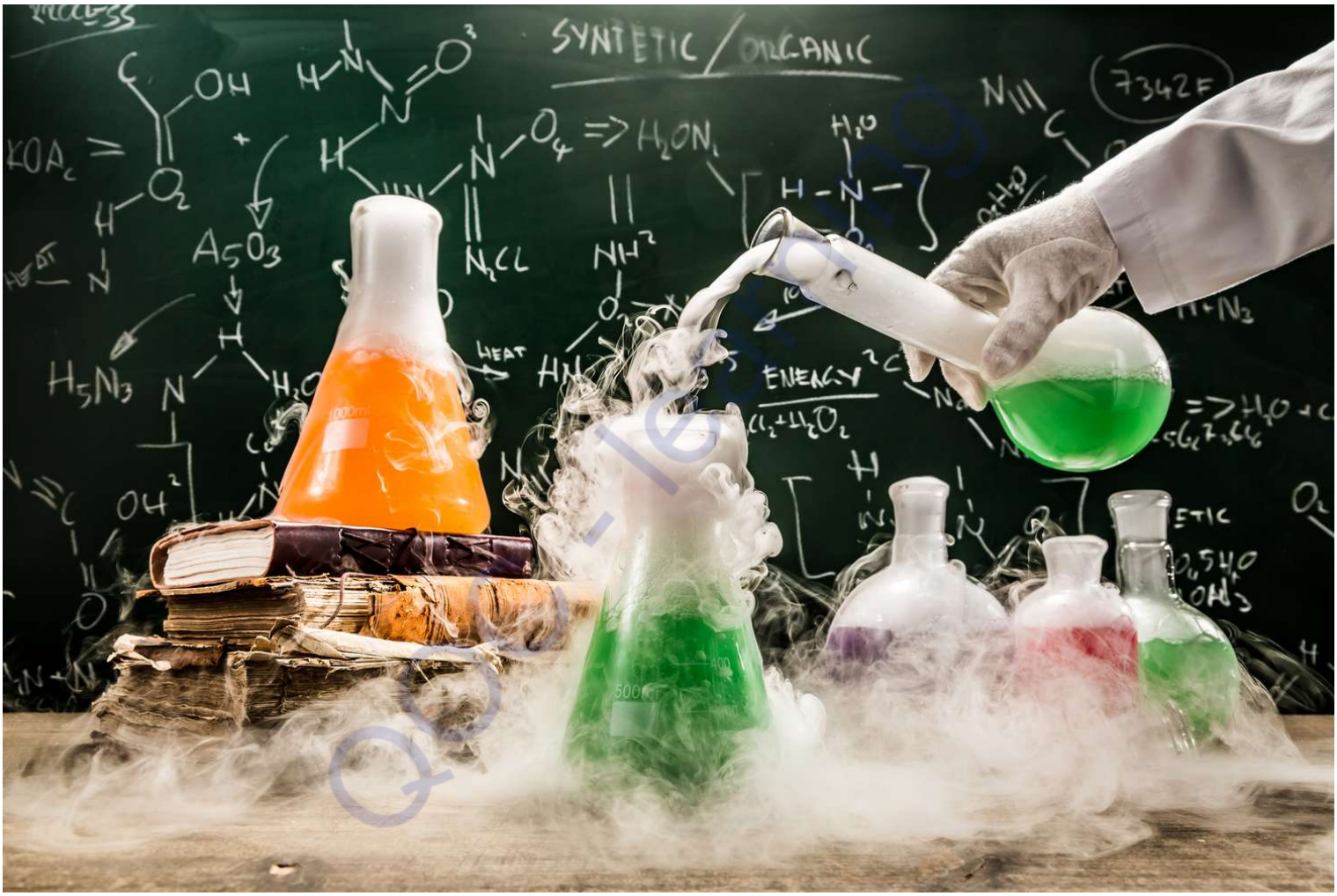
Unit 1



1.3 Formulae, equations and amounts of substance

Key terms

- **Atom**: An atom is the smallest particle of an element that cannot be broken down further by chemical means.
- **Element**: Elements are the simplest chemical substances which cannot be decomposed into simpler chemicals by heating or using electricity.
- **Ion**: An ion is an atom, or group of atoms, which has become electrically charged by the loss or gain of one or more electrons.
- **Molecule**: A group of atoms held together by covalent bonds. Molecules may be elements or compounds.
- **Compound**: A substance formed in a chemical change when two or more elements are joined together.
- **Empirical formulae**: An empirical formula shows the simplest whole number ratio of the atoms of different elements in a compound.
- **Molecular formulae**: The molecular formula gives the actual number of atoms of each element in a molecule.

Writing balanced equations

* The number of moles should be the same on both sides of an equation.

Example: Write down the equation for the extraction of iron from hematite using a reducing agent.

$Fe_2O_3 + CO \rightarrow Fe + CO_2$ (Write the equation)

$\downarrow\downarrow$

$Fe_2O_3 + 3CO \rightarrow 2Fe + 3CO_2$ (Balance it)

$\downarrow\downarrow$

$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$ (Add state symbols)

Ionic equation-Example

$Cu^{2+}_{(s)} + 2Cl^-_{(aq)} \rightarrow CuCl_{2(aq)}$

* Ionic equations must balance for charge!!!

Steps
- Write the ions separately for solutions of ionic compounds
- Write full molecular formulae for solids and all covalent substances
- Cancel the spectator ions

Key terms

- **Relative atomic mass**: A_r is the average mass of an element relative to $\frac{1}{12}$th of the mass of an atom of the isotope carbon-12.
- **Amount of substance**: is a physical quantity (symbol n) which is measured in the unit mole (symbol mol).

- **Molar mass**: is the mass of one mole of a chemical - the unit is $g\,mol^{-1}$.
- **Parts per million**: a unit of measure of the amount of dissolved solids in a solution in terms of a ratio between the number of parts of solids to a million parts of total volume (ppm). 1000 ppm is 1000 mg per liter.

Amounts in solutions

$$\text{concentration}/g\,dm^{-3} = \frac{\text{mass of solute}/g}{\text{volume of solution}/dm^3}$$

$$\text{concentration}/mol\,dm^{-3} = \frac{\text{amount of solute}/mol}{\text{volume of solution}/dm^3}$$

$$\text{concentration}/ppm = \frac{\text{amount of solute}/g}{1 \text{ million grams of solute}}$$

Calculations involving equations

An equation tells a lot!

Steps in solving problems using equations:

Step 1: Write the balanced equation for the reaction.
Step 2: Write down the amounts in moles of the relevant reactants and products in the equation
Step 3: Convert these amounts in moles of the relevant reactants and products to masses.
Step 4: Scale the masses to the quantities required.

Example

What mass of iron can be obtained from 1.0 kg of hematite?

→ Step 1: $Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 2Fe_{(s)} + 3CO_{2(g)}$

→ Step 2: 1 mol Fe_2O_3 → 2 mol Fe

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

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

So, 159.6 g Fe_2O_3 → 2×55.8 g Fe = 111.6 g Fe

→ Step 4: 159.6 g Fe_2O_3 → 111.6 g Fe

1.0 g Fe_2O_3 → $\frac{111.6}{159.6}$ g Fe

= 0.70 g Fe (2 s.f)

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

The Avogadro Constant

The Avogadro constant is the number of atoms, molecules or ions in one mole of a substance. In fact, the molar mass (1 mole) of every element contains the same number of atoms. Experiments show that the Avogadro constant, L, is $6.02 \times 10^{23}\ mol^{-1}$.

number of molecules = moles × Avogadro constant

number of ions = moles × Avogadro constant × number of those ions in the formula

Yields and atom economies

If there are no losses during a chemical reaction, the starting reactants are converted to the required products. Converting all of the limiting reagent to the desired product gives a 100% yield.

- A limiting reagent: is a substance which is present in an amount which limits the theoretical yield.

✳ Few reactions are so efficient and many give low yields. There are various reasons why yields are not 100%:

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

Percentage yield

Yield calculations are used to assess the efficiency of a chemical process.

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

Atom economy

Atom economy is a measure of how efficiently a chemical reaction converts the atoms in its reactants to atoms in the product.

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

Amounts of gases

The gas laws describe the behaviour of gases and are summarised by the ideal gas equation. Ideal gases are gases which obey the ideal gas equation.

The ideal gas equation

$$pV = nRT$$

p: Pressure in Pa
V: Volume in m^3
n: Number of moles in mole
R: Constant → $8.31\ J\,mol^{-1}K^{-1}$
T: Temperature in Kelvin

The molar volume of gases

The molar volume of a gas is the volume of 1 mol of the gas under stated conditions. At room temperature and atmospheric pressure, the molar volume of all gases is $24.0\ dm^3\,mol^{-1}$.

volume of gas / cm^3 = amount of gas / mol × 24000 / $cm^3\,mol^{-1}$

Empirical formulae

The empirical formula shows the simplest ratio in which atoms combine.

Steps

1- Find the combining masses (in grams) by experiment.
2- Change grams to moles of atoms.
3- This tells you the ratio in which atoms combine.
4- So you can write a formula.

Note: If the combining masses are given in percentages, follow the same steps. The percentages, in effect, show the combining masses in a 100g sample of the compound.

Molecular formulae

The molecular formula gives the actual number of atoms of each element in a molecule.

Steps

1- First, find the empirical formula.
2- Calculate $\frac{M_r}{\text{empirical mass}}$ for the compound. This gives a number, n.
3- Multiply the numbers in the empirical formula by n.

Measuring enthalpy changes

The energy given out or taken in during many chemical reactions can be measured and this makes it possible to calculate enthalpy changes.

The energy transferred to a material can be calculated using this expression:

energy transferred /J = mass /g × specific heat capacity /J g^{-1} K^{-1} × temperature rise /K

$$Q = mc\Delta T$$

- The specific heat capacity of a material, c, is the energy needed to raise the temperature of 1g of the material by 1K.

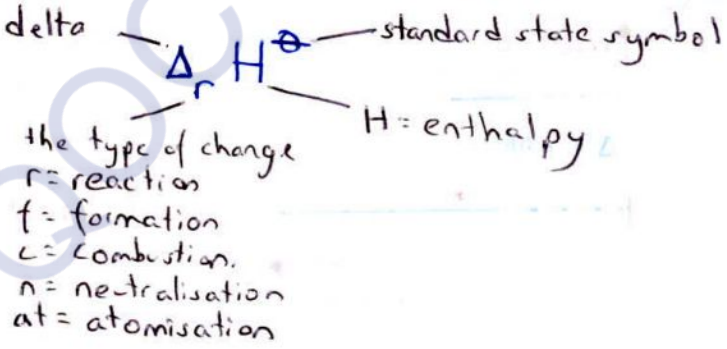
For water c = 4.18 J g^{-1} K^{-1}

Standard enthalpy changes

The standard conditions are:

- a pressure of 100 kPa
- a stated temperature that is usually 298 K (25°C)
- substances in their standard (most stable) state at 100 kPa pressure and the stated temperature
- solutions with a concentration of 1 mol dm^{-3}

Any enthalpy change measured under standard conditions is described as a standard enthalpy change and given the symbol $\Delta H^{\ominus}_{298}$ or simply $\Delta H^{\ominus}$, pronounced 'delta H standard'.



- The standard enthalpy change of a reaction, $\Delta_r H^{\ominus}$, is the energy transferred when the molar quantities of reactants as stated in the equation react under standard conditions.
- The standard enthalpy change of combustion of a substance, $\Delta_c H^{\ominus}$ is the enthalpy change when one mole of the substance burns completely in oxygen under stated conditions.

Example

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta_c H^{\ominus} = -394\ kJ\ mol^{-1}$$

Shorthand form: $\Delta_c H^{\ominus}[CH_{4(g)}] = -890\ kJ\ mol^{-1}$

1.4 ENERGETICS

Energy changes

Thermochemistry is the study of energy changes in chemistry. Energy changes from chemical reactions are of great practical importance. Whenever a change occurs in a system, there is almost always an energy change involving transfer of energy between the system and its surroundings.

- An enthalpy change: ΔH is the overall energy changed with the surroundings when a change happens at constant pressure and the final temperature is the same as the starting temperature. ($kJ\ mol^{-1}$)

Enthalpy changes

Exothermic changes

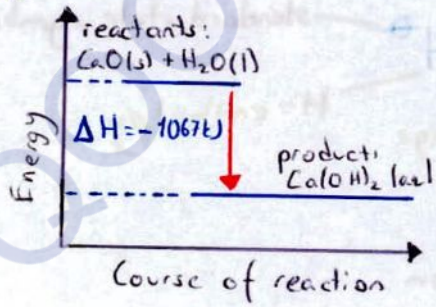
Exothermic changes give out energy that often just heats up the surroundings. Burning is an obvious exothermic chemical reaction. Hot packs used in self-warming drinks and in treating rheumatic conditions also involve exothermic reactions.

* The sign of ΔH for exothermic reactions is always negative.

An example:

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2\,(aq)} \quad \Delta H = -1067\ kJ\ mol^{-1}$$

→ The energy changes in reactions can be summarised in enthalpy level diagrams:

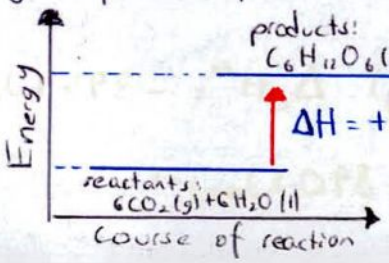


* Chemists measure changes in enthalpy. Energy level diagrams show the difference in enthalpy between the reactants and the products.

