CHAPTER 1: Atomic Structure

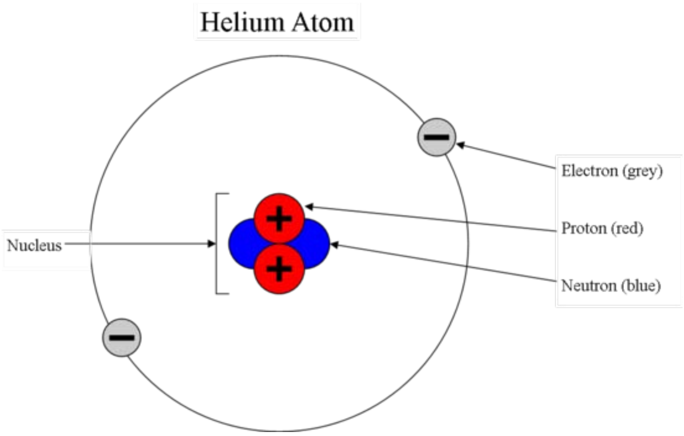
1.1 Inside the Atom
1.2 Isotopes

Learning outcomes:

(a) *identify and describe protons, neutrons and electrons in terms of their relative charges and relative masses.*
(b) *deduce the behaviour of beams of protons, neutrons and electrons in electric fields.*
(c) *describe the distribution of mass and charges within an atom.*
(d) *deduce the numbers of protons, neutrons and electrons present in both atoms and ions given proton and nucleon numbers (and charge).*
(e) (i) *describe the contribution of protons and neutrons to atomic nuclei in terms of proton number and nucleon number.*
  (ii) *distinguish between isotopes on the basis of different numbers of neutrons present*
  (iii) *recognise and use the symbolism* $^{x}_{y}A$ *where x is the nucleon number and y is the proton number.*

1.1 Inside the Atom

Sub-atomic particles



1) Electrons revolve around in region of space called orbitals.

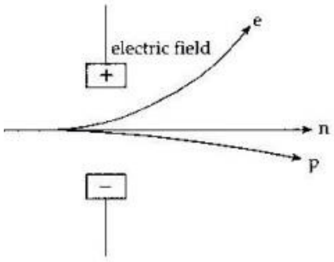
2) Electrons **do not** move in fixed orbits.

3) The nucleus is made up of **protons and neutrons** which contains almost all the mass of the atom. This is because the mass of electrons is very small compared to others.

4) The nucleus is positively-charged because of the protons. Electrons, being negatively-charged, surround the nucleus.

Particles	Relative mass	Relative Charge	Charge / C
Protons, p	1	+1	$+1.6 \times 10^{-19}$
Neutron, n	1	0	0
Electron, e	$\frac{1}{1836}$	-1	-1.6×10^{-19}

Behaviour of sub-atomic particles in electric field



1) Proton will be deflected towards the **negative plate** because it is **positively-charged**.

2) Electron will be deflected towards the **positive plate** because it is **negatively-charged**.

3) Neutron will **not** be deflected and continue in their direction of motion because it is **neutral**(not charged).

4) **Angle of deflection of electron > Angle of deflection of proton** because the mass of electron is smaller than proton. (angle of deflection is inversely proportional to charge/mass ratio)

5) Conclusion:
   i. Protons are positively-charged
   ii. Electrons are negatively-charged
   iii. Neutrons are neutral
   iv. Protons are much heavier than electron

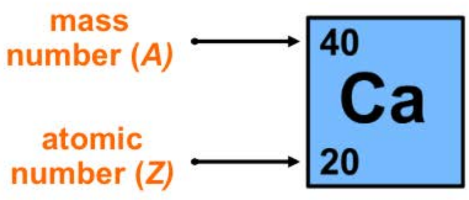
Nucleon number and proton number

1) *Proton number* is the total number of protons in an atom.

2) *Nucleon number* is the total number of protons and neutrons in an atom.

3) Proton number is also known as atomic number while nucleon number is also known as mass number.

4) In a neutral atom, the total number of protons **equals** to the total number of electrons.



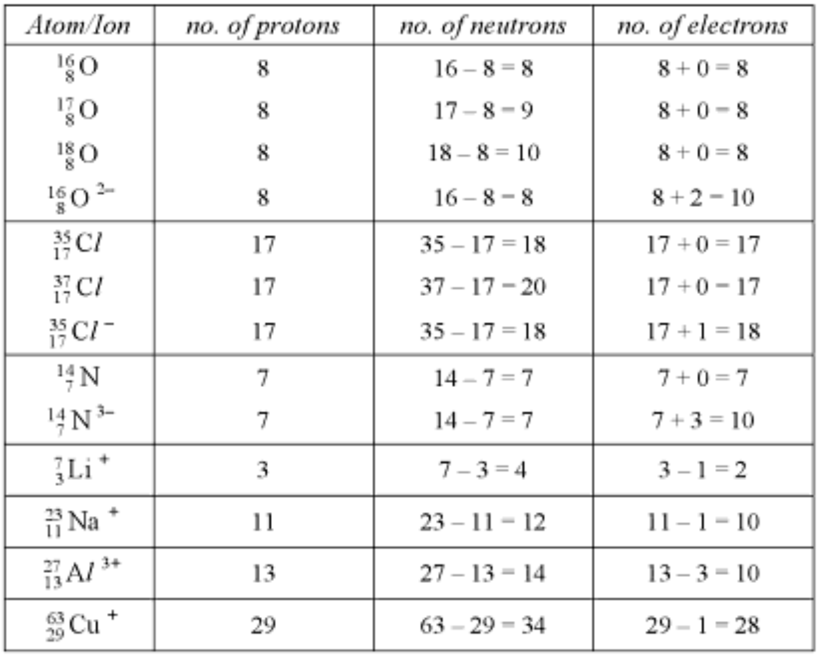
5) When an atom gains or loses electrons, a cation or anion will be formed.

6) *Cation* is a positively-charged ion. It is formed when an atom **loses** electron(s).
In cation, the number of protons is more than the number of electrons.

7) *Anion* is a negatively-charged ion. It is formed when an atom **gains** electron(s).
In anion, the number of electrons is more than the number of protons.

8) An atom or ion is said to be
   i. **isoelectronic** if they have the same number of electrons.
   ii. **isotonic** if they have the same number of neutrons.
   iii. **isotopic** if they have the same number of protons.

To deduce the number of protons, neutrons and electrons in an atom/ion



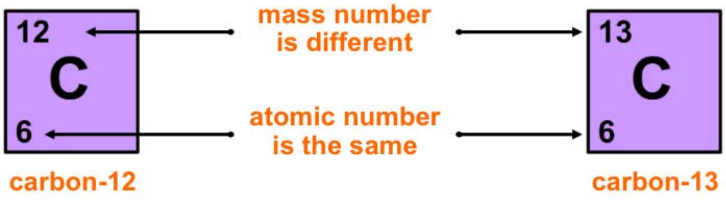
Atom/Ion	*no. of protons*	*no. of neutrons*	*no. of electrons*
$^{16}_{8}\mathrm{O}$	8	16 – 8 = 8	8 + 0 = 8
$^{17}_{8}\mathrm{O}$	8	17 – 8 = 9	8 + 0 = 8
$^{18}_{8}\mathrm{O}$	8	18 – 8 = 10	8 + 0 = 8
$^{16}_{8}\mathrm{O}^{2-}$	8	16 – 8 = 8	8 + 2 = 10
$^{35}_{17}\mathrm{C}l$	17	35 – 17 = 18	17 + 0 = 17
$^{37}_{17}\mathrm{C}l$	17	37 – 17 = 20	17 + 0 = 17
$^{35}_{17}\mathrm{C}l^{-}$	17	35 – 17 = 18	17 + 1 = 18
$^{14}_{7}\mathrm{N}$	7	14 – 7 = 7	7 + 0 = 7
$^{14}_{7}\mathrm{N}^{3-}$	7	14 – 7 = 7	7 + 3 = 10
$^{7}_{3}\mathrm{Li}^{+}$	3	7 – 3 = 4	3 – 1 = 2
$^{23}_{11}\mathrm{Na}^{+}$	11	23 – 11 = 12	11 – 1 = 10
$^{27}_{13}\mathrm{A}l^{3+}$	13	27 – 13 = 14	13 – 3 = 10
$^{63}_{29}\mathrm{Cu}^{+}$	29	63 – 29 = 34	29 – 1 = 28

1.2 Isotopes

Isotopes

1) *Isotopes* are atoms of the same element with the same number of proton but different number of neutron.

Example:

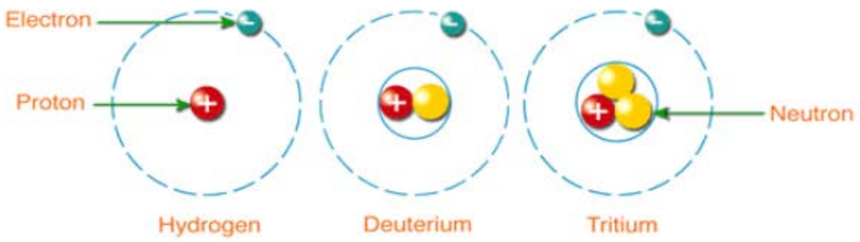


2) Isotopes have the **same**:
   1. number of protons and electrons
   2. electronic configuration
   3. chemical properties(because they have the same number of electrons)

3) Isotopes have **different**:
   1. number of neutrons and nucleon number
   2. mass
   3. density
   4. molecular speed

4) Isotopes can be stable or unstable. Unstable isotopes are called radioactive isotopes(radioisotopes).

Isotopic symbol	$^{1}_{1}H$	$^{2}_{1}H$	$^{3}_{1}H$
Name	Protium	Deuterium	Tritium
Proton	1	1	1
Neutron	0	1	2
Electron	1	1	1



CHAPTER 2: Atoms, Molecules and Stoichiometry

Learning outcomes:

(a) *define and use the terms relative atomic, isotopic, molecular and formula masses, based on the C-12 scale.*
(b) *define and use the term mole in terms of the Avogadro constant.*
(c) *analyse mass spectra in terms of isotopic abundances [knowledge of the working of the mass spectrometer is not required].*
(d) *calculate the relative atomic mass of an element given the relative abundances of its isotopes, or its mass spectrum.*
(e) *define and use the terms empirical and molecular formulae.*
(f) *calculate empirical and molecular formulae, using combustion data or composition by mass.*
(g) *write and/or construct balanced equations.*
(h) *perform calculations, including use of the mole concept, involving:*
  (i) *reacting masses (from formulae and equations).*
  (ii) *volumes of gases (e.g. in the burning of hydrocarbons).*
  (iii) *volumes and concentrations of solutions.*
  When performing calculations, candidates' answers should reflect the number of significant figures given or asked for in the question. When rounding up or down, candidates should ensure that significant figures are neither lost unnecessarily nor used beyond what is justified.
(i) *deduce stoichiometric relationships from calculations such as those in (h).*

2.1 Mass of Atoms and Molecules

Concept of relative mass

1) Relative mass is an indication of how heavy is an atom compared to another atom which is used as a standard model.

2) Relative mass is expressed in atomic mass unit(a.m.u).

3) C-12 was chosen to be the standard model because:
   i. it is the most abundant isotope of carbon.
   ii. it is a solid, easy to handle and easily available.

4) C-12 was assigned a mass of exactly 12 a.m.u.. This is known as C-12 scale.

5) For example, an atom which is 3.5 times heavier than a C-12 atom would have a relative mass of $(3.5 \times 12) = 42$ a.m.u.. That means, this atom is 42 times heavier than the mass of ($1/12 \times$ the mass of C-12 atom).

Relative isotopic mass

1) *Relative isotopic mass* is the mass of an isotope measured on a scale in which a carbon-12 atom has a mass of exactly 12 units.

Relative atomic mass, Ar

1) *Relative atomic mass, Ar* is the weighted average relative masses of all its isotopes measured on a scale in which a carbon-12 atom has a mass of exactly 12 units.

$$\boxed{\text{Relative atomic mass, Ar} = \frac{\text{Average mass of one atom of the element}}{\text{Mass of one atom of carbon-12}} \times 12}$$

Example:

Ratio of Cl-35 to Cl-37 is 3:1. If you have 4 typical atoms of chlorine, total mass is (35 x 3) + (37 x 1) = 142. So, the average mass of the isotopes is 142/4 = 35.5.

This implies that 35.5 is the **relative atomic mass** of chlorine while 35 is the **relative mass** of Cl-35 and 37 is the **relative mass** of Cl-37.

Relative molecular mass, Mr

1) *Relative molecular mass, Mr* is the weighted average of the masses of the molecules measured on a scale in which a carbon-12 atom has a mass of exactly 12 units.

2) It should only be applied to substances which exist as molecules.

3) It is found by adding up all the relative atomic masses of all the atoms present in the molecule.

4) Examples:
   i. Mr (H_2O) = 2(1) + 16 = 18
   ii. Mr ($CHCl_3$) = 12 + 1 + 3(35.5) = 119.5

Relative formula mass, Mr

1) *Relative formula mass, Mr* is the weighted average of the masses of the formula units measured on a scale in which a carbon-12 atom has a mass of exactly 12 units.

2) It works for both ionic and covalent compounds.

3) Examples:
   i. Mr (NaCl) = 23 + 35.5 = 58.5
   ii. Mr ($CuSO_4 \cdot H_2O$) = 64 + 32+ 4(16) +5[2(1) + 16] = 249.5

2.2 Mass Spectrometer

What is mass spectrometer?

1) A mass spectrometer is used to determine:
   - a. relative isotopic mass
   - b. relative abundance of isotopes
   - c. relative atomic mass
   - d. relative molecular mass
   - e. structural formula of compounds

Determination of relative atomic mass using mass spectrometer

1) Five steps:

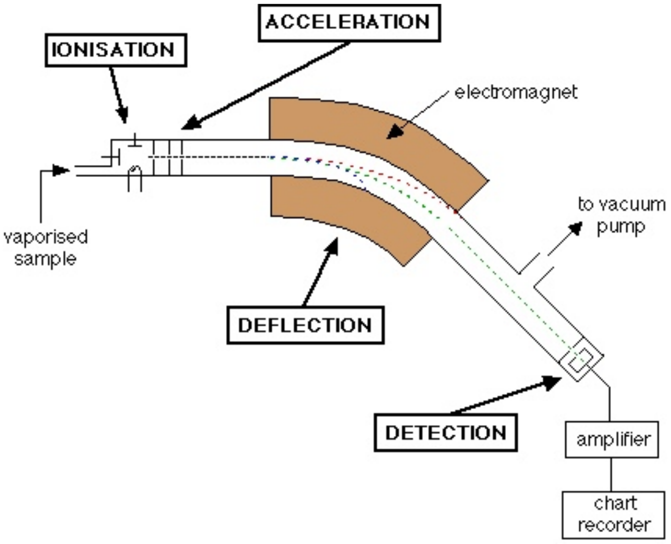
i. Vaporisation
- atoms are vaporised to form **gaseous atoms**.

ii. Ionisation
- gaseous atoms are bombarded with high energy electrons to form positive ions.

iii. Acceleration
- the ions are accelerated so that they have the same kinetic energy.

iv. Deflection
- ions are deflected by a magnetic field. The amount of deflection depends on:
  1) the mass of the ion
  2) the amount of positive charge on it
- **the larger the mass, the smaller the deflection.**
- **the higher the charge, the larger the deflection.**
- the two factors combine into **mass/charge ratio (m/e or m/z)**.
- the smaller the value of m/e, the larger the deflection.

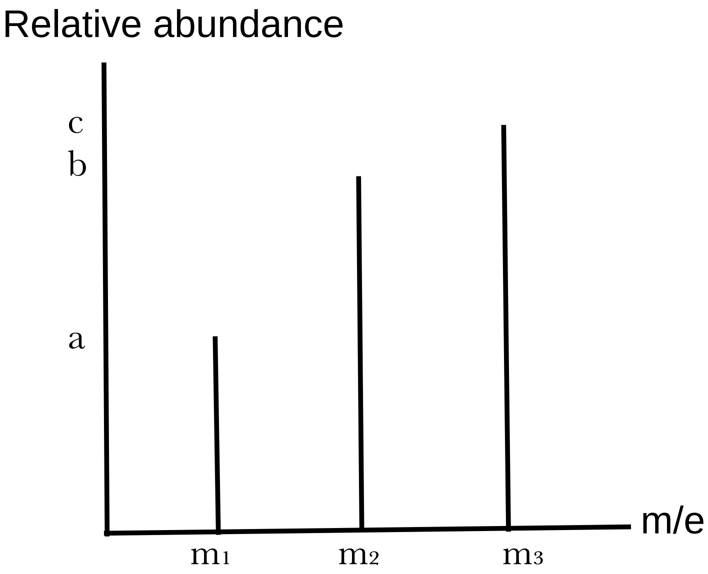
v. Detection
- the beam of ions are detected electrically.
- the data are fed into the computer and the mass spectrum is produced.



Side note

1) Ionisation chamber is **vacuum** so that the ions produced can run freely without knocking air molecules.

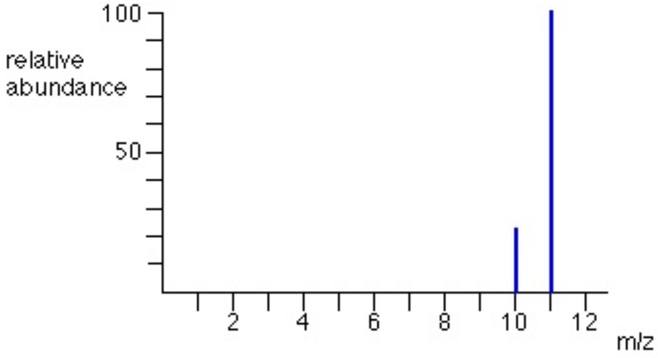
Mass spectrum (How to calculate relative atomic mass, Ar from it?)



$$\boxed{Ar = \frac{(m_1 \times a) + (m_2 \times b) + (m_3 \times c)}{a + b + c}}$$

Example:

The mass spectrum of boron, B is as shown, given the relative abundances:
B-10 : 23
B-11 : 100



$$Ar = \frac{(23 \times 10) + (100 \times 11)}{23 + 100}$$

$$= 10.8$$

2.3 Amount of Substance

The mole and the Avogadro constant

1) A *mole* of a substance is the amount of substance that contains the same amount of stated elementary units as there are atoms is 12 g of C-12.

2) The number of atoms is 12 g of C-12 is 6.02×10^{23} . This number is also known as the **Avogadro's constant, *L***.

3) Examples:
   - i. 1 mol of He contains 6.02×10^{23} He **atoms**.
   - ii. 1 mol of CO_2 contains 6.02×10^{23} CO_2 **molecules** but $3 \times (6.02 \times 10^{23})$ **atoms**.
   - iii. 1 mol of NaCl contains 6.02×10^{23} NaCl units, Na^+ and Cl^- ions.

Moles and mass

$$\boxed{\text{No. of mole / mol} = \frac{\text{Mass / g}}{\text{Molar mass / g mol}^{-1}}}$$

Moles and volumes

1) Volume occupied by a gas depends on the amount of gas, temperature and pressure. In other words the volume of a gas is not fixed.

2) *Avogadro's Law* states that for equal volumes of all gases, under the same conditions, contain the same number of moles.

3) Hence, equal number of moles of any gas, under the same conditions, would occupy the same volume. It does not depend on the nature of gas.

4) At room temperature of 20 ℃ and a pressure of 1 atm, one mole of any gas occupies 24 dm^3.

5) At standard temperature and pressure (s.t.p), which is 0 ℃ and 1 atm, one mole of any gas occupies 22.4 dm^3.

$$\boxed{\text{No.of mole / mol} = \frac{\text{Volume of a gas / dm}^3}{\text{Molar volume / dm}^3\text{ mol}^{-1}}}$$

6) i. Complete combustion of hydrocarbon produces water and carbon dioxide. The general equation is as follow:

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow \ xCO_2 + \left(\frac{y}{2}\right) H_2O$$

   ii. In incomplete combustion, the possible products are carbon dioxide, carbon monoxide, carbon soot and water.

Moles and concentration of solutions

1) A *solution* is a homogeneous mixture of two or more substance.

2) The substance presents in small quantity is called the solute while the substance present is larger quantity is called the solvent.

3) *Concentration* is the amount of solute present in a fixed quantity of solution.

4) Concentration is expressed in terms of g dm^{-3}. Concentration in mol dm^{-3} is called molar concentration or **molarity**.

$$\text{Concentration / g dm}^{-3} \quad \frac{\text{Mass of solute / g}}{\text{Volume of solution / dm}^{3}}$$

$$\text{Molarity / mol dm}^{-3} \quad \frac{\text{Concentration / g dm}^{-3}}{\text{Molar mass of solute / g mol}^{-1}}$$

$$\text{No. of moles / mol} = \frac{\text{Volume / cm}^{3} \ \text{X} \ \text{Molarity / mol dm}^{-3}}{1000}$$

2.4 Empirical Formula and Molecular Formula

Percentage composition by mass

$$\text{Percentage composition by mass / \%} = \frac{\text{Ar x No.of mole of that element}}{\text{Molar mass of compound}} \ \text{X } 100\%$$

Empirical formula

1) *Empirical formula* is a chemical formula that shows the simplest ratio of the atoms that combine to form a molecule.

2) Steps to find empirical formula:
   i. Find the mass of each element.
   ii. Find the number of mole of each element (divide by its Ar).
   iii. Find the simplest ratio (divide by the smallest number).
   iv. Construct the empirical formula using the simplest ratio.

   [If a decimal or fraction exists, round up or eliminate the fraction]
   [Never assume a formula]

3) Some facts:
   i. The formula for an ionic compound is always its empirical formula.
   ii. The empirical formula and molecular formula for simple inorganic molecules are often the same.
   iii. Organic molecules have different empirical and molecular formula.

Molecular formula

1) *Molecular formula* is a chemical formula that shows the actual number of atoms that combine to form the compound.

2) In order to deduce the molecular formula of a compound, we need to know:
   i. the relative formula mass of the compound.
   ii. the empirical formula of the compound.

Principle of conservation of mass

1) Mass is neither created nor destroyed during a chemical reaction. Therefore the total mass of the reactants is equal to the total mass of the products in a closed system.

2) For example, the total mass of iodine in the reactants is equal to the total mass of iodine in the products.

3) This can be used to solve problems in calculating the empirical formula.

2.5 Stoichiometry and Equations

Stoichiometry

1) Stoichiometry is the proportion of things either reacting or combining.

2) In compounds, it refers to the ratio in which the atoms are combined together. For example, water, H_2O has a stoichiometry of 2 hydrogen to 1 oxygen.

3) It also refers to the reacting proportions in a chemical equation. For example:

$$2H_2 + O_2 \rightarrow 2H_2O$$

The stoichiometry shows that 2 moles of hydrogen react with 1 mole of oxygen to form 2 moles of water.

Ionic equations

1) Steps to construct net ionic equations:
   i. Write the balanced molecular equation.
   ii. Write the complete ionic equation by splitting it into ions(if possible).
   iii. Cancel out the spectator ions. (Spectator ions are ions that present in the mixture but do not participate in the reaction.)
   iv. Write down the 'leftovers', that is the net ionic equation.

Chemical equation: $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$

Complete ionic equation: $H^+\cancel{Cl^-}_{(aq)} + \cancel{Na^+}OH^-_{(aq)} \rightarrow \cancel{Na^+}\cancel{Cl^-}_{(aq)} + H_2O_{(l)}$

Net ionic equation: $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$

FAQ 1: When to split compounds into ions?

1) Only split aqueous ionic compounds. For example, NaCl(aq) and HCl(aq)
2) Do not split solid ionic compounds and covalent compounds, as well as metals. For example, NaCl(s), H_2O(l), Mg(s) and HCl(g)

FAQ 2: How to identify spectator ions?

1) The ions present on both sides of the equation are spectator ions.

CHAPTER 3: Electrons in Atoms

3.1 Sub-shells and Atomic Orbitals
3.2 Electronic Configuration
3.3 Ionisation Energy

Learning outcomes:

- *(a) describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals.*
- *(b) describe the shapes of s and p orbitals.*
- *(c) state the electronic configuration of atoms and ions given the proton number (and charge), using the convention* $1s^2 2s^2 2p^6$ *etc.*
- *(d) (i) explain and use the term ionisation energy.*
  - *(ii) explain the factors influencing the ionisation energies of elements.*
  - *(iii) explain the trends in ionisation energies across a Period and down a Group of the Periodic Table.*
- *(e) deduce the electronic configurations of elements from successive ionisation energy data.*
- *(f) interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table.*

3.1 Sub-shells and Atomic Orbitals

Principle quantum shell

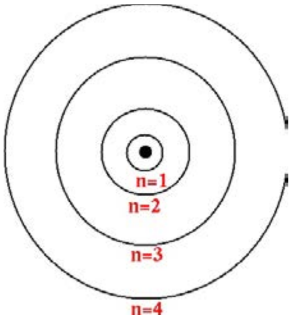
1) Electrons are arranged outside the nucleus in **energy levels** or **principle quantum shell, n**.

2) The principal quantum shells are numbered according how far are they from the nucleus.

3) The lowest energy level, n = 1 is closest to the nucleus, the energy level n = 2 is further out, and so on.

4) The electrons in energy level further away from the nucleus have more energy and held less tightly by the nucleus.

5) Electrons **do not** move in fixed circular paths, they occupy a space called the atomic orbitals.



The circles represent energy levels

6) The total number of electrons that can occupy any principal shell is $2n^2$, where n is the principal quantum number.

Quantum sub-shells

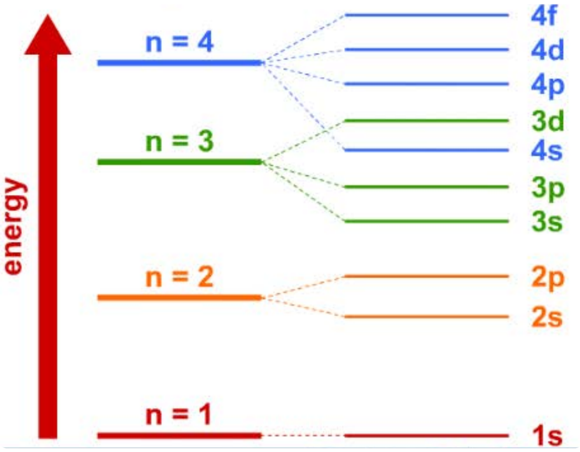
1) The principal quantum shells, apart from the first, are split into sub-shells. Each principle quantum shell contains a different number of sub-shells.

2) The first energy level contains one sub-shell, the second energy level contains two and so on.

3) The sub-shells are distinguished by letters s, p, d, f and so on.

4) The energy of electrons in the sub-shells increases in the order $s < p < d < f$.

Principal quantum shell	Maximum number of electrons	Number of sub-shells	Name of sub-shells
K, n = 1	2	1	1s
L, n = 2	8	2	2s, 2p
M, n = 3	18	3	3s, 3p, 3d
N, n = 4	32	4	4s, 4p, 4d, 4f



The impossibility of drawing orbits for electrons

1) Heisenberg Uncertainty Principle says, you cannot know with certainty where an electron is and where it is going next.

2) This makes it impossible to draw out an orbit or pathway in which the electrons move.

Atomic orbitals

1) An *atomic orbital* is a region of space around the nucleus where the probability of finding a particular electron is maximum (>95%).

2) The sub-shells are split further into orbitals where the electrons are placed.

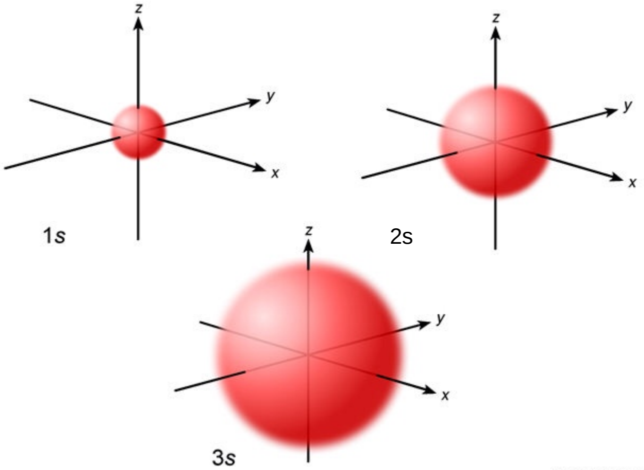
3) The number of orbital in each sub-shell depends on the sub-shells.
   s - one orbital {s}
   p - three orbitals {p_x, p_y, p_z}
   d - five orbitals {d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$, d_{z^2}}

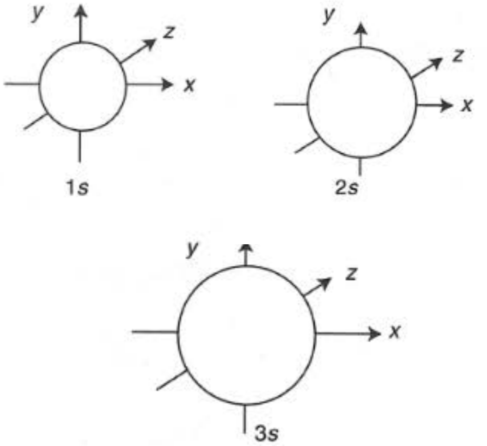
4) Orbitals having the same energy are called degenerate orbitals. For example, p_x, p_y and p_z are degenerate orbitals.

5) The concept of orbitals arises from the fact that an electron has dual nature. It behaves as a particle as well as a wave.

6) In the **nth** principal quantum shell, there are **n** sub-shells, **n^2** orbitals and a maximum of **$2n^2$** electrons.

The s orbital



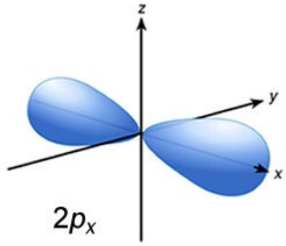


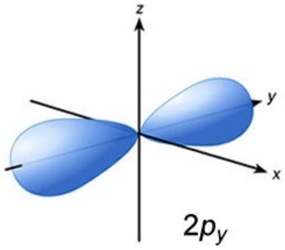
1) All the s orbitals are **spherical** and **non-directional**.

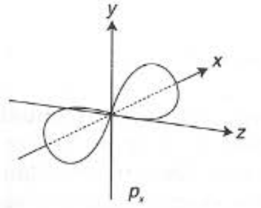
2) The shaded region represents the region in which the chance of finding the s electron is more than 95%.

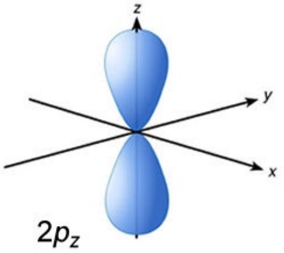
3) The size of the s orbital increases in the order 1s < 2s < 3s < 4s.

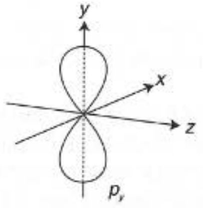
The p orbital

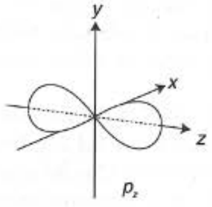


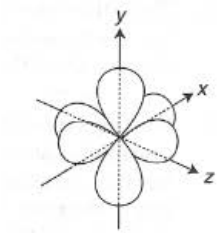










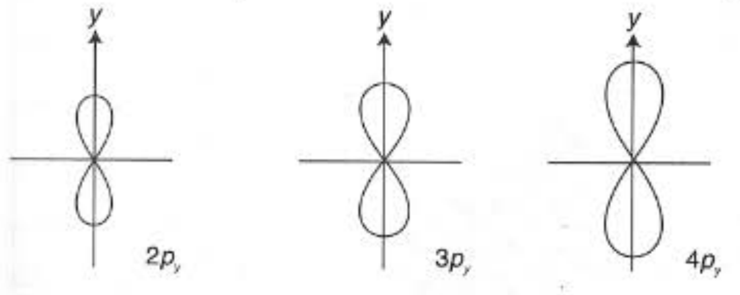


1) All the p orbitals are **dumb-bell shaped** and **directional**.

2) p orbitals are only available from the second principal quantum shell and onwards.

3) There are 3 types of p orbitals, p_x, p_y and p_z. All 3 different types of p orbitals are perpendicular to each other along the x, y and z axes.

4) Going to a higher energy level, the 'lobes' of the p orbital become longer.



3.2 Electronic Configuration

Ways to represent electronic configuration

Electronic configuration describes how the electrons in an atom/ion are arranged in their shells, sub-shells and orbitals.

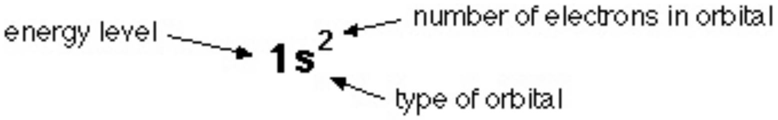
1) Using 'electrons-in-boxes':

	1s	2s	$2p_x$	$2p_y$	$2p_z$		1s	2s	$2p_x$	$2p_y$	$2p_z$
B	↑↓	↑↓	↑			O	↑↓	↑↓	↑↓	↑	↑
C	↑↓	↑↓	↑	↑		F	↑↓	↑↓	↑↓	↑↓	↑
N	↑↓	↑↓	↑	↑	↑	Ne	↑↓	↑↓	↑↓	↑↓	↑↓

2) Using energy levels:

B	2,3	Na	2,8,1
C	2,4	Mg	2,8,2
N	2,5	Al	2,8,3
Ne	2,8	Ar	2,8,8

3) Using s, p, d and f notation:



			or ***FULL electronic configurations***:
B	$1s^2\,2s^2\,2p^1$	B	$1s^2\,2s^2\,2p_x^1\,2p_y^0\,2p_z^0$
C	$1s^2\,2s^2\,2p^2$	C	$1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^0$
N	$1s^2\,2s^2\,2p^3$	N	$1s^2\,2s^2\,2p_x^1\,2p_y^1\,2p_z^1$
O	$1s^2\,2s^2\,2p^4$	O	$1s^2\,2s^2\,2p_x^2\,2p_y^1\,2p_z^1$
F	$1s^2\,2s^2\,2p^5$	F	$1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^1$
Ne	$1s^2\,2s^2\,2p^6$	Ne	$1s^2\,2s^2\,2p_x^2\,2p_y^2\,2p_z^2$

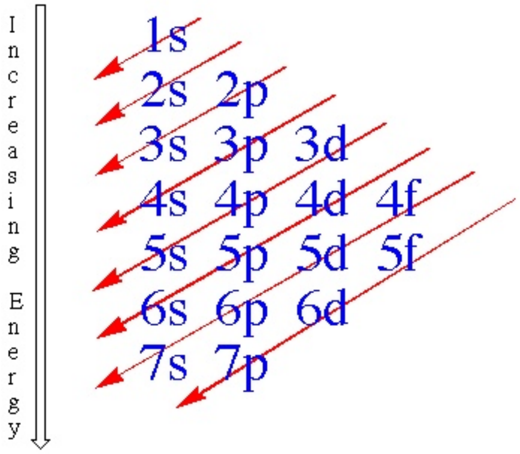
4) Using the noble gas 'core':

B	$[He]\,2s^2\,2p^1$	Na	$[Ne]\,3s^1$
C	$[He]\,2s^2\,2p^2$	Mg	$[Ne]\,3s^2$
N	$[He]\,2s^2\,2p^3$	Al	$[Ne]\,3s^2\,3p^1$

Filling in the orbitals

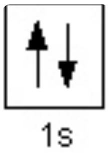
1) Three general rules of filling the orbitals are:

i. *Aufbau Principle* states that in the ground state of an atom, the electrons must occupy the orbitals in the order of **increasing energy**.



[Note: 4s has a slightly lower energy than 3d, therefore electrons are filled in 4s orbital first before the 3d orbitals.]

ii. *Pauli's Exclusion Principle* states that an orbital can only accommodate a maximum of **two** electrons only. The two electrons must have opposite spins.



iii. *Hund's Rule* states that in a set of degenerate orbitals, electrons must occupy the orbital **singly first before pairing**. The reason is because, two electrons occupying the same orbital will experience repulsion.

rather than

2) Electronic configuration of the elements (up to Z = 38)

Element	*Energy Level*	*s, p, d, f notation*	*Period No.*	*Group No.*	*Remarks*
$_{1}$H	1	$\mathbf{1s^1}$	1	I	
$_{2}$He	2	$\mathbf{1s^2}$	1	II	
$_{3}$Li	2, 1	$1s^2\ \mathbf{2s^1}$	2	I	
$_{4}$Be	2, 2	$1s^2\ \mathbf{2s^2}$	2	II	
$_{5}$B	2, 3	$1s^2\ \mathbf{2s^2\ 2p^1}$	2	III	
$_{6}$C	2, 4	$1s^2\ \mathbf{2s^2\ 2p^2}$	2	IV	
$_{7}$N	2, 5	$1s^2\ \mathbf{2s^2\ 2p^3}$	2	V	half-filled 2p-orbitals
$_{8}$O	2, 6	$1s^2\ \mathbf{2s^2\ 2p^4}$	2	VI	
$_{9}$F	2, 7	$1s^2\ \mathbf{2s^2\ 2p^5}$	2	VII	
$_{10}$Ne	2, 8	$1s^2\ \mathbf{2s^2\ 2p^6}$	2	0	noble gas
$_{11}$Na	2, 8, 1	$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^1}$	3	I	
$_{12}$Mg	2, 8, 2	$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2}$	3	II	
$_{13}$A*l*	2, 8, 3	$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^1}$	3	III	
$_{14}$Si	2, 8, 4	$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^2}$	3	IV	
$_{15}$P	2, 8, 5	$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^3}$	3	V	half-filled 3p-orbitals
$_{16}$S	2, 8, 6	$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^4}$	3	VI	
$_{17}$C*l*	2, 8, 7	$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^5}$	3	VII	
$_{18}$Ar	2, 8, 8	$1s^2\ 2s^2\ 2p^6\ \mathbf{3s^2\ 3p^6}$	3	0	noble gas
$_{19}$K	2, 8, 8, 1	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{4s^1}$	4	I	4s filled first before 3d
$_{20}$Ca	2, 8, 8, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ \mathbf{4s^2}$	4	II	
$_{21}$Sc	2, 8, 9, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{1}}\ \mathbf{4s^2}$	4	TE	
$_{22}$Ti	2, 8, 10, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{2}}\ \mathbf{4s^2}$	4	TE	
$_{23}$V	2, 8, 11, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{3}}\ \mathbf{4s^2}$	4	TE	
$_{24}$Cr	2, 8, 12, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{5}}\ \mathbf{4s^1}$	4	TE	half-filled 3d & 4s
$_{25}$Mn	2, 8, 13, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{5}}\ \mathbf{4s^2}$	4	TE	
$_{26}$Fe	2, 8, 14, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{6}}\ \mathbf{4s^2}$	4	TE	
$_{27}$Co	2, 8, 15, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7\ \mathbf{4s^2}$	4	TE	
$_{28}$Ni	2, 8, 16, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{8}}\ \mathbf{4s^2}$	4	TE	
$_{29}$Cu	2, 8, 18, 1	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{10}}\ \mathbf{4s^1}$	4	TE	filled 3d & half-filled 4s
$_{30}$Zn	2, 8, 18, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{\mathbf{10}}\ \mathbf{4s^2}$	4	TE	
$_{31}$Ga	2, 8, 18, 3	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ \mathbf{4s^2\ 4p^1}$	4	III	
$_{32}$Ge	2, 8, 18, 4	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ \mathbf{4s^2\ 4p^2}$	4	IV	
$_{33}$As	2, 8, 18, 5	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ \mathbf{4s^2\ 4p^3}$	4	V	
$_{34}$Se	2, 8, 18, 6	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ \mathbf{4s^2\ 4p^4}$	4	VI	
$_{35}$Br	2, 8, 18, 7	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ \mathbf{4s^2\ 4p^5}$	4	VII	
$_{36}$Kr	2, 8, 18, 8	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ \mathbf{4s^2\ 4p^6}$	4	0	noble gas
$_{37}$Rb	2, 8, 18, 8, 1	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ \mathbf{5s^1}$	5	I	
$_{38}$Sr	2, 8, 18, 8, 2	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ \mathbf{5s^2}$	5	II	

3) The odd ones (K, Sc, Cr and Cu):

i. For potassium, 4s is filled before 3d because 4s has a **lower energy level** than 3d.

ii. For scandium (to zinc, the d-block elements), the energy level of 3d and 4s are **reversed**. 4s is at a higher energy level now. This is because once the 3d orbital(s) is/are filled, the 3d electrons **repel** the 4s electrons to a higher energy level.

iii. For chromium, the electronic configuration is $[Ar]3d^5 4s^1$ instead of $[Ar]3d^4 4s^2$. This is because orbitals that are **fully filled or half filled have extra stability** due to their symmetrical charge distribution.

iv. For copper, the electronic configuration is $[Ar]3d^{10} 4s^1$ instead of $[Ar]3d^9 4s^2$. The reason is the same as stated in (iii).

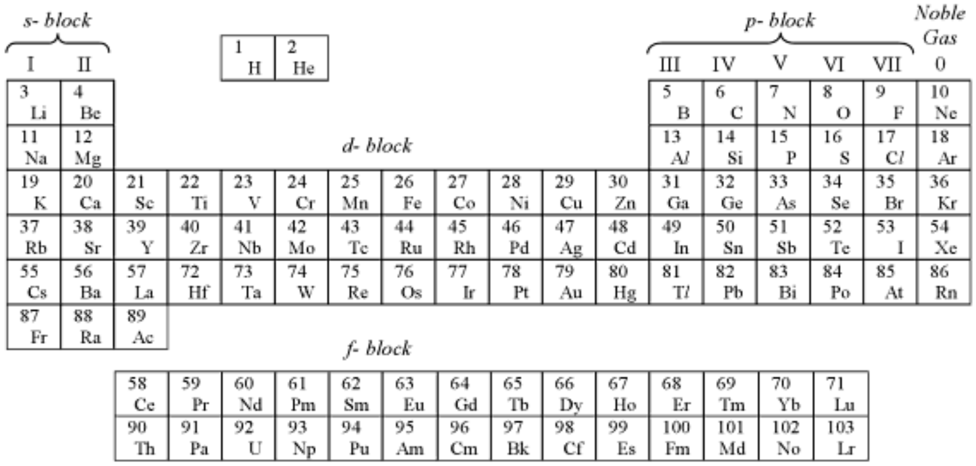
Electronic configuration of ions

1) In the formation of cation, the electrons are removed in the order of decreasing energy (the reverse of filling in).

2) For the d-block elements, the electrons in 4s is removed first before 3d. This is because once the 3d orbital is filled, the 4s electrons are repelled to a higher energy level than 3d.

3) In the formation of anion, the electrons are added in the same manner as filling the electrons.

Orbitals and the Periodic Table



1) The elements in the Periodic Table can be divided into four blocks according to their valence shell electronic configuration.

2) The s-block elements have their valence electron(s) in the s orbital.

3) The p-block elements have their valence electrons in the p orbital.

4) The d-block elements have d orbitals filling.

5) The f-block elements have f orbitals filling.

Some useful facts

1) The valence electrons always appear at the end of the electronic configuration. (but not necessary the last one).

2) The valence electrons are large responsible for the chemical properties of an element.

3) The **number of valence electron** will indicate the **group number** of that element in the Periodic Table.

4) The **outermost quantum shell number** will indicate the **period** of that element in the Periodic Table.

3.3 Ionisation Energy

What is ionisation energy?

1) The *1st ionisation energy, ΔH_{i1}* is the energy needed to remove one electron from each atom in one mole of the atoms of the element in the **gaseous state** to form one mole of gaseous 1+ ions.

2) The general unit for ionisation energy is kJ mol^{-1}.

$$Ca(g) \rightarrow Ca^{+}(g) + e^{-} \quad ; \Delta H_{i1} = +590 \text{ kJ mol}^{-1}$$

3) If a second electron is removed from the gaseous 1+ ions, it is the 2nd ionisation energy, ΔH_{i2}.

$$Ca^{+}(g) \rightarrow Ca^{2+}(g) + e^{-} \quad ; \Delta H_{i2} = +1150 \text{ kJ mol}^{-1}$$

4) The *2nd ionisation energy, ΔH_{i2}* is the energy needed to remove one electron from each gaseous 1+ ion in one mole of the ions to form one mole of gaseous 2+ ion.

5) The continuos removal of electrons until the nucleus is left only will result in successive ionisation energies.

Factors affecting the ionisation energy

1) **Charge on the nucleus (Number of proton)**
- The greater the number of proton in the nucleus, the greater the amount of positive charge.
- The greater the positive charge, the **greater the attractive force** between the nucleus and outer electrons.
- More energy is needed to overcome the attractive force. So, the ionisation energy is higher.
- **The greater the nuclear charge, the higher the ionisation energy.**

2) **Distance between nucleus and outer electrons (Size of atom/ion)**

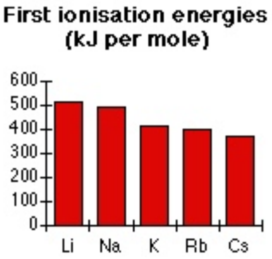
- The larger the size of the atom, the greater the distance between the nucleus and the outer electrons.
- The greater the distance between the nucleus and the outer electrons, the **weaker the attractive force** between nucleus and outer electrons.
- Furthermore, the outer electrons experience greater shielding effect by the inner electrons.
- Less energy is required to overcome the attractive force. So, the ionisation energy is lower.
- **The greater the distance between nucleus and outer electrons, the lower the ionisation energy.**

3) **Shielding effect by the inner electrons**

- All electrons are negatively-charged, so they repel each other. Electrons in full inner shells will repel the outer electrons and so prevent the full nuclear charge being felt by the outer electrons. This is called shielding or screening.
- The greater the shielding effect, the **weaker the attractive force** between the nucleus and outer electrons.
- Less energy is required to overcome the attractive force. So, the ionisation energy os lower.
- **The greater the shielding effect, the lower the ionisation energy.**

Pattern of ionisation down a Group

1) The first ionisation energy **decreases** down a Group.



2) This is because the atomic size increases and hence the distance between the nucleus and outer electrons increases. The outer electrons also experience a greater shielding effect.

