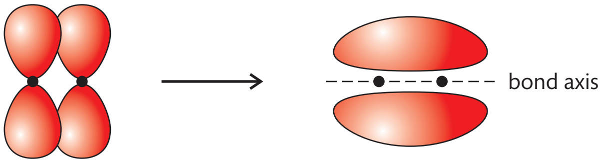


Figure 14.2 *Formation of pi bond by sideways overlap of p orbitals. The electron density is greatest in two regions above and below the bond axis.*

In a double bond one bond is a sigma bond and the other is a pi bond.

In a triple bond one bond is a sigma bond and the other two are pi bonds.

Understanding: Formal charge (FC) can be used to decide which Lewis (electron dot) structure is preferred from several. The FC is the charge an atom would have if all atoms in the molecule had the same electronegativity. FC = (number of valence electrons) – $\frac{1}{2}$(number of bonding electrons) – (number of non-bonding electrons). The Lewis (electron dot) structure with the atoms having FC values closest to zero is preferred.

- Formal charge (FC):
  - is a measure of whether an atom has gained or lost electrons in forming covalent bonds
  - is the number of valence electrons on the unbonded atom (V) – (half the number of bonding electrons (B) on the bonded atom in the molecule + the number of non-bonding electrons (L) on the bonded atom in the molecule):

    $FC = V - (\frac{1}{2}B + L)$
  - allows the best Lewis structure to be determined for a molecule when there is more than one possible Lewis structure.

Hints for success: The sum of the formal charges on all the atoms in a Lewis structure must equal the overall charge on the Lewis structure.

Skill: Application of FC to ascertain which Lewis (electron dot) structure is preferred from different Lewis (electron dot) structures.

To determine the **preferred** (best) Lewis structure for a molecule or molecular ion:

Step 1: Calculate the formal charges for every atom in each Lewis structure.

Step 2: Identify the structure that has the smallest formal charges. This is the preferred structure.

If there is more than one preferred structure after Step 2:

Step 3: Identify the structure that has the most negative formal charge on the most electronegative atom. This is the preferred structure.

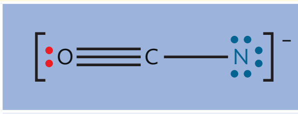
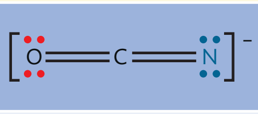
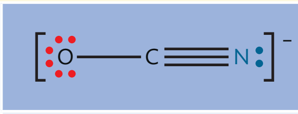
General vocabulary

preferred best or most desirable

Worked example

Three possible Lewis structures for the cyanate ion (OCN^-) are shown. Determine which Lewis structure is the best by determining the formal charges of the atoms in each structure.

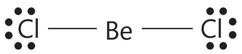
Solution

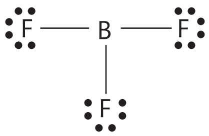
			
Step 1	$FC(O) = 6 - (\frac{1}{2}(6) + 2) = +1$ $FC(C) = 4 - \frac{1}{2}(8) = 0$ $FC(N) = 5 - (\frac{1}{2}(2) + 6) = -2$	$FC(O) = 6 - (\frac{1}{2}(4) + 4) = 0$ $FC(C) = 4 - \frac{1}{2}(8) = 0$ $FC(N) = 5 - (\frac{1}{2}(4) + 4) = -1$	$FC(O) = 6 - (\frac{1}{2}(2) + 6) = -1$ $FC(C) = 4 - \frac{1}{2}(8) = 0$ $FC(N) = 5 - (\frac{1}{2}(6) + 2) = 0$
Step 2	Large FC of −2 on N *Not the best structure*	Small FCs of 0 and −1 *Equal best structure*	Small FCs of 0 and −1 *Equal best structure*
Step 3		FC of −1 is on less electronegative N *Not the best structure*	FC of −1 is on more electronegative O *The best structure*

Understanding: Exceptions to the octet rule include some species having incomplete octets and expanded octets.

- **Incomplete octets**:
  - occur when an atom has *fewer than* eight electrons in its valence shell
  - can happen for small atoms such as beryllium and boron.

    $BeCl_2$ and BF_3 have incomplete octets:





- **Expanded octets**:
  - occur when an atom has *more than* eight electrons in its valence shell
  - can happen for atoms that have empty d orbitals and are able to accept electron pairs from other atoms
  - can happen for atoms that are in the third or higher periods.
- To draw Lewis structures for compounds with expanded octets:
  - follow the rules provided on page 48 until Step 4
  - change Step 5 to:

    If extra electrons are required they are added as pairs *to the central atom*.

Subject vocabulary

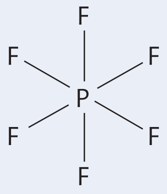
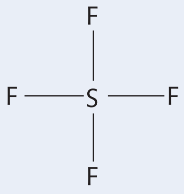
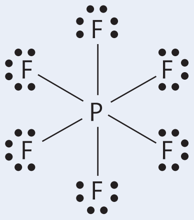
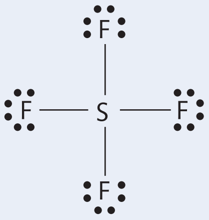
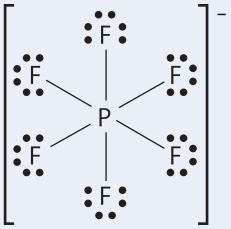
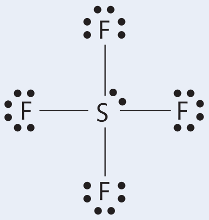
incomplete octets happen when the valence shells of atoms have fewer than eight electrons

expanded octets happen when the valence shells of atoms have more than eight electrons

Worked example

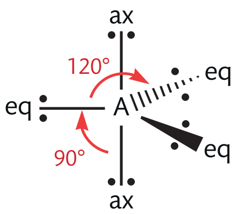
Deduce the Lewis (electron dot) structures for PF_{6}^{-} and SF_4.

Following the steps in the flow chart on page 48 (modified at Step 5):

	PF_6^-	SF_4
Step 1: Total valence electrons	5 + (6 × 7) + 1 = 48	6 + (4 × 7) = 34
Steps 2 and 3: Skeletal structure with bonds shown as lines		
Step 4: Complete octets around each atom		
Step 5: Add extra pairs to central atom if required (add brackets and charge to structures of charged species)		

Skill: Deduction using VSEPR theory of the electron domain geometry and molecular geometry with five and six electron domains and associated bond angles.

- VSEPR theory can also be applied to Lewis structures with five and six electron domains around the central atom.
- Five electron domains:
  - repel each other to give a *trigonal bipyramidal* electron domain geometry
  - have two electron domains in **axial positions** (ax) at 180° to each other
  - have three electron domains in the **equatorial plane** (eq) at 120° to each other
  - have a 90° angle between the axial and equatorial electron domains.

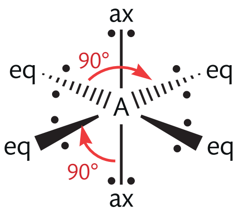


- Six electron domains:
  - repel each other to give an *octahedral* electron domain geometry
  - have two electron domains in axial positions (ax) at 180° to each other
  - have four electron domains in the equatorial plane (eq) at 90° to each other
  - have a 90° angle between all electron domains.

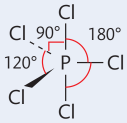
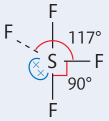
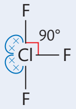
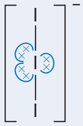
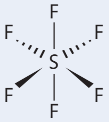
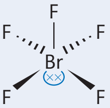
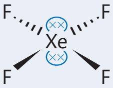
Subject vocabulary

axial positions atoms that are bonded to the central atom and are positioned along the vertical axis of a molecule are in the axial positions

equatorial plane the plane that is at 90 degrees to the vertical axis of a molecule is the equatorial plane



- The molecular geometry for a compound with expanded octets:
  - depends on the electron domain geometry
  - depends on the number of bonded and unbonded electron domains.

Electron domain geometry	Number of electron domains	Number of bonded domains	Number of unbonded domains	Molecular geometry	Example
trigonal bipyramidal	5	5	0	trigonal bipyramidal	
		4	1	see-saw (unsymmetrical tetrahedron)	
		3	2	T-shaped	
		2	3	linear	
octahedral	6	6	0	octahedral	
		5	1	square pyramidal	
		4	2	square planar	

Understanding: Delocalization involves electrons that are shared by/between more than one pair in a molecule or ion as opposed to being localized between a pair of atoms.

Understanding: Resonance involves using two or more Lewis (electron dot) structures to represent a particular molecule or ion. A resonance structure is one of two or more alternative Lewis (electron dot) structures for a molecule or ion that cannot be described fully with one Lewis (electron dot) structure alone.

- **Resonance** occurs when a molecule has two or more Lewis structures; for example ozone (O_3) has two possible Lewis structures:

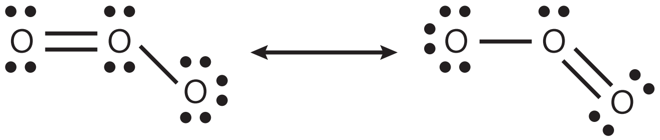


Figure 14.3 *Resonance structures of ozone (O_3).*

A double-headed arrow is drawn between the two structures to show that resonance is happening.

- Experimental evidence shows that the O–O bonds in ozone (O_3):
  - are the same length
  - are longer than a double bond
  - are shorter than a single bond.
- This experimental evidence shows that the pi bond (and the pair of pi electrons in the bond):
  - is not localized between one pair of atoms
  - is shared equally between the two possible bonding positions
  - is **delocalized**.
- The true structure that results from the delocalization of the pi electrons is known as a **resonance hybrid**.

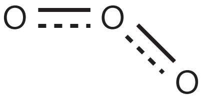


Figure 14.4 *In a resonance hybrid the dashed lines represent delocalized pi electrons.*

- **Bond order**:
  - is a measure of the strength of a bond
  - is equal to the number of bonding pairs between two atoms:
    - a single bond has a bond order of 1
    - a double bond has a bond order of 2
    - a triple bond has a bond order of 3.
- The higher the bond order between two atoms:
  - the stronger the bond
  - the shorter the bond:

    e.g. a C=C bond has a bond order of 2 and a C≡C bond has a bond order of 3. The C≡C bond is stronger and shorter than the C=C bond.
- The bonds in oxygen (O_2):
  - have a higher order than the bonds in ozone (O_3)
  - are stronger than the bonds in ozone (O_3)
  - are harder to **dissociate** (break) than the bonds in ozone (O_3)
  - need UV light of a higher energy (shorter wavelength) to break them than the bonds in ozone (O_3).

Subject vocabulary

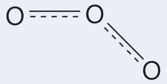
resonance when a molecule has more than one Lewis structure

delocalized not held in one position

resonance hybrid the true structure that results from resonance and the delocalization of pi electrons

bond order the number of bonding pairs of electrons between two atoms

dissociate to break bonds and separate atoms in a molecule

	Oxygen	Ozone
	O=O	
Bond order	2	1.5
Bond enthalpy	498 kJ mol^{-1}	364 kJ mol^{-1}
Bond strength of one bond	$\frac{498 \times 10^3\,\text{J mol}^{-1}}{6.02 \times 10^{23}\,\text{mol}^{-1}} = 8.27 \times 10^{-19}\,\text{J}$	$\frac{364 \times 10^3\,\text{J mol}^{-1}}{6.02 \times 10^{23}\,\text{mol}^{-1}} = 6.05 \times 10^{-19}\,\text{J}$
Wavelength of light needed to break the bond	$\lambda = \frac{hc}{E}$ $= \frac{6.63 \times 10^{-34}\,\text{J s} \times 3.00 \times 10^8\,\text{m s}^{-1}}{8.27 \times 10^{-19}\,\text{J}}$ $= 2.42 \times 10^{-7}\,\text{m}$ $= 242\,\text{nm}$	$\lambda = \frac{hc}{E}$ $= \frac{6.63 \times 10^{-34}\,\text{J s} \times 3.00 \times 10^8\,\text{m s}^{-1}}{6.05 \times 10^{-19}\,\text{J}}$ $= 3.30 \times 10^{-7}\,\text{m}$ $= 330\,\text{nm}$

Skill: Description of the mechanism of the catalysis of ozone depletion when catalysed by CFCs and NO_x.

- Ozone (O_3):
  - is a very important component of the atmosphere
  - has been **depleted** in the atmosphere by chemicals released because of human activities.

  The depletion of ozone has serious health **consequences** as harmful UV wavelengths that would normally be absorbed by ozone are able to reach the Earth's surface.
- Nitrogen monoxide (NO):
  - is formed when nitrogen (N_2) reacts with oxygen (O_2) in car engines because of the high temperatures:

    $N_2(g) + O_2(g) \rightarrow 2NO(g)$
  - is a **free radical** (contains an unpaired electron)
  - is very reactive.

Hints for success: A dot is added to the chemical formula of a free radical to signify an unpaired electron, e.g. nitrogen monoxide is written as NO•.

- Nitrogen monoxide reacts with ozone in a two-step mechanism:

  Step 1: $\cancel{NO\bullet(g)} + O_3(g) \rightarrow \cancel{NO_2(g)} + O_2(g)$

  Step 2: $\cancel{NO_2(g)} + O(g) \rightarrow \cancel{NO\bullet(g)} + O_2(g)$

  Overall reaction: $O_3(g) + O(g) \rightarrow 2O_2(g)$
- Nitrogen monoxide (NO•):
  - reacts in Step 1 and is formed again in Step 2
  - is a catalyst in the reaction
  - can take part in many reactions and destroy many ozone molecules.
- **Chlorofluorocarbons** (CFCs) are substances that were commonly used as **refrigerants**, **aerosols**, solvents, and in making plastics.

General vocabulary

depleted	lowered in amount or concentration
consequences	the negative results of an action

Subject vocabulary

free radical	a chemical species that contains one or more unpaired electrons
chlorofluorocarbons	organic compounds (halogenoalkanes) that contain both chlorine and fluorine substituents
refrigerants	substances used as coolants in refrigerators
aerosols	substances used in spray cans

- Freon (CCl_2F_2):
  - was a commonly used chlorofluorocarbon
  - breaks down in the upper atmosphere and releases a chlorine atom:
    $CCl_2F_2(g) \rightarrow CF_2Cl(g) + Cl(g)$
- Chlorine atoms:
  - have unpaired electrons and are free radicals ($Cl\bullet$)
  - can then react with ozone in a two-step mechanism:
    Step 1: $\cancel{Cl\bullet(g)} + O_3(g) \rightarrow \cancel{ClO\bullet(g)} + O_2(g)$
    Step 2: $\cancel{ClO\bullet(g)} + O\bullet(g) \rightarrow \cancel{Cl\bullet(g)} + O_2(g)$
    Overall reaction: $O_3(g) + O(g) \rightarrow 2O_2(g)$
- The chlorine radical ($Cl\bullet$):
  - reacts in Step 1 and is formed again in Step 2
  - is a catalyst in the reaction
  - can take part in many reactions and destroy many ozone molecules.

14.2 Hybridization

Essential idea:

Hybridization results from the mixing of atomic orbitals to form the same number of new equivalent hybrid orbitals that can have the same **mean** energy as the contributing atomic orbitals.

Synonym

mean .... average

Understanding: A hybrid orbital results from the mixing of different types of atomic orbitals on the same atom.

- Hybrid orbitals:
  - are used in bonding (not atomic orbitals)
  - are formed from the mixing, or **hybridization**, of s and p atomic orbitals.
- The number of hybrid orbitals formed is equal to the number of atomic orbitals that mix to form the hybrids.
- There are three types of hybrid orbitals: sp^3, sp^2, and sp hybrids.
- Sigma bonds are formed from the overlap of hybrid orbitals.
- Pi bonds are formed from the overlap of **unhybridized** p orbitals.

Subject vocabulary

hybridization the mixing of atomic orbitals to make hybrid orbitals

unhybridized atomic orbitals that do not mix to form hybrid orbitals are unhybridized

Skill: Explanation of the formation of sp^3, sp^2, and sp hybrid orbitals in methane, ethane, and ethyne.

- Methane, CH_4: sp^3 hybridization

  sp^3 hybridization:
  - occurs when one s orbital mixes with three p orbitals
  - forms four sp^3 hybrids that are equal in energy and are at 109.5° to each other.

Figure 14.5 *sp^3 hybridization.*

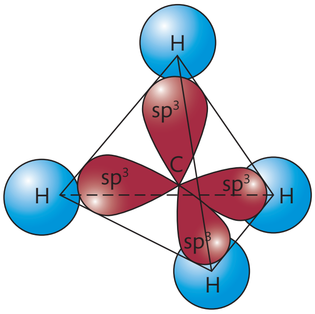


Figure 14.6 *Structure of methane. The tetrahedral shape is formed by the four sp^3 hybrid orbitals, which each overlap with the s orbital of an H atom. All bonds are sigma bonds.*

- Ethene, C_2H_4: sp^2 hybridization

  sp^2 hybridization:
  - occurs when one s orbital mixes with two p orbitals
  - forms three sp^2 hybrids that are equal in energy and are at 120° to each other
  - has one p orbital that is unhybridized.

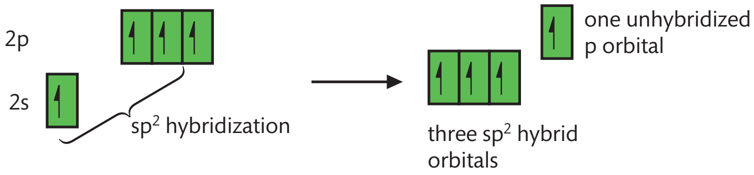


Figure 14.7 *sp^2 hybridization.*

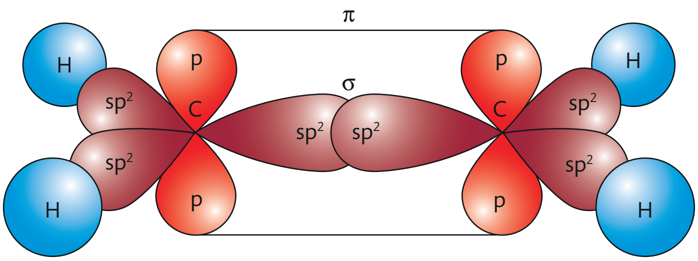


Figure 14.8 *Structure of ethene. The three sp^2 hybrid orbitals on each carbon atom form a triangular planar shape, overlapping to form one C–C and two C–H sigma bonds. The unhybridized p orbitals on each carbon atom overlap to form a pi bond.*

- Ethyne, C_2H_2: sp hybridization

  sp hybridization:
  - occurs when the s orbital mixes with one p orbital
  - forms two sp hybrids that are equal in energy and are at 180° to each other
  - has two p orbitals that are unhybridized.

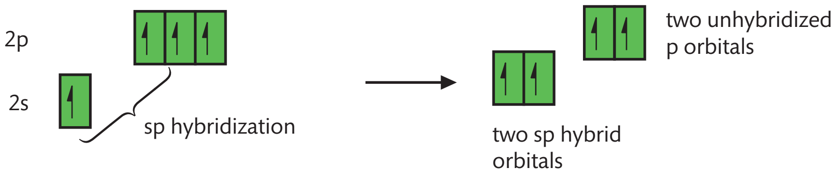


Figure 14.9 *sp hybridization.*

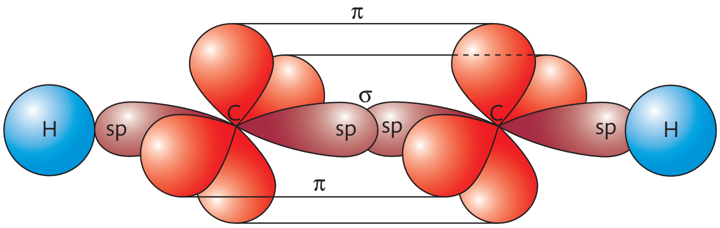


Figure 14.10 *Structure of ethyne. The two sp hybrid orbitals on each carbon atom form a linear shape, overlapping to form one C–C and one C–H sigma bonds. The unhybridized p orbitals on each carbon atom overlap to form two pi bonds.*

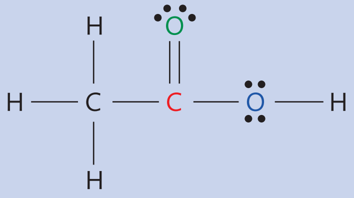
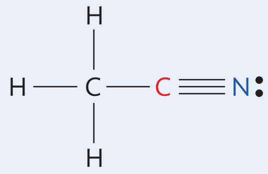
Skill: Identification and explanation of the relationship between Lewis (electron dot) structures, electron domains, molecular geometries, and types of hybridization.

- The examples given above show the relationship between the electron domain geometry of an atom and the type of hybridization.

Example	Hybridization of carbon atoms	Number of electron domains	Electron domain geometry
methane	sp^3	4	tetrahedral
ethene	sp^2	3	trigonal planar
ethyne	sp	2	linear

Worked example

Determine the hybridization for the carbon, oxygen, and nitrogen atoms in ethanoic acid, CH_3COOH, and ethanenitrile, CH_3CN.

	CH_3COOH				CH_3CN		
Lewis structure							
Atom in structure	C	C	O	O	C	C	N
Number of electron domains	4	3	3	4	4	2	2
Hybridization	sp^3	sp^2	sp^2	sp^3	sp^3	sp	sp

Topic 15: Energetics/thermochemistry

15.1 Energy cycles

Essential idea:

The concept of the energy change in a single-step reaction being equivalent to the summation of smaller steps can be applied to changes involving ionic compounds.

Understanding: Representative equations (e.g. $M^+(g) \rightarrow M^+(aq)$) can be used for enthalpy/energy of hydration, ionization, atomization, electron affinity, lattice, covalent bond, and solution.

The **lattice enthalpy** ($\Delta H^{\ominus}_{\text{lat}}$) of an ionic compound is the enthalpy change that occurs when one mole of the solid compound is broken into its gaseous ions:

$$MX(s) \rightarrow M^+(g) + X^-(g)$$

Hints for success: Values for lattice enthalpies are given in section 18 of the IB data booklet.

Lattice enthalpies are difficult to measure directly but they can be calculated from the enthalpies of other reactions using a **Born–Haber cycle**.

Subject vocabulary

lattice enthalpy the enthalpy change that occurs when one mole of an ionic solid is broken into its gaseous ions

Born–Haber cycle an enthalpy cycle that relates the lattice enthalpy and enthalpy of formation of an ionic solid using a series of one-step processes

enthalpy of formation the enthalpy change that occurs when one mole of a compound in its standard state is formed from its elements in their standard states

enthalpy of atomization the enthalpy change that occurs when one mole of a gaseous atom is formed from the element in its standard state

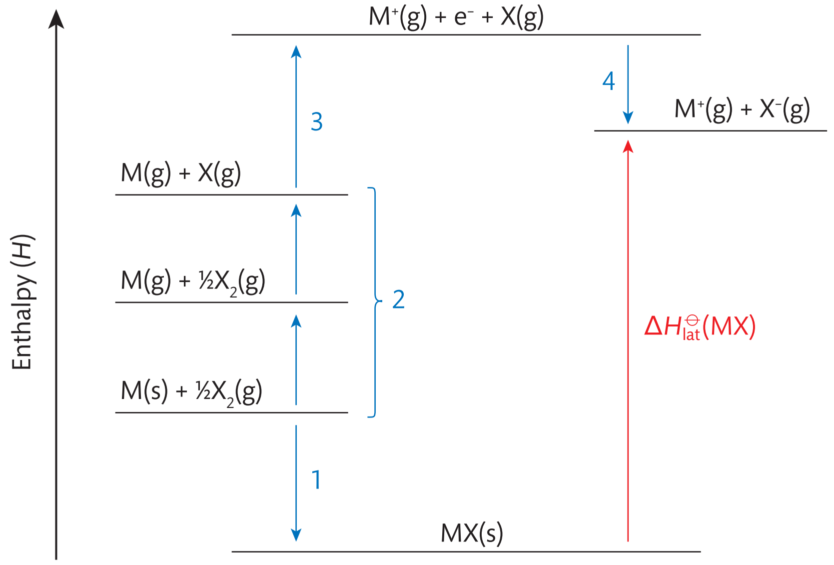


Figure 15.1 *The Born–Haber cycle for an ionic salt MX. M represents the metal and X represents the non-metal.*

Hints for success: In a Born–Haber cycle arrows going up represent endothermic processes. Arrows going down represent exothermic processes.

There are four steps required to create a Born–Haber cycle.

1. **Enthalpy of formation** ($\Delta H_f^{\ominus}$): the enthalpy change that occurs when one mole of a compound in its standard state is formed from its elements in their standard states.
2. **Enthalpy of atomization** ($\Delta H^{\ominus}_{\text{atom}}$): the enthalpy change that occurs when one mole of a gaseous atom is formed from the element in its standard state.

Subject vocabulary

sublime convert directly from solid to gas

first ionization energy the enthalpy change that occurs when one mole of electrons is removed from one mole of gaseous atoms

first electron affinity the enthalpy change that occurs when one mole of electrons is added to one mole of gaseous atoms

Metals exist as solids in their standard states. The enthalpy of atomization for a metal is the energy required to **sublime** the solid:

$\mathrm{M(s)} \rightarrow \mathrm{M(g)}$

$\Delta H_{\mathrm{atom}} = \Delta H_{\mathrm{sublimation}}$

Non-metals usually exist as diatomic gaseous molecules in their standard states, i.e. $\mathrm{X_2(g)}$. The enthalpy of atomization for a diatomic gas is half the X–X bond enthalpy:

$\frac{1}{2}\mathrm{X_2(g)} \rightarrow \mathrm{X(g)}$

$\Delta H_{\mathrm{atom}} = \frac{1}{2}\Delta E(\mathrm{X{-}X})$

3. **First ionization energy** ($\Delta H_{\mathrm{i}}^{\ominus}$): the enthalpy change that occurs when one mole of electrons is removed from one mole of gaseous atoms:

   $\mathrm{M(g)} \rightarrow \mathrm{M(g)} + \mathrm{e^-}$

4. **First electron affinity** ($\Delta H_{\mathrm{e}}^{\ominus}$): the enthalpy change that occurs when one mole of electrons is added to one mole of gaseous atoms:

   $\mathrm{X(g)} + \mathrm{e^-} \rightarrow \mathrm{X^-(g)}$

Hints for success: First electron affinities for non-metals are exothermic.

From the Born–Haber cycle we can see that the lattice enthalpy is related to the enthalpies of the other reactions:

$$\begin{aligned}\Delta H_{\mathrm{lat}}(\mathrm{MX}) &= -1 + 2 + 3 + 4 \\ &= -\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{MX}) + \Delta H_{\mathrm{atom}}^{\ominus}(\mathrm{M}) + \Delta H_{\mathrm{atom}}^{\ominus}(\mathrm{X}) + \Delta H_{\mathrm{i}}^{\ominus}(\mathrm{M}) + \Delta H_{\mathrm{e}}^{\ominus}(\mathrm{X}).\end{aligned}$$

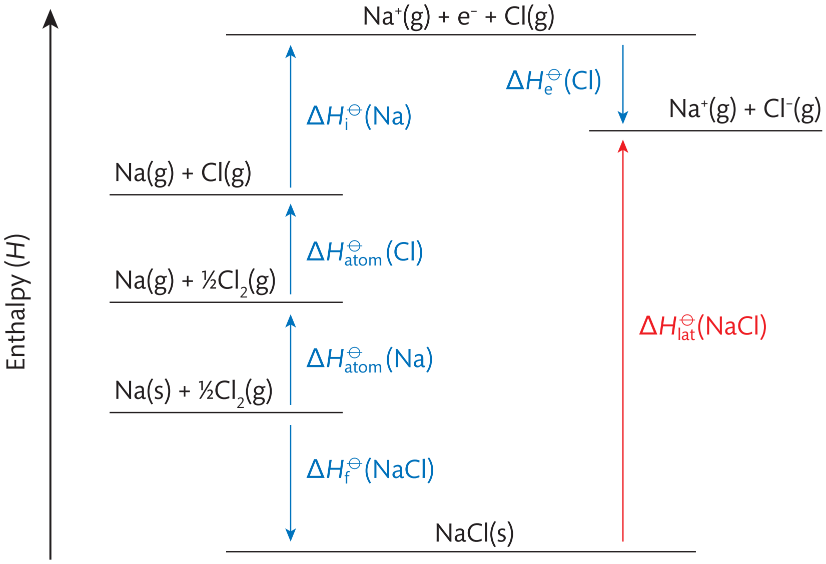
The total atomization energy (2 in Figure 15.1) includes the atomization of the metal (M) and the non-metal (X).