Endothermic changes

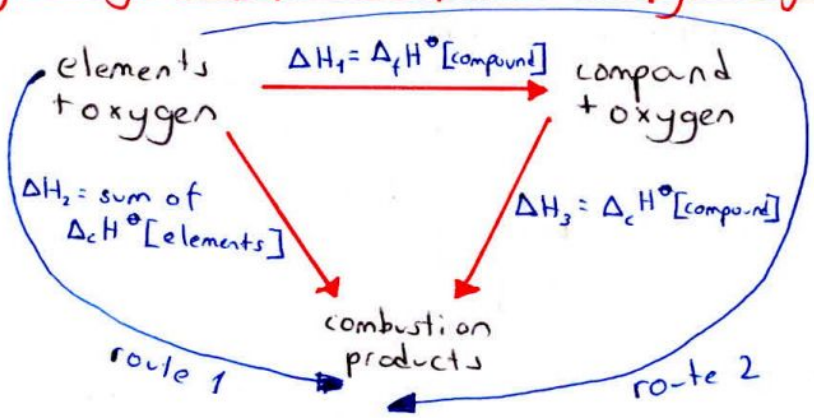
Endothermic changes take in energy from the surroundings. They are the opposite of endothermic changes. Twist a cold pack and it gets cold. When chemicals in the cold pack react, they take in energy and the pack gets cold.

* The sign of ΔH for endothermic reactions is always positive.



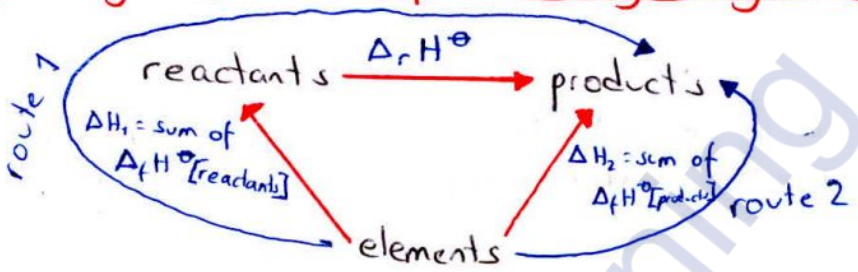
→ An enthalpy level diagram for photosynthesis

Enthalpy changes of formation from enthalpy changes of combustion



Hence, $\Delta H_2 = \Delta H_1 + \Delta H_3$

Enthalpy changes of reaction from enthalpy changes of formation



According to Hess's Law:

$$\Delta H_1 + \Delta_r H^\ominus = \Delta H_2$$

Rearranging gives:

$$\Delta_r H^\ominus = \Delta H_2 - H_1$$

So:

$$\Delta_r H^\ominus = \text{sum of } \Delta_r H^\ominus[\text{products}] - \text{sum of } \Delta_f H^\ominus[\text{reactants}]$$

* Do not learn these formulae parrot fashion. Check with the Hess cycle each time.

Note: In general, chemists expect that a reaction will go if it is exothermic.

Enthalpy changes and bonding

- Bond breaking is endothermic. - Bond making is exothermic.

During reactions, the bonds in reactants break and then new bonds form in the products. This means that the enthalpy change of a reaction is the energy difference between bond-breaking and bond making process.

- The bond enthalpy of a particular bond is the energy required to break one mole of the bonds in a substance in the gaseous state.
- The mean bond enthalpy of the X-Y bond is the mean value of the bond enthalpy values ~~of the bond enthalpy values~~ for the X-Y bond averaged across a wide range of compounds.

Unknown bond enthalpies can be calculated given the enthalpy change for a reaction involving the compound which includes the bond together with other relevant bond enthalpies, however this has limitations and values may not match with experimental data as discussed in the relevant practical objective.

- **The standard enthalpy change of formation** of a compound, $\Delta_f H^\ominus$, is the enthalpy change when one mole of the compound forms from its elements under standard conditions with the elements and the compound in their standard (stable) states.

* The elements and the compound formed must be in their stable states. The more stable state of an element is chosen where there are allotropes such as graphite and diamond.

* One important consequence of the definition of standard enthalpy changes of formation is that, for an element, $\Delta_f H^\ominus = 0\ kJ\ mol^{-1}$ because there is no change, and therefore no enthalpy change, when an element forms from itself.

$$\Delta_f H^\ominus [O_2(g)] = 0$$

- **The standard enthalpy change of neutralisation** is the enthalpy change when the acid and alkali in the equation for the reaction neutralise each other under standard conditions to form one mole of water.

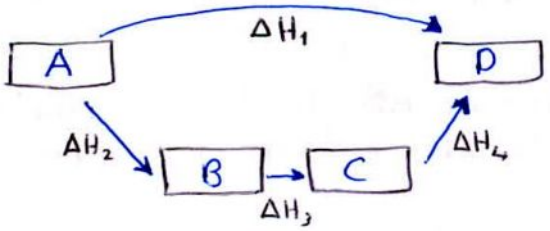
- **The standard enthalpy change of atomisation** of an element, $\Delta_{at} H^\ominus$, is the enthalpy change when one mole of gaseous atoms is formed from the element under standard conditions.

$$\frac{1}{2} H_2(g) \rightarrow H(g) \quad \Delta_{at} H^\ominus = +218\ kJ\ mol^{-1}$$

$$\Delta_{at} H^\ominus [\tfrac{1}{2} H_2(g)] = +218\ kJ\ mol^{-1}$$

Hess's Law and the indirect determination of enthalpy changes

Hess's Law states that the enthalpy change in converting reactants to products is the same regardless of the route taken, provided that the initial and final conditions are the same.



* According to Hess's law:

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4$$

* Hess's Law is a chemical version of the law of conservation of energy.

* Hess's Law can be used to calculate:

- standard enthalpy changes of formation from standard enthalpy changes of combustion
- standard enthalpy changes of reaction from standard enthalpy changes of formation.

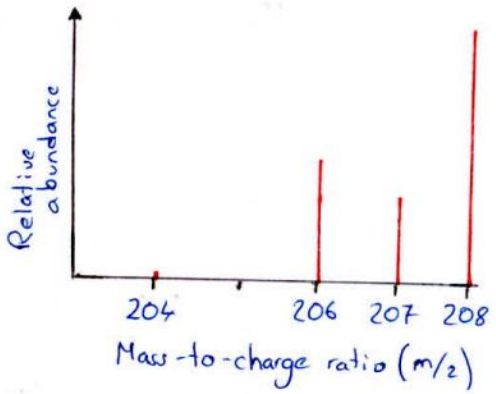
Mass Spectra

Mass spectrometry is an analytical chemistry technique that helps identify the amount and type of chemicals present in a sample by measuring the mass-to-charge ratio (m/z) and abundance of gas-phase ions.

A mass spectrometer is used. It separates atoms and molecules according to their mass, and also shows the relative numbers of the different atoms and molecules present.

The mass-to-charge ratio (m/z): is the ratio of the relative mass, m, of an ion to its charge, z, where z is the number of charges. Spectrometers usually operate so that most ions produced have the value of $z = 1$.

Mass spectrum of lead (Pb)



Isotopic composition: lead-204, lead 206, lead-207, lead 208 (4 isotopes)

Ratio of isotopes: 0.1 : 1.6 : 1.1 : 3.4 = 1 : 16 : 11 : 34

Percentage abundance: lead-204: 1.61
lead-206: 25.8
lead-207: 17.2
lead-208: 54.8

$$A_r \text{ of lead} = \frac{(1.61 \times 204) + (25.8 \times 206) + (17.2 \times 207) + (54.8 \times 208)}{100}$$

$$= 207.2$$

Steps in a mass spectrometer

1- Ionization of the sample by bombardment with electrons or other methods

→ Before atoms, or molecules, can be separated and detected in a mass spectrometer, they must be converted to positive ions in the gaseous state.

$$e^- + X \longrightarrow X^+ + e^- + e^-$$

(e^-: fast-moving electron; X: atom in sample vapour; X^+: positive ion; e^-: electron knocked out of X; e^-: slower-moving electron)

2- Mass analyser separating ions by mass-to-charge ratio

3- Ion detector giving an electrical signal which is converted to a digital response that is stored in a computer. The output is usually a stick diagram.

✳ Mass spectrometers can also be used to study molecules. Bombarding electrons not only ionise the molecules, but also break them into fragments. Because of the high vacuum inside the mass spectrometer, it is possible to study these molecular fragments and ions which do not normally exist. As a result the mass spectrum consists of a 'fragmentation pattern'. When analysing molecular compounds, the peak of the ion with the highest mass is usually the whole molecule ionised. So the mass of this 'parent ion' or 'molecular ion', M^+, is the relative molecular mass of the compound.

$$e^- + M_{(g)} \longrightarrow M^+ + e^- + e^-$$

(e^-: high-energy electron; $M_{(g)}$: molecule in sample; M^+: molecular ion; $e^- + e^-$: electrons)

1.5 ATOMIC STRUCTURE AND THE PERIODIC TABLE

Key Terms

- **Relative atomic mass:** A_r is the average mass of an atom of an element relative to $\frac{1}{12}$th of the mass of an atom of the isotope carbon-12.
- **Relative isotopic mass:** is the mass of one atom of an isotope relative to $\frac{1}{12}$th of the mass of an atom of the isotope carbon-12.
- **Relative molecular mass:** The relative molecular mass of an element or compound is the sum of the relative atomic masses of all the atoms in its molecular formula. (for molecular compounds)
- **Relative formula mass:** The relative formula mass of a compound is the sum of the relative atomic masses of all atoms in its formula. (for ionic compounds)

Note: All these values are relative so they do not have units.

* But why is calculation of atomic mass based on carbon-12?

→ A standard is needed to calculate the atomic mass of any element, so it could have been any element. In fact, initially it was hydrogen-1 and then oxygen-16. However, using hydrogen-1 led to inaccuracies and oxygen-17 is abundant too. Therefore, scientists agreed to use carbon-12 because of its coherence to Avogadro's principle, its stability and abundance. Carbon-12 also more accurately defines a mass for hydrogen, and it is unbound in its ground state.

*Recall from IGCSE: Relative atomic mass calculation

$$\text{relative atomic mass } (A_r) = \left(\begin{matrix}\%\text{ abundance}\\ \text{of 1. isotope}\end{matrix} \times \text{mass number}\right) + \left(\begin{matrix}\%\text{ abundance}\\ \text{of 2. isotope}\end{matrix} \times \text{mass number}\right) + \text{etc...}$$

Example

magnesium-24: 78.6%.
magnesium-25: 10.1%.
magnesium-26: 11.3%.

Q: Calculate the A_r of magnesium.

$$= \frac{(78.6 \times 24) + (10.1 \times 25) + (11.3 \times 26)}{100} = 24.3 \text{ (3s.f)}$$

*Recall from IGCSE: Relative molecular and formula mass calculation

Example

→ $M_r(H_2SO_4) = 2 \times A_r(H) + A_r(S) + 4 \times A_r(O)$

$= (2 \times 1.0) + 32.1 + (4 \times 16.0) = 98.1$

→ $M_r(Mg(NO_3)_2) = A_r(Mg) + 2 \times [A_r(N) + 3 \times A_r(O)]$

$= 24.3 + 2 \times (14.0 + 48.0) = 148.3$

Ionisation energies

As mentioned before, an ionisation energy is the energy needed to remove one mole of electrons from one mole of gaseous atoms, or ions, of an element. Ionisation energies are always endothermic. They could be shown by equations:

for sodium:

$Na_{(g)} \rightarrow Na^+_{(g)} + e^-$ first ionisation energy = +496 kJ mol^{-1}

$Na^+_{(g)} \rightarrow Na^{2+}_{(g)} + e^-$ second ionisation energy = +4563 kJ mol^{-1}

$Na^{2+}_{(g)} \rightarrow Na^{3+}_{(g)} + e^-$ third ionisation energy = +6913 kJ mol^{-1}

→ This goes on. The ionization energies for an element always get more endothermic. This is not suprising because, having moved one electron, it is more difficult to remove a second electron from the positive ion formed.

Note: It is easier to remove outer electrons than inner electrons because they are shielded from the full attraction of the positive nucleus by inner electrons.

Evidence for sub-shells of electrons

By studying the first ionization energies of successive elements in the periodic table, it is possible to compare how easy it is to remove an electron from the highest energy level in the atoms of these elements. This provides us with evidence for the arrangement of electrons in sub-shells.

Electrons in energy levels

The electrons in atoms are grouped together in energy levels or quantum shells. "$n = x$" is used to label these main shells.