3) These two factors **outweigh** the increasing nuclear charge.

4) The above factors causes the attractive force between nucleus and outer electrons to decrease, less energy is required to overcome the weaker attractive force. Hence, the ionisation energy is lower.

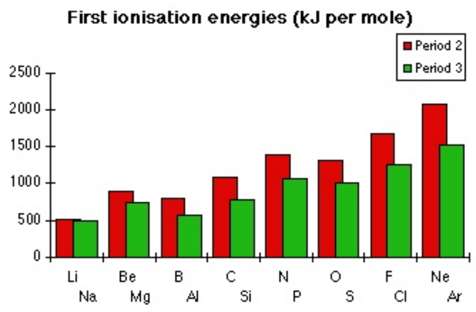
Pattern of ionisation energy across a Period

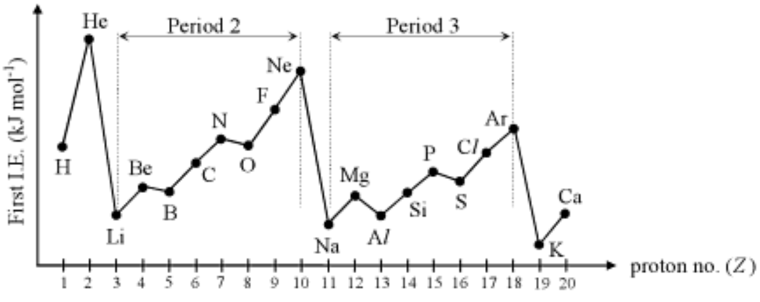
1) The general trend of ionisation energy across a Period is **increasing**.

2) This is because, across a Period, the number of proton in the nucleus increases by one therefore the nuclear charge increases.

3) However, the distance between the nucleus and outer electrons decreases across a Period and the outer electrons experience the same amount of shielding.

4) The above factors causes the attractive force between nucleus and outer electrons to increase, more energy is required to overcome the stronger attractive force. Hence, the ionisation energy is higher.





The drop between (Be-B) and (Mg-Al)

1) There is a slight decrease in first ionisation energy between beryllium-born and magnesium-aluminium.

2) This is because the fifth electron in boron is located in the 2p sub-shell, which is slightly further away from the nucleus. The outer electron in boron is shielded by the $1s^2$ as well as $2s^2$ electrons.

Be : $1s^2 2s^2$ B : $1s^2 2s^2 \mathbf{2p^1}$

3) The decrease in first ionisation energy between magnesium and aluminium has the same reason, except that everything is happening at the third energy level.

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

The drop between (N-O) and (P-S)

1) There is a slight decrease in first ionisation energy between nitrogen-oxygen and phosphorus-sulphur.

2) This is because the electron being removed in oxygen is from the orbital which contains **a pair** of electrons. The extra repulsion between the pair of electrons results in less energy needed to remove the electron. This is called **spin-pair repulsion**.

N : $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ O : $1s^2 2s^2 \mathbf{2p_x^2} 2p_y^1 2p_z^1$

3) The decrease in first ionisation energy between phosphorus and sulphur has the same reason, except that everything is happening at the third energy level.

P : $1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$ S : $1s^2 2s^2 2p^6 3s^2 \mathbf{3p_x^2} 3p_y^1 3p_z^1$

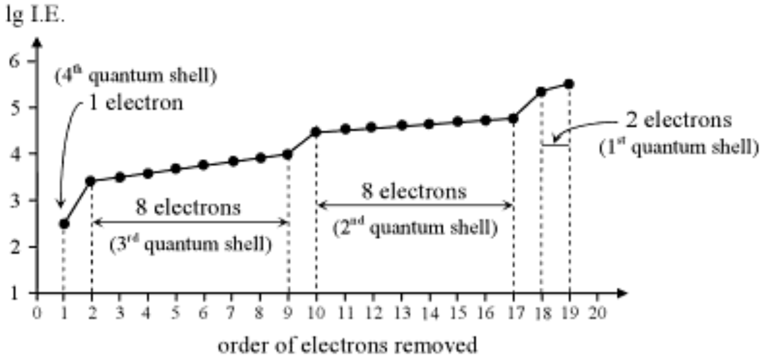
Successive ionisation energy

1) The following data can be obtained from successive ionisation energy:
   i. Total number of electrons in an atom.
      - is equal to the number of separate ionisation energies possessed by the atom.

   ii. Number of principal quantum shells occupied and the number of electrons in each.
      -by looking the big difference between two successive ionisation energies.

   iii. Number of sub-shells occupied and the number of electrons in each.

2) Successive ionisation energies get larger because removing an electron from a positive ion with increasing positive charge is going to be more difficult due to the increasing attractive force.



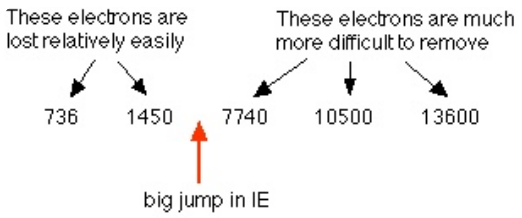
3) There is a relatively big increase in ionisation energy between the first and second electron being removed. This suggests that the second electron being removed is from a principal quantum shell closer to the nucleus.

4) The big jump occurs three times, so there are four principal quantum shells occupied by this atom.

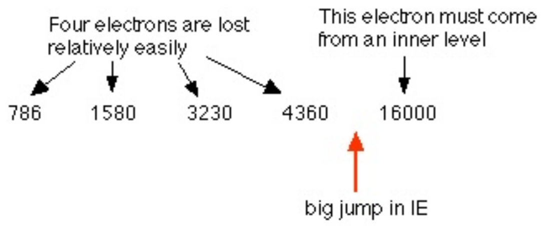
5) After the big jumps, there is a steady increase in ionisation energy, this suggests that the electrons being removed come from the same principal quantum shell.

6) The electronic configuration for this atom can be written as 2,8,8,1.

7) Two more examples:

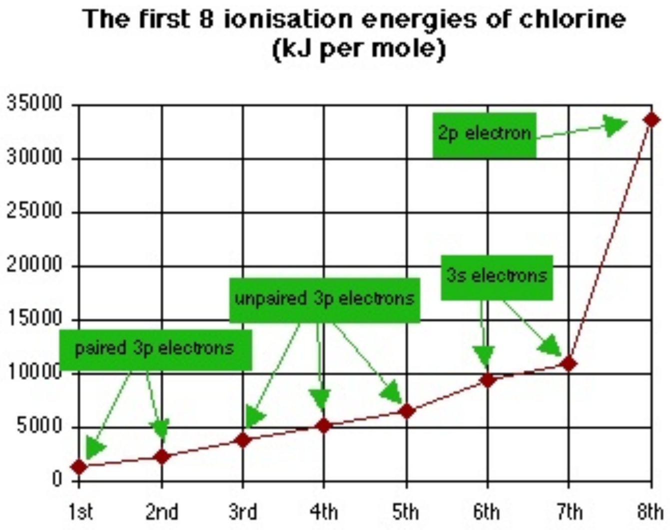


This element comes from Group 2 of the Periodic Table



This element comes from Group 14 of the Periodic Table

Looking at the pattern in more detail



1) The electronic configuration of chlorine is $1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^2 3p_z^1$.

2) Between the second and third ionisation energy, there is a slight increase in difference in ionisation energy. This is because the first two electrons being removed come from the orbitals which contain a paired electrons. The extra repulsion between the electrons result in the ionisation energy being lower.

3) There is also a slight increase in difference in ionisation energy between the fifth and sixth electron being removed. This is because the sixth electron being removed comes from the 3s sub-shell, which is slightly closer to the nucleus.

4) The drastic increase in ionisation energy between the seventh and eighth electrons suggests that the eighth electron comes from a principal quantum shell closer to the nucleus.

CHAPTER 4: Chemical Bonding

Learning outcomes:

(a) *describe ionic (electrovalent) bonding, as in sodium chloride and magnesium oxide, including the use of 'dot-and-cross' diagrams.*
(b) *describe, including the use of 'dot-and-cross' diagrams,*
  (i) *covalent bonding, as in hydrogen, oxygen, chlorine, hydrogen chloride, carbon dioxide, methane, ethene.*
  (ii) *co-ordinate (dative covalent) bonding, as in the formation of the ammonium ion and in the* Al_2Cl_6 *molecule.*
(c) *explain the shapes of, and bond angles in, molecules by using the qualitative model of electron-pair repulsion (including lone pairs), using as simple examples:* BF_3 *(trigonal),* CO_2 *(linear),* CH_4 *(tetrahedral),* NH_3 *(pyramidal),* H_2O *(non-linear),* SF_6 *(octahedral),* PF_5 *(trigonal bipyramid).*
(d) *describe covalent bonding in terms of orbital overlap, giving* σ *and* π *bonds, including the concept of hybridisation to form sp,* sp^2 *and* sp^3 *orbitals.*
(e) *explain the shape of, and bond angles in, ethane and ethene in terms of* σ *and* π *bonds.*
(f) *predict the shapes of, and bond angles in, molecules analogous to those specified in (c) and (e).*
(g) *describe hydrogen bonding, using ammonia and water as simple examples of molecules containing N-H and O-H groups.*
(h) *understand, in simple terms, the concept of electronegativity and apply it to explain the properties of molecules such as bond polarity and the dipole moments of molecules.*
(i) *explain the terms bond energy, bond length and bond polarity and use them to compare the reactivities of covalent bonds.*
(j) *describe intermolecular forces (van der Waals' forces), based on permanent and induced dipoles, as in* $CHCl_3(l)$; $Br_2(l)$ *and the liquid noble gases.*
(k) *describe metallic bonding in terms of a lattice of positive ions surrounded by mobile electrons.*

(l) describe, interpret and/or predict the effect of different types of bonding (ionic bonding, covalent bonding, hydrogen bonding, other intermolecular interactions, metallic bonding) on the physical properties of substances.

(m) deduce the type of bonding present from given information.

(n) show understanding of chemical reactions in terms of energy transfers associated with the breaking and making of chemical bonds.

4.1 Ionic Bonding

Formation of ionic bond

1) *Ionic bond* is the electrostatic force of attraction between oppositely-charged ions formed by the complete transfer of electrons from an atom to another atom.

2) Ionic bond is also called electrovalent bond.

3) i. An atom(usually a metal) that loses electron(s) will form a positive ion(cation).
   ii. The electron is then **transferred** to another atom.
   iii. The atom that gains the electron(usually a non-metal) will form a negative ion(anion).
   iv. The cations and anions are then attracted by strong electrostatic force of attraction. The force of attraction constitutes the ionic bond.

4) The force of attraction between cation and anion is very strong, therefore ionic bond is a very strong bond.

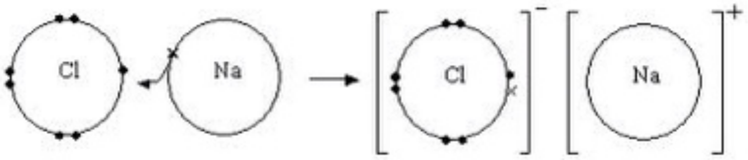
5) Ionic bonds are non-directional, each cation will attract any neighbouring anion and vice versa to form a huge ionic lattice.

6) The compound formed as a result of ionic bond is called ionic compound. An example is sodium chloride, NaCl.

Dot-and-cross diagram

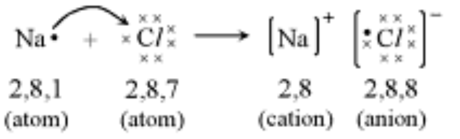
1) A dot-and-cross diagram shows:
   i. the outer electron shell only.
   ii. that the charge of the ion is spread evenly using a square bracket.
   iii. the charge of each ion.

2) It is also called the Lewis diagram.



3) Using dot-and-cross diagram to represent the formation of ionic bond:

Formation of sodium chloride (NaC*l*)



[*No electrons* are shown in the 'dot-and-cross' diagram of cations – since the valence electrons are transferred completely to the anions.]

- Na atom loses an electron to form Na^+, which has a stable neon structure (2,8).
- C*l* atom gains an electron to form Cl^-, which has a stable argon structure (2,8,8).
- ***Electrostatic attraction*** between Na^+ and Cl^- ions constitutes the ionic bond.

Strength of ionic bonds

1) The strength of ionic bond is a measure of the electrostatic force of attraction between the ions.

2) The force of attraction between the oppositely-charged ions is proportional to the charge on the ions and inversely proportional to the square of distance between the ions.

$$E \propto \frac{(Q^+)\,(Q^-)}{d^2}$$

3) The strength of ionic bond is manifested in the melting point of the ionic compound.

4) i. For instance, the melting point of NaCl is higher than NaBr.
   ii. This is because the size of Br^- ion is larger than Cl^- ion. Therefore the distance between Br^- and Na^+ is larger than that of between Cl^- and Na^+.
   iii. As a result, the electrostatic force of attraction between Na^+ and Cl^- is stronger than that of between Na^+ and Br^- ion.

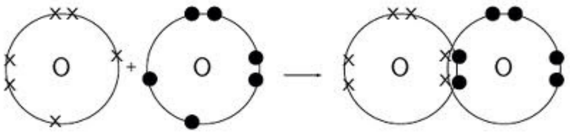
5) i. The melting point of NaCl is lower than $MgCl_2$.
   ii. This is because Mg^{2+} ion has a higher charge than Na^+ ion. Besides that, the size of Mg^{2+} ion is smaller than Na^+ ion.
   iii. The above two factors causes the electrostatic force of attraction between Mg^{2+} and Cl^- to be stronger than that of between Na^+ and Cl^-.

4.2 Covalent Bonding

Formation of covalent bond

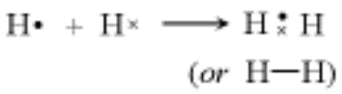
1) *Covalent bond* is the electrostatic force of attraction that two neighbouring nuclei have for a localised pair of electrons shared between them.

2) Covalent bond is formed without transferring electrons, instead, the atoms **share** their valence electron(s) to achieve duplet/octet electronic configuration.

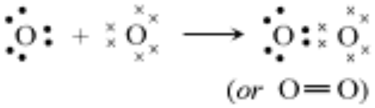


3) The shared pair of electrons constitutes the covalent bond.

4) Using dot-and-cross diagram to represent the formation of covalent bond:



Formation of hydrogen gas, H_2

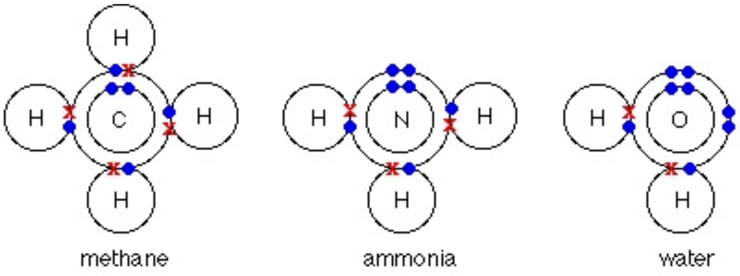


Formation of oxygen gas, O_2

Single bond

1) Single bond is formed when **one pair** of electrons is shared between two atoms.

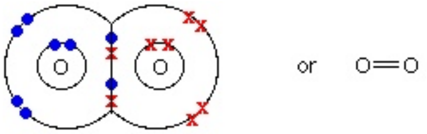
2) Examples of compounds with single bonds:

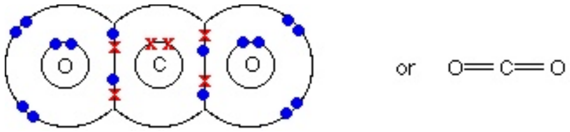


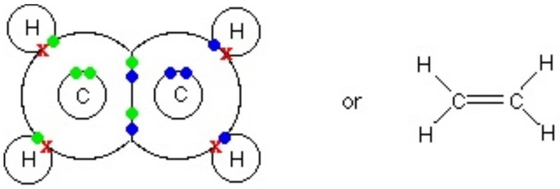
Double bond

1) Double bond is formed when **two pairs** of electrons are shared between two atoms.

2) Examples of compounds with double bonds:



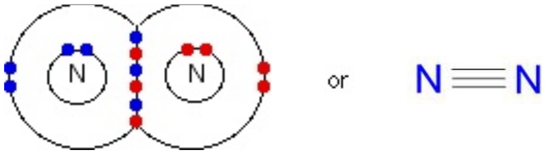




Triple bond

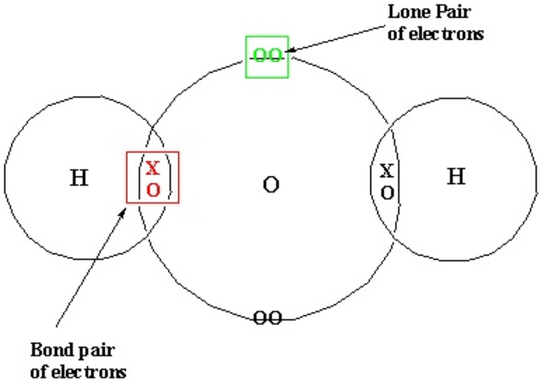
1) Triple bond is formed when **three pairs** of electrons are shared between two atoms.

2) Examples of compounds with triple bonds:



Lone pair and bond pair of electrons

1) The pair of electrons used in covalent bonding is called the bond pair while the pair of electrons not used in covalent bonding is called the lone pair.

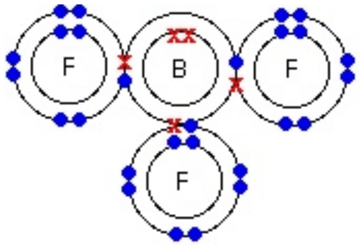


Octet-deficient and expanded octet species

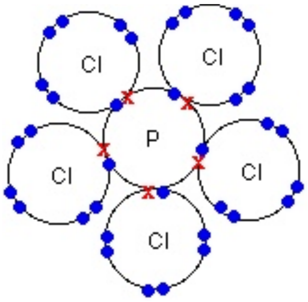
1) In general, atoms tend to share their electrons to a achieve a duplet/octet electronic configuration - the octet rule.

2) i. In octet-deficient species, the central atom has **less** than eight electrons.
   ii. Some examples are boron trifluoride, BF_3 and nitrogen monoxide, NO.

4) i. In expanded octet species, the central atom has **more** than eight electrons.
   ii. An example is phosphorus(V) chloride, PCl_5.
   iii. This is possible only for Period 3 elements and beyond, this is because starting from Period 3, the atoms have **empty d orbitals** in the third energy level to accommodate more than eight electrons.



Octet deficient



Expanded octet

Co-ordinate bond (dative covalent bond)

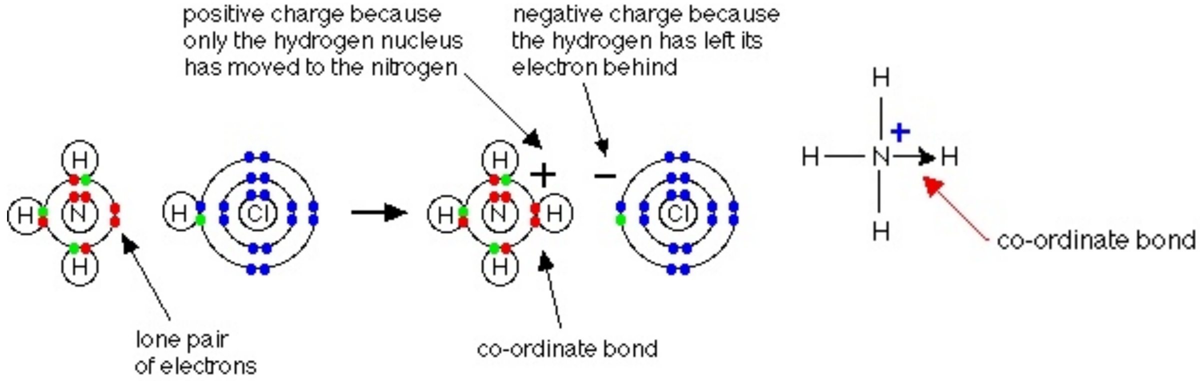
1) A co-ordinate bond is formed when one atom provides **both** the electrons needed for a covalent bond.

2) Conditions of forming a co-ordinate bond:
   i. one atom has a **lone pair** of electrons.
   ii. another atom has an **unfilled orbital** to accept the lone pair, in other words, an electron-deficient species.

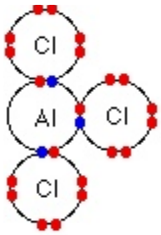
3) Once the bond is formed, it is identical to the other covalent bonds. It does not matter where the electrons come from.

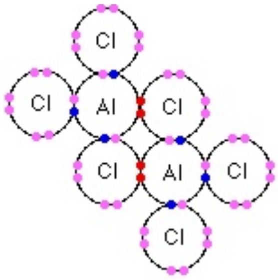
4) In a displayed formula, a co-ordinate bond is represented by an arrow, the head of the arrow points away from the lone pair which forms the bond.

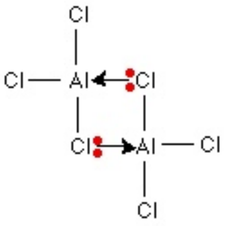
5) An example is the reaction between ammonia and hydrogen chloride. In this reaction, ammonium ion is formed by the transfer of hydrogen ion(an octet deficient species) from hydrogen chloride to the lone pair of electrons in the ammonia molecule.



6) Another example is aluminium chloride. At high temperature, it exists as $AlCl_3$. At low temperature(around 180-190°C), it exists as Al_2Cl_6, a dimer(two molecules joined together). This is possible because lone pairs of electrons from the chlorine atom form co-ordinate bonds with the aluminium atom.







Tips to draw dot-and-cross diagram for covalent molecules

1) Identify the central atom and terminal atom(s). For example, in ammonia, the nitrogen is the central atom while the hydrogens are the terminal atoms.

2) During the sharing of electrons, the terminal atoms **must** attain octet configuration(or duplet for hydrogen) but not necessarily for the central atom.

3) i. If the central atom is from Period 2 of the Periodic Table, the total number of electrons surrounding it **cannot exceed eight**(but can less than eight).
   ii. If the central atom is from Period 3 and beyond, the total number of electrons surrounding it **can exceed eight**.

4) i. For polyatomic anions, the negative charge will be distributed among the **most electronegative** atom(s). This is to decrease the charge density on a particular atom and to stabilise the ion.
   ii. For polyatomic cation, the positive charge will be distributed among the **less electronegative** atom(s). The reason is same as above.

5) If the terminal atom already has octet configuration(for example, Cl^-), it will contribute two electrons to the central atom to form a co-ordinate bond.

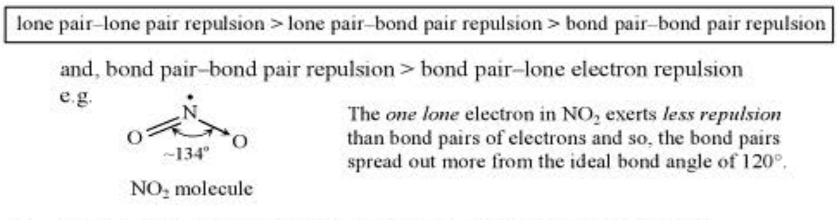
4.3 Shapes of Molecules

Valence shell electron pair repulsion(VSEPR) theory

1) All electrons are negatively-charged, so they will repel each other when they are close together.

2) So, a pair of electrons in the bonds surrounding the central atom in a molecule will repel the other electron pairs. This repulsion forces the pairs of electrons apart until the repulsive forces are minimised.

3) The amount of repulsion is as follow:



lone pair–lone pair repulsion > lone pair–bond pair repulsion > bond pair–bond pair repulsion

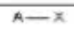
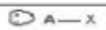
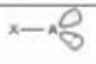
and, bond pair–bond pair repulsion > bond pair–lone electron repulsion

e.g.

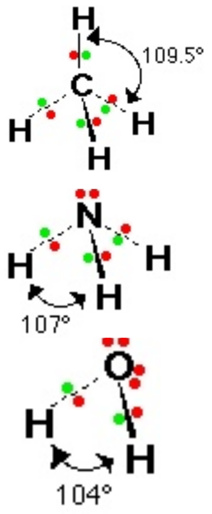
NO_2 molecule

The *one lone* electron in NO_2 exerts *less repulsion* than bond pairs of electrons and so, the bond pairs spread out more from the ideal bond angle of 120°.

4) General steps to determine the shape of a molecule:
   i. determine the number of valence electrons in the central atom.
   ii. find the total number of electrons surrounding the central atom by adding the number of shared electrons to it. (Dot-and-cross diagram might be necessary)
   iii. find the number of electron pairs by dividing the total number of electrons by two.
   iv. determine how many pairs is/are bond pairs and lone pairs. (A double bond or triple bond is counted as one bond pair)
   v. refer to the table to obtain the shape of the molecule

Total Domains	Generic Formula	Picture	Bonded Atoms	Lone Pairs	Molecular Shape	Electron Geometry	Example	Hybridi -zation	Bond Angles
1	AX		1	0	Linear	Linear	H_2	s	180
2	AX_2		2	0	Linear	Linear	CO_2	sp	180
	AXE		1	1	Linear	Linear	CN^-		
3	AX_3		3	0	Trigonal planar	Trigonal planar	$AlBr_3$	sp^2	120
	AX_2E		2	1	Bent	Trigonal planar	$SnCl_2$		
	AXE_2		1	2	Linear	Trigonal planar	O_2		
4	AX_4		4	0	Tetrahedral	Tetrahedral	$SiCl_4$	sp^3	109.5
	AX_3E		3	1	Trigonal pyramid	Tetrahedral	PH_3		
	AX_2E_2		2	2	Bent	Tetrahedral	$SeBr_2$		
	AXE_3		1	3	Linear	Tetrahedral	Cl_2		
5	AX_5		5	0	Trigonal bipyramid	Trigonal bipyramid	AsF_5	sp^3d	90 and 120
	AX_4E		4	1	See Saw	Trigonal bipyramid	SeH_4		
	AX_3E_2		3	2	T shape	Trigonal bipyramid	ICl_3		
	AX_2E_3		2	3	Linear	Trigonal bipyramid	BrF_2^-		
6	AX_6		6	0	Octahedral	Octahedral	$SeCl_6$	sp^3d^2	90
	AX_5E		5	1	Square pyramid	Octahedral	IF_5		
	AX_4E_2		4	2	Square planar	Octahedral	XeF_4		

Effect of lone pair on bond angle



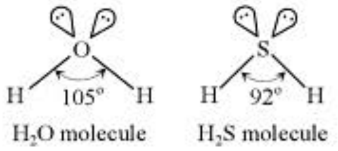
1) For methane, ammonia and water, the electron pair geometries are tetrahedral. However, the molecular geometries are different.

2) In methane, all the bonds are identical, repulsion between the bonds is the same. Thus, methane has a perfect tetrahedral structure with bond angle **109.5°**.

3) In ammonia, the repulsion between the lone pair and the bond pairs is stronger than in methane. This forces the bond angle to decrease slightly to **107°**.

4) In water, there are two lone pairs and thus the repulsion is the greatest, the two bond pairs are pushed closer to one another and the bond angle is reduced to **104.5°**.

Effect of electronegativity on bond angle



1) Water and hydrogen sulfide have the same general shape with the same number of bond pairs and lone pairs. However, their bond angles are different.

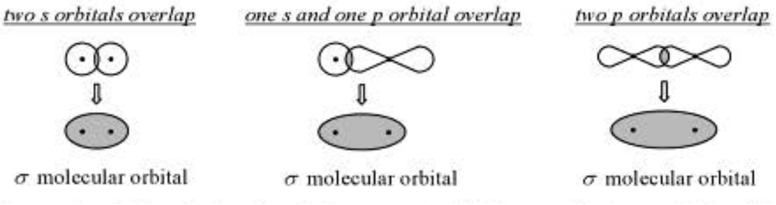
2) This is because oxygen has a higher electronegativity than sulphur. The bond pairs of electrons are closer to the oxygen atom compared to the sulfur atom.

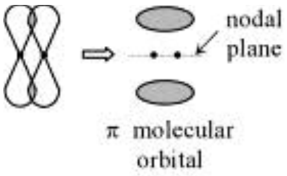
3) This results in **greater repulsion** in the O-H bonds than in the S-H bonds. Therefore, the bond angle increases from 92.5° to 104.5°.

Sigma(σ) bond and pi(π) bond

1) A sigma bond is formed by orbitals from two atoms overlapping **end-to-end**.

2) In a sigma bond, the electron density is concentrated between the two nuclei.



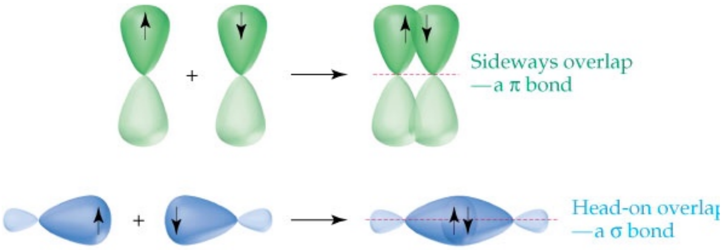


3) A pi bond is formed by the p orbitals from two atoms overlapping **sideways**.

4) In a pi bond, there are two regions of high electron density alongside the nuclei.

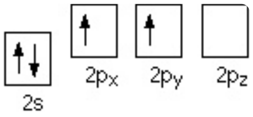
5) A pi bond is weaker than a sigma bond because the overlapping of charge clouds is less than in a sigma bond.

6) In covalent molecules, **single bonds** are sigma bonds(**σ**), a **double bond** consists of one sigma bond and one pi bond(**1σ, 1π**), and a **triple bond** consists of one sigma bond and two pi bonds(**1σ, 2π**).



Hybridisation

1) *Hybridisation* is the mixing of atomic orbitals to produce a new set of hybrid orbitals of equivalent energies. This is a theory used to account for the discrepancies in explaining the shapes of covalent molecules.

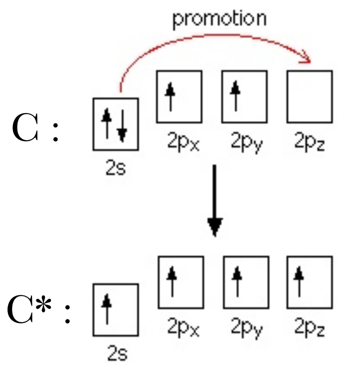


2) There is a problem with simple view on methane, CH_4. Methane has two unpaired electrons only in its outer shell to share with the hydrogen atoms, but the formula of methane is not CH_2.

3) The concept of hybridisation is used to account for this discrepancy.

4) General steps in hybridisation:
   i. promotion of electron.
   ii. mixing of orbitals to produce a new set of hybrid orbitals of equivalent energies(sp, sp^2 or sp^3 hybrid orbitals)
   iii. forming of a new molecular orbital.

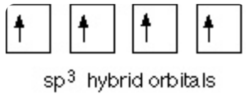
sp^3 hybridisation



1) An example of compound which undergoes sp^3 hybridisation is methane, CH_4.

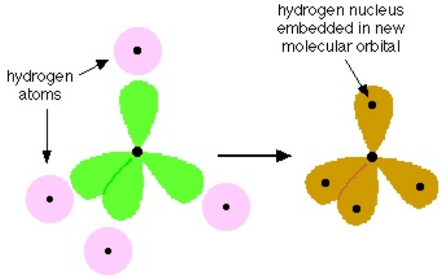
2) The carbon atom uses some energy to **promote** one of its electron from 2s to empty 2p orbital so that there are **four unpaired electrons** for covalent bonding.

3) The carbon now is said to be in an **excited state(C*)**.



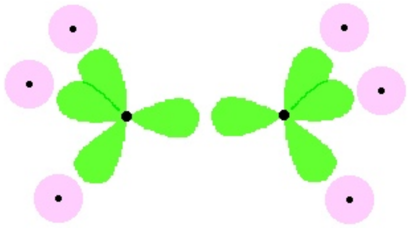
4) The orbitals then 'mix' or **hybridise** to produce **four hybrid orbitals of equivalent energies**. The new orbitals are called sp^3 hybrid orbitals because they are made from one s orbital and three p orbitals.

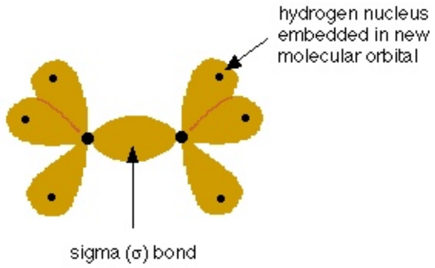
5) Each hybrid orbital has one big lobe and one small lobe. They rearrange themselves so that they are as far as possible to form a tetrahedral geometry. The hybrid orbitals are 109.5° apart.



6) The s orbitals from the hydrogen atoms then overlap with the four hybrid orbitals to form **four sigma bonds** because the overlapping is end-to-end. All the bonds are identical.

7) Another example is ethane, C_2H_6. The two carbon atoms undergo sp^3 hybridisation to form four hybrid orbitals. The two carbon atoms are bonded by overlapping one of their hybrid orbitals. The remaining ones then overlap with the s orbitals of the hydrogen atoms.



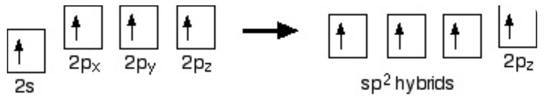


8) The bond angle is approximately 109.5°. This is an approximation because all the bonds are not identical.

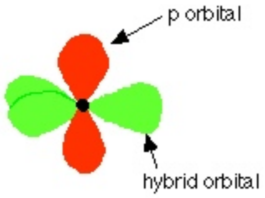
sp^2 hybridisation

1) An example of compound which undergoes sp^2 hybridisation is ethene, C_2H_4.

2) The same thing happens as in sp^3 hybridisation, except that this time the carbon atoms 'mix' or hybridise **three of the four orbitals only** because the carbon atom is bonding with three other atoms only.

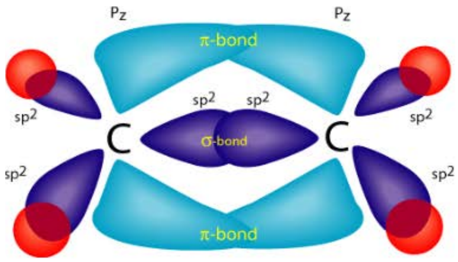


3) This produces **three sp^2 hybrid orbitals** because they are made from one s orbital and two p orbitals. Another p orbital **remains unchanged** and it is perpendicular to the plane containing the hybrid orbitals.

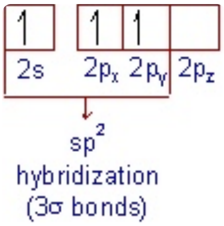


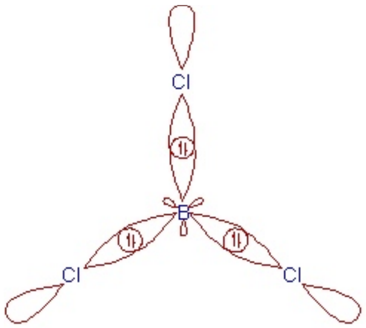
4) The hybrid orbitals rearrange themselves so that they are as far as possible, that is, a trigonal planar arrangement, the hybrid orbitals are 120° apart.

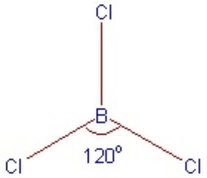
5) The hybrid orbitals then overlap with s orbitals from the hydrogen atoms and another hybrid orbital from the other carbon atom to form **five sigma bonds**. The remaining p orbitals overlap sideways to form **a pi bond**. A **double bond** is formed between the two carbon atoms.



6) Another example is boron trichloride, BCl_3. The boron atom undergoes sp^2 hybridisation to produce three sp^2 hybrid orbitals. The hybrid orbitals rearrange themselves to form a trigonal planar geometry. The p orbitals from chlorine atoms then overlap with the hybrid orbitals to form three sigma bonds.



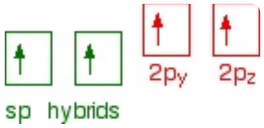


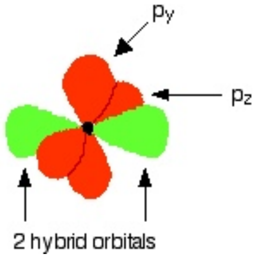


sp hybridisation

1) An example of compound which undergoes sp hybridisation is ethyne, C_2H_2.

2) The same thing happens as in sp^3 and sp^2 hybridisation, except that this time the carbon atoms 'mix' or hybridise **two of the four orbitals** only because the carbon atom is bonding with two other atoms only.

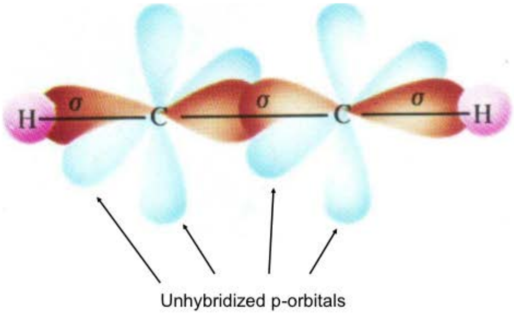


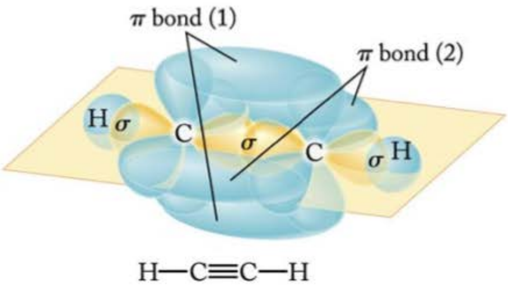


3) This produces **two sp hybrid orbitals** because they are made from one s orbital and one p orbital. The other two p orbitals **remain unchanged** and they are perpendicular to each other and to the two hybrid orbitals.

4) The hybrid orbitals rearrange themselves so that they are as far as possible, that is, a linear arrangement, the hybrid orbitals are 180° apart.

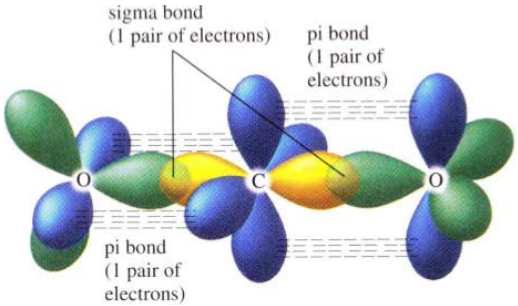
5) The hybrid orbitals overlap with the s orbitals from the hydrogen atoms and to the hybrid orbital from the other carbon atom to form **three sigma bonds**. The remaining p orbitals overlap sideways to form **two pi bonds**. A **triple bond** is formed between the two carbon atoms.





Example of covalent molecule with multiple hybridisations

1) In carbon dioxide, CO_2, the carbon atom undergoes sp hybridisation while the oxygen atoms undergo sp^2 hybridisation. The overlapping of the hybrid and p orbitals are shown in the diagram.



4.4 Electronegativity, Bond Polarity, Bond Length and Bond Energy

Electronegativity

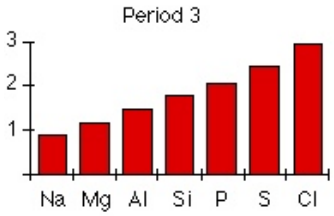
1) *Electronegativity* is the ability of an atom which is covalently bonded to the other atom to attract the bond pair of electrons towards itself.

2) The more electronegative an atom is, the higher the tendency of that atom to attract the bond pair of electrons towards itself.

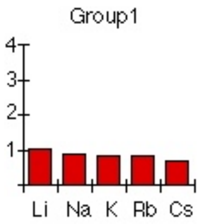
3) The Pauling scale is commonly used to quantify the value of electronegativity of a particular element.

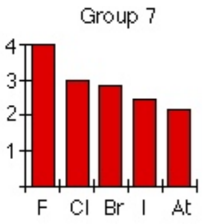
4) **Fluorine** is the most electronegative element because of its small size, followed by **oxygen** and **nitrogen**.

Trends of electronegativity values in the Periodic Table



1) i. The value of electronegativity **increases** across a Period(from left to right).
   ii. This is because the number of proton increases across a Period. Therefore the amount of positive charge in the nucleus also increases.
   iii. The shielding effect by inner electrons remains constant.
   iv. Therefore the attraction towards the bond pair of electrons increases, making it more electronegative.





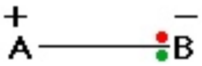
2) i. The value of electronegativity **decreases** down a Group.
   ii. This is because the size of the atoms increases down a Group. Therefore the distance between the nucleus and the bond pair of electrons also increases.
   iii. The shielding effect by inner electrons is also greater.
   iv. Therefore the attraction towards the bond pair of electrons decreases, making it less electronegative.

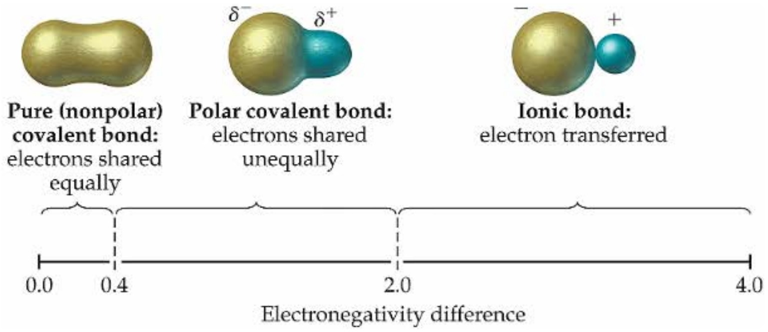
Bond Polarity

1) i. When two covalently-bonded atoms have the same electronegativity, the electron cloud is evenly distributed between the two atoms.
   ii. The bond is described as a 'pure' covalent bond or non-polar bond.
   iii. Some examples are H_2, Cl_2 and Br_2.

2) i. However, when an atom is more electronegative than the other, the more electronegative atom will attract the bond pair of electrons more towards itself. The electron cloud is not evenly distributed or **distorted**.
   ii. The more electronegative end acquires a partial negative charge while the less electronegative end acquires a partial positive charge.
   iii. The bond is said to be **polarised**, or, a polar bond.
   iv. Some examples of compound which contain polar bond(s) are HCl and CH_4.
   v. The molecule is described as 'covalent with some ionic character'.

3) i. When the electronegativity difference between the two atoms is very great, the less electronegative atom will lose its electrons and the more electronegative atom will gain the electrons.
   ii. An ionic bond will be formed.





Polar and non-polar molecules

1) A molecule is polar, and thus, has a dipole moment($\mu \neq 0$) if:
   i. the bonds are polarised
   ii. the dipole of the bonds do not cancel out each other(in other words, it is asymmetrical)

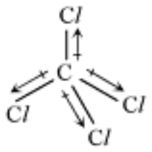
2) The *dipole moment*, μ is the product of charges and the distance between the centre of the charges.

3) Examples:

H_2O

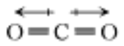
Individual dipoles do ***not*** cancel out; so molecule has a dipole moment.

CCl_4

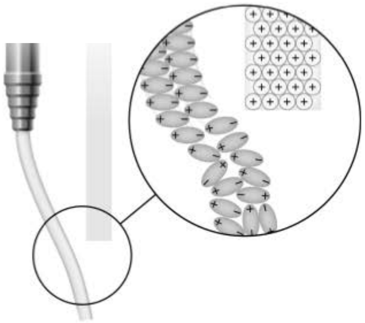


Individual dipoles cancel each other; so molecule has ***no*** dipole moment.

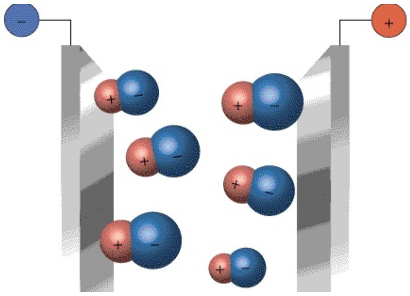
CO_2



Individual dipoles cancel each other; so molecule has ***no*** dipole moment.



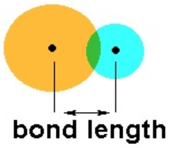
4) A liquid containing polar molecules **can be deflected** by a charged rod brought near to it. This is because there is a positive end and a negative end in polar molecules. So, irregardless of the charge on the rod, one end of the molecule will always be attracted towards the charged rod.



5) When polar molecules are placed in an electric field, the positive end of the molecule will face towards the negative terminal while the negative end of the molecule will face towards the positive terminal.

6) Generally, polar molecules are more reactive than non-polar molecules because many chemical reactions are started by a reagent attacking an electrically-charged end of the polar molecule. An example is CO is more reactive than N_2 although both of them have triple bonds because CO is polar while N_2 is not.

<u>Bond length and bond energy</u>



1) *Bond length* is the distance between two nuclei of two atoms joined by a covalent bond.

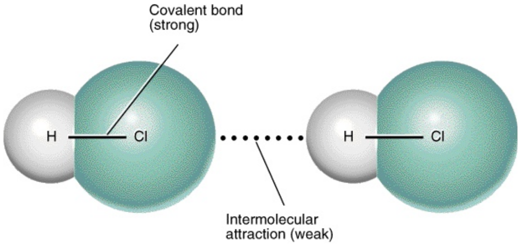
2) *Bond energy* is the energy needed to break one mole of covalent bonds between two atoms in the gaseous state.

$$A\text{-}B(g) \rightarrow A(g) + B(g) \qquad \Delta H^\circ = +x\ \mathrm{J}$$

4) i. The **shorter** the bond length, the **stronger** is the bond.
ii. The **greater** the bond energy, the **stronger** is the bond.
iii. Hence, the **shorter** and bond length, the **greater** the bond energy.

4.5 Intermolecular Forces

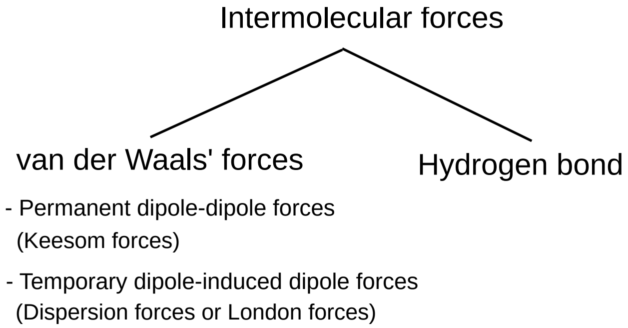
Intermolecular and intramolecular forces



1) i. Intramolecular force is the force of attraction that hold individual atoms together **in a molecule**.
   ii. Commonly referred to as covalent bonds.