Hints for success: Enthalpy values are added when following the direction of arrows in the Born–Haber cycle and subtracted when going against an arrow.

Skill: Construction of Born–Haber cycles for group 1 and 2 oxides and chlorides.

Born–Haber cycle for NaCl

Figure 15.2 *The Born–Haber cycle for sodium chloride, NaCl.*



$$\Delta H_{\mathrm{lat}}^{\ominus}(\mathrm{NaCl}) = -\Delta H_{\mathrm{f}}^{\ominus}(\mathrm{NaCl}) + \Delta H_{\mathrm{atom}}^{\ominus}(\mathrm{Na}) + \Delta H_{\mathrm{atom}}^{\ominus}(\mathrm{Cl}) + \Delta H_{\mathrm{i}}^{\ominus}(\mathrm{Na}) + \Delta H_{\mathrm{e}}^{\ominus}(\mathrm{Cl})$$

Worked example

Determine the lattice enthalpy of NaCl using the following information and the IB data booklet.

$\Delta H_f^{\ominus}(\text{NaCl}) = -411\ \text{kJ mol}^{-1}$ $\Delta H_{\text{atom}}^{\ominus}(\text{Na}) = +107\ \text{kJ mol}^{-1}$

Solution

From the IB data booklet:

$\Delta H_i^{\ominus}(\text{Na}) = +496\ \text{kJ mol}^{-1}$ $\Delta H_e^{\ominus}(\text{Cl}) = -349\ \text{kJ mol}^{-1}$ $E(\text{Cl–Cl}) = +242\ \text{kJ mol}^{-1}$

$$\Delta H_{\text{atom}}^{\ominus}(\text{Cl}) = \tfrac{1}{2}E(\text{Cl–Cl}) = \tfrac{1}{2} \times +242\ \text{kJ mol}^{-1} = +121\ \text{kJ mol}^{-1}$$

$$\begin{aligned}\Delta H_{\text{lat}}^{\ominus}(\text{NaCl}) &= -\Delta H_f^{\ominus}(\text{NaCl}) + \Delta H_{\text{atom}}^{\ominus}(\text{Na}) + \Delta H_{\text{atom}}^{\ominus}(\text{Cl}) + \Delta H_i^{\ominus}(\text{Na}) + \Delta H_e^{\ominus}(\text{Cl})\\ &= [-(-411) + 107 + 121 + 496 - 349]\ \text{kJ mol}^{-1}\\ &= +786\ \text{kJ mol}^{-1}\end{aligned}$$

Hints for success: Ionization energy and electron affinity values are found in section 8 of the IB data booklet. Bond enthalpies are found in section 11.

Born–Haber cycle for MgO

The Born–Haber cycle for MgO involves two more processes than the cycle for NaCl:

Second ionization energy ($\Delta H_{2i}^{\ominus}$): the enthalpy change that occurs when one mole of electrons is removed from one mole of gaseous 1+ ions:

$$\text{M}^{+}(g) \rightarrow \text{M}^{2+}(g) + e^{-}$$

Second electron affinity ($\Delta H_{2e}^{\ominus}$): the enthalpy change that occurs when one mole of electrons is added to one mole of gaseous 1– ions:

$$\text{X}^{-}(g) + e^{-} \rightarrow \text{X}^{2-}(g)$$

(Second electron affinities are always endothermic as it takes energy to add a negative electron to a negative ion.)

Subject vocabulary

second ionization energy the enthalpy change that occurs when one mole of electrons is removed from one mole of gaseous 1+ ions

second electron affinity the enthalpy change that occurs when one mole of electrons is added to one mole of gaseous 1– ions

The first and second ionization energies of an atom can be combined and represented as a single arrow in a Born–Haber cycle.

The first and second electron affinities of an atom can also be combined and represented by a single arrow.

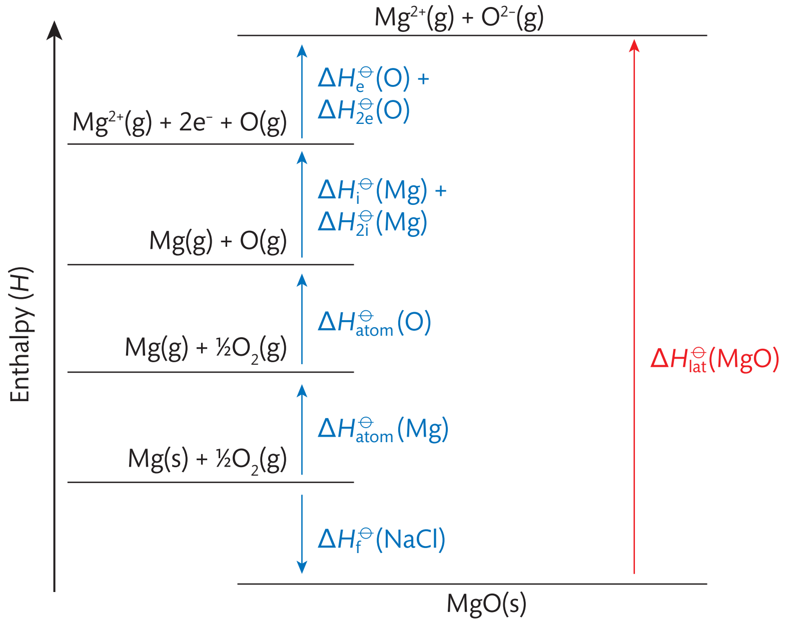


Figure 15.3 *The Born–Haber cycle for magnesium oxide, MgO.*

$$\Delta H_{\text{lat}}^{\ominus}(\text{MgO}) = -\Delta H_f^{\ominus}(\text{MgO}) + \Delta H_{\text{atom}}^{\ominus}(\text{Mg}) + \Delta H_{\text{atom}}^{\ominus}(\text{O}) + \Delta H_i^{\ominus}(\text{Mg}) + \Delta H_{2i}^{\ominus}(\text{Mg}) + \Delta H_e^{\ominus}(\text{O}) + \Delta H_{2e}^{\ominus}(\text{O})$$

Worked example

Determine the enthalpy of formation of MgO using the following information and the IB data booklet.

Solution

$\Delta H^{\ominus}_{\text{atom}}(\text{Mg}) = +148\,\text{kJ mol}^{-1}$ $\Delta H^{\ominus}_{2\text{i}}(\text{Mg}) = +1451\,\text{kJ mol}^{-1}$

From the IB data booklet:

$\Delta H_{\text{i}}^{\ominus}(\text{Mg}) = +738\,\text{kJ mol}^{-1}$, $\Delta H_{\text{e}}^{\ominus}(\text{O}) = -141\,\text{kJ mol}^{-1}$

$\Delta H^{\ominus}_{2\text{e}}(\text{O}) = +753\,\text{kJ mol}^{-1}$

$\Delta H^{\ominus}_{\text{lat}}(\text{MgO}) = +3791\,\text{kJ mol}^{-1}$

$\Delta H^{\ominus}_{\text{atom}}(\text{O}) = \frac{1}{2}E(\text{O=O}) = \frac{1}{2} \times +498\,\text{kJ mol}^{-1} = +249\,\text{kJ mol}^{-1}$

$\Delta H_{\text{f}}^{\ominus}(\text{MgO}) = \Delta H^{\ominus}_{\text{atom}}(\text{Mg}) + \Delta H^{\ominus}_{\text{atom}}(\text{O}) + \Delta H_{\text{i}}^{\ominus}(\text{Mg}) + \Delta H^{\ominus}_{2\text{i}}(\text{Mg}) + \Delta H_{\text{e}}^{\ominus}(\text{O}) + \Delta H^{\ominus}_{2\text{e}}(\text{O}) - \Delta H^{\ominus}_{\text{lat}}(\text{MgO})$

$\Delta H_{\text{f}}^{\ominus}(\text{MgO}) = [+148 + 249 + 738 + 1451 - 141 + 753 - 3791]\,\text{kJ mol}^{-1} = -593\,\text{kJ mol}^{-1}$

Understanding: Enthalpy of solution, hydration enthalpy, and lattice enthalpy are related in an energy cycle.

Water is a highly polar molecule and is strongly attracted to the charged ions in an ionic solid. Ionic solids dissolve in water because the ionic bonds that hold the cations and anions together are broken and the ions become surrounded by water molecules:

$$\text{MX(s)} \xrightarrow{\text{H}_2\text{O}} \text{M}^{+}(\text{aq}) + \text{X}^{-}(\text{aq})$$

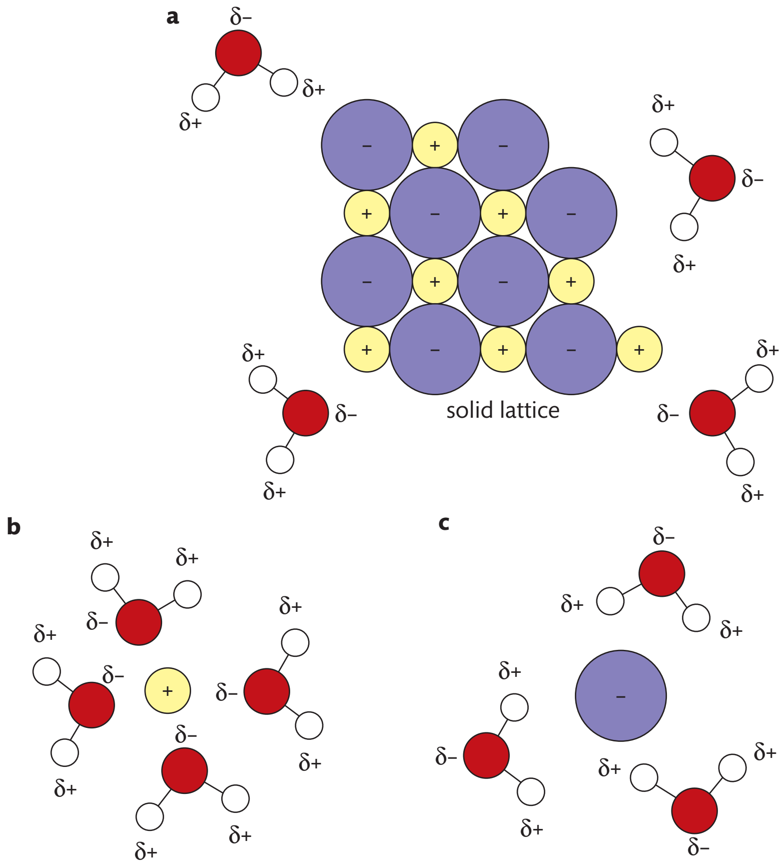


Figure 15.4 *Ionic compounds generally dissolve in the polar solvent water.* ***(a)*** *Ionic lattices are often broken up by polar water molecules. At the contact surface, partial charges in the water molecules are attracted to ions of opposite charge in the lattice, which may cause them to dislodge from their positions.* ***(b)*** *The partially negatively charged oxygen atoms in the polar water molecules are attracted to the positive ions.* ***(c)*** *The partially positively charged hydrogen atoms in the polar water molecules are attracted to the negative ions.*

The **enthalpy of solution** ($\Delta H^{\ominus}_{sol}$) is the enthalpy change that occurs when one mole of an ionic solid is dissolved in water to **infinite dilution** under standard conditions.

Hints for success: Values for enthalpies of solution are given in section 19 of the IB data booklet.

An enthalpy cycle can be created using the enthalpy of solution and treating how the solid dissolves as a two-step process:

1. breaking the ionic solid into gaseous ions

   $MX(s) \rightarrow M^{+}(g) + X^{-}(g)$

   The enthalpy change for this step is the lattice enthalpy ($\Delta H_{lat}{}^{\ominus}$). This step is endothermic as gaseous ions are less stable than the ionic solid.

2. **hydration** of the gaseous ions

   $M^{+}(g) \rightarrow M^{+}(aq)$ $\quad$ $X^{-}(g) \rightarrow X^{-}(aq)$

   (Overall: $M^{+}(g) + X^{-}(g) \rightarrow M^{+}(aq) + X^{-}(aq)$)

   This step involves the hydration enthalpies of the two ions being dissolved, and it is exothermic because hydrated ions are more stable than gaseous ions.

   Hydration enthalpy ($\Delta H^{\ominus}_{hyd}$) is the enthalpy change that occurs when one mole of a gaseous ion is dissolved in water to infinite dilution under standard conditions.

Hints for success: Values for enthalpies of hydration are given in section 20 of the IB data booklet.

A **dissolution energy cycle** can be constructed using the enthalpy of solution, lattice enthalpy, and the hydration enthalpies of the ions.

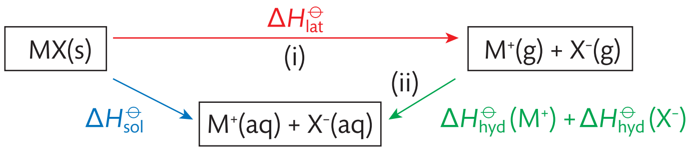


Figure 15.5 *The dissolution energy cycle for an ionic solid MX. M represents the metal and X represents the non-metal.*

Applying Hess's Law:
$$\begin{aligned}\Delta H^{\ominus}_{sol} &= \Delta H(i) + \Delta H(ii)\\ &= \Delta H^{\ominus}_{lat} + \Delta H^{\ominus}_{hyd}(M^{+}) + \Delta H^{\ominus}_{hyd}(X^{-})\\ &= \Delta H^{\ominus}_{lat} + \Sigma\Delta H^{\ominus}_{hyd}\end{aligned}$$

Enthalpies of solution:

- are endothermic when $\Delta H^{\ominus}_{lat} > \Sigma\Delta H^{\ominus}_{hyd}$
- are exothermic when $\Delta H^{\ominus}_{lat} < \Sigma\Delta H^{\ominus}_{hyd}$

Skill: Construction of energy cycles from hydration, lattice, and solution enthalpy, for example dissolution of solid NaOH or NH_4Cl in water.

Skill: Calculation of enthalpy changes from Born-Haber or dissolution energy cycles.

Subject vocabulary

enthalpy of solution the enthalpy change that occurs when one mole of an ionic solid is dissolved in water to infinite dilution under standard conditions

infinite dilution a solution that is so dilute that solute particles only interact with solvent and do not interact with each other

hydration the process by which ions become surrounded by water molecules

hydration enthalpy the enthalpy change that occurs when one mole of a gaseous ion is dissolved in water to infinite dilution under standard conditions

dissolution energy cycle an enthalpy cycle that relates lattice enthalpy, enthalpy of solution, and hydration enthalpy

Worked example

Construct the dissolution cycle for sodium hydroxide (NaOH) and determine the enthalpy of solution of sodium hydroxide (NaOH) using the following information and the IB data booklet:

$\Delta H^{\ominus}_{\text{lat}}(\text{NaOH}) = +900\ \text{kJ mol}^{-1}$

Solution

Start by constructing a dissolution energy cycle for NaOH showing the relationship between the lattice enthalpy, enthalpy of solution, and hydration enthalpies of the ions.

$$\begin{tikzcd}
\boxed{\text{NaOH(s)}} \arrow[rr, "\Delta H^{\ominus}_{\text{lat}}(\text{NaOH})", "\text{(i)}"'] \arrow[dr, "\Delta H^{\ominus}_{\text{sol}}(\text{NaOH})"'] & & \boxed{\text{Na}^+\text{(g)} + \text{OH}^-\text{(g)}} \arrow[dl, "\text{(ii)}"', "\Delta H^{\ominus}_{\text{hyd}}(\text{Na}^+) + \Delta H^{\ominus}_{\text{hyd}}(\text{OH}^-)"] \\
& \boxed{\text{Na}^+\text{(aq)} + \text{OH}^-\text{(aq)}} &
\end{tikzcd}$$

From section 20 in the IB data booklet: $\Delta H^{\ominus}_{\text{hyd}}(\text{Na}^+) = -424\ \text{kJ mol}^{-1}$ $\quad \Delta H^{\ominus}_{\text{hyd}}(\text{OH}^-) = -519\ \text{kJ mol}^{-1}$

$$\begin{aligned}
\Delta H^{\ominus}_{\text{sol}}(\text{NaOH}) &= \Delta H^{\ominus}_{\text{lat}}(\text{NaOH}) + \Delta H^{\ominus}_{\text{hyd}}(\text{Na}^+) + \Delta H^{\ominus}_{\text{hyd}}(\text{OH}^-) \\
&= +900\ \text{kJ mol}^{-1} + (-424\ \text{kJ mol}^{-1}) + (-519\ \text{kJ mol}^{-1}) \\
&= -43\ \text{kJ mol}^{-1}
\end{aligned}$$

Skill: Relate size and charge of ions to lattice and hydration enthalpies.

Lattice enthalpies are related to the strength of the ionic bonding between the cation and anion. The stronger the ionic bond, the larger the lattice enthalpy.

The size of lattice enthalpies depends on:

(i) the ionic radius of the ions: *smaller ions give larger lattice enthalpies*

← decreasing size of anion

↑ decreasing size of cation

	F^-	Cl^-	Br^-	I^-
Li^+	1049	864	820	764
Na^+	930	790	754	705
K^+	829	720	691	650
Rb^+	795	695	668	632
Cs^+	759	670	647	613

The lattice enthalpies of the Group 1 halides/kJ mol^{-1}

(ii) the charge on the ions: *bigger charges give larger lattice enthalpies*

	$\Delta H^{\ominus}_{\text{lat}}$ / kJ mol^{-1}		**$\Delta H^{\ominus}_{\text{lat}}$ / kJ mol^{-1}**	**Explanation of difference**
NaCl	1049	**$MgCl_2$**	2540	$MgCl_2$ has more than double the lattice enthalpy of NaCl, as Mg^{2+} has double the charge of Na^+ and a smaller ionic radius.
CaF_2	2651	**CaO**	3401	CaO has a higher lattice enthalpy than CaF_2, as O^{2-} has double the charge of F^-. The value is less than double as O^{2-} has a larger ionic radius than F^-.

Hydration enthalpies depend on the strength of the attraction between the ions and the water molecules.

The size of hydration enthalpies depends on:

(i) the ionic radius of the ions: *smaller ions give larger hydration enthalpies*

decreasing size of cation

Cations	$\Delta H^{\ominus}_{hyd}$ / kJ mol^{-1}
Li^+	−538
Na^+	−424
K^+	−340
Rb^+	−315

Anions	$\Delta H^{\ominus}_{hyd}$ / kJ mol^{-1}
F^-	−504
Cl^-	−359
Br^-	−328
I^-	−287

decreasing size of anion

(ii) the charge on the ions: *bigger charges give larger hydration enthalpies*

Cations	$\Delta H^{\ominus}_{hyd}$ / kJ mol^{-1}
Na^+	−424
Mg^{2+}	−1963
Al^{3+}	−4741

15.2 Entropy and spontaneity

Essential idea:

A reaction is spontaneous if the overall transformation leads to an increase in total entropy (system plus surroundings). The direction of spontaneous change always increases the total entropy of the universe at the expense of the energy available to do useful work. This is known as the second law of thermodynamics.

General vocabulary

transformation change

Understanding: Entropy (*S*) refers to the distribution of available energy among the particles. The more ways the energy can be distributed, the higher the entropy.

Subject vocabulary

entropy a measure of disorder. Entropy has the symbol *S* and units J K^{-1} mol^{-1}

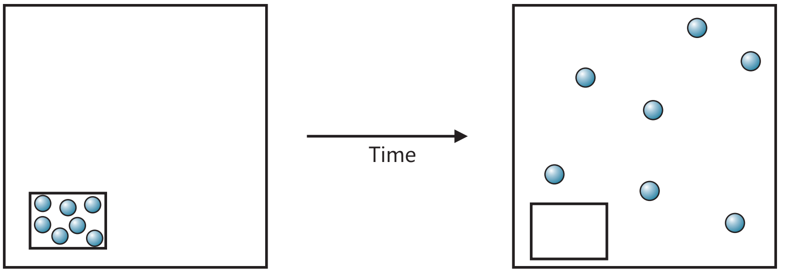
Synonym

disorder .... randomness

dispersed ...... spread out

Entropy (*S*) is a measure of **disorder**.

- It has units of J K^{-1} mol^{-1}.
- It is equal to zero at absolute zero (0 K).
- It increases as temperature increases.
- A greater disorder (and higher entropy) occurs when there are more ways to distribute energy through the system. When entropy increases, energy is **dispersed** and is not available to do useful work.



All gas particles are concentrated in small volume. This is an ordered state with low entropy.

The gas particles are dispersed throughout the room. This is a disordered state with high entropy.

Figure 15.6 *Particles naturally adopt a more disordered state with higher entropy. A random system allows the energy to be distributed in more ways than one (the different ways in which particles are separated). This illustrates the second law of thermodynamics: spontaneous processes always occur with an increase in the entropy of the universe.*

Understanding: Entropy of gas > liquid > solid under the same conditions.

Solids, liquids, and gases that are under the same conditions of temperature and pressure have different entropies.

INCREASING ENTROPY →

Solid	**Liquid**	**Gas**
• Particles in fixed positions	• Particles can move	• Particles move freely
• Little distribution of energy	• Some distribution of energy	• Large distribution of energy
• Lower disorder (highly ordered)	• More disordered	• Highly disordered
• Low entropy	• Higher entropy	• Highest entropy

Skill: Prediction of whether a change will result in an increase or decrease in entropy by considering the states of the reactants and products.

Worked example

Predict the entropy change (ΔS) for the following reactions or processes:

(i) $Br_2(l) \rightarrow Br_2(g)$

(ii) $Ag^+(aq) + Br^-(aq) \rightarrow AgBr(s)$

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

(iv) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

Solution

(i) ΔS is positive because a gaseous product is made from a liquid reactant.

(ii) ΔS is negative because a solid product is made from aqueous reactants.

(iii) ΔS is negative because a liquid product is made from gaseous reactants.

(iv) ΔS is negative because there are fewer gas molecules on the products side.

Skill: Calculation of entropy changes (ΔS) from given standard entropy values ($S^\ominus$).

The standard entropy change ($\Delta S^\ominus$) that occurs for a reaction is the difference between the total standard entropy ($S^\ominus$) of all the products and the total standard entropy of all the reactants:

$$\Delta S^\ominus = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$$

Hints for success: Standard entropy values are given in section 12 of the IB data booklet.

Worked example

Calculate the standard entropy change ($\Delta S^\ominus$) that occurs for the following reaction using the information provided and the IB data booklet.

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$ $\quad S^\ominus(O_2) = +205.0\,J\,K^{-1}\,mol^{-1}$

Solution

From section 12 in the IB data booklet:

$S^\ominus(CH_4) = +186\,J\,K^{-1}\,mol^{-1}$, $S^\ominus(CO_2) = +213.8\,J\,K^{-1}\,mol^{-1}$, $S^\ominus(H_2O(l)) = +70.0\,J\,K^{-1}\,mol^{-1}$

$$\begin{aligned}\Delta S^\ominus &= \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})\\ &= [S^\ominus(CO_2) + 2S^\ominus(H_2O(l))] - [S^\ominus(CH_4) + 2S^\ominus(O_2)]\\ &= [+213.8 + 2 \times 70.0]\,J\,K^{-1}\,mol^{-1} - [+186 + 2 \times 205.0]\,J\,K^{-1}\,mol^{-1}\\ &= -242\,J\,K^{-1}\,mol^{-1}\end{aligned}$$

Hints for success: The $S^\ominus$ values for a compound must be multiplied by the coefficient of that compound.

Understanding: Gibbs free energy (*G*) relates the energy that can be obtained from a chemical reaction to the change in enthalpy (ΔH), change in entropy (ΔS), and absolute temperature (*T*).

We have seen two factors that favour a spontaneous reaction:

- ΔH is negative
- ΔS is positive.

But some reactions that are spontaneous have a positive ΔH or negative ΔS, for example:

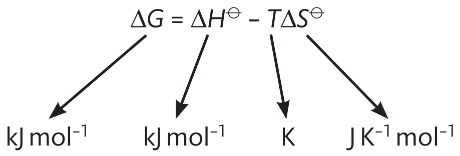
- $H_2O(s) \rightarrow H_2O(l)$ $\Delta H^{\ominus} = +6.0\ \text{kJ mol}^{-1}$
- $H_2(g) + C_2H_4(g) \rightarrow C_2H_6(g)$ $\Delta S^{\ominus} = -121\ \text{J K}^{-1}\ \text{mol}^{-1}$

So how can we predict if a reaction will be spontaneous or not spontaneous?

The change in **Gibbs free energy** (ΔG) that occurs determines whether a reaction is spontaneous or not:

Subject vocabulary

Gibbs free energy the energy of a reaction that is available to do work



These are the units that are typically given with each term in the equation.

Hints for success: When using $\Delta G = \Delta H^{\ominus} - T\Delta S^{\ominus}$ the units of $\Delta S^{\ominus}$ must be converted to $\text{kJ K}^{-1}\ \text{mol}^{-1}$ to be consistent with the units of ΔG and $\Delta H^{\ominus}$.

The change in Gibbs free energy (ΔG) is the amount of energy that is available to do useful work as a result of the reaction.

The sign of ΔG tells us if the reaction is spontaneous or not:

- If ΔG is **negative**: *the reaction is spontaneous.*
- If ΔG is **positive**: *the reaction is not spontaneous.*

The sign of ΔG depends on the values of ΔH and ΔS as well as temperature (*T*).

ΔH	ΔS	$\Delta G\ (= \Delta H - T\Delta S)$	**Comments**
Positive (endothermic)	Negative (less disordered products)	Always positive	Non-spontaneous at all temperatures *(Products are always less stable and less disordered than reactants)*
Negative (exothermic)	Positive (more disordered products)	Always negative	Spontaneous at all temperatures *(Products are always more stable and more disordered than reactants)*

ΔH	ΔS	ΔG (= $\Delta H - T\Delta S$)	**Comments**
Positive (endothermic)	Positive (more disordered products)	Negative at high temperatures	Spontaneous at high temperatures *(Products are less stable but large increase in disorder at high temperatures)*
		Positive at low temperatures	Not spontaneous at low temperatures *(Products are less stable and only a small increase in disorder at low temperatures)*
Negative (exothermic)	Negative (less disordered products)	Positive at high temperatures	Not spontaneous at high temperatures *(Products are more stable but large decrease in disorder at high temperatures)*
		Negative at low temperatures	Spontaneous at low temperatures *(Products are more stable and only a small decrease in disorder at low temperatures)*

Skill: Application of $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$ in predicting spontaneity and calculation of various conditions of enthalpy and temperature that will affect this.