Each quantum shell can hold only a limited number of electrons:

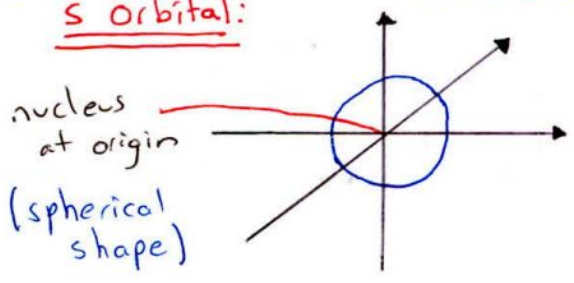
- the $n=1$ shell can hold 2 electrons
- the $n=2$ shell can hold 8 electrons
- the $n=3$ shell can hold 18 electrons
- the $n=4$ shell can hold 32 electrons

→ These main shells are further divided into 4 sub-shells: **s, p, d and f**

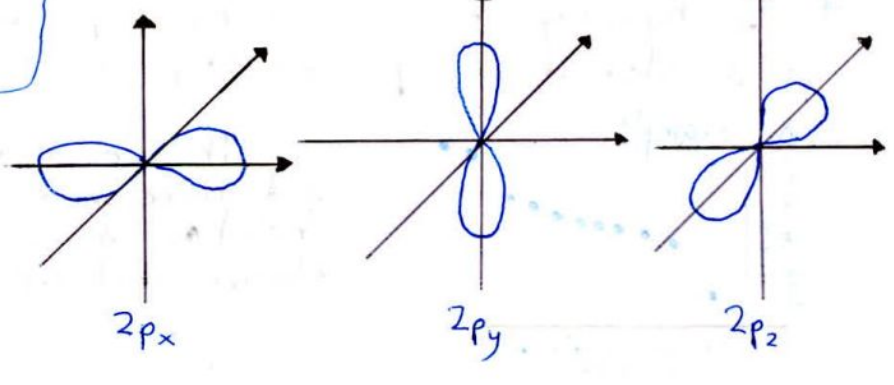
→ The sub-shells are further divided into atomic orbitals. Each orbital is defined by its:

- energy level
- shape
- direction in space ($\mp \frac{1}{2}$)

s orbital:



p orbitals: (dumbell shaped)



Uses of mass spectrometers

By carefully interpreting data from mass spectrometers, chemists can deduce:

- the isotopic composition of elements
- the relative atomic masses of elements
- the relative molecular masses of compounds.

So, mass spectrometers identify elements and compounds and therefore have numerous uses, such as in:

- Radioactive dating
- Space research
- Sport: to detect use of anabolic steroids
- Pharmaceutical industry: to provide an identifier to compounds synthesised for possible identification as drugs.

Key terms

- An ionisation energy: is the energy needed to remove one mole of electrons from ~~atoms~~ one mole of gaseous atoms, or ions, of an element.
- Atomic energy levels: are the energies of electrons in atoms. According to quantum theory, each electron in an atom has a definite. When atoms gain or lose energy, the electrons jump from one energy level to another.
- Shielding: is an effect of inner electrons which reduces the pull of the nucleus on the electrons in the outer shell of an atom. Thanks to shielding, the electrons in the outer shell are attracted by an 'effective nuclear charge' which is less than the full charge on the nucleus.

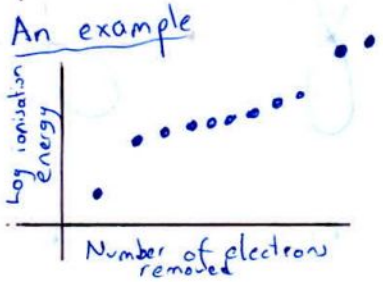
Evidence for the electronic structure of atoms

A particular amount of energy is required to remove electrons from the atoms of an element. By varying the intensity of the beam of electrons which is used to remove electrons, scientists can figure out the ionization energies of the atoms of an element. When represented on an log ionisation energy against number of electrons removed graph, a pattern forms. There are big jumps between two atomic energy levels. This provides an evidence for the existence of quantum shells. From these measurements, scientists can predict the electron structures of atoms.

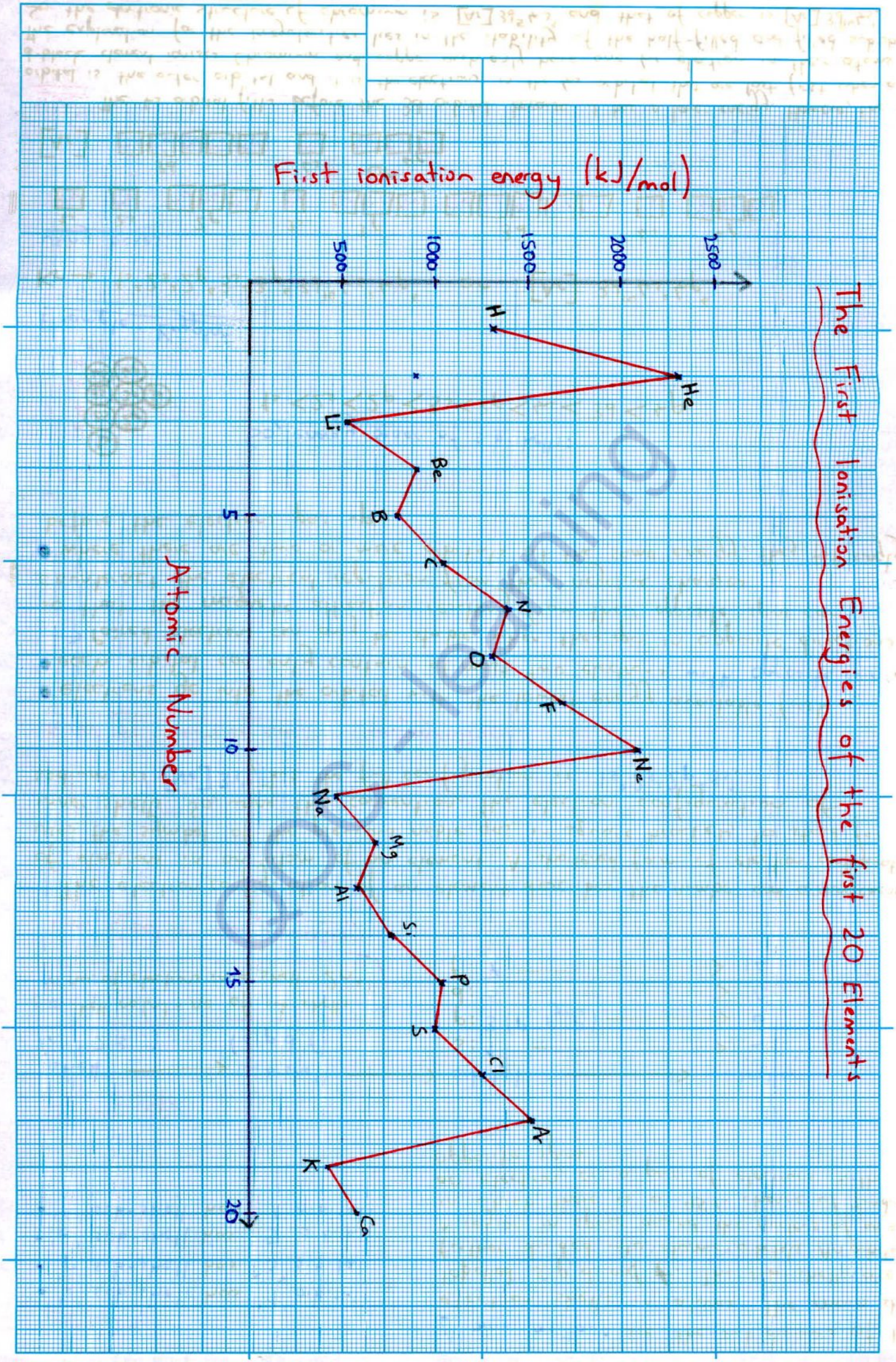
* Note: The quantum shells of electron correspond to the periods of elements in the periodic table.

* Note: By noting where the first big jump comes in the successive ionisation energies of an element, it is possible to predict the group to which the element belongs.

An example



→ This element is sodium as it has 11 electrons and three shells. The different energy levels (= quantum shells) are obvious. The first big jump is after the first electron which tells us sodium belongs to Group I.


First ionisation energy (kJ/mol)
500
1000
1500
2000
2500
Atomic Number
5
10
15
20
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
The First Ionisation Energies of the first 20 Elements

Orbitals

- 's' sub-shell has '1' orbital
- 'p' sub-shell has '3' orbitals
- 'd' sub-shell has '5' orbitals
- 'f' sub-shell has '7' orbitals

Atomic orbitals: are the sub-divisions of the electron shells in atoms. The main shells labelled s, p, d and f. The sub-shells are further divided into atomic orbitals. An orbital is a region in space around the nucleus of an atom in which there is a 95% chance of finding an electron, or a pair of electrons with opposite spins.

To sum up,

shell (n = 1, 2, 3...) → sub-shell (s, p, d, f) → orbital → electron

- s: 1 → 2
- p: 3 (p_x, p_y, p_z) → 6
- d: 5 → 10
- f: 7 → 14

* shell no (n) = no. of sub-shells
* no. of electrons in a shell = $2n^2$

The electron configuration

The electron configuration of an element describes the number and arrangement of electrons in an atom of an element. A shortened form of electron configuration uses the symbol of the previous noble gas, in square brackets, to stand for inner shells. So, using this convention, the electron configuration of sodium is $[Ne]3s^1$, but the full configuration is $1s^2 2s^2 2p^6 3s^1$.

Rules of writing electron configuration

- electrons go into the orbital with the lowest energy available first
- each orbital can only contain at most two electrons with opposite spins.

→ Paired electrons can only be stable when they spin in opposite directions so that the magnetic attraction resulting from their opposite spins can counteract the electrical repulsion from their negative charges. → Hund's rule

- where there are two or more orbitals at the same energy, they fill singly before the electrons pair up.

The energy order of the sub-shells

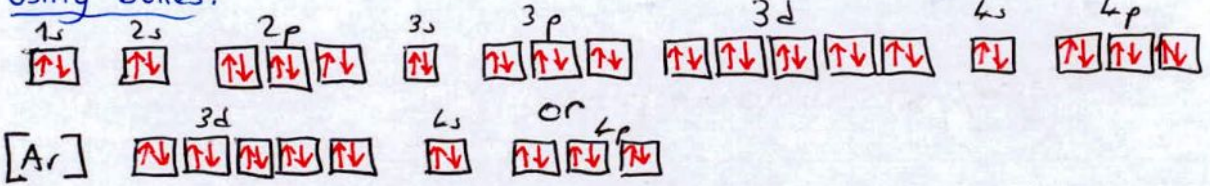
So, energy order of sub-shells:

$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p$

Example: Krypton

Kr → $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ or $[Ar]\ 3d^{10} 4s^2 4p^6$

using boxes:

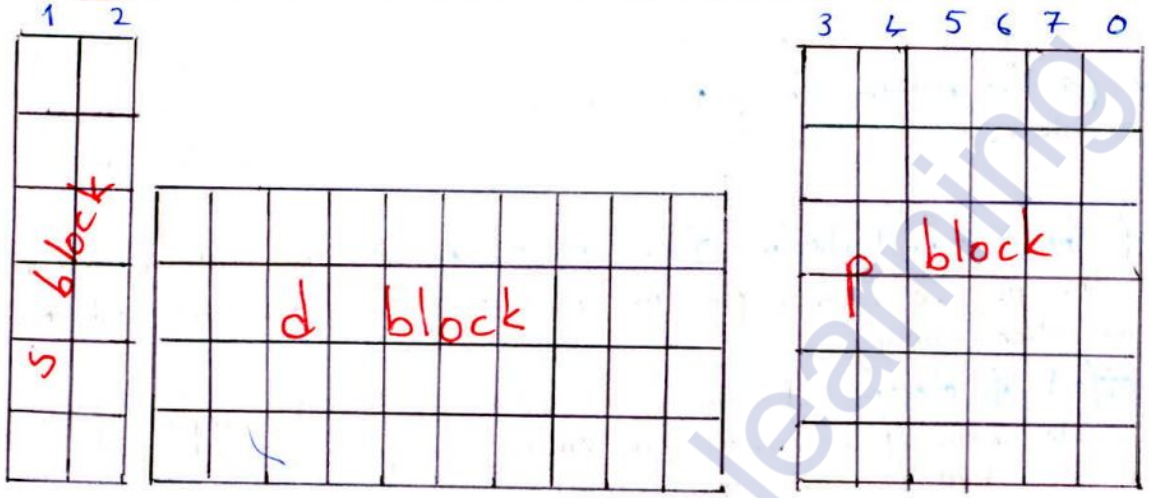


Note: The 4s orbital fills before the 3d orbital because it has a lower energy. However, the 4s orbital is the outer orbital and it is the electrons in the 4s orbital that are lost first when a d-block element ionises. Chromium and copper each only have one 4s electron in their atoms. The explanation for the irregularities lies in the stability of the half-filled and filled sub-shells. So the electronic structure of chromium is $[Ar]3d^5 4s^1$ and that of copper is $[Ar]3d^{10} 4s^1$.

Melting temperatures

- The melting temperature of an element depends on both its structure and the type of bonding between its atoms. In metals, the bonding between atoms is strong, so their melting temperatures are usually high. The more shared delocalised electrons, the stronger the bonding and the higher the melting temperature. Therefore, melting temperatures rise from Group 1 to Group 2 to Group 3.
- In Group 4, the elements carbon and silicon have giant covalent structures and this means that the melting temperatures of them are very high.
- The non-metal elements in Groups 5, 6, 7 and 0 form simple molecules. The intermolecular forces between these simple molecules are weak, so these elements have low melting temperatures.

Electron Structures and the Periodic Table



* (Recall)!

Periodic Properties

The elements in the periodic table are arranged in order of increasing atomic number and they show several trends called periodic properties. There are numerous trends including:

- Ionisation energy
- Melting temperatures
- Electronegativity
- Electron affinity

For now, we'll just look at ionisation energies and melting temperatures.

First Ionisation Energies

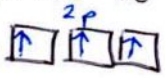
Periodicity in the first ionisation energies of the first 20 elements is illustrated on the graph in the previous page.

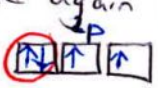
→ The ionisation energy of an atom is determined by three atomic properties:

- **The size of the positive nuclear charge:** As the positive nuclear charge increases, its attraction for outermost electrons increases and this tends to increase the ionisation energy.
- **The distance of the outermost electron from the nucleus:** As this distance increases, the attraction of the positive nucleus for the negative electron decreases and this tends to reduce ionisation energy.
- **The shielding effect of electrons:** Electrons in inner shells exert a repelling effect on electrons in the outer shells of an atom. This reduces the pull of the nucleus on electrons in the outer shell, lowering the ionisation energies.