2) Intermolecular force is the force of attraction **between one molecule and the neighbouring molecule**.

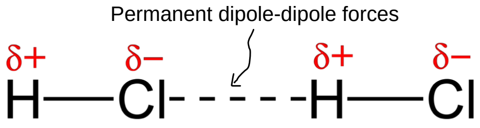
3) There are several types of intermolecular forces:



4) Intermolecular forces are **much weaker** than intramolecular forces.

5) Intermolecular forces are responsible for the melting and boiling points of substances, as well as their physical states.

Permanent dipole-dipole forces(Keesom forces)



1) Polar molecules have a negative end and a positive end. The oppositely-charged ends will attract one another. The forces of attraction is called permanent dipole-dipole forces.

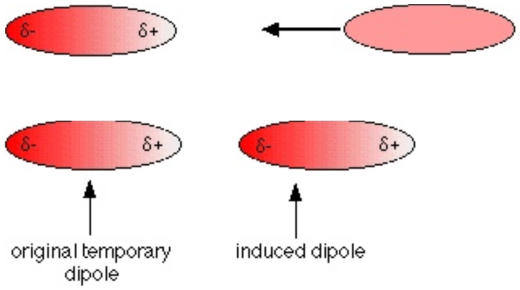
2) **Only polar molecules** will experience permanent dipole-dipole forces.

Temporary dipole-induced dipole forces(Dispersion forces or London forces)

1) Electrons are mobile, and constantly revolving around the nucleus. Even in non-polar molecules, there is a high possibility that at any given instant, the electron density is higher on one side than the other.

2) This will result in the formation of **temporary dipole**(or instantaneous dipole) because it only lasts for just a tiny fraction of time.

3) In the next instance, the distribution of electron density will change and the molecule has a new temporary dipole.



4) The temporary dipole set up can distort the electron charge clouds of the neighbouring molecules, giving rise to **induced dipoles**.

5) The forces of attraction between temporary dipoles and induced dipoles give rise to dispersion forces.

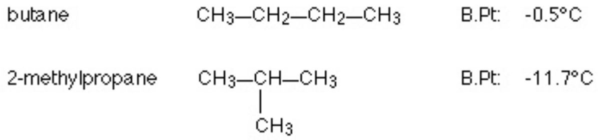
6) **All molecules(polar and non-polar)** will experience dispersion forces. For polar molecules, permanent dipole-dipole forces exist **in addition** with dispersion forces.

Factors affecting strength of dispersion forces

1) **Number of electrons in the molecule(Size of molecule)**
   - As the number of electrons increases, the size of the molecule also increase.
   - This causes the attraction between the nucleus and the electrons to get weaker, the electrons become progressively easier to be distorted.
   - This causes more temporary dipoles to be set up and the dispersion forces get stronger.
   - The boiling point of halogens increases going down the Group. The size of the molecules increases and thus the van der Waals' forces become stronger.

2) **Number of contact points between the molecules(Surface area)**
   - For two molecules of the same number of electrons, the one which has a larger surface area has more contact points between the molecules.
   - The more contact points between molecules, more temporary dipoles can be set up and the dispersion forces become stronger.

- Butane is a **long chain** molecule while 2-methypropane is more **spherical** (more compact). This causes the number of contact point between butane molecules to be more than in 2-methypropane.
- Therefore the van der Waals' forces of attraction in butane is stronger than in 2-methypropane. This causes the boiling point of butane to be higher.



butane	$CH_3—CH_2—CH_2—CH_3$	B.Pt:	-0.5°C
2-methylpropane	$CH_3—CH(CH_3)—CH_3$	B.Pt:	-11.7°C

Hydrogen bonding

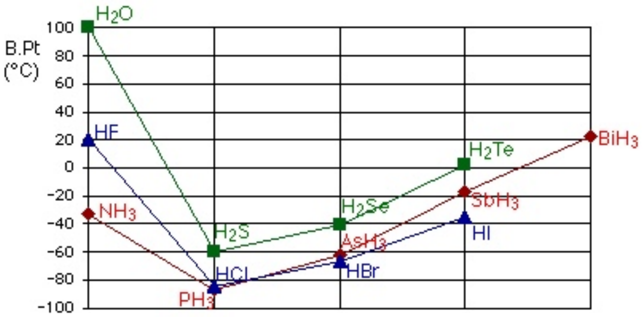
1) *Hydrogen bond* is the electrostatic force of attraction between a hydrogen atom (which is covalently bonded to a small and highly electronegative atom) and the lone pair of electrons of another small and highly electronegative atom.

2) The 'small and highly electronegative atoms' are fluorine, oxygen and nitrogen.

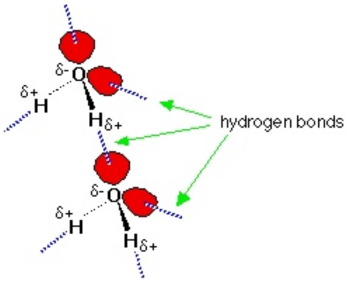
3) The conditions necessary for forming hydrogen bonds:
   i. a **hydrogen atom** bonded **directly** to a **small and electronegative atom**, causing it to acquire a significant amount of partial positive charge.
   ii. a **lone pair** of electrons from the small and electronegative atom.

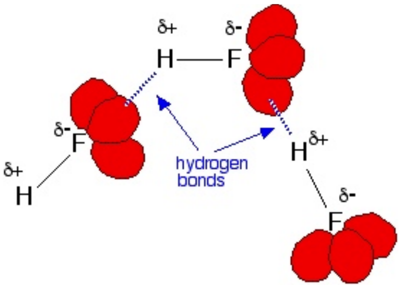
4) The attraction between the hydrogen atom and the lone pair of electrons constitutes the hydrogen bond.

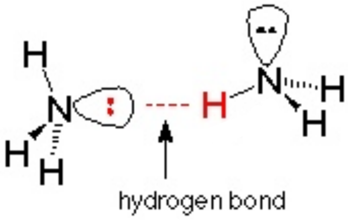
5) The evidence of hydrogen bonding:
   - H_2O, HF and NH_3 have exceptionally high boiling points compared to other compounds with greater number of electrons.
   - This suggests that there must be an additional intermolecular force other than van der Waals' forces exists between them.
   - This additional intermolecular force is called the hydrogen bond.



6) H_2O has a higher boiling point compared to NH_3 and HF. This is because a H_2O molecule can form, on average four hydrogen bonds. In NH_3, the number of hydrogen bonds is restricted by the one lone pair of electrons in the NH_3 molecule. In HF, it is restricted by the number of hydrogen atoms.



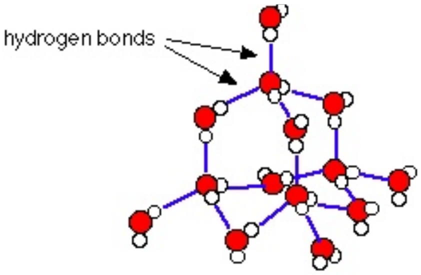




The peculiar properties of water

1) **Solid ice is less dense than liquid water**

- Most solids are denser than their liquids, this is because in the solid state, the molecules are packed closer and occupies smaller volume.
- However, solid ice is less dense than liquid water.
- This is because in the solid state, the water molecules are bonded to each other through hydrogen bonding to form a **giant 3-dimensional tetrahedral structure**. This structure has a lot of **empty spaces** in between the water molecules.
- When heat is supplied, some of the hydrogen bond breaks down and the rigid structure collapses, filling up the spaces in between them, thus decreasing the volume occupied and increasing its density.



2) **Solubility of substances in water**

- Most covalent compounds are not soluble water while ionic compounds are.
- However, some covalent compounds are soluble in water because they can form hydrogen bonds with water, some examples are ammonia and alcohols

3) **High boiling point of water**

- The boiling point of water is exceptionally high compared to other Group 16 hydrides(see graph at page 21).
- This is because water molecules are capable of forming hydrogen bonds between themselves. This additional type of intermolecular forces increases its boiling point significantly.

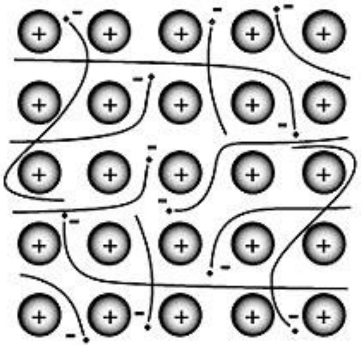
4) **High surface tension and viscosity**

- Water has a high viscosity. This is because hydrogen bonding reduces the ability of water to slide over each other, making it more viscous.
- Water has a high surface tension. This is because hydrogen bonds also exert a significant downward force at the surface of liquid.

4.6 Metallic Bonding

Metallic bonds

1) *Metallic bond* is the electrostatic force of attraction between the delocalised electrons and the positive metal ions.



2) Take sodium as an example, in the solid state, sodium atoms are packed so closely together that the 3s orbitals(containing an electron) overlap with one another to form a giant molecular orbital.

3) The 3s electrons is then free to move throughout the lattice structure, it is no longer bound to any sodium atom. The electrons are said to be **delocalised**. The delocalised electrons are sometimes referred to as **'sea of delocalised electrons'**.

4) The attraction between the delocalised electrons and the positive metal ions constitutes the metallic bond.

Factors affecting the strength of metallic bonds

1) **Number of electrons in the sea of delocalised electrons**
   - The **more** the number of electrons delocalised, the **stronger** the metallic bond.
   - For example, the melting point of magnesium is higher than sodium.
   - This is because one magnesium atom can donate two electrons from its outer shell into the sea of delocalised electrons while sodium can only donate one.
   - There is twice amount of delocalised electrons in magnesium than in sodium. So, the metallic bond in magnesium is stronger due to the stronger attraction.

2) **Size of the metal**
   - The **smaller** the size of the metal, the **stronger** the metallic bond.
   - For example, the melting point of magnesium is lower than beryllium although both of them have two electrons delocalised per atom.
   - This is because the size of magnesium is bigger, causing the attraction between the delocalised electrons and the positive nucleus to be weaker. The shielding effect in magnesium is also more than in beryllium.
   - So, the metallic bond in magnesium is weaker than in beryllium.

4.7 Bonding and Physical Properties of Substances

Physical state at room temperature

1) **Ionic compounds**
   - Ionic compounds are solids at room temperature, this is because the ionic bond holding the oppositely-charged ions is very strong, a lot of energy is required to overcome the strong forces of attraction.

2) **Covalent compounds**
   - Most simple covalent molecules(like water and ammonia) are liquids or gases at room temperature. This is because the intermolecular force between the molecules is weak, little energy is required to overcome it.
   - Some simple covalent molecules(like iodine) are solids because the intermolecular force between them is strong enough.
   - For giant covalent structures(like diamond and silicon dioxide), they are solids at room temperature. This is because the covalent bonds holding the atoms are very strong, a lot of energy is required to overcome it.

3) **Metals**
   - Metals(except mercury) are solids at room temperature. This is because the metallic bond holding the metal ions is very strong, a lot of energy is required to overcome it.

Electrical conductivity

1) **Ionic compounds**
   - Ionic compounds do not conduct electricity in the solid state, this is because the ions are not free to move.
   - In the molten or aqueous state, it conducts electricity because the ions are free to move(mobile ions are present).

2) **Covalent compounds**
   - Simple covalent molecules do not conduct electricity because the ions are **not free to move**.
   - Some giant covalent structures(like graphite) are able to conduct electricity because the electrons are free to move(delocalised). (See also Chapter 5)

3) **Metals**
- Metals conduct electricity because the delocalised electrons are free to move.

Solubility

1) **Ionic compounds**
- Most ionic compounds are soluble in water(polar solvents) and insoluble in non-polar solvents.
- This is because in non-polar solvents, the molecules are held together by weak intermolecular forces. The ionic bonds in ionic compounds are much stronger and the energy needed to break them is high. If ion-solvent bonds are formed, the energy released is **not enough to compensate** the energy absorbed, making the entire structure **unstable**.
  [Note: To form ion-solvent bonds, the ion-ion(ionic bond) and solvent-solvent (van der Waal's forces) bonds must be broken first.]
- While in polar molecules, there is an attraction between polar molecules and the ions. So, the energy released when ion-solvent bonds are formed is **enough to compensate** the energy needed to break the strong ionic bonds.

2) **Covalent compounds**
- This is because when a covalent molecule is dissolved in a non-polar solvent, the molecule-solvent attraction is strong enough to compensate the energy needed to break the weak van der Waal's forces between covalent molecules.
- While when dissolved in polar solvents, the energy needed to break the attractions in polar solvents is too high. The energy released when molecule-solvent attraction set up is not enough to compensate it. This makes the structure to gain energy overall, making it less stable.
- Some covalent compounds react with water rather than dissolving in it. For example, hydrogen chloride reacts with water to form hydrogen ions and chloride ions, and the ions are soluble.

3) **Metals**
- Metals do not dissolve in polar and non-polar solvents.
- However, some metals like sodium and calcium can react with water.

CHAPTER 5: States of Matter

Learning outcomes:

(a) state the basic assumptions of the kinetic theory as applied to an ideal gas.
(b) explain qualitatively in terms of intermolecular forces and molecular size:
  (i) the conditions necessary for a gas to approach ideal behaviour.
  (ii) the limitations of ideality at very high pressures and very low temperatures.
(c) state and use the general gas equation $pV = nRT$ *in calculations, including the determination of Mr.*
(d) describe, using a kinetic-molecular model: the liquid state, melting, vaporisation, vapour pressure.
(e) describe, in simple terms, the lattice structure of a crystalline solid which is:
  (i) ionic, as in sodium chloride, magnesium oxide.
  (ii) simple molecular, as in iodine.
  (iii) giant molecular, as in silicon(IV) oxide and the graphite and diamond allotropes of carbon.
  (iv) hydrogen-bonded, as in ice.
  (v) metallic, as in copper.
  [the concept of the 'unit cell' is not required]
(f) explain the strength, high melting point and electrical insulating properties of ceramics in terms of their giant molecular structure.
(g) relate the uses of ceramics, based on magnesium oxide, aluminium oxide and silicon(IV) oxide, to their properties (suitable examples include furnace linings, electrical insulators, glass, crockery).
(h) discuss the finite nature of materials as a resource and the importance of recycling processes.
(i) outline the importance of hydrogen bonding to the physical properties of substances, including ice and water (for example, boiling and melting points, viscosity and surface tension).
(j) suggest from quoted physical data the type of structure and bonding present in a substance.

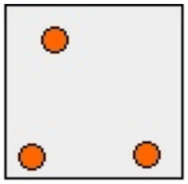
5.1 The Gaseous State

Kinetic theory of gases

1) Assumptions made in the kinetic theory of gases as applied to **ideal gases**:
   - The gas particles have **zero intermolecular forces** between them.
   - The gas particles behave as point particles which have **negligible volume**.
   - The gas particles are in constant random motion, colliding with each other and the wall of the container frequently.
   - All collisions between the gas particles are perfectly elastic.
   - Pressure is due to the collision of gas particles with the wall of container.

2) In the gaseous state, the particles can **move freely** and are **far apart**.

3) A gas has **no fixed shape and volume**, it takes the shape of container and always fills it. The volume of a gas depends on its pressure, temperature and number of moles.



gas

Ideal gas and real gas

1) A real gas is most like an ideal gas at:
   i. **low pressures**
      - At low pressures, the distance between gas particles is large and the volume of the gas particles is negligible(very small compared to the volume of the container).
      - Intermolecular forces are also negligible at low pressures.

   ii. **high temperatures(well above its boiling point)**
      - At high temperatures, the gas particles have negligible intermolecular forces between them because they have sufficient energy to overcome it.

2) However, an ideal gas **does not exist**, because:
   i. there are intermolecular forces between the gas particles.
   ii. the volume occupied by the gas particles is not zero.

3) A real gas shows biggest deviation from an ideal gas at:
   i. **high pressures**
      - At high pressures, the gas particles are packed close together, thus the volume occupied by the gas particles is not negligible.
      - The intermolecular forces between them is also not negligible.

ii. **low temperature**

- At low temperatures, the gas particles are packed close together, thus the volume occupied by the gas particles is not negligible.
- The intermolecular forces between them is also not negligible because they do not have sufficient energy to overcome it.

The general gas equation

- The general gas equation gives the relationship between the *volume* of a given mass of gas and the prevailing conditions (*temperature*, *pressure*).

$\boxed{pV = nRT}$ where

p = pressure in Pa (or N m^{-2})
V = volume in m^3
n = no. of moles of gas
R = gas constant (8.31 J K^{-1} mol^{-1})
T = temperature in K

Side note
1) 1 atm = 1.01×10^5 Pa
2) (x) °C = (x + 273) K
3) 1 m^3 = 1000 dm^3
= 1000000 cm^3
4) At s.t.p:
- p = 1.01×10^5 Pa
- T = 273 K

- The general gas equation, $pV = nRT$, can be expressed as

$$pV = \frac{m}{M}RT \quad \left[\text{since } n = \frac{m}{M} \quad \text{where } m = \text{mass in g},\ M = \text{molar mass in g mol}^{-1}\right]$$

$$\Rightarrow \boxed{M = \frac{m}{pV}RT}$$

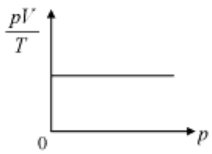
Hence, the general gas equation can be used to determine M_r.

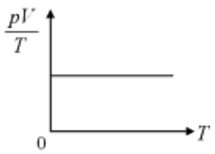
If the density, ρ, of the gas is given, then $\boxed{M = \rho\frac{RT}{p}}$ since $\rho = \frac{m}{V}$.

- An ***ideal gas*** obeys the general gas equation, $pV = nRT$, *exactly*.

For a fixed mass of ideal gas,

➢ $\frac{pV}{T} = nR$ OR $\frac{pV}{T} = \text{constant}$.



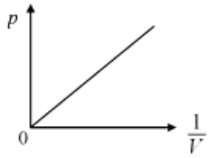


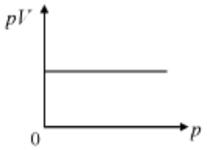
$$\boxed{\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}}$$

➢ At *constant temperature*, $pV = \text{constant}$ OR $V \propto \frac{1}{p}$.

$$\boxed{p_1V_1 = p_2V_2}$$

← Boyle's Law

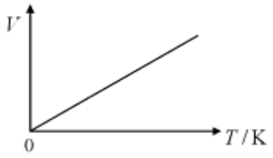


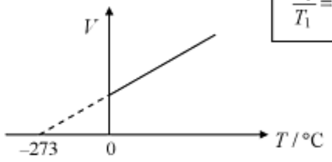


➢ At *constant pressure*, $\frac{V}{T} = \text{constant}$ OR $V \propto T$.

$$\boxed{\frac{V_1}{T_1} = \frac{V_2}{T_2}}$$

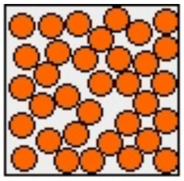
← Charles' Law





5.2 The Liquid State

Kinetic theory of liquids



liquid

1) In liquids, the particles are packed **quite closely** together but in a **fairly random arrangement**(gaps are present between them). So, the particles have limited movements.

2) A liquid has **fixed volume** but do not have fixed shape.

3) Intermolecular forces are present between the particles, its strength is stronger than in the gaseous state but weaker than in the solid state.

Melting and freezing

1) When a solid is heated, the energy is absorbed by the particles and they vibrate about their fixed positions **more vigorously**.

2) Then, a point is reached where the particles have energy high enough to overcome the attractive forces that hold them in fixed positions. They break away from their fixed positions and move freely.

3) The solid then becomes a liquid, this process is called **melting**. The temperature at which this process happens is called the **melting point**.

4) In freezing, the reverse happens. The liquid particles lose energy until they do not have enough energy to move freely. They are held together in fixed positions again. The liquid **solidifies**.

Boiling(vapourisation) and condensation

1) When a liquid is heated, the vapour pressure of the liquid increases until eventually it is **equal** to the atmospheric pressure. Bubbles of vapour will form in the body of liquid.

2) The bubbles then rise to the surface of the liquid, burst open and escape into the atmosphere as a gas. The liquid **boils**.

3) This happens because when a liquid is heated, the particles absorb energy until it is sufficient to overcome the forces of attraction between them. The particles break away from the fairly close arrangement of the liquid and boils.

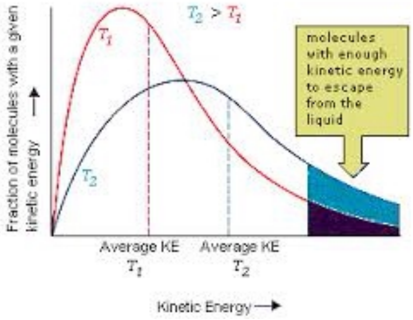
4) This process is called **boiling**. The temperature at which this process happens is called the **boiling point**.
   i. Boiling point depends on external pressure. If a liquid boils under a pressure lower than the atmospheric pressure(1 atm), it will boil faster.
   ii. Conversely, if it boils at a pressure higher than the atmospheric pressure, it will boil slower.

5) In condensation, the reverse happens, the particles lose energy and experience increasing attractive force. They move slower and become closer together when temperature is sufficiently low. The gas **liquefies**.

Evaporation and vapour pressure

1) The energy distribution of particles in the liquid state follows a shape similar to the normal distribution.

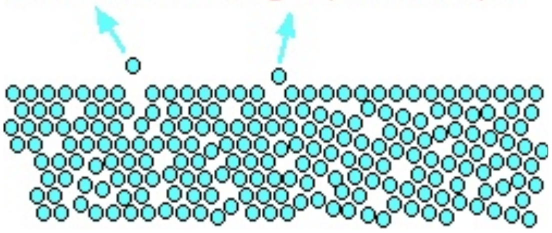
2) The average energy is governed by the temperature. The higher the temperature, the higher the average energy.



3) Some particles have energy higher than the average while some have lower. The more energetic particles at the surface of the liquid can be moving fast enough and eventually overcome the attractive forces and escape into the atmosphere. They **evaporate** to form vapour(Vapour is the gas form of a particle below its boiling point).

4) Unlike boiling, evaporation only takes place on the **surface** of the liquid.

5) In an open container, the liquid will evaporate until none is left.

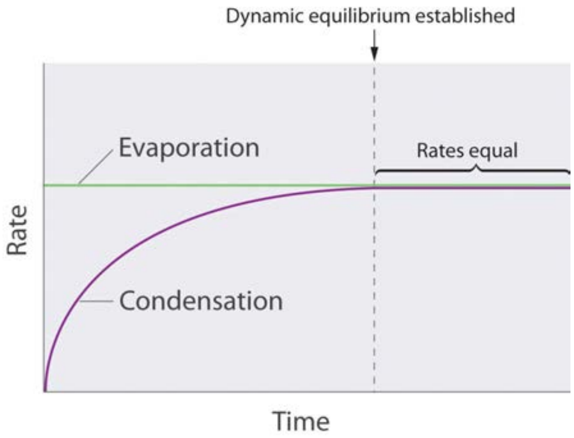


6) However, a different thing happens when the liquid is evaporated in a closed container.

7) At first, liquid particles with higher energy escape from the surface of the liquid to become vapour. The vapour particles will collide with the wall of container. The collisions exert a pressure called **vapour pressure**.

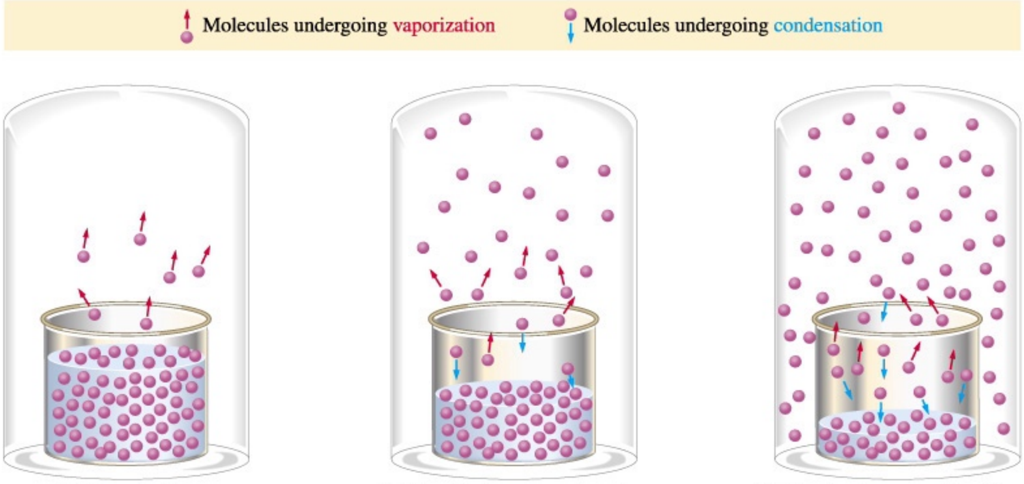
8) As more and more particles escape, the vapour particles become close together. Eventually the particles with lower energy will not be able to overcome the attractive forces between them. The vapour begins to condense and return to liquid.

9) Eventually the vapour particles return to liquid at the **same rate** as the liquid particles evaporate to form vapour. An **equilibrium** is reached. At this equilibrium, the concentration of liquid particles and vapour particles remains constant.



10) In this situation, the vapour pressure is **maximum** and is called the **saturated vapour pressure**.

11) Vapour pressure will increase when temperature is increased. At higher temperature, more liquid can undergo evaporation. The vapour particles are more energetic and collide with the wall of container harder and more frequently. This causes the pressure exerted to be higher.



(a) Vaporization

(b) Vaporization rate > condensation rate

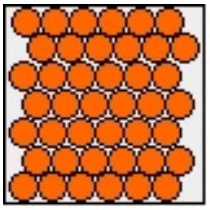
(c) Vaporization rate = condensation rate

5.3 The Solid State

Kinetic theory of solids

1) In solids, very strong forces of attraction hold the particles in **fixed positions** and **close to each other**. Hence, particles in the solid state can only rotate and cannot translate.

2) A solid has **fixed shape and volume**.



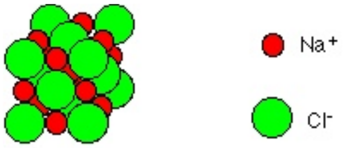
solid

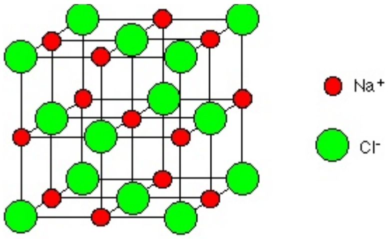
3) The structure of solids can be crystalline or amorphous.
   i. In **crystalline solids**, the particles are arranged in a regular and orderly pattern called a lattice structure.
   ii. In **amorphous solids**, the particles do not have a regular and orderly arrangement. Examples are rubber and plastic.

Ionic lattices

1) An example of ionic lattice is sodium chloride, NaCl, where strong ionic bonds hold the Na^+ and Cl^- ions rigidly in place in the solid lattice.

2) Sodium chloride has a **face-centred cubic structure**. In this structure, each ion is surrounded by **six** other oppositely-charged ions. So, sodium chloride is described as 6:6-co-ordinated.

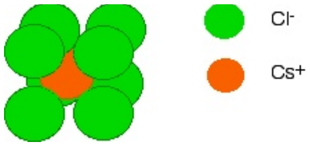


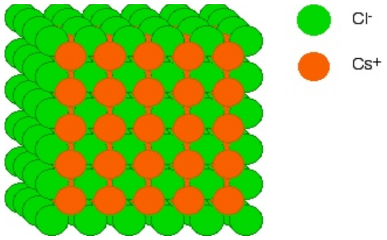


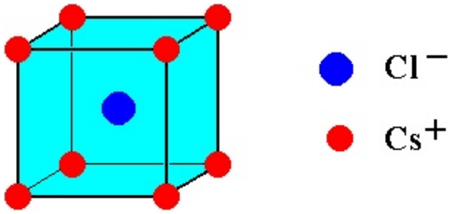
3) Some other examples with face-centred cubic structure are magnesium chloride and magnesium oxide.

4) Another example is caesium chloride, CsCl, which has a **body-centred cubic structure**. In this structure, each ion is surrounded by **eight** other oppositely-charged ions. So, caesium chloride is described as 8:8-co-ordinated.

5) This is just like layers of oppositely-charged ions stacking on each other.







6) Properties of ionic compounds:(For more detailed discussions, see Chapter 4)

i. **They are hard**

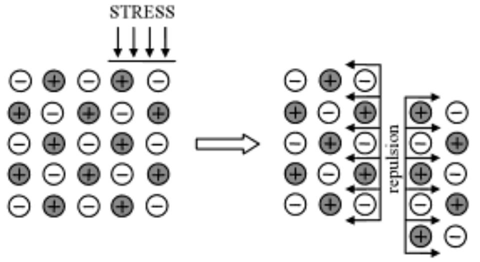
- This is because the ionic bonds within are very strong. A lot of energy is required to split them apart.

ii. **They have high melting and boiling points**

- This is because the ionic bonds within are very strong. A lot of energy is required to break the bonds.

iii. **They are brittle**

- This is because when a stress is applied, the layers of ions may be **displaced** by the force.
- This brings ions with the same charge together and the repulsion between them causes the crystal to split.



Arrangement of one layer of ions before displacement. *Arrangement of ions after displacement.*

iv. **They conduct electricity in the molten or aqueous state**

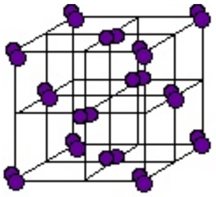
- This is because in the molten or aqueous state, free moving ions are present to carry the current.

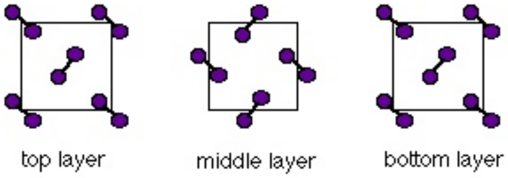
v. **Many of them are soluble in water(polar solvents) but insoluble in non-polar solvents**

- This is because when ion-polar solvent attraction is set up, the energy released is enough to compensate the energy needed to break the ionic bonds.

Simple molecular lattices

1) An example of simple molecular lattice is iodine, I_2. Solid iodine has a face-centred cubic structure.





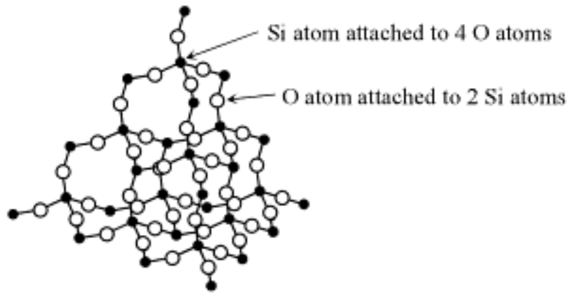
2) Weak van der Waals' forces of attraction hold the individual iodine molecules together.

3) Properties of simple molecular solids:(For more detailed discussions, see Chapter 4)
   i. **They do not conduct electricity in any state**
      - This is because there are no free electrons to carry the current.
   ii. **They have low melting and boiling points**
      - This is because the van der Waals' forces of attraction between them is weak, little energy is required to overcome it.
   iii. **They are soluble in non-polar solvents but insoluble in water(polar solvents)**
      - This is because the molecule-non-polar solvent attraction set up is enough to compensate the energy needed to break the weak van der Waals' forces of attraction between the simple molecules.

Giant covalent lattices

1) In giant covalent structures, **all the atoms are covalently-bonded to each other**, linking the whole structure. An example of giant covalent lattice is silicon(IV) oxide or silicon dioxide, SiO_2.

2) In silicon dioxide, each silicon atom is covalently-bonded to **four** oxygen atoms in a tetrahedral arrangement while each oxygen atom is covalently-bonded to **two** silicon atoms in a V-shaped(bent) arrangement.

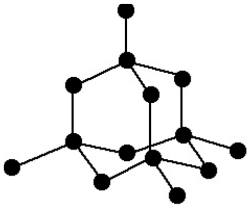


3) Properties of silicon dioxide:
   i. **Very high melting and boiling points**
      - The covalent bonds holding the atoms are very strong, a lot of energy is required to break these strong bonds.
   ii. **Very hard**
      - This is because of the need to break the strong covalent bonds
   iii. **Does not conduct electricity**
      - This is because there are no delocalised electrons to move around and carry the current. All the electrons are held tightly to the atoms.

4) Another two examples are diamond and graphite. Both of them are **allotropes of carbon**.

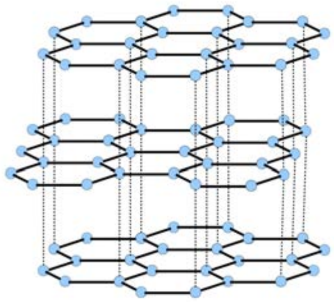
5) *Allotropes* are different crystalline or molecular forms of the same element in the same physical state, having different atomic arrangement.

6) In diamond, all the carbon atoms undergo sp^3 hybridisation and covalently-bonded to **four** other carbon atoms in a tetrahedral arrangement. This network of carbon extends throughout the whole structure.



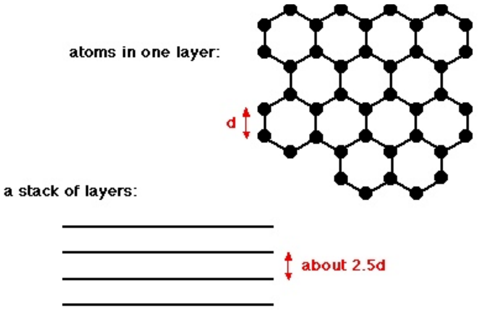
7) The properties of diamond are same as the ones in silicon dioxide.

8) In graphite, the carbon atoms undergo sp^2 hybridisation. Each carbon atom is covalently-bonded to **three** other carbon atoms in a trigonal planar arrangement **within each layer**, forming hexagons.



9) The unhybridised p orbital in each planar layers overlap sideways **to form a giant molecular orbital above and below each layer**. The electrons are then **delocalised**, free to move between the layers of carbon. However, the electrons cannot move from one layer to another.

10) The distance between carbon atoms between the layers is **greater** than the distance between carbon atoms in each layer.



11) Properties of graphite:
   i. **Very high melting and boiling points**
      - This is because the covalent bonds holding the carbon atoms with each layer is very strong, a lot of energy is required to overcome the strong forces of attraction.
      - In fact, it has a higher melting point than diamond because of the additional attraction between the delocalised electrons and the nucleus. Dispersion forces are also present, this is because the delocalised electrons can set up a temporary dipole easily.
   ii. **Soft and slippery**
      - Layers of carbons can slide over easily, this is because the intermolecular forces between the layers are very weak.

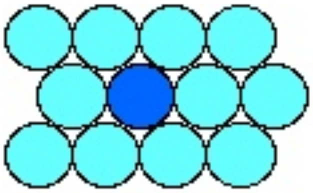
- Because of this, graphite is often used as pencil 'leads' and lubricants.

iii. **Conducts electricity**

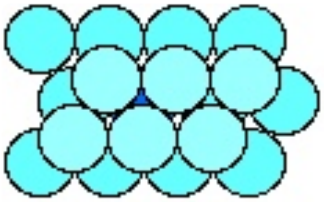
- It can conduct electricity in the direction parallel to each layer but not perpendicular to it.
- This is because the delocalised electrons are free to move between the layers but not from one layer to another.

Metallic lattices

1) An example of metallic lattice is copper, Cu. In copper, each copper atom is surrounded by **twelve** other copper atoms. Therefore, copper is a 12-co-ordinated metal.



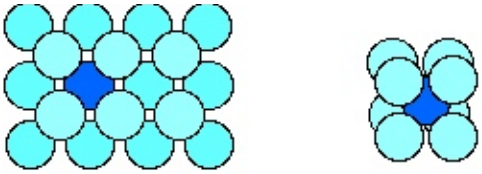
Six copper atoms surround it in a layer



Three other copper atoms surround it up and down.

3) The copper atoms are bonded to each other through strong metallic bonding. (For more information about metallic bonding, refer Chapter 4)

4) Another example is sodium. In sodium, each sodium atom is surrounded by **eight** other sodium atoms only. Therefore, sodium is a 8-co-ordinated metal.



In the first diagram, no atoms are touching each other in a layer.

5) Properties of metals:

i. **High melting and boiling points**

- This is because the metallic bonds are very strong, a lot of energy is required to break these strong bonds.

ii. **Conducts heat and electricity**

- This is because delocalised electrons are present and free to move.

iii. **Ductile and malleable**

- Metals are **ductile(can be pulled into wires)** and **malleable(can be hammered into different shapes)**. This is because the layers of metals can slide over each other, the broken metallic bonds can be immediately replaced by the new ones.

5.4 Ceramics

Ceramics

1) A *ceramic* is an inorganic non-metallic solid which is prepared by heating a substance or mixture of substances to a high temperature.

2) Ceramics often contain silicon dioxide, magnesium oxide and aluminium oxide. This gives ceramics their giant covalent or ionic structures.

3) Properties of ceramics:
   i. **Very high melting and boiling points**
      - This is because most ceramics contain giant covalent or ionic structures. The covalent or ionic bonds holding them together is very strong, a lot of energy is required to overcome it.
   ii. **Does not conduct electricity or heat**
      - This is because there are no delocalised electrons or free moving ions present. Therefore most of them are electrical insulators.
   iii. **Chemically unreactive**
      - This is because all the electrons are held firmly in strong covalent bonds and not available for a reaction.
   iv. **Very hard**
      - This is because the ionic or covalent bonds holding them is very strong.

Uses of ceramics

1) Ceramics containing **magnesium oxide** are used:
   - as electrical insulators in industrial electrical cables.
   - as a refractory in furnace linings because it has a high melting point.
   - in fire-resistant wall boards.

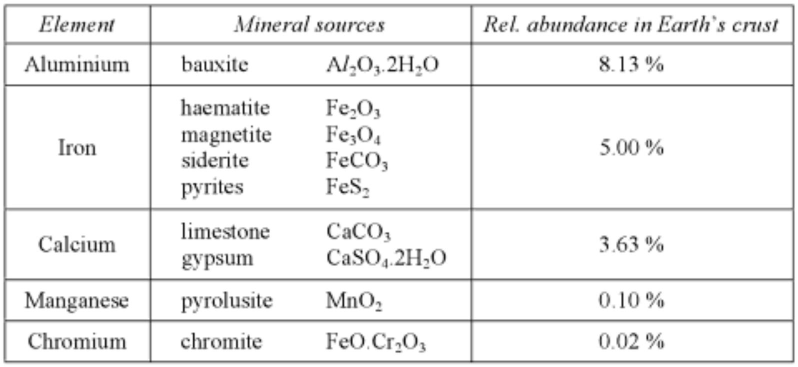
2) Ceramics containing **aluminium oxide** are used:
   - as a refractory in furnace linings because it has a high melting point.
   - as an abrasive for grinding hard materials because they do not conduct heat or melt when heat is given off during grinding.
   - in transparent aluminium oxide-scandium windows.
   - in high temperature and high voltage electrical insulators.
   - in the replacement of artificial hip joints.

3) Ceramics containing **silicon dioxide** are used:
   - as a refractory in furnace linings because it has a high melting point.
   - as a abrasive, for example in sandpaper.
   - in the manufacture of glass.

5.5 Conserving Materials

Why conserve materials?

1) There is only a limited supply of metal ores in the Earth. Therefore metals are **finite resources**. They do not get replaced once they are used up.



Element	*Mineral sources*		*Rel. abundance in Earth's crust*
Aluminium	bauxite	$Al_2O_3.2H_2O$	8.13 %
Iron	haematite magnetite siderite pyrites	Fe_2O_3 Fe_3O_4 $FeCO_3$ FeS_2	5.00 %
Calcium	limestone gypsum	$CaCO_3$ $CaSO_4.2H_2O$	3.63 %
Manganese	pyrolusite	MnO_2	0.10 %
Chromium	chromite	$FeO.Cr_2O_3$	0.02 %

Ways to conserve materials

1) One way to conserve materials is through **recycling**.

2) Advantages of recycling:
   i. Recycling saves new resources.
   ii. Recycling reduces the amount of waste materials to be disposed off.
   iii. Recycling saves energy because less energy is needed to recycle metals than to extract it from their ores.
   iv. Recycling protects the environment because it reduces pollution associated with product manufacture, disposal and littering. For example, the process of extracting metals produces gases which can lead to acid rain.

3) Two metals that can be recycled easily are copper and aluminium. Glass can also be recycled easily.

4) Another way to conserve materials is **using renewable resources**. Examples are like water, wood, sunlight, wind and etcetera.

CHAPTER 6: Chemical Energetics

Learning outcomes:

(a) *explain that some chemical reactions are accompanied by energy changes, principally in the form of heat energy; the energy changes can be exothermic (ΔH, negative) or endothermic.*
(b) *explain and use the terms:*
  (i) *enthalpy change of reaction and standard conditions, with particular reference to: formation, combustion, hydration, solution, neutralisation, atomisation.*
  (ii) *bond energy (ΔH positive, i.e. bond breaking).*
(c) *calculate enthalpy changes from appropriate experimental results, including the use of the relationship enthalpy change, $\Delta H = -mc\Delta T$.*
(d) *apply Hess' Law to construct simple energy cycles, and carry out calculations involving such cycles and relevant energy terms, with particular reference to:*
  (i) *determining enthalpy changes that cannot be found by direct experiment, e.g. an enthalpy change of formation from enthalpy changes of combustion.*
  (ii) *average bond energies.*
(e) *construct and interpret a reaction pathway diagram, in terms of the enthalpy change of the reaction and of the activation energy.*

6.1 Enthalpy Changes

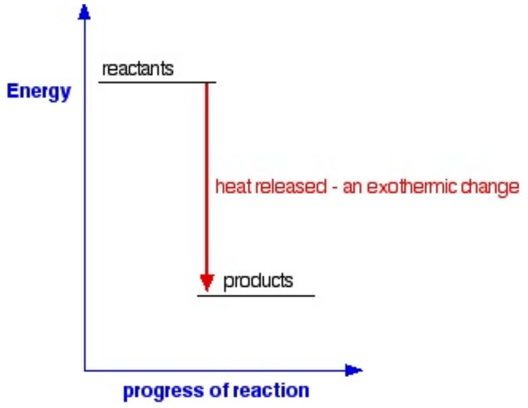
Exothermic and endothermic reactions

1) Most chemical reactions are accompanied by energy changes. Some absorbs energy while some releases it.

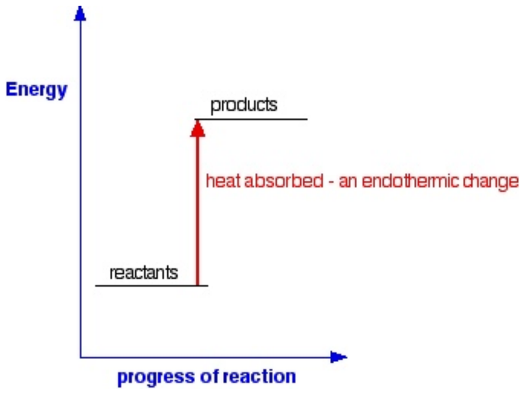
2) An *exothermic reaction* is a reaction that **releases energy** to the surroundings. Therefore the product contain **less** energy with respect to the reactants. The energy is released as heat energy, so the surroundings **warm up**.

3) An *endothermic reaction* is a reaction that **absorbs energy** from the surroundings. Therefore the products contain **more** energy with respect to the reactants. The energy is absorbed as heat energy, so the surroundings **cool down**.

4) An energy level diagram shows the relative energies of the products and reactants. The higher its energy, the higher its position.



An exothermic reaction



An endothermic reaction

5) i. Examples of exothermic reactions are neutralisation, combustion, dissolving anhydrous salts and the reaction between acids and metal carbonates.
   ii. Examples of endothermic reactions are atomisation, photosynthesis, dissolving crystalline salts and thermal decomposition.

Enthalpy changes

1) *Enthalpy*, H is an indication of the total energy of a substance and it cannot be measured directly. However, enthalpy change, ΔH is measurable.

2) *Enthalpy change of a reaction*, ΔH is the heat change(heat is absorbed or evolved) when a chemical reaction takes place.

3) i. In exothermic reactions, the enthalpy change is **always negative**.($\Delta H < 0$)
   ii. In endothermic reactions, the enthalpy change is **always positive**.($\Delta H > 0$)

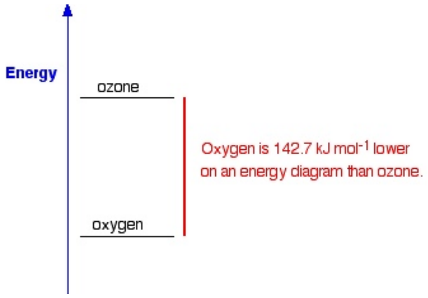
Energetic stability of a system

1) Exothermic reactions are more energetically favourable than endothermic ones because a system with lower energy content is more stable.

2) Thus, the more negative the ΔH value, the more stable the system is.

3) For example, oxygen,O_2 is energetically more stable than ozone, O_3. Their relative positions on the energy level diagram are as follow:

4) But ozone does not convert to oxygen immediately in atmosphere, this is because ozone is **kinetically stable** although it is energetically unstable with respect to the products. The activation energy is not sufficient for the reaction to take place.



Oxygen is 142.7 kJ mol^{-1} lower on an energy diagram than ozone.

Measuring enthalpy changes

1) Enthalpy changes can be measured experimentally by measuring the temperature change as a reaction proceeds. Two common examples are measuring the enthalpy change of neutralisation and combustion.