Worked example

Calculate the value of $\Delta G^\ominus$ for the reaction of ethanol (CH_3CH_2OH) and oxygen (O_2) to produce ethanoic acid (CH_3COOH) and water (H_2O) at 298 K using the $\Delta H_f^\ominus$ and $S^\ominus$ values in section 12 of the IB data booklet.

Predict whether the reaction will be spontaneous or non-spontaneous at this temperature.

$CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O\ (l)$ $\qquad S^\ominus(O_2) = +205.0\ J\ K^{-1}\ mol^{-1}$

Solution

$$\Delta H^\ominus = \Sigma\Delta H_f^\ominus(\text{products}) - \Sigma\Delta H_f^\ominus(\text{reactants})$$

$$= [\Delta H_f^\ominus(CH_3COOH) + \Delta H_f^\ominus(H_2O)] - [\Delta H_f^\ominus(CH_3CH_2OH) + \Delta H_f^\ominus(O_2)]$$

$$= [-484 + -285.8]\,kJ\,mol^{-1} - [-278 + 0]\,kJ\,mol^{-1}$$

$$= -492\,kJ\,mol^{-1}$$

$$\Delta S^\ominus = \Sigma S^\ominus(\text{products}) - \Sigma S^\ominus(\text{reactants})$$

$$= [S^\ominus(CH_3COOH) + S^\ominus(H_2O(l)] - [S^\ominus(CH_3CH_2OH) + S^\ominus(O_2)]$$

$$= [+160 + +70.0]\,J\,K^{-1}\,mol^{-1} - [+161 + +205.0]\,J\,K^{-1}\,mol^{-1}$$

$$= -136\,J\,K^{-1}\,mol^{-1}$$

$$= -0.136\,kJ\,K^{-1}\,mol^{-1}$$

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$

$= -492\ \text{kJ mol}^{-1} - [298\ \text{K} \times -0.136\ \text{kJ K}^{-1}\ \text{mol}^{-1}]$

$= -451\ \text{kJ mol}^{-1}$

Because the value of $\Delta G^{\ominus}$ is negative, the reaction is spontaneous at 298 K.

Gibbs free energies of formation

The change in Gibbs free energy (ΔG) for a reaction can also be calculated using standard Gibbs free energies of formation:

- $\Delta G^{\ominus}_{\text{reaction}} = \Sigma\Delta G_f^{\ominus}(\text{products}) - \Sigma\Delta G_f^{\ominus}(\text{reactants})$

Subject vocabulary

standard Gibbs free energy of formation the change in Gibbs free energy that occurs when one mole of a compound is formed from its elements in their standard states

The **standard Gibbs free energy of formation** ($\Delta G_f^{\ominus}$) is the change in Gibbs free energy that occurs when one mole of a substance is formed from its constituent elements in their standard states under standard conditions, for example:

- $\Delta G_f^{\ominus}(CH_4)$ is the change in Gibbs free energy that occurs for the reaction:
  $C(s) + 2H_2(g) \rightarrow CH_4(g)$
- $\Delta G_f^{\ominus}(MgCl_2)$ is the change in Gibbs free energy that occurs for the reaction:
  $Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$

Hints for success: Standard Gibbs free energy of formation values are given in section 12 of the IB data booklet.

- $\Delta G_f^{\ominus}$ of all *elements* in their standard states is zero, for example $\Delta G_f^{\ominus}(N_2) = 0$.

Worked example

Calculate the value of $\Delta G^{\ominus}$ for the reaction of ethanol (CH_3CH_2OH) and oxygen (O_2) to produce ethanoic acid (CH_3COOH) and water (H_2O) at 298 K using the $\Delta G_f^{\ominus}$ and $S^{\ominus}$ values in section 12 of the IB data booklet.

$CH_3CH_2OH(l) + O_2(g) \rightarrow CH_3COOH(l) + H_2O(l)$

Hints for success: The $\Delta G_f^{\ominus}$ values for a compound must be multiplied by the coefficient of that compound.

Solution

$\Delta G^{\ominus} = \Sigma\Delta G_f^{\ominus}(\text{products}) - \Sigma\Delta G_f^{\ominus}(\text{reactants})$

$= [\Delta G_f^{\ominus}(CH_3COOH) + \Delta G_f^{\ominus}(H_2O)] - [\Delta G_f^{\ominus}(CH_3CH_2OH) + \Delta G_f^{\ominus}(O_2)]$

$= [-390 + -237.1]\ \text{kJ mol}^{-1} - [-175 + 0]\ \text{kJ mol}^{-1}$

$= -452\ \text{kJ mol}^{-1}$

Skill: Relation of ΔG to position of equilibrium.

$$\overset{\displaystyle\xrightarrow{\text{Forward reaction}}}{\underset{\displaystyle\xleftarrow[\text{Reverse reaction}]{}}{\mathrm{A + B \rightleftharpoons C + D}}}$$

(i) When ΔG is **negative** the reaction is spontaneous in the *forward* direction.

(ii) When ΔG is **positive** the reaction is spontaneous in the *reverse* direction.

(iii) When $\Delta G = 0$ the forward and reverse reactions are **both** spontaneous and they are happening at the same time. This occurs for **equilibrium reactions**. These are discussed in more detail in Chapter 7.

Subject vocabulary

equilibrium reaction a reaction in which the forward and reverse reactions are ocurring at the same time

Topic 16: Chemical kinetics

16.1 Rate expression and reaction mechanism

Essential idea:

Rate expressions can only be determined empirically. They limit possible reaction mechanisms. In particular cases, such as a linear chain of elementary reactions, no equilibria, and only one significant activation barrier, the rate equation is equivalent to the slowest step of the reaction.

Understanding: Reactions may occur by more than one step, and the slowest step determines the rate of reaction (rate-determining step/RDS).

Although we write reactions as if they occur in one single step this rarely happens. Consider the reaction:

$BrO_3^-(aq) + 5Br^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

If this reaction happened in a single step it would require *one* BrO_3^- ion, *five* Br^- ions and *six* H^+ ions colliding at the same time. *Twelve* particles colliding is impossible. Almost all collisions involve only two particles.

Subject vocabulary

elementary step a single step in a reaction mechanism

reaction mechanism a description of a reaction as a series of elementary steps

reaction intermediate a species made in one elementary step and used in another step. It does not appear in the overall equation for the reaction

rate-determining step the slowest elementary step in a reaction mechanism

Reactions occur via a series of **elementary steps** involving one or two reactant particles. The overall sequence of steps is known as the **reaction mechanism**.

Elementary steps in a reaction mechanism add together to give the overall reaction.

A possible two-step reaction mechanism for the reaction $2NO(g) + O_2(g) \rightarrow NO_2(g)$ is:

Step 1: $NO(g) + NO(g) \rightarrow N_2O_2(g)$

Step 2: $N_2O_2\ (g) + O_2(g) \rightarrow 2NO_2(g)$

Overall: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

N_2O_2 is a **reaction intermediate** because it is a product in one step and is used as a reactant in another step. Reaction intermediates do not appear in the overall equation.

Experimental evidence can show if a reaction mechanism is possible but cannot prove that it is the correct mechanism.

Example: if N_2O_2 is observed experimentally when NO reacts with O_2 then the reaction mechanism above is possible. However, it would not prove that this is the actual mechanism because other reaction mechanisms might also predict the formation of N_2O_2.

Elementary steps in a reaction mechanism occur with different rates. The **rate-determining step** (RDS) is the slowest step and it controls the overall rate of the reaction because it has the largest activation energy.

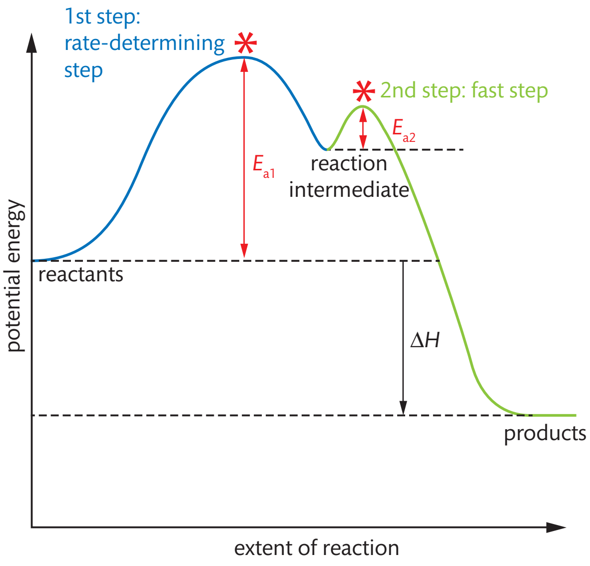


Figure 16.1 *Potential energy level profile showing a two-step reaction.*

Understanding: The molecularity of an elementary step is the number of reactant particles taking part in that step.

The **molecularity** of an elementary step is given by the number of particles in that step.

For *elementary steps* a **rate expression** has the form:

rate = $k[A]^x[B]^y$, where:

- k is the **rate constant** for the elementary step
- A and B represent the reactant particles in the elementary step
- x and y are equal to the coefficients of the reactants in the elementary step.

Elementary step	Number of reactant particles	Molecularity	Rate expression for elementary step
A → products	1	unimolecular	rate = $k[A]$
2A → products	2	bimolecular	rate = $k[A]^2$
A + B → products	2	bimolecular	rate = $k[A][B]$

Understanding: The order of a reaction can be either integer or fractional in nature. The order of a reaction can describe, with respect to a reactant, the number of particles taking part in the rate-determining step.

The rate expression for a *reaction* cannot be predicted from its stoichiometry and has to be determined experimentally. It can be written as:

- rate = $k[A]^m[B]^n$, where:
  - m and n relate to the number of each reactant involved in the RDS
  - m is the **order of reaction** with respect to reactant A
  - n is the order of reaction with respect to reactant B.

Subject vocabulary

molecularity the number of particles in an elementary step

rate expression a mathematical equation that shows how the rate depends on the concentrations of the reactants

rate constant a constant that relates the rate of a reaction to the concentrations of the reactants

order of reaction the number of particles of a particular reactant that are involved in the rate-determining step

Subject vocabulary

overall order of reaction the total number of reactant particles that are involved in the rate-determining step

The **overall order of the reaction** is the sum of the coefficients in the rate expression. It represents the total number of reactant species involved in the RDS.

Overall rate expression	Reaction order with respect to A	Reaction order with respect to B	Overall reaction order
rate = $k[A]^1[B]^0$ $= k[A]$	first order	zero order	first order
rate = $k[A]^1[B]^1$	first order	first order	second order
rate = $k[A]^2[B]^0$ $= k[A]^2$	second order	zero order	second order
rate = $k[A]^1[B]^2$	first order	second order	third order

Worked example

Determine the reaction order for each reactant and the overall reaction order for the reaction:

$NO(g) + H_2(g) \rightarrow H_2NO(g)$

The experimentally determined rate expression is rate = $[NO]^2[H_2]$.

Solution

Reaction order with respect to NO = 2 (second order).

Reaction order with respect to H_2 = 1 (second order).

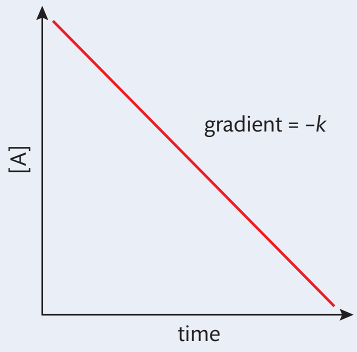
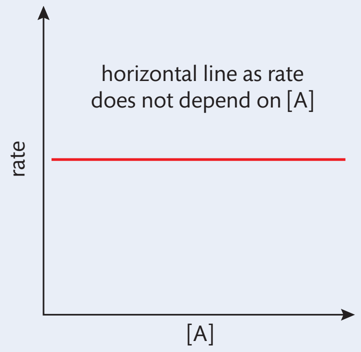
Overall reaction order = 2 + 1 = 3 (third order).

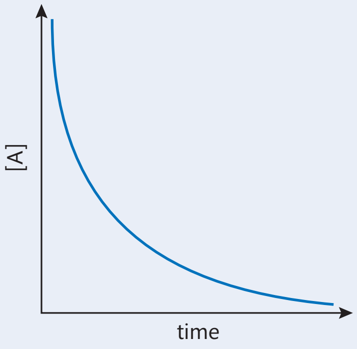
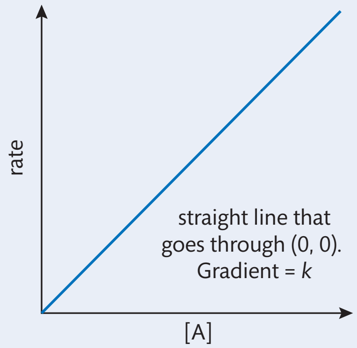
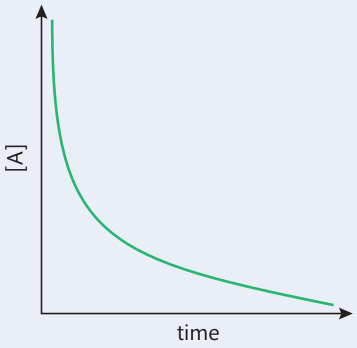
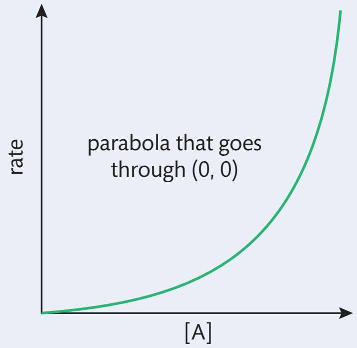
Hints for success: Notice how the coefficients in the rate expression cannot be predicted from the reaction stoichiometry.

Skill: Sketching, identifying, and analysing graphical representations for zero-, first-, and second-order reactions.

Reactions that are zero order, first order, and second order give different graphs when:

- concentration is plotted against time
- rate is plotted against concentration.

Overall reaction order	Rate expression	Concentration–time graph	Rate–concentration graph
zero order	rate = $k[A]^0$ $= k$		

Overall reaction order	Rate expression	Concentration–time graph	Rate–concentration graph
first order	rate = $k[A]^1$ $= k[A]$		 straight line that goes through (0, 0). Gradient = k
second order	rate = $k[A]^2$		 parabola that goes through (0, 0)

The concentration–time and rate–concentration graphs for the different orders are compared below. Note that the concentration–time graph for a second-order reaction decreases more quickly than for a first-order reaction.

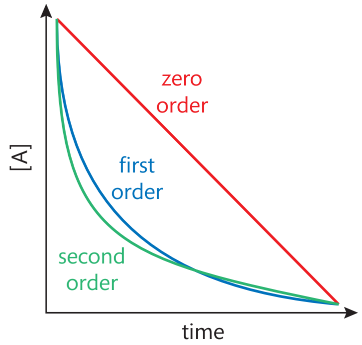


Figure 16.2 *Concentration–time graphs for zero-, first-, and second-order reactions.*

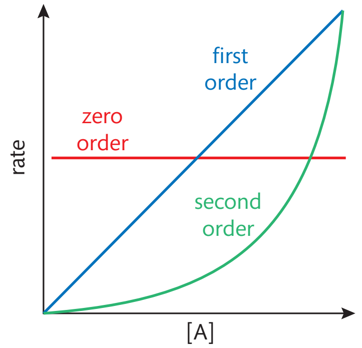


Figure 16.3 *Rate–concentration graphs for zero-, first-, and second-order reactions.*

Understanding: Rate equations can only be determined experimentally

The orders of reaction for each reactant in a reaction can be determined experimentally using the **initial rates method**.

(i) Measure the initial rate of reaction for a set of reactant concentrations.

(ii) Change the concentration of one reactant only. Measure the initial rate of reaction for this new set of concentrations. *Repeat for each reactant*.

Subject vocabulary

initial rates method a method for determining orders of reaction. The concentrations of reactants are changed one at a time and the effect on the initial rate of reaction is observed

(iii) Compare the initial rates in steps **(i)** and **(ii)**.

	Change in initial rate of zero-order reaction	Change in initial rate of first-order reaction	Change in initial rate of second-order reaction
[A] doubles	no change	rate doubles (×2)	rate increases ×4
[A] triples	no change	rate triples (×3)	rate increases ×9
[A] increases four-fold	no change	rate increases four-fold (×4)	rate increases ×16

Skill: Deduction of the rate expression for an equation from experimental data and solving problems involving the rate expression.

Worked example

Use the data in the table below to work out the order of reaction with respect to reactants A and B, and so write the rate expression for this reaction.

Experiment number	Initial concentrations / mol dm^{-3}		Initial rate of reaction / mol dm^{-3} s^{-1}
	[A]	[B]	
1	0.10	0.10	2.0×10^{-4}
2	0.20	0.10	4.0×10^{-4}
3	0.30	0.10	6.0×10^{-4}
4	0.30	0.20	2.4×10^{-3}
5	0.30	0.30	5.4×10^{-3}

Solution

The concentration of B is constant in the first three experiments, so we can use these to deduce the effect of A on the rate of the reaction. We can find the change in rate by dividing one value by the other. Comparing experiments 1 and 2, doubling [A] leads to a doubling of the rate; from experiments 1 and 3, tripling [A] leads to a tripling of the rate. So the reaction must be first order with respect to A.

The concentration of A is held constant in the last three experiments, so these are used to deduce the effect of B on the rate. Comparing experiments 3 and 4, doubling [B] leads to a quadruple (2^2) change in the rate; comparing experiments 3 and 5, tripling [B] leads to a nine-fold (3^2) change in the rate. So the reaction must be second order with respect to B.

Therefore the rate expression for this reaction is rate = $k\,[A]\,[B]^2$.

Skill: Evaluation of proposed reaction mechanisms to be consistent with kinetic and stoichiometric data.

If the RDS is not the first step then its rate expression may include an intermediate. This can be substituted using the concentrations of the reactants in a previous step, for example:

Step 1: A + B → intermediate

Step 2: Intermediate → products **RDS**

Rate expression for RDS = k[intermediate]

From step 1 we see that [intermediate] depends on [A] and [B]

[intermediate] $\propto$ [A][B]

= k[A][B]

Worked example

Nitrogen dioxide (NO_2) reacts with carbon monoxide (CO) to form nitrogen oxide (NO) and carbon dioxide (CO_2):

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

The rate expression determined experimentally is rate = $k[NO_2]^2$.

Determine which of the two mechanisms below is possible by determining the rate expression for each mechanism and comparing it to the experimental result.

Reaction mechanism 1

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$ (slow)

Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$

Overall: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Reaction mechanism 2

Step 1: $NO_2(g) + NO_2(g) \rightarrow NO(g) + NO_3(g)$

Step 2: $NO_3(g) + CO(g) \rightarrow NO_2(g) + CO_2(g)$ (slow)

Overall: $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Solution

Reaction mechanism 1

Rate expression for RDS = $k[NO_2]^2$ because RDS is step 1

Overall rate expression = $k[NO_2]^2$

Reaction mechanism 2

Step 2 is RDS

Rate expression for RDS = $k[NO_3][CO]$

NO_3 is a reaction intermediate; from step 1: $[NO_3] \propto [NO_2]^2$

Overall rate expression = $k[NO_2]^2[CO]$

Mechanism 1 is a possible reaction mechanism because it gives a rate expression that is the same as the experimental rate expression.

Understanding: The value of a rate constant (k) is affected by temperature and its units are determined from the overall order of the reaction.

When the concentrations of reactants are kept constant, the rate of a reaction increases with temperature. As rate = $k[A]^x$ this means that the rate constant must increase with temperature. (This will be discussed in more detail in the next section.)

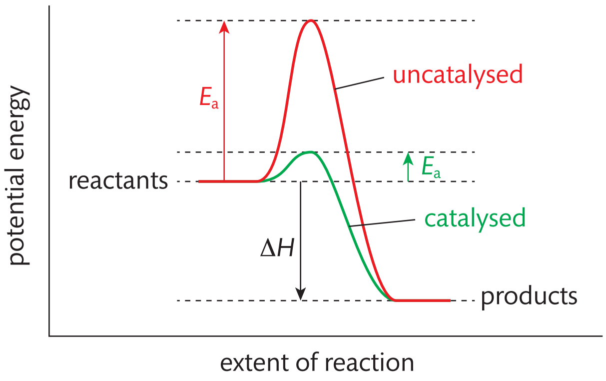
The units of the rate constant depend on the order of reaction:

Zero order	**First order**	**Second order**	**Third order**
rate = k k = rate	rate = $k[\text{A}]$ $k = \frac{\text{rate}}{[\text{A}]}$	e.g. rate = $k[\text{A}]^2$ $k = \frac{\text{rate}}{[\text{A}]^2}$	e.g. rate = $k[\text{A}]^3$ $k = \frac{\text{rate}}{[\text{A}]^3}$
units of k = units of rate = $\text{mol dm}^{-3}\ \text{s}^{-1}$	units of k $= \frac{\text{units of rate}}{\text{units of [ ]}}$ $= \frac{\text{mol dm}^{-3}\ \text{s}^{-1}}{\text{mol dm}^{-3}}$ $= \text{s}^{-1}$	units of k $= \frac{\text{units of rate}}{\text{units of [ ]}^2}$ $= \frac{\text{mol dm}^{-3}\ \text{s}^{-1}}{(\text{mol dm}^{-3})^2}$ $= \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$	units of k $= \frac{\text{units of rate}}{\text{units of [ ]}^3}$ $= \frac{\text{mol dm}^{-3}\ \text{s}^{-1}}{(\text{mol dm}^{-3})^3}$ $= \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$

Understanding: Catalysts alter a reaction mechanism, introducing a step with lower activation energy.

When a catalyst is added to a reaction it provides a different reaction pathway that has a lower activation energy (E_a). This means that the rate of reaction will be faster for a catalysed reaction.

Figure 16.4 *The potential energy profile for a catalysed and an uncatalysed reaction.*



16.2 Activation energy

Essential idea:

The activation energy of a reaction can be determined from the effect of temperature on reaction rate.

Understanding: The Arrhenius equation uses the temperature dependence of the rate constant to determine the activation energy.

Understanding: The frequency factor (or pre-exponential factor, *A*) takes into account the frequency of collisions with proper orientations.

The **Arrhenius equation** shows how the rate constant (k) for a reaction depends on temperature (T), in kelvin, and the activation energy (E_a):

$$k = Ae^{\frac{-E_a}{RT}}$$

where R is the universal gas constant, 8.31 $\mathrm{J\,K^{-1}\,mol^{-1}}$

- A is the **frequency factor** (or pre-exponential factor), which is the frequency of collisions that occur with the correct orientation for the reaction to happen.
- The units of A are the same as the units of k and depend on the order of the reaction.

Skill: Describing the relationships between temperature and rate constant, frequency factor, and complexity of molecules colliding.

From the Arrhenius equation the following relationships can be determined:

- $k \propto e^{\frac{-1}{T}}$: this means that the value of the rate constant (k) increases as the temperature (T) increases
- $k \propto A$: this means that the value of the rate constant (k) increases as the frequency factor (A) increases.

The value of A decreases as reactants increase in **complexity** and contain more atoms. When reactants contain more atoms the probability that the collision occurs with the correct orientation and happens at the **reactive site** of the molecule decreases.

Skill: Using the Arrhenius equation $k = Ae^{\frac{-E_a}{RT}}$

Worked example

The reaction

$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$

has an activation energy (E_a) of 1.0×10^2 kJ mol^{-1}. At 20 °C the rate constant $k = 2.0 \times 10^{-5}\ \mathrm{s^{-1}}$.

Use this information to determine the frequency factor (A) for this reaction at 20 °C.

Subject vocabulary

Arrhenius equation an equation that shows how the rate constant of a reaction depends on the activation energy and the temperature

frequency factor (also known as the pre-exponential factor) the frequency of collisions between reactant particles that occur with the correct orientation for the reaction to happen

reactive site the part of a molecule where the reaction happens

General vocabulary

complexity level of complication

Solution

To solve this problem:

E_a must be converted to J mol^{-1} because R has units of $\text{J K}^{-1}\,\text{mol}^{-1}$.

T must be converted to kelvin (K).

$$k = Ae^{\frac{-E_a}{RT}}$$

$$A = \frac{k}{e^{\frac{-E_a}{RT}}} = \frac{2.0 \times 10^{-5}\,\text{s}^{-1}}{e^{-\frac{1.0 \times 10^{5}\,\text{J mol}^{-1}}{8.314\,\text{J K}^{-1}\,\text{mol}^{-1} \times 293\,\text{K}}}} = 1.3 \times 10^{13}\,\text{s}^{-1}$$

Understanding: A graph of $\frac{1}{T}$ against ln k is a linear plot with gradient $\frac{-E_a}{R}$ and intercept ln A.

The Arrhenius equation $k = Ae^{\frac{-E_a}{RT}}$ can be converted to a linear form using logarithms:

$$k = Ae^{\frac{-E_a}{RT}}$$

$$\ln k = \left(\frac{-E_a}{R}\right)\frac{1}{T} + \ln A$$

This is in the form of the equation of a line ($y = mx + c$) so a graph of ln k vs $\frac{1}{T}$ will give a straight line with gradient = $\frac{-E_a}{R}$ and y intercept = ln A.

Skill: Determining and evaluating values of activation energy and frequency factors from data.

Skill: Analysing graphical representations of the Arrhenius equation in its linear form: ln $k = \frac{-E_a}{RT}$ + ln A

Worked example

The following data were obtained for the decomposition reaction of hydrogen iodide (HI) to hydrogen (H_2) and iodine (I_2).

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

Temperature /°C	Rate constant /$\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$	Temperature /°C	Rate constant /$\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$
283	3.52×10^{-7}	427	1.16×10^{-3}
356	3.02×10^{-5}	508	3.95×10^{-2}
393	2.19×10^{-4}		

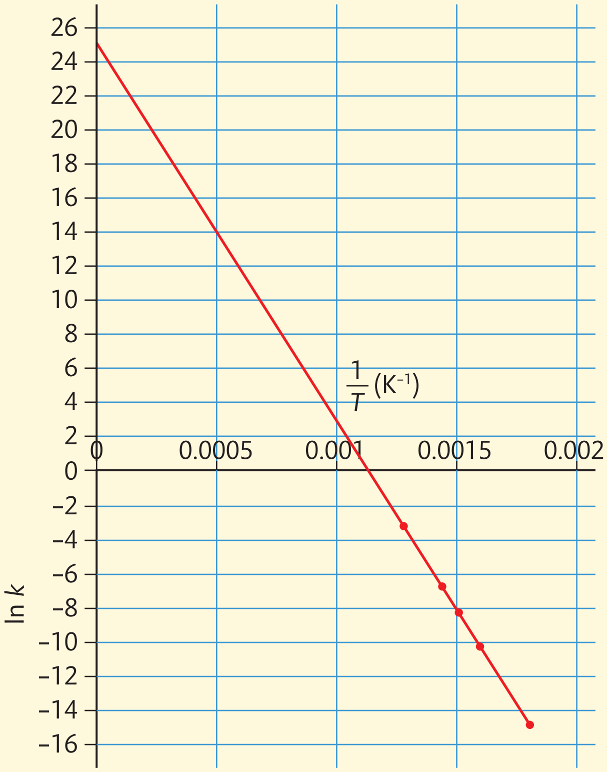
Use these data to determine the activation energy (E_a) and frequency factor (A) for the reaction.

Solution

Convert the data in the table and plot ln k vs $1/T$. (Note: the temperature must be converted from °C to kelvin.)