* The Trend

↦ The general trend is increasing first ionization energy across the periods. However, the rising trend is not smooth. There is a 2-3-3 pattern, which reflects the way in which electrons feed into s and p orbitals and whether they are single or paired up. P orbitals have higher energy than an s orbital in the same period, so ionisation energy tends to be lower. On the other hand, it is easier to remove an electron from its pair because of the repulsion of the other electron. For these reasons, the first ionisation energy decreases from beryllium to boron and again from nitrogen to oxygen.

Illustration: $^{15}_{7}N$ → 

$^{16}_{8}O$ 

→ An electron is paired in $_{8}O$ and it takes less energy to remove it rather than any single electron in $_{7}N$. So, oxygen has a lower first ionization energy despite its higher positive nuclear charge.

↦ The first ionisation energies of elements decrease with increasing atomic number in every group of the periodic table due to increasing distance of the outermost electron from the nucleus and the shielding effect of electrons in the inner shells.

Migration of Ions

The movement of ions can be observed during the electrolysis of coloured compounds.

-Electrolysis: is the decomposition of a compound by electricity. The compound which is decomposed is called an electrolyte and it is described as being electrolysed.

Electrolysis of copper (II) chromate (VI)

If a green solution of copper (II) chromate (VI) is electrolysed in a U-tube, the solution around the cathode turns blue and the solution around the anode turns yellow. This is because blue $Cu^{2+}(aq)$ cations are attracted by the negative cathode and migrate towards it. At the same time, yellow $CrO_4^{2-}(aq)$ ions are attracted by the positive anode and migrate towards it. This provides an evidence for the existence of ions.

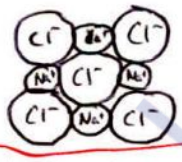
Ionic Bonding

-Ionic Bonding refers to the strong net electrostatic forces between oppairtely charged ions in a lattice.

An ionic crystal is a giant lattice containing billions of positive and negative ions packed together in a regular pattern.

A lattice: is a regular three-dimensional arrangement of atoms or ions in a crystal.

Sodium Chloride Crystal:



: strong electrostatic force of attraction

: weak electrostatic force of attraction

$d_1 < d_2$

✳ The strength of the electrostatic attractions between ions depends on the charges of the ions and their radii. Ions with high charges and small radii produce the strongest electrostatic attractions. In mathematical terms:

$$F \propto \frac{Q_1 \times Q_2}{d^2}$$

Ionic Radii

X-ray diffraction methods are used to study ionic compounds and to measure the spacing between ions in crystals. From the diffraction patterns, it is possible to calculate the radii of individual atoms. The radius of the positive ion of an element is smaller than its atomic radius because it loses electrons from its outer shell when turning into an ion. The radius of the negative ion of an element is larger than its atomic radius because electrons are added to the outer shell.

Trends

✳ Ionic radii increase with increase in atomic number down the group. From one element to the next, the elements have an additional filled shell of electrons.

✳ Ionic radii decrease for consecutive isoelectronic ions.

-Isoelectronic: means having the same electron structure.

→ From N^{3-} to Al^{3+}, the nuclear charge is increasing from 7 protons to 13 protons but the electron structure of all the ions is identical. The increasing nuclear charge attracts the electrons more strongly, pulling them closer, and the ionic radii decrease.

1.6 Bonding

Investigating Structure and Bonding

X-rays could be used to investigate crystal structures because their wavelengths are about the same distance between atoms in a crystal. A narrow beam of X-rays is directed at a crystal of the substance being studied. The atoms or ions in the crystal scatter the X-rays producing a pattern of diffracted rays. The diffracted X-rays were originally photographed using X-ray film but can now be recorded electronically. From the diffraction pattern produced, it is possible to deduce the three-dimensional crystal structure by studying the pattern of dots. Once the arrangement of the atoms or ions in a substance is known and also how they are held together (structure and bonding) - then the properties of a substance can be explained.

Types of Structure

Broadly speaking there are two types of structure - giant structures and simple molecular structures.

- Giant structures: are crystal structures in which all the atoms or ions are linked by a network of strong bonding extending throughout the crystal.
- Simple molecular structures: consist of groups of atoms held together by strong covalent bonding within the molecules, but with weak forces of attraction between the molecules (known as intermolecular forces).
- Intermolecular forces: are weak attractive forces between molecules.

Types of Bonding

There are three types of bonding:

- Ionic bonding
- Covalent bonding
- Metallic bonding

Note: For each type of bonding, its strength depends on electrostatic attractions between positive and negative charges.

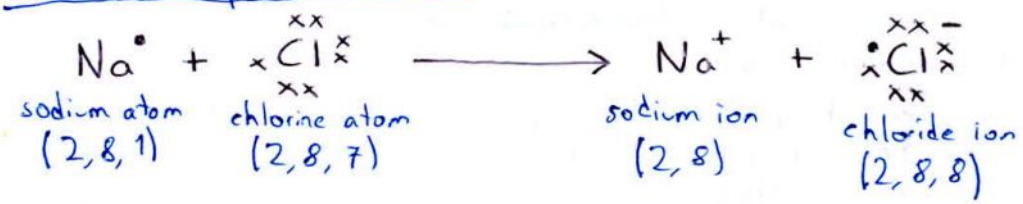
① Ionic Bonding and Structures

* Atoms into ions

Compounds of metals with non-metals are composed of ions. When compounds form between metals and non-metals, the metal atoms lose electrons and become cations (positive ions). At the same time, the non-metal atoms gain electrons and become anions (negative ions).

→ Dot-and-cross diagrams are used to represent the formation of ionic compounds.

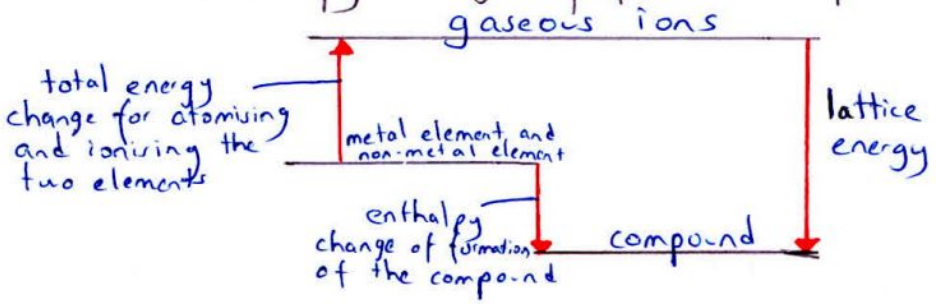
+ Formation of sodium chloride



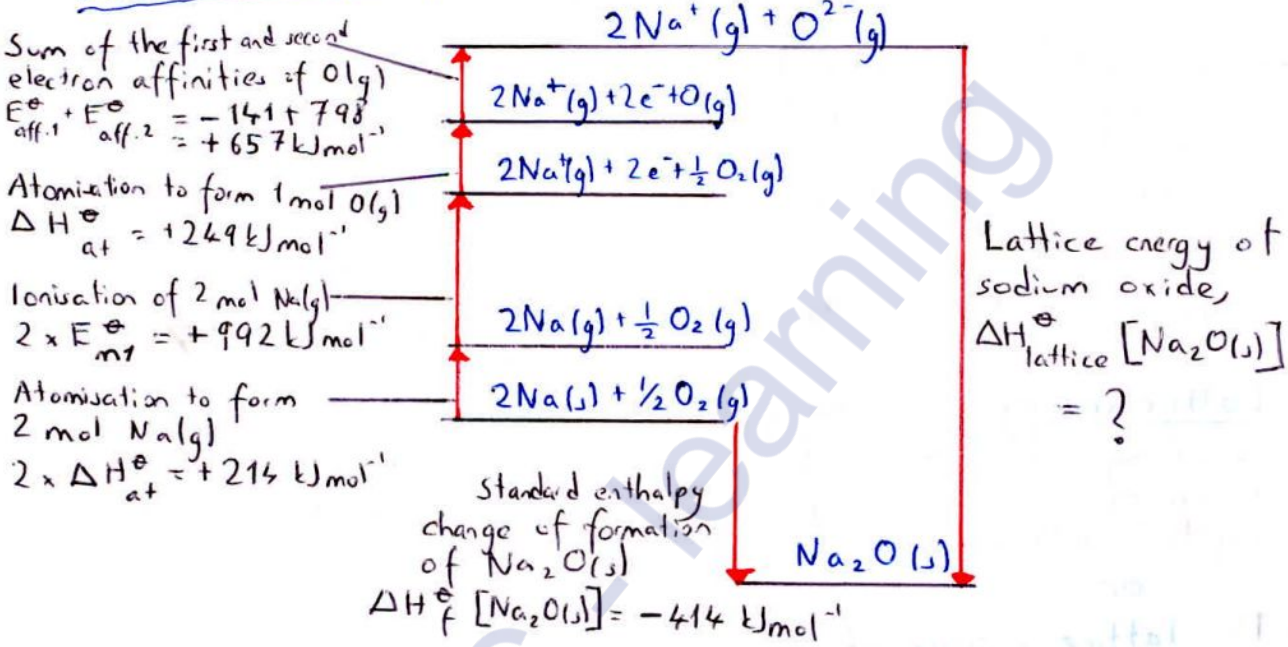
sodium atom (2, 8, 1) + chlorine atom (2, 8, 7) → sodium ion (2, 8) + chloride ion (2, 8, 8)

Born-Haber cycles

Born-Haber cycles are an application of Hess's Law. A Born-Haber cycle identifies all the enthalpy changes which contribute to the standard enthalpy change of formation of a compound.



Born-Haber cycle for sodium oxide



✳ Remember that an exothermic change in one direction becomes an endothermic change, with the opposite sign, in the reverse direction and vice versa.

Hence,

$$\Delta H^{\ominus}_{lattice}[Na_2O(s)] = (-657 - 249 - 992 - 214 - 414)\ kJ\,mol^{-1}$$

$$= -2526\ kJ\,mol^{-1}$$

Energy changes and ionic bonding

Formation of sodium chloride (NaCl)

- sodium starts as a giant structure of atoms
- energy is required to separate the sodium atoms (the enthalpy change of atomisation)
- energy is required to remove electrons (the first ionisation energy) to form sodium ions
- chlorine consists of molecules
- energy is required to separate the chlorine atoms (the enthalpy change of atomisation)
- energy is involved (the electron affinity) in adding one electron to each chlorine atom to form a chloride ion.

Ionic crystals are stable because of the large release of energy when oppositely charged ions come together forming a crystal lattice.

This is called the lattice energy, $\Delta H^{\ominus}_{lattice}$, of the ionic compound.

For sodium chloride, it is summarised by the equation

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)} \quad \Delta H^{\ominus}_{lattice}[NaCl_{(s)}] = -787\ kJ\,mol^{-1}$$

- Lattice energy is the energy which would be given out to the surroundings if 1 mole of a compound could form directly from free gaseous ions coming together and arranging themselves into a crystal lattice.

or

- The lattice energy of an ionic solid is the standard enthalpy change when one mole of the compound forms free gaseous ions.

- The first electron affinity of an element is the energy change when each atom in one mole of gaseous atoms gains one electron to form one mole of gaseous ions with a single negative charge.

For example, $O_{(g)} + e^- \rightarrow O^-_{(g)}$

$$E^{\ominus}_{aff.1} = -141\ kJ\,mol^{-1}$$

* The gain of the first electron is exothermic, but adding the second electron to a negatively charged ion is endothermic.

For example, $O^-_{(g)} + e^- \rightarrow O^{2-}_{(g)}$

$$E^{\ominus}_{aff.2} = +798\ kJ\,mol^{-1}$$

The lattice energy is greater if:

- the charges on the ions are large
- the ions are small allowing them to get closer to each other

$$F \propto \frac{Q_1 \times Q_2}{d^2}$$

The stability of ionic compounds

Almost all the compounds of metals with non-metals are ionic, and these compounds have standard enthalpy changes of formation which are exothermic. This means that the compounds are at a lower energy level and therefore more stable than their elements.

An ionic compound will have an exothermic standard enthalpy of formation if its negative lattice energy can outweigh the total energy needed to produce gaseous ions from the elements.

Using a Born-Haber cycle with theoretical values for lattice energies, it is possible to calculate the standard enthalpy change of formation for compounds which do not normally exist.

Considering $MgCl \rightarrow \Delta_f H^\ominus [MgCl(s)] = -94 kJ mol^{-1}$

However,

$$\Delta_f H^\ominus [MgCl_2(s)] = -641 kJ mol^{-1}$$

$\Delta_f H^\ominus [MgCl_2(s)]$ is more exothermic than $\Delta_f H^\ominus [MgCl(s)]$.

Therefore, $MgCl_2(s)$ is more stable than $MgCl(s)$ and it will form in preference in any reaction between magnesium and chlorine.

(2) Covalent Bonding and Structures

~A covalent bond is the strong electrostatic attraction between two nuclei and the shared pair of electrons between them.

→ Ionic bonding always produces giant structures of ionic lattices. Covalent bonding can also produce giant structures, called giant covalent lattices, but can also lead to simple molecular structures.

Giant covalent structures

A few non-metals - including diamond, graphite and silicon - consist of giant structures of atoms held together by covalent bonding.

Diamond

Diamond is an allotrope of carbon. It is made of carbon atoms, held in a strong lattice. A carbon atom bonds to four others. Each outer atom then bonds to three more an so on.