2) The formulae:

$$\boxed{\text{Heat energy absorbed or released} = mc\Delta T}$$

where m = mass of substance(or solution)/g
c = specific heat capacity of solution/J g^{-1} °C^{-1}
(c is normally assumed to be 4.18 J g^{-1} °C^{-1})
ΔT = change in temperature/°C

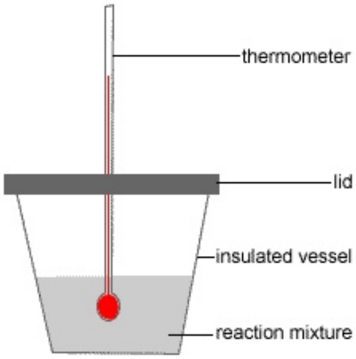
$$\boxed{\Delta H = \frac{\text{heat energy absorbed or released}}{\text{no. of moles of the limiting reagent}}}$$

Unit = kJ mol^{-1}

3) Assumptions made in this calculation:
- The density of all aqueous solution is 1 g cm^{-3}. Thus, numerically, 1 cm^3 = 1 g.
- The solution has the same specific heat capacity as water(4.18 J g^{-1} °C^{-1}).

4) An example - to calculate the enthalpy change of the reaction between sodium hydroxide, NaOH(aq) and hydrochloric acid, HCl(aq).

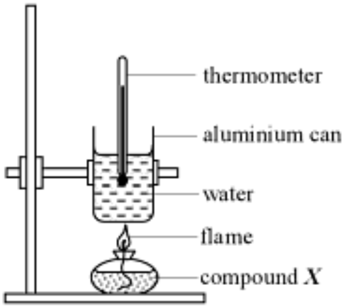
$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$



i. Pour 25 cm^3 of NaOH into 25 cm^3 of HCl in a polystyrene cup(polystyrene cup is used because it is a good heat insulator). Both solutions have concentrations of 1.0 mol dm^{-3}.
ii. Measure the initial and maximum temperature reached.
iii. For example, the mean initial temperature of both solutions is 18.1 °C and the maximum temperature reached is 24.8 °C. Then, ΔT = 6.7 °C.
iv. Mass of both solutions is (25+25) **x** 1 = 50 g since density = mass/volume.
v. Therefore heat released = 50 **x** 4.18 **x** 6.7 = 1400 J = 1.4 kJ
vi. Number of moles of water = 0.025 mol
vii. Therefore ΔH = -(1.4/0.025) = -56 kJ mol^{-1}

5) Another example - to calculate the enthalpy change of the reaction of combustion of ethanol, C_2H_5OH.

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(g)$



i. In this experiment, a spirit burner is used to combust the flammable liquid ethanol. The heat evolved is used to heat up the water, the maximum temperature reached is then measured.
ii. Mass of water = 250 g
Initial temperature of water = 19.5 °C
Maximum temperature of water = 23.7 °C
Initial mass of ethanol = 41.36 g
Final mass of ethanol = 41.18 g
iii. Therefore, ΔT = 4.2 °C and m = 250 g.
iv. Heat released = 250 **x** 4.18 **x** 4.2 = 4389 J = 4.389 kJ
v. Number of moles of ethanol burned = 0.18/46 = 0.0039 mol
vi. Therefore ΔH = -(4.389/0.0039) = -1100 kJ mol^{-1} (2 s.f)

6.2 Standard Enthalpy Changes

The standard condition

1) To make comparison of enthalpy changes a fair comparison, same conditions must be used. These are called the **standard conditions**:
   - A pressure of **100 kPa**(approximately atmospheric pressure).
   - A temperature of **298 K or 25 °C**.
   - Where solutions are involved, a concentration of **1.0 mol dm^{-3}**.
   - Every substance involved must be in its **normal physical state** at 100 kPa and 298 K. For example, water is in liquid, not ice or steam.
   - If allotropes are involved, the allotrope which is more energetically stable is used. For example, for carbon, graphite is chosen over diamond because graphite is energetically more stable than diamond.

2) Standard enthalpy changes can be represented by the symbol $\Delta H°$. This refers that the reaction is carried out under standard conditions. For example:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad ; \quad \Delta H° = -890.3 \text{ kJ mol}^{-1}$$

Various enthalpy changes

1) Enthalpy changes are described according to the type of reaction. Examples:
   - standard enthalpy change of reaction, $\Delta H°_r$ (in general)
   - standard enthalpy change of formation, $\Delta H°_f$
   - standard enthalpy change of combustion, $\Delta H°_c$
   - standard enthalpy change of neutralisation, $\Delta H°_n$
   - standard enthalpy change of atomisation, $\Delta H°_{at}$
   - standard enthalpy change of solution, $\Delta H°_{sol}$
   - standard enthalpy change of hydration, $\Delta H°_{hyd}$

Standard enthalpy change of reaction, $\Delta H°_r$

1) *Standard enthalpy change of reaction,* $\Delta H°_r$ is the enthalpy change when the amount of reactants shown in the equation react to give products under standard condition. The reactants and products must be in their standard states.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \quad ; \quad \Delta H°_r = -576 \text{ kJ mol}^{-1}$$

2) The equation shows that 576 kJ of energy is released when two moles of hydrogen react with one mole of oxygen to give two moles of water.

3) This is a theoretical reaction, it does not happen in practice. The enthalpy change can be found by applying Hess' law.

Standard enthalpy change of formation, ΔH°_f

1) *Standard enthalpy change of formation,* ΔH°_f is the enthalpy change when one mole of a compound is formed from its elements under standard condition. The reactants and products must be in their standard states.

$$2Fe(s) + 1\tfrac{1}{2}O_2(g) \rightarrow Fe_2O_3(s) \quad ; \quad \Delta H^\circ_f\,[\,Fe_2O_3(s)\,] = -824.5 \text{ kJ mol}^{-1}$$

2) By definition, the standard enthalpy change of formation of an element is zero.

3) The standard enthalpy change of formation can be exothermic or endothermic.

Standard enthalpy change of combustion, ΔH°_c

1) *Standard enthalpy change of combustion,* ΔH°_c is the enthalpy change when one mole of a substance is burnt in excess oxygen under standard conditions. The reactants and products must be in their standard states.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \quad ; \quad \Delta H^\circ_c\,[\,CH_4(g)\,] = -890.3 \text{ kJ mol}^{-1}$$

2) The standard enthalpy change of combustion is always exothermic.

Standard enthalpy change of neutralisation, ΔH°_n

1) *Standard enthalpy change of neutralisation,* ΔH°_n is the enthalpy change when one mole of water is formed by the reaction of an acid with an alkali under standard conditions.

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l) \quad ; \quad \Delta H^\circ_n = -57.1 \text{ kJ mol}^{-1}$$

2) For any acid-alkali reaction, the ionic equation is:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

3) The enthalpy change of neutralisation between strong acids and strong bases is a constant(-57.1 kJ mol^{-1}). This is because all strong acids and strong bases dissociate completely in water to form aqueous ions.

4) So, neutralisation between strong acids and strong bases involves the same reaction, that is, H^+ reacts with OH^- to form H_2O. The other ions present are just simply spectator ions. They do not take part in the reaction. Hence, the heat released is the same.

5) However, the enthalpy change of neutralisation between sulfuric acid and sodium hydroxide is more exothermic(-66.8 kJ mol^{-1}) than expected. This is because the enthalpy change of dilution of sufuric acid is significant. When sulfuric acid is added to sodium hydroxide, the acid is diluted in the process and heat is released.

6) The enthalpy change of neutralisation involving weak acids or weak bases is less than 57.1 kJ mol^{-1}. For example:

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l) \quad ; \quad \Delta H^\circ_n = -56.1 \text{ kJ mol}^{-1}$$

$$NaOH(aq) + HCN(aq) \rightarrow NaCN(aq) + H_2O(l) \quad ; \quad \Delta H^\circ_n = -11.7 \text{ kJ mol}^{-1}$$

7) This is because weak acids and weak bases only partially dissociated in water. For example:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq) \quad ; \quad \Delta H^\circ = \text{positive}$$

8) On addition of strong base such as NaOH, the OH^- ions react with H^+ from the dissociation of CH_3COOH. The removal of H^+ ions causes the position of equilibrium to shift to the right and more CH_3COOH molecules dissociate. However the dissociation of CH_3COOH is an endothermic process, hence, some energy is absorbed and the enthalpy change overall is less negative.

9) The standard enthalpy change of neutralisation is always exothermic.

Standard enthalpy change of atomisation, ΔH°_{at}

1) *Standard enthalpy change of atomisation,* ΔH°_{at} is the enthalpy change when one mole of gases atoms is formed from its element under standard conditions.

$$\tfrac{1}{2}H_2(g) \rightarrow H(g) \quad ; \quad \Delta H^\circ_{at}\,[\,\tfrac{1}{2}H_2\,] = +218 \text{ kJ mol}^{-1}$$

$$Na(s) \rightarrow Na(g) \quad ; \quad \Delta H^\circ_{at}\,[\,Na\,] = +107 \text{ kJ mol}^{-1}$$

2) By definition, the standard enthalpy change of atomisation of the noble gases is zero because all of them exist as monoatomic gases at standard conditions.

3) The standard enthalpy change of atomisation of diatomic gases(example: O_2, Cl_2, N_2 and F_2) is equal to half the value of their bond energies.

4) The standard enthalpy change of atomisation is always endothermic.

Standard enthalpy change of solution, $\Delta H°_{sol}$

1) *Standard enthalpy change of solution,* $\Delta H°_{sol}$ is the enthalpy change when one mole of solute is dissolved in a solvent to form an infinitely dilute solution under standard conditions.

$$NaCl(s) + aq \rightarrow NaCl(aq) \quad ; \quad \Delta H°_{sol} = +6.0 \text{ kJ mol}^{-1}$$
$$NaOH(s) + aq \rightarrow NaOH(aq) \quad ; \quad \Delta H°_{sol} = -44.5 \text{ kJ mol}^{-1}$$

2) An infinitely dilute solution is one which does not produce any further enthalpy change when more solvent is added.

3) The standard enthalpy change of solution can be exothermic or endothermic.

Standard enthalpy change of hydration, $\Delta H°_{hyd}$

1) *Standard enthalpy change of hydration,* $\Delta H°_{hyd}$ is the enthalpy change when one mole of gases ions dissolves in water to form hydrated ions of infinite dilution under standard conditions.

$$Ca^{2+}(g) + aq \rightarrow Ca^{2+}(aq) \quad ; \quad \Delta H°_{hyd} = -1650 \text{ kJ mol}^{-1}$$

2) Water is a polar molecule, this means that it has a negative end and a positive end. The negative end of the water molecule will be attracted to the cations while the positive end of the water molecule will be attracted to the anions.

3) The attraction set up is called the ion-dipole forces.

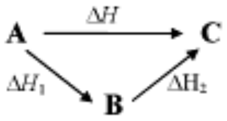
4) The standard enthalpy change of hydration is always exothermic.

6.3 Hess' Law

Hess' law and Hess' cycle

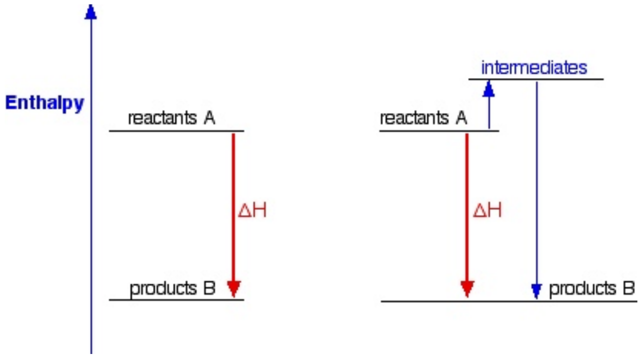
1) *Hess' law* states that the total enthalpy change in a chemical reaction is independent of the route which the reaction takes place as long as the initial and final conditions are the same.

2) For example, the enthalpy change of reaction from **A** to **C** is the same whether the reaction takes place in one stage(**A** to **C**) or two stages(**A** to **B** then to **C**).



By Hess' Law, $\Delta H = \Delta H_1 + \Delta H_2$

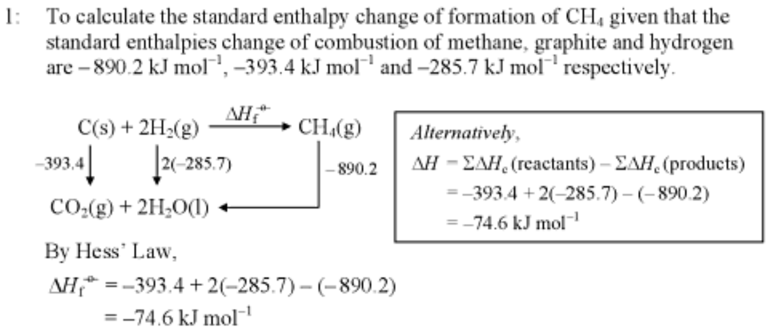
3) This is because the enthalpy change of a chemical reaction depends only on the difference between enthalpy of the products and the reactants. It does not depend on how the reaction took place.



4) Hess' law is useful to calculate enthalpy changes that cannot be measured directly from experiments(theoretical reactions that will not occur under standard conditions).

5) Steps to construct a Hess' cycle:
   i. Write down the equation for the enthalpy change that you are asked to find and write ΔH on top of the arrow.
   ii. Use the information that you have been given to complete a cycle.
   iii. Find the direct route and indirect route. The routes should not go against any arrows. (Equations may be reversed when necessary, but do not forget to reverse the sign as well.)
   iv. Apply Hess' law and form an equation to solve for ΔH.

6) Examples:



1: To calculate the standard enthalpy change of formation of CH_4 given that the standard enthalpies change of combustion of methane, graphite and hydrogen are $-890.2\ kJ\ mol^{-1}$, $-393.4\ kJ\ mol^{-1}$ and $-285.7\ kJ\ mol^{-1}$ respectively.

$$\begin{tikzcd} C(s) + 2H_2(g) \arrow[r, "\Delta H_f^{\circ}"] \arrow[d, "-393.4"', "2(-285.7)"] & CH_4(g) \arrow[dl, "-890.2"] \\ CO_2(g) + 2H_2O(l) & \end{tikzcd}$$

Alternatively,

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

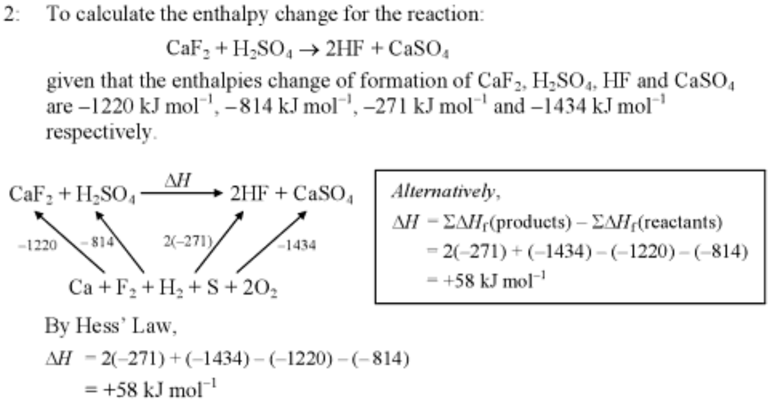
$= -393.4 + 2(-285.7) - (-890.2)$

$= -74.6\ kJ\ mol^{-1}$

By Hess' Law,

$\Delta H_f^{\circ} = -393.4 + 2(-285.7) - (-890.2)$

$= -74.6\ kJ\ mol^{-1}$



2: To calculate the enthalpy change for the reaction:

$$CaF_2 + H_2SO_4 \rightarrow 2HF + CaSO_4$$

given that the enthalpies change of formation of CaF_2, H_2SO_4, HF and $CaSO_4$ are $-1220\ kJ\ mol^{-1}$, $-814\ kJ\ mol^{-1}$, $-271\ kJ\ mol^{-1}$ and $-1434\ kJ\ mol^{-1}$ respectively.

$$\begin{tikzcd} CaF_2 + H_2SO_4 \arrow[r, "\Delta H"] & 2HF + CaSO_4 \\ Ca + F_2 + H_2 + S + 2O_2 \arrow[u, "-1220", "-814"'] \arrow[ur, "2(-271)", "-1434"'] & \end{tikzcd}$$

Alternatively,

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

$= 2(-271) + (-1434) - (-1220) - (-814)$

$= +58\ kJ\ mol^{-1}$

By Hess' Law,

$\Delta H = 2(-271) + (-1434) - (-1220) - (-814)$

$= +58\ kJ\ mol^{-1}$

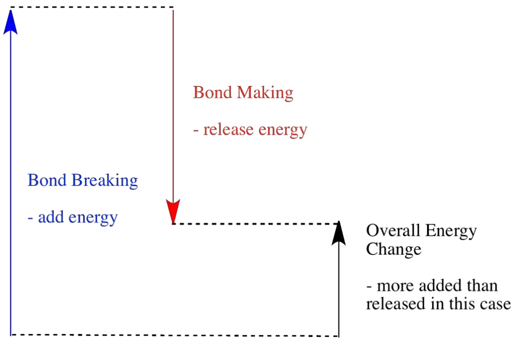
6.4 Bond Energy

Bond breaking and bond forming

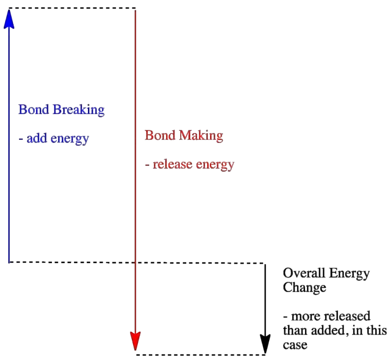
1) i. Breaking bonds needs energy, energy is absorbed from the surroundings. Therefore, bond breaking is an endothermic process.
   ii. Forming bonds releases energy to the surroundings. Therefore, bond forming is an exothermic process.

2) i. If the energy needed to break bonds is **less than** the energy released when new bonds are formed, then the reaction will be exothermic
   ii. If the energy needed to break bonds is **more than** the energy released when new bonds are formed, then the reaction will be endothermic.

3) In most chemical reactions, bonds have to be broken first and then reformed into a new compound.



An endothermic reaction



An exothermic reaction

Bond energy

1) *Bond energy, E* is the energy needed to break one mole of covalent bonds between two atoms in the gaseous state.

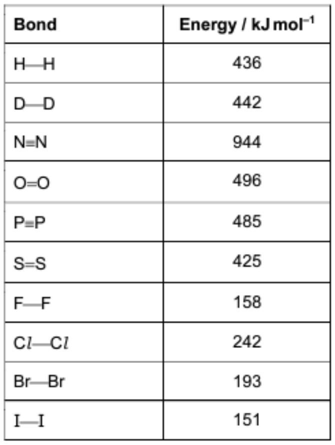
$$Br\text{-}Br(g) \rightarrow 2Br(g) \quad ; \quad E(Br\text{-}Br) = +193 \text{ kJ mol}^{-1}$$

2) Bond energy is often called bond enthalpy or bond dissociation energy.

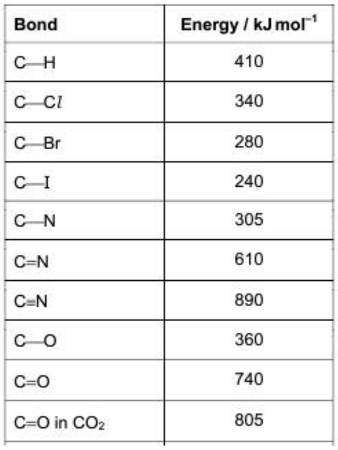
Average bond energy

1) Bond energy is often affected by the presence of other atoms in the molecule. For example, the O-H bond in water has a different bond energy value than the O-H bond in ethanol. Even in the same molecule, for example, CH_4, the energy needed to break all the C-H bonds are not identical.

2) Therefore, bond energies are taken from a number of bonds of the same type from different environment and average out to get the **average bond energy**. The values are not always accurate.



Bond	Energy / kJ mol^{-1}
H—H	436
D—D	442
N≡N	944
O=O	496
P≡P	485
S=S	425
F—F	158
C*l*—C*l*	242
Br—Br	193
I—I	151

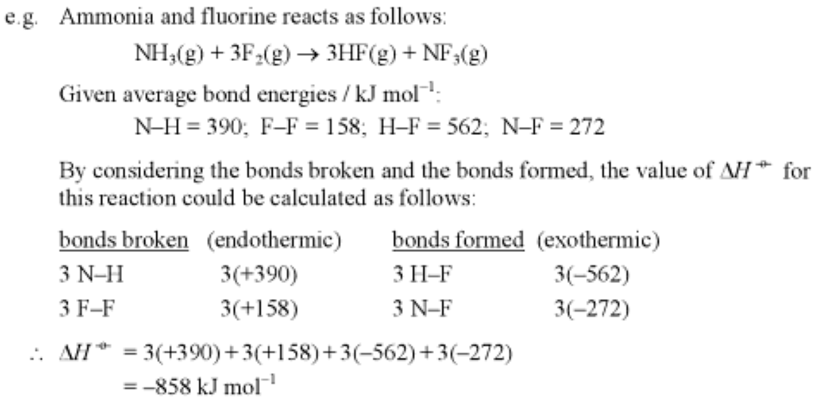


Bond	Energy / kJ mol^{-1}
C—H	410
C—C*l*	340
C—Br	280
C—I	240
C—N	305
C=N	610
C≡N	890
C—O	360
C=O	740
C=O in CO_2	805

Hess' law involving average bond energy

1) Average bond energies can also be used to estimate enthalpy changes of reactions involving covalent molecules

2) Example:



e.g. Ammonia and fluorine reacts as follows:

$$NH_3(g) + 3F_2(g) \rightarrow 3HF(g) + NF_3(g)$$

Given average bond energies / kJ mol^{-1}:

N–H = 390; F–F = 158; H–F = 562; N–F = 272

By considering the bonds broken and the bonds formed, the value of $\Delta H^{\ominus}$ for this reaction could be calculated as follows:

bonds broken	(endothermic)	bonds formed	(exothermic)
3 N–H	3(+390)	3 H–F	3(–562)
3 F–F	3(+158)	3 N–F	3(–272)

$$\therefore \Delta H^{\ominus} = 3(+390) + 3(+158) + 3(-562) + 3(-272)$$
$$= -858 \text{ kJ mol}^{-1}$$

3) If the given reactants or products are not in the gaseous state, **enthalpy change of vaporisation** or **enthalpy change of fusion** must be considered because the non-gaseous compounds needed to be converted to the gaseous state. Changing from other states to the gaseous state needs to absorb extra energy.

CHAPTER 7: Redox Reactions and Electrolysis

7.1 Oxidation and Reduction
7.2 Electrolysis

Learning outcomes:

- *(a) (i) calculate oxidation numbers of elements in compounds and ions.*
  - *(ii) describe and explain redox processes in terms of electron transfer and/or changes in oxidation number (oxidation state).*
  - *(iii) use changes in oxidation numbers to help balance chemical equations.*
- *(b) explain, including the electrode reactions, the industrial processes of:*
  - *(i) the electrolysis of brine, using a diaphragm cell.*
  - *(ii) the extraction of aluminium from molten aluminium oxide/cryolite.*
  - *(iii) the electrolytic purification of copper.*

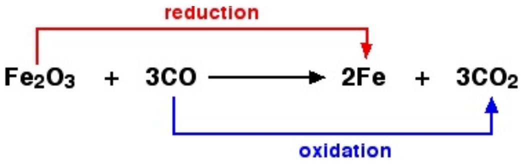
7.1 Oxidation and Reduction

Redox reactions

1) *Oxidation* is:
   - i. gain of oxygen
   - ii. loss of hydrogen
   - iii. loss of electrons
   - iv. increase in oxidation number

2) *Reduction* is:
   - i. gain of hydrogen
   - ii. loss of oxygen
   - iii. gain of electrons
   - iv. decrease in oxidation number

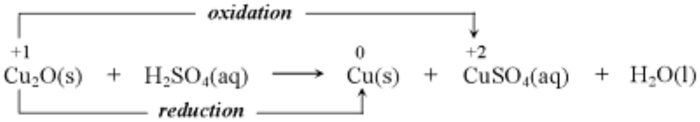
3) Oxidation and reduction always occur simultaneously in a chemical reaction. Such reaction is called a **redox reaction**. In a redox reaction, one substance must be oxidised and another must be reduced.



4) i. An *oxidising agent* is a substance which oxidises another substance and **itself is reduced**.
   ii. A *reducing agent* is a substance which reduces another substance and **itself is oxidised**.

5) In short, an oxidising agent undergoes reduction while a reducing agent undergoes oxidation.

6) **Disproportionation** is a redox reaction in which both oxidation and reduction occurs on the same atom. The atom is simultaneously oxidised and reduced.



Oxidation state (oxidation number) of a substance

1) Oxidation state shows that total number of electrons which have been removed from or added to **an element** to get to its present state.

2) i. When electrons have been removed, the oxidation number increases.(positive)
   ii. When electrons have been added, the oxidation number decreases.(negative)

3) i. Since removing electrons is an oxidation process, therefore oxidation is the increase in oxidation number
   ii. Since adding electrons is a reduction process, therefore reduction is the decrease in oxidation number.

3) For example, from V to V^{2+}, two electrons have been removed, therefore the oxidation state of is +2. From V to V^{3+}, three electrons have been removed, therefore the oxidation state is +3. Removing another electron gives:

$$V^{3+} + H_2O \rightarrow VO^{2+} + 2H^+ + e^-$$

Four electrons have been removed starting from V, therefore the oxidation state is +4. In all cases, V has been oxidised.

4) Another example, from S to S^{2-}, two electrons have been added, therefore the oxidation state is -2. S is said to have been reduced.

Rules to determine oxidation numbers of a substance

1) All atoms in an atom, molecule or ion can be given an oxidation number.

2) The rules to determine the oxidation number of a substance:
   i. All **free atoms** in elements have an oxidation number of **zero**.
   e.g.

$$\overset{0}{\mathrm{Mg}} \quad \overset{0}{\mathrm{Fe}} \quad \overset{0}{\mathrm{O_2}} \quad \overset{0}{\mathrm{H_2}} \quad \overset{0}{\mathrm{P_4}} \quad \overset{0}{\mathrm{Cl_2}}$$

   ii. For **simple ions**, the oxidation number is the same as the **charge** on the ion.
   e.g.

$$\overset{+1}{\mathrm{Na^+}} \quad \overset{+3}{\mathrm{Al^{3+}}} \quad \overset{+2}{\mathrm{Mg^{2+}}} \quad \overset{-2}{\mathrm{O^{2-}}} \quad \overset{-2}{\mathrm{S^{2-}}} \quad \overset{-1}{\mathrm{Cl^-}}$$

   iii. For **polyatomic ion**, the **sum** of all the oxidation numbers of the atoms in the ion is equal to the **charge** of the ion.

e.g. MnO_4^- : $\therefore\ 1(+7) + 4(-2) = -1$

$Cr_2O_7^{2-}$: $\therefore\ 2(+6) + 7(-2) = -2$

NO_2^+ : $\therefore\ 1(+5) + 2(-2) = +1$

iv. For a **neutral covalent molecule**, the sum of all the oxidation numbers of the atoms in the molecule is equal to **zero**.

e.g. $\overset{+1\ -2}{H_2O}$ $\overset{+6\ -2}{SO_3}$ $\overset{+1\ -1}{HCl}$

Also, the more electronegative atom is always given a negative oxidation number while the less electronegative atom is given a positive one.

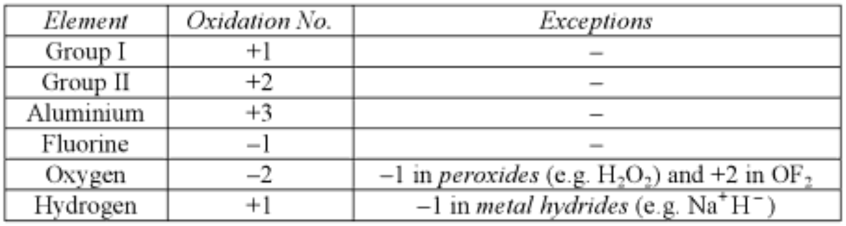
v. For **Group I and Group II elements**, their oxidation number are always +1 and +2 respectively. For aluminium, it is always +3.

vi. For **hydrogen**, its oxidation number is always +1 except in metal hydrides. For example, NaH, where its oxidation number is -1.

vii. For **oxygen**, its oxidation number is always -2 except in peroxides and fluorine compounds. For example, BaO_2, where its oxidation number is -1.

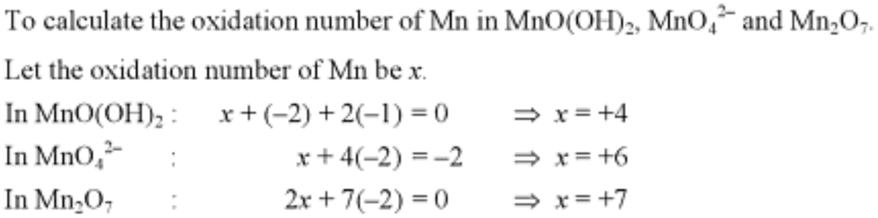
viii. For **fluorine**, its oxidation number is always -1, with no exceptions.

3) A summary:



Element	*Oxidation No.*	*Exceptions*
Group I	+1	–
Group II	+2	–
Aluminium	+3	–
Fluorine	–1	–
Oxygen	–2	–1 in *peroxides* (e.g. H_2O_2) and +2 in OF_2
Hydrogen	+1	–1 in *metal hydrides* (e.g. Na^+H^-)

4) To work out the oxidation number of a particular atom in a molecule/ ion, find the sum of all the oxidation number of the atoms present and equate it to zero/ charge of the ion. An example:



To calculate the oxidation number of Mn in $MnO(OH)_2$, MnO_4^{2-} and Mn_2O_7.

Let the oxidation number of Mn be x.

In $MnO(OH)_2$: $x + (-2) + 2(-1) = 0 \Rightarrow x = +4$

In MnO_4^{2-} : $x + 4(-2) = -2 \Rightarrow x = +6$

In Mn_2O_7 : $2x + 7(-2) = 0 \Rightarrow x = +7$

Balancing redox equations

1) There are two methods to balance complicated redox equations:
   i. Using electron half-equations.
   ii. Using changes in oxidation number.

2) **Using electron half-equations**:
   i. In this method, the redox equation is divided into two half-equations. One for oxidation and another for reduction.
   ii. Steps**(in acidic condition)**:
      - Divide the equation or information given into two half-equations.
      - Balance all other elements other than oxygen and hydrogen.
      - Balance the oxygen by adding H_2O to the appropriate side of the equation.
      - Balance the hydrogen by adding H^+ to the appropriate side of the equation.
      - Balance the charge by adding electrons to the appropriate side of the equation.
      - Combine two half-equations such that the electrons cancel out each other.
   iii. An example:

Q: Balance and complete this equation:

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

A: 1) Divide into two equations:

$Cr_2O_7^{2-} \rightarrow Cr^{3+}$..........reduction
$Fe^{2+} \rightarrow Fe^{3+}$................oxidation

2) Balance the atoms:

$Cr_2O_7^{2-} \rightarrow \mathbf{2}Cr^{3+}$
$Fe^{2+} \rightarrow Fe^{3+}$

3) Balance the oxygen:

$Cr_2O_7^{2-} \rightarrow 2Cr^{3+} \mathbf{+ 7H_2O}$
$Fe^{2+} \rightarrow Fe^{3+}$

4) Balance the hydrogen:

$Cr_2O_7^{2-} \mathbf{+14H^+} \rightarrow 2Cr^{3+} + 7H_2O$
$Fe^{2+} \rightarrow Fe^{3+}$

5) Balance the charge:

$Cr_2O_7^{2-} +14H^+ \mathbf{+ 6e^-} \rightarrow 2Cr^{3+} + 7H_2O$
$Fe^{2+} \rightarrow Fe^{3+} \mathbf{+ e^-}$

6) Cancel the electrons and combine the equations:

$[\ Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O\ ] \times 1$

$[\ Fe^{2+} \rightarrow Fe^{3+} + e^-\ ] \times 6$

the combine....

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$+\ 6Fe^{2+} \rightarrow 6Fe^{3+} + 6e^-$

\---

$Cr_2O_7^{2-} + 14H^+ + 6e^- + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+} + 6e^-$

same number of electrons on both sides, cancel it....

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

is the final answer.

iv. Steps(**in alkaline condition**):

- Balance the equation as if it happens in an acidic condition first.
- Add OH^- to both sides of the equation to react with all the H^+ to form H_2O.
- Cancel the excess H_2O on either side of the equation.

Note: If it is obvious enough that OH^- must be added in order to balance the equation, then add OH^- instead.

3) **Using changes in oxidation number**:

i. This method utilises the fact that an increase in certain amount of oxidation number in a substance must be accompanied by a decrease in same amount of oxidation number in another substance.

ii. An example:

Q: Balance and complete this equation:

$$Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$$

A: 1) Calculate the changes in oxidation number:

For Cr: +6 to +3, change is -3

For Fe: +2 to +3, change is +1

2) Balance the changes:

For Cr: -3(**1**) = -3

For Fe: +1(**3**) = +3

$1Cr_2O_7^{2-} + 3Fe^{2+} \rightarrow 1Cr^{3+} + 3Fe^{3+}$

3) Multiply everything by 2 except $Cr_2O_7^{2-}$ because there are already two atoms of chromium inside it.

$Cr_2O_7^{2-} + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+}$

4) Balance the oxygen and hydrogen:

$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$ is the final answer.

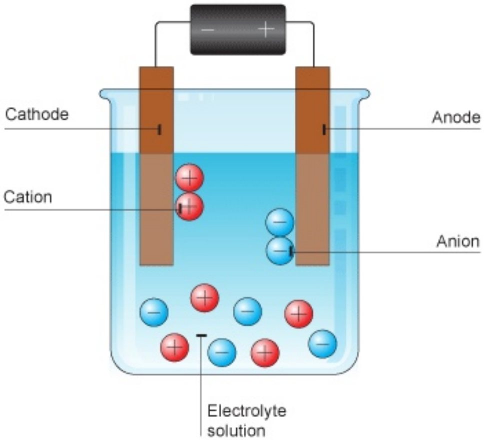
7.2 Electrolysis

Electrolytic cells

1) *Electrolysis* is the decomposition of a compound into its elements by an electric current.

2) Uses of electrolysis:
   - to extract useful metals from their ores.
   - to produce useful by-products such as chlorine gas.
   - to purify metals.

3) Electrolysis is carried out in an electrolytic cell. An electrolytic cell consists of:
   i. the *electrolyte* which is the compound being decomposed. It is either a **molten** ionic compound or a concentrated **aqueous solution** of ions. Solid ionic compounds and covalent compounds cannot be used because they do not conduct electricity.
   ii. the *electrodes* which are rods made from graphite or a metal which conducts electricity to and from the electrolyte.
      - *anode* is the positive electrode.
      - *cathode* is the negative electrode.
   iii. external power supply of direct current and a complete d.c. circuit.



Redox reactions in electrolysis

1) During electrolysis, the **cations are attracted to the cathode** while the **anions are attracted to the anode**.

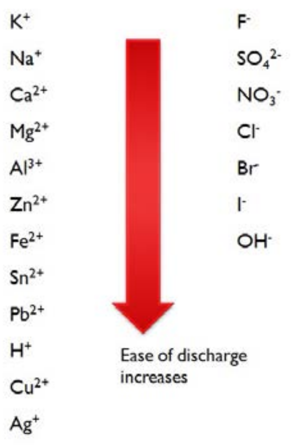
2) i. At the cathode, cations gain electrons and are reduced. **Reduction occurs at the cathode**.
   ii. At the anode, anions lose electrons and are oxidised. **Oxidation occurs at the anode**.

3) A simple example is the electrolysis of molten sodium chloride:
   i. At the cathode: $Na^+ + e^- \rightarrow Na$...........gain electrons, reduction.
   ii. At the anode: $2Cl^- \rightarrow Cl_2 + 2e^-$...........lose electrons, oxidation.
   iii. Sodium metal and chlorine gas are produced.

4) For electrolysis of aqueous sodium chloride:
   i. In an aqueous solution of sodium chloride, four types of ions are present (Na^+, Cl^-, H^+ and OH^-).
   ii. However, only one type of ion can be discharged at each electrode.

5) Factors that determine the selective discharge of ions in an electrolytic cell:
   i. **Position of the ion in the electrochemical series**
      - the lower it is in the electrochemical series, the higher the possibility for it to be discharged.
   ii. **Concentration of the ions**
      - the higher the concentration of the ion, the higher the possibility for it to be discharged.

The Electrochemical Series



6) For electrolysis of aqueous sodium chloride:
   i. At the cathode: $2H^+ + 2e^- \rightarrow H_2$............because H^+ is lower in the electrochemical series.
   ii. At the anode: $4OH^- \rightarrow O_2 + 2H_2O + 4e^-$.............because OH^- is lower in the electrochemical series.

Extraction of aluminium from bauxite ore

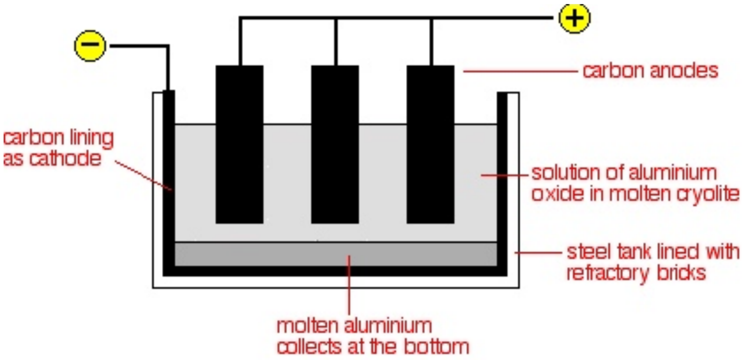
1) Bauxite is **impure aluminium oxide**, Al_2O_3. The impurities are iron oxides, silicon dioxide and titanium dioxide. Bauxite is the major aluminium ore.

2) The first step is to purify the bauxite to get pure aluminium oxide, Al_2O_3.

3) Molten aluminium oxide is electrolysed in a solution of cryolite, Na_3AlF_6 to give out the required aluminium metal.

4) The function of dissolving aluminium oxide in large amount of cryolite is to:
   i. **lower the melting point** of the electrolyte from about 2140 °C to 970 °C.
   ii. improve the electrical conductivity of the electrolyte.

5) Electrolysis of aluminium oxide is carried out in long narrow cells using carbon (graphite) electrodes.



6) At the cathode: $Al^{3+} + 3e^- \rightarrow Al$..........reduction
   At the anode: $2O^{2-} \rightarrow O_2 + 4e^-$...........oxidation
   Overall equation: **$4Al^{3+} + 6O^{2-} \rightarrow 4Al + 3O_2$ or $2Al_2O_3 \rightarrow 4Al + 3O_2$**

7) Aluminium is denser than the electrolyte. It drops to the bottom of the electrolytic cell and is removed using a suction tube or through a tap hole.

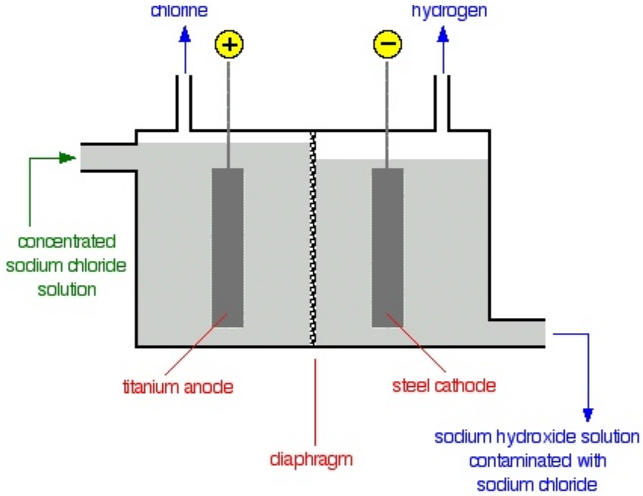
8) The oxygen gas released will oxidise the hot carbon electrodes to carbon dioxide and carbon monoxide. So the electrodes have to be replaced from time to time.

9) Some environmental issues related:
   i. The carbon monoxide gas produced is poisonous.
   ii. Large amount of energy is needed because the current needed to electrolyse the electrolyte is very high.

Electrolysis of brine

1) Brine is **concentrated aqueous solution of sodium chloride**. It is obtained from sea water or by dissolving rock salt in water.

2) Electrolysis of brine is used **to produce chlorine, hydrogen and sodium hydroxide**. A diaphragm cell is used to carry out this reaction.



3) The electrolyte level in the anode compartment is kept higher than in the cathode compartment. This ensures the flow of the solution is always towards the cathode compartment. This reduces the possibility of sodium hydroxide solution formed moving back as they are to be collected.

4) The ions present in the aqueous solution of sodium chloride are Na^+, Cl^-, H^+ and OH^-. H^+ and OH^- comes from the slight ionisation of water.

$$H_2O \rightleftharpoons H^+ + OH^-$$

5) At the cathode: $2H^+ + 2e^- \rightarrow H_2$.........because H^+ is lower in the electrochemical series.

At the anode: $2Cl^- \rightarrow Cl_2 + 2e^-$..........because Cl^- is in a far more greater concentration than OH^-.

Overall: **$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2$**

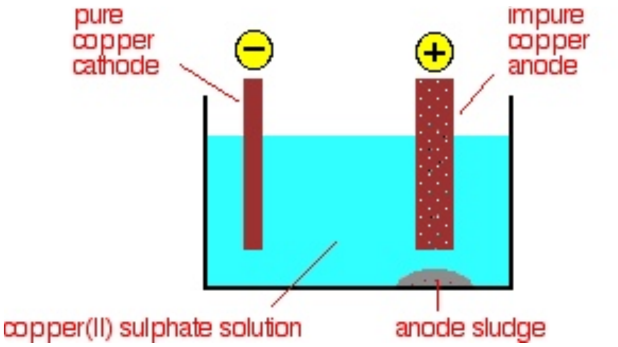
6) As more and more H^+ are removed, more are formed from the ionisation of water because the position of equilibrium shifts to the right. The H^+ formed are being removed again until none is left.

7) At the same time, more and more OH^- are being produced. When all the H^+ are removed, only OH^- and Na^+ are left in the electrolyte and NaOH is formed.

Electrolytic purification of copper

1) Copper is purified to be used for electrical wiring because 99.99% of purity is required for efficient transmission of electrical energy. Even small amounts of impurity reduces its conductivity greatly.

2) Electrolytic purification of copper is carried out in cells using:
   i. an electrolyte of **copper(II) sulfate solution** acidified with sulfuric acid.
   ii. an anode of **impure copper**.
   iii. a cathode of **pure copper**.



3) At the anode: $Cu \rightarrow Cu^{2+} + 2e^-$
   At the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

4) The result is the transfer of copper from the anode to the cathode. As a result, **the cathode gets thicker and the anode get thinner**. The impurities in the anode settle down as anode 'sludge'.

5) The concentration of copper(II) sulfate solution **does not change** because the number of moles of Cu^{2+} ions formed at the anode is exactly the same as the number of moles of Cu^{2+} ions discharged at the cathode.

CHAPTER 8: Chemical Equilibria

Learning outcomes:

(a) explain, in terms of rates of the forward and reverse reactions, what is meant by a reversible reaction and dynamic equilibrium.
(b) state Le Chatelier's Principle and apply it to deduce qualitatively (from appropriate information) the effects of changes in temperature, concentration or pressure, on a system at equilibrium.
(c) state whether changes in concentration, pressure or temperature or the presence of a catalyst affect the value of the equilibrium constant for a reaction.
(d) deduce expressions for equilibrium constants in terms of concentrations, K_c*, and partial pressures,* K_p*. [treatment of the relationship between* K_p *and* K_c *is not required]*
(e) calculate the values of equilibrium constants in terms of concentrations or partial pressures from appropriate data.
(f) calculate the quantities present at equilibrium, given appropriate data (such calculations will not require the solving of quadratic equations).
(g) describe and explain the conditions used in the Haber process and the Contact process, as examples of the importance of an understanding of chemical equilibrium in the chemical industry.
(h) show understanding of, and use, the Brønsted-Lowry theory of acids and bases, including the use of the acid-I, base-II concept.
(i) explain qualitatively the differences in behaviour between strong and weak acids and bases and the pH values of their aqueous solutions in terms of the extent of dissociation.

8.1 Dynamic Equilibria

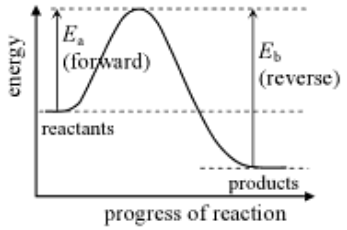
Reversible reactions

1) A reversible reaction is one which can proceed in both directions, as indicated by the "⇌" sign. For example:

$$H_2 + I_2 \rightleftharpoons 2HI \qquad 2SO_2 + O_2 \rightleftharpoons 2SO_3$$

2) In a reversible reaction, the reactants react to form the products. The products in turn also react to re-form the reactants. A mixture of reactants and products is present, an **equilibrium** is established between them.

3) Whether a reaction is reversible or not depends on its activation energy. If the activation energy of the backward reaction is very high, the reaction is not reversible.

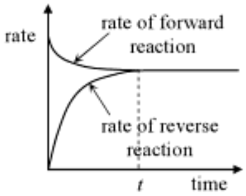


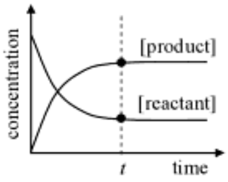
Characteristics of equilibrium

1) An equilibrium have four particular features under constant conditions:
   i. **It is dynamic**
   - *Dynamic equilibrium* is a situation where the **rate of forward reaction becomes equal to the rate of reverse reaction** and the amount of substance present to do not vary with time as long as the conditions remain the same.
   - In the microscopic scale, the reactants and products are continuously reacting but in the macroscopic scale, there seem to be no change at all.

   ii. **The concentrations of the reactants and products remain constant**
   - This is because at equilibrium, the rate of forward reaction equals to the rate of backward reaction.
   - For example, $H_2 + I_2 \rightleftharpoons 2HI$

   At equilibrium, for every one mole of the reactants get converted to two moles of products, two moles of the products are re-forming the reactants.





iii. **It requires a closed system**
- A closed system is one which none of the substances can be added or removed, but energy can move in and out freely.
- In an open system, the products formed will escape, this will not allow them to react and re-form the reactants, an equilibrium will never be reached.

8.2 Factors Affecting Chemical Equilibria

Position of equilirbium

1) The position of equilibrium refers to the relative amount of products and reactants present in an equilibrium mixture.