Temperature/°C	Temperature/K	$\frac{1}{T}$/K^{-1}	k/mol^{-1} dm^3 s^{-1}	ln k
283	556	1.80×10^{-3}	3.52×10^{-7}	−14.8
356	629	1.59×10^{-3}	3.02×10^{-5}	−10.4
393	666	1.50×10^{-3}	2.19×10^{-4}	−8.4
427	700	1.43×10^{-3}	1.16×10^{-3}	−6.8
508	781	1.28×10^{-3}	3.95×10^{-2}	−3.2

Plotting ln k vs $1/T$ gives:



The equation of the line shown in the graph can be determined using a graphing calculator:

$$\ln k = -2.24 \times 10^4 \times \frac{1}{T} + 25.3$$

$E_a = -R \times \text{gradient} = -8.31\,\text{J K}^{-1}\,\text{mol}^{-1} \times -2.24 \times 10^4\,\text{K}$

$= 1.86 \times 10^5\,\text{J mol}^{-1}$

$= 186\,\text{kJ mol}^{-1}$

y intercept = ln A = 25.3

$A = e^{25.3} = 9.72 \times 10^{10}\,\text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$

Topic 17: Equilibrium

17.1 The equilibrium law

Essential idea:

The position of equilibrium can be quantified by the equilibrium law. The equilibrium constant for a particular reaction only depends on the temperature.

Understanding: Le Châtelier's principle for changes in concentration can be explained by the equilibrium law.

Subject vocabulary

homogeneous equilibrium an equilibrium reaction in which all the reactants and products are in the same state

General vocabulary

quantify to make a numerical measurement of a quantity

Skill: Solution of homogeneous equilibrium problems using the expression for K_c.

The equilibrium law allows us to **quantify** the position of equilibrium.

The value of K_c for a particular reaction can be calculated from the equilibrium concentrations of reactants and products.

Worked example

Hydrogen can be prepared by the combination of carbon monoxide and water at 500 °C. At equilibrium the concentrations in the reaction mixture were found to be:

$[CO]$ 0.150 mol dm^{-3} $[H_2O]$ 0.0145 mol dm^{-3}

$[H_2]$ 0.200 mol dm^{-3} $[CO_2]$ 0.0200 mol dm^{-3}

Calculate the equilibrium constant for the reaction at this temperature.

Solution

First write the equation for the reaction, making sure it is correctly balanced:

$$CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g)$$

Next write the equilibrium expression:

$$K_c = \frac{[H_2][CO_2]}{[CO][H_2O]}$$

Now substitute the given values for each component:

$$K_c = \frac{(0.200)(0.0200)}{(0.150)(0.0145)} = 1.84$$

Hints for success: Equilibrium constants do not have units.

Hints for success:
ICE stands for:
Initial
Change
Equilibrium

The ICE method can be used to calculate K_c using initial and equilibrium concentrations.

1 Write the balanced equation.

2 Under the equation, write in the values of the concentrations of each component using three rows: *initial*, *change*, and *equilibrium*.

- *Initial* represents the concentration originally placed in the flask; unless stated otherwise, we assume the initial product concentration is zero.

- *Change* represents the amount that reacts to reach equilibrium. A minus sign for reactants represents a decrease in concentration as they are used up, and a plus sign for products represents an increase in concentration as they form. The changes that occur must be in the same ratio as the coefficients in the balanced equation, so if we know one of the change values we can deduce the others.
- *Equilibrium* is the concentration present in the equilibrium mixture. This can be calculated by applying the amount of change to the initial concentration for each component.

  equilibrium concentration = initial concentration ± change in concentration

3 Write the expression for K_c from the balanced equation. Substitute the values for equilibrium concentration and calculate K_c.

Worked example

A student placed 0.20 mol of $PCl_3(g)$ and 0.10 mol of $Cl_2(g)$ into a 1.0 dm^3 flask at 350 °C. The reaction, which produced PCl_5, was allowed to come to equilibrium, at which time it was found that the flask contained 0.12 mol of PCl_3. What is the value of K_c for this reaction?

Solution

1 Write the equation for the reaction.

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$$

2 Insert the data under the equation in the three rows for initial, change, and equilibrium. In this example, the numbers in black are data that were given in the question and numbers in blue have been **derived** as explained below.

Synonyms

derived .... calculated

	$PCl_3(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$PCl_5(g)$
initial (mol dm^{-3})	0.20		0.10		0.00
change (mol dm^{-3})	−0.08		−0.08		+0.08
equilibrium (mol dm^{-3})	0.12		0.02		0.08

The change in concentration of PCl_3, the amount that reacted to reach equilibrium, is 0.20 − 0.12 = 0.08. It is given a minus sign to show that the concentration decreases by this amount. As PCl_3 and Cl_2 react in a 1 : 1 ratio and form a 1 : 1 ratio with PCl_5, the same change in concentration must apply to Cl_2 and PCl_5. The equilibrium concentrations are calculated by applying the change amount to the initial values.

3 $$K_c = \frac{[PCl_5]}{[PCl_3]\,[Cl_2]} = \frac{0.08}{0.12 \times 0.02} = 33$$

Equilibrium concentrations can be calculated using K_c.

Worked example

The reaction:

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

has K_c = 0.500 at 350 K. If the concentrations at equilibrium are:

[CO] 0.200 mol dm^{-3}

$[H_2]$ 0.155 mol dm^{-3}

what is the equilibrium concentration of CH_3OH?

Solution

Write the equilibrium expression:

$$K_c = \frac{[CH_3OH]}{[CO]\,[H_2]^2}$$

Substitute the data from the question and solve the equation to give the unknown concentration.

$$0.500 = \frac{[CH_3OH]}{(0.200)\,(0.155)^2}$$

Therefore $[CH_3OH] = 0.00240\ mol\,dm^{-3}$ or $2.40 \times 10^{-3}\ mol\,dm^{-3}$

Equilibrium concentrations can be calculated using initial concentrations when K_c is very small.

When K_c is very small, the change in concentration of reactants and products (x) will also be very small:

$$[A]_{equilibrium} = [A]_{initial} - x \approx [A]_{initial}$$

Worked example

The thermal decomposition of water has a very small value of K_c. At 1000 °C, $K_c = 7.3 \times 10^{-18}$ for the reaction

$$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$$

A reaction is set up at this temperature with an initial H_2O concentration of $0.10\ mol\,dm^{-3}$. Calculate the H_2 concentration at equilibrium.

Solution

We need to know the change in concentration of H_2, so we could assign this as x. But from the stoichiometry of the reaction, this would make change in $[O_2] = \frac{1}{2}x$. So it will make the calculation easier if we proceed as follows:

let change in concentration of $H_2 = 2x$

therefore change in concentration of $O_2 = x$

so change in concentration of $H_2O = -2x$ (due to the 2 : 2 : 1 stoichiometry)

Insert the relevant data from the question under the equation.

	$2H_2O(g)$	$\rightleftharpoons$	$2H_2(g)$	+	$O_2(g)$
initial ($mol\ dm^{-3}$)	0.10		0.00		0.00
change ($mol\ dm^{-3}$)	$-2x$		$+2x$		$+x$
equilibrium ($mol\ dm^{-3}$)	$0.10 - 2x$		$2x$		x
	≈ 0.10				

The approximation $[H_2O]_{initial} \approx [H_2O]_{equilibrium}$ follows from the very small value of K_c.

Write the equilibrium expression and substitute the equilibrium concentrations.

$$K_c = \frac{[H_2]^2[O_2]}{[H_2O]^2} = \frac{(2x)^2\,x}{(0.10)^2} = 7.3 \times 10^{-18}$$

This can now be solved for x.

$$4x^3 = (7.3 \times 10^{-18})(0.010) = 7.3 \times 10^{-20}$$

$$x = 2.6 \times 10^{-7}$$

The equilibrium concentration of H_2 can now be calculated.

$$[H_2]_{equilibrium} = 2x = 5.2 \times 10^{-7}\ mol\,dm^{-3}$$

Understanding: The position of equilibrium corresponds to a **maximum** value of entropy and a **minimum** in the value of Gibbs free energy.

Understanding: The Gibbs free energy change of a reaction and the equilibrium constant can both be used to measure the position of an equilibrium reaction and are related by the equation $\Delta G^\ominus = -RT\ln K$.

General vocabulary

maximum	the largest value
minimum	the smallest value

$\Delta G^\ominus$ is the difference in Gibbs free energy between the products and reactants under standard conditions. It is measured in $\mathrm{kJ\,mol^{-1}}$.

$\Delta G^\ominus = G^\ominus(\text{products}) - G^\ominus(\text{reactants})$

The total Gibbs free energy of the reaction mixture can be calculated *for any stage* of the reaction:

total Gibbs free energy = Gibbs free energy of reactants present + Gibbs free energy of products present

The minimum in the total Gibbs free energy occurs:

- at the maximum entropy of the reaction mixture
- at the equilibrium position of the reaction.

Skill: Relationship between $\Delta G^\ominus$ and the equilibrium constant.

From Figures 17.1 and 17.2 we can see that the position of equilibrium is related to $\Delta G^\ominus$.

If $\Delta G^\ominus$ is negative:

- the minimum in total Gibbs free energy is positioned closer to the right of the graph where there are more products than reactants
- the equilibrium mixture contains more products than reactants
- the equilibrium constant is greater than 1 ($K_c > 1$).

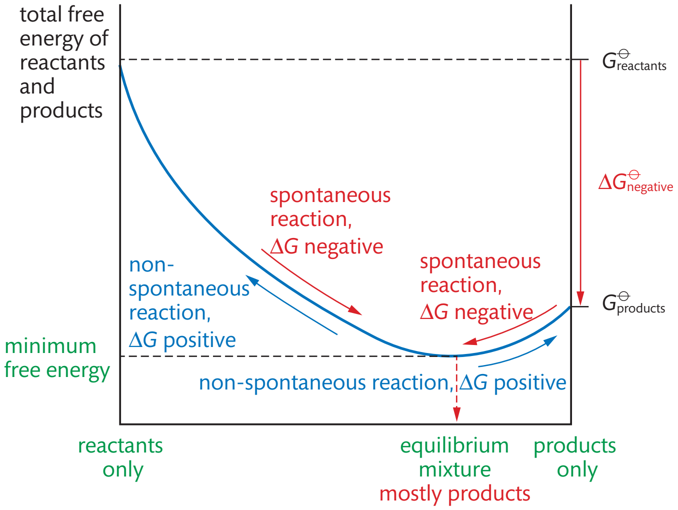
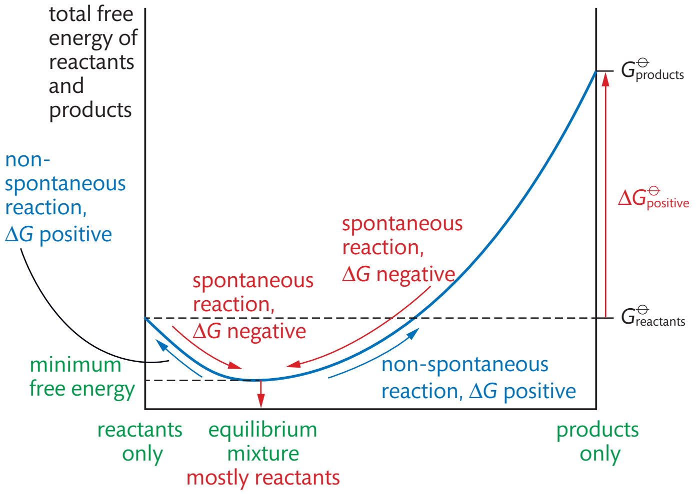


Figure 17.1 *The change in total Gibbs free energy during a reaction with negative $\Delta G^\ominus$.*

If $\Delta G^\ominus$ is positive:

- the minimum in total Gibbs free energy is positioned closer to the left of the graph where there are more reactants than products
- the equilibrium mixture contains more reactants than products
- the equilibrium constant is less than 1 ($K_c < 1$).

Figure 17.2 *The change in total Gibbs free energy during a reaction with positive* $\Delta G^\ominus$.



Hints for success: When using $\Delta G^\ominus = -RT\ln K_c$ the value of $\Delta G^\ominus$ must be converted from $kJ\,mol^{-1}$ to $J\,mol^{-1}$ to be consistent with the units of R ($J\,K^{-1}\,mol^{-1}$).

The relationship between $\Delta G^\ominus$ and K_c is given by the equation:

$$\Delta G^\ominus = -RT\ln K_c$$

where R is the universal gas constant ($8.31\,J\,K^{-1}\,mol^{-1}$), T is the temperature in kelvin (K), and K_c is the equilibrium constant for the reaction.

Skill: Calculations using the equation $\Delta G^\ominus = -RT\ln K$.

Worked example

The reaction between nitrogen (N_2) and hydrogen (H_2) to form ammonia (NH_3) is an equilibrium reaction. At 298 K the value of K_c is 1.45×10^{-6}.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Use this information to determine the value of the standard change in Gibbs free energy ($\Delta G^\ominus$) for this reaction at 298 K.

Solution

$$\Delta G^\ominus = -RT\ln K_c$$

$$= -8.31\,J\,K^{-1}\,mol^{-1} \times 298\,K \times \ln(1.45 \times 10^{-6})$$

$$= -33\,300\,J\,mol^{-1}$$

$$= -33.3\,kJ\,mol^{-1}$$

Worked example

The esterification reaction that produces ethyl ethanoate has a free energy change $\Delta G^\ominus = -4.38\,kJ\,mol^{-1}$.

$CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(aq)$

Calculate the value of the equilibrium constant of this reaction at 298 K.

Solution

$$\Delta G^\ominus = -RT\ln K_c$$

$$\Delta G^\ominus = -4.38\,kJ\,mol^{-1} = -4.38 \times 1000\,J\,mol^{-1}$$

$$\therefore\ -4.38 \times 1000\,J\,mol^{-1} = -(8.31\,J\,K^{-1}\,mol^{-1}) \times (298\,K) \times \ln K_c$$

$$\ln K_c = \frac{-4380\,J\,mol^{-1}}{2476\,J\,mol^{-1}} = 1.77$$

$$\therefore\ K_c = e^{1.77} = 5.9$$

Topic 18: Acids and bases

18.1 Lewis acids and bases

Essential idea:

The acid–base concept can be extended to reactions that do not involve proton transfer.

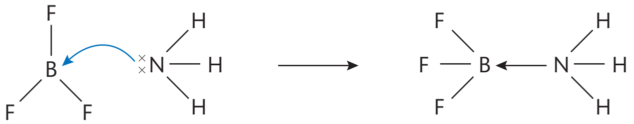
Understanding: A Lewis acid is a lone pair acceptor and a Lewis base is a lone pair donor.

The Lewis theory of acids and bases is based on the donation of a lone pair of electrons:

- a **Lewis base** *donates* the lone pair of electrons
- a **Lewis acid** *accepts* the lone pair of electrons.

Understanding: When a Lewis base reacts with a Lewis acid a coordinate bond is formed.

A **coordinate bond** is formed when one compound donates both of the electrons to form a covalent bond. Because a Lewis base donates a *pair* of electrons to a Lewis acid, the bond that forms is a coordinate bond.



electron pair acceptor

Lewis acid

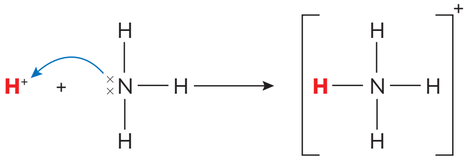
electron pair donor

Lewis base

coordinate bond

the direction of the arrow shows that N donates the electron pair to B

Brønsted–Lowry acids and bases are also Lewis acids and bases:



electron pair acceptor/ Lewis acid

proton donor/ Brønsted–Lowry acid

electron pair donor/ Lewis base

proton acceptor/ Brønsted–Lowry base

Understanding: A nucleophile is a Lewis base and an electrophile is a Lewis acid.

Nucleophiles and **electrophiles** are terms used to describe chemical species based on their reactivity.

Subject vocabulary

Lewis base a substance that is an electron pair donor

Lewis acid a substance that is an electron pair acceptor

coordinate bond (also known as a dative bond) a covalent bond in which one atom donates both of the electrons that are shared in the bond

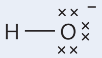
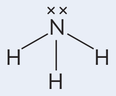
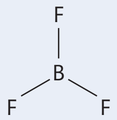
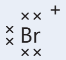
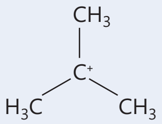
Subject vocabulary

nucleophiles electron-rich species that can act as Lewis bases and donate electron pairs to form coordinate bonds

electrophiles electron-poor species that can act as Lewis acids and accept electron pairs to form coordinate bonds

Hints for success: Reactions involving nucleophiles and electrophiles are discussed in Chapter 10.

Skill: Application of the Lewis acid-base theory to inorganic and organic chemistry to identify the role of the reacting species.

Nucleophiles	Electrophiles
Electron-rich species Donate electron pairs to form coordinate bonds Are Lewis bases	Electron-poor species Accept electron pairs to form coordinate bonds Are Lewis acids
Examples: OH^-, NH_3, Cl^-   	Examples: BF_3, Br^+, $(CH_3)_3C^+$   

18.2 Calculations involving acids and bases

Essential idea:

The equilibrium law can be applied to acid–base reactions. Numerical problems can be simplified by making assumptions about the relative concentrations of the species involved. The use of logarithms is also significant here.

Understanding: The expression for the dissociation constant of a weak acid (K_a) and a weak base (K_b).

For a weak acid, HA:

$HA(aq) + H_2O(l) \rightleftharpoons A^-(aq) + H_3O^+(aq)$

The equilibrium expression for this reaction is:

$$K_a = \frac{[A^-][H_3O^+]}{[HA]}$$

- $[H_2O]$ is not included in the expression because it is a constant.
- K_a is known as the **acid dissociation constant**.

Hints for success: Like all equilibrium constants, acid dissociation constants and base dissociation constants do not have units.

For a weak base, B:

$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

The equilibrium expression for this reaction is:

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

- $[H_2O]$ is not included in the expression because it is a constant.
- K_b is known as the **base dissociation constant**.

Subject vocabulary

acid dissociation constant a measure of the strength of a weak acid that relates the equilibrium concentrations of the weak acid and its conjugate base in solution

base dissociation constant a measure of the strength of a weak base that relates the equilibrium concentration of the weak base and its conjugate acid in solution

Understanding: For a conjugate acid–base pair, $K_a \times K_b = K_w$.

For the conjugate acid–base pair HA/A^-:

$$K_a(HA) = \frac{[A^-][H_3O^+]}{[HA]} \qquad K_b(A^-) = \frac{[HA][OH^-]}{[A^-]}$$

$$K_a(HA) \times K_b(A^-) = \frac{\cancel{[A^-]}[H_3O^+]}{\cancel{[HA]}} \times \frac{\cancel{[HA]}[OH^-]}{\cancel{[A^-]}}$$

$$= [H_3O^+][OH^-]$$

$$= K_w$$

This relationship is true for any conjugate acid–base pair: $K_a(HA) \times K_b(A^-) = K_w$.

Example: NH_4^+/NH_3: $K_a(NH_4^+) \times K_b(NH_3) = K_w$

The value of K_w changes with temperature. This means that the $[H^+]$ and pH of a neutral solution also change with temperature:

Temperature / °C	K_w	[H⁺] in pure water ($\sqrt{K_w}$)	pH of pure water ($-\log_{10}[H^+]$)
0	1.5×10^{-15}	0.39×10^{-7}	7.47
10	3.0×10^{-15}	0.55×10^{-7}	7.27
20	6.8×10^{-15}	0.82×10^{-7}	7.08
25	1.0×10^{-14}	1.00×10^{-7}	7.00
30	1.5×10^{-14}	1.22×10^{-7}	6.92
40	3.0×10^{-14}	1.73×10^{-7}	6.77
50	5.5×10^{-14}	2.35×10^{-7}	6.63

Understanding: The relationship between K_a and pK_a is $pK_a = -\log K_a$ and between K_b and pK_b is $pK_b = -\log K_b$.

Logarithms are used to convert K_a and K_b values to numbers that are easier to compare:

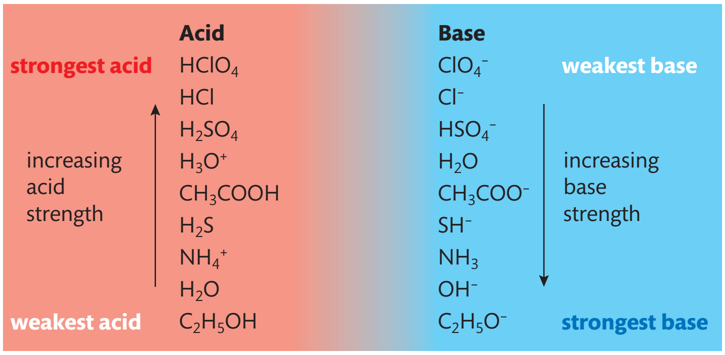
- $pK_a = -\log_{10} K_a$ $\qquad K_a = 10^{-pK_a}$
- $pK_b = -\log_{10} K_b$ $\qquad K_b = 10^{-pK_b}$

For a conjugate acid–base pair:

$pK_a(HA) + pK_b(A^-) = 14.00$

Skill: Discussion of the relative strengths of acids and bases using values of K_a, pK_a, K_b, and pK_b.

An inverse relationship exists between the strength of a weak acid and the strength of its conjugate base.



Acid	Base
$HClO_4$	ClO_4^-
HCl	Cl^-
H_2SO_4	HSO_4^-
H_3O^+	H_2O
CH_3COOH	CH_3COO^-
H_2S	SH^-
NH_4^+	NH_3
H_2O	OH^-
C_2H_5OH	$C_2H_5O^-$

Figure 18.1 *The relative strengths of some acids and their conjugate bases in aqueous solution.*

Skill: Solution of problems involving [$H^+(aq)$], [$OH^-(aq)$], pH, pOH, K_a, pK_a, K_b, and pK_b.

Problems involving acid and base equilibria can be solved using the same methods used for equilibrium problems.

The following points are to remind you of some key points and guide you in all the calculations that follow:

- The given concentration of an acid or base is its *initial* concentration – before dissociation occurs.
- The pH (or pOH) of a solution refers to the concentration of H^+ ions (or OH^- ions) at *equilibrium*.
- The concentration values substituted into the expressions for K_a and K_b must be the *equilibrium* values for all reactants and products.
- When the extent of dissociation is very small (very low value for K_a or K_b) it is appropriate to use the approximations:

$$[\text{acid}]_{\text{initial}} \approx [\text{acid}]_{\text{equilibrium}}$$

$$[\text{base}]_{\text{initial}} \approx [\text{base}]_{\text{equilibrium}}$$

Calculating K_a from initial and equilibrium concentrations

Worked example

Calculate K_a at 298 K for a 0.01 mol dm^{-3} solution of ethanoic acid (CH_3COOH). It has a pH of 3.4 at this temperature.

Solution

Write the equation for the dissociation of the acid. Insert the data in three rows: initial, change, and equilibrium. As in Chapter 17, numbers in black are data that were given in the question, numbers in blue have been derived.

From the pH we get the [H^+] at equilibrium:

pH 3.4 $\Rightarrow [H^+] = 10^{-3.4} = 4.0 \times 10^{-4}$ mol dm^{-3}

From the stoichiometry of the reaction we know that $[H^+] = [CH_3COO^-]$

	$CH_3COOH(aq)$	$\rightleftharpoons$	$CH_3COO^-(aq)$	+	$H^+(aq)$
initial (mol dm^{-3})	0.01		0.00		0.00
change (mol dm^{-3})	-4.0×10^{-4}		$+4.0 \times 10^{-4}$		$+4.0 \times 10^{-4}$
equilibrium (mol dm^{-3})	$0.01 - (4.0 \times 10^{-4})$ ≈ 0.01		4.0×10^{-4}		4.0×10^{-4}

The approximation $0.01 \approx 0.01 - (4.0 \times 10^{-4})$ is valid within the precision of this data.

Write the expression for K_a and substitute the equilibrium values.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(4.0 \times 10^{-4})^2}{0.01} = 1.6 \times 10^{-5}$$

Calculating K_b from initial and equilibrium concentrations

Worked example

Calculate the K_b for a 0.100 mol dm^{-3} solution of methylamine, CH_3NH_2, at 25 °C . Its pH is 11.80 at this temperature.

Solution

At 25 °C (298 K), pH + pOH = 14.00. Therefore pH 11.80 $\Rightarrow$ pOH = 2.20

$[OH^-] = 10^{-pOH} = 10^{-2.20} = 6.3 \times 10^{-3}$ mol dm^{-3}

From the stoichiometry of the reaction $[OH^-] = [CH_3NH_3^+]$

	$CH_3NH_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CH_3NH_3^+(aq)$	+	$OH^-(aq)$
initial (mol dm^{-3})	0.100				0.000		0.000
change (mol dm^{-3})	−0.0063				+0.0063		+0.0063
equilibrium (mol dm^{-3})	0.0937				0.00630		0.00630

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} = \frac{(0.0063)^2}{0.0937} = 4.24 \times 10^{-4}$$

Calculating pH using K_a and initial concentration

Worked example

A 0.75 mol dm^{-3} solution of ethanoic acid has a value for $K_a = 1.8 \times 10^{-5}$ at a specified temperature. What is its pH at this temperature?

Solution

To calculate pH we need to know $[H^+]$ at equilibrium, and therefore the amount of dissociation of the acid that has occurred: this is the 'change' amount in the reaction.

So let the change in concentration of $CH_3COOH = -x$

Therefore change in concentration of CH_3COO^- and $H^+ = +x$

	$CH_3COOH(aq)$	$\rightleftharpoons$	$CH_3COO^-(aq)$	+	$H^+(aq)$
initial (mol dm^{-3})	0.75		0.00		0.00
change (mol dm^{-3})	$-x$		$+x$		$+x$
equilibrium (mol dm^{-3})	$0.75 - x$		x		x
	≈ 0.75				

As K_a is very small, x, the amount of dissociation, is also extremely small and it is valid to approximate $[CH_3COOH]_{initial} \approx [CH_3COOH]_{equilibrium}$.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x^2}{0.75} = 1.8 \times 10^{-5}$$

Therefore $x = \sqrt{1.8 \times 10^{-5} \times 0.75} = 3.7 \times 10^{-3}$

$[H^+] = 3.7 \times 10^{-3} \Rightarrow$ pH = 2.4

Calculating pH using K_b and initial concentration

Worked example

A 0.20 mol dm^{-3} aqueous solution of ammonia has K_b of 1.8×10^{-5} at 298 K .
What is its pH?

Solution

Let the change in concentration of $NH_3 = -x$

Therefore change in concentration of NH_4^+ and $OH^- = +x$

	$NH_3(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	+	$OH^-(aq)$
initial (mol dm^{-3})	0.20				0.00		0.00
change (mol dm^{-3})	$-x$				$+x$		$+x$
equilibrium (mol dm^{-3})	$0.20 - x$ ≈ 0.20				x		x

As K_b is very small, x, the amount of dissociation, is also extremely small, and so it is valid to approximate $[NH_3]_{initial} \approx [NH_3]_{equilibrium}$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.20} = 1.8 \times 10^{-5}$$

Therefore $x = \sqrt{1.8 \times 10^{-5} \times 0.20} = 1.9 \times 10^{-3}$

$[OH^-] = 1.9 \times 10^{-3}$

$pOH = -\log_{10}(1.9 \times 10^{-3}) = 2.72$

Therefore at 298 K, pH = 14.00 – 2.72 = 11.28

18.3 pH curves

Essential idea:

pH curves can be investigated experimentally but are mathematically determined by the dissociation constants of the acid and base. An indicator with an appropriate end-point can be used to determine the **equivalence point** of the reaction.

Subject vocabulary

equivalence point where stoichiometricallly equal amounts of acid and base have neutralized each other

buffer solutions solutions that resist any change in pH when small amounts of acid or base are added

General vocabulary

composition make-up, ingredients

Understanding: The **composition** and action of a buffer solution.