- Properties:

1- It is very hard, because each atom is held in place by four strong covalent bonds.

2- For the same reason, it has a very high melting point.

3- It does not conduct electricity because the electrons in its covalent bonds are localised between pairs of atoms.

- Uses:

1- in tools for drilling and cutting

2- For jewellery

Testing the ionic model - ionic or covalent?

One way in which chemists can test their theories and models is by comparing predictions from their theoretical models with the values obtained by experiment.

Born-Haber cycles are very helpful in this respect. The experimental lattice energy calculated from a Born-Haber cycle can be compared with the theoretical value calculated using the laws of electrostatics and assuming that the only bonding in the crystal is ionic.

Pure ionic bonding arises solely from the electrostatic forces between the ions in a crystal. There should be a close agreement between theoretical and experimental values of the lattice energies to say this is the case. The experimental values are sometimes much larger than the theoretical values which assume the only bonding is ionic. The bonding is significantly stronger than that predicted by a pure ionic model. This suggests that there is some covalent bonding as well as ionic bonding in these substances.

Polarisation of ions

Polarisation is the distortion of the electron cloud in a molecule or ion by a nearby charge.

In ionic compounds, positive metal ions will attract the outermost electrons of negative ions, pulling electrons into the space between the ions. This distortion of the electron clouds around anions by positively charged cations is an example of polarisation. Polarisation of anions by positive metal ions gives rise to some electron sharing – that is, to a degree of covalent bonding.

Polarising power gives an indication of the extent to which a positive ion is able to distort the electron cloud around a neighboring negative ion.

* The polarisability of an anion depends on its size.

→ The larger the negative ion and the larger its charge, the more polarisable it becomes. So, iodide ions are more polarisable than fluoride ions.

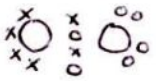
* The polarising power of a cation depends on its radius and charge.

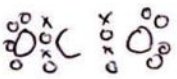
→ The larger the charge on a cation and the smaller its radius, the greater its charge density. The greater the charge density the greater the polarising power of the ion. A metal with a higher polarising power attracts the bonding electrons in neighbouring ions more strongly. This pull on the electrons of an ion distorts the bonding such as in a carbonate and makes it easier to break up the negative ion into an oxide ion and carbon dioxide.

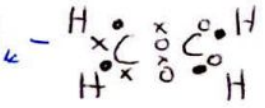
Multiple bonds

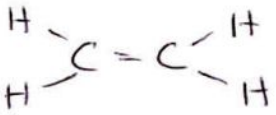
One shared pair of electrons makes a single bond. Double bonds and triple bonds are possible with two or three shared pairs, respectively.

* With two electron pairs involved in the bonding, there is a region of high electron density between the two atoms joined by a double bond.

O_2 –  $O=O$

CO_2 –  $O=C=O$

C_2H_4 – 

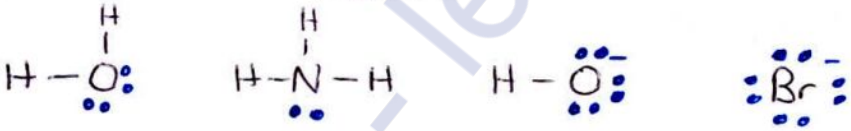


Lone pairs of electrons

In many molecules, there are atoms with pairs of electrons in their outer shells which are not involved in the bonding between atoms in the molecule.

Lone pairs of electrons:

- affect the shapes of molecules
- form dative covalent bonds
- are important in the chemical reactions of some compounds including water and ammonia.

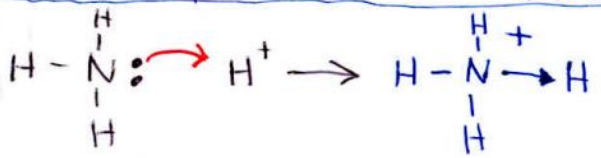


Dative covalent bonds

A dative covalent bond is a bond in which two atoms share a pair of electrons, both the electrons being donated by one atom.

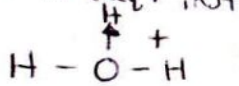
A pair of electrons is donated to an atom and the atom accepts the electron pair into a vacant orbital. Once formed, there is no difference between a dative covalent bond and a covalent bond.

Formation of an ammonium ion, NH_4^+



Oxonium ion

When an acid dissolves in water, aqueous hydrogen ions called oxonium ions are formed. A lone pair of electrons on a water molecule forms a dative covalent bond with a hydrogen ion from an acid. The formula of the oxonium ion is H_3O^+. It is often more convenient to write $H^+(aq)$ instead, but remember that the hydrogen ion is hydrated.

 : Oxonium ion

Graphite

Graphite is an allotrope of carbon too. In graphite, each carbon atom forms covalent bonds with three others.

- Properties:

1- It is soft and slippery. That is because the sheets can slide over each other easily.
2- It is a good conductor of electricity, unlike other giant covalent structures. That is because each carbon atom has four outer electrons, but forms only three bonds. So, the fourth electron is delocalised and free to move through the graphite, carrying charge.

- Uses:

1- As a lubricant for engines and locks
2- For pencil
3- For electrodes, and connecting brushes in generators

Silica (Si_2O)

Silica occurs naturally as quartz, the main mineral in sand. Each silicon atom bonds covalently to form silica with two oxygen atoms.

- Properties:

1- Hard, can scratch things
2- Hard, lets light through
3- High melting point

- Uses:

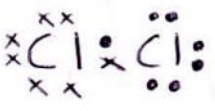
1- In sandpaper
2- For making glass and lenses
3- In bricks for lining furnaces

Simple molecular structures

In most non-metal elements, atoms are joined together in small molecules such as hydrogen, (H_2), nitrogen (N_2), and sulfur (S_8). Simple molecular compounds such as water and carbon dioxide exist too.

The covalent bonds holding atoms together within these simple molecular structures are strong, so the molecules do not break up into atoms easily. However, the intermolecular forces are weak, so it is quite easy to separate them. This means that molecular substances are often liquids or gases at room temperature.

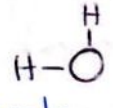
Dot-and-cross diagrams

Cl_2 – 

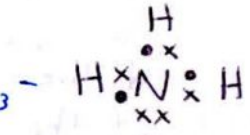
Cl – Cl

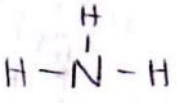
chlorine

H_2O – 



water

NH_3 – 



ammonia

1.7 Introductory organic chemistry

Organic chemistry is the study of carbon compounds. Inorganic chemistry is the study of all the 91 naturally occuring chemical elements and their compounds, including carbon and a few of its simple compounds such as carbon dioxide.

Hazard and risk in organic chemistry

- Hazard: The hazard presented by a substance or activity is its potential to do harm. This potential is absolute.

- Risk: The risk associated with a particular hazard is the chance that it will actually cause harm. Risk is affected by a number of things, in particular the nature of the hazard involved and the level of exposure. A hazardous substance can be safe to use if the risks are minimised.

Risk assessment with organic compounds

There are a number of hazards particularly associated with organic chemicals. Many of these chemicals are poisonous and/or carcinogenic. Many are flammable. As a result, when working with organic chemicals it is very important to carry out full risk assessment. The purpose of this is to identify the risks of using hazardous chemicals and reduce them as far as possible.

Ways of reducing risk

- Working on a smaller scale: For example:
  - There is less risk of inhaling fumes with smaller amounts of chemicals because there are fewer fumes.
  - If heat is given out, this will be less for smaller quantities of reactants.
  - Smaller quantities are easier to transfer from one container to another without spillage.
- Taking specific precautions or using alternative techniques depending on the properties of hazardous substances you are using: One way of reducing risk is to use the lowest possible concentration of a solution to achieve a particular reaction. Using a low concentration considerably reduces the risks for a hazardous substance. At lower concentrations the chemicals are irritant rather than corrosive, so the hazard level is reduced.
- Using alternative methods with less hazardous substances: Sometimes it is possible to substitute chemicals and still study the same basic reaction. The reaction may be lower but if the risk is also substantially lower these disadvantages are worthwhile.
- Careful use of safety measures
- Changing the conditions under which a reaction takes place

③ Metallic Bonding and Structures

Metals are very important and useful materials. They consist of giant lattices of metal ions in a sea of delocalised electrons.

- Delocalised electrons: are bonding electrons which are not fixed in a bond between two atoms. They are free to move and are shared by many atoms.
- Metallic bonding: is the strong electrostatic attraction between metal ions and the sea of delocalised electrons.

The properties of metals

All the properties of metals can be explained and interpreted in terms of their close-packed structure and delocalised electrons.

- High melting and boiling temperatures: Metal atoms are closely packed with strong forces of attraction between the positive ions and delocalised electrons. So, it takes a lot of energy to move the positive ions away from their positions in the giant lattice.
- High densities: The atoms are closely packed with as little space between them as possible.
- Good conductors of heat: When a metal is heated, energy is transferred to the electrons. The delocalised electrons in the heated region move around faster and conduct the heat rapidly to other parts of the metal.
- Good conductors of electricity: When a potential difference is applied across a metal, the delocalised electrons are attracted to the positive electrode and flow through the metal. This flow of electrons is an electric current.
- Malleable: When a force is applied to a metal, lines or layers of atoms can slide over each other. This is known as slip. After slipping, the atoms settle into close-packed positions again.

Representing organic compounds

Apart from empirical and molecular formulae, organic compounds are also represented with their structural formula, displayed formula, and **skeletal formula**.

- Structural formula: Formula which shows both the number of atoms in a molecule and the way in which they are arranged relative to each other.
- Displayed formula: Formula which show both the relative placing of the atoms and the number of bonds between them.
- Skeletal formula: Formula which simply shows the bonds and the functional group.

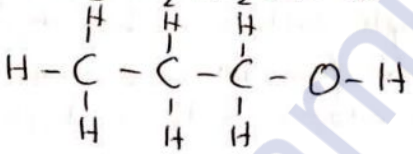
Example - propan-1-ol

empirical formula C_3H_8O

molecular formula C_3H_8O

structural formula $CH_3CH_2CH_2OH$ or $C_2H_5CH_2OH$

displayed formula



skeletal formula

* Space-filling models can also be used to model a molecule in three dimensions because you need to know not only what type of bonds are present but also how they are arranged in space.

IUPAC nomenclature

A rigorous system of naming is used for both organic and inorganic compounds, according to rules drawn up by IUPAC (the International Union of Pure and Applied Chemistry).

- Naming aliphatic compounds

- For an aliphatic compound, the first part of the name refers to the number of carbon atoms in the carbon chain or, if the molecule is branched, the number of carbon atoms in the longest carbon chain.

Prefix	Number of carbon atoms in the main carbon chain
meth-	1
eth-	2
prop-	3
but-	4
pent-	5

Prefix	Number of carbon atoms in the main carbon chain
hex-	6
hept-	7
oct-	8
dec-	10

The properties of carbon atom

The electronic structure of the carbon atom in the ground state is $1s^2 2s^2 2p^2$, which means that the carbon atom needs to gain four electrons to achieve a noble gas configuration. Once the four bonds are made, the outer shell electrons form a fully shared octet, the inner shell is complete and there are no lone pairs or empty orbitals, so carbon atoms do not bond to more than four other atoms.

The bonding of carbon and the strength of its bonds produce a great diversity of organic compounds.

Organic families

Classifying organic compounds

The first major division is based on the arrangement of the carbon chain itself.

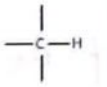
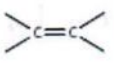
- Aliphatic molecules contain straight or branched chain carbon skeletons.
- Alicyclic molecules consist of closed rings of carbon atoms which may contain single or multiple carbon-carbon bonds.
- Arenes are all derived from benzene molecule and contain a benzene ring with six carbon atoms in their structure.

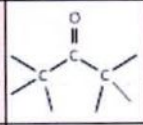
* As well as these families of organic chemicals can be identified by the possession of a particular functional group.

- A functional group: is an atom or group of atoms that is typical for a particular organic family and which determines the chemical properties of the molecule.

The different functional groups

Each homologous series has a general formula which describes the number of carbon atoms and relationships to the other atoms.

Homologous series	General formula	Functional group	Example
Alkanes	C_nH_{2n+2}		CH_3CH_3 (ethane)
Alkenes	C_nH_{2n}		CH_2CH_2 (ethene)
Alkynes	C_nH_{2n-2}		CHCH (ethyne)
Alcohols	$C_nH_{2n+1}OH$		C_2H_5OH (ethanol)

Homologous series	General formula	Functional group	Example
Halogenoalkanes	$C_nH_{2n+1}X$ X is a halogen		CH_3Cl (chloromethane)
Aldehydes	RCHO		CH_3CHO (ethanal)
Ketones	RCOR		CH_3COCH_3 (propanone)
Carboxylic acids	$C_nH_{2n+1}COOH$		CH_3CH_2COOH (propanoic acid)

Isomerism in organic molecules

Another reason why carbon forms so many compounds is that it is sometimes possible to join the same atoms together in different ways. These different arrangements of atoms are called structural isomers.

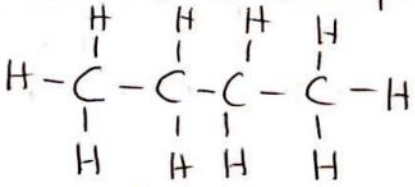
- Structural isomers: are compounds with the same molecular formula but different structural formula.