Le Chatelier's principle

1) *Le Chatelier's principle* states that if a change is made to a system in equilibrium, the system reacts in such a way so as to oppose the change and a new equilibrium is established.

2) In other words, "whatever done to the system, the system does the opposite".

Effect of change in concentration

$$A + B \rightleftharpoons C + D$$

1) When something is added or removed, the system will does the opposite so as to remove or replace it.

2) When the concentration of A or B increases, by Le Chatelier's principle, the position of equilibrium shifts to the right **to decrease the concentration** back. More C and D are being formed.

3) When the concentration of A or B decreases, by Le Chatelier's principle, the position of equilibrium shifts to the left **to increase the concentration** back. More A and B are being formed.

Effect of change in pressure

$$2A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

1) Changes in pressure will only affect reactions between gases.

2) When the pressure of a system is altered, the system will respond to neutralise the change.

3) When the pressure is increased, by Le Chatelier's principle, the position of equilibrium shifts to the right **to reduce the total number of molecules** and to decrease the pressure.

4) When the pressure is decreased, by Le Chatelier's principle, the position of equilibrium shifts to the left **to increase the total number of molecules** and to increase the pressure.

5) i. Increased pressure favours the reaction which produces fewer molecules.
   ii. Decreased pressure favours the reaction which produces more molecules.

6) If there are equal number of molecules on each side of the equation, changes in pressure **will not** affect the position of equilibrium. However, it will still affect the rate of reaction.

Effect of change in temperature

$$A + B \rightleftharpoons C + D \qquad \Delta H^\circ = \text{enthalpy change of forward reaction}$$

1) If heat is introduced to the system, the system will respond to neutralise the change, either by absorbing or releasing heat.

2) If $\Delta H^\circ > 0$ (endothermic reaction):
   i. When temperature is increased, by Le Chatelier's principle, the position of equilibrium shifts to the right **to remove the extra heat** (the endothermic reaction is favoured).
   ii. When temperature is reduced, by Le Chatelier's principle, the position of equilibrium shifts to left **to release heat** (the forward reaction, an exothermic reaction is favoured).

3) i. Increased temperature favours endothermic reaction.
   ii. Decreased temperature favours exothermic reaction.

Effect of catalyst

1) Catalysts **will not affect** the position of equilibrium. This is because a catalyst increases both the rate of forward and reverse reaction.

2) However, catalysts can speed up the time taken to reach equilibrium.

8.3 Equilibrium Constants

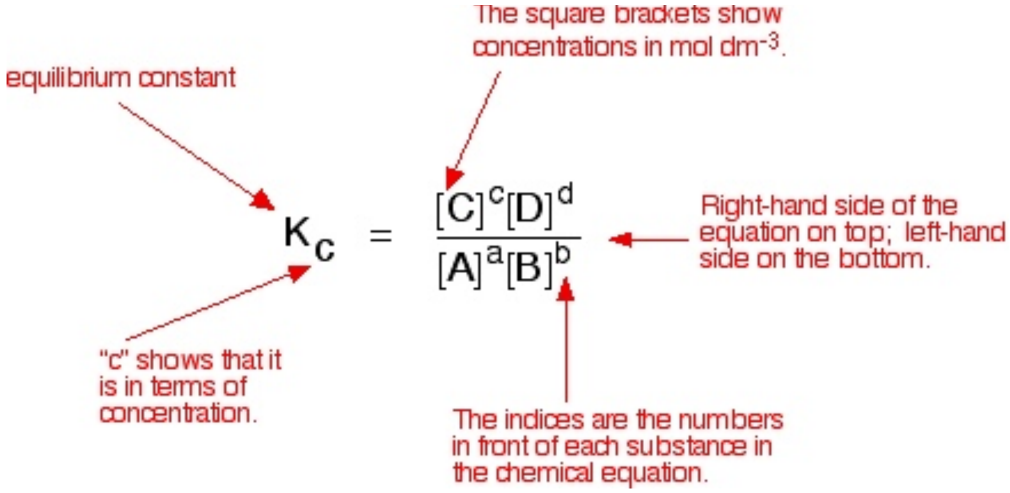
Equilibrium constants, K_c and K_p

1) *Equilibrium constant* is the value of the reaction quotient when the reaction has reached equilibrium. Alternatively, it can also be defined as the measure of the extent in which reactants are converted into products.

2) At any given temperature, every reaction has a specific value of equilibrium constant which is independent of changes in concentration, pressure, use of catalyst or the amount of reactants you start with.

3) Equilibrium constant expressed in concentration is called K_c while expressed in partial pressure is called K_p.

4) For any reaction: $aA + bB \rightleftharpoons cC + dD$



5) For reaction involving gases, equilibrium constant can be expressed in terms of partial pressures.

$$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g) \text{ ....(1)}$$

$$K_p = \frac{P_C{}^c \times P_D{}^d}{P_A{}^a \times P_B{}^b}$$

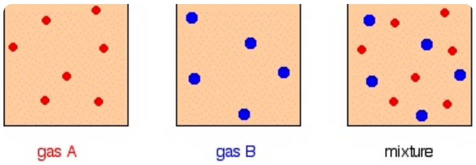
Mole fraction and partial pressures

1) From equation (1), the mole fraction of A is given by:

$$x_A = \frac{\text{number of moles of gas A}}{\text{total number of moles of gas}}$$

2) The partial pressure of a gas A in a mixture of gases is the pressure that gas A will exert, if gas A alone was to occupy the same volume at the same temperature. It is given by:

$$P_A = \text{mole fraction of A} \times \text{total pressure}$$
$$P_A = x_A \times P$$



More about K_c and K_p

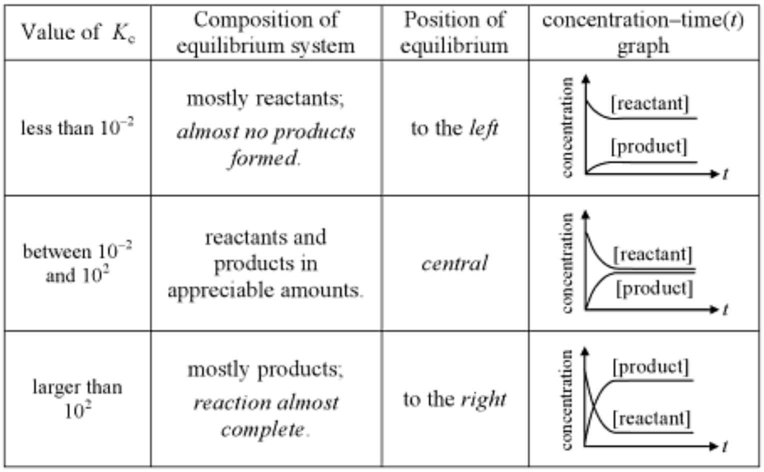
1) Note:

i. Concentration of liquids and solids are omitted in the expression of K_p and K_c.

ii. State symbols are not essential in writing the expressions.

2) The magnitude of K_p and K_c gives the measure of the extent of equilibrium, it does not give any information about the rate of reaction.

$$\text{Since } K_c \propto \frac{[\text{products}]}{[\text{reactants}]}$$



Value of K_c	Composition of equilibrium system	Position of equilibrium	concentration–time(t) graph
less than 10^{-2}	mostly reactants; *almost no products formed.*	to the *left*	concentration [reactant] [product] t
between 10^{-2} and 10^{2}	reactants and products in appreciable amounts.	*central*	concentration [reactant] [product] t
larger than 10^{2}	mostly products; *reaction almost complete.*	to the *right*	concentration [product] [reactant] t

3) Examples on writing an expression for K_p and K_c.

e.g.

1. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\quad K_p = \dfrac{(p_{HI})^2}{(p_{H_2})(p_{I_2})}$ (no units)
2. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ $\quad K_c = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ $\dfrac{(mol\,dm^{-3})^2}{(mol\,dm^{-3})^3}$ (***units***: $dm^3\,mol^{-1}$)
3. $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ $\quad K_c = \dfrac{[SO_2]^2[O_2]}{[SO_3]^2}$ $\dfrac{(mol\,dm^{-3})^3}{(mol\,dm^{-3})^2}$ (***units***: $mol\,dm^{-3}$)
4. $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$ $\quad K_c = \dfrac{[H_2]^4}{[H_2O]^4}$ (no units)
5. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $\quad K_p = p_{CO_2}$ (***units***: atm or Pa)

Factors affecting the value of K_p and K_c

1) In short, the equilibrium constants are constants at constant temperature. **Only temperature can affect the value of K_c and K_p.**

2) i. For endothermic reaction, the value of K_c or K_p **increases** with increasing temperature.
ii. For exothermic reaction, the value of K_c or K_p **decreases** with increasing temperature.

[Note: Statement (g) is omitted in this section and is discussed in Chapter 13]

8.4 Theory of Acids and Bases

The Arrhenius theory

1) According to Arrhenius theory:
i. An *acid* is a substance which ionises in water to give hydrogen ions, H^+.
ii. A *base* is a substance which ionises in water to give hydroxide ions, OH^-.

2) Limitations of this theory:
i. When ammonia gas reacts with hydrogen chloride gas, ammonium chloride is produced. Although this really is an acid-base reaction but it contradicts with the Arrhenius theory because no H^+ or OH^- is produced.

The Brønsted-Lowry theory

1) According to the Brønsted-Lowry theory:
   i. An *acid* is a **proton donor**.
   ii. A *base* is a **proton acceptor**.

2) A proton is a hydrogen ion, H^+.

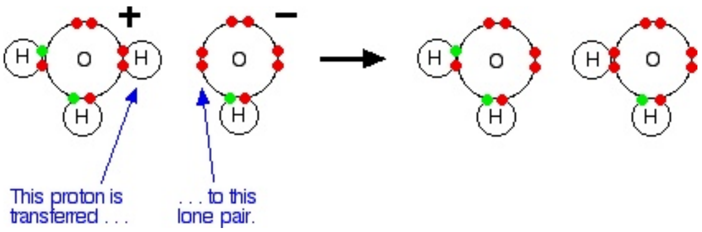
3) For example, when hydrogen chloride dissolves in water to form hydrochloric acid, the following reaction occurs:

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)............(2)$$

HCl is acting as an **acid** because it has donated a proton. H_2O is acting as a **base** because it has accepted a proton.

4) When the acidic solution reacts with a base, what is actually functioning as an acid is the hydroxonium ion, H_3O^+.

$$H_3O^+ + OH^- \rightarrow 2H_2O$$



H_3O^+ is acting as an acid because it has donated a proton. OH^- Is acting as a base because it has accepted a proton.

5) Brønsted-Lowry acids and bases do not nave to involve aqueous solutions.

Conjugate pairs

1) When ammonia gas dissolves in water, the reaction that occurs is reversible:

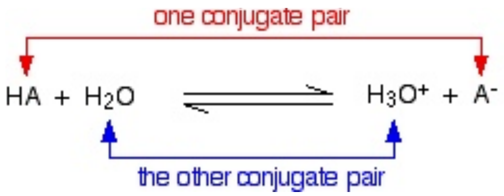
$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)..............(3)$$

In the forward reaction, H_2O is acting as an **acid** because it has donated a proton and NH_3 is acting as a **base** because it has accepted a proton.
In the backward reaction, OH^- is acting as a **base** because it has accepted a proton and NH_4^+ is acting as an **acid** because it has donated a proton.

2) Therefore OH^- is the **conjugate base** of the acid H_2O while NH_4^+ is the **conjugate acid** of the base NH_3.

3) In general:
   i. Every acid has a conjugate base, this is the particle left when the acid has given away its proton.
   ii. Every base has a conjugate acid, this is the particle left when the base has accepted a proton.

$$\underset{\textit{acid}}{HA(aq)} + \underset{\textit{base}}{H_2O(l)} \rightleftharpoons \underset{\textit{conjugate acid}}{H_3O^+(aq)} + \underset{\textit{conjugate base}}{A^-(aq)}$$



4) Alternatively, the acid-I, base-II terminology can also be used:
   i. HA is **acid-I** and A^- is **base-I**, they are one conjugate pair.
   ii. H_2O is **base-II** and H_3O^+ is **acid-II**, they are another conjugate pair.

5) Substances which can behave as an acid as well as base are described as **amphoteric**. One example is water:
   i. In reaction (2), water is behaving as a base.
   ii. In reaction (3), water is behaving as an acid.

Strength of acids and bases

1) i. A *strong acid* is one which **dissociates completely** in a solution.

$$HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

   ii. This produces high concentration of hydroxonium ions. Therefore the pH of the solution is very low, pH ≈ 1.
   iii. Examples of strong acids are HCl, H_2SO_4 and HNO_3.

2) i. A *strong base* is one which **dissociates completely** in a solution.

$$NaOH(s) + aq \rightarrow NaOH(aq)$$

   ii. This produces high concentration of hydroxide ions. Therefore the pH of the solution is very high, pH ≈ 14.
   iii. Examples are Group I metal hydroxides.

3) i. A *weak acid* is one which **dissociates partially** in a solution.

$$CH_3COOH(l) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

   ii. This produces very low concentration of hydroxonium ions, the position of equilibrium is far over the left. Therefore the pH of the solution is higher, pH ≈ 3.
   iii. Examples are organic acids.

4) i. A *weak base* is one which **dissociates partially** in a solution.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

ii. This produces very low concentration of hydroxide ions, the position of equilibrium is far over the left. Therefore the pH of the solution is lower, pH ≈ 12.
iii. Examples are ammonia, amines and some hydroxides of transition metals.

5) Note:
i. Strength of acids and bases is defined in terms of **degree of dissociation** while concentration is defined as the **number of moles per unit volume**.
ii. Therefore a weak acid in high concentration is still classified as a weak acid.
iii. Also, a strong acid in low concentration is still classified as a strong acid.

CHAPTER 9: Rate of Reaction

9.1 Rate of Reaction
9.2 Factors Affecting Rate of Reaction
9.3 Catalysis

Learning outcomes:

(a) *explain and use the terms: rate of reaction, activation energy and catalysis.*
(b) *explain qualitatively, in terms of collisions, the effect of concentration changes on the rate of a reaction.*
(c) *show understanding, including reference to the Boltzmann distribution, of what is meant by the term activation energy.*
(d) *explain qualitatively, in terms both of the Boltzmann distribution and of collision frequency, the effect of temperature change on the rate of a reaction*
(e) (i) *explain that, in the presence of a catalyst, a reaction has a different mechanism, i.e. one of lower activation energy.*
  (ii) *interpret this catalytic effect in terms of the Boltzmann distribution.*
(f) *describe enzymes as biological catalysts (proteins) which may have specific activity.*

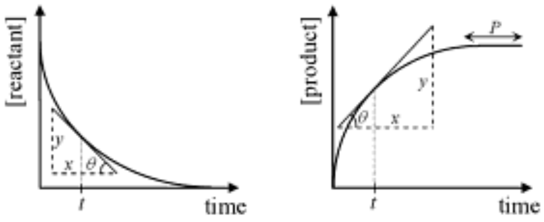
9.1 Rate of Reaction

What is the rate of reaction?

1) *Rate of reaction* is the change in concentration of reactants or products per unit time. It refers to the rate of product formed or the rate of reactant used up.

2) A balanced chemical equation gives no information about the rate of reaction. It has to be measured experimentally.

3) The rate of reaction can also be obtained by calculating the **gradient** of a concentration-time graph.



Rate of reaction at time t

= gradient of graph at time t

= tan θ

$= \frac{y}{x}$

4) The higher the gradient(the steeper the graph), the higher the rate of reaction.

5) The gradient of the graph decreases with time, this shows that the **rate of reaction is inversely proportional to time**. Which means, the rate of reaction decreases as the reaction proceeds.

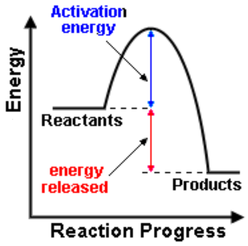
Collision theory

1) The *collision theory* states that, for the particles to react with each other, they must **collide** in the **correct orientation** with **energy greater than or equal to the activation energy**.

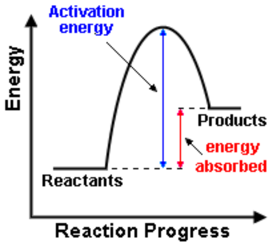
2) The *activation energy* is the minimum energy that that the reacting particles must possess for a successful collision to take place.

3) Every reaction has a specific activation energy.

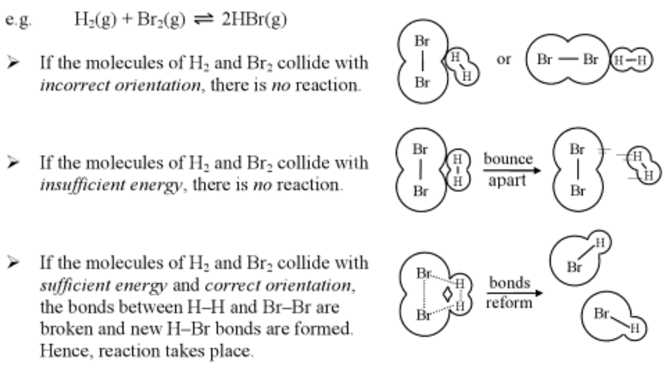
4) If the collision results in the reactants changing into products, it is said to be an effective(or successful) collision.



Exothermic reaction



Endothermic reaction



e.g. $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$

- If the molecules of H_2 and Br_2 collide with *incorrect orientation*, there is *no* reaction.
- If the molecules of H_2 and Br_2 collide with *insufficient energy*, there is *no* reaction.
- If the molecules of H_2 and Br_2 collide with *sufficient energy* and *correct orientation*, the bonds between H–H and Br–Br are broken and new H–Br bonds are formed. Hence, reaction takes place.

9.2 Factors Affecting the Rate of Reaction

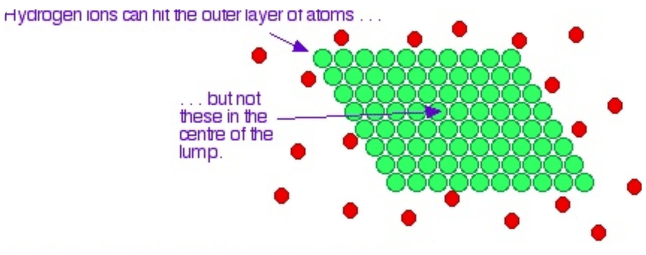
How to increase the rate of reaction?

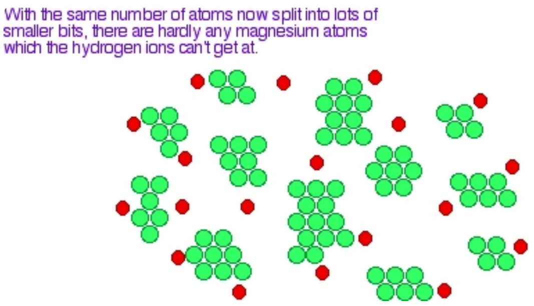
1) According to the collision theory, the rate of reaction will increase if:
   i. the frequency of collision and effective collision increases.
   ii. the proportion of particles with energy greater than activation energy increases.

Effect of surface area

1) The **larger** the surface area of the reactant particles, the **higher** the rate of reaction.

2) This is because the surface area exposed for collision is larger, **frequency of collision** between the reactant particles **increases** and hence the **frequency of effective collision also increases**. More products are formed per unit time and hence the rate of reaction increases.

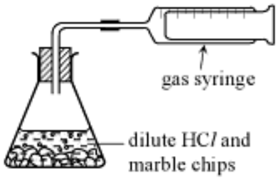


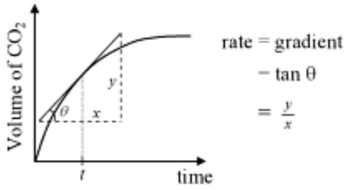


3) For example, the reaction between hydrochloric acid and marble chips(calcium carbonate) is as follow:

$$HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

The rate of reaction can be found by measuring the volume of CO_2 gas given out per unit time. The volume of CO_2 is determined at regular intervals. The set up of apparatus is as follow:





It is found that powdered marble chips react faster than big lumps of marble chips

4) This is because powdered marble chips are smaller in size and hence have a larger total surface area.

Effect of concentration

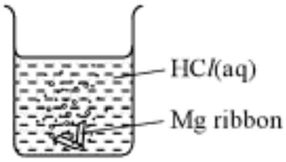
1) The **higher** the concentration of the reactant particles, the **higher** the rate of reaction.

2) This is because in a more concentrated solution, there are **more reactant particles per unit volume**. The **frequency of collision** between the reactant particles **increases** and hence the **frequency of effective collision also increases**. More products are formed per unit time and hence the rate of reaction is higher.

3) For example, the reaction between magnesium ribbon and hydrochloric acid is as follow:

$$Zn(s) + HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

The rate of reaction can be found by measuring the time taken for the magnesium ribbon to disappear from sight.



It is found that when HCl has a higher concentration, the time taken for the magnesium ribbon to disappear is shorter.

4) Since rate of reaction is inversely proportional to time, the shorter the time, the higher the rate of reaction.

5) There are also times where increasing the concentration does not help in increasing the rate of reaction:
   i. **Reactions involving only a single reactant particle splitting**
      - The rate of reaction is not governed by the rate of collision between them.
      - The rate is governed by the **amount of energy** possessed by the reactant particles.
      - If a large proportion of the particles have energy **greater than activation energy**, more particles will split up per unit time and hence the rate of reaction is higher.
   ii. **Where a catalyst is working as fast as it can**
      - If a high enough concentration of reactant particles is mixed with a small amount of catalyst, the reaction proceeds.
      - The rate of reaction will not increase if the concentration of the reactant particles is increased because the **catalyst is saturated**.
      - The rate of reaction can be increased by adding more catalysts.

Effect of pressure

1) The **higher** the pressure of the system, the **higher** the rate of reaction.

2) The explanation is the same as the one in the effect of concentration. However, increasing the pressure will only increase the rate of a reaction **involving gases**. Changing the pressure of a reaction which involves only solid or liquid has no effect on it.

Effect of temperature

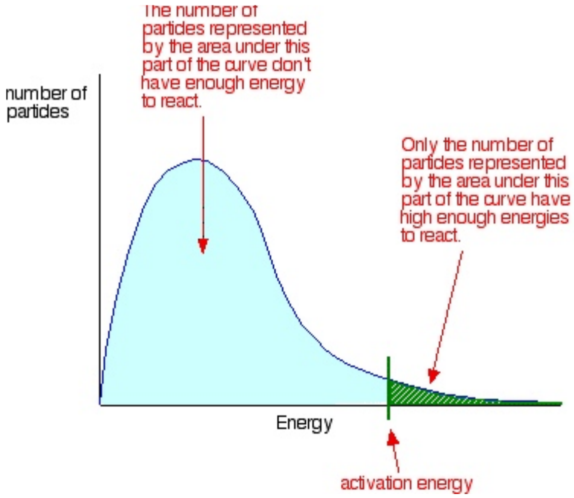
1) The **higher** the temperature of the reacting system, the **higher** the rate of reaction.

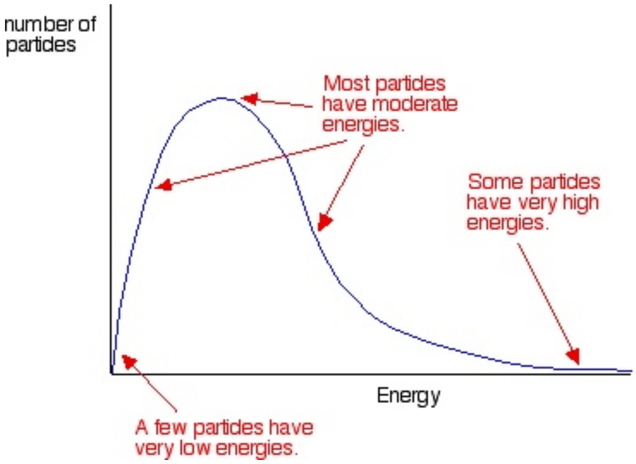
2) This is because at higher temperature, the **average kinetic energy of the particles increases**, so:
   i. more reacting particles have energy equal to or greater than the activation energy. (This is the major reason)
   ii. the reacting particles travel at higher speed, the frequency of collision between the reacting particles increases. (This is the minor reason)

   This causes the frequency of effective collision to increase. More products are formed per unit time and hence, the rate of reaction is higher.

3) In fact, the rate of reaction doubles for every increase in 10 °C.

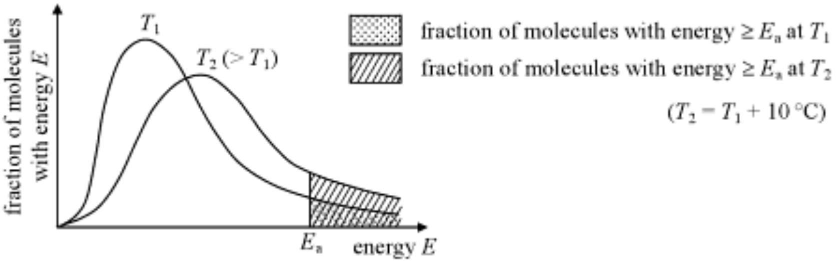
4) The effect of temperature on rate of reaction can be shown in a Maxwell-Boltzmann distribution curve. A typical curve looks like this:





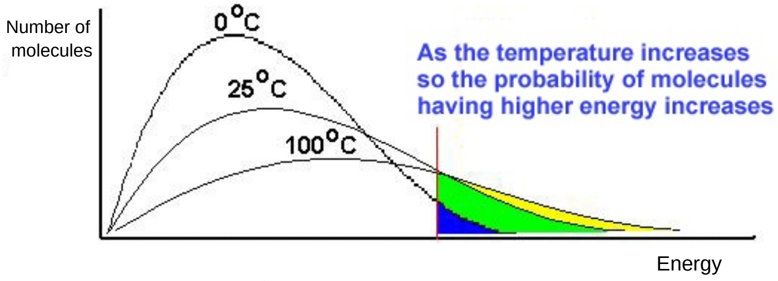
5) The area under the curve represents the **total number of molecules**, it is constant if no additional molecules are added.

6) An increase in temperature increases the number of particles with higher energy, the curve shifts to the right. So that there are more particles with energy greater than the activation energy, as illustrated below:



There are more particles with energy greater than the activation energy at T2

7) When drawing the curve at a higher temperature, the height of the curve should reduce so that the area under the curve remains constant.



9.3 Catalysis

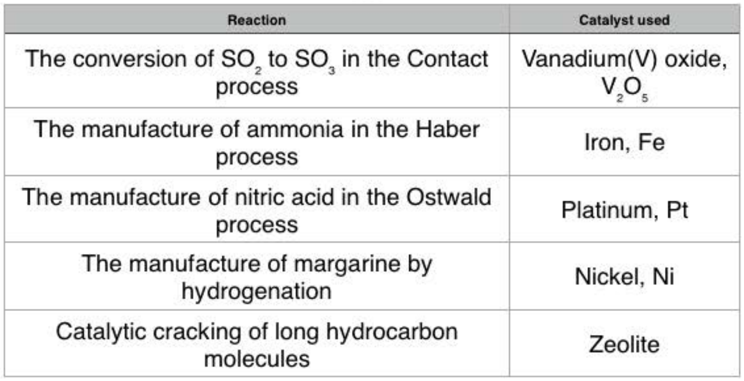
What is a catalyst?

1) A *catalyst* is a substance that increases the rate of reaction but is chemically unchanged at the end of the reaction.

2) *Catalysis* is the increase in the rate of chemical reaction by a catalyst.

3) Characteristics of catalysts:
   i. Catalysts are needed in small amounts only. This is because a catalyst is not used up at the end of a reaction, the same catalyst can be used to catalyse a large number of reactions.
   ii. Catalysts do not initiate the reaction, they accelerate it.
   iii. Catalysts do not alter the enthalpy change of a reaction.
   iv. Catalysts can be poisoned by impurities, thus losing its catalytic abilities.
   v. Most catalysts are transition metals or compounds of them.
   vi. Catalysts are usually specific, a reaction can only be catalysed by a specific catalyst.

4) Examples of catalysts used in industries:

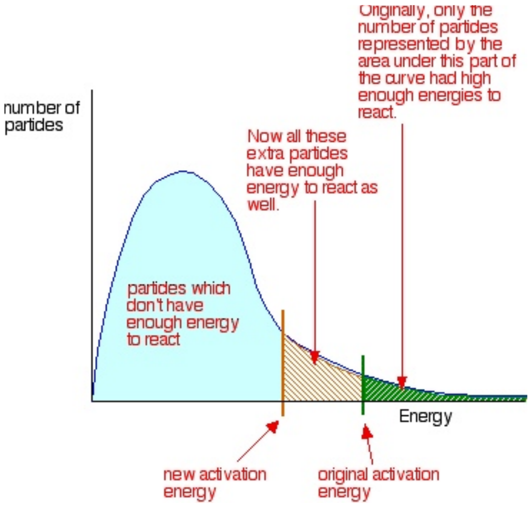


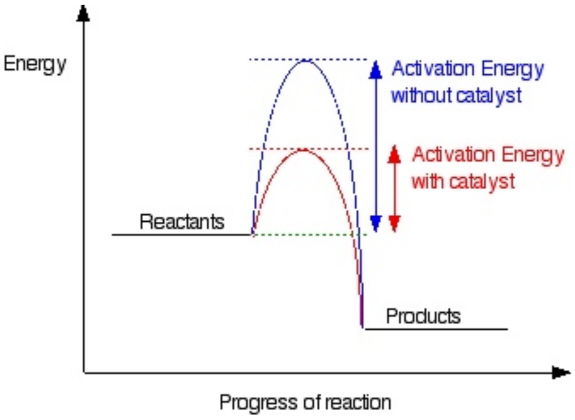
Reaction	Catalyst used
The conversion of SO_2 to SO_3 in the Contact process	Vanadium(V) oxide, V_2O_5
The manufacture of ammonia in the Haber process	Iron, Fe
The manufacture of nitric acid in the Ostwald process	Platinum, Pt
The manufacture of margarine by hydrogenation	Nickel, Ni
Catalytic cracking of long hydrocarbon molecules	Zeolite

The role of catalyst

1) A catalyst works by **providing an alternative route** for the reaction to occur. This alternative route has a **lower activation energy**. This increases the proportion of reacting particles with energy greater than the activation energy. As a result, the frequency of effective collision increases. More products are formed on per unit time and the rate of reaction is higher.

2) A catalyst neither alters the energies of reacting particles nor lower the original activation energy. It provides an **alternative route with lower activation energy**.





3) An example is the decomposition of hydrogen peroxide into water and oxygen.

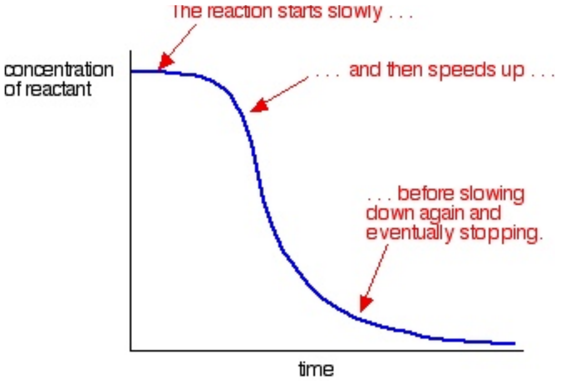
$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

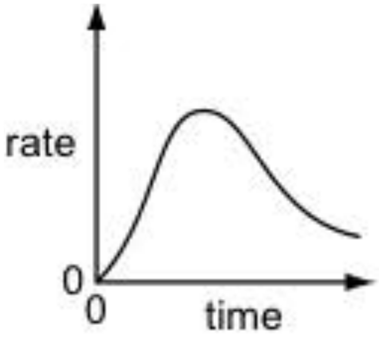
The reaction proceeds very slowly at room temperature and there are no observable changes. However, when a little manganese(VI) oxide, MnO_2 is added, effervescence is seen immediately. This suggests that oxygen gas is released.

Autocatalysis

1) For most reactions, the rate of reaction decreases with time because the concentration of reactants decreases.

2) However in some reactions, one of the **products can act as a catalyst** for that reaction. In these reactions, the rate is low at the beginning because there is no catalyst but increases as soon as the product(catalyst) is being formed. After that, the rate decreases again because the concentration of reactant decreases.

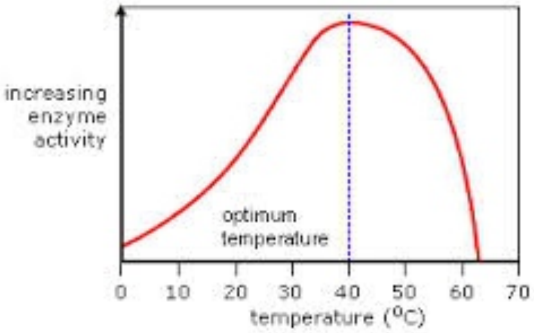


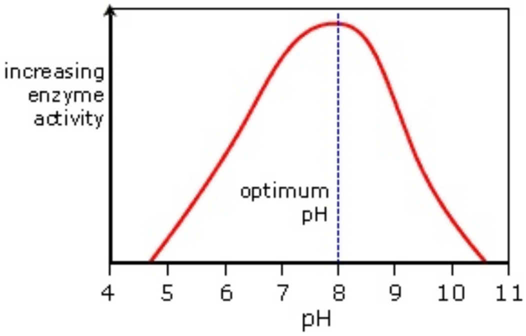


Enzymes as catalysts

1) *Enzymes* are proteins which have catalytic function and can act as biological catalysts that catalyses biological reactions in living organisms.

2) i. Enzymes are **highly specific**, catalysing only one type of reaction.
   ii. Enzymes are also very sensitive to changes in pH and temperature. Most enzymes can only function in a small range of temperature(usually 37 °C, the body temperature) and pH.

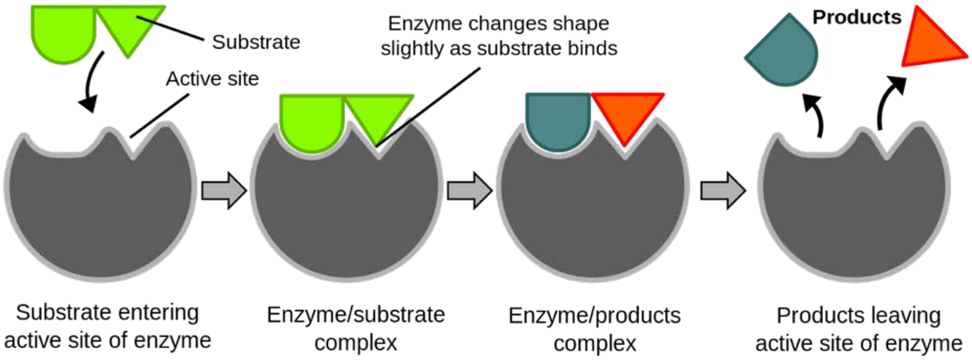




   iii. Enzymes are super-efficient catalysts, they are much more efficient compared to inorganic catalysts.

3) Enzymes function via the **lock-and-key mechanism**. According to this model, the substrate(reactant) molecule and the active site of the enzyme have complementary shapes so that the substrate fits in precisely.

4) The substrate binds to the active site of the enzyme just like a key binds to a lock. Bond-breaking and bond-forming processes then take place, transforming the substrate into products.



CHAPTER 10: Chemical Periodicity

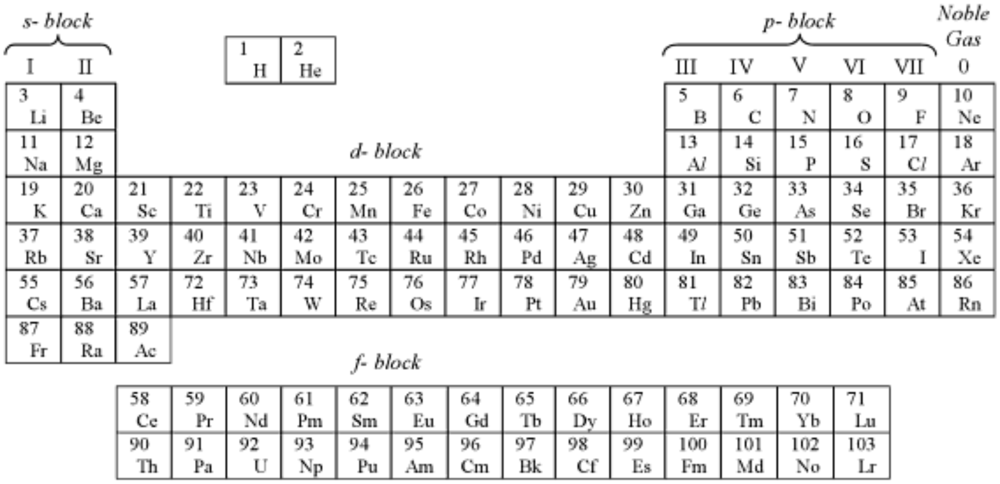
Learning outcomes:

- *(a) describe qualitatively (and indicate the periodicity in) the variations in atomic radius, ionic radius, melting point and electrical conductivity of the elements (see the Data Booklet).*
- *(b) explain qualitatively the variation in atomic radius and ionic radius.*
- *(c) interpret the variation in melting point and in electrical conductivity in terms of the presence of simple molecular, giant molecular or metallic bonding in the elements.*
- *(d) explain the variation in first ionisation energy.*
- *(e) describe the reactions, if any, of the elements with oxygen (to give* Na_2O, MgO, Al_2O_3, P_4O_{10}, SO_2, SO_3*), chlorine (to give* $NaCl$, $MgCl_2$, Al_2Cl_6, $SiCl_4$, PCl_5*) and water (Na and Mg only).*
- *(f) state and explain the variation in oxidation number of the oxides and chlorides in terms of their valence shell electrons.*
- *(g) describe the reactions of the oxides with water. [treatment of peroxides and superoxides is not required]*
- *(h) describe and explain the acid/base behaviour of oxides and hydroxides including, where relevant, amphoteric behaviour in reaction with sodium hydroxide (only) and acids.*
- *(i) describe and explain the reactions of the chlorides with water.*
- *(j) interpret the variations and trends in (f), (g), (h), and (i) in terms of bonding and electronegativity.*
- *(k) suggest the types of chemical bonding present in chlorides and oxides from observations of their chemical and physical properties.*
- *(l) predict the characteristic properties of an element in a given group by using knowledge of chemical periodicity*
- *(m) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information about physical and chemical properties.*

10.1 Periodicity in Physical Properties

What is periodicity?

1) *Periodicity* is the recurrence of similar properties at regular intervals when the elements are arranged in increasing atomic number.



s- block

d- block

p- block

Noble Gas

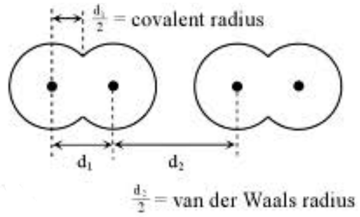
I	II											III	IV	V	VI	VII	0
				1 H	2 He												
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac															

f- block

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

Variation in size of atoms

1) *Covalent radius* is half the internuclear distance between two like atoms bonded by a single covalent bond.



2) *Van der Waal's radius* is half the average distance between two adjacent non-bonded atoms.

3) For example, the covalent radius of Cl_2 is 0.099 nm while the van der Waal's radius of Cl_2 is 0.180 nm.
Note: van der Waal's radius is always larger than covalent radius.

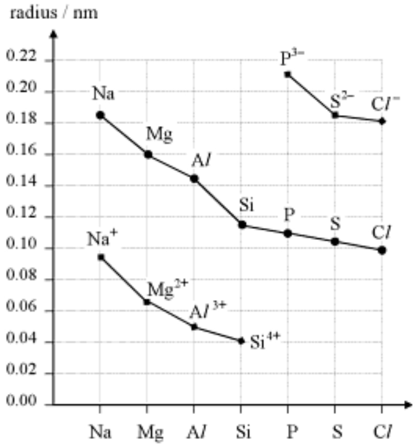
4) *Metallic radius* is half the distance between two like metal atoms bonded by metallic bond.

5) All these measurable quantities can be given a general name called 'atomic radii'.

6) Across Period 3, the atomic radius **decreases** gradually. This is because the **nuclear charge increases** while the **shielding effect remains constant**. The outer electrons are more attracted towards the nucleus, making the atoms smaller.

7) For comparison, metallic radii are used for Na, Mg and Al, covalent radii are used for Si, P, S and Cl. For argon, van der Waal's radius is used(argon do not form any bonds)
Note: This trend excludes argon because comparing van der Waal's radius with covalent and metallic radius is not fair.

Variation in ionic radius



1) Cations are formed when an atom loses electron(s). In Period 3, Na, Mg, Al and Si form cations by losing electron(s) to achieve stable octet electronic configuration. The ions formed are Na$^+$, Mg^{2+}, Al^{3+} and Si^{4+} respectively.

2) Cations are **smaller** than their respective atoms because a whole layer of electrons are lost. The remaining electrons are attracted more strongly towards the centre by the same nuclear charge.

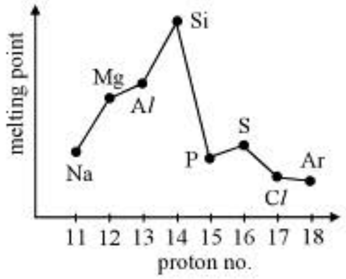
3) Anions are formed when an atom gains electron(s). In Period 3, P, S and Cl form anions by gaining electron(s) to achieve stable octet electronic configuration. The ions formed are P^{3-}, S^{2-} and Cl$^-$ respectively.

4) Anions are **bigger** than their respective atoms because they have more electrons than protons. The electrons are held less strongly by the nucleus. Besides, a repulsion is created between the electrons when a new electron is introduced and this causes the ion to expand.

5) **Anions are bigger than cations** because anions have one more shell of electrons compared to cations.

6) In the isoelectronic series(from Na$^+$ to Si^{4+} and P^{3-} to Cl$^-$), the ionic radius **decreases** gradually. This is because the same number of electrons are attracted more strongly by the increasing nuclear charge.

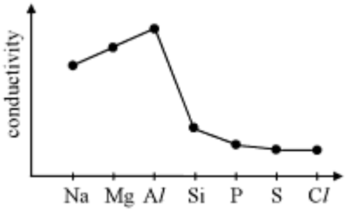
Variation in melting and boiling points



1) Across a Period,
   i. melting point **increases from Na to Al** because the strength of the metallic bond increases.
   ii. melting point of Si is **highest** because Si has a **giant covalent structure**, a lot of energy is required to overcome the strong covalent bonds.
   iii. melting points of P, S, Cl and Ar are **lower** because these have **simple molecular structures**, only weak van der Waal's forces of attraction exist between them.

2) Melting point of S > P > Cl > Ar because these elements exist as S_8, P_4, Cl_2 and Ar respectively. S_8 contains the **most number of electrons**, followed by P_4, Cl_2 and Ar. Van der Waal's forces get stronger with increasing number of electrons.

Variation in electrical conductivity



1) Across the Period, the elements change from metals(Na to Al) to semi-metal(Si) and then to non-metals(P to Ar).

2) Electrical conductivity is highest is metals, lower in semi-metals and lowest in non-metals(Most non-metals do not conduct electricity at all).

3) The electrical conductivity of Period 3 elements:
   i. **increases from Na to Al** because the number of electrons contributed by per atom to the sea of delocalised electrons increases from one in Na, two in Mg and three in Al. There are more electrons to conduct electricity.
   ii. **decreases from Al onwards**. Si is a semi-metal therefore it is a semi-conductor. The remaining elements do not conduct electricity because there are no mobile electrons.

Variation is first ionisation energy

(Refer Chapter 3)

10.2 Periodicity in Chemical Properties

Reaction with oxygen gas, O_2

1) **Sodium** burns on heating with an **orange-yellow flame** to form white sodium oxide.

$$4Na(s) + O_2(g) \rightarrow 2Na_2O(s)$$

2) **Magnesium** burns on heating with a **brilliant white flame** to form white magnesium oxide.

$$2Mg(s) + O_2(g) \rightarrow 2MgO(s)$$

3) An oxide layer will form on the **aluminium** when it is exposed to air, this oxide layer prevents aluminium from reacting. However, if powdered aluminium is used, it burns on heating with **white flames** to form white aluminium oxide.

$$4Al(s) + 3O_2(g) \rightarrow 2Al_2O_3(s)$$

4) **Silicon** burns slowly at red heat to form silicon(VI) oxide or silicon dioxide.

$$Si(s) + O_2(g) \rightarrow SiO_2(s)$$

5) **Phosphorus** burns on heating with a **white flame** to form clouds of white covalent oxides, phosphorus(III) oxide and phosphorus(V) chloride.

$P_4(s) + 3O_2(g) \rightarrow P_4O_6(s)$; if oxygen gas is limited

$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$; if oxygen gas is in excess

6) **Sulfur** burns on heating with a **blue flame** to form sulfur dioxide gas.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

Under suitable conditions, sulfur dioxide can be converted to sulfur trioxide.(See also the Contact process)

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

7) **Chlorine** forms several oxides(Cl_2O and Cl_2O_7), but it will not react directly with oxygen.

8) **Argon** does not react with oxygen to form any oxides.

9) Going across Period 3, the **reactivity towards oxygen decreases** because the reducing power(tendency to be oxidised) of the elements decreases.

Reaction with chlorine gas, Cl_2

1) **Sodium** burns on heating in chlorine gas with an **orange-yellow flame** to form white sodium chloride.

$$2Na(s) + Cl_2(g) \rightarrow 2NaCl(s)$$

2) **Magnesium** burns on heating in chlorine gas with a **brilliant white flame** to form white magnesium chloride.

$$Mg(s) + Cl_2(g) \rightarrow MgCl_2(s)$$

3) **Aluminium** burns on heating to form ionic aluminium chloride.

$$2Al(s) + 3Cl_2(g) \rightarrow 2AlCl_3(s)$$

At temperature about 180 °C, aluminium chloride converts to a molecular form, Al_2Cl_6, a dimer of covalent $AlCl_3$. At even higher temperature, Al_2Cl_6 breaks into simple $AlCl_3$ molecules.

$$2Al(s) + 3Cl_2(g) \rightarrow Al_2Cl_6(g)$$

4) **Silicon** burns slowly in chlorine gas at red heat to form covalent silicon(IV) chloride or silicon tetrachloride, a colourless liquid which vaporises.

$$Si(s) + Cl_2(g) \rightarrow SiCl_4(l)$$

5) **Phosphorus** burns in chlorine gas to produce a mixture of two chlorides, phosphorus(III) chloride, PCl_3 and phosphorus(V) chloride, PCl_5. In excess chlorine gas, PCl_5 is the major product.

$$P_4(s) + 6Cl_2(g) \rightarrow 4PCl_3(l) \quad \text{; if chlorine gas is limited}$$

$$P_4(s) + 10Cl_2(g) \rightarrow 4PCl_5(s) \quad \text{; if chlorine gas is in excess}$$

PCl_3 is a fuming liquid while PCl_5 is an off-white solid.