Buffer solutions:

- show little change in pH when small amounts of acid or base are added to them
- contain a conjugate pair of a weak acid/base.

Skill: While the nature of the acid-base buffer always remains the same, buffer solutions can be prepared by either mixing a weak acid/base with a solution of a salt containing its conjugate, or by partial neutralization of a weak acid/base with a strong acid/base.

Buffers can be prepared in two different ways:

- mixing a weak acid (or base) with the salt of its conjugate base (or acid)
- adding base (acid) to a weak acid (base) and converting some of the weak acid (base) to its conjugate base (acid).

Both methods will result in a buffer solution of the same nature being formed, as the solution made will contain the same conjugate acid–base pair.

Buffers

Acidic buffers (pH < 7)	Basic buffers (pH > 7)
Made by:	Made by:
• mixing a weak acid with a salt of its conjugate base	• mixing a weak base with a salt of its conjugate acid
OR	OR
• converting some of a weak acid to its conjugate base by adding strong base.	• converting some of a weak base to its conjugate acid by adding strong acid.

Mixing equal amounts of ethanoic acid (CH_3COOH) and sodium ethanoate ($NaCH_3COO$) creates an acidic buffer solution. An acid–base equilibrium exists between the CH_3COOH and CH_3COO^-:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

Adding H^+ to the solution will shift the equilibrium to the left and the excess H^+ is accepted by the CH_3COO^- and removed from the solution:

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

Adding OH^- to the solution removes H^+ and shifts the equilibrium to the right. The H^+ that is removed by the OH^- is replaced by the dissociation of CH_3COOH:

$$CH_3COOH \rightarrow CH_3COO^- + H^+$$

The $[H^+]$ and pH change very little because of these buffering reactions that remove excess H^+ or replace H^+ that is depleted.

Skill: Prediction of the relative pH of aqueous salt solutions formed by the different combinations of strong and weak acid and base.

The pH of a salt solution depends on the acid–base properties of the cations and anions.

Neutralization reaction	Example of parent acid and base	Salt formed	Acid–base properties of ions	Type of salt solution	pH of salt solution
strong acid and strong base	$HCl(aq) + NaOH(aq)$	$NaCl(aq)$	both ions have no acid–base reaction	neutral	7
weak acid and strong base	$CH_3COOH(aq) + NaOH(aq)$	$NaCH_3COO(aq)$	anion is a weak base; $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$	basic	>7
strong acid and weak base	$HCl(aq) + NH_3(aq)$	$NH_4Cl(aq)$	cation is a weak acid; $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$	acidic	<7
weak acid and weak base	$CH_3COOH(aq) + NH_3(aq)$	$NH_4CH_3COO(aq)$	anion is a base and cation is an acid	depends on K_a(cation) and K_b(anion)	depends on K_a(cation) and K_b(anion)

Understanding: The characteristics of pH curves produced by different combinations of strong and weak acids and bases.

Understanding: The buffer region on the pH curve represents the region where small additions of acid or base result in little or no change in pH.

The changes in pH that happen during an acid–base titration can be monitored using a pH meter. **pH curves** are the graphs of pH against volume of solution added during a titration and they have different shapes for the following combinations:

- strong acid and strong base
- weak acid and strong base
- strong acid and weak base
- weak acid and weak base.

The equivalence point is where stoichiometrically equivalent amounts of acid and base have been combined. The equivalence point can be determined in pH curves from the **point of inflection**.

Skill: The general shapes of graphs of pH against volume for titrations involving strong and weak acids and bases, with an explanation of their important features.

Subject vocabulary

pH curves graphs of pH against volume of acid or base added in an acid–base titration

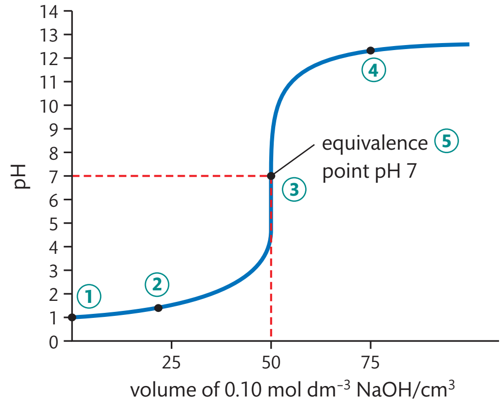
General vocabulary

point of inflection a point on a graph where the shape of the curve changes from concave to convex

1 Titration of a strong acid and a strong base

Figure 18.2 *Titration curve for strong acid–strong base.*

pH curve for the titration of 50.0 cm^3 of 0.10 mol dm^{-3} HCl with 0.10 mol dm^{-3} NaOH



The following points can be deduced from the graph:

① initial pH = 1 (pH of 0.10 mol dm^{-3} HCl)

② pH changes only gradually until equivalence

③ very sharp jump in pH at equivalence: from pH 3 to pH 11

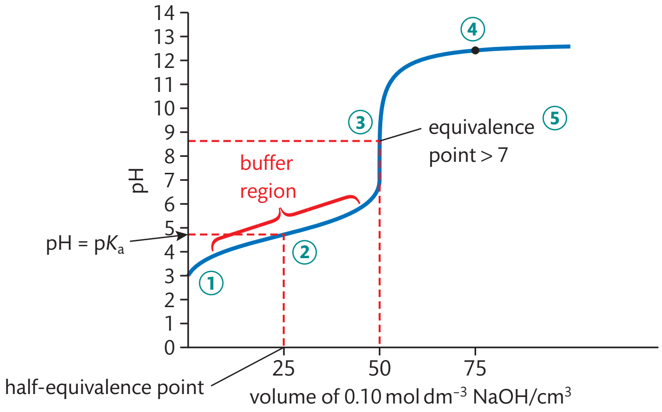
④ after the equivalence point the curve flattens out at a high value (pH of strong base).

⑤ *pH at equivalence = 7*

2 Titration of a weak acid and a strong base

Figure 18.3 *Titration curve for weak acid–strong base.*

pH curve for the titration of 50.0 cm^3 of 0.10 mol dm^{-3} CH_3COOH with 0.10 mol dm^{-3} NaOH



The following points can be deduced from the graph:

① pH > 1 (pH of 0.10 mol dm^{-3} weak acid)

② Addition of the strong base converts some of the weak acid to its conjugate base and creates a buffer. pH stays almost constant through the buffer region where both HA and A$^-$ are present. At half-equivalence point (25.0 cm^3); pH = pK_a

③ jump in pH at equivalence from about pH 7.0 to 11.0, which is not as much of a jump as for a strong acid–strong base titration

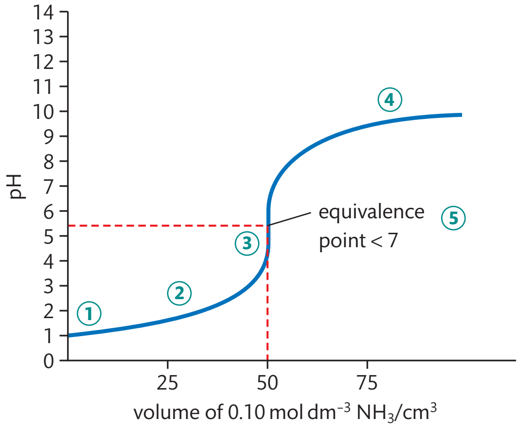
④ after the equivalence point the curve flattens out at a high value (pH of strong base).

⑤ *pH at equivalence is > 7*

3 Titration of a strong acid and a weak base

pH curve for the titration of 50.0 cm^3 of 0.10 mol dm^{-3} HCl with 0.10 mol dm^{-3} NH_3

Figure 18.4 *Titration curve for strong acid–weak base.*



The following points can be deduced from the graph:

① initial pH = 1 (pH of 0.10 mol dm^{-3} HCl)

② pH stays relatively constant through the buffer region to equivalence

③ jump in pH at equivalence from about pH 3.0 to 7.0

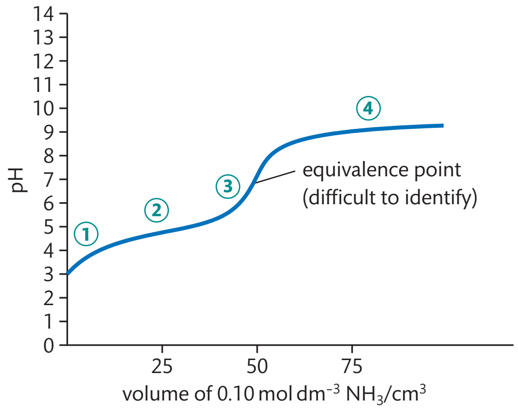
④ after the equivalence point the curve flattens out at a fairly low pH (pH of weak base).

⑤ *pH at equivalence is < 7*

4 Titration of a weak acid and a weak base

pH curve for the titration of 50.0 cm^3 of 0.10 mol dm^{-3} CH_3COOH with 0.10 mol dm^{-3} NH_3

Figure 18.5 *Titration curve for weak acid–weak base.*



The following points can be deduced from the graph:

① pH > 1 (pH of 0.10 mol dm^{-3} weak acid)

② addition of base causes the pH to rise steadily

③ change in pH at the equivalence point is much less sharp than in the other titrations

④ after the equivalence point the curve flattens out at a fairly low pH (pH of weak base).

⑤ *pH at equivalence point is difficult to determine*

Understanding: An acid–base indicator is a weak acid or a weak base for which the components of the conjugate acid–base pair have different colours.

Indicators are weak acids or weak bases. The acid (HIn) has a different colour to the conjugate base (In^-):

$$HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq)$$

Colour A Colour B

Figure 18.6 *Methyl orange indicator changes colour when added to an acid or alkali. It turns red in acid (left) and yellow in alkali (right).*

Understanding: The relationship between the pH range of an acid–base indicator that is a weak acid and its pK_a value.

The acid dissociation constant of an indicator is:

$$K_a = \frac{[H^+][In^-]}{[HIn]}$$

When $[HIn] = [In^-]$: $K_a = [H^+]$ and $pH = pK_a(HIn)$

The colour of a solution containing an indicator depends on pH:

pH	[HIn]	Colour of solution
$pH < pK_a$	$[HIn] > [In^-]$	Colour of HIn
$pH = pK_a$	$[HIn] = [In^-]$	Mix of HIn and In^-
$pH > pK_a$	$[HIn] < [In^-]$	Colour of In^-

A distinct colour change is observed over a small **pH range** for any indicator. Different indicators have different pH ranges where the colour change occurs because they have different pK_a values.

Subject vocabulary

pH range (for indicators) the pH range at which an intermediate colour is observed because both the indicator and its conjugate base are present

Hints for success: The colours, pK_a, and pH ranges of various indicators are given in section 22 of the IB data booklet.

Skill: Selection of an appropriate indicator for a titration, given the equivalence point of the titration and the end-point of the indicator.

If an indicator is added to an acid–base titration, the **end-point** is observed when the colour of the solution changes.

If an appropriate indicator is used, the end-point will be the same as the equivalence point.

The steps for determining the appropriate indicator for an acid–base titration are:

- determine which combination of acid and base is reacting
- based on the graph of this combination estimate the pH values for the steep portion of the curve that occurs around the equivalence point
- choose an indicator with a pH range that lies within the steep portion of the pH curve.

Reactants in titration	pH range at equivalence	Example of suitable indicators	pK_a	pH range of indicator and colour change
strong acid + strong base	3–11	phenolphthalein	9.50	8.2–10.0; colourless to pink
		methyl orange	3.46	3.2–4.4; red to yellow
weak acid + strong base	7–11	phenolphthalein	9.50	8.2–10.0; colourless to pink
		phenol red	8.00	6.6–8.0; yellow to red
strong acid + weak base	3–7	methyl orange	3.46	3.2–4.4; red to yellow
		bromophenol blue	4.10	3.0–4.6; yellow to blue
weak acid + weak base	this combination of acid and base does not give a significant change in pH at equivalence, so there is no suitable indicator to use here			

Subject vocabulary

end-point the volume of acid (or base) added when the indicator first changes colour in an acid–base titration

Topic 19: Redox processes

19.1 Electrochemical cells

Essential idea:

Energy conversions between electrical and chemical energy lie at the core of electrochemical cells.

Understanding: A voltaic cell generates an electromotive force (EMF) resulting in the movement of electrons from the anode (negative electrode) to the cathode (positive electrode) via the external circuit. The EMF is termed the cell potential ($E^{\ominus}$).

The **electromotive force** (EMF) of a voltaic cell:

- is also known as the cell potential
- is the **potential difference** between the anode and cathode
- has the symbol E ($E^{\ominus}$ is used for standard conditions)
- changes with different combinations of half-cells.

Subject vocabulary

electromotive force the voltage generated by any source of electrical energy

potential difference the difference in voltage between the anode and cathode in a cell

standard hydrogen electrode a reference half-cell that is used to measure the electrode potentials of other half-cells

electrode potential the EMF that is generated by a half-cell when it is connected to the standard hydrogen electrode

standard conditions a set of consistent reaction conditions that is used when measuring cell potentials

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Understanding: The standard hydrogen electode (SHE) consists of an inert platinum electrode in contact with 1 mol dm^{-3} hydrogen ion and hydrogen gas at 100 kPa and 298 K. The standard electrode potential ($E^{\ominus}$) is the potential (voltage) of the reduction half-equation under standard conditions measured relative to the SHE. Solute concentration is 1 mol dm^{-3} or 100 kPa for gases. The $E^{\ominus}$ of the SHE is 0 V.

The **standard hydrogen electrode** (SHE):

- is a half-cell that can be combined with other half-cells to make a voltaic cell
- is used as a reference half-cell
- has a standard **electrode potential** of 0 V
- has a redox equilibrium between aqueous H^+ ions and $H_2(g)$:

  $2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$
- uses an inert platinum electrode
- uses **standard conditions**.

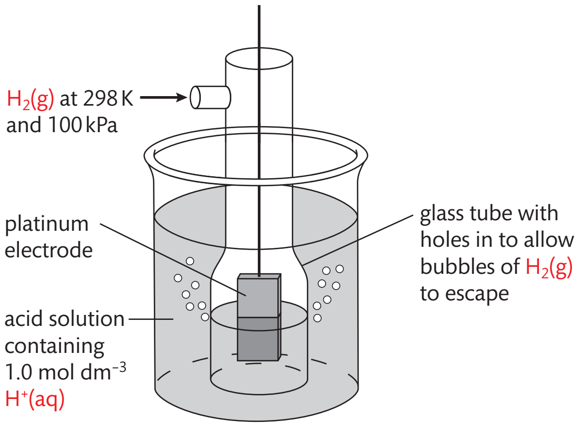


Figure 19.1 *The standard hydrogen electrode (SHE).*

Electrode potentials are affected by temperature, concentration, and pressure. This means that a standard set of conditions must be used when measuring electrode potentials.

Standard conditions for electrochemical cells are:

- a concentration of 1.0 mol dm^{-3} for all solutions
- a pressure of 100 kPa for all gases
- a temperature of 298 K
- a platinum electrode if the half-cell does not include a metal.

The **standard electrode potential** ($E^{\ominus}$) of a half-cell is the EMF that is measured when it is connected to a SHE to make a voltaic cell under standard conditions.

Subject vocabulary

standard electrode potential the EMF that is generated by a half-cell when it is connected to the standard hydrogen electrode under standard conditions

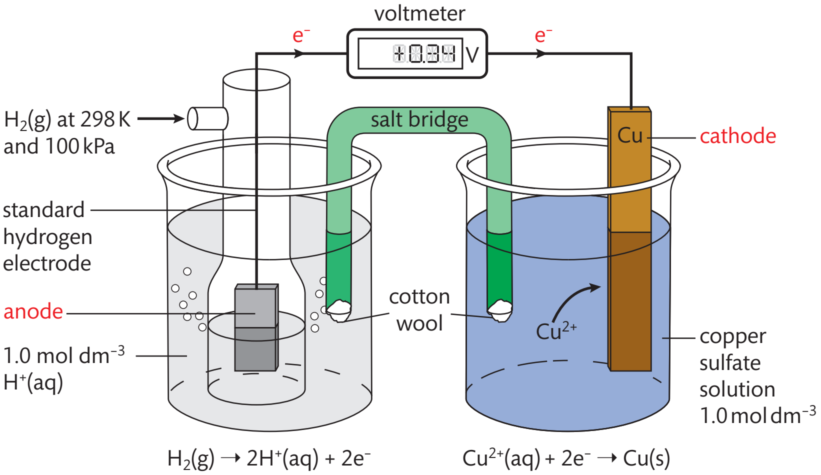


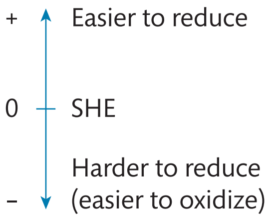
Figure 19.2 *Measuring the standard electrode potential for $Cu^{2+}(aq)/Cu(s)$.*

$E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{half-cell}} - E^{\ominus}_{\text{SHE}}$

Because $E^{\ominus}_{\text{SHE}} = 0$, $E^{\ominus}_{\text{cell}} = E^{\ominus}_{\text{half-cell}}$

$E^{\ominus}_{\text{half-cell}}$ values:

- are always given for the reduction reaction of the half-cell
- do not depend on the number of electrons involved in the reduction reaction
- are positive when the half-cell is more easily reduced than the SHE
- are negative when the half-cell is harder to reduce than the SHE.



	Oxidized species		Reduced species	$E^{\ominus}$ / V, at 298 K
increasing tendency to occur as reduction ↓	$Zn^{2+}(aq) + 2e^-$	⇌	Zn(s)	−0.76
	$H^+(aq) + e^-$	⇌	½$H_2(g)$	0.00
	$Cu^{2+}(aq) + 2e^-$	⇌	Cu(s)	+0.34
	$Ag^+(aq) + e^-$	⇌	Ag(s)	+0.80

Hints for success: $E^{\ominus}$ values are given for a large number of half-cells in section 24 of the IB data booklet.

When two half-cells are combined:

- reduction will occur at the half-cell with the more positive $E^{\ominus}$ value
- oxidation will occur at the half-cell with the more negative $E^{\ominus}$ value.

Example: If $Cu^{2+}(aq)/Cu(s)$ and $Ag^{+}(aq)/Ag(s)$ half-cells were connected:

- reduction would occur at the $Ag^{+}(aq)/Ag(s)$ half-cell: $Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$
- oxidation would occur at the $Cu^{2+}(aq)/Cu(s)$ half-cell: $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^{-}$.

Skill: Calculation of cell potentials using standard electrode potentials.

Cell potentials can be calculated for any voltaic cell using the standard electrode potentials of the half-cells:

$$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$$

where $E^{\ominus}_{red}$ is the standard electrode potential of the half-cell where reduction occurs

and $E^{\ominus}_{ox}$ is the standard electrode potential of the half-cell where oxidation occurs.

Worked example

Calculate the EMF for a voltaic cell constructed from a zinc half-cell and a copper half-cell, and identify the anode and cathode. Write the equation for the overall cell reaction.

Solution

Standard electrode potential data for these half-cells at 298 K are:

$Zn^{2+}(aq) + 2e^{-} \rightleftharpoons Zn(s)$ $\qquad E^{\ominus} = -0.76\ V$

$Cu^{2+}(aq) + 2e^{-} \rightleftharpoons Cu(s)$ $\qquad E^{\ominus} = +0.34\ V$

So the copper half-cell will be reduced (higher value for $E^{\ominus}$), and the zinc half-cell will be oxidized. Electrons flow from zinc to copper.

$$E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$$

$$E^{\ominus}_{cell} = E^{\ominus}_{Cu^{2+}} - E^{\ominus}_{Zn^{2+}} = +0.34 - (-0.76)\ V = +1.10\ V$$

The zinc half-cell is the anode and the copper half-cell is the cathode.

$$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$$

Hints for success: When using $E^{\ominus}_{cell} = E^{\ominus}_{red} - E^{\ominus}_{ox}$ use the reduction $E^{\ominus}$ values in section 24 of the IB data booklet exactly as they are given: do not change the signs.

Understanding: When aqueous solutions are electrolysed, water can be oxidized to oxygen at the anode and reduced to hydrogen at the cathode.

When aqueous solutions are **electrolysed** water can be:

- reduced at the cathode:

  $2H_2O(l) + 2e^{-} \rightarrow H_2(g) + 2OH^{-}(aq)$ $\qquad E^{\ominus} = -0.83\ V$
- oxidized at the anode:

  $2H_2O(l) \rightarrow 4H^{+}(aq) + O_2(g) + 4e^{-}$ $\qquad -E^{\ominus} = -1.23\ V$

Subject vocabulary

electrolysed converted into simpler compounds using electrolysis

Because this is an *oxidation* reaction the sign of the electrode potentials has been reversed to convert it from a reduction potential to an *oxidation* potential.

Skill: Explanation of the products formed during the electrolysis of aqueous solutions.

When aqueous solutions of a salt are electrolysed there is more than one reaction possible at both the anode and cathode:

- Cathode
  - reduction of the cation: $M^+(aq) + e^- \rightarrow M$
  - reduction of water: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$
- Anode
  - oxidation of the anion: $A^-(aq) \rightarrow A + e^-$
  - oxidation of water: $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$

Subject vocabulary

electrolysis a process in which electrical current is used to make non-spontaneous redox reactions occur

Electrolysis of NaCl(aq)

The possible reactions at the electrodes are:

- Cathode: $2Na^+(aq) + 2e^- \rightarrow Na(s)$ $E^{\ominus} = -2.71\text{ V}$
  $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^{\ominus} = -0.83\text{ V}$
- Anode: $2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $-E^{\ominus} = -1.36\text{ V}$
  $2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$ $-E^{\ominus} = -1.23\text{ V}$

Low concentration of NaCl(aq)

	Reaction occurring at electrode	Explanation
cathode	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	The reaction with the most positive reduction potential is favoured
anode	$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$	The reaction with the most positive oxidation potential is favoured
Overall equation $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$		*Observations* Colourless $H_2(g)$ bubbles at cathode Colourless $O_2(g)$ bubbles at anode

High concentration of NaCl(aq)

	Reaction occurring at electrode	Explanation
cathode	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	The reaction with the most positive reduction potential is favoured
anode	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$	The two possible oxidation reactions have similar potentials At high $[Cl^-]$ the oxidation of Cl^- is favoured
Overall equation $2H_2O(l) + 2NaCl(aq) \rightarrow 2H_2(g) + Cl_2(g) + 2NaOH(aq)$		*Observations* Colourless $H_2(g)$ bubbles at cathode Green $Cl_2(g)$ bubbles at anode pH increases as OH^- formed

Electrolysis of $CuSO_4(aq)$

When aqueous solutions of copper sulfate are electrolysed, the products depend upon the type of electrode used (inert electrodes or copper electrodes).

Inert electrodes (graphite or platinum)

The possible reactions at the electrodes are:

● Cathode:	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E^\ominus = +0.34\,V$
	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$E^\ominus = -0.83\,V$
● Anode:	$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(g) + 2e^-$	$-E^\ominus = -2.01\,V$
	$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$	$-E^\ominus = -1.23\,V$

	Reaction occurring at electrode	**Explanation**
cathode	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	The reaction with the most positive reduction potential is favoured
anode	$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$	The reaction with the most positive oxidation potential is favoured
Overall equation $2CuSO_4(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq) + 2SO_4^{2-}(aq)$		*Observations* Pink/brown metal layer of Cu(s) forms on cathode Blue colour of solution fades as $Cu^{2+}(aq)$ is depleted Colourless $O_2(g)$ bubbles at anode pH decreases as H^+ formed

Copper electrodes

The possible reactions at the electrodes are;

● Cathode:	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	$E^\ominus = +0.34\,V$
	$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$	$E^\ominus = -0.83\,V$
● Anode:	$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(g) + 2e^-$	$-E^\ominus = -2.01\,V$
	$2H_2O(l) \rightarrow 4H^+(aq) + O_2(g) + 4e^-$	$-E^\ominus = -1.23\,V$
	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	$-E^\ominus = -0.34\,V$

	Reaction occurring at electrode	**Explanation**
cathode	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	The reaction with the most positive reduction potential is favoured
anode	$Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$	The reaction with the most positive oxidation potential is favoured
Overall equation No overall change is observed (the Cu^{2+} reduced at the cathode is replaced by the Cu^{2+} formed by oxidation of Cu(s) at the anode)		*Observations* Pink/brown metal layer of Cu(s) forms on cathode Cu anode reduces in mass as it oxidizes to Cu^{2+} Blue colour of solution is constant No change in pH

Understanding: $\Delta G^\ominus = -nFE^\ominus$. When $E^\ominus$ is positive, $\Delta G^\ominus$ is negative, indicating of a spontaneous process. When $E^\ominus$ is negative, $\Delta G^\ominus$ is positive, indicating of a non-spontaneous process. When $E^\ominus$ is 0, $\Delta G^\ominus$ is 0.

The cell potential of a voltaic cell is related to the Gibbs free energy change for the overall redox reaction occurring in the cell:

$\Delta G^\ominus = -nFE^\ominus$

where $\Delta G^\ominus$ is the difference in the standard free energy of reactants and products

n is the number of moles of electrons transferred in the reaction

F is the **Faraday constant** (96 500 C mol^{-1})

$E^\ominus$ is the standard cell potential.

Subject vocabulary

Faraday constant the total charge carried by one mole of electrons. It has the symbol F and has a value of 96 500 C mol^{-1}

Hints for success: The value of the Faraday constant is given in section 2 of the IB data booklet. It represents the total charge carried by one mole of electrons.

This means that the cell potential, $E^\ominus_{\text{cell}}$, also indicates if the redox reaction occurring is spontaneous or non-spontaneous.

Hints for success: In Topic 15 we saw that $-\Delta G^\ominus \rightarrow$ spontaneous, $+\Delta G^\ominus \rightarrow$ not spontaneous.

$E^\ominus_{\text{cell}}$	$\Delta G^\ominus$	Spontaneous or not spontaneous
positive	negative	spontaneous
negative	positive	not spontaneous (reverse reaction is spontaneous)
zero	zero	cell is at equilibrium

Skill: Determination of standard free-energy changes ($\Delta G^\ominus$) using standard electrode potentials.

Worked example

Calculate the standard free-energy change at 298 K for the zinc–copper voltaic cell, which has a standard cell potential of +1.10 V.

Solution

First write the equation for the overall cell reaction, as we need to know the number of electrons transferred. We deduced this on page 212.

$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$

$$\Delta G^\ominus = -nFE^\ominus$$

$$= -2\ (\text{mol e}^-) \times 96\,500\ (\text{C mol}^{-1}) \times 1.10\ (\text{V})$$

$$= 212\,000\ \text{J}$$

$$\therefore\ \Delta G^\ominus = -212\ \text{kJ}$$

Understanding: Current, duration of electrolysis, and charge on the ion affect the amount of product formed at the electrodes during electrolysis.

The amount of product that is produced in an electrolysis reaction depends on:

- the amount of current (measured in amperes, A)
- the amount of time that the current is flowing (measured in seconds)
- the charge on the ion being oxidized or reduced.

Skill: Determination of the relative amounts of products formed during electrolytic processes.

Worked example

How many grams of copper are formed on the cathode of an electrolytic cell containing $CuCl_2(aq)$ if a current of 2.00 A is run for 15 minutes?

How many grams of copper would be formed if CuCl(aq) was used instead of $CuCl_2(aq)$?