It is useful to divide structural isomers into three different types:

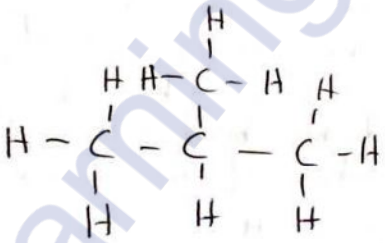
- Chain isomers have different chains of carbon atoms
- Position isomers have different positions of the same functional group.
- Functional group isomers have different functional groups.

Examples

- Structural isomers of C_4H_{10}

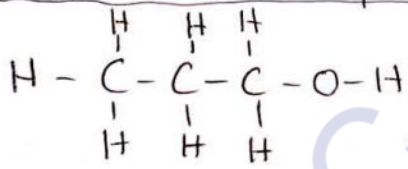


butane

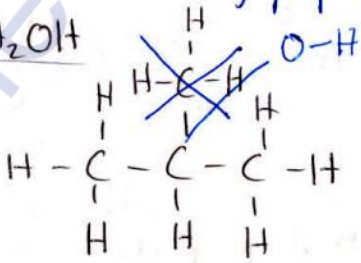


2-methyl propane

- Position isomers of CH_3CH_2OH

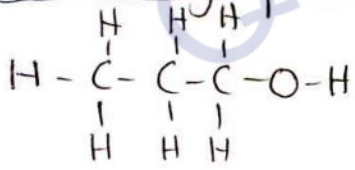


propan-1-ol

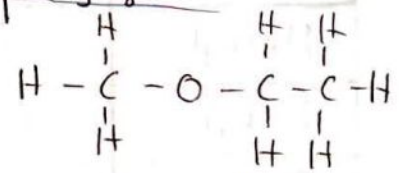


propan-2-ol

- Functional group isomers of C_3H_8O



propan-1-ol
(an alcohol)



methoxyethane
(an ether)

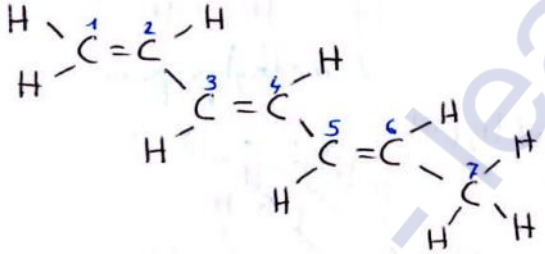
Stereoisomerism

Another form of isomerism is stereoisomerism. It arises when the three-dimensional arrangement of the bonds in a molecule allow different possible orientations in space.

- The second part of the name, the suffix, refers to the functional group of the homologous series to which the molecule belongs

Suffix	Homologous series
-ane	alk**ane**
-ene	alk**ene**
-ol	alcoh**ol**
-oic	carboxyl**ic** acid
-al	**al**dehyde
-one	ket**one**

- The organic families other than the alkanes contain double or triple bonds or other functional groups. Numbers are used to show where in the carbon chain the functional group is. For example, in an alkene the parent or main carbon chain is taken to be the longest one in which the double bond occurs. It is numbered from the end that gives the first carbon of the double bond.



$\Longrightarrow$ hepta-1, 3, 5-triene

- The position of a side chain, that are often alkyl groups, such as methyl, ethyl, propyl, is again indicated by the lowest possible number, to show which carbon atom in the parent chain it is attached.

Alkyl group	Formula
Methyl	CH_3-
Ethyl	CH_3CH_2-
Propyl	$CH_3CH_2CH_2-$
Butyl	$CH_3CH_2CH_2CH_2-$

- If more than one side chain is attached then the name of the compound includes the side groups in alphabethical order:
  * butyl, ethyl, hexyl, methyl, pentyl and propyl
- If two side chains are attached to the same carbon atom then the number of the carbon atom is repeated in the name. If there are two metyl groups the compound is described as dimethyl, and if there are three methyl side chains it becomes trimethyl, etc.

-Reforming

Reforming converts straight-chain alkanes into branched-chain or cyclic alkanes or arenes such as benzene and methylbenzene, and turns cyclic alkanes into arenes. H_2 is a valuable by-product of the process. The catalyst for this process is often one or more of the precious metals such as platinum and rhodium supported on an inert material such as aluminium oxide. The process operates at about 500°C.

The chemical properties of the alkanes

Althagh they combust well, alkanes are unreactive. The reason for this lack of reactivity is that both C-C and C-H bonds involve a very even sharing of electrons, since the electronegativities of carbon and hydrogen are very close. This means that the bonds in the molecules of the alkanes are not polar to any extent, and there are no charges to attract other polar or ionic species. Almost all of the reactions of the alkanes occur due to formation of free radicals, which contain an unpaired electron.

Bond fission

Breaking bond is also known as bond fission. In organic chemistry we almost always talk about the breaking and making of covalent bonds with varying degrees of polarity or ionic character. Within a covalent bond, two electrons are shared between two atoms. When that bond is broken during a chemical reaction there are two ways in which the electrons may be shared out.

-Homolytic fission

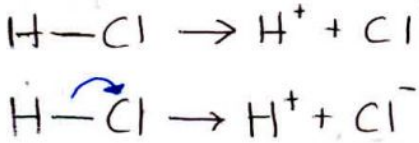
Homolytic fission involves the equal sharing out of the electrons in the bond, so that each of the participants in the bond recieves one electron when the bond splits.

To show what exactly is going on in chemical reactions, curly arrows are used. The most common use of curly arrows is to show the movement of pairs of electrons.

*The important point is that althagh neither atom has an overall charge, these free radicals with their unpaired electrons are extremely reactive. This is because the unpaired electron has a very strong tendency to pair up with an electron from another substance. The equal sharing of the electrons of homolytic fission usually occurs in situations where there is little or no ionic character in the covalent bond.

-Heterolytic fission

Heterolytic fission involves an unequal sharing of the electrons of the covalent bond, so that both electrons go to one atom. This results in two charged particles - the atom receiving the electrons gaining a negative charge and the other atom gaining a positive charge. Heterolytic fission is usually seen when the covalent bond already has a degree of polarity.



Alkanes

The alkanes are a family of saturated hydrocarbons. They are saturated because they have no double or triple bonds between the carbon atoms, so they contain the maximum amount of hydrogen possible. They are hydrocarbons because they contain only carbon and hydrogen atoms. All these hydrocarbons have certain properties in common:

- They are insoluble in water.
- They all burn, and in sufficient oxygen they give carbon dioxide and water as the only combustion products.

* The general formula of alkanes: C_nH_{2n+2}
* The single most important source of the alkanes is crude oil (a fossil fuel).

Using crude oil

The crude oil is a mixture of many different hydrocarbons. It is of little use without processing. Alkanes are obtained from fractional distillation, cracking and reformation of crude oil.

- Fractional distillation of crude oil

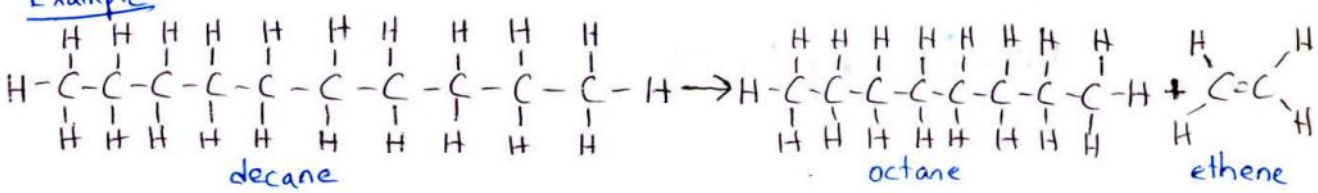
Petroleum is boiled and the vapours are cooled and liquefied at particular temperatures. The liquid collected over each range of temperatures is known as a fraction. This process provides five major fractions:

- refinery gas - used mainly as a fuel or as a starting point for other organic synthases.
- gasoline - used as fuel for the internal combustion engines that power cars and in the production of other organic chemicals.
- kerosene - used as fuel for aircraft engines.
- diesel oil / gas oil - used both in the diesel engines and as a fuel for industrial boilers.
- residue - used as fuel for the furnaces of power stations or large ships, or it can be further fractioned to yield lubricating oils and waxes and a solid material which we know as the bitumen used to surface roads.

- Cracking

Cracking, also known as catalytic cracking, is the breaking down of long chain alkanes into shorter chain molecules which are more useful as fuels and compounds in industry. Catalysts such as zeolites are used to reduce the temperature needed for reactions to take place. When conducted at high temperatures in presence of steam, a higher proportion of alkenes is produced. When conducted in the presence of a a catalyst, higher yields of branched and cyclic alkanes are produced.

Example



Combustion and air pollution

The complete combustion of fuels containing alkanes provides energy to heat homes and to power vehicles but also releases carbon dioxide into the atmosphere. This carbon dioxide is enhancing the greenhouse effect and is responsible for global warming and climate change.

Air pollution from motor vehicles

Engines that burn petrol or diesel fuels can pollute the air for three main reasons:

- they do not burn the fuel completely
- the fuel contains impurities
- they run at such a high temperature that nitrogen and oxygen in the air can react.

- Incomplete combustion

Carbon monoxide may be produced that combines strongly with haemoglobin so that blood can carry less oxygen. In low doses this puts a strain on the heart; in higher doses, it kills.

$$CH_{4(g)} + 1\tfrac{1}{2}\, O_{2(g)} \rightarrow CO_{(g)} + 2H_2O_{(l)}$$

- Impurities in the fuel

The two main impurities are sulfur and nitrogen. Oxides of these elements, which form during internal combustion in the car engine, dissolve in water in the atmosphere and lead to acid rains. Nitrogen dioxide, an oxide of nitrogen, might also break down into nitrogen monoxide and oxygen radicals. These radicals react with oxygen gas to form ozone. Ozone is itself a serious pollutant but it also reacts with hydrocarbon particles in the air to form a smog.

+ Catalytic converters

Catalytic converters improve air quality by removing the pollutants that would otherwise be released from car exhausts. In the presence of a catalyst such as rhodium, platinum or palladium, carbon monoxide and unburned hydrocarbons react with nitrogen oxides to form CO_2 and H_2O.

$$2CO_{(g)} + 2NO_{(g)} \rightarrow 2CO_{2(g)} + N_{2(g)}$$

$$C_8H_{18(g)} + 25NO_{(g)} \rightarrow 8CO_{2(g)} + 12\tfrac{1}{2}\, N_{2(g)} + 9H_2O_{(g)}$$

Alternative fuels

Chemists are starting to seek out for alternative fuels, not only because fossil fuels cause a lot of environmental pollution, but also as they are non-renewable, that is they are being consumed faster than they are being replenished. This is leading to a global energy gap. Alternative are:

- Biofuel: This involves burning ethanol produced by maize instead of petrol. It is carbon neutral, as plants will be cropped to produce ethanol which will in turn absorb CO_2 from the atmosphere. Some say, it's not ethical. We should feed people rather than cars.
- Electric power for cars
- Hydrogen fuel cell: It is very environmentally-friendly, yet it possesses danger to people due to the fact that hydrogen is an explosive gas.

Combustion of alkanes

When alkanes are heated in a plentiful supply of air, complete combustion occurs. Alkanes are energetically unstable with respect to their oxidation products, water and carbon dioxide, so once lit they will burn completely. Alkanes only burn when they are in the gaseous state so solid and liquid alkanes tend to be less flammable than gaseous ones.

If an alkane is burnt without plenty of oxygen, incomplete combustion occurs. The products of an incomplete combustion may include carbon or potentially fatal gas carbon monoxide.

The mechanism of free radical substitution by chlorine

The alkanes react with chlorine, but only with an input energy in the form of sunlight or ultraviolet light. The light provides the input of energy needed to break the hydrocarbon bonds. This, combined with the very rapid reaction that follows, is typical of a reaction that takes place by a free-radical mechanism.

Steps

1- Initiation

The Cl–Cl bond is easier to break than the C–H bond. Light provides the energy to split the chlorine molecules into atoms – in other words initiate the reaction. The splitting of the chlorine molecules is an example of homolytic fission.

$$Cl_2 \rightarrow Cl\bullet + Cl\bullet \qquad \Delta H = +243\ kJ\ mol^{-1}$$

2- Propagation

1) Chlorine free radicals react with methane molecules, combining with one of the hydrogen atoms to form hydrogen chloride and another free radical:

$$CH_4 + Cl\bullet \rightarrow CH_3\bullet + HCl \qquad \Delta H = -19\ kJ\ mol^{-1}$$

2) The methyl free radical then reacts with another chlorine molecule to form chloromethane and a chlorine free radical:

$$CH_3\bullet + Cl_2 \rightarrow CH_3Cl + Cl\bullet \qquad \Delta H = -103\ kJ\ mol^{-1}$$

The process is then repeated hundreds of times in these propagation reactions that produce another free radical. This rapid and repeated propagation results in a chain reaction, an explosive process.

3- Termination

The propagating steps of this reaction continue until there is a termination step. This is a reaction between two free radicals – a highly exothermic process.

$$Cl\bullet + Cl\bullet \rightarrow Cl_2 \qquad \Delta H = -243\ kJ\ mol^{-1}$$
$$CH_3\bullet + Cl\bullet \rightarrow CH_3Cl \qquad \Delta H = -346\ kJ\ mol^{-1}$$
$$CH_3\bullet + CH_3\bullet \rightarrow C_2H_6 \qquad \Delta H = -347\ kJ\ mol^{-1}$$

* If there is a plentiful supply of chlorine then further substitutions of the methane will take place to give di-, tri- and tetrachloromethane.