6) **Sulfur** burns in chlorine gas to produce disulfur dichloride, an orange, evil-smelling liquid.

$$2S(s) + Cl_2(g) \rightarrow S_2Cl_2(l)$$

7) **Chlorine** obviously does not react with chlorine gas.

8) **Argon** does not react with chlorine gas to form any chlorides.

Reaction with water, H_2O

1) **Sodium** catches fire in cold water and a violently exothermic reaction occurs to form sodium hydroxide and hydrogen gas.

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

2) **Magnesium** reacts very slowly with cold water, taking several days to collect a test tube of hydrogen gas and a weakly alkaline magnesium hydroxide solution.

$$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g) \quad \text{; very slow}$$

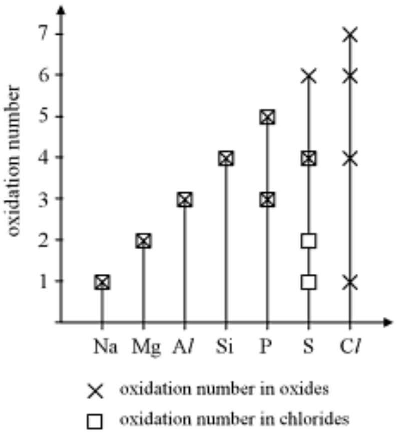
However, it reacts rapidly with steam to produce magnesium hydroxide and hydrogen gas.

$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g) \quad \text{; very fast}$$

Variation in oxidation number of Period 3 oxides and chlorides

1) Oxidation number of a Period 3 oxide or chloride corresponds to the **number of electrons used for bonding**. It is always positive because oxygen is more electronegative than any of the element.

2) The maximum oxidation number is the **same as Group number**. This corresponds to the total number of valence electrons.



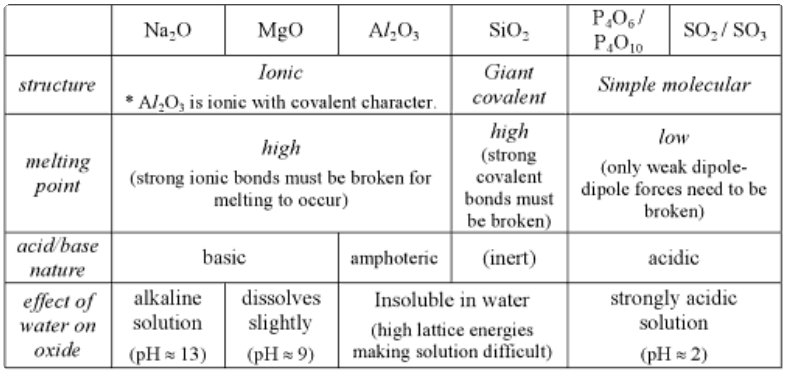
3) i. In the oxides, the maximum oxidation number increases from +1 in Na to +6 in S.
   ii. In the chlorides, the maximum oxidation number increases from +1 in Na to +5 in P.

4) Phosphorus and sulfur show several oxidation numbers because they can expand their octet through the excitation of electrons to the empty 3d orbitals.

5) For example:
   i. In SO_2, S has oxidation number +4 because only four electrons are used for bonding.
   ii. In SO_3, S has oxidation number +6 because all six electrons are used for bonding.

10.3 Period 3 Oxides

Summary of the properties of Period 3 oxides.



	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_6 / P_4O_{10}	SO_2 / SO_3
structure	*Ionic* * Al_2O_3 is ionic with covalent character.			*Giant covalent*	*Simple molecular*	
melting point	*high* (strong ionic bonds must be broken for melting to occur)			*high* (strong covalent bonds must be broken)	*low* (only weak dipole-dipole forces need to be broken)	
acid/base nature	basic		amphoteric	(inert)	acidic	
effect of water on oxide	alkaline solution (pH ≈ 13)	dissolves slightly (pH ≈ 9)	Insoluble in water (high lattice energies making solution difficult)		strongly acidic solution (pH ≈ 2)	

Reaction with water, H_2O

1) **Sodium oxide** reacts exothermically with cold water to form sodium hydroxide. A **strongly alkaline** solution of sodium hydroxide is produced.

$$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq) \quad ; pH = 13$$

2) **Magnesium oxide** reacts **slightly** with water to the extent that it is almost insoluble. A **weakly alkaline** solution of magnesium hydroxide is produced.

$$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq) \quad ; pH = 9$$

3) **Aluminium oxide** does not react or dissolve in water due to its high lattice energy.

4) **Silicon dioxide** does not react or dissolve in water due to the strong covalent bonds.

5) Phosphorus oxides react with water to form **acidic solutions**(pH = 2).
Phosphorus(III) oxide reacts with water to form phosphorous acid.

$$P_4O_6(s) + 6H_2O(l) \rightarrow 4H_3PO_3(aq)$$

Phosphorus(V) oxide reacts with water to form phosphoric(V) acid.

$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

6) Sulfur oxides react with water to form **acidic solutions**(pH = 2).
Sulfur dioxide reacts with water to give sulfurous acid or sulfuric(IV) acid.

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

Sulfur trioxide reacts violently with water to form a mist of sulfuric acid.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

Acid-base behaviour of Period 3 oxides

1) Going across Period 3, the nature of the oxide changes from **basic(Na_2O, MgO)** to **amphoteric(Al_2O_3)** then to **acidic(SiO_2, P_4O_6/P_4O_{10}, SO_2/SO_3)**. The **acidity of the oxides increases** across the Period.

2) **Sodium and magnesium oxides** are **basic oxides**, they react with acid to give the corresponding **salts and water**.

$$Na_2O(s) + 2HCl(aq) \rightarrow 2NaCl(aq) + H_2O(l)$$
$$MgO(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2O(l)$$

3) **Aluminium oxide** is **amphoteric**, it can react with **both acid and base**. Aluminium oxide reacts with hot and concentrated acids to give salt and water

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

Aluminium oxide reacts with hot and concentrated sodium hydroxide to give sodium aluminate.

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow \underset{\text{sodium aluminate}}{2NaAl(OH)_4(aq)}$$

4) **Silicon dioxide** is an **acidic oxide**, it reacts with hot and concentrated sodium hydroxide to give a colourless solution of sodium silicate.

$$SiO_2(s) + 2NaOH(aq) \rightarrow \underset{\text{sodium silicate}}{Na_2SiO_3(aq)} + H_2O(l)$$

5) Phosphorus oxides are **acidic oxides**, they react with alkalis to form salts and water.
Phosphorus(III) oxide reacts with sodium hydroxide to form sodium phosphate(III) and water.

$$P_4O_6(s) + 12NaOH(aq) \rightarrow 4Na_3PO_3(aq) + 6H_2O(l)$$

Phosphorus(V) oxide reacts with sodium hydroxide to form sodium phosphate(V) and water.

$$P_4O_{10}(s) + 12NaOH(aq) \rightarrow 4Na_3PO_4(aq) + 6H_2O(l)$$

6) Sulfur oxides are **acidic oxides**, they react with alkalis to form salt and water.
Sulfur dioxide reacts with sodium hydroxide to form sodium sulfate(IV) and water.

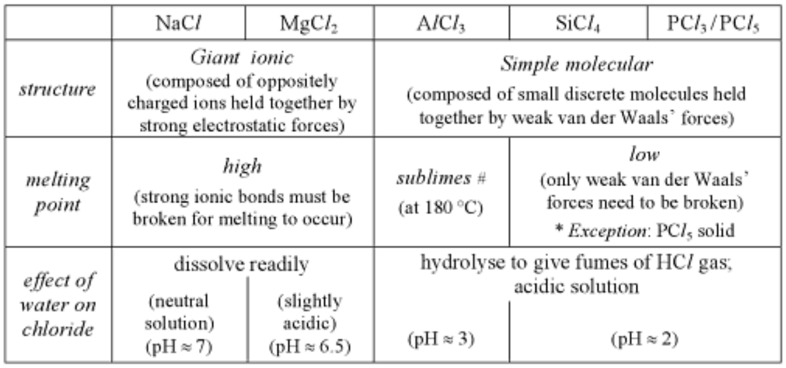
$$SO_2(g) + 2NaOH(aq) \rightarrow Na_2SO_3(aq) + H_2O(l)$$

Sulfur trioxide reacts with sodium hydroxide to form sodium sulfate(VI) and water.

$$SO_3(g) + 2NaOH(aq) \rightarrow Na_2SO_4(aq) + H_2O(l)$$

10.4 Period 3 Chlorides

Summary of the properties of Period 3 chlorides



	NaCl	$\mathrm{MgCl_2}$	$\mathrm{AlCl_3}$	$\mathrm{SiCl_4}$	$\mathrm{PCl_3/PCl_5}$
structure	*Giant ionic* (composed of oppositely charged ions held together by strong electrostatic forces)		*Simple molecular* (composed of small discrete molecules held together by weak van der Waals' forces)		
melting point	*high* (strong ionic bonds must be broken for melting to occur)		*sublimes* # (at 180 °C)	*low* (only weak van der Waals' forces need to be broken) * *Exception*: $\mathrm{PCl_5}$ solid	
effect of water on chloride	dissolve readily (neutral solution) (pH ≈ 7)	(slightly acidic) (pH ≈ 6.5)	hydrolyse to give fumes of HCl gas; acidic solution (pH ≈ 3)	(pH ≈ 2)	

Reaction with water, H_2O

1) **Sodium chloride** dissolves in water to form a **neutral solution** of sodium chloride.

$$\mathrm{NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)} \quad ;\ \mathrm{pH} = 7$$

2) **Magnesium chloride** dissolves in water with slight hydrolysis to form a solution of magnesium chloride.

$$\mathrm{MgCl_2(s) + 6H_2O \rightarrow \underbrace{[Mg(H_2O)_6]^{2+}(aq)}_{\text{hexaaquamagnesium ions}} + 2Cl^-(aq)}$$

$$\mathrm{[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5(OH)]^+(aq) + H_3O^+(aq)} \quad ;\ \mathrm{pH} = 6.5$$

3) **Aluminium chloride**, $AlCl_3$ hydrolyses in water to give an acidic solution, white fumes of hydrogen chloride gas are formed.

$$\mathrm{AlCl_3(s) + 6H_2O(l) \rightarrow [Al(H_2O)_6]^{3+}(aq) + 3Cl^-(aq)}$$

$$\mathrm{[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)} \quad ;\ \mathrm{pH} = 3$$

4) **Silicon tetrachloride** undergoes complete hydrolysis in water to form a strongly acidic solution, white fumes of hydrogen chloride gas are formed.

$$\mathrm{SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(g)} \quad ;\ \mathrm{pH} = 2$$

5) **Phosphorus(III) chloride** reacts violently with water in a hydrolysis reaction to give a strongly acidic solution and fumes of hydrogen chloride gas.

$$\mathrm{PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(g)} \quad ;\ \mathrm{pH} = 2$$

Phosphorus(V) chloride is an off-white ionic solid at room temperature and sublimes at 163 °C to give phosphorus(III) chloride and chlorine gas.

$$PCl_5(s) \rightleftharpoons PCl_3(l) + Cl_2(g)$$

It reacts violently with water in a hydrolysis reaction to give a strongly acidic solution and fumes of hydrogen chloride gas.

$$PCl_5(s) + 4H_2O(l) \rightarrow H_3PO_4(aq) + 5HCl(g) \quad ; pH = 2$$

6) The **acidity of the chlorides increases** across the Period as the nature of the chlorides changes from ionic to covalent.

CHAPTER 11: Group II

Learning outcomes:

(a) *describe the reactions of the elements with oxygen, water and dilute acids.*
(b) *describe the behaviour of the oxides, hydroxides and carbonates with water and with dilute acids.*
(c) *describe the thermal decomposition of the nitrates and carbonates.*
(d) *interpret, and make predictions from, the trends in physical and chemical properties of the elements and their compounds.*
(e) *explain the use of magnesium oxide as a refractory lining material*
(f) *describe and explain the use of lime in agriculture.*

11.1 Physical Properties of Group II Elements

Introduction to Group II elements

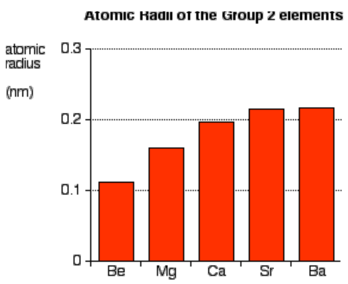
1) Group II elements(also called the 'alkaline earth metals') are s-block elements with a characteristic outer shell configuration ns^2.

Group II elements		*Atomic no.*	*Electronic configuration*
beryllium	Be	4	$1s^2\,\mathbf{2s^2}$
magnesium	Mg	12	$1s^2\,2s^2\,2p^6\,\mathbf{3s^2}$
calcium	Ca	20	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,\mathbf{4s^2}$
strontium	Sr	38	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^6\,\mathbf{5s^2}$
barium	Ba	56	$[Xe]\,\mathbf{6s^2}$

2) Group II elements are very reactive metals. They have low electronegativity and are readily oxidised, they **always** exhibit an oxidation state of +2 in their compounds. This is because the two outer s electrons are readily lost during a reaction to achieve a noble gas configuration.

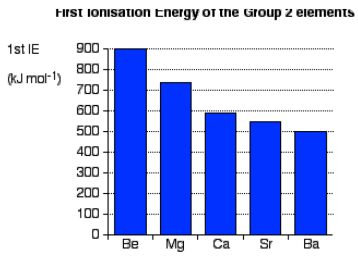
$$M \rightarrow M^{2+} + 2e^- \quad ; \text{where } M = \text{A Group II element}$$

Variation in atomic radius



1) The atomic radius **increases** going down the Group. This is because going down the Group, each succeeding element has **one more shell of electrons**. The distance between nucleus and outer electrons are progressively further.

Variation in first ionisation energy

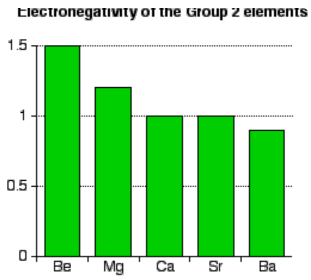


1) The first ionisation energy **decreases** down the Group. This is because the distance between nucleus and outer electrons increases, and the outer electrons are more shielded.

2) These two factors outweigh the increasing nuclear charge. So, the attractive force between nucleus and outer electrons decreases and less energy is required to remove the electron.

Variation in electronegativity

1) Electronegativity **decreases** down the Group. This is because the distance between the nucleus and the bonded pair of electrons increases down the Group. Therefore the electrons are held less strongly by the nucleus.


Electronegativity of the Group 2 elements

2) In other words, the reducing power(and reactivity) increases down the Group.

11.2 Reactions of Group II Elements

Reaction with oxygen gas, O_2

1) All Group II elements(except beryllium) burn in oxygen with a bright flame to form monoxides.

$2M(s) + O_2(g) \rightarrow 2MO(s)$; where M = A Group II element

2) i. $2Mg(s) + O_2(g) \rightarrow 2MgO(s)$; burns with brilliant white flame
ii. $2Ca(s) + O_2(g) \rightarrow 2CaO(s)$; burns with brick red flame
iii. $2Sr(s) + O_2(g) \rightarrow 2SrO(s)$; burns with crimson red flame
iv. $2Ba(s) + O_2(g) \rightarrow 2BaO(s)$; burns with apple green flame


Magnesium burning


Calcium burning


Strontium burning


Barium burning

Reaction with water, H_2O

1) All Group II elements(except beryllium) reacts with water to form hydroxides and hydrogen gas.

   $M(s) + 2H_2O(l) \rightarrow M(OH)_2(aq) + H_2(g)$; where M = A Group II element

2) i. **Beryllium** has no reaction with cold water or steam even at red heat due to the formation of protective oxide layer on its surface.

   ii. **Magnesium** reacts very slowly with cold water, taking several days to collect a test tube of hydrogen gas and a weakly alkaline magnesium hydroxide solution.

   $$Mg(s) + 2H_2O(l) \rightarrow Mg(OH)_2(aq) + H_2(g) \quad \text{; very slow, pH = 9}$$

   However, it reacts rapidly with steam to produce magnesium oxide and hydrogen gas. This is because the hydroxide formed thermally decompose into an oxide.

   $$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g) \quad \text{; very fast}$$

   iii. **Calcium**, **strontium** and **barium** reacts vigorously with cold water to give hydroxides.

   $$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + H_2(g)$$
   $$Sr(s) + 2H_2O(l) \rightarrow Sr(OH)_2(aq) + H_2(g)$$
   $$Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$$

   Note:

   i. $Ca(OH)_2$ appears as white precipitate. It is sparingly soluble therefore a weakly alkaline solution will also be formed.

3) The reactivity of the elements with water **increases** down the Group. In other words, they become **more soluble** going down the Group.

Reaction with acids

1) All Group II elements react with acid to give hydrogen gas and the corresponding salt.

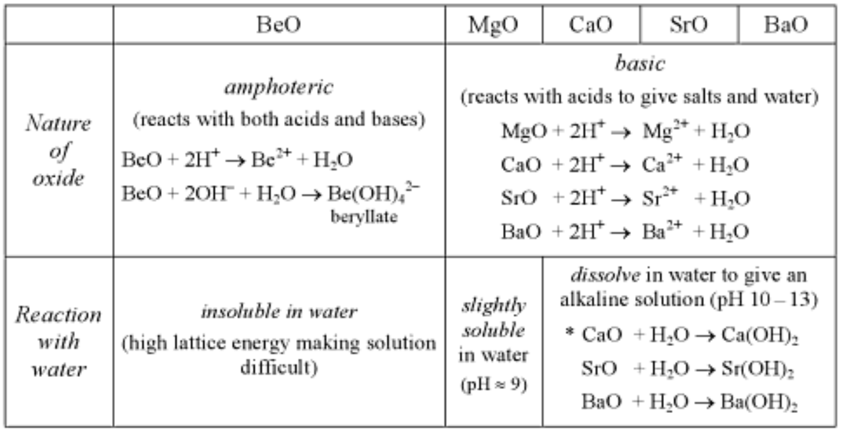
   $M(s) + H^+(aq) \rightarrow M^{2+}(aq \text{ or } s) + H_2(g)$; where M = A Group II element

2) i. Beryllium reacts slowly with acids and has no reaction at room temperature.

   ii. The rest of Group II metals react with **increasing vigorous** going down the Group.

11.3 Group II Oxides, Hydroxides and Carbonates

Group II oxides



	BeO	MgO	CaO	SrO	BaO
Nature of oxide	*amphoteric* (reacts with both acids and bases) $BeO + 2H^+ \rightarrow Be^{2+} + H_2O$ $BeO + 2OH^- + H_2O \rightarrow Be(OH)_4^{2-}$ beryllate	*basic* (reacts with acids to give salts and water) $MgO + 2H^+ \rightarrow Mg^{2+} + H_2O$ $CaO + 2H^+ \rightarrow Ca^{2+} + H_2O$ $SrO + 2H^+ \rightarrow Sr^{2+} + H_2O$ $BaO + 2H^+ \rightarrow Ba^{2+} + H_2O$			
Reaction with water	*insoluble in water* (high lattice energy making solution difficult)	*slightly soluble* in water (pH ≈ 9)	*dissolve* in water to give an alkaline solution (pH 10 – 13) * $CaO + H_2O \rightarrow Ca(OH)_2$ $SrO + H_2O \rightarrow Sr(OH)_2$ $BaO + H_2O \rightarrow Ba(OH)_2$		

1) All Group II oxides(except beryllium oxide) reacts with water, at least to some extent to give the corresponding hydroxides.

2) i. Beryllium oxide is insoluble because Be^{2+} ion is a very small and highly charged ion, thus making the lattice energy of BeO exceptionally high.
   ii. Magnesium oxide is only slightly soluble in water, producing a weakly alkaline solution.
   iii. Addition of calcium oxide with water is a very vigorous and exothermic reaction.

3) All Group II oxides(except beryllium oxide) are **basic**. They react with acids to give the corresponding salt and water.

4) Beryllium oxide, on the other hand, is amphoteric. It reacts with both acid and base.

Group II hydroxides

1) Group II hydroxides are not very soluble, and they do not react with water. However, the solubility **increases** down the Group.

2) i. Magnesium hydroxide is only slightly soluble in water, with a pH of about 9.
   ii. Calcium hydroxide(slaked lime) is moderately soluble to give a solution called "lime water".

3) Group II hydroxides behave as a base and react with acids to give the corresponding salt and water.

Group II carbonates

1) Group II carbonates are mainly insoluble, and they do not react with water. The solubility **decreases** down the Group.

2) Group II carbonates react with acid to form salt, carbon dioxide and water.
$MCO_3(s) + H^+ \rightarrow M^{2+}(aq\ or\ s) + CO_2(g) + H_2O(l)$; where M = A Group II element

11.4 Thermal Decomposition

Thermal decomposition of Group II salts

1) In general, compounds with **high charge density cation** and **large anion size** tend to decompose more easily(less stable on heat) due to the **greater polarisation of anion by the cation**.

2) Thermal decomposition of Group II salts **decreases** down the Group. In other words, the thermal stability of Group II salts **increases** down the Group.

3) This is because going down the Group, the cation size increases while the anion size remains unchanged. Therefore the charge density and polarising power of cation decreases and the anion cloud is less polarised. The compound is more stable on heating.

4) Group II salts are less stable compared to Group I salts due to the higher charge density of M^{2+} ion.

Thermal decomposition of Group II nitrates

1) All Group II nitrates decompose on heating to give the corresponding metal oxide, brown nitrogen monoxide gas and oxygen gas.
$2M(NO_3)_2(s) \rightarrow 2MO(s) + 4NO_2(g) + O_2(g)$; where M = A Group II element

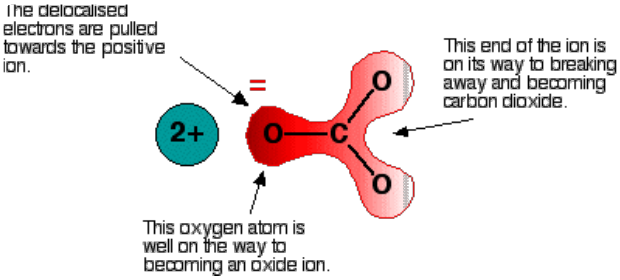
2) Thermal stability of Group II nitrates **increases** down the Group. This is because the cation size increases down the Group, this reduces the charge density and polarising power of cation. The nitrate ion is less polarised and the compound is more stable.

Thermal decomposition of Group II carbonates

1) All Group II carbonates decompose on heating to give the corresponding metal oxide and carbon dioxide gas.

$$MCO_3(s) \rightarrow MO(s) + CO_2(g) \quad ; \text{where } M = \text{A Group II element}$$

2) Thermal stability of Group II carbonates **increases** down the Group. This is because the cation size increases down the Group, this reduces the charge density and polarising power of cation. The carbonate ion is less polarised and the compound is more stable.



11.5 Uses of Group II Compounds

1) Some ceramics contain magnesium oxide, MgO and they can be used as:
   i. electrical insulators in industrial electrical cables.
   ii. a refractory in furnace linings because it has a high melting point.(However, it cannot be used in furnaces where acid is present due to its basic nature)
   iii. in fire-resistant wall boards.

2) Calcium compounds have many uses, this includes:
   i. calcium carbonate(limestone) to make cement.
      - It is roasted in a lime kiln so that it decomposes into calcium oxide, CaO (quicklime). The cement made is mixed with rocks to make concrete.
   ii. using calcium hydroxide/oxide/carbonate to treat acidic soil as they react with acids.

CHAPTER 12: Group VII

__Learning outcomes:__

(a) describe the colours of, and the trend in volatility of chlorine, bromine and iodine.
(b) interpret the volatility of the elements in terms of van der Waals' forces.
(c) describe the relative reactivity of the elements as oxidising agents.
(d) describe and explain the reactions of the elements with hydrogen.
(e) (i) describe and explain the relative thermal stabilities of the hydrides.
  (ii) interpret these relative stabilities in terms of bond energies.
(f) describe and explain the reactions of halide ions with
  (i) aqueous silver ions followed by aqueous ammonia.
  (ii) concentrated sulfuric acid.
(g) outline a method for the manufacture of chlorine from brine by a diaphragm cell.
(h) describe and interpret in terms of changes of oxidation number the reaction of chlorine with cold, and with hot, aqueous sodium hydroxide.
(i) explain the use of chlorine in water purification.
(j) state the industrial importance and environmental significance of the halogens and their compounds (e.g. for bleaches, PVC, halogenated hydrocarbons as solvents, refrigerants and in aerosols).

12.1 Physical Properties of Group VII Elements

Introduction to Group VII elements

1) Group VII elements(also called the '**halogens**') are p-block elements with a characteristic outer shell configuration of ns^2np^5.

Group VII elements		*Atomic no.*	*Electronic configuration*
fluorine	F	9	$1s^2\,\mathbf{2s^2\,2p^5}$
chlorine	Cl	17	$1s^2\,2s^2\,2p^6\,\mathbf{3s^2\,3p^5}$
bromine	Br	35	$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,\mathbf{4s^2\,4p^5}$
iodine	I	53	$[Kr]\,4d^{10}\,\mathbf{5s^2\,5p^5}$
astatine	At	85	$[Xe]\,4f^{14}\,5d^{10}\,\mathbf{6s^2\,6p^5}$

2) Some common physical properties of the halogens are as follow:

	Colour and state at r.t.	*b.p. / °C*	*Solubility*	
			in water	*in organic solvent*
F_2	pale yellow gas	–188	–	–
Cl_2	yellow-green gas	–35	moderately soluble	yellow solution
Br_2	dark red liquid	58	slightly soluble	orange-brown solution
I_2	black solid	183	insoluble	violet/purple solution

Note:

i. Bromine is a dark red liquid but forms reddish-brown gas.

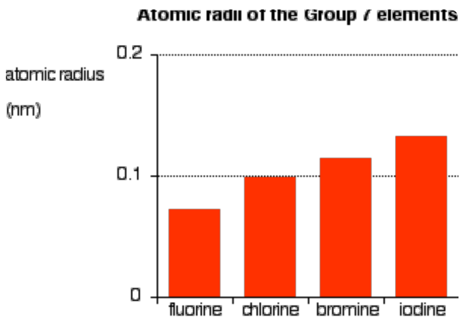
ii. Iodine is a black solid but forms a **purple vapour** on gentle heating.

iii. The trend is the halogens get **darker** going down the Group.

iv. Iodine is insoluble in water but it dissolves in potassium iodide, KI solution due to the formation of I_3^- ion.

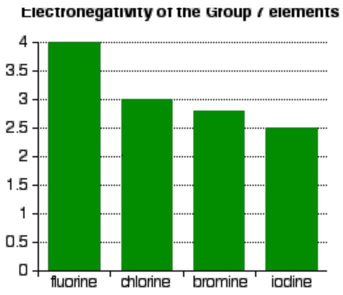
v. In organic solvents, halogens exist as free molecules, X_2.

Variation in atomic radius



1) The atomic radius of halogens **increases** going down the Group. This is because going down the Group, each succeeding element has **one more shell of electrons**. The distance between nucleus and outer electrons are progressively further.

Variation in electronegativity

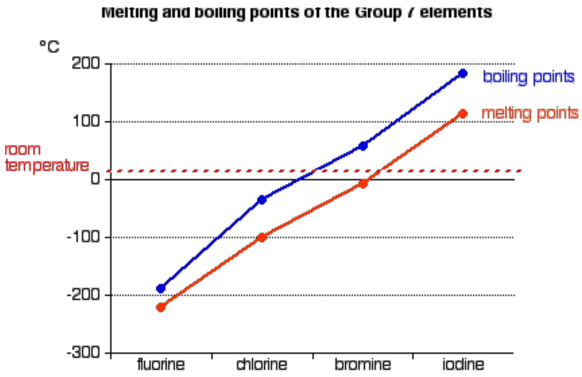


1) The electronegativity of halogens **decreases** down the Group. This is because going down the Group, the distance between the nucleus and bonding electrons increases. Therefore the electrons are attracted less strongly by the nucleus.

2) Fluorine is the most electronegative element, and is assigned an electronegativity of 4.0 on the Pauling scale.

3) In other words, the oxidising power(and reactivity) decreases down the Group.

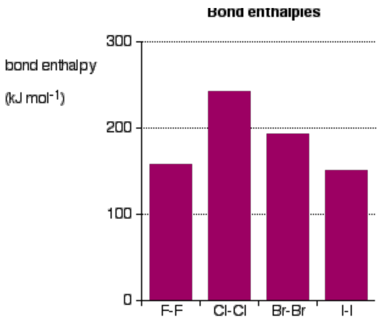
Variation in volatility



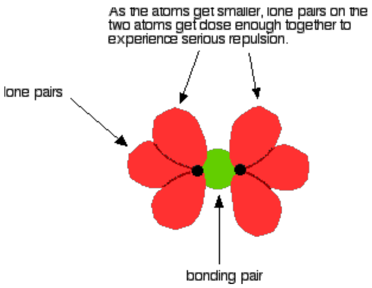
1) The volatility of halogens **decreases** down the Group. This is because going down the Group, the number of electrons in the halogen molecules increases. More temporary dipoles can be set up and the **strength of van der Waal's forces increases**.

2) Hence the boiling point increases and the halogens become less volatile.

Variation in bond enthalpy



1) Excluding fluorine, the bond enthalpy of halogens **decreases** down the Group. This is because going down the Group, the **distance between the nucleus and bonding pair of electrons increases**. The bonding electrons are less attracted and as a result, the covalent bond gets weaker. Less energy is required to break the bond.



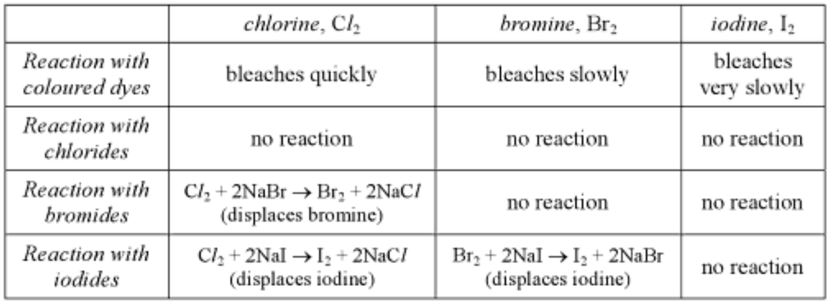
2) The bond enthalpy is exceptionally low because F_2 is a very small molecule with six lone pairs of electrons. The **repulsion** created between these electrons reduces the energy needed to break the covalent bond.

12.2 Reactions of Group VII Elements

Halogens as oxidising agent

1) Halogens are powerful oxidising agents. However, the oxidising ability **decreases** down the Group. Therefore, F_2 is the most powerful oxidising agent while I_2 is the weakest.

2) This is reflected in their ability to oxidise other halide ions, as follow:



	chlorine, Cl_2	*bromine*, Br_2	*iodine*, I_2
Reaction with coloured dyes	bleaches quickly	bleaches slowly	bleaches very slowly
Reaction with chlorides	no reaction	no reaction	no reaction
Reaction with bromides	$Cl_2 + 2NaBr \rightarrow Br_2 + 2NaCl$ (displaces bromine)	no reaction	no reaction
Reaction with iodides	$Cl_2 + 2NaI \rightarrow I_2 + 2NaCl$ (displaces iodine)	$Br_2 + 2NaI \rightarrow I_2 + 2NaBr$ (displaces iodine)	no reaction

Note:

i. **A halogen can oxidise the halide ion below it** on the Periodic Table, fluorine is excluded in this argument because it is too powerful as an oxidising agent and will oxidise water into oxygen.

ii. If chlorine is able to displace bromide ion from its aqueous solution, this indicates that chlorine has a higher tendency to be reduced and to accept electrons to form ions.

Reaction with hydrogen gas, H_2

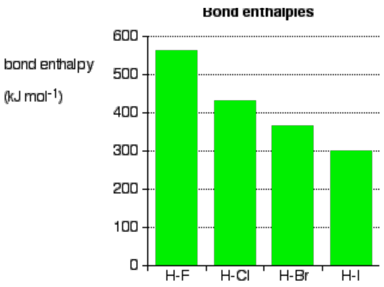
1) All halogens react with hydrogen gas to form hydrides, HX.

$$H_2 + X_2 \rightarrow 2HX \quad ; \text{where } X = \text{A halogen}$$

2) i. $H_2(g) + F_2(g) \rightarrow 2HF(g)$; explosive reaction under all temperature
ii. $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$; explosive reaction under sunlight
iii. $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$; slow reaction on heating
iv. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; an equilibrium mixture is obtained

3) The reactivity of halogens towards hydrogen gas decreases down the Group due to the decrease in oxidising ability of the halogens.

Thermal stability of hydrogen halides, HX



1) The thermal stability of the hydrogen halides, HX **decreases** down the Group. This is because the size of the atom increases and so the **strength of the H-X bond decreases**. In other words, the hydrogen halides become less stable on heating going down the Group.

2) i. Hydrogen iodide decomposes easily on heating, thick purple fumes of I_2 are observed.
   ii. Hydrogen bromide decomposes slightly, little orange-brown of Br_2 is observed.
   iii. Hydrogen chloride and fluoride are stable on heating.

3) When hydrogen halides decompose, X^- ions are oxidised. The ease of oxidation down the Group indicates the increase in reducing ability of X^- ion. Hence, I^- is the strongest reducing agent while F^- is the weakest.

Reaction with aqueous sodium thiosulfate, $Na_2S_2O_3$

1) Chlorine and bromine can oxidise sodium thiosulfate, $Na_2S_2O_3$ to sodium sulfate, Na_2SO_4. The oxidation number of sulfur changes from +2 to +6.

$$4Cl_2 + S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Cl^-$$
$$4Br_2 + S_2O_3^{2-} + 5H_2O \rightarrow 2SO_4^{2-} + 10H^+ + 8Cl^-$$

2) However, iodine can only oxidise sodium thiosulfate to sodium tetrathionate, $Na_2S_4O_6$. The oxidation number of sulfur changes from +2 to +2.5.

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Reaction with aqueous iron(II) ions, Fe^{2+}

1) Chlorine and bromine would oxidise Fe^{2+} to Fe^{3+} but not iodine.

$$Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$$
$$Br_2 + 2Fe^{2+} \rightarrow 2Br^- + 2Fe^{3+}$$

Reaction with iron, Fe

1) i. When chlorine gas is passed over hot iron, iron(III) chloride is formed. The oxidation number of iron changes from 0 to +3.

$Cl_2 + Fe \rightarrow FeCl_3$; rapid and vigorous reaction

ii. When bromine vapour is passed over hot iron, iron(III) chloride is formed. The oxidation number of iron changes from 0 to +3.

$Br_2 + Fe \rightarrow FeBr_3$; less rapid and vigorous reaction

iii. When iodine vapour is passed over hot iron, iron(II) chloride is formed. The oxidation number of iron changes from 0 to only +2.

$I_2 + Fe \rightarrow FeI_2$; even less vigorous

Reaction with hot and cold alkali

1) Chlorine undergoes **disproportionation** when it reacts with alkali. In this reaction, chlorine is **simultaneously oxidised and reduced**.

2) In cold alkali(15 °C), the reaction is as follow:

$$Cl_2(aq) + 2NaOH(aq) \rightarrow NaCl(aq) + NaClO(aq) + H_2O(l)$$

The ionic equation is:

$$Cl_2(aq) + 2OH^-(aq) \rightarrow Cl^-(aq) + ClO^-(aq) + H_2O(l)$$

3) In cold alkali, the oxidation number of chlorine changes from **0** in Cl_2 to **-1** in Cl^-(reduction) and **+1** in ClO^-(oxidation).

4) In hot alkali(70 °C), the reaction is as follow:

$$3Cl_2(aq) + 6NaOH(aq) \rightarrow 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$$

The ionic equation is:

$$3Cl_2(aq) + 6OH^-(aq) \rightarrow 5Cl^-(aq) + ClO_3^-(aq) + 3H_2O(l)$$

5) In hot alkali, the oxidation number of chlorine changes from **0** in Cl_2 to **-1** in Cl^-(reduction) and **+5** in ClO_3^-(oxidation).

6) This reaction is the result of disproportionation of chlorate(I) ions in the presence of heat.

$$3ClO^-(aq) \rightarrow 2Cl^-(aq) + ClO_3^-$$

7) Bromine and iodine react in a similar manner. However, the bromate(I) and iodate(I) ions formed disproportionate readily at all temperatures.

12.3 Reactions of Halide Ions

Introduction to halide ions, X^-

1) The halogens are typical non-metals, they:
   i. form singly charge negative ions, X^-.
   ii. form ionic compounds with metals and covalent compounds with non-metals.

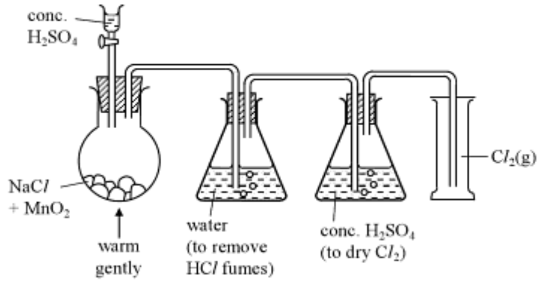
Preparation of halogens in the laboratory

1) Halogens can be prepared in the laboratory by the oxidation of X^- ions using manganese(IV) oxide, MnO_2 in the presence of concentrated sulfuric acid.

$$2X^- + MnO_2 + 4H^+ \rightarrow X_2 + Mn^{2+} + 2H_2O \quad ; \text{where } X = \text{A halogen}$$

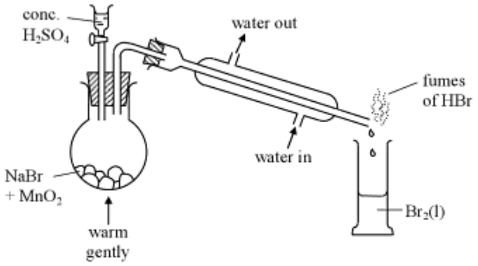
2) The apparatus needed is shown below:

Laboratory preparation of chlorine: $2Cl^- + MnO_2 + 4H^+ \rightarrow Cl_2 + Mn^{2+} + 2H_2O$

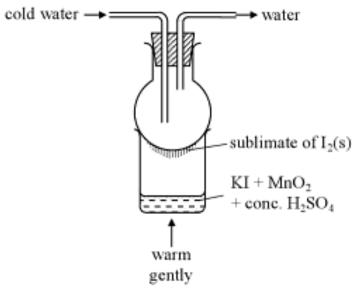


Note:
i. In each case, hydrogen halide is also formed from the reaction of X^- with H_2SO_4 and must be removed in order to obtain pure halogen.

Laboratory preparation of bromine: $2Br^- + MnO_2 + 4H^+ \rightarrow Br_2 + Mn^{2+} + 2H_2O$



Laboratory preparation of iodine: $2I^- + MnO_2 + 4H^+ \rightarrow I_2 + Mn^{2+} + 2H_2O$



Test for halide ions(reaction with silver ion, Ag^+)

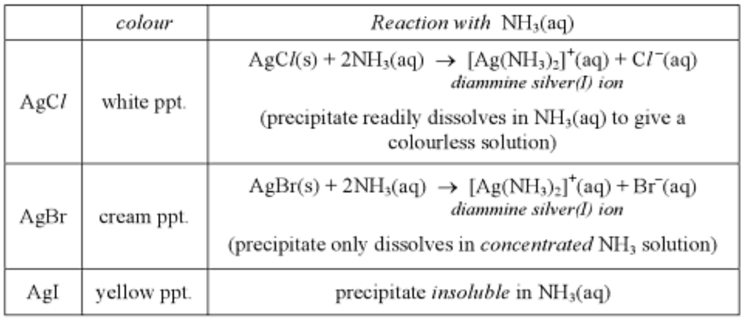
1) Halide ions are colourless in their aqueous solutions and a test is needed to identify their presence.

2) **Silver ions, Ag^+** can be used to test halide ions because the silver halide is formed as precipitate.

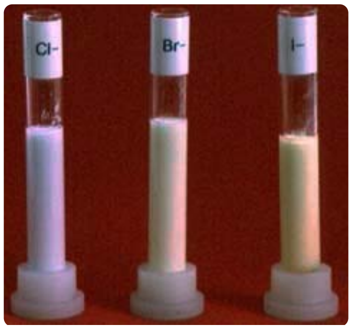
$$Ag^+(aq) + X^-(aq) \rightarrow AgX(aq \text{ or } s) \quad ; \text{where } X = \text{A halogen}$$

The silver halides formed can be differentiated by:
   - i. their colour.
   - ii. their reaction with dilute aqueous ammonia, NH_3.

3) The test is summarised below: (Fluoride does not form precipitates)

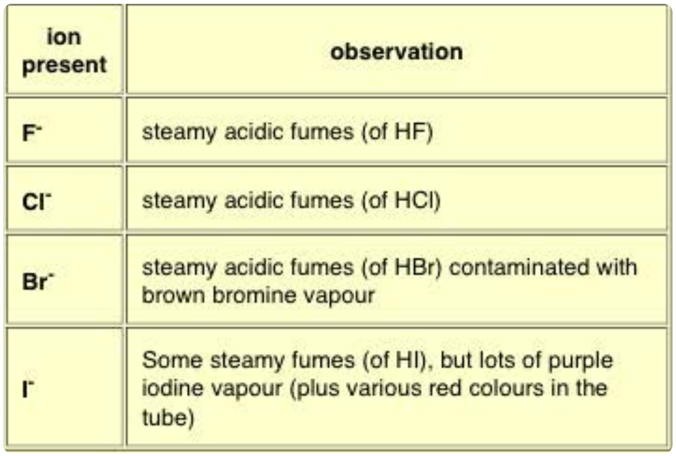


	colour	*Reaction with* $NH_3(aq)$
$AgCl$	white ppt.	$AgCl(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Cl^-(aq)$ *diammine silver(I) ion* (precipitate readily dissolves in $NH_3(aq)$ to give a colourless solution)
AgBr	cream ppt.	$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+(aq) + Br^-(aq)$ *diammine silver(I) ion* (precipitate only dissolves in *concentrated* NH_3 solution)
AgI	yellow ppt.	precipitate *insoluble* in $NH_3(aq)$



4) NH_3 is used as a confirmatory test as cream and white precipitate may be hard to distinguish.

5) Alternatively, concentrated sulfuric acid can be used to test halide ions:

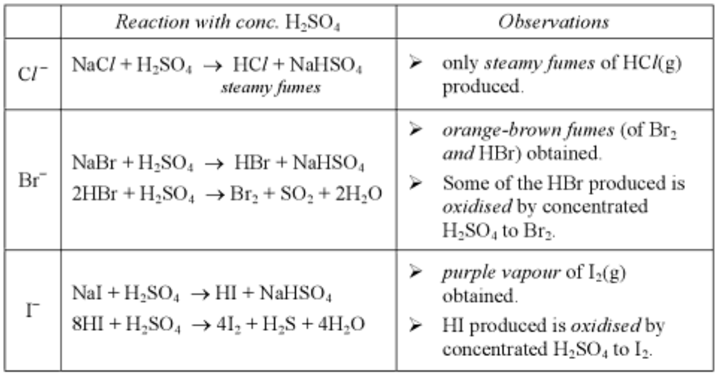


ion present	**observation**
F^-	steamy acidic fumes (of HF)
Cl^-	steamy acidic fumes (of HCl)
Br^-	steamy acidic fumes (of HBr) contaminated with brown bromine vapour
I^-	Some steamy fumes (of HI), but lots of purple iodine vapour (plus various red colours in the tube)

Note:
- i. F^- and Cl^- can be differentiated using the silver ion test.
- ii. The chemistry of this test is explained next.

Reaction with concentrated sulfuric acid, H_2SO_4

1) When halides(NaX) are reacted with concentrated sulfuric acid, the following happens:



	Reaction with conc. H_2SO_4	*Observations*
Cl^-	$NaCl + H_2SO_4 \rightarrow \underset{\textit{steamy fumes}}{HCl} + NaHSO_4$	➢ only *steamy fumes* of $HCl(g)$ produced.
Br^-	$NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$ $2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$	➢ *orange-brown fumes* (of Br_2 *and* HBr) obtained. ➢ Some of the HBr produced is *oxidised* by concentrated H_2SO_4 to Br_2.
I^-	$NaI + H_2SO_4 \rightarrow HI + NaHSO_4$ $8HI + H_2SO_4 \rightarrow 4I_2 + H_2S + 4H_2O$	➢ *purple vapour* of $I_2(g)$ obtained. ➢ HI produced is *oxidised* by concentrated H_2SO_4 to I_2.

2) The **ease of oxidation of halide ions increases** from Cl^- to I^- because the tendency to be oxidised(the reducing power) increases. The HBr and HI produced are oxidised to Br_2 and I_2 respectively while the HCl produced is not. (HI is oxidised readily while HBr is not)

3) To prepare HI or HBr, phosphoric acid, H_3PO_4 is used instead because all halides react to give the corresponding hydrides.

$$2NaX + H_3PO_4 \rightarrow 2HX + Na_2HPO_4 \quad ; \text{where } X = \text{A halogen}$$

12.4 Uses of Halogens

1) Chlorine is used in the **chlorination of water to kill bacteria**. The chlorine undergoes disproportionation.

$$Cl_2(aq) + H_2O(l) \rightarrow HCl(aq) + HClO(aq)$$

Chloric(I) acid, HClO produced decomposes slowly to produce reactive oxygen atoms that kill bacteria in water.

$$HClO \rightarrow HCl + O$$

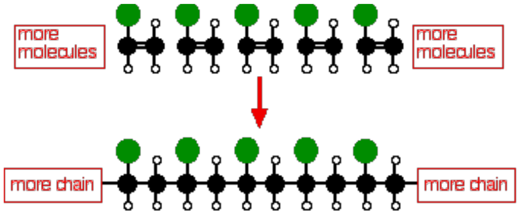
2) **Bleach** is an equal mixture of sodium chloride, NaCl and sodium chlorate(I), NaClO. Sodium chlorate(I) is a powerful oxidising agent and bleaches dye and other coloured molecules by oxidising them.