Solution

	$CuCl_2(aq)$	CuCl(aq)
Step 1: Determine the total charge (Q) produced by the current flow: $Q = It$	$Q = It$ $= 2.00\,A \times 900\,s$ $= 1800\,C$	$Q = It$ $= 2.00\,A \times 900\,s$ $= 1800\,C$
Step 2: Determine the number of moles of electrons contained in the total charge: $n(e^-) = \frac{Q}{F}$	$n(e^-) = \frac{Q}{F}$ $= \frac{1800\,C}{96\,500\,C\,mol^{-1}}$ $= 0.01865\,mol$	$n(e^-) = \frac{Q}{F}$ $= \frac{1800\,C}{96\,500\,C\,mol^{-1}}$ $= 0.01865\,mol$
Step 3: Use the balanced oxidation (or reduction) reaction to determine the moles of product formed	$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $n(Cu) = \frac{n(e^-)}{2}$ $= \frac{0.01865\,mol}{2}$ $= 9.33 \times 10^{-3}\,mol$	$Cu^+(aq) + e^- \rightarrow Cu(s)$ $n(Cu) = n(e^-)$ $= 0.01865\,mol$
Step 4: Determine the mass of product formed: $m = nM$	$m(Cu) = nM$ $= 9.33 \times 10^{-3}\,mol \times 63.55\,g\,mol^{-1}$ $= 0.593\,g$	$m(Cu) = nM$ $= 0.01865\,mol \times 63.55\,g\,mol^{-1}$ $= 1.19\,g$

Hints for success: The equation $Q = It$ is not provided in the IB data booklet so you need to memorize this equation.

Understanding: Electroplating involves the electrolytic coating of an object with a metallic thin layer.

Electroplating is when a layer of a metal is **deposited** on an object made of a different metal or another conductive material such as graphite.

Electroplating uses an electrolytic cell that contains:

- a salt solution containing the cations of the metal to be deposited onto the object
- a cathode made of the conducting object that will be electroplated
- an anode made of the metal being electroplated.

Subject vocabulary

electroplating a process that uses electrolysis to deposit a layer of metal on another conducting object

General vocabulary

deposited placed on top of

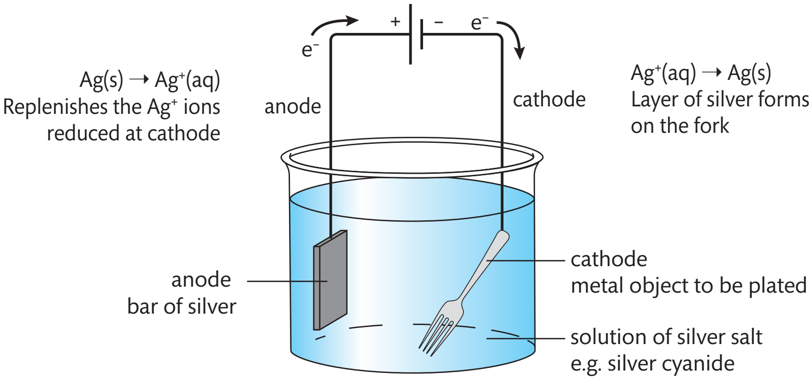


Figure 19.3 *Apparatus for electroplating silver.*

Topic 20: Organic chemistry

20.1 Types of organic reactions

Essential idea:

Key organic reaction types include nucleophilic substitution, electrophilic addition, electrophilic substitution, and redox reactions. Reaction mechanisms vary and help in understanding the different types of reactions taking place.

Nucleophilic substitution reactions

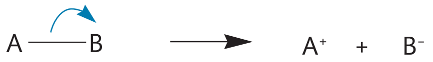
Skill: Outline of the difference between protic and aprotic solvents.

Reactions can be affected by the nature of the solvent used:

- polar **aprotic** solvents are polar solvents that are unable to form hydrogen bonds. Examples: propanone (CH_3COCH_3), ethanenitrile (CH_3CN).
- polar **protic** solvents are polar solvents that are able to form hydrogen bonds. Examples: water (H_2O), methanol (CH_3OH), ammonia (NH_3).

A curly arrow (↷) shows the movement of a pair of electrons in a reaction mechanism.

Heterolytic fission is the breaking of a covalent bond with one atom getting both electrons. This forms a cation and an anion:

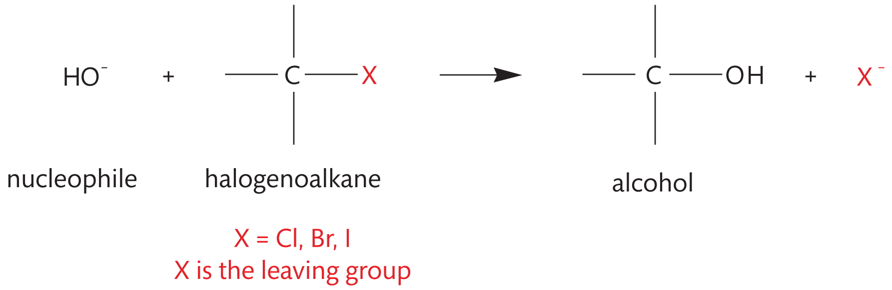


$A{-}B \longrightarrow A^+ + B^-$

(The curly arrow shows the bond breaking and the pair of electrons moving onto B.)

Nucleophilic substitution reactions happen when a **leaving group** is substituted by a nucleophile. The reaction mechanism involves heterolytic fission of the bond between the leaving group and a carbon atom.

The reaction of halogenoalkanes with hydroxide ions to make alcohols is a nucleophilic substitution reaction:



There are two nucleophilic substitution reaction mechanisms: S_N1 and S_N2.

Skill: Explanation of why hydroxide is a better nucleophile than water.

The negative charge on the hydroxide ion, OH^-, means it is more strongly attracted to positive charges. This makes it a better nucleophile than water, which is a neutral molecule.

Subject vocabulary

aprotic	unable to donate an H^+ or form hydrogen bonds
protic	able to donate an H^+ or form hydrogen bonds
heterolytic fission	the breaking of a covalent bond to form a cation and an anion
nucleophilic substitution reactions	a reaction in which a leaving group is substituted by a nucleophile
leaving group	the atom or group that is substituted by a nucleophile in a nucleophilic substitution reaction

Understanding: S_N2 represents a nucleophilic bimolecular substitution reaction. It involves a concerted reaction with a transition state.

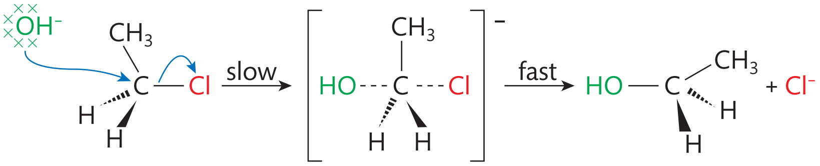
Understanding: For S_N2, rate = k[halogenoalkane][nucleophile]. S_N2 is stereospecific, with an inversion at the carbon.

Understanding: S_N2 reactions are best conducted using aprotic polar solvents.

S_N2:

- means 2nd-order nucleophilic substitution
- is a one-step reaction that occurs through a transition state
- is a bimolecular reaction (has two species involved in the rate-determining step)
- has the rate equation: rate = k[halogenoalkane][nucleophile].

The reaction between OH^- and CH_3CH_2Cl occurs by an S_N2 mechanism.



unstable transition state

Comments on the S_N2 mechanism:

- This mechanism is favoured for primary halogenoalkanes.
- Although the mechanism shows a fast and slow part this is a **concerted** reaction and there is only one step.
- The one step that occurs is the rate-determining step and it involves two reactants, OH^- and CH_3CH_2Cl:

  rate = $k[OH^-][CH_3CH_2Cl]$
- The transition state must be drawn inside square brackets. If the transition state has a charge this must be written at the top right of the brackets.
- The reaction is **stereospecific**. The alcohol is always **inverted** at the central carbon compared to the halogenoalkane.
- The reaction works best with aprotic polar solvents because they cannot form hydrogen bonds to the nucleophile, which would slow down the reaction.

Subject vocabulary

S_N2 second-order nucleophilic substitution reaction

stereospecific produces a particular stereoisomer

inverted of the opposite orientation

General vocabulary

concerted occurs in one step

Understanding: S_N1 represents a nucleophilic unimolecular substitution reaction. It involves a carbocation intermediate.

Understanding: The rate-determining step (slow step) in an S_N1 reaction depends only on the concentration of the halogenoalkane, rate = k[halogenoalkane].

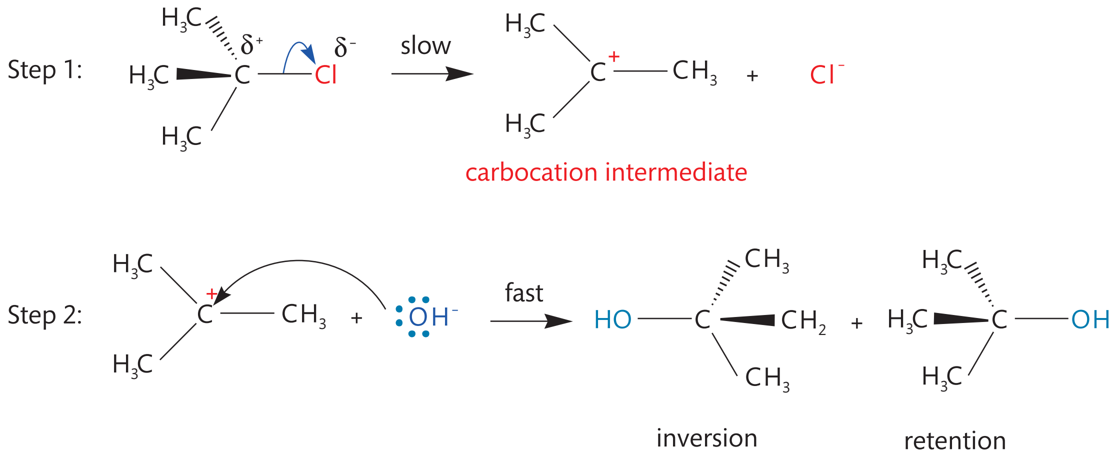
Understanding: S_N1 reactions are best conducted using protic polar solvents.

Skill: Deduction of the mechanism of the nucleophilic substitution reactions of halogenoalkanes with aqueous sodium hydroxide in terms of S_N1 and S_N2 mechanisms.

S_N1:

- means 1st-order nucleophilic substitution
- is a two-step reaction that occurs through a carbocation intermediate
- is a unimolecular reaction (has one species involved in the rate-determining step)
- has the rate equation: rate = k[halogenoalkane].

The reaction between OH^- and $(CH_3)_3Cl$ occurs by an S_N1 mechanism:



Comments on the S_N1 mechanism:

- This mechanism is favoured for tertiary halogenoalkanes because the tertiary carbocation is most stable due to the inductive effect of neighbouring carbon atoms.
- The first step is the rate-determining step and it involves one reactant, $(CH_3)_3Cl$:
  rate = $k[(CH_3)_3Cl]$
- The carbocation is sp^2 hybridized so the carbon centre is trigonal planar. This means the nucleophile can attack from above or below the plane and there will be a 50:50 mix of inversion and retention in the alcohol product.
- The S_N1 mechanism is not stereospecific because retention and inversion products are both formed.

Subject vocabulary

S_N1 first-order nucleophilic substitution reaction

carbocation intermediate a reaction intermediate that has a positive charge present on a carbon atom

inductive effect stabilizing of a positive charge by the donation of electron density by neighbouring atoms

retention keeping the same orientation

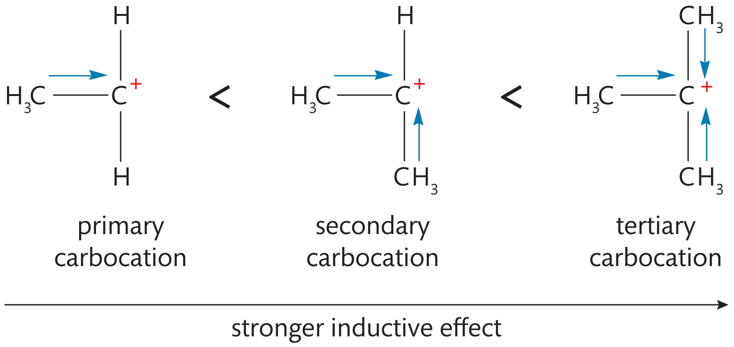
inversion having the opposite orientation

- The reaction works best with protic polar solvents because they can stabilize the carbocation through **ion–dipole interactions**. Polar protic solvents can also surround the leaving group and prevent it from recombining with the carbocation.

Carbocations and the inductive effect

The inductive effect happens when carbon atoms bonded to the positively charged carbon donate electron density and stabilize the carbocation. The more carbons bonded to the charged carbon, the stronger the inductive effect and the more stable the carbocation.

The stability of carbocations increases in the order:



Understanding: For tertiary halogenoalkanes the predominant mechanism is S_N1 and for primary halogenoalkanes it is S_N2. Both mechanisms occur for secondary halogenoalkanes.

Type of halogenoalkane	Reaction mechanism	Comments
tertiary	S_N1	Carbon in C–X bond not accessible to nucleophile attack via S_N2 due to **steric hindrance** Tertiary carbocation is stable so will react via S_N1
secondary	S_N1 and S_N2	Carbon in C–X bond accessible to nucleophile attack via S_N2 Secondary carbocation is less stable but still reacts via S_N1
primary	S_N2	Carbon in C–X bond easily accessible to nucleophilic attack via S_N2 Primary carbocation is not stable so will not react via S_N1

Skill: Explanation of how the rate depends on the identity of the halogen (the leaving group), whether the halogenoalkane is primary, secondary, or tertiary, and the choice of solvent.

Subject vocabulary

ion–dipole interactions the electrostatic attraction between an ion and a dipole

steric hindrance the blocking of a reaction site on a molecule by other parts of the molecule such as alkyl side chains

Factors affecting the rate of nucleophilic substitution reactions of halogenoalkanes.

Factor	**Observed rates (slowest → fastest)**	**Explanation**
Identity of leaving group	C–F < C–Cl < C–Br < C–I	Rate depends on C–X bond strength as this determines if X^- can easily act as a leaving group C–I is a weak bond so I^- is a good leaving group and it reacts fastest C–F is a strong bond so F^- is a poor leaving group and it reacts slowest
Type of halogenoalkane	primary < secondary < tertiary S_N2 S_N1 and S_N2 S_N1	S_N1 reactions are faster than S_N2 reactions
Type of solvent	S_N1: polar aprotic < polar protic S_N2: polar protic < polar aprotic	Polar protic solvents can stabilize the carbocation in S_N2 reactions and speed up the reaction Polar protic solvents can hydrogen bond to the nucleophile in S_N2 reactions and slow down the reaction

Electrophilic addition reactions

Understanding: An electrophile is an electron-deficient species that can accept electron pairs from a nucleophile. Electrophiles are Lewis acids.

Electrophiles:

- are electron-deficient species
- have a positive charge or a partial positive charge
- are attracted to electron-rich pi bonds
- can act as Lewis acids and accept electron pairs.

Subject vocabulary

Markovnikov's rule a rule for predicting the products formed in the addition reactions of unsymmetrical alkenes

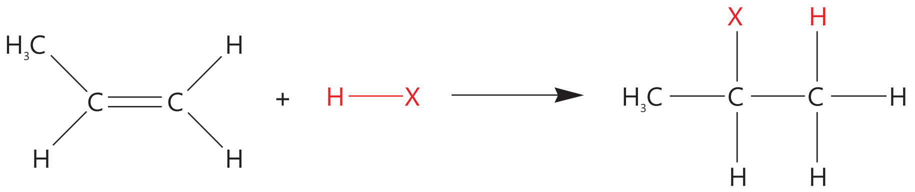
unsymmetrical alkene an alkene that has different substituents on the two carbons making the double bond

interhalogen a diatomic molecule containing two halogens, e.g. ICl, ClBr

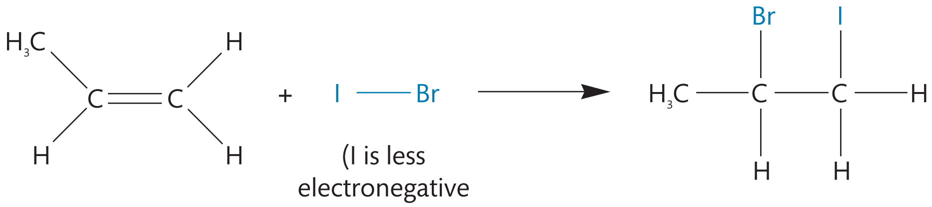
Understanding: Markovnikov's rule can be applied to predict the major product in electrophilic addition reactions of unsymmetrical alkenes with hydrogen halides and interhalogens. The formation of the major product can be explained in terms of the relative stability of possible carbocations in the reaction mechanism.

Markovnikov's rule predicts the products for addition reactions of **unsymmetrical alkenes** with hydrogen halides (e.g. HBr) and **interhalogens** (e.g. IBr).

Hydrogen halides: *the hydrogen will attach to the alkene carbon that is already bonded to the larger number of hydrogens.*



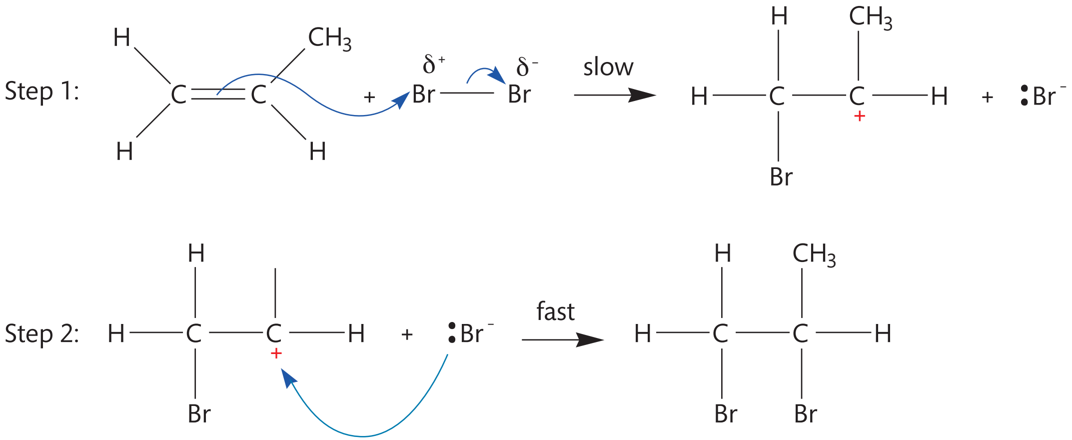
Interhalogens: *the less electronegative halogen will attach to the alkene carbon that is bonded to the smaller number of carbons.*



(I is less electronegative than Br)

Skill: Deduction of the mechanism of the electrophilic addition reactions of alkenes with halogens/interhalogens and hydrogen halides.

The electrophilic addition of Br_2 to an alkene is a two-step mechanism:



Comments on the electrophilic addition mechanism:

Step 1

- The electrons in the pi (π) bond are attracted to the δ+ of an instantaneous dipole on Br_2.
- The Br–Br bond breaks heterolytically and Br^- forms.
- Br adds to the alkene carbon that creates the most stable carbocation. This is the carbocation that has the positive charge on the carbon atom that is bonded to the most carbons. (It will be stabilized by a larger inductive effect.)

Step 2

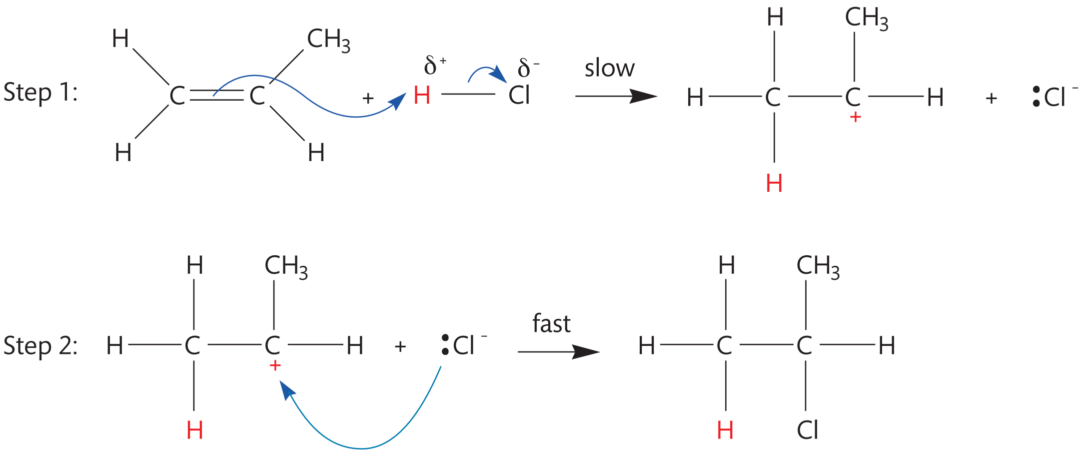
- Br^- acts as a nucleophile and attacks the carbocation.

The electrophilic additions of hydrogen halides and interhalogens to an alkene both occur by an electrophilic addition mechanism

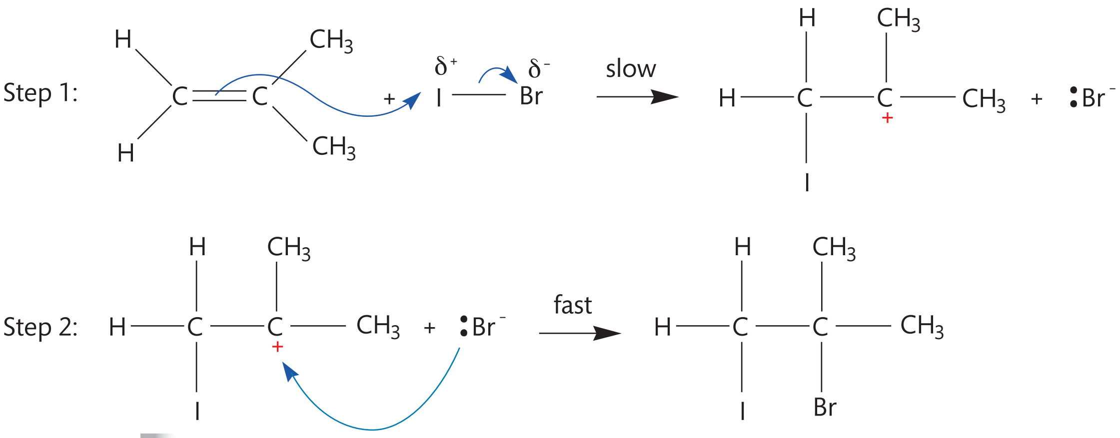
Step 1

- The pi electrons are attracted to the partial positive charge on the addition reactant.
- The reactant adds to the carbon that gives the most stable carbocation.

Example: Addition of HCl to propene



Example: Addition of IBr to 2-methylpropene



Electrophilic substitution reactions

Understanding: Benzene is the simplest aromatic hydrocarbon (or arene) and has a delocalized structure of π bonds around its ring. Each carbon to carbon bond has a bond order of 1.5. Benzene is susceptible to attack by electrophiles.

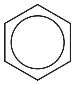
Aromatic hydrocarbons (**arenes**) are ring structures that contain delocalized π bonds.

Subject vocabulary

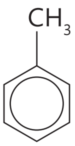
aromatic hydrocarbons hydrocarbons that contain ring structures with delocalized π bonds

arenes molecules that are aromatic hydrocarbons

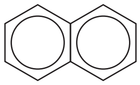
Examples include:



benzene



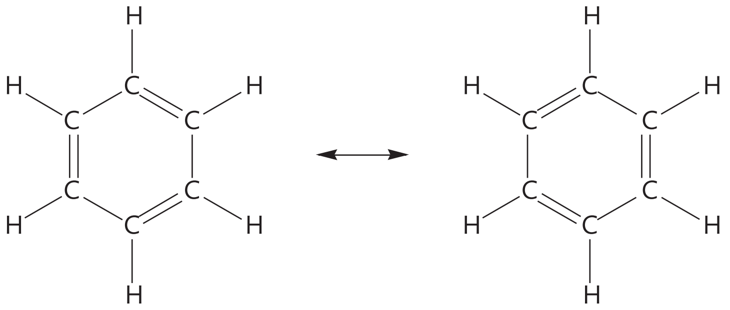
methylbenzene
(toluene)



naphthalene

Benzene:

- is unsaturated because it contains π bonds
- has two resonance structures:

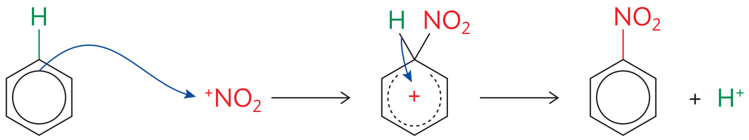


(*Because benzene exists as a hybrid of the two resonance structures the C–C bond order is 1.5.*)

- is **aromatic** (the three π bonds in the ring are delocalized)
- attracts electrophiles because the benzene ring is electron rich due to the delocalized pi electrons.

Skill: Deduction of the mechanism of the nitration (electrophilic substitution) reaction of benzene (using a mixture of concentrated nitric acid and sulfuric acid).

The **nitration** of benzene occurs by an electrophilic substitution reaction. The electrophile NO_2^+ is produced from a mixture of HNO_3 and H_2SO_4.



$$C_6H_6 + HNO_3 \xrightarrow[50\,°C]{\text{conc. } H_2SO_4} C_6H_5NO_2 + H_2O$$

Comments on the electrophilic substitution mechanism:

- The electrons in a delocalized π bond on the benzene are attracted to the positive charge of the electrophile.
- The carbocation intermediate formed is stabilized by the positive charge being delocalized over the carbons in the ring.

Subject vocabulary

aromatic	having a ring structure with delocalized π bonds
nitration	an electrophilic substitution reaction in which an NO_2 group replaces an H atom

Reduction reactions

Understanding: Carboxylic acids can be reduced to primary alcohols (via the aldehyde). Ketones can be reduced to secondary alcohols. Typical reducing agents are lithium aluminium hydride (used to reduce carboxylic acids) and sodium borohydride.

Reduction reactions involve the gain of electrons. In organic chemistry, reduction reactions also involve the gain of hydrogen atoms or loss of oxygen atoms.

Common reducing agents used in organic chemistry are:

- sodium borohydride ($NaBH_4$) in water or alcohol solutions
- lithium aluminium hydride ($LiAlH_4$) in **anhydrous** (dry) solvents.

Subject vocabulary

anhydrous not containing any water

Hints for success:
[+H] can be used to represent a reducing agent when writing reduction reactions.

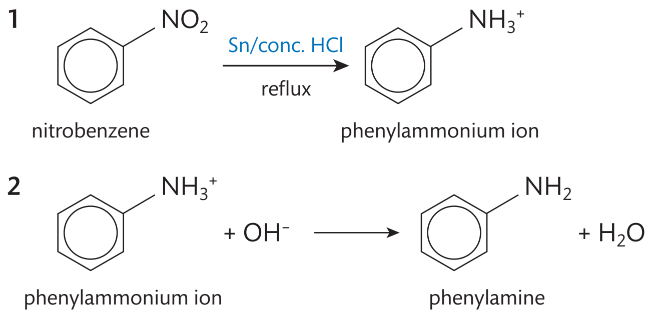
$NaBH_4$ is the safer reducing agent so it is used for most reactions. However, the reduction of carboxylic acids needs $LiAlH_4$ because it is a stronger reducing agent.

Skill: Writing reactions of carbonyl-containing compounds: aldehydes and ketones to primary and secondary alcohols, and carboxylic acids to aldehydes, using suitable reducing agents.