Reactions of the alkenes

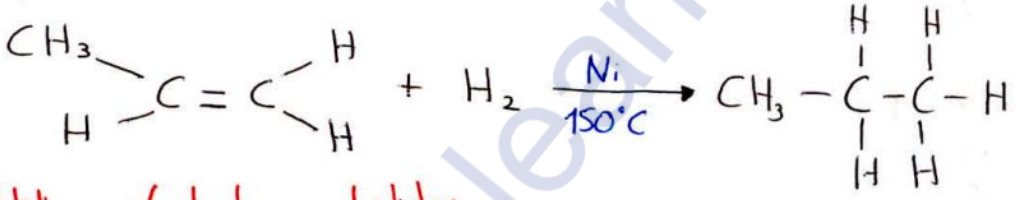
Due to the presence of carbon-carbon double bonds, alkenes undergo addition reactions rather than substitution reactions of the alkanes. The reactions of the alkenes do not involve free radicals. Instead, heterolytic fission of the double bond occurs, and this is what determines how the molecules behave. The high electron density associated with the double bond means that the alkenes are attacked by both electrophiles and oxidising agents.

- Electrophiles: An electrophile is an electron-deficient species that can form a new covalent bond, using an electron pair provided by the carbon compound. The most common electrophilic agent is the proton, H^+.

Addition reactions of the alkenes

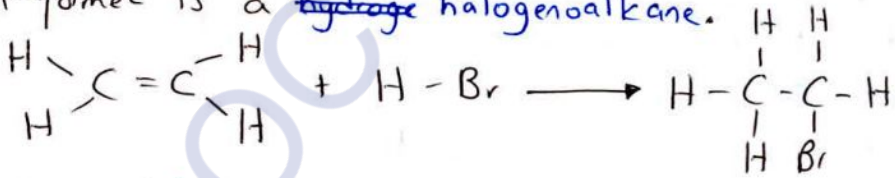
- Addition of hydrogen

Hydrogen adds to C=C double bonds in alkenes at room temperature in the presence of a platinum or palladium catalyst, or on heating to 150°C in the presence of a nickel catalyst. This process is known as catalytic hydrogenation and is used in the manufacture of margarine from unsaturated vegetable oils in palm seeds and sunflower seeds.



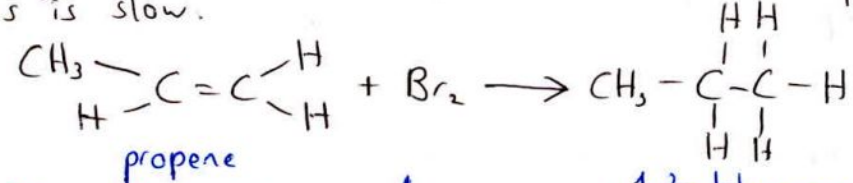
- Addition of hydrogen halides

Hydrogen halides react readily with alkenes at room temperature. The product formed is a ~~hydroge~~ halogenoalkane.

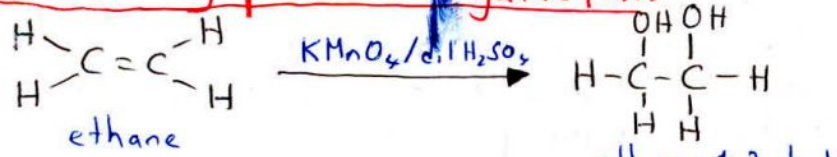


- Addition of halogens

Chlorine and bromine add rapidly to alkenes at room temperature. The products are dichloroalkanes and dibromoalkanes. Fluorine reacts explosively with small alkenes, but the reaction of iodine with alkenes is slow.



- Oxidation by potassium manganate (VII)



* The reaction of the alkenes with acidified potassium manganate (VII) solution involves both addition across the double bond and oxidation.

→ The products of the reaction are alkanediols, and the manganate (VII) solution is decolorised in the process, turning from purple to colourless. This reaction can be used to distinguish the alkenes from the alkanes. Alkanes do not react.

Alkenes

Alkenes are a family of unsaturated hydrocarbons. They are unsaturated because they do not contain the maximum amount of hydrogen possible, since they have at least one C=C double bond.

* The general formula of alkenes: C_nH_{2n}

The carbon-carbon double bond

In a carbon-carbon single bond, also known as σ bond, the electron cloud is symmetrical about the central axis of the molecule. Because it lies along the line joining the two carbon atoms, the σ bond **can rotate** about this axis, so the two ends of a such molecule are free to rotate relative to each other.

In the carbon-carbon double bond the geometry is different. For instance, the ethene molecule $CH_2=CH_2$ is flat. The double bond in ethene involves a σ bond plus a second bond which has its electron density concentrated in two regions on either side of the axis of the bond, above and below the plane of the molecule. This second bond is known as a π bond. This bond does not allow rotation around the axis.

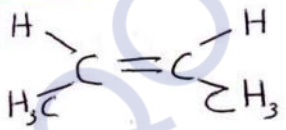
→ Molecules containing C=C bond(s) are:

- Reactive.
- Show geometric isomerism.

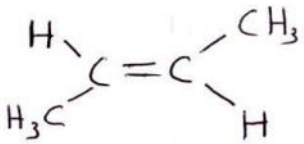
Geometric isomerism

The lack of free rotation around the double bond results in molecules known as geometric isomers. Geometric isomers occur when components of the molecule are arranged on different sides of the molecule. The traditional way of naming geometric isomers is known as cis-trans isomerism. In the cis isomer, similar groups are on the same side of the double bond. In the trans isomer, similar groups are on the opposite sides of the double bond.

Example - but-2-ene

(a) 

cis-but-2-ene

(b) 

trans-but-2-ene

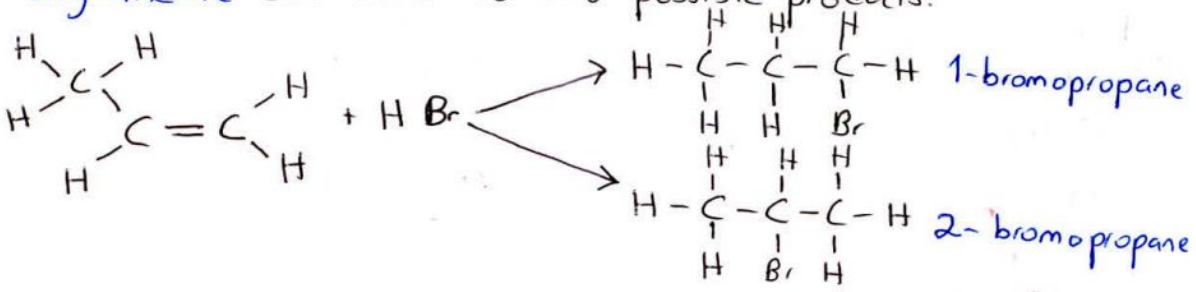
* Geometric isomers frequently show different physical properties. Their melting and boiling temperatures as well as the density of the compound are often affected.

E-Z isomerism

The cis-trans system has some limitations because it does not work for all geometric isomers. The IUPAC system for naming geometric isomers is now the system of E-Z isomerism. In the E-Z system, groups attached around a carbon-carbon double bond are ranked based on their atomic number. The atom with the highest number has the highest priority. If the two higher-priority groups are on the same side on two different ends they are zusammen and this is the Z-isomer. If the highest-priority groups are on the opposite sides of the rigid bond then they are entgegen and this is the E-isomer.

+ Addition to unsymmetrical alkene - propene

The addition of hydrogen halides to alkenes, such as propene, which are asymmetric can lead to two possible products.



In this case, the major product formed is 2-bromopropane, with a smaller amant of the alternative 1-bromopropane. The likely products of the addition of hydrogen halides to asymmetric alkenes can be predicted using Markovnikov's rule:

- When HX adds across an asymmetric dable bond, the major product formed is the molecule in which hydrogen adds to the carbon atom in the double bond with the greater number of hydrogen atoms already attached to it.

Modern theories can explain which of the two products is more likely to form by considering the mechanism of the reaction and the relative stability of intermediates (carbocations) formed.

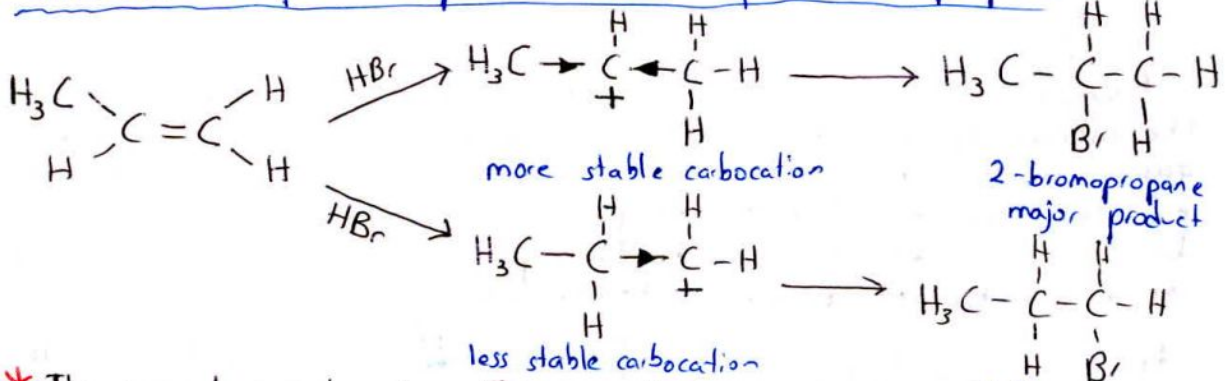
Intermediates: are atoms, molecules, ions or free radicals which do not appear in the overall equation for a reaction, but which are formed during one step of a reaction and then used up in the next.

Carbocation: the positively charged ion left when carbon has lost electrons in an electrophilic attack. A series containing a positive charge produced by the heterolytic fission of a covalent bond.

The stability of a carbocation depends on the number of alkyl groups attached, because these alkyl groups exert an inductive effect on the carbocation.

* A primary carbocation has one alkyl group attached to C+.
* A secondary carbocation has two alkyl groups attached to C+ and is more stable than a primary carbocation.
* A tertiary carbocation has three alkyl groups attached to C+ and is more stable than a secondary or a primary carbocation.

- The mechanism for electrophilic addition of HBr to propene

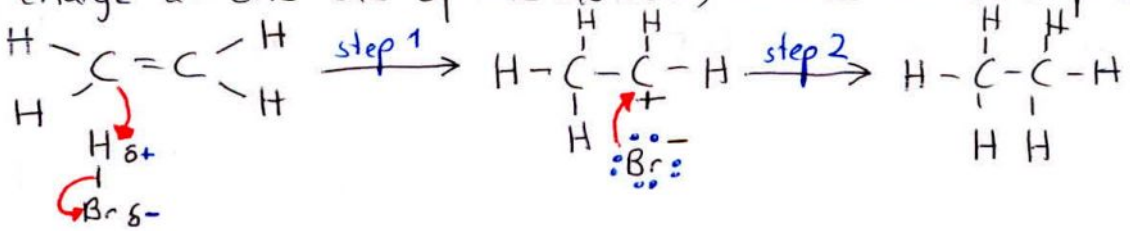


* The secondary carbocation has two alkyl groups pushing electrons towards the positively charged carbon atom. By contrast, the primary carbocation has only one alkyl group pushing electrons. This extra inductive effect helps to stabilise the secondary ion slightly more by reducing its positive charge.

Mechanism for electrophilic addition to alkenes

+ The addition of hydrogen bromide to ethene

Hydrogen bromide molecules are polar. The hydrogen atom, with its δ+ charge at one end of the molecule, acts as an electrophile.



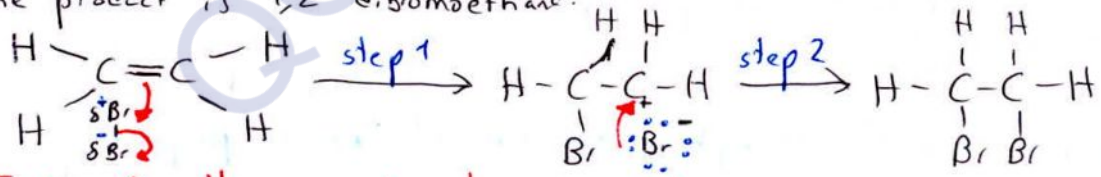
Step 1: An HBr molecule approaches an ethene molecule. The δ+ hydrogen end of the HBr is attracted towards the electron-rich double bond. As the HBr molecule gets even closer, the heterolytic fission of the π bond occurs. The electrons in the π bond form a covalent bond to the hydrogen atom, and at the same time, heterolytic fission of the HBr bond also occurs. Electrons in the H-Br bond are taken over by the bromide atom, producing a Br^- ion.

Step 2: The other product of step 1 is a highly reactive carbocation $CH_3CH_2^+$ which reacts with the bromide ion; a pair of electrons from Br^- is used to form a covalent bond with the electron-deficient carbon of this carbocation. This rapid second step forms bromoethane, CH_3CH_2Br.

- A carbocation: is a reactive species which contains a carbon atom which has a positive charge.