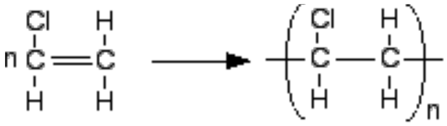
3) i. Halogens are also used in **chlorofluorocarbons(CFCs)**. CFCs are widely used as refrigerants, propellants and aerosols. They are also used as solvents for dry cleaning and generating foamed plastics like expanded polystyrene or polyurethane foam.

ii. Unfortunately, CFCs are largely responsible for destroying the ozone layer. In the high atmosphere, the carbon-chlorine bonds break to give chlorine free radicals and these radicals destroy the ozone. CFCs are now being replaced by less environmentally harmful compounds.

4) i. **Plastic PVC**(poly(chloroethene) or polyvinyl chloride) are made from halogen compounds.

ii. Poly(chloroethene) is made through polymerisation of organic molecules, the organic molecule is chloroethene, CH_2CHCl. These organic molecules join together repeatedly to form the polymer.




$$n\,\begin{matrix}Cl & & H\\ | & & |\\ C & = & C\\ | & & |\\ H & & H\end{matrix} \longrightarrow \left(\begin{matrix}Cl & & H\\ | & & |\\ -C & - & C-\\ | & & |\\ H & & H\end{matrix}\right)_n$$

iii. Poly(chloroethene) is used to make a wide range of things including guttering, plastic windows, electrical cable insulation, sheet materials for flooring and other uses, footwear, clothing, and so on.

5) Bromine and iodine are often used in the manufacture of dyes and drugs.

CHAPTER 13: Nitrogen and Sulfur

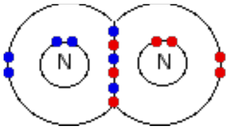
13.1 Nitrogen Compounds
13.2 Environmental Consequences of Using Nitrogen Compounds
13.3 Sulfur Compounds

Learning outcomes:

(a) explain the lack of reactivity of nitrogen.
(b) describe and explain:
  (i) the basicity of ammonia.
  (ii) the structure of the ammonium ion and its formation by an acid-base reaction.
  (iii) the displacement of ammonia from its salts.
(c) describe the Haber process for the manufacture of ammonia from its elements, giving essential operating conditions, and interpret these conditions (qualitatively) in terms of the principles of kinetics and equilibria.
(d) state the industrial importance of ammonia and nitrogen compounds derived from ammonia.
(e) state and explain the environmental consequences of the uncontrolled use of nitrate fertilisers.
(f) state and explain the natural and man-made occurrences of oxides of nitrogen and their catalytic removal from the exhaust gases of internal combustion engines.
(g) explain why atmospheric oxides of nitrogen are pollutants, including their catalytic role in the oxidation of atmospheric sulfur dioxide.
(h) describe the formation of atmospheric sulfur dioxide from the combustion of sulfur contaminated carbonaceous fuels.
(i) state the role of sulfur dioxide in the formation of acid rain and describe the main environmental consequences of acid rain.
(j) state the main details of the Contact process for sulfuric acid production.
(k) describe the use of sulfur dioxide in food preservation.

13.1 Nitrogen Compounds

The lack of reactivity of nitrogen



1) Nitrogen, N_2 exists as a diatomic molecule, two nitrogen atoms are bonded by a triple bond.

2) Nitrogen is **very unreactive** because the **bond energy is very high** (about +944 kJ mol^{-1}) and reactions involving nitrogen tend to break the entire bond.

3) However, nitrogen still undergoes the following reactions:
   i. When nitrogen and oxygen are struck by lightning in the atmosphere, nitrogen monoxide, NO is produced. In this case, the lightning provides the activation energy required to start the reaction.

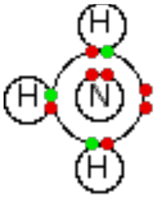
$$N_2(g) + O_2(g) \rightarrow 2NO(g) \quad ; \Delta H = +181 \text{ kJ mol}^{-1}$$

   ii. Magnesium nitride, Mg_3N_2 is formed when magnesium is heated in nitrogen. The reaction is exothermic because the ionic bond formed is much stronger than the original bonds and a net energy is released.

$$3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s) \quad ; \Delta H = -461 \text{ kJ mol}^{-1}$$

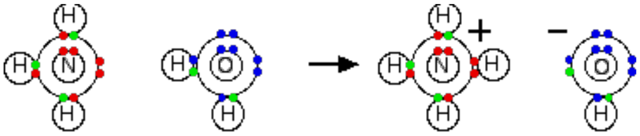
4) Carbon monoxide, CO with a triple bond and similarly high bond energy is more reactive because:
   i. **it has a dipole moment** hence the molecule is **polar**. They are more attractive to nucleophiles or electrophiles and this initiates a reaction to occur.
   ii. the reaction involving carbon monoxide **will normally not break the entire triple bond**. Instead, the bond is partially broken to produce a double-bonded carbon dioxide, CO_2.

Ammonia, NH_3 and its reactions



1) Ammonia, NH_3 is a trigonal pyramidal molecule with a net dipole moment, hence the molecule is polar.

2) Ammonia is a **weak base**, it is also a **Brønsted-Lowry base**, hence it is capable of accepting a hydrogen ion to form ammonium ion, NH_4^+.



3) i. **Ammonia reacts with acids** to form ammonium salts. For example, the reaction between ammonia and hydrogen chloride, HCl gas:

$$NH_3(g) + HCl(g) \rightarrow NH_4^+Cl^-$$

ii. **Ammonium salts react with bases** to liberate ammonia gas, salt and water is also formed. This is because ammonia is a weak base, the proton accepted is easily removed again. For example, the reaction between ammonium sulfate, $(NH_4)_2SO_4$ and calcium oxide, CaO:

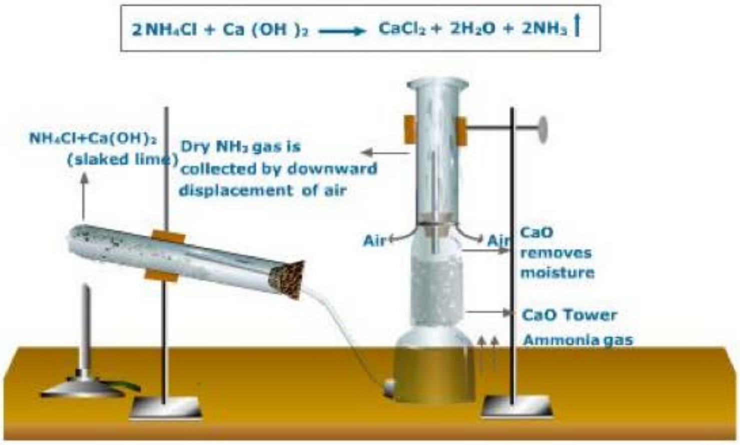
$$2NH_4Cl(s) + Ca(OH)_2(s) \rightarrow CaCl(s) + 2NH_3(g) + 2H_2O(l)$$

The ionic equation is:

$$NH_4^+(aq\ or\ s) + OH^-(aq) \rightarrow NH_3(g) + H_2O(l)$$

This is also a **common test for ammonium ions** in a compound. When a suspected compound is warmed with sodium hydroxide, NaOH solution, ammonia gas will be released if it contains ammonium ions. The ammonia gas can be confirmed by using a red litmus paper.

iii. This reaction can also be used **to prepare ammonia** in school laboratories, the setup is as follow:



Note:

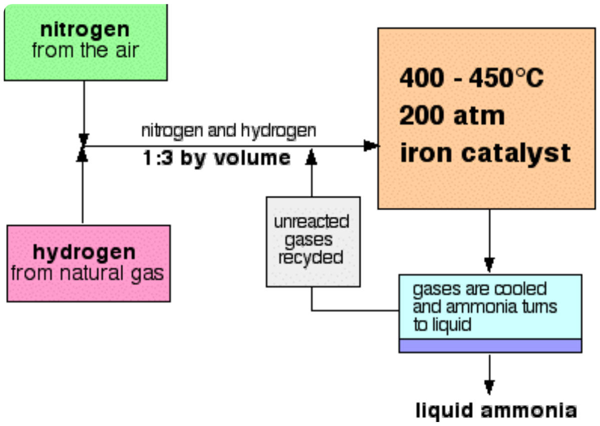
i. This reaction is also known as the displacement of ammonia.

ii. Calcium oxide, CaO is used as a drying agent. Other drying agents like calcium chloride, $CaCl_2$ and sulfuric acid, H_2SO_4 are not used because they react with ammonia.

Manufacture of ammonia - the Haber process

1) The Haber process is used **to manufacture ammonia** on a large scale. A brief summary of the Haber process:

$$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g) \quad ; \Delta H = -92 \text{ kJ mol}^{-1}$$



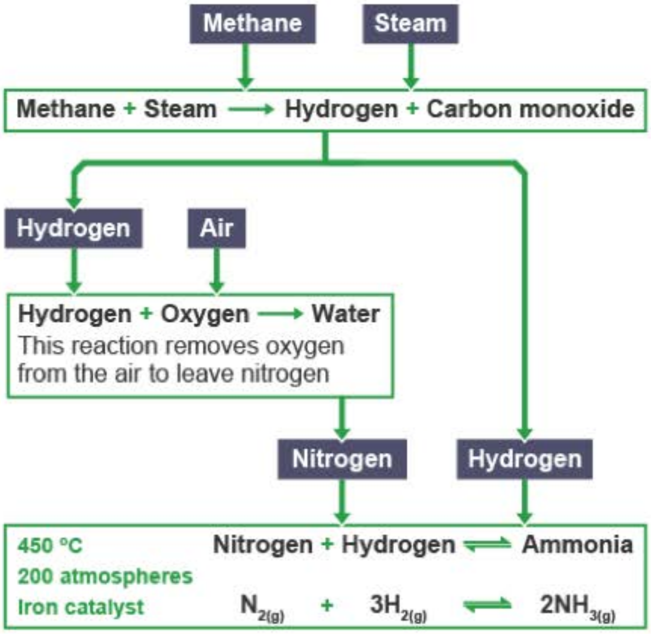
2) i. Hydrogen gas is obtained by reacting methane, CH_4(natural gas) with steam at around 700 °C and the presence of nickel as catalyst.

$$CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$$

ii. Nitrogen gas is obtained by the purification of air. Air which contains mostly a mixture of nitrogen and oxygen gas is reacted with hydrogen gas at high temperature. Oxygen from the air will react with hydrogen to form water.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Oxygen gas is removed, leaving only nitrogen gas behind.



3) The required conditions for optimum yield are:
   i. **(400 - 450) ºC**.
   ii. **200 atm (equivalent to 20000 kPa)**.
   iii. **Presence of fine iron as catalyst**.

4) Nitrogen and oxygen gas are fed into the reactor in a ratio of **1:3**, which is the one demanded by the equation. Excess of reactants are not used because it wastes the space in the reactor and decrease the efficiency of the catalyst, since the excess reactants will have nothing to react with.

5) i. The production of ammonia is an exothermic reaction in equilibrium. According to Le Chatelier's principle, in order to shift the position of equilibrium to the right as much as possible(to increase the yield), **a low temperature should be used**. However, (400 - 450) ºC is not a low temperature.
   ii. A low temperature will **decrease the rate of reaction** albeit having a high yield. The reaction will take a long time to complete and it is not economically plausible.
   iii. Hence, (400 - 450) ºC is the **compromise temperature** that produces a good enough yield in a short time.

6) i. According to Le Chatelier's principle, the position of equilibrium will shift to the right if the **pressure is increased** because there are less molecules on the right of the equation. Besides, a high pressure can also **increase the rate of reaction**. Hence, a high pressure, 200 atm is used.
   ii. Higher pressures are not used because:
      - it is **expensive** to build and maintain the pipes and generators to withstand the pressure, this increases the production cost.
      - there is a risk of the pipes exploding.
   iii. Hence, 200 atm is the **compromise pressure** chosen on economic grounds.

7) A catalyst of fine iron is used to **increase the rate of reaction**. Although it has no effect on the position of equilibrium, it is essential because without it, the reaction will too long to complete.

8) Under these conditions, about 15% of nitrogen and hydrogen converts to ammonia. Unreacted molecules are recycled again so that the overall percentage conversion is about 98%.

Industrial use of ammonia and nitrogen compounds derived from ammonia

1) i. Ammonia can be used **to make fertilisers**. Common fertilisers include ammonium sulfate, ammonium nitrate, ammonium phosphate and urea, $CO(NH_2)_2$.
   ii. This is because they contain the element nitrogen. Nitrogen is essential for plants to grow healthy.

2) Ammonia is also **a precursor for most nitrogen-containing compounds**. One famous example is the manufacture of nitric acid, HNO_3 by the oxidation of ammonia in the Ostwald process.

3) Nitric acid has several uses:
   i. To make fertilisers such as ammonium nitrate(the main use).
   ii. To make explosives such as TNT.
   iii. To be used in the manufacture of dyes, polymers and drugs.

13.2 Environmental Consequence of Using Nitrogen Compounds

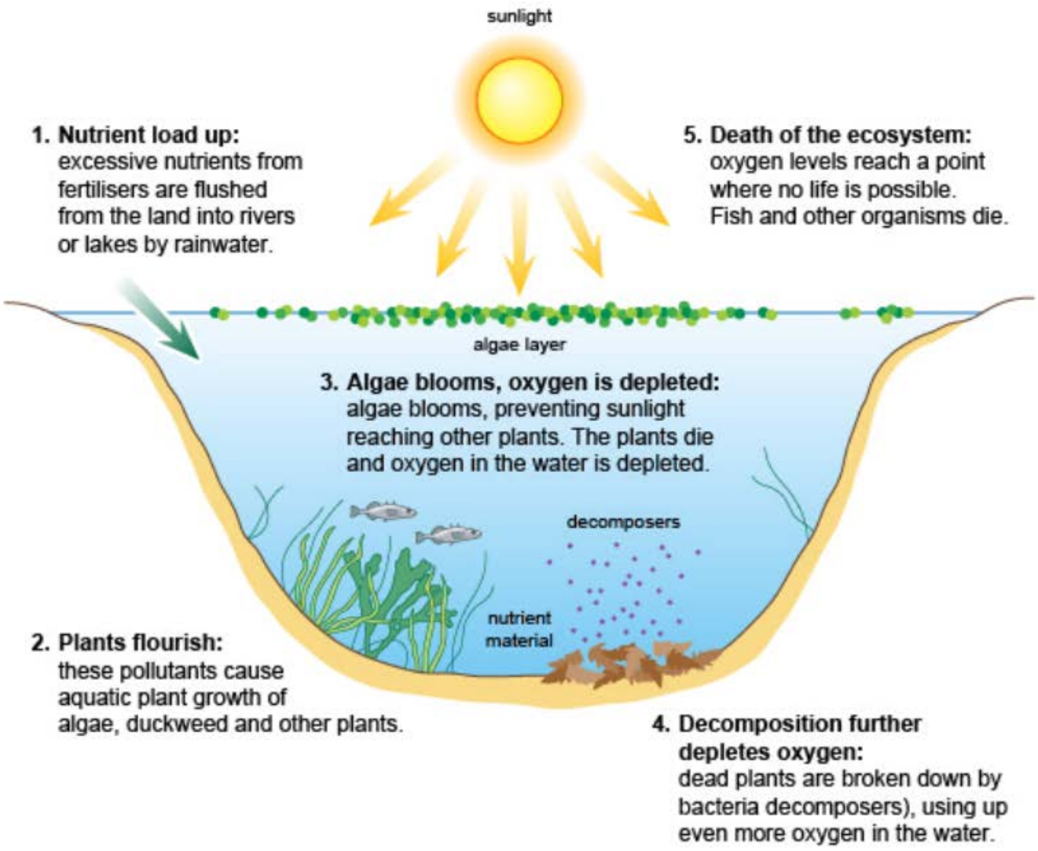
Excessive use of nitrate fertilisers

1) When excessive nitrate or ammonium fertilisers are used, the unabsorbed ones will dissolve in rain water and it leaches into lakes and rivers.

2) An excess of these chemicals in the waters can **promote the growth of algae**, eventually causing an algae bloom. The algae grow exponentially across the surface of water, **blocking sunlight** from the reach of aquatic plants and causes the plants to die.

3) The algae grow faster than being consumed, eventually a large number of algae die without being consumed. When their remains decompose, the process takes up a lot of oxygen from the water. The oxygen level in the water will eventually reach a level where no life can sustain.

4) This process of excess growth leading to the destruction of life in the water is known as **eutrophication**.



5) Since nitrates are soluble in water, removing them from drinking water is very expensive. High levels of nitrates in drinking water can cause a disease in young babies called **'blue baby syndrome'**. Nitrates in water can also potentially cause **stomach cancer**.

Oxides of nitrogen as pollutants

1) i. Nitrogen monoxide, NO is formed when electric spark is passed through a medium of nitrogen and oxygen.
 ii. This happens in the atmosphere during lightning storms. In petrol engines, it is formed when sparks are used to ignite the petrol.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

 iii. It can be removed in petrol engines using a **catalytic converter**. A catalytic converter uses expensive metals like platinum as a catalyst to convert harmful pollutants into non-harmful substances. In this case, it converts the harmful nitrogen monoxide and carbon monoxide into non-harmful nitrogen and carbon dioxide gases.

$$2NO(g) + 2CO(g) \rightarrow N_2(g) + CO_2(g)$$

2) i. Nitrogen monoxide is converted to nitrogen dioxide, NO_2 in the atmosphere.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

ii. Nitrogen dioxide **acts as a catalyst** in the conversion of sulfur dioxide, SO_2 into sulfur trioxide, SO_3.

$$SO_2(g) + NO_2(g) \rightarrow SO_3(g) + NO(g)$$

iii. Sulfur dioxide and sulfur trioxide are the main causes of acid rain. Sulfur dioxide oxidises into sulfur trioxide and sulfur trioxide reacts with water in the atmosphere to form sulfuric acid.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

iv. The sulfuric acid then fall on earth as **acid rain**.

v. The nitrogen monoxide reacts with water in the atmosphere to re-form nitrogen dioxide and the cycle repeats.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

13.3 Sulfur Compounds

Uses and formation of sulfur dioxide, SO_2 and its consequences

1) Atmospheric sulfur dioxide is formed during the **burning of fossil fuels**. Fossil fuels like coal and oil all contain sulfur compounds, and when the coal or the oil product are burned, sulfur dioxide is produced.

2) As discussed above, sulfur dioxide in the atmosphere can cause acid rain. The consequences of acid rain include:
   i. the **corrosion of limestone buildings** as the calcium carbonate reacts with the acid.
   ii. the **corrosion of ironwork** as the iron reacts with the acid.
   iii. the acidification of lakes and rivers leading to the **death of aquatic life**. This is complicated by the fact that a fall in pH dissolves aluminium ions from the soil. Aluminium ions are toxic to fish.
   iv. **damage to trees**. This again is partly the result of aluminium ions being toxic to plants.

3) On the other hand, sulfur dioxide can be used **as food preservative** in, for example, wine and dried fruit and vegetable. It has two functions:
   i. It **slows oxidation of the food** by oxygen in the air.
   ii. It also **kills bacteria**.

Manufacture of sulfuric acid - the Contact process

1) The Contact process:
   i. makes sulfur dioxide.
   ii. converts the sulfur dioxide into sulfur trioxide.
   iii. converts the sulfur trioxide into concentrated sulfuric acid.

2) The sulfur dioxide, SO_2 can be made by using two methods:
   i. Burning sulfur in an excess of air.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

   ii. Heating sulfide ores like pyrite in an excess of air.

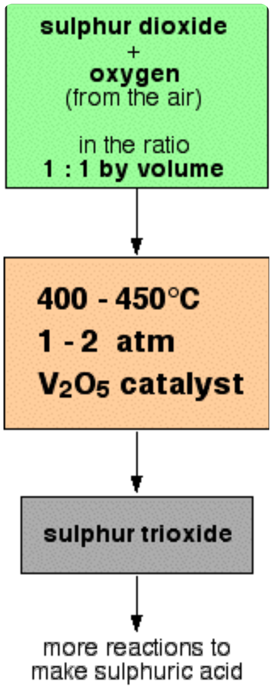
$$4FeS_2(s) + 11O_2(g) \rightarrow 2Fe_2O_3(s) + 8SO_2(g)$$

3) The sulfur dioxide made is then converted into sulfur trioxide. This is the key process in the Contact process.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \quad ; \Delta H = -196 \text{ kJ mol}^{-1}$$

4) The required conditions to achieve this are:
   i. **(400 - 450) °C**.
   ii. **(1 - 2) atm (equivalent to about 101 kPa)**.
   iii. **Presence of vanadium(V) oxide, V_2O_5 as catalyst**.

4) i. Sulfur dioxide and oxygen gas are fed into the reactor in a ratio of **1:1**. An excess of oxygen is used to shift the position of equilibrium to the right.
   ii. Higher proportions of oxygen are not used because it wastes the space in the reactor and decrease the efficiency of the catalyst, since the excess oxygen will have nothing to react with.



5) i. The production of sulfur trioxide is an exothermic reaction in equilibrium. According to Le Chatelier's principle, in order to shift the position of equilibrium to the right as much as possible(to increase the yield), **a low temperature should be used**. However, (400 - 450) °C is not a low temperature.
   ii. A low temperature will **decrease the rate of reaction** albeit having a high yield. The reaction will take a long time to complete and it is not economically plausible.

iii. Hence, (400 - 450) °C is the **compromise temperature** that produces a good enough yield in a short time.

6) i. According to Le Chatelier's principle, the position of equilibrium will shift to the right if the **pressure is increased** because there are less molecules on the right of the equation. Besides, a high pressure can also **increase the rate of reaction**.
ii. However, the reaction is done almost at atmospheric pressure. This is because even at this relatively low pressure, the conversion rate is already about 99.5 %. Increasing the pressure will only result in minor improvements.
ii. Higher pressures are not used because:
- it is **expensive** to build and maintain the pipes and generators to withstand the pressure, this increases the production cost.
- there is a risk of the pipes exploding.

7) A catalyst of vanadium(V) oxide, V_2O_5 is used to **increase the rate of reaction**. Although it has no effect on the position of equilibrium, it is essential because without it, the reaction will too long to complete.

8) i. Then, sulfur trioxide is first converted into **oleum or fuming sulfuric acid**. This is done by dissolving sulfur trioxide in concentrated sulfuric acid.

$$H_2SO_4(l) + SO_3(g) \rightarrow H_2S_2O_7(l)$$

ii. It is then reacted with water to produce sulfuric acid.

$$H_2S_2O_7(l) + H_2O(l) \rightarrow 2H_2SO_4(l)$$

9) In the last step, water cannot just react with sulfur trioxide. This is because **a mist of poisonous and uncontrollable sulfuric acid** will be formed. Dissolving it in concentrated sulfuric acid is a more gentle and safe way.

CHAPTER 14: An Introduction to Organic Chemistry

Learning outcomes:

(a) interpret, and use the general, structural, displayed and skeletal formulae of the following classes of compound:
  - *(i) alkanes and alkenes.*
  - *(ii) halogenoalkanes.*
  - *(iii) alcohols (including primary, secondary and tertiary).*
  - *(iv) aldehydes and ketones.*
  - *(v) carboxylic acids and esters.*

[Candidates will be expected to recognise the shape of the benzene ring when it is present in organic compounds. Knowledge of benzene or its compounds is not required for AS.]

(b) interpret, and use the following terminology associated with organic reactions:
  - *(i) functional group.*
  - *(ii) homolytic and heterolytic fission.*
  - *(iii) free radical, initiation, propagation, termination.*
  - *(iv) nucleophile, electrophile.*
  - *(v) addition, substitution, elimination, hydrolysis.*
  - *(vi) oxidation and reduction.*

[in equations for organic redox reactions, the symbols [O] and [H] are acceptable]

(c) (i) describe the shapes of the ethane and ethene molecules.
  - *(ii) predict the shapes of other related molecules.*

(d) explain the shapes of the ethane and ethene molecules in terms of σ and π carbon-carbon bonds.

(e) describe structural isomerism, and its division into chain, positional and functional group isomerism.

(f) describe stereoisomerism, and its division into geometrical (cis-trans) and optical isomerism.

(g) describe cis-trans isomerism in alkenes, and explain its origin in terms of restricted rotation due to the presence of π bonds.

(h) explain what is meant by a chiral centre and that such a centre gives rise to optical isomerism

(i) identify chiral centres and/or cis-trans isomerism in a molecule of given structural formula.

(j) deduce the possible isomers for an organic molecule of known molecular formula.

(k) deduce the molecular formula of a compound, given its structural, displayed or skeletal formula.

14.1 Organic Compounds

What is organic chemistry?

1) Organic chemistry is the study of carbon compounds (excluding simple compounds like CO, CO_2, CO_3^{2-}, HCO_3^-).

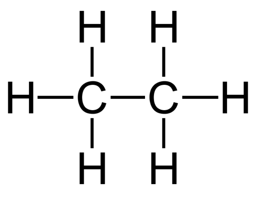
Formulae of organic compounds

1) There are five ways in which organic compounds/molecules can be presented:
   i. Empirical formula
   ii. Molecular formula
   iii. Structural formula
   iv. Displayed formula
   v. Skeletal formula

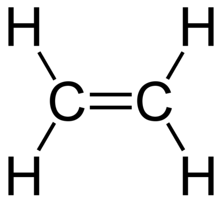
2) i. **Empirical formula** gives the **simplest ratio** of the number of atoms of each element present in the compound.
   ii. **Molecular formula** gives the **actual number** of atoms of each element present in the compound.
   iii. These two formulae are least useful and rarely used in organic chemistry because they do not reveal much information about the compounds.

3) **Structural formula** shows the **order** of the atoms joined together in an organic compound. These formulae are usually written in one line.
   Examples: Ethane - CH_3CH_3
   Ethene - $CH_2=CH_2$ (only double and triple bonds are shown)
   Ethanoic acid - CH_3COOH
   2-methylpentane - $CH_3CH(CH_3)CH_2CH_3$

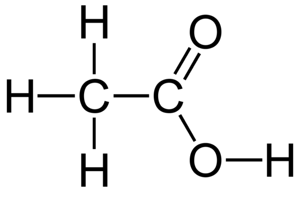
4) **Displayed formula** shows the **order** of the atoms joined together, as well as the **orientation** of the atoms and bond angles.
   Examples:



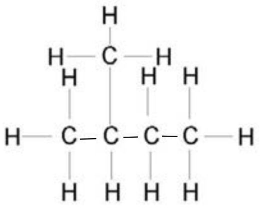
Ethane



Ethene

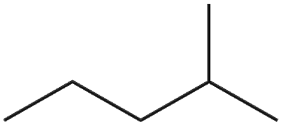


Ethanoic acid

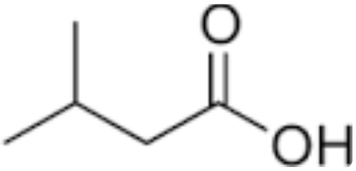


2-methylbutane

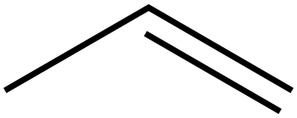
5) **Skeletal formula** shows only the functional groups. The carbon and hydrogen atoms are simplified and hidden. In a skeletal formula:
   i. there is a carbon atom **at each junction** and **at the end of the bond**, there is no carbon atom at a place occupied by another functional group.
   ii. there is **enough hydrogen atoms** bonded to each carbon so that each carbon has four bonds only.



2-methylpentane

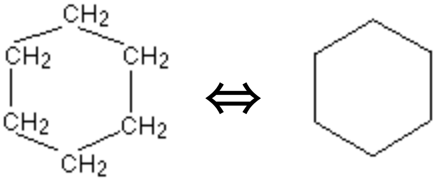


3-methylbutanoic acid

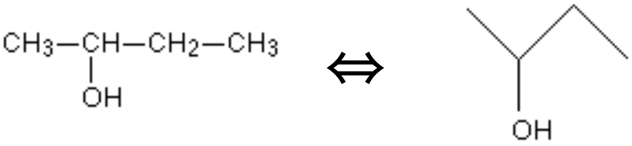


Propene

Benzene



Cyclohexane



$$CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_2-CH_3$$

2-methylbutanol

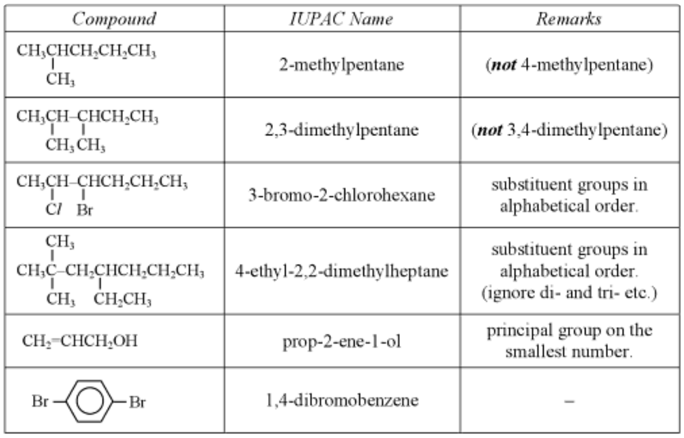
6) It is essential to learn to convert between different formulae of the same compound.

Names of organic compounds

1) Organic compounds are named systematically according to the IUPAC (**I**nternational **U**nion of **P**ure and **A**pplied **C**hemistry) nomenclature.

2) For details, **refer to the attached document** at the end of the notes.

3) Some examples to fill the page:



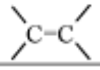
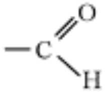
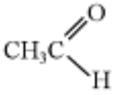
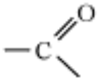
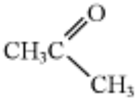
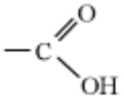
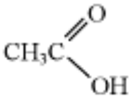
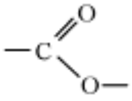
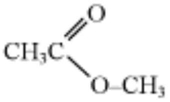
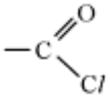
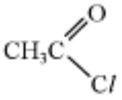
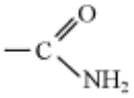
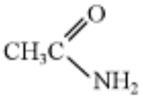
Compound	*IUPAC Name*	*Remarks*
$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2CH_2CH_3$	2-methylpentane	(***not*** 4-methylpentane)
$CH_3\underset{\displaystyle CH_3}{\underset{\vert}{C}}H-\underset{\displaystyle CH_3}{\underset{\vert}{C}}HCH_2CH_3$	2,3-dimethylpentane	(***not*** 3,4-dimethylpentane)
$CH_3\underset{\displaystyle Cl}{\underset{\vert}{C}}H-\underset{\displaystyle Br}{\underset{\vert}{C}}HCH_2CH_2CH_3$	3-bromo-2-chlorohexane	substituent groups in alphabetical order.
$CH_3\overset{\displaystyle CH_3}{\overset{\vert}{\underset{\displaystyle CH_3}{\underset{\vert}{C}}}}-CH_2\underset{\displaystyle CH_2CH_3}{\underset{\vert}{C}}HCH_2CH_2CH_3$	4-ethyl-2,2-dimethylheptane	substituent groups in alphabetical order. (ignore di- and tri- etc.)
$CH_2{=}CHCH_2OH$	prop-2-ene-1-ol	principal group on the smallest number.
Br—⌬—Br	1,4-dibromobenzene	–

Functional groups

1) A *functional group* is a group of atoms in an organic compound that determines the chemistry of that particular compound.

2) A *homologous series* is a series of compounds with the same functional group, and the adjacent members differ in the number of carbon atoms.

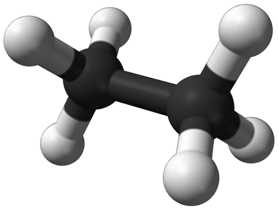
Some common functional groups and their associated types of compounds:

Homologous series	*Functional group*	*prefix or suffix*	*Example*
Alkene		-ene	$H_2C{-}CH_2$ eth**ene**
Alkyne	$—C{\equiv}C—$	-yne	$H{-}C{\equiv}C{-}H$ eth**yne**
Halogen compound	$–X$ (X = F, C*l*, Br, I)	halo-	$CH_3CH_2{-}Cl$ **chloro**ethane
Alcohol	$–OH$	-ol	$CH_3CH_2{-}OH$ ethan**ol**
Ether	$–O–$	alk**oxy**-	$CH_3OCH_2CH_3$ meth**oxy**ethane
Aldehyde		-al	 ethan**al**
Ketone		-one	 propan**one**
Carboxylic acid		-oic acid	 ethan**oic acid**
Ester		-oate	 methyl ethan**oate**
Acid chloride		-oyl chloride	 ethan**oyl chloride**
Amide		-amide	 ethan**amide**
Amine	$–NH_2$	-amine	$CH_3CH_2{-}NH_2$ ethyl**amine**
Nitrile	$–C{\equiv}N$	-nitrile	$CH_3CH_2{-}CN$ propane**nitrile**

[Note: You do not need to memorise the table above at this moment.]

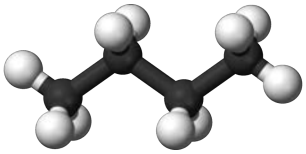
Bonding in organic molecules

1) Carbon atoms which are sp^3 hybridised(typically forming 4 bonds) have the atoms bonded to it arranged in **tetrahedral shape** with a bond angle of 109.5°.

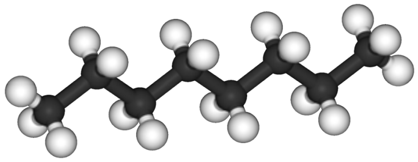


2) One such example is ethane. In an ethane molecule, the two carbon atoms undergo sp^3 hybridisation. All other atoms are bonded to the carbon atoms via σ bonds. All bond angles are 109.5°.

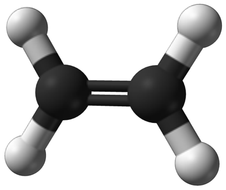
3) If the carbon chain is longer, all the bond angles are still 109.5°, the molecule has a zig-zag shape.



Butane



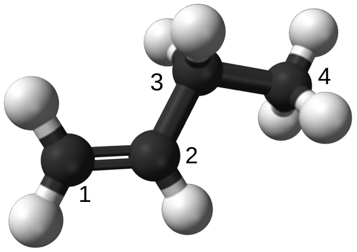
Octane



4) Carbon atoms which are sp^2 hybridised(typically forming 3 bonds) have the atoms bonded to it arranged in a **trigonal planar shape** with bond angle 120°.

5) One such example is ethene. In an ethene molecule, the two carbon atoms undergo sp^2 hybridisation. The two carbon atoms are connected via σ and π bonds, a double bond is formed between the two carbon atoms. The bond angle is 120°.

6) If the carbon chain is longer, depending on the number of double bonds, a mixture of trigonal planar and tetrahedral shape is possible. However, each carbon atoms can only have either one.



7) Observe the but-1,2-ene molecule beside. Carbon 1 and 2 are sp^2 hybridised, so the atoms around it have a trigonal planar arrangement. Carbon 3 and 4 are sp^3 hybridised, so the atoms around it have a tetrahedral arrangement.

[Note : For greater detail on hybridisation and bonding, refer Chapter 4]

14.2 Organic Reactions

Reactions that organic compounds undergo

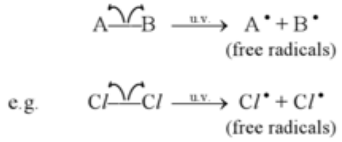
1) Organic reactions are classified using two ways:
   i. By the type of reagent used:
      - Nucleophilic
      - Electrophilic
   ii. By what happens during the reaction:
      - Addition
      - Substitution
      - Elimination

2) Some common reactions:
   - Free-radical substitution
   - Electrophilic addition
   - Electrophilic substitution
   - Nucleophilic addition
   - Nucleophilic substitution
   - Redox (oxidation and reduction)
   - Hydrolysis
   [Note : You do not need to be familiar with these names at this moment.]

Homolytic and heterolytic bond fission

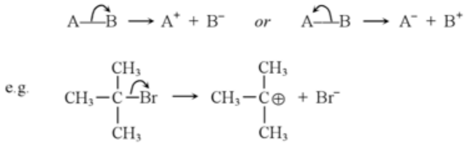
1) Organic reactions involve the breaking of covalent bonds. There are two ways in which a covalent bond can be broken, by homolytic or heterolytic fission.

2) *Homolytic fission* is the breaking of a covalent bond in such a way that one electron goes to each atom, forming free-radicals.



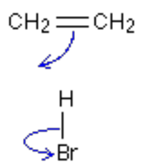
3) A *free-radical* is an atom or a group of atoms with an unpaired electrons formed from the homolytic fission of a covalent bond and is very reactive.

4) *Heterolytic fission* is the breaking of a covalent bond in such a way that both electrons go to the same atom, forming cation and anion.



Curly arrows

1) Curly arrows are used in organic chemistry to represent the **movement of electron(s)**. It is often used in the presentation of an organic mechanism.



2) The tail of the arrow shows where the electron(s) originates from while the head shows the place where electron(s) is/are moved to. The electrons can either originate **from a lone pair or from a bond**.

3) Half arrows show the movement of **one** electron while a full arrow shows the movement of **two** electrons. In the diagram above, the first is a half arrow while the second is a full arrow.

4) Curly arrows can only be used to represent the movement of electron(s), they may not be used for other purposes to avoid ambiguity.

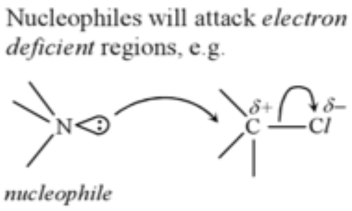
Nucleophiles and electrophiles

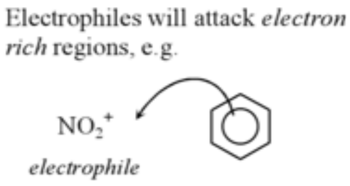
1) A *nucleophile* is a species which contains a lone pair of electrons and is attracted to regions of positive charge or electron-deficient sites. They are often negatively-charged or carry a partial negative charge.

2) Some examples of nucleophiles are NH_3, CN^-, OH^-, Cl^-, Br^- and H_2O.

3) An *electrophile* is an electron-deficient species which can accept electrons and is attracted to regions of negative charge or electron-rich sites. They are often positively-charged or carry a partial positive charge.

4) Some examples of electrophiles are H^+, Br^+, Cl^+ and NO_2^+.


Nucleophiles will attack *electron deficient* regions, e.g.


Electrophiles will attack *electron rich* regions, e.g.

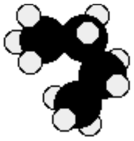
[Note : A benzene ring is an electron-rich region]

14.3 Isomerism

What are isomers?

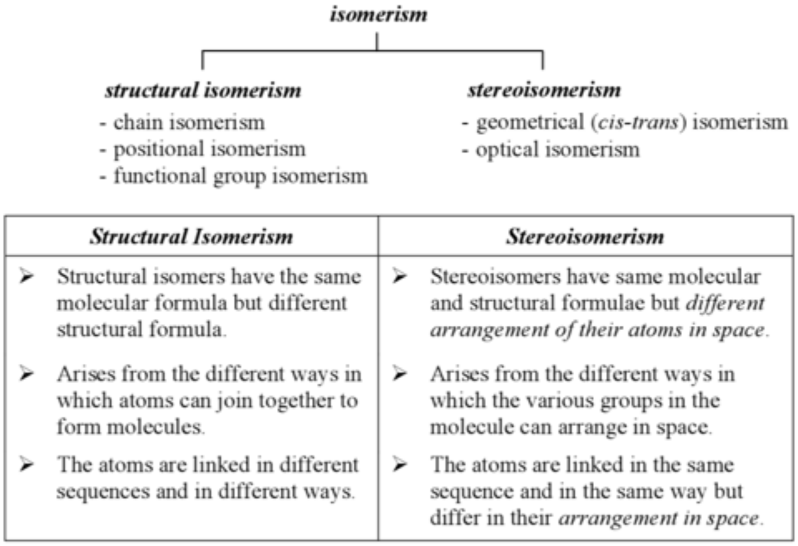
1) *Isomers* are two or more compounds with the same molecular formula but a different arrangement of atoms in space. Organic molecules which exhibit this property show isomerism.

2) **This excludes any different arrangements which are simply due to the molecule rotating** as a whole, or rotating about particular bonds. For example, both of the following are the same molecule. They are not isomers, both are butane.



3) Isomers **must have different names**. A good way to identify isomers is by naming the molecules, molecules with the same name are not isomers.

4) There are two types of isomerism
   i. Structural isomerism
   ii. Stereoisomerism



isomerism

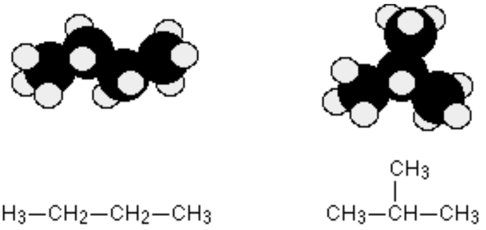
structural isomerism
- chain isomerism
- positional isomerism
- functional group isomerism

stereoisomerism
- geometrical (*cis-trans*) isomerism
- optical isomerism

Structural Isomerism	***Stereoisomerism***
➢ Structural isomers have the same molecular formula but different structural formula.	➢ Stereoisomers have same molecular and structural formulae but *different arrangement of their atoms in space*.
➢ Arises from the different ways in which atoms can join together to form molecules.	➢ Arises from the different ways in which the various groups in the molecule can arrange in space.
➢ The atoms are linked in different sequences and in different ways.	➢ The atoms are linked in the same sequence and in the same way but differ in their *arrangement in space*.

Structural isomerism

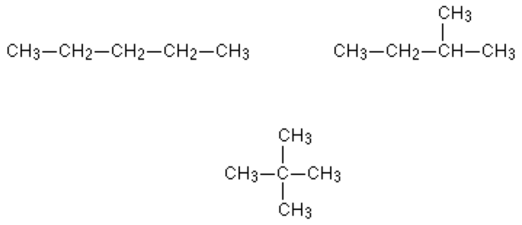
1) **Chain isomerism** arises due to the **different arrangement of carbon atoms in a chain**. The carbon atoms may be arranged in a straight chain or branched chain.



$CH_3-CH_2-CH_2-CH_3$

$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_3$

Isomers of butane, C_4H_{10}



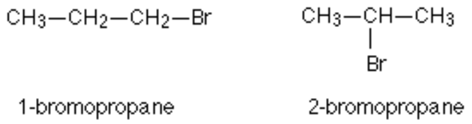
$CH_3-CH_2-CH_2-CH_2-CH_3$

$CH_3-CH_2-\overset{\overset{CH_3}{|}}{C}H-CH_3$

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

Isomers of pentane, C_5H_{12}

2) **Positional isomerism** arises due to **different positions of functional group** in the carbon chain.



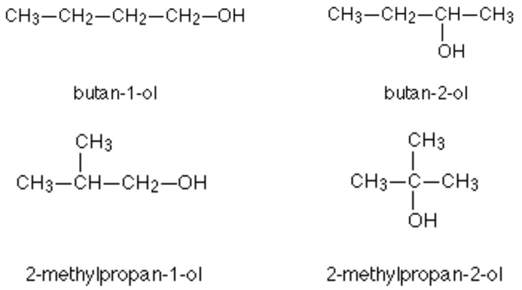
$CH_3-CH_2-CH_2-Br$

1-bromopropane

$CH_3-\underset{\underset{Br}{|}}{C}H-CH_3$

2-bromopropane

Isomers of C_3H_7Br



$CH_3-CH_2-CH_2-CH_2-OH$

butan-1-ol

$CH_3-CH_2-\underset{\underset{OH}{|}}{C}H-CH_3$

butan-2-ol

$CH_3-\overset{\overset{CH_3}{|}}{C}H-CH_2-OH$

2-methylpropan-1-ol

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3$

2-methylpropan-2-ol

Isomers of butanol, C_4H_9OH

3) **Functional isomerism** arises due to **different functional groups**.