Starting compound	Reduction products	Example
carboxylic acid	aldehyde → primary alcohol	$CH_3COOH \xrightarrow{[+H]} CH_3CHO \xrightarrow{[+H]} CH_3CH_2OH$ ethanoic acid, ethanal, ethanol carboxylic acid, aldehyde, primary alcohol
ketone	secondary alcohol	$(CH_3)_2CO \xrightarrow{[+H]} (CH_3)_2CHOH$ propanone, propan-2-ol ketone, secondary alcohol

Skill: Conversion of nitrobenzene to phenylamine via a two-stage reaction.

Nitrobenzene can be converted to phenylamine in a two-stage reaction. The reducing agent is a mixture of tin metal (Sn) and concentrated hydrochloric acid (HCl).



Comments on the conversion of nitrobenzene to phenylamine:

- The acidic conditions in the first stage means that the product is the phenylammonium ion.
- The addition of OH^- in the second stage results in an acid–base reaction that converts the phenylammonium ion to phenylamine.

20.2 Synthetic routes

Essential idea:

Organic synthesis is the systematic preparation of a compound from a widely available starting material or the synthesis of a compound via a synthetic route that can often involve a series of different steps.

Understanding: The synthesis of an organic compound begins from a readily available starting material via a series of discrete steps. Functional group **interconversions** are the basis of such synthetic routes.

Organic synthesis involves making a compound from readily available starting materials using a series of reactions. The reactions convert the functional groups present on the starting material into the functional groups needed for the product.

The different conversions of functional groups that have been covered in this section can be summarized in a diagram:

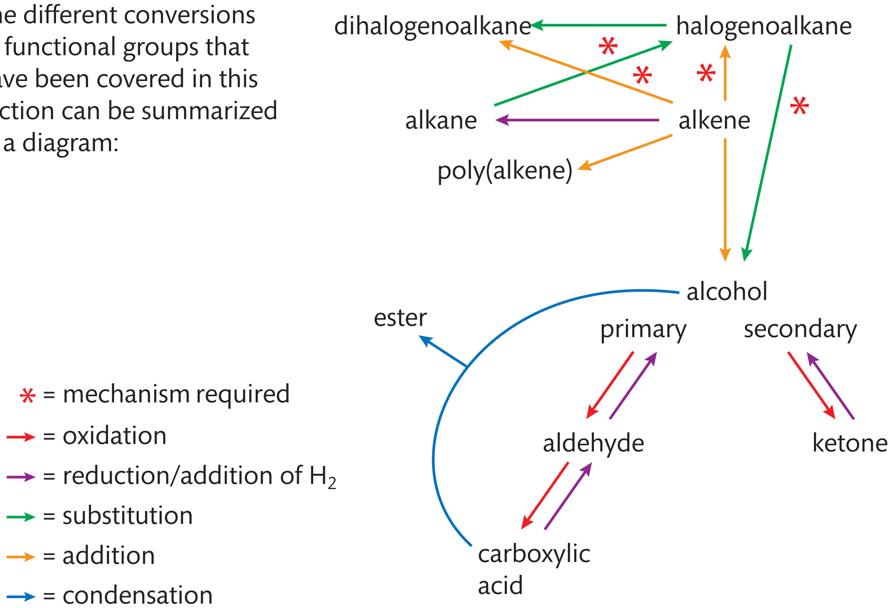


Figure 20.1 *Some pathways of conversion of organic compounds.*

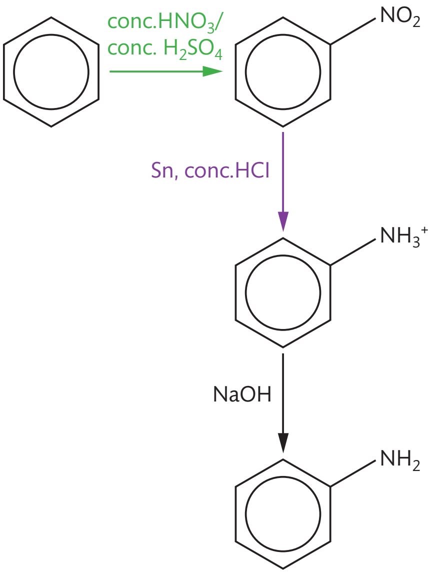


Figure 20.2 *Some more pathways of conversion of organic compounds.*

General vocabulary

interconversions changes from one to another

Subject vocabulary

organic synthesis the process of making an organic compound from readily available starting materials using a series of reactions

Understanding: Retro-synthesis of organic compounds.

Retro-synthesis involves looking at the target molecule and working backwards, step by step, to determine what would be suitable **precursors** (simpler compounds) based on the functional groups that can be converted. This stepwise process also allows a suitable starting material to be identified:

target molecule → precursor 1 → precursor 2 → ……… → starting material

Subject vocabulary

retro-synthesis working backwards from a target molecule to determine the stepwise conversions and starting materials needed for its synthesis

precursors simple compounds used as starting materials to make larger compounds

Skill: Deduction of multi-step synthetic routes given starting reagents and the product(s).

Worked example

Explain how propyl propanoate can be synthesized from a single carboxylic acid. Give equations and conditions for all reactions, and state the type of reaction occurring at the functional group at each step.

Solution

Start by analysing the target molecule: the ester is the result of condensation between propanoic acid, C_2H_5COOH, and propanol, C_3H_7OH.

- Starting with C_2H_5COOH, a portion of it is reduced to C_3H_7OH by heating with $LiAlH_4$ in dry ether followed by aqueous acid. The conditions must be applied for long enough to complete the reduction reaction via the aldehyde.
- Another portion of C_2H_5COOH is reacted with the alcohol produced above. The mixture is heated with a catalyst of concentrated H_2SO_4.

$$C_2H_5COOH \xrightarrow[\text{2 aqueous } H^+]{\text{1 } LiAlH_4 \text{ in dry ether}} C_3H_7OH$$ reduction

$$C_2H_5COOH + C_3H_7OH \overset{\text{conc. } H_2SO_4}{\rightleftharpoons} C_2H_5COOC_3H_7 + H_2O$$ condensation

Worked example

You are required to make butanone starting from any alkene of your choice. Show the steps involved in retro-synthesis to determine the identity of the alkene.

Solution

Butanone, $CH_3COC_2H_5$, is a ketone. It can be made by oxidizing a secondary alcohol.

$CH_3COC_2H_5 \Rightarrow CH_3CH(OH)C_2H_5$ oxidation using $H^+/K_2Cr_2O_7$

The secondary alcohol is made by substitution of a secondary halogenoalkane.

$CH_3CH(OH)C_2H_5 \Rightarrow CH_3CH(Br)C_2H_5$ substitution using NaOH

The secondary halogenoalkane is made by addition to an alkene according to Markovnikov rules.

$CH_3CH(Br)C_2H_5 \Rightarrow CH_2{=}CHCH_2CH_3$ addition using HBr

Therefore but-1-ene is the starting material.

(The secondary alcohol could be made directly by hydration of the alkene, but is likely to give a better yield via the halogenoalkane.)

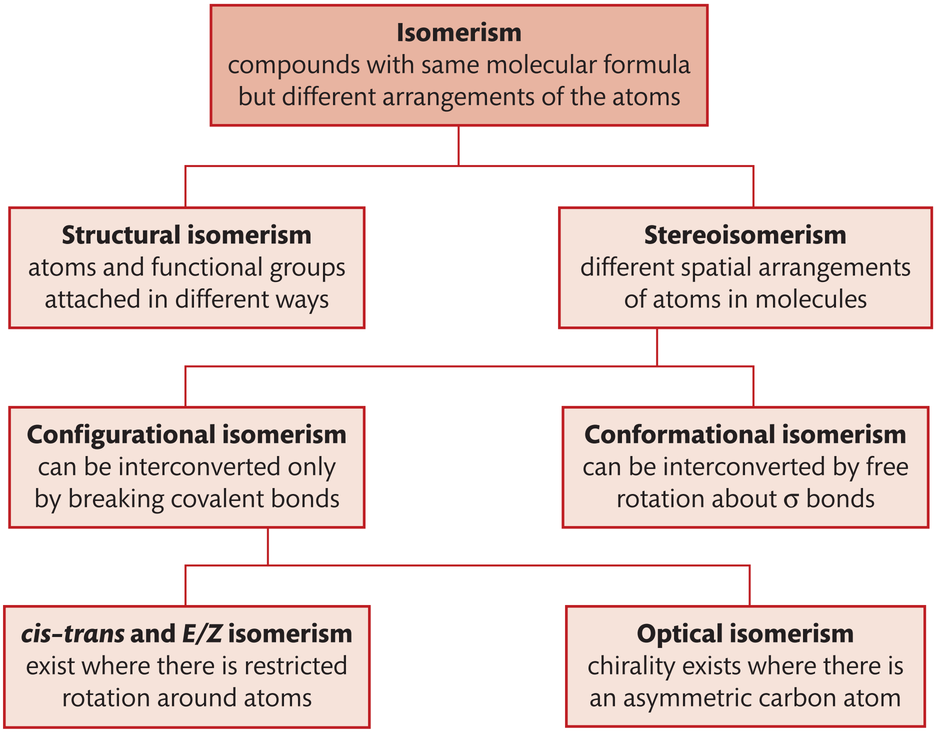
20.3 Stereoisomerism

Essential idea:

Stereoisomerism involves isomers which have different arrangements of atoms in space but do not differ in connectivity or bond multiplicity (whether single, double, or triple) between the isomers themselves.

Understanding: Stereoisomers are subdivided into two classes. Conformational isomers interconvert by rotation about a σ bond and configurational isomers interconvert only by breaking and reforming a bond. Configurational isomers are further subdivided into *cis–trans*, *E*/*Z*, and optical isomers.

Isomers are compounds with the same molecular formula but different arrangements of the atoms. There are different types of isomers:



Understanding: *Cis–trans* isomers can occur in alkenes or cycloalkanes (or heteroanalogues) and differ in the positions of atoms (or groups) relative to a reference plane.

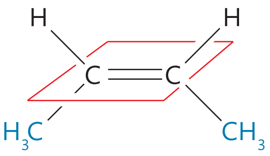
Skill: Explanation of stereoisomerism in non-cyclic alkenes and C3 and C4 cycloalkanes.

Because free rotation cannot happen around a double bond the substituent groups on an alkene are in fixed positions relative to each other.

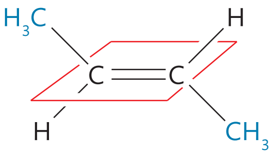
When there are different substituent groups on each end of the alkene, ***cis*** **and *trans* isomers** are possible. A reference plane drawn through the double bond is used to define whether the isomer is *cis* or *trans*.

- *cis* isomers: similar substituents are on the same side of the reference plane
- *trans* isomers: similar substituents are on opposite sides of the reference plane.

Example: but-2-ene has *cis* and *trans* isomers:



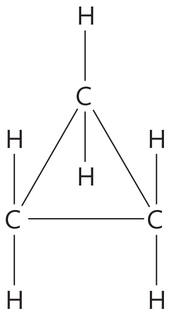
cis-but-2-ene



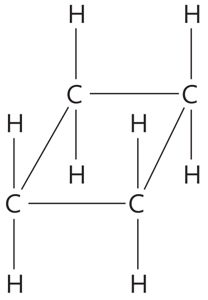
trans-but-2-ene

Hints for success: *trans* means on *opposite* sides, *cis* means on the *same* side.

Cycloalkanes are ring structures made up of carbons that are linked together by single bonds. Cycloalkanes have the general formula C_nH_{2n}, e.g.

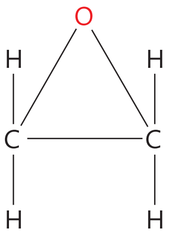


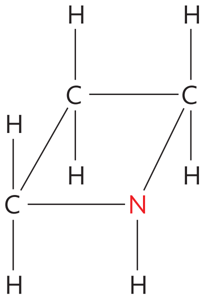
cyclopropane



cyclobutane

Heteroanalogues of cycloalkanes are ring structures where a carbon has been replaced by a different (hetero) atom, e.g.





cis and *trans* isomers also occur for cycloalkanes and their heteroanalogues.

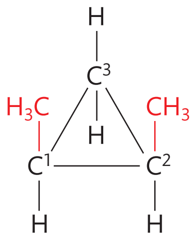
Subject vocabulary

cis **isomers** isomers where the substituents are on the same side of a double bond in an alkene or on the same side in a ring compound

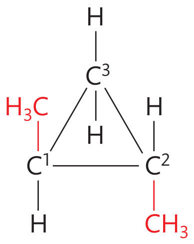
trans **isomers** isomers where the substituents are on the opposite sides of a double bond in an alkene or on the opposite sides in a ring compound

cycloalkanes alkanes in which the carbon atoms are linked to form a ring structure

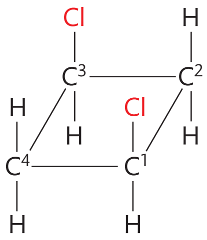
heteroanalogues cycloalkanes in which a carbon atom is replaced by another atom such as O or N (a heteroatom)



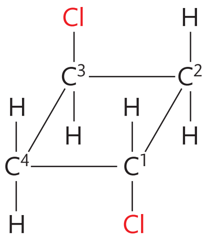
cis-1,2-dimethylcyclopropane



trans-1,2-dimethylcyclopropane



cis-1,3-dichlorocyclobutane



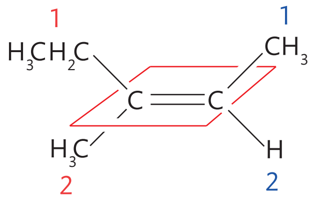
trans-1,3-dichlorocyclobutane

Understanding: According to IUPAC, *E*/*Z* isomers refer to alkenes of the form $R^1R^2C{=}CR^3R^4$ ($R^1 \neq R^2$, $R^3 \neq R^4$) where neither R^1 nor R^2 need be different from R^3 or R^4.

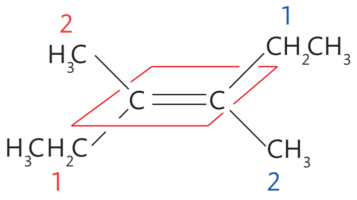
When all the substituents on an alkene are different it may not be possible to assign the isomers as being *cis* or *trans*.

E or *Z* isomers are identified based on the **priorities** of the substituents on each end of the alkene. Atoms with a larger atomic number have a higher priority. e.g. Cl has a higher priority than C. For alkyl chains a higher priority is assigned to longer chains, e.g. a butyl group has a higher priority than a methyl group.

- *Z* isomers: the highest priority groups are on the same side of the reference plane.
- *E* isomers: the highest priority groups are on opposite sides of the reference plane.



(*Z*)-3-methylpent-2-ene



(*E*)-3,4-dimethylhex-3-ene

General vocabulary

priorities	order of importance

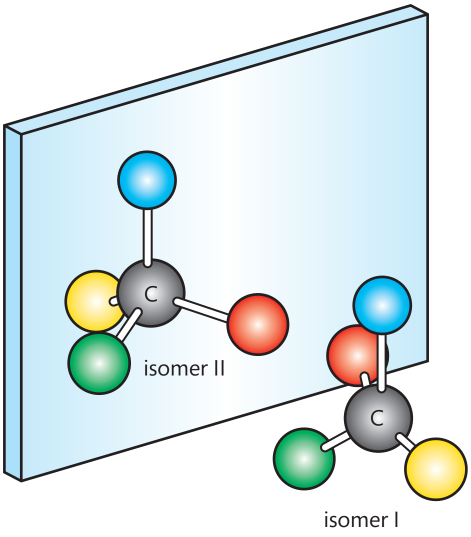
Understanding: A chiral carbon is a carbon joined to four different atoms or groups.

A **chiral carbon** (or asymmetric carbon) is bonded to four different groups or atoms. This arrangement has two isomers that are **non-superimposable** mirror images of each other.

Subject vocabulary

chiral carbon	a carbon atom that has four different groups attached to it
non-superimposable	cannot be placed on top of each other to give the same arrangement

Figure 20.3 *An asymmetric, or chiral, carbon atom, shown in black, is bonded to four different atoms or groups – shown here in different colours. This gives rise to two configurations that are mirror images of each other.*



Understanding: An optically active compound can rotate the plane of polarized light as it passes through a solution of the compound. Optical isomers are enantiomers. Enantiomers are non-superimposable mirror images of each other. Diastereomers are not mirror images of each other.

Optical isomers:

- contain a chiral carbon
- are **chiral molecules**
- are also called **enantiomers**
- are non-superimposable mirror images of each other
- rotate **plane-polarized light** in opposite directions (are **optically active**)
- have identical physical properties
- have the same chemical properties *except for their reactions with other chiral molecules.*

Subject vocabulary

optical isomers isomers that rotate plane-polarized light in opposite directions

chiral molecules a molecule that contains chiral carbons and rotates plane-polarized light

enantiomers optical isomers

plane-polarized light light that only oscillates in one plane

optically active rotating plane-polarized light

Skill: Description and explanation of optical isomers in simple organic molecules.

Butan-2-ol and 2-chlorobutane both contain a chiral carbon. This means they both have two optical isomers:

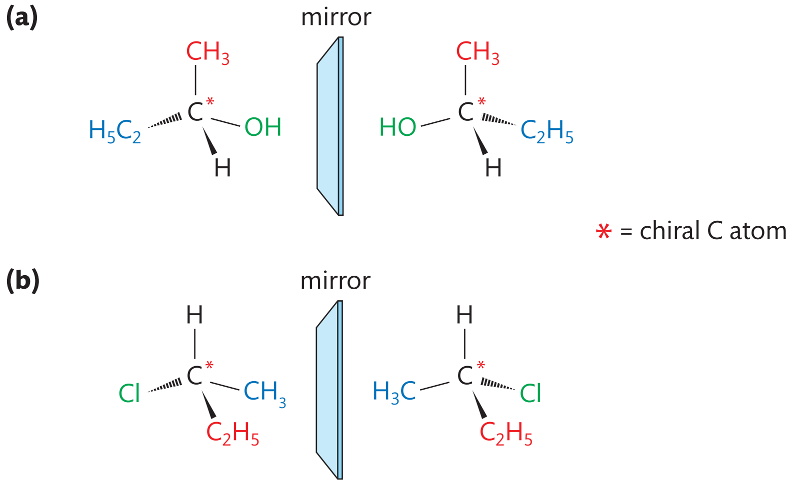


Figure 20.4 *Enantiomers of **(a)** butan-2-ol and **(b)** 2-chlorobutane.*

Skill: Comparison between the physical and chemical properties of enantiomers.

Diastereomers:

- contain more than one chiral carbon
- do not have opposite configurations at all chiral carbons
- are not mirror images of each other
- have different physical and chemical properties.

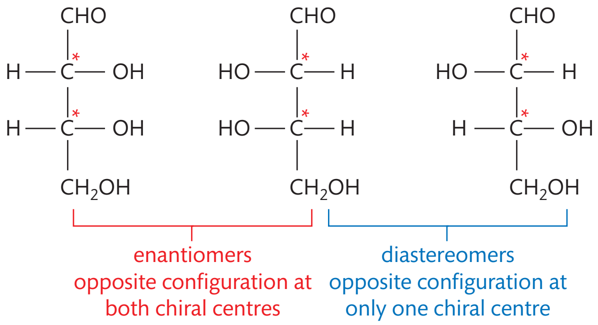


Figure 20.5 *Examples of four-carbon sugars showing the difference between enantiomers and diastereomers. Red asterisks mark the position of chiral carbon atoms. Note the diagram is simplified to two-dimensional representation for this purpose.*

Subject vocabulary

diastereomers isomers that contain more than one chiral carbon and are not mirror images of each other

polarimeter an instrument that measures the rotation of plane-polarized light

Skill: Distinction between optical isomers using a polarimeter.

A **polarimeter** measures how much the plane of polarized light rotates when it passes through solutions containing optical isomers.

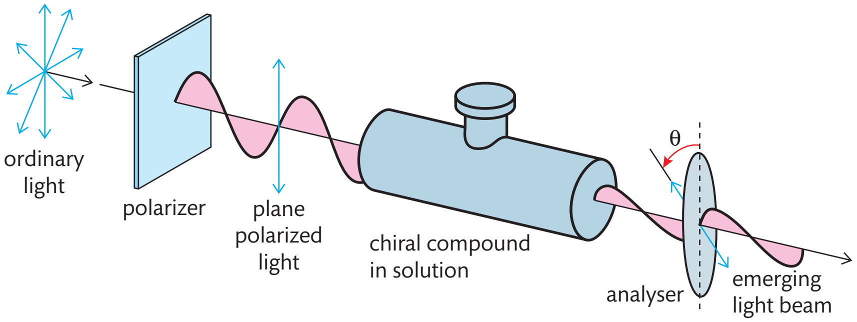


Figure 20.6 *Schematic representation of a polarimeter.*

Features of a polarimeter:

- light is plane polarized using a polarizer
- the plane-polarized light passes through a solution of the optical isomer
- an analyser measures the angle (θ) through which the plane of the polarized light has been rotated by the solution.

The two optical isomers of a chiral compound are identified by the direction in which they rotate polarized light in a polarimeter, e.g.

- (+)-butan-2-ol rotates plane-polarized light in a clockwise direction ($+\theta$)
- (–)-butan-2-ol rotates plane-polarized light in an anti-clockwise direction ($-\theta$)

Understanding: A racemic mixture (or racemate) is a mixture of two enantiomers in equal amounts and is optically inactive.

A **racemic mixture** (racemate) is a mixture that contains equal amounts of two enantiomers.

One enantiomer will rotate plane-polarized light in a clockwise direction. The other enantiomer rotates the plane-polarized light *an equal amount* in the anti-clockwise direction.

This means that there is no overall rotation of the plane-polarized light and racemic mixtures are **optically inactive**.

Subject vocabulary

racemic mixture a mixture that contains equal amounts of two optical isomers

optically inactive not rotating plane-polarized light

Topic 21: Measurement and analysis

21.1 Spectroscopic identification of organic compounds

Essential idea:

Although spectroscopic characterization techniques form the backbone of structural identification of compounds, typically no one technique results in a full structural identification of a molecule.

Understanding: Structural identification of compounds involves several different analytical techniques including IR, ^{1}H NMR, and MS.

- Different analytical techniques identify different structural features of a compound. To determine the overall structure of a compound the information obtained from different techniques must often be combined.

Technique	Structural information identified by technique
Percentage composition	The *empirical formula* of a compound can be calculated from the percentage composition. See the Worked example on page 10.
Mass spectroscopy (MS)	The *molecular formula* can be determined from the mass of the molecular ion if the empirical formula is known. A possible structure can be determined from the masses of the fragments in the fragmentation pattern. See the Worked example on page 139.
Infrared spectroscopy (IR)	The *covalent bonds* present in the molecule can be determined from the peaks in the IR spectrum, e.g. ● a strong peak at 1600 cm^{-1} indicates a C=O bond is present ● a broad peak at 3200–3600 cm^{-1} indicates an O–H bond is present
Nuclear magnetic resonance (^{1}H NMR)	The number of different *hydrogen chemical environments* is determined from the number of signals in the ^{1}H NMR spectrum. The *number of hydrogen atoms in each chemical environment* is determined from the integrated area of each signal. See the Worked example on page 142. The *identity of neighbouring atoms* for each chemical environment can be deduced from the chemical shifts of the signal associated with each chemical environment. See the Worked example on page 237. The *number of hydrogen atoms on neighbouring carbon atoms* for each chemical environment can be determined from the splitting pattern of the signal in a **high-resolution ^{1}H NMR** spectrum. See the Worked example on page 237.

Subject vocabulary

high-resolution ^{1}H NMR ^{1}H NMR spectroscopy that shows the splitting of peaks that occurs due to the effect of protons on neighbouring atoms

Subject vocabulary

diffraction pattern regions of high and low intensity caused by the interference of two or more electromagnetic waves

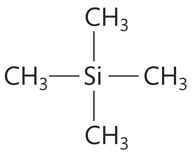
reference standard a substance that gives a reliable measured value that other substances can be compared to

splitting pattern the pattern of peaks that are observed for signals in a ^{1}H NMR spectrum

Technique	Structural information identified by technique
X-ray spectroscopy	X-rays deflected by the atoms in a crystal produce a **diffraction pattern**. The three-dimensional structure of the solid is determined from the diffraction pattern.

Understanding: In a high-resolution ^{1}H NMR spectrum, single peaks present in low resolution can split into further clusters of peaks.

Skill: Explanation of the use of tetramethylsilane (TMS) as the reference standard.



$$(CH_3)_4Si$$

Figure 21.1 *Tetramethylsilane (TMS). Each of the 12 hydrogen atoms is bonded to a carbon atom, which in turn is bonded to two other hydrogen atoms. The silicon atom is bonded to four methyl groups. All the hydrogen atoms are in the same environment so only one signal is recorded.*

Tetramethylsilane (TMS) is used as a **reference standard** in ^{1}H NMR.

The peak observed for TMS in an ^{1}H NMR spectrum is assigned a chemical shift of zero. The chemical shifts (δ) of other signals in the spectrum are defined relative to TMS:

$$\delta = \left(\frac{\nu - \nu_0}{\nu_0}\right) \times 10^6 \text{ ppm}$$

ν_0 = the frequency of the radiowaves absorbed by the hydrogen nuclei in TMS.

ν = the frequency of the radiowaves absorbed by the hydrogen nuclei in the compound.

- In *low-resolution* ^{1}H NMR a single peak is observed for each hydrogen chemical environment.
- In *high-resolution* ^{1}H NMR the peaks observed for each hydrogen chemical environment are split into smaller peaks to create a **splitting pattern**.

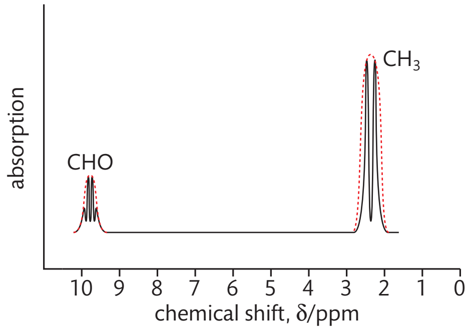


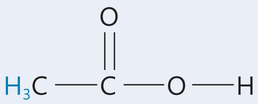
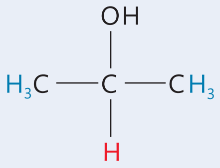
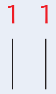
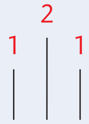
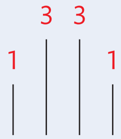
Figure 21.2 *The high-resolution ^{1}H NMR spectrum of ethanal. The dotted lines show the low-resolution spectrum.*

The total integrated area for all of the peaks in the splitting pattern is proportional to the number of hydrogen atoms in the chemical environment.

The splitting pattern observed for each chemical environment depends on the number of hydrogen atoms on the *neighbouring* carbon atoms. (Hydrogen atoms on N and H atoms do not cause splitting.)

In the table below:

- the blue H are the hydrogen atoms generating the ^{1}H NMR signal shown in the final column
- the red H are the neighbouring hydrogen atoms that cause the splitting pattern.

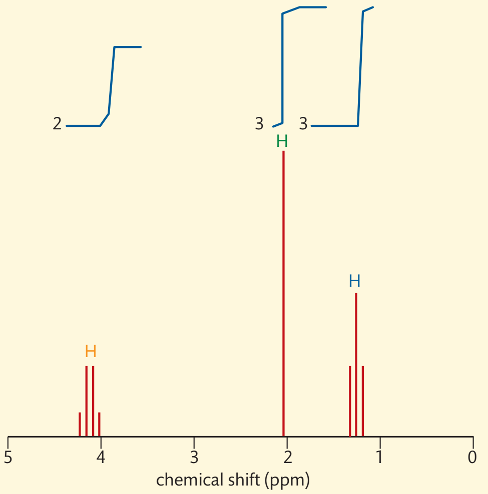
Number of hydrogen atoms on neighbouring carbon atoms	Example	Name of splitting pattern	Shape of splitting pattern and relative intensities
0	 $H_3C-\overset{\overset{O}{\|}}{C}-O-H$	singlet	
1	 $H_3C-\underset{\overset{\mid}{H}}{\overset{\underset{\mid}{OH}}{C}}-CH_3$	doublet	
2	H_3C-CH_2-OH	triplet	
3	H_3C-CH_2-OH	quartet	

Worked example

The ^1H NMR spectrum of a compound with the empirical formula C_2H_4O is shown.