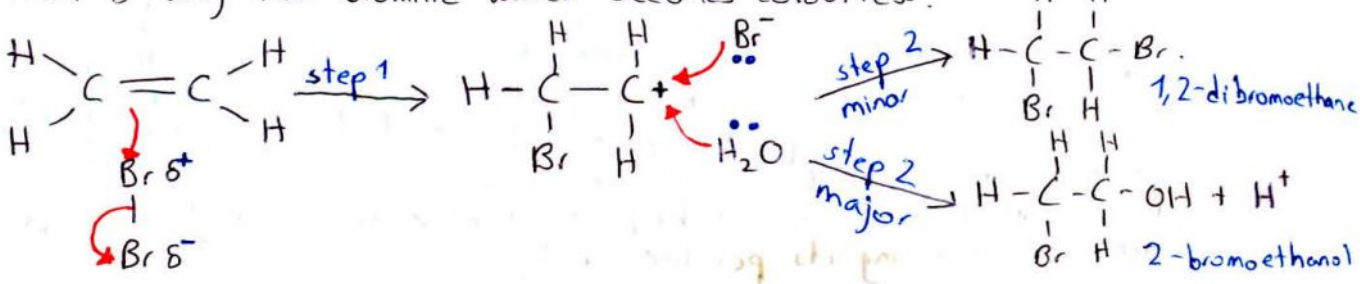
+ The addition of bromine to ethene

The addition of bromine to ethene is also an electrophilic addition. Bromine molecules are not polar, but they become polarised as they approach the electron-rich region of the double bond. Electrons in the double bond repel electrons in the bromine molecule, so the end of the bromine molecule becomes δ+ and electrophilic. In this case, the product is 1,2-dibromoethane.



+ Testing for alkenes using bromine water

Bromine water, an aqueous solution of bromine is used as a test for the alkenes. If you shake an alkene with bromine water, or bubble a gaseous alkene through bromine water, you will see the solution become colourless. This demonstrates the presence of carbon-carbon double bond because an addition reaction takes place across the double bond, which is why the bromine water becomes colourless.



The properties of polymers

The properties of polymers depend on the chains of monomers from which they are made.

- The average length of the polymer chain – tensile strength and melting temperatures increase with the length of the chain
- Branching of the chain – branched chains cannot pack together as regularly as straight chains, so polymers with highly branched chains tend to have low tensile strengths, low melting temperature and low density.
- The presence of intermolecular forces between chains – these are of immense importance in natural polymers and also affect synthetics. If there are more strong intermolecular forces between the chains, the polymer will be strong and tend to have a high melting temperature.
- Cross-links between chains – these chemical bonds holding the chains together make a polymer very rigid, hard and brittle, usually with a very high melting temperature.

Polymer problems and solutions

Polymers have some downsides including:

- The energy costs – polymers are produced from chemicals obtained from fossil fuels. These hidden energy costs of polymer products are very high, because large amounts of energy are used both in the production of the polymers and the manufacture of goods made from them.
- The resources used – because many polymer products are made from alkenes from fossil fuels, they use up valuable resources.
- Disposal problems – synthetic polymers are not easy to dispose of. They are causing a substantial waste problem as they do not decay and accumulate in the nature. They also release harmful gases when they burn.

Solutions:

+ Renewable energy sources

Making polymer products uses fossil fuels and energy. Using renewable energy sources in their manufacture is therefore a good option. If electricity generated from nuclear, solar or wind power is used instead of fossil fuels the environmental effect is greatly reduced.

+ Reducing use of polymer products

Reusing polymer products is an effective way of reducing energy costs. For years many plastic products have been disposable, single-use only items. By developing polymer products designed to be used for a much longer time, the energy costs, carbon footprint and resources can be greatly reduced.

- Carbon footprint: A carbon footprint is defined as a measure of the impact that a particular human activity has on the environment in terms of the amount of greenhouse gases produced.

+ Recycling

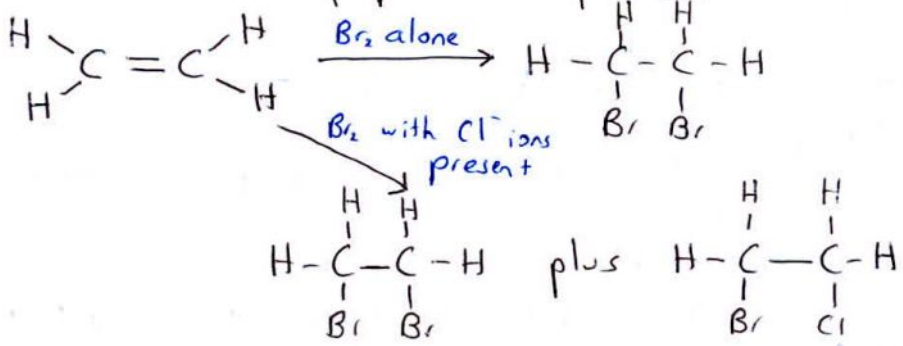
Many plastics are very difficult to dispose of in a way that does not damage the environment. Recycling not only reduces the need for plastics disposal – it also reduces the demand for the production of new plastics.

Mechanical recycling: Physically breaking down plastics into smaller pieces before reprocessing.

Chemical recycling: Chemically breaking down polymers into monomer units for reuse.

Evidence for the reaction mechanisms

Scientists hypothesised that organic reactions often involve the formation of several different intermediate species as atoms are added or removed. They have some concrete evidence for the existence of the intermediate carbocation in both the reaction of hydrogen bromide with propene and the reaction of bromine with ethene. This evidence comes from the observation that if competing nucleophiles are present in the reaction mixture, a mixture of products is formed.



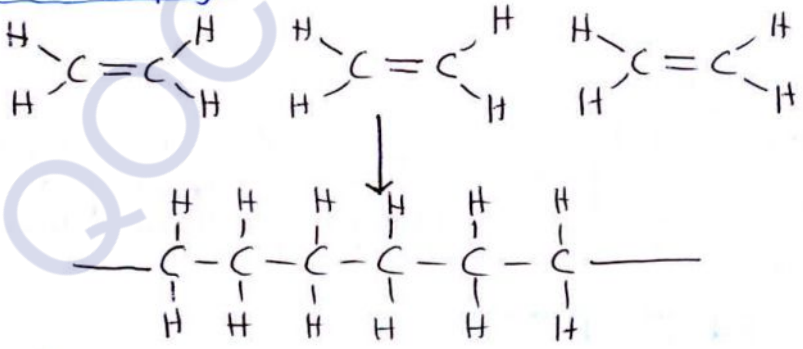
Polymerisation

A polymer is a very large molecule made up of long chains of smaller units joined together. These smaller units are known as monomers. The alkenes and their derivatives, with their reactive double bonds, are some of the main sources of monomers in the production of many commercial polymers.

The synthesis of polymers

Alkenes undergo addition polymerisation to form polymers. Two monomer units, which are usually identical, react together across a double bond. The double bonds break and the carbon atoms of the repeating units link together to form a long chain.

Example – Formation of poly(ethene)



There are two types of polythene, namely low-density polythene and high-density polythene.

- Low-density polythene: Ethene polymer with branded chains – low density, low melting temperature. It forms when ethene is polymerised at a high temperature and pressure.
- High-density polythene: Ethene polymer with relatively few branched chains so relatively dense with higher melting temperature than low density polythene. It forms when ethene is polymerised using a catalyst which lowers the temperature and pressure needed for the reaction to occur.

The Periodic Table of Elements

1	2											3	4	5	6	7	0 (8)
							1.0 H hydrogen 1										(18) 4.0 He helium 2
(1)	(2)											(13)	(14)	(15)	(16)	(17)	
6.9 Li lithium 3	9.0 Be beryllium 4											10.8 B boron 5	12.0 C carbon 6	14.0 N nitrogen 7	16.0 O oxygen 8	19.0 F fluorine 9	20.2 Ne neon 10
23.0 Na sodium 11	24.3 Mg magnesium 12	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	27.0 Al aluminium 13	28.1 Si silicon 14	31.0 P phosphorus 15	32.1 S sulfur 16	35.5 Cl chlorine 17	39.9 Ar argon 18
39.1 K potassium 19	40.1 Ca calcium 20	45.0 Sc scandium 21	47.9 Ti titanium 22	50.9 V vanadium 23	52.0 Cr chromium 24	54.9 Mn manganese 25	55.8 Fe iron 26	58.9 Co cobalt 27	58.7 Ni nickel 28	63.5 Cu copper 29	65.4 Zn zinc 30	69.7 Ga gallium 31	72.6 Ge germanium 32	74.9 As arsenic 33	79.0 Se selenium 34	79.9 Br bromine 35	83.8 Kr krypton 36
85.5 Rb rubidium 37	87.6 Sr strontium 38	88.9 Y yttrium 39	91.2 Zr zirconium 40	92.9 Nb niobium 41	95.9 Mo molybdenum 42	[98] Tc technetium 43	101.1 Ru ruthenium 44	102.9 Rh rhodium 45	106.4 Pd palladium 46	107.9 Ag silver 47	112.4 Cd cadmium 48	114.8 In indium 49	118.7 Sn tin 50	121.8 Sb antimony 51	127.6 Te tellurium 52	126.9 I iodine 53	131.3 Xe xenon 54
132.9 Cs caesium 55	137.3 Ba barium 56	138.9 La* lanthanum 57	178.5 Hf hafnium 72	180.9 Ta tantalum 73	183.8 W tungsten 74	186.2 Re rhenium 75	190.2 Os osmium 76	192.2 Ir iridium 77	195.1 Pt platinum 78	197.0 Au gold 79	200.6 Hg mercury 80	204.4 Tl thallium 81	207.2 Pb lead 82	209.0 Bi bismuth 83	[209] Po polonium 84	[210] At astatine 85	[222] Rn radon 86
[223] Fr francium 87	[226] Ra radium 88	[227] Ac* actinium 89	[261] Rf rutherfordium 104	[262] Db dubnium 105	[266] Sg seaborgium 106	[264] Bh bohrium 107	[277] Hs hassium 108	[268] Mt meitnerium 109	[271] Ds darmstadtium 110	[272] Rg roentgenium 111							

Key

relative atomic mass
atomic symbol
name
atomic (proton) number

Elements with atomic numbers 112-116 have been reported but not fully authenticated

140 Ce cerium 58	141 Pr praseodymium 59	144 Nd neodymium 60	[147] Pm promethium 61	150 Sm samarium 62	152 Eu europium 63	157 Gd gadolinium 64	159 Tb terbium 65	163 Dy dysprosium 66	165 Ho holmium 67	167 Er erbium 68	169 Tm thulium 69	173 Yb ytterbium 70	175 Lu lutetium 71
232 Th thorium 90	[231] Pa protactinium 91	238 U uranium 92	[237] Np neptunium 93	[242] Pu plutonium 94	[243] Am americium 95	[247] Cm curium 96	[245] Bk berkelium 97	[251] Cf californium 98	[254] Es einsteinium 99	[253] Fm fermium 100	[256] Md mendelevium 101	[254] No nobelium 102	[257] Lr lawrencium 103

* Lanthanide series

* Actinide series

Energy recovery

Energy recovery is methods of recovering some of the energy used in the production of polymer products by burning them as fuels for electricity production, for example.

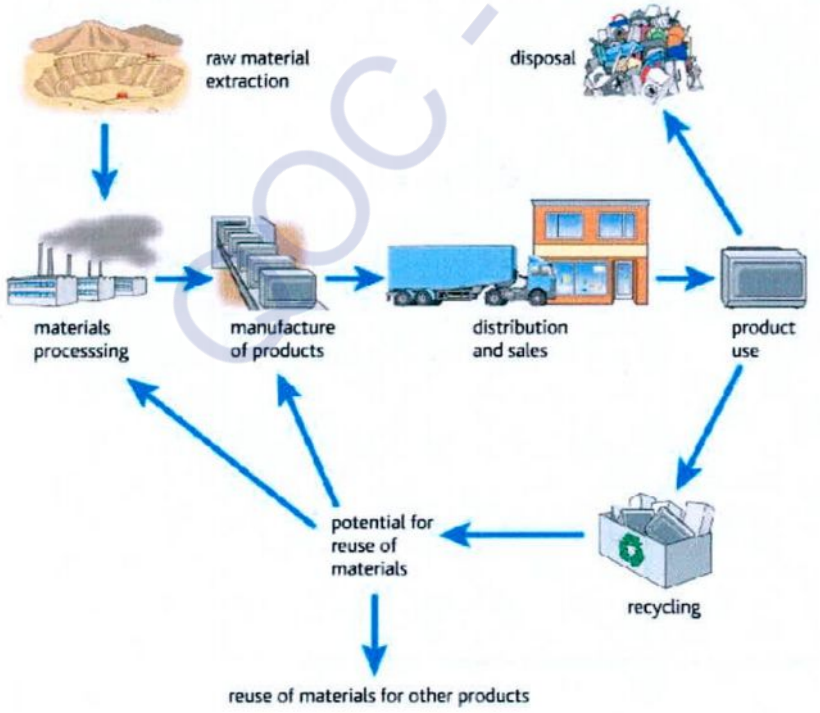
In the process of energy recovery, incinerators are used which operate at very high temperatures to prevent toxin production. Polymers contain a great deal of stored energy so they are a high-energy fuel source. The heat produced in the incinerators can be used to drive the generation of electricity and to produce hot water for heating in combined heat and power systems.

There are a number of other ways in which the energy from polymer products can be recovered and reused. These include pyrolysis and gasification.

- Pyrolysis: Method of breaking down polymers using heat in the absence of oxygen. The formation of charcoal from wood is an example.
- Gasification: Gasification involves the breakdown of solid hydrocarbons in a limited oxygen atmosphere to produce syngas. This is mainly a mixture of hydrogen and carbon monoxide, which can be used as feedstock in a wide range of different chemical processes.

Life cycle analysis

Increasingly, industry is using a life cycle analysis of polymer products to quantify the effect they have on the environment. The product's life cycle is examined from the extraction of the raw materials used in its manufacture to the costs of recycling, reusing or disposing of it at the end of its useful life.



→ This type of analysis makes it possible to identify where improvements can be made in a process to reduce the environmental impact, and also to compare two different polymer products and decide which to use on the basis of its life cycle impact on the environment.