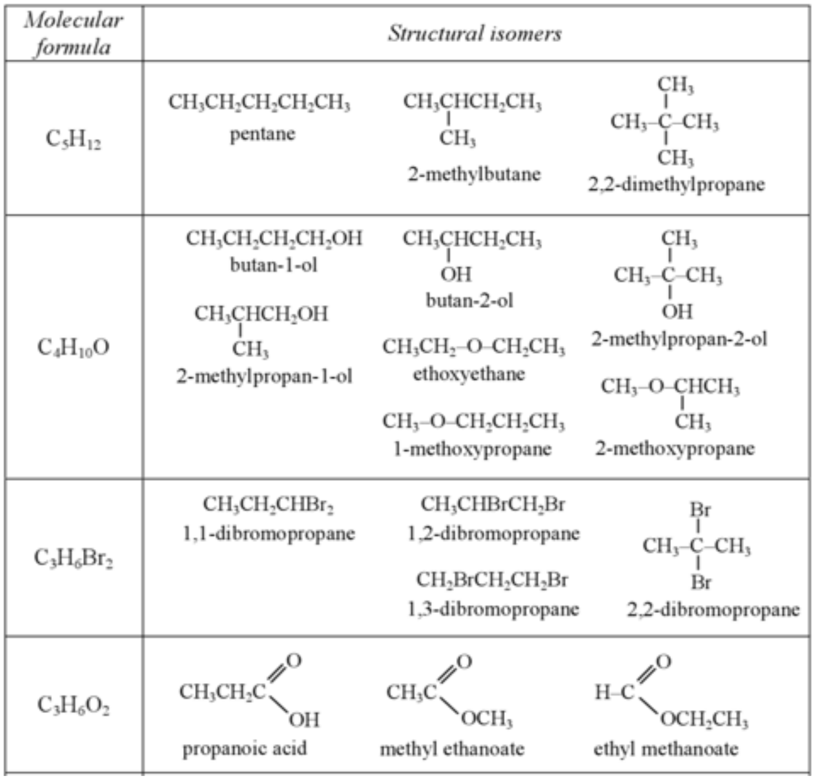
propanal

propanone

Some isomers of C_3H_6O

[Note : Propanal is an aldehyde while propanone is a ketone, they belong to different homologous series]

4) More examples:

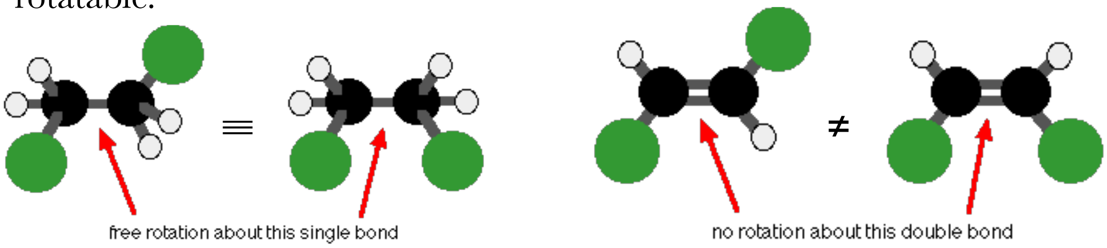


Molecular formula	*Structural isomers*		
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$ pentane	$CH_3\underset{CH_3}{C}HCH_2CH_3$ 2-methylbutane	$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$ 2,2-dimethylpropane
$C_4H_{10}O$	$CH_3CH_2CH_2CH_2OH$ butan-1-ol $CH_3\underset{CH_3}{C}HCH_2OH$ 2-methylpropan-1-ol	$CH_3\underset{OH}{C}HCH_2CH_3$ butan-2-ol $CH_3CH_2-O-CH_2CH_3$ ethoxyethane $CH_3-O-CH_2CH_2CH_3$ 1-methoxypropane	$CH_3-\overset{CH_3}{\underset{OH}{C}}-CH_3$ 2-methylpropan-2-ol $CH_3-O-\underset{CH_3}{C}HCH_3$ 2-methoxypropane
$C_3H_6Br_2$	$CH_3CH_2CHBr_2$ 1,1-dibromopropane	$CH_3CHBrCH_2Br$ 1,2-dibromopropane $CH_2BrCH_2CH_2Br$ 1,3-dibromopropane	$CH_3-\overset{Br}{\underset{Br}{C}}-CH_3$ 2,2-dibromopropane
$C_3H_6O_2$	$CH_3CH_2C\begin{matrix}/\!\!/O\\ \backslash OH\end{matrix}$ propanoic acid	$CH_3C\begin{matrix}/\!\!/O\\ \backslash OCH_3\end{matrix}$ methyl ethanoate	$H-C\begin{matrix}/\!\!/O\\ \backslash OCH_2CH_3\end{matrix}$ ethyl methanoate

Stereoisomerism - Geometrical (*cis-trans* or E-Z) isomerism

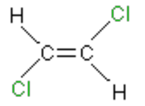
1) Geometrical isomerism arises due to the **rotation about a bond is restricted**. It is common in compounds containing **carbon-carbon double bond(C=C bond)** and certain **ring systems**.

2) i. A C=C bond cannot be rotated due to the **presence of π bond**. A π bond will break if a rotation occurs. Conversely, a carbon-carbon single bond is rotatable.

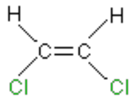


ii. In ring systems, rotation about a bond is restricted due to the **linkage of the ring** because the C-C bond is now part of the ring system.

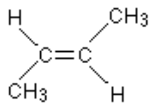
3) Geometrical isomers occur in pairs, differing from each other in the **positioning of the two groups across the double bond**.
   i. A *cis*-isomer has the two groups on the **same side** of the double bond.
   ii. A *trans*-isomer has the two groups on the **opposite sides** of the double bond.



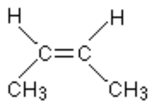
trans-1,2-dichloroethene



cis-1,2-dichloroethene



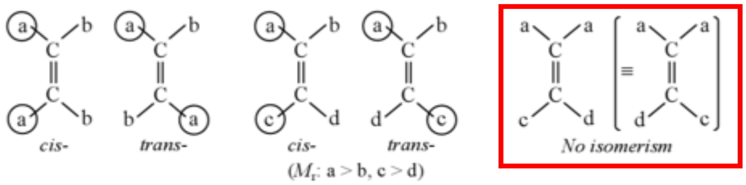
trans-but-2-ene



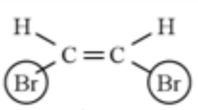
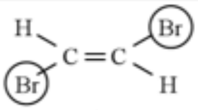
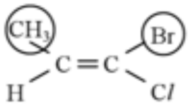
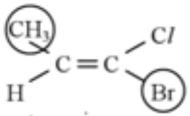
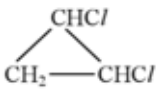
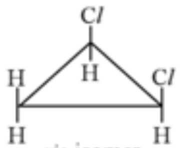
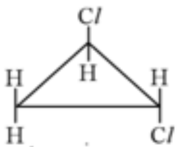
cis-but-2-ene

4) To identify geometrical(*cis*-*trans*) isomers, it is essential to draw the groups around the double bond showing the correct bond angles(120°).

5) Geometrical(*cis*-*trans*) isomerism **cannot exist if either carbon carries identical groups**. In short, to have geometrical isomers, it is essential to have two different groups on the left and two different groups on the right.

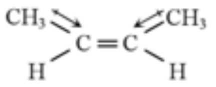


6) More examples:

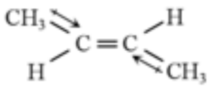
Compound	*Geometrical (cis-trans) isomers*	*Remarks*
BrCH=CHBr	 *cis*-isomer  *trans*-isomer	–
$CH_3CH=CClBr$	 *cis*-isomer  *trans*-isomer	In the *cis*-isomer, the group of ***higher priority*** (higher M_r) on each C are on the same side of C=C bond.
 1,2-dichloro cyclopropane	 *cis*-isomer  *trans*-isomer	–

7) Geometrical isomers have similar(not identical) chemical properties but different physical properties.

8) *cis*-isomer generally has a **higher boiling point** than *trans*-isomer. This is because dipoles in a *cis*-isomer do not cancel out each other, causing the entire molecule to have a **net dipole moment** and it is **polar**. Permanent dipole-dipole forces exist and more energy is required to overcome it.



cis- isomer:
bond moments do ***not*** cancel out;
molecule has a net dipole moment
and so, is *polar*.



trans- isomer:
bond moments cancel each other;
molecule has no net dipole
moment and so, is *non-polar*.

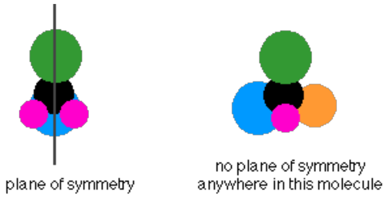
9) *trans*-isomer generally has a **higher melting point** than *cis*-isomer. This is because in the solid state, trans-isomers pack more efficiently in the crystalline lattice due to its shape.

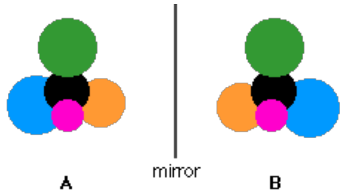
Stereoisomerism - Optical isomerism

1) Optical isomerism arises due to the **ability of compounds to rotate the plane of polarisation of a plane-polarised light**.

2) A compound is said to be **optically-active**(optical isomerism exists) if it rotates the plane of polarised light. If it does not, it is said to be optically-inactive.

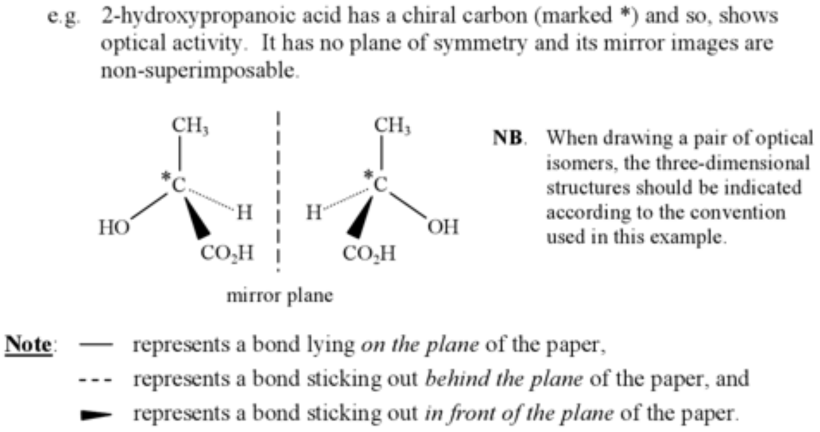
3) For a compound to be optically active:
   i. It needs to have an **asymmetrical carbon** with **four different groups** attached to it so that there is no plane of symmetry. The carbon atoms with four different groups attached to it is called the **chiral carbon or chiral centre**.
   ii. The isomers must be mirror-images of each other and are non-superimposable. That is, no matter how the molecules are rotated, they never fully resemble each other.





A and B are optical isomers

4) An example:



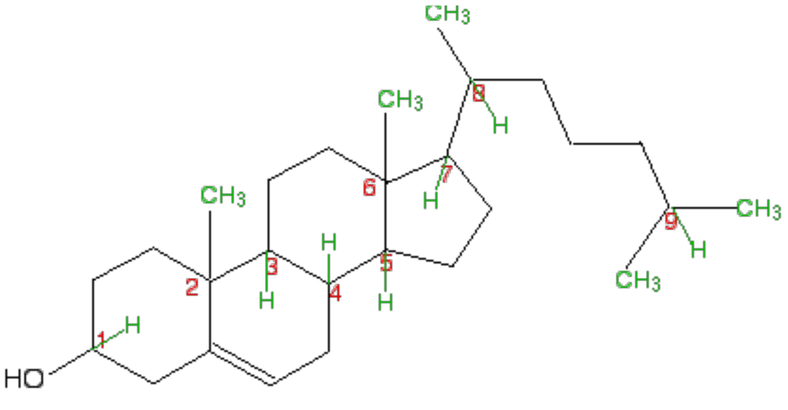
e.g. 2-hydroxypropanoic acid has a chiral carbon (marked *) and so, shows optical activity. It has no plane of symmetry and its mirror images are non-superimposable.

NB. When drawing a pair of optical isomers, the three-dimensional structures should be indicated according to the convention used in this example.

Note: — represents a bond lying *on the plane* of the paper,
--- represents a bond sticking out *behind the plane* of the paper, and
▶ represents a bond sticking out *in front of the plane* of the paper.

5) To identify optical isomers:

i. In chain systems, check which carbon has four different groups attached to it.
ii. In ring systems, check also which carbon has four different groups attached to it. A different group here can be identified by **tracking around that ring** from a particular carbon atom in either clockwise or anti-clockwise direction. If the pattern along the way is the same, that carbon atom is not chiral, and the converse is also true.
iii. An example:



Only carbon 9 is not a chiral carbon in this cholesterol molecule

NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry is the chemistry of carbon compounds. Carbon has the ability to bond with itself to form long chains and, as a result, millions of compounds from simple hydrocarbons to large biomolecules such as proteins, lipids, carbohydrates, and nucleic acids. Originally it was believed that these compounds had to come from a living organism, now they are synthesized in the laboratory.

The simplest organic compounds are composed of carbon and hydrogen and are known as hydrocarbons. There are four types, or classes, of hydrocarbons:

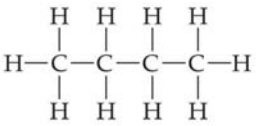
Alkanes: contain all C-C single bonds. These are known as **saturated hydrocarbons**.

Alkenes: contain at least one C=C double bond.

Alkynes: contain at least one C≡C triple bond. Both alkenes and alkynes are known as **unsaturated hydrocarbons**

Aromatic hydrocarbons: contain a benzene structure

Lewis structures of alkanes look like this:



These are also called structural formulas. Since these take up a lot of space, condensed structural formulas are used.

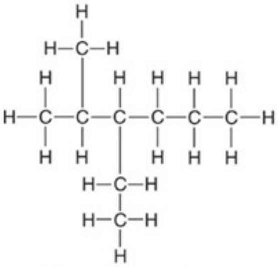
$$H_3C-CH_2-CH_2-CH_3$$

or

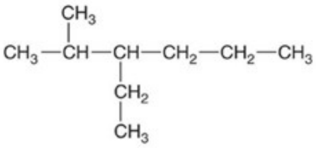
$$CH_3CH_2CH_2CH_3$$

Even simpler than condensed structures are skeletal or line structures:

There are a range of structures used to represent organic compounds:

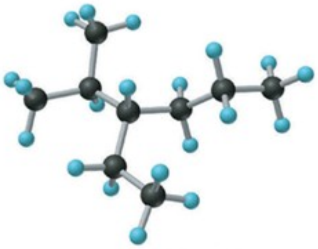


Expanded formula

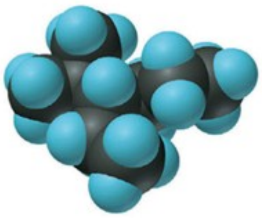


$$CH_3-CH(CH_3)-CH(CH_2CH_3)-CH_2-CH_2-CH_3$$

Condensed formula



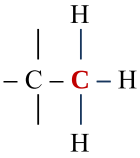
Ball-and-stick model



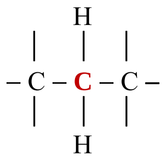
Space-filling model

Before we start naming organic compounds, it is important to understand how carbon atoms are bonded. Every carbon atom will try to form 4 bonds.

A carbon atom on the end of a chain of single bonded carbon atoms will be bonded to one carbon atom and three hydrogen atoms:

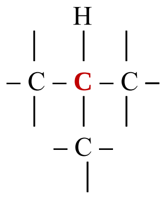


A carbon atom in the middle of a chain of single bonded carbon atoms will be bonded to two carbon atoms and two hydrogen atoms.



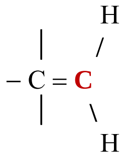
$-\mathrm{C}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{C}-$

A carbon atom bonded to 3 other single bonded carbon atoms will be bonded to one hydrogen.



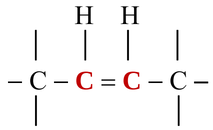
$-\mathrm{C}-\underset{-\mathrm{C}-}{\overset{\mathrm{H}}{\mathrm{C}}}-\mathrm{C}-$

A carbon atom on the end of a chain that is double bonded to another carbon atom be bonded to two hydrogen atoms.



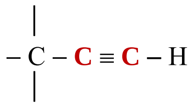
$-\mathrm{C}=\mathrm{C}\begin{smallmatrix}\mathrm{H}\\ \mathrm{H}\end{smallmatrix}$

A carbon atom in the middle of a chain of that is double bonded to another carbon atom will be bonded to one carbon atom and one hydrogen atom.



$-\mathrm{C}-\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}-\mathrm{C}-$

A carbon atom on the end of a chain that is triple bonded to another carbon atom will be bonded to one hydrogen atom. The second carbon atom in that chain is only bonded to another carbon atom, but no hydrogen atoms.



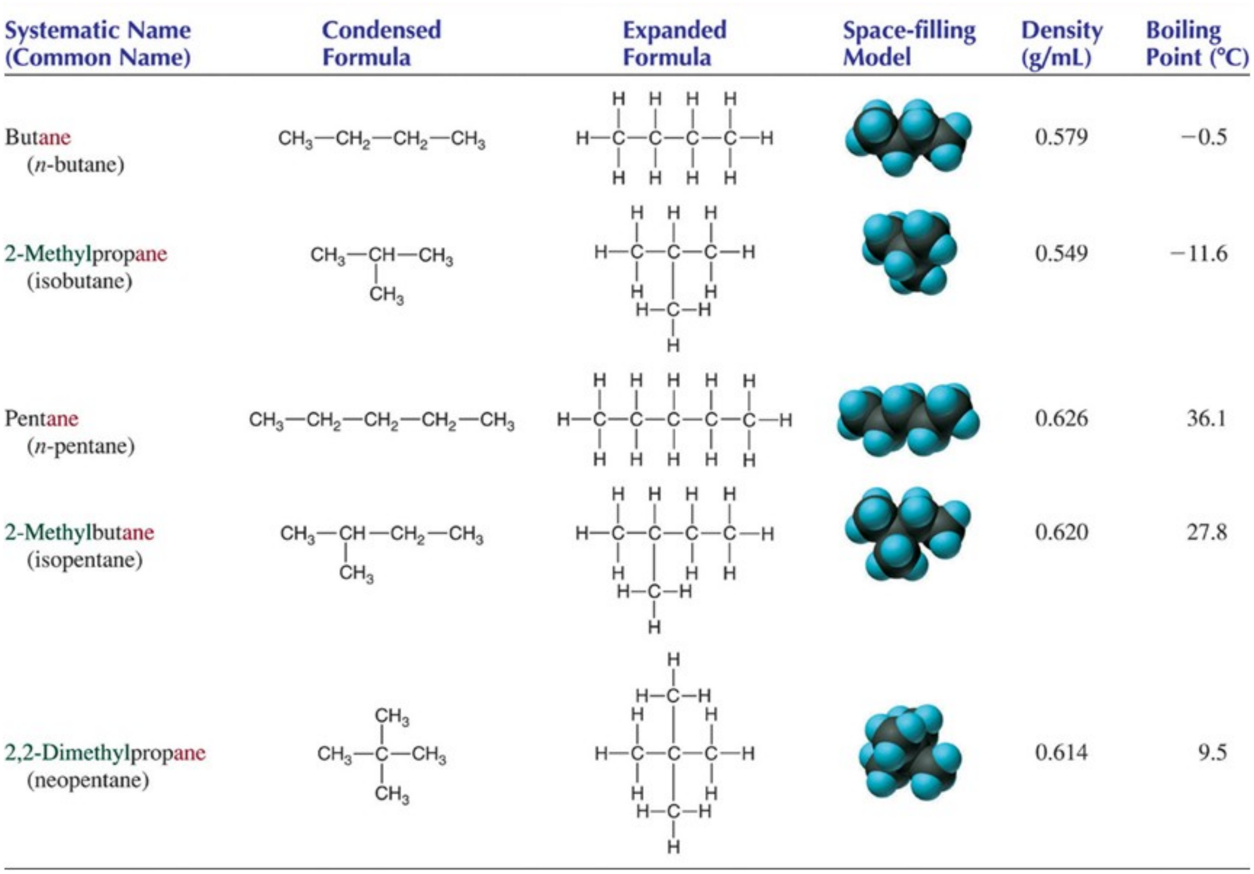
$-\mathrm{C}-\mathrm{C}\equiv\mathrm{C}-\mathrm{H}$

I. Naming Saturated Hydrocarbons - The Alkanes

The names of the alkanes are derived from the Greek prefix for the particular number of carbon atoms in the compound with an -ane ending. The names of the first ten alkanes are given in the following table.

Molecular Formula	**Condensed Structural Formula**	**Name**	**Boiling Point (°C)**
CH_4	CH_4	Methane	−161
C_2H_6	CH_3CH_3	Ethane	−89
C_3H_8	$CH_3CH_2CH_3$	Propane	−44
C_4H_{10}	$CH_3CH_2CH_2CH_3$	Butane	−0.5
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	Pentane	36
C_6H_{14}	$CH_3CH_2CH_2CH_2CH_2CH_3$	Hexane	68
C_7H_{16}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$	Heptane	98
C_8H_{18}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Octane	125
C_9H_{20}	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Nonane	151
$C_{10}H_{22}$	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	Decane	174

Not all the alkanes are straight chained compounds, as shown in the previous table, they can have side chains or branches. These variations of compounds which have the same number of carbon and hydrogen atoms, but a different arrangement are known as **isomers**. Some isomers are shown in the diagram below.



Systematic Name (Common Name)	Condensed Formula	Expanded Formula	Space-filling Model	Density (g/mL)	Boiling Point (°C)
Butane (*n*-butane)	$CH_3-CH_2-CH_2-CH_3$			0.579	−0.5
2-Methylpropane (isobutane)	$CH_3-CH-CH_3$ CH_3			0.549	−11.6
Pentane (*n*-pentane)	$CH_3-CH_2-CH_2-CH_2-CH_3$			0.626	36.1
2-Methylbutane (isopentane)	$CH_3-CH-CH_2-CH_3$ CH_3			0.620	27.8
2,2-Dimethylpropane (neopentane)	CH_3 CH_3-C-CH_3 CH_3			0.614	9.5

Rules for Naming of Branched Hydrocarbons.

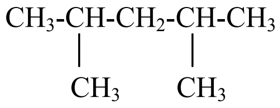
There are four parts to the name of a branched hydrocarbon

1. The **parent chain**: Tells how many carbons are in the longest continuous chain.
   meth = 1 eth = 2 prop = 3 but = 4 pent = 5
2. The **suffix**: Tells what type of compound it is.
   ane = an alkane ene = an alkene yne = an alkyne
3. The **prefix**: Tells what groups, or branches are attached to the parent chain.
   methyl = $-CH_3$ ethyl = $-CH_2-CH_3$ propyl = $-CH_2-CH_2-CH_3$
4. The **location**: Tells where groups, or branches, are attached to the parent chain.

   2 = 2nd carbon atom 3 = 3rd carbon atom 4 = 4th carbon atom

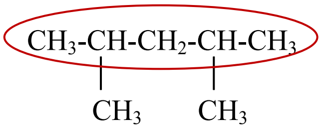
   Note: alkyl groups, or branches cannot be located on the 1st or last carbon

Example 1:



$$\mathrm{CH_3\text{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}\text{-}CH_2\text{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}\text{-}CH_3}$$

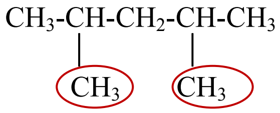
1. Select as the **parent chain** the LONGEST CONTINUOUS CHAIN of carbon atoms. The compound is considered to have been derived from the parent structure by the replacement of hydrogens by various alkyl groups.



$$\mathrm{CH_3\text{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}\text{-}CH_2\text{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}\text{-}CH_3}$$

The longest continuous chain of carbon atoms in this example contains five carbon atoms. Since the carbon atoms in this compound all contain The alkane that contains five carbon atoms is **pentane**.

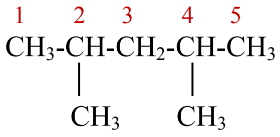
2. Identify the branches, or side chains, attached to the parent chain.



$$\mathrm{CH_3\text{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}\text{-}CH_2\text{-}\underset{\underset{\displaystyle CH_3}{|}}{CH}\text{-}CH_3}$$

Both branches consist of single carbon atoms, there are called **methyl** groups

3. Starting from either end of the longest carbon chain, number the carbon atoms in the parent chain consecutively so that the alkyl groups (or branches) are attached to the carbon atoms with the lowest possible numbers.



$$\mathrm{\overset{1}{CH_3}\text{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{2}{CH}}\text{-}\overset{3}{CH_2}\text{-}\underset{\underset{\displaystyle CH_3}{|}}{\overset{4}{CH}}\text{-}\overset{5}{CH_3}}$$

For this compound, it makes no difference which end you start the numbering. In both cases the alkyl groups, or branches are attached to the second and fourth carbon atoms in the parent chain.

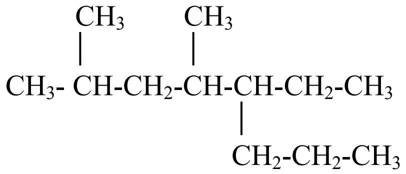
4. Name the compound in order of: number of carbon atom-alkyl group attached(number of carbon atom-alkyl group attached- etc...) name of parent compound. If there are several different alkyl groups attached to the parent chain, name them in order of increasing size or in alphabetical order.

The name for this compound looks like it would be called would be called 2-methyl-4-methylpentane, however, all branches with the same name are grouped together. The number of these branches have a prefix:

di = 2 tri = 3 tetra = 4 penta = 5

But, each branch needs a specified location, so, the correct name is **2,4-dimethylpentane**

Example 2

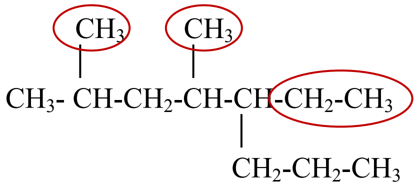


$CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}CH(CH_2\text{-}CH_2\text{-}CH_3)\text{-}CH_2\text{-}CH_3$

In this compound, the longest continuous chain is **8 carbon atoms long**. Note that the longest continuous chain does not have to be straight. This longest chain is **oct-** (for 8 carbons)

All the bonds are single bonds, so this is an alkane. The suffix is **-ane**

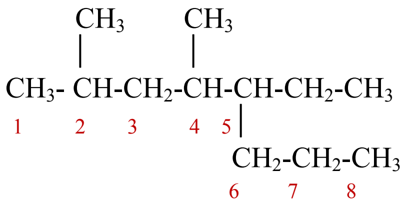
This parent chain is **octane**



$CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}CH(CH_2\text{-}CH_2\text{-}CH_3)\text{-}CH_2\text{-}CH_3$

There are three branches attached to the parent chain. Two of these are **methyl** groups and one is an **ethyl** group.

Number the carbon atoms, so that the groups are attached to the carbon atoms with the lowest possible numbers.



$CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH(CH_3)\text{-}CH(CH_2\text{-}CH_2\text{-}CH_3)\text{-}CH_2\text{-}CH_3$

The two methyl groups in this compound are attached on the 2nd and 4th carbon atoms and the ethyl group is attached to the 5th carbon atom.

This compound is named **5-ethyl-2,4-dimethyloctane**. Note that the branches are named in alphabetical order.

II. Naming Unsaturated Hydrocarbons – Alkenes and Alkynes

Rules for Naming Alkenes and Alkynes

Alkenes contain at least one carbon to carbon double bond. The suffix used is **–ene**.

Alkynes contain at least one carbon to carbon triple bond. The suffix used is **–yne**.

Naming is the same as used for alkanes, except that the parent structure is the longest continuous chain of carbon atoms that contains the carbon-carbon double bond or triple bond. The name is derived by changing the suffix of the corresponding alkane name to **–ene** for an alkene and **–yne** for an alkyne and a number is added to denote the location of the multiple bond.

Example:

$$CH_3{-}CH{=}CH{-}CH_3$$

The longest continuous chain in this compound contains four carbon atoms. The parent structure would be named **but + ene** (to denote the double bond)

Number the carbon atoms in' the longest chain in such a way that the carbon atoms containing the double bond have the lowest possible numbers.

$$\overset{1}{C}H_3{-}\overset{2}{C}H{=}\overset{3}{C}H{-}\overset{4}{C}H_3$$

For this compound, the numbering should start on the left side so the double bond will be located between carbon atom no. 2 and carbon atom no. 3. Although the double bond involves two carbon atoms, its position is designated by the number of the first doubly-bonded carbon atom when numbering from the end of the parent chain nearest the double bond. So, this compound would be named **2-butene**.

Example:

$$CH_3{-}CH_2{-}CH{=}CH_2$$

In this compound the double bond is located between the 1st and 2nd carbon atoms. The compound is named **1-butene**.

Example:

$$CH_3{-}CH{=}CH{-}CH{=}CH_2$$

The longest continuous chain in this compound contains five carbon atoms. The parent structure would be named **pent-** however, the compound contains **two** carbon-carbon double bonds. The number of double bonds, if greater than 1, is denoted by a prefix added to the suffix.

di = 2 tri = 3 tetra = 4

The p[aren't chain is named **pentadiene** Note that an "a" is added to the name to make it easier to pronounce.

Number the carbon atoms in' the longest chain in such a way that the carbon atoms containing the double bond have the lowest possible numbers.

$$\overset{5}{C}H_3{-}\overset{4}{C}H{=}\overset{3}{C}H{-}\overset{2}{C}H{=}\overset{1}{C}H_2$$

For this compound, the numbering should start on the right side so the double bonds will be located between carbon atom no. 1 and carbon atom no. 2 and carbon atom no. 3 and carbon atom no. 4. The name of the compound is **1,3-pentadiene**

Example

$CH_3–CH_2–C≡CH$

The longest continuous chain in this compound contains four carbon atoms. The parent structure would be named **but + yne** (to denote the triple bond)

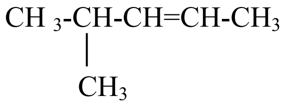
Number the carbon atoms in' the longest chain in such a way that the carbon atoms containing the triple bond have the lowest possible numbers.

$$\overset{4}{CH_3}–\overset{3}{CH_2}–\overset{2}{C}≡\overset{1}{CH}$$

For this compound, the numbering should start on the right side so the triple bond will be located between carbon atom no. 1 and carbon atom no. 2. This compound would be named **1-butyne**.

If the compound is branched, the name is determined similar to that used for the alkanes.

Example.



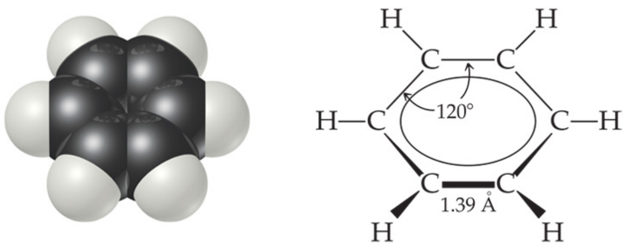
$$CH_3\text{-}\underset{\underset{CH_3}{|}}{CH}\text{-}CH\text{=}CH\text{-}CH_3$$

This compound is named **4-methyl-2-pentene**. Note that the double bond takes precedence in naming.

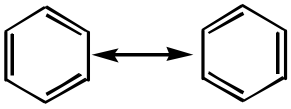
III. Naming Aromatic Compounds

Aromatic Compounds are cyclic hydrocarbons containing a benzene structure.

AROMATIC
Benzene C_6H_6

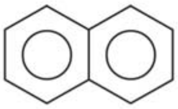


Benzene can be represented by the resonance structures:



The actual structure of benzene, however, is a resonance hybrid of these two structure usually written as:

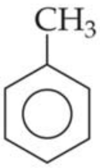
Benzene rings can be fused together. These compounds have common names.



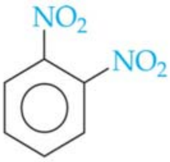
Naphthalene

Anthracene

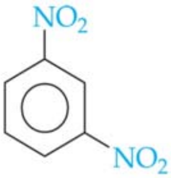
An aromatic compound which is formed by having an alkyl group attached to a benzene ring is named by prefixing the alkyl group name to the word benzene. An example of this is named **methylbenzene** or **toluene**



If there are only two groups attached to the benzene ring, their relative positions can be designated by numbers or by the terms ortho, meta. or para, abbreviated o-, m-, or p-.



1,2-dinitrobenzene
ortho-dinitrobenzene



1,3-dinitrobenzene
meta-dinitrobenzene

1,4-dinitrobenzene
para-dinitrobenzene

Ortho = the 1 and 2 positions on the ring (adjacent carbon atoms)
Meta = the 1 and 3 positions on the ring (alternate carbon atoms)
Para = the 1 and 4 positions on the ring (opposite carbon atoms)

IV. Naming Functional Group Compounds

Derivatives are formed by replacing one or more of the hydrogens in a hydrocarbon by a FUNCTIONAL GROUP. The functional group is responsible for giving what is ordinarily an inactive compound the characteristic chemical and physical properties of another class of compounds.

A. Halogen Derivatives of Hydrocarbons

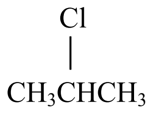
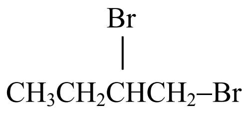
Functional Group: - X (F, Cl, Br, I)

General Formula: R-X

Naming of Halides

Halogens attached to a hydrocarbon chain are named by replacing the -ine ending of the halogen name with **–o.** When naming a compound, halogens are named in the same manner as alkyl group branches.

Examples:

$CH_3\text{-}Br$	$CH_3CH_2\text{-}I$	 $CH_3CH(Cl)CH_3$	 $CH_3CH_2CH(Br)CH_2\text{–}Br$
bromomethane	iodoethane	2-chloropropane	1,2-dibromobutane

B. Oxygen Derivatives of the Hydrocarbons

These functional group compounds contain at least one oxygen atom in its structure.

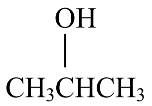
1. Alcohols

Functional Group: –OH

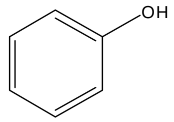
General Formula: R–OH

Naming of alcohols:
Number the-longest carbon chain so that the -OH group is attached to the carbon atom with the lowest possible number. Name the parent compound by using the alkane name and replacing the -e ending with an **-ol** ending. Indicate the position of the hydroxyl. group with a number in any alcohol containing three or more carbon atoms.

Examples:

CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$	 $CH_3CH(OH)CH_3$
methanol	ethanol	1-propanol	2-propanol
(methyl alcohol)	(ethyl alcohol)	(propyl alcohol)	(isopropyl alcohol)

Aromatic alcohols are called phenols and contain the structure:



2. Ethers

Functional Group: –O–
General formula: R–O–R

Naming of ethers
Ethers are commonly named by naming each group attached to the oxygen followed by the word **ether**. If one group has no simple name, the ether can be named as an alkoxy derivative of the larger group.

Examples:

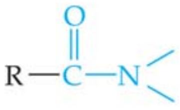
$CH_3\text{-}O\text{-}CH_3$	$CH_3\text{-}O\text{-}CH_2CH_3$	$CH_3CH_2\text{-}O\text{-}CH_2CH_3$
dimethyl ether	methyl ethyl ether	diethyl ether
(methoxymethane)	(methoxyethane)	(ethoxyethane)

3. Carbonyl Compounds

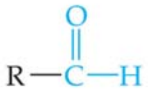
Carbonyl compounds all contain a **= O**

This includes several types of compounds:

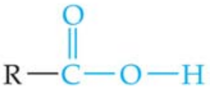
- Aldehydes
- Ketones
- Carboxylic acids
- Esters
- Amides



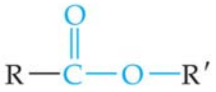
Amide



Aldehyde



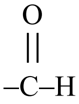
Carboxylic acid

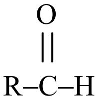


Ester

Ketone

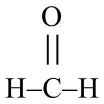
a) Aldehydes

Functional Group: 
$-\overset{O}{\overset{||}{C}}-H$

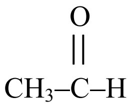
General formula: 
$R-\overset{O}{\overset{||}{C}}-H$ or shorthand as –CHO (The oxygen is bonded to a terminal carbon atom)

Naming of aldehydes:
Number the-longest carbon chain starting with the -CHO group. Name the parent compound by using the alkane name and replacing the -e ending with an **-al** ending.

Examples:

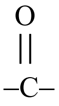

$H-\overset{O}{\overset{||}{C}}-H$

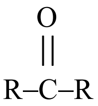
methanal
(methyl aldehyde)


$CH_3-\overset{O}{\overset{||}{C}}-H$

ethanal
(ethyl aldehyde also known as acetaldehyde)

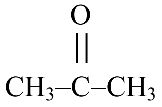
b) Ketones

Functional Group: 
$-\overset{O}{\overset{||}{C}}-$

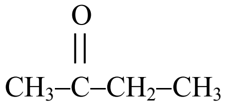
General formula: 
$R-\overset{O}{\overset{||}{C}}-R$ (The oxygen is bonded to a carbon atom in the middle of the chain)

Naming of Ketones:
Number the-longest carbon chain starting so that the –C=O group is attached to the carbon atom with the lowest number. Name the parent compound by using the alkane name and replacing the -e ending with an **-one** ending.

Examples:

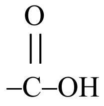

$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_3}$

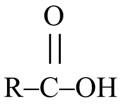
propanone
(dimethyl ketone or
acetone)


$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}CH_2{-}CH_3}$

2-butanone
(methylethyl ketone)

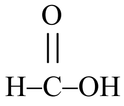
c) Carboxylic acids

Functional Group: 
$\mathrm{{-}\overset{\overset{O}{\|}}{C}{-}OH}$

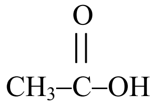
General formula: 
$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}OH}$ or shorthand as –COOH (The carboxyl group is bonded to a terminal carbon atom)

Naming of acids:
Number the-longest carbon chain starting with the -COOH group. Name the parent compound by using the alkane name and replacing the -e ending with an **–oic acid** ending.

Examples:


$\mathrm{H{-}\overset{\overset{O}{\|}}{C}{-}OH}$

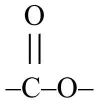
methanoic acid
(formic acid)

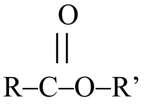

$\mathrm{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH}$

ethanoic acid
(acetic acid)

d) Esters

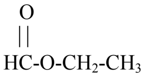
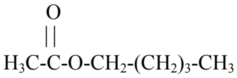
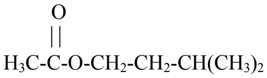
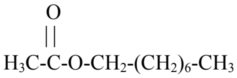
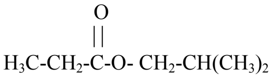
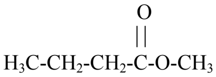
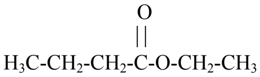
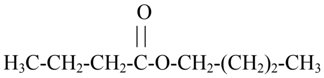
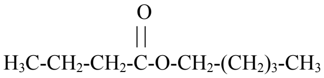
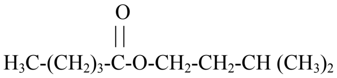
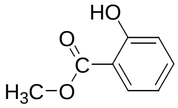
An ester is formed from the combination of a carboxylic acid and an alkanol. They are often highly aromatic compounds and are used for flavors and fragrances.

Functional Group: 
$\mathrm{{-}\overset{\overset{O}{\|}}{C}{-}O{-}}$

General formula: 
$\mathrm{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}R'}$ (The R’ may be the same or different from R)

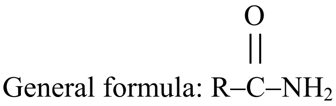
Naming of esters
Esters are usually named by naming the R’ group [from an alcohol] as an akyl group first followed by the acid name [the R-C group] with ending **-oate**. Esters are often called by their common names.

Examples of esters and their flavor/odor properties are given in the table below.

Formula	Common name	IUPAC name	Flavor/odor
 $H\overset{O}{\overset{\Vert}{C}}-O-CH_2-CH_3$	ethyl formate	ethyl methanoate	rum
 $H_3C-\overset{O}{\overset{\Vert}{C}}-O-CH_2-(CH_2)_3-CH_3$	n-amyl acetate	pentyl ethanoate	pears, bananas
 $H_3C-\overset{O}{\overset{\Vert}{C}}-O-CH_2-CH_2-CH(CH_3)_2$	isoamyl acetate	3-methylbutyl ethanoate	pears, bananas
 $H_3C-\overset{O}{\overset{\Vert}{C}}-O-CH_2-(CH_2)_6-CH_3$	n-octyl acetate	octyl ethanoate	oranges
 $H_3C-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2-CH(CH_3)_2$	isobutyl propionate	2-methylpropyl propanoate	rum
 $H_3C-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_3$	methyl butyrate	methyl butanoate	apples
 $H_3C-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2-CH_3$	ethyl butyrate	ethyl butanoate	pineapples
 $H_3C-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2-(CH_2)_2-CH_3$	n-butyl butyrate	butyl butanoate	pineapples
 $H_3C-CH_2-CH_2-\overset{O}{\overset{\Vert}{C}}-O-CH_2-(CH_2)_3-CH_3$	n-amyl butyrate	pentyl butanoate	apricots
 $H_3C-(CH_2)_3-\overset{O}{\overset{\Vert}{C}}-O-CH_2-CH_2-CH(CH_3)_2$	isoamyl valerate	3-methylbutyl butanoate	apples
	methyl salicylate	methyl 2-hydroxybenzoate	oil of wintergreen

e) Amides

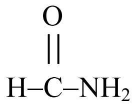

Functional Group: $-\overset{O}{\overset{\Vert}{C}}-\underset{\vert}{\overset{\vert}{N}}:$


General formula: $R-\overset{O}{\overset{\Vert}{C}}-NH_2$

Naming of Amides

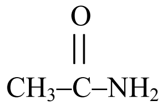
Amides are commonly named similar to a carboxylic acid, replacing the **–oic acid** suffix with **amide.**

Examples:



$H-\overset{\overset{O}{||}}{C}-NH_2$

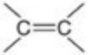
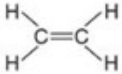
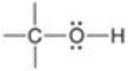
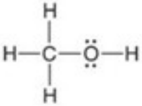
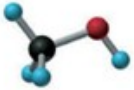
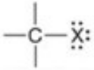
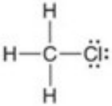
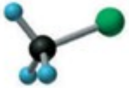
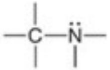
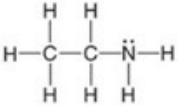
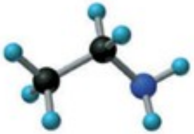
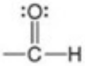
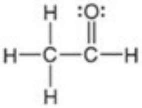
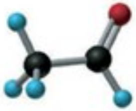
formamide
(methylamide)

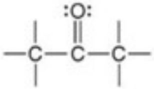
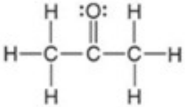
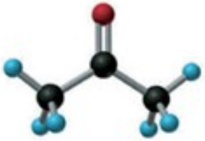
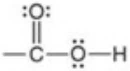
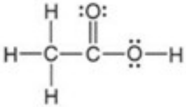
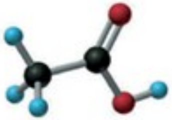
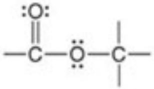
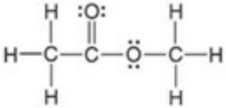
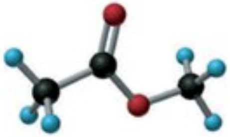
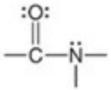
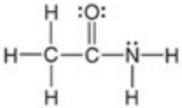
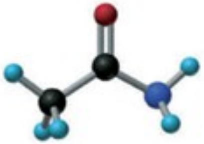
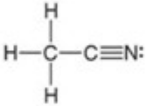


$CH_3-\overset{\overset{O}{||}}{C}-NH_2$

ethanamide
(ethylamide or acetamide)

A summary of the functional group compounds, their structures and names is listed in tables on the next two pages.

Functional Group	Compound Type	Suffix or Prefix of Name	Example		Systematic Name (Common Name)
	alkene	-ene			ethene (ethylene)
—C≡C—	alkyne	-yne	H—C≡C—H		ethyne (acetylene)
	alcohol	-ol			methanol (methyl alcohol)
 (X=halogen)	haloalkane	halo-			chloromethane (methyl chloride)
	amine	-amine			ethylamine
	aldehyde	-al			ethanal (acetaldehyde)

Functional Group	Compound Type	Suffix or Prefix of Name	Example		Systematic Name (Common Name)
	ketone	-one			2-propanone (acetone)
	carboxylic acid	-oic acid			ethanoic acid (acetic acid)
	ester	-oate			methyl ethanoate (methyl acetate)
	amide	-amide			ethanamide (acetamide)
$-C\equiv N:$	nitrile	-nitrile			ethanenitrile (acetonitrile, methyl cyanide)

CHAPTER 15: Hydrocarbons

Learning outcomes:

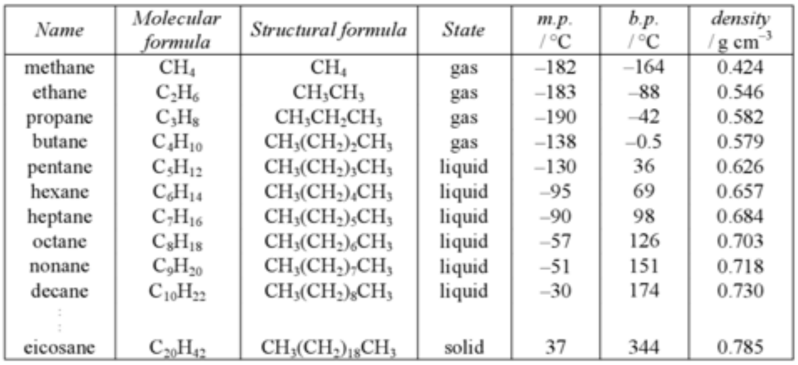
(a) *show awareness of the general unreactivity of alkanes, including towards polar reagents.*
(b) *describe the chemistry of alkanes as exemplified by the following reactions of ethane:*
  (i) *combustion.*
  (ii) *substitution by chlorine and by bromine.*
(c) *describe the mechanism of free-radical substitution at methyl groups with particular reference to the initiation, propagation and termination reactions.*
(d) *describe the chemistry of alkenes as exemplified, where relevant, by the following reactions of ethene and propene (including the Markovnikov addition of asymmetric electrophiles to propene):*
  (i) *addition of hydrogen, steam, hydrogen halides and halogens.*
  (ii) *oxidation by cold, dilute, acidified manganate(VII) ions to form the diol.*
  (iii) *oxidation by hot, concentrated, acidified manganate(VII) ions leading to the rupture of the carbon-to-carbon double bond in order to determine the position of alkene linkages in larger molecules.*
  (iv) *polymerisation.*
(e) *describe the mechanism of electrophilic addition in alkenes, using bromine/ethene and hydrogen bromide/propene as examples.*
(f) *explain the use of crude oil as a source of both aliphatic and aromatic hydrocarbons.*
(g) *suggest how 'cracking' can be used to obtain more useful alkanes and alkenes of lower Mr from larger hydrocarbon molecules.*
(h) *describe and explain how the combustion reactions of alkanes led to their use as fuels in industry, in the home and in transport.*
(i) *recognise the environmental consequences of:*
  (i) *carbon monoxide, oxides of nitrogen and unburnt hydrocarbons arising from the internal combustion engine and of their catalytic removal.*
  (ii) *gases that contribute to the enhanced greenhouse effect.*

15.1 Introduction to Alkanes

What is an alkane?

1) A *hydrocarbon* is a compound containing carbon and hydrogen atoms only. Examples of hydrocarbons are alkanes, alkenes, alkynes and arenes.

2) Alkanes are **saturated hydrocarbons**, the carbon atoms are