(a) Deduce the molecular formula of the compound.

(b) Use section 27 of the IB data booklet to identify a structure that is consistent with the ^1H NMR spectrum and account for the number of peaks and the splitting patterns in the spectrum.

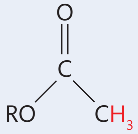
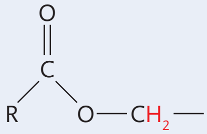


Solution

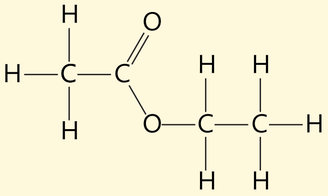
(a) The ^1H NMR spectrum shows the presence of eight hydrogen atoms so the molecular formula is $C_4H_8O_2$. The hydrogens are in three different chemical environments, in a 2 : 3 : 3 ratio.

From the formula, IHD = 1, so there is either a ring or one double bond.

(b)

Chemical shift / ppm	Integration	Type of proton	Splitting pattern	Structural information
1.0–1.5	3H	$-CH_3$	triplet	CH_3 next to CH_2
2.0–2.5	3H		singlet	CH_3 next to CO
3.8–4.1	2H		quartet	OCH_2 next to CH_3

The correct structure is $CH_3COOCH_2CH_3$



Skill: Deduction of the structure of a compound given information from a range of analytical characterization techniques (X-ray crystallography, IR, ^{1}H NMR, and MS).

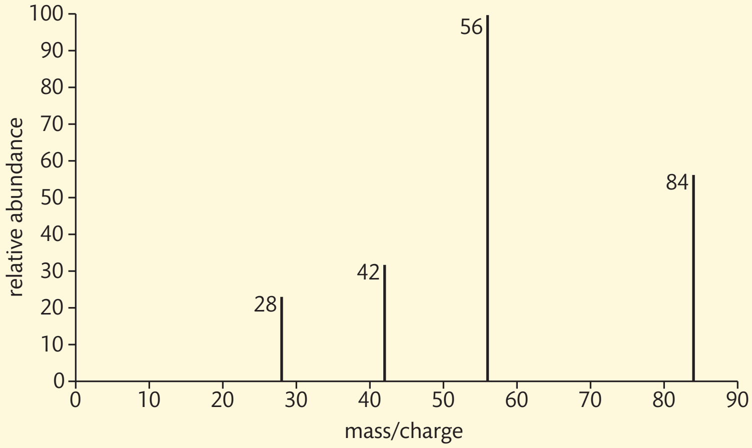
Worked example

(a) An unknown compound is found to have the following composition:

	% composition by mass
C	85.6
H	14.4

Deduce the empirical formula of the compound.

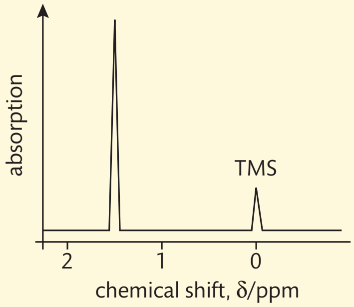
(b) The mass spectrum of the compound is shown below. Deduce the molecular formula and the IHD of the compound.



(c) Is the molecule likely to contain a CH_3 group? Explain your answer.

(d) The infrared spectrum shows one absorption close to 2900 cm^{-1}, but there is no absorption close to 1600 cm^{-1}. State what can be deduced from this information.

(e) Deduce the molecular structure from the ^1H NMR spectrum shown.



Solution

(a) To find the empirical formula calculate the relative number of moles:

	C	H
mass / g	85.6	14.4
moles	$=\frac{85.6}{12.01}$ $= 7.13$	$=\frac{14.4}{1.01}$ $= 14.3$
simple ratio	$=\frac{7.13}{7.13}$ $= 1.00$	$=\frac{14.4}{7.13}$ $= 2.02$

The empirical formula is CH_2.

(b) The mass spectrum shows a parent ion at 84. The molecular formula is C_nH_{2n}.

$n(12.01) + 2n(1.01) = 84$

$14.03n = 84$

$n = \frac{84}{14.03} = 5.99$

The molecular formula is C_6H_{12}.

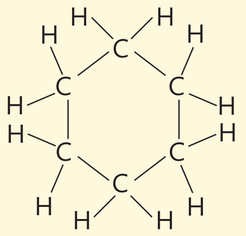
The saturated non-cyclic compound with six carbons is C_6H_{14}, so the IHD = 1. The molecule contains a C=C or a ring.

(c) The absence of peaks at 15 or 69 (84 – 15) suggests that the molecule probably does not contain a methyl group.

(d) The absorption close to 2900 cm^{-1} is due to the C–H bond.

The absence of an absorbance at 1600 cm^{-1} suggests that the molecule does not contain a C=C bond. It must, therefore, have a ring structure.

(e) The NMR spectra shows only one peak, so all the hydrogen atoms are in the same chemical environment. This confirms that the molecule has a ring structure. It is cyclohexane.



Understanding: The structural technique of single-crystal X-ray crystallography can be used to identify the bond lengths and bond angles of crystalline compounds.

- **Single-crystal X-ray crystallography**:
  - shines **monochromatic** X-rays at a **crystal** of a compound
  - records the diffraction pattern generated by the X-rays that are **scattered** by the atoms in the **crystalline** compound
  - uses the diffraction pattern to map the electron density in the crystal and determine the structure of the compound along with bond lengths and bond angles.

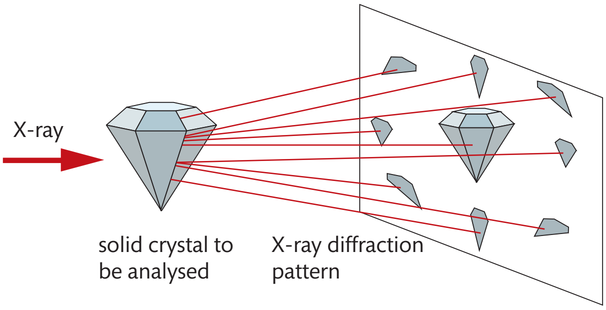


Figure 21.3 *Electromagnetic waves, such as X-rays, are diffracted when they interfere with each other due to the presence of objects in their path.*

- The diffraction pattern shows regions of:
  - high intensity where scattered X-rays are **in phase** and **constructively interfere**

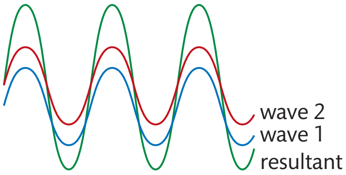


Figure 21.4 *Constructive interference occurs when the waves are in phase: Waves reinforce each other to produce a region of high-intensity X-rays on the screen.*

  - low intensity where scattered X-rays are **out of phase** and **destructively interfere**.

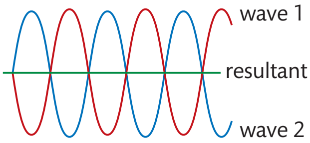


Figure 21.5 *Destructive interference occurs when the waves are out of phase. Waves cancel each other out to produce a region of low-intensity X-rays on the screen.*

Subject vocabulary

single-crystal X-ray crystallography a technique that records the diffraction pattern generated by X-rays scattered by a crystal and uses this to determine the structure of the compound

monochromatic (light) with one specific wavelength

crystal a solid in which all the individual species (ions, atoms, or molecules) are in a highly ordered arrangement

scattered deflected from the original direction

crystalline having the properties of a crystal

in phase when two waves are in phase the peaks and troughs of both waves occur at the same position

constructively interfere add together to give a wave with a larger amplitude

out of phase when two waves are out of phase the peaks of one wave occur at the same position as the troughs of the other wave

destructively interfere cancel each other completely and no wave exists after they combine

- Scattered X-rays will be in phase or out of phase depending on:
  - the wavelength of the X-rays (λ)
  - the angle that the X-rays hit the surface of the crystal (θ), which is known as the **incident angle**
  - the distance between the atoms in the crystal (*d*).

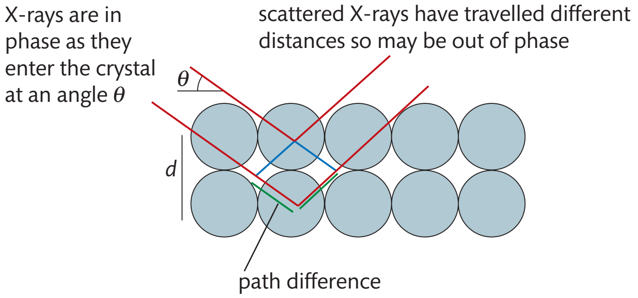


Figure 21.6 *The angle of diffraction at which constructive interference occurs (θ) depends on the wavelength of the incident radiation (λ) and the interatomic distance (d).*

- An **electron density map** can be determined from the diffraction pattern and this shows where the atoms are located. The positions of hydrogen atoms cannot be determined directly using X-ray crystallography because they have a low electron density and do not diffract X-rays.

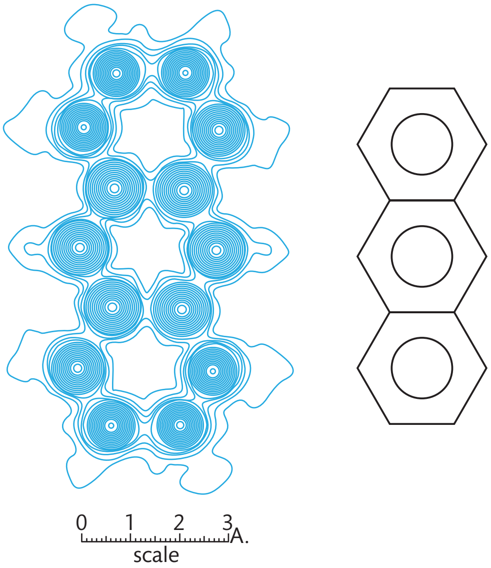


Figure 21.7 *The electron density map of anthracene and its molecular structure. The carbon–carbon bond lengths and angles can be obtained directly from the map. The high electron density between the atoms shows the presence of covalent bonding.*

Subject vocabulary

incident angle that angle at which X-rays hit the surface of a crystal

electron density map a representation (or map) of where electrons are in a compound

The investigation

During your two-year IB Chemistry course, you are expected to carry out an individual scientific investigation, sometimes known as an exploration. This must be written up as a full report, and contributes to your final assessment on the course.

The investigation will be based on a topic of your own interest, and have a purposeful research question and scientific rationale. Your approach and methodology may rely on the collection of primary data through experimental work, or it may involve analysis of secondary data. Possibilities include the use of spreadsheets for analysis and modelling, extraction and analysis of data from a database, or the use of open-ended simulations. The investigation may also use a mix of approaches and data sources. In all cases, the investigation is marked according to the same five criteria, which are summarized below. Note the following general points:

- The written investigation is marked by your teacher (internally).
- The reports of a sample of students from your class will be re-marked by the IB, a process known as moderation, which ensures that the same standards are applied across all candidates.
- The mark awarded for your investigation contributes 20% towards your final IB result.
- The investigation is expected to take approximately 10 hours to complete.
- The investigation should be about 6 to 12 pages in length in regular font size.
- The investigation can be based on a topic within the course content, or it can be on extension material beyond the topic specifications in the IB Chemistry guide.

The investigation should provide clear evidence of the knowledge and skills that you have acquired with respect to the Nature of Science, and an awareness of the aims of the course. You also have the opportunity here to demonstrate the attributes of the IB learner profile.

The assessment criteria

The investigation will be marked using a best-fit approach to match the level of work with the descriptors given as mark bands. Each criterion is marked separately, and makes a specific contribution to the final mark out of 24 (later scaled to 20% of the overall IB assessment), as shown below.

	Personal engagement	Exploration	Analysis	Evaluation	Communication
mark out of 24	2	6	6	6	4
% of IA mark	8%	25%	25%	25%	17%

The marking descriptors for each criterion are shown below, with some additional notes for guidance.

Personal engagement

Mark	Descriptor
0	The student's report does not reach a standard described by the descriptors below.
1	The evidence of personal engagement with the exploration is limited with little independent thinking, initiative, or creativity. The justification given for choosing the research question and/or the topic under investigation does not demonstrate personal significance, interest, or curiosity. There is little evidence of personal input and initiative in the designing, implementation, or presentation of the investigation.

Your report should include some background to the choice of your investigation and what inspired you in the planning. Maybe it was something that you thought about in class, or during an experiment, or something you read? You will be credited for an investigation that is innovative and somewhat unique, that shows evidence of independent thinking and creativity in any or all stages. Try to demonstrate personal interest and genuine enthusiasm in your report.

Exploration

Mark	Descriptor
0	The student's report does not reach a standard described by the descriptors below.
1–2	The topic of the investigation is identified and a research question of some relevance is stated but it is not focused. The background information provided for the investigation is superficial or of limited relevance and does not aid the understanding of the context of the investigation. The methodology of the investigation is only appropriate to address the research question to a very limited extent since it takes into consideration few of the significant factors that may influence the relevance, reliability, and sufficiency of the collected data. The report shows evidence of limited awareness of the significant safety, ethical, or environmental issues that are relevant to the methodology of the investigation*.
3–4	The topic of the investigation is identified and a relevant but not fully focused research question is described. The background information provided for the investigation is mainly appropriate and relevant and aids the understanding of the context of the investigation. The methodology of the investigation is mainly appropriate to address the research question but has limitations since it takes into consideration only some of the significant factors that may influence the relevance, reliability, and sufficiency of the collected data. The report shows evidence of some awareness of the significant safety, ethical, or environmental issues that are relevant to the methodology of the investigation*.

* This indicator should only be applied when appropriate to the investigation.

Your report must have a clearly stated and focused research question, and give the scientific context of the work. This means relating it to your knowledge of the topic studied. The methodology used must show how relevant data are collected, taking into account factors that influence reliability of results. Consider control variables, choice of apparatus, and how many data will be sufficient for useful analysis. Note that five data points are usually considered necessary to establish a trend line. Where appropriate, make sure that you have demonstrated awareness of related health, safety, and environmental issues. References to sources must, of course, be properly quoted.

Analysis

Mark	Descriptor
0	The student's report does not reach a standard described by the descriptors below.
1–2	The report includes insufficient relevant raw data to support a valid conclusion to the research question. Some basic data processing is carried out but is either too inaccurate or too insufficient to lead to a valid conclusion. The report shows evidence of little consideration of the impact of measurement uncertainty on the analysis. The processed data are incorrectly or insufficiently interpreted so that the conclusion is invalid or very incomplete.
3–4	The report includes relevant but incomplete quantitative and qualitative raw data that could support a simple or partially valid conclusion to the research question. Appropriate and sufficient data processing is carried out that could lead to a broadly valid conclusion but there are significant inaccuracies and inconsistencies in the processing. The report shows evidence of some consideration of the impact of measurement uncertainty on the analysis. The processed data are interpreted so that a broadly valid but incomplete or limited conclusion to the research question can be deduced.

In this part of the report you must record data, both qualitative and quantitative, and demonstrate how the data are processed. This includes showing accuracy in calculations, the correct use of units, and consideration of the impact of error propagation. Data should be put into a table where possible. Graphs must be clearly titled, have appropriate scales and labelled axes with units, and show accurately plotted data points. Suitable best-fit lines or curves need to be marked distinctly. Your processed data need to be interpreted carefully in the context of the research question to develop a valid conclusion.

Evaluation

Mark	Descriptor
0	The student's report does not reach a standard described by the descriptors below.
1–2	A conclusion is outlined which is not relevant to the research question or is not supported by the data presented. The conclusion makes superficial comparison to the accepted scientific context. Strengths and weaknesses of the investigation, such as limitations of the data and sources of error, are outlined but are restricted to an account of the practical or procedural issues faced. The student has outlined very few realistic and relevant suggestions for the improvement and extension of the investigation.
3–4	A conclusion is described which is relevant to the research question and supported by the data presented. A conclusion is described which makes some relevant comparison to the accepted scientific context. Strengths and weaknesses of the investigation, such as limitations of the data and sources of error, are described and provide evidence of some awareness of the methodological issues* involved in establishing the conclusion. The student has described some realistic and relevant suggestions for the improvement and extension of the investigation.

You must give a conclusion that is both justified by the results presented, and puts the findings in a broader context. This involves comparison with literature values and accepted data sources. This is a good place to show off your relevant scientific knowledge, and you should aim to include molecular level explanations for your findings where possible. Full consideration of errors is essential, and should lead you to evaluate the methodology chosen and suggest relevant modifications. Make sure that the modifications are specific to the weaknesses identified. A table with three columns can help you to keep this part of the report focused, as shown in the example below:

Error/design limitation	Impact on results	Suggested modification
some of the CO_2 collected by displacement of water may have dissolved in the water	volume of CO_2 measured is less than the volume released by the reaction	collect gas over warm water to reduce its solubility

Communication

Mark	Descriptor
0	The student's report does not reach a standard described by the descriptors below.
1–2	The presentation of the investigation is unclear, making it difficult to understand the focus, process, and outcomes. The report is not well structured and is unclear: the necessary information on focus, process, and outcomes is missing or is presented in an incoherent or disorganized way. The understanding of the focus, process, and outcomes of the investigation is obscured by the presence of inappropriate or irrelevant information. There are many errors in the use of subject-specific terminology and conventions*.

* For example, incorrect/missing labelling of graphs, tables, images; use of units, decimal places.

A good scientific report communicates in clear and concise language with no unnecessary comments. There is no fixed narrative style or outline of sub-headings expected, but your report should follow a logical sequence and make correct use of the subject-specific terms. Scientific journal articles provide a good source of ideas for how to structure your report. This criterion will be judged based on the communicative quality of the report as a whole.

Making the most of your Internal Assessment opportunity

1 Start early

Your school will give guidance on when you are expected to work on your investigation and will probably set internal deadlines. But you can start thinking about possible topics from the beginning of the course, and research ideas and approaches. Keep a record of your resources and outlines, and allow your ideas to develop as your knowledge grows in the course.

2 Be aware of the criteria

As you choose your research question and design your investigation, keep a close eye on the assessment criteria that are given here. Remember the marks that you are given are decided by how well your work matches these specific descriptors, so keep checking that your investigation matches them closely.

3 Seek and follow feedback

Your teacher may give you some guidance on your early ideas and suggest modifications. Don't be afraid to ask for help as you develop your plan, as this could make your work more efficient and will not affect your assessment.

4 Be enthusiastic!

This is your chance to put the Nature of Science into action. You are in charge of your choice of topic, and have the flexibility here to be creative, so enjoy it fully.

Chemistry Extended Essay

The Extended Essay is a compulsory part of the IB Diploma. It is an independent 40-hour research project in an IB subject of your choice. The final essay is up to 4000 words of formally presented, structured writing.

An Extended Essay in chemistry must have a clear chemical emphasis, for example a Chemistry Extended Essay in an area such as biochemistry will be assessed on its chemical and not its biological content. It should include chemical principles and theory.

Some advice

Before you start

Read a copy of the subject-specific details of an Extended Essay in chemistry, including the assessment criteria. Read some previous essays and try to identify their strengths and weaknesses. Draw up a list of possible research questions, including the techniques you would use to address these questions. Many of the best essays are written by students investigating relatively simple phenomena using apparatus and materials that can be found in most school laboratories.

You may find it useful to consider some of the following techniques when planning your research; it is often appropriate to use a combination of two or more of these approaches:

- titration: acid–base or redox
- chromatography: paper, partition, thin-layer, column
- electrophoresis
- spectrophotometry
- measuring mass or volume changes
- calorimetry
- qualitative and quantitative analysis
- separation and purification techniques in organic chemistry
- use of data-logging probes for some of the above.

The research question

The research question is the key to a successful Extended Essay. You should choose a topic that interests you as you will be spending 40 hours on this. Your question must be sharply focused. For example, *What is the ratio of oxygen and chlorine produced at the anode during the electrolysis of different concentrated solutions of aqueous sodium chloride solution?* is better than *What happens during the electrolysis of salt?*

The research process

- Safety is a priority. Don't do anything in the laboratory without checking with your supervisor.
- Use a range of resources to find out what others have done in the area. Textbooks should never be the only source of information.
- Keep written records of everything that you do and make a note of all references, including the date when internet sites were accessed, so that you can build up your footnotes and bibliography as you go along.

- Record all experimental data, including the dates when the experiments were performed and any uncertainties in your measurements. In your preliminary investigations, write down any problems and challenges you encountered and record any modifications. Use your imagination to design new equipment if necessary.

While writing the essay

Make sure that you address your stated research question and the Extended Essay assessment criteria.

- Include explanations of any theory not covered in the IB Subject Guide, including the chemistry of any specialized techniques you have used.
- Use the appropriate chemical language and make sure that all chemical equations are balanced.
- Include sufficient details of any experimental procedure to allow others to repeat the work.
- Check any calculations and make sure that all experimental data are presented correctly.
- Discuss the limitations of the experimental method and any systematic errors.
- Consider any questions which are unresolved at the end of your research and suggest new questions and areas for possible further investigation.
- Let your enthusiasm and interest for the topic show and emphasize clearly your own personal contribution.
- Ensure that your word count is close to 4000. You will often find you can cut quite a number of words as you polish your essay at the end.

After completing the essay

- Check and proofread the final version carefully.
- Use the assessment criteria to grade your essay. Are you satisfied with the grade you award yourself?

The assessment criteria

Overview of the assessment criteria for the Extended Essay

Criterion A: Focus and method	Criterion B: Knowledge and understanding	Criterion C: Critical thinking	Criterion D: Presentation	Criterion E: Engagement
• Topic • Research question • Methodology	• Context • Subject-specific terminology and concepts	• Research • Analysis • Discussion and evaluation	• Structure • Layout	• Process • Research focus
Marks	**Marks**	**Marks**	**Marks**	**Marks**
6	6	12	4	6

Total marks available: 34

The Extended Essay criteria and advice to achieve high marks for each criterion

Criterion and marks	Advice/questions to ask yourself
A: Focus and method (6 marks) • Topic • Research question • Methodology	Assess the explanation of the focus of the research (this includes the topic and the research question), how the research will be undertaken, and how the focus is maintained throughout the essay. You can also formulate your research question as a statement or as a hypothesis. It is good practice to use the introduction to lead into the research question, which should be highlighted so that it is obvious.
B: Knowledge and understanding (6 marks) • Context • Subject-specific terminology and concepts	Assess the extent to which the research relates to the subject area/discipline used to explore the research question, and the way in which this knowledge and understanding is demonstrated through the use of appropriate terminology and concepts. • Have you explained how your research question relates to a specific subject you selected for the extended essay? You are not expected to explain basic chemistry, but you are expected to show that you fully understand the relevant principles and ideas and can apply them correctly. Have you used relevant terminology and concepts throughout your essay as they relate to your particular area of research? • Is it clear that the sources you are using are relevant and appropriate to your research question? • Do you have a range of sources or have you relied on one particular type, for example internet sources? • Is there a reason why you might not have a range? Is this justified?

Criterion and marks	Advice/questions to ask yourself
C: Critical thinking (12 marks) Research Analysis Discussion and evaluation	For non-experimental essays include details of how you selected your data. Distinguish between primary sources (personal communications, interviews) and secondary sources (textbooks, newspaper articles, reviews). You should comment on the reliability of your sources. It is good practice to show an awareness of a range of possible approaches which could have been used in answering the research question. Also explain why the chosen approach was adopted. You should provide sufficient information for any experimental work to be repeated. It should be clear which experiments you have designed and which you have altered, adapted, or improved from existing methods. A thorough understanding of the reliability of all data used to support the argument should be shown. Inadequate experimental design or any systematic errors should be analysed. Uncertainties in physical data should be evaluated and discussed. Approximations in models should be accounted for and all assumptions examined thoroughly. Where possible, the quality of sources accessed or data generated should be verified by secondary sources or by direct calculations.
D: Presentation (4 marks) • Structure • Layout	• Have you chosen a font that will be easy for examiners to read on-screen? • Is your essay double-spaced and size 12 font? • Are the title and research question mentioned on the cover page? • Are all pages numbered? • Have you prepared a correct table of contents? • Do the page numbers in the table of contents match the page numbers in the text? • Are all figures and tables properly numbered and labelled? • Does your bibliography contain only the sources cited in the text? • Did you use the same reference system throughout the essay? • Does the essay have fewer than 4000 words? • Is all the material presented in the appendices relevant and necessary? • Have you proofread the text for spelling and grammar errors? Correct chemical should be used consistently. Relevant chemical formulas (including structural formulas), balanced equations (including state symbols), and mechanisms should be included. The correct units for physical quantities must always be given. For experiments where numerical results are calculated from data obtained by changing one of the variables, try to show one example of the calculation. The remainder can be displayed in tabular or graphical form. The conclusion must be consistent with the argument presented. It should not repeat material in the introduction or introduce new points to the argument. It is a good idea to consider unresolved questions and to suggest areas for further investigation.

Criterion and marks	Advice/questions to ask yourself
E: Engagement (6 marks) ● Process ● Research focus	Have you demonstrated your engagement with your research topic and the research process? Have you highlighted challenges you faced and how you overcame them? Will the examiner get a sense of your intellectual and skills development? Will the examiner get a sense of your creativity and intellectual initiative? Will the examiner get a sense of how you responded to actions and ideas in the research process? You should also demonstrate that you understand the theory behind any techniques or apparatus used and also identify possible weaknesses.

Bibliography and references

It is required that you acknowledge all sources of information and ideas in an approved academic manner. Essays that omit a bibliography or that do not give references are unacceptable. Your supervisor or school librarian will be able to give you advice on which format to follow. One acceptable format is:

Author(s), Year, *Title*, Place of publication, Publisher.

C. Brown and M. Ford, 2014, *Higher Level Chemistry, 2nd edition*, UK, Pearson Baccalaureate.

Internet references should include the title of the extract used as well as the website address, the date it was accessed, and, if possible, the author. You should always exercise caution when using information from websites that do not give references or that cannot be cross-checked against other sources. The more important a particular point is to the essay, the more the quality of its source needs to be evaluated.

Viva voce

After you have handed in the final version you may be given a short interview or *viva voce* by your supervisor, who is required to write a report on your project. This is an opportunity to discuss the successes and challenges of the project, and for you to reflect on what you have learned from the experience.

World Studies Extended Essay

As you think about topics for an Extended Essay in chemistry, it may be that you find an area of current global interest that overlaps with another subject. In this case, it may be appropriate to submit the essay as World Studies, which is a separate IB Extended Essay subject. An essay in World Studies must have the following characteristics:

- it must focus on an *issue of contemporary global significance*
- it must involve an in-depth *interdisciplinary study*, making reference to at least two IB subjects.

The approach to a World Studies Extended Essay is to identify a global issue and find a local example that lends itself to research and analysis, using the methodologies of two different subjects. This gives a grounded appreciation and understanding of the issue under study. As part of the research, you are encouraged to keep records of your thoughts and ideas in the 'researcher's reflection space'. This helps to show development in your global perspective and some of the challenges in the research.

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ISBN 978-1-292-13453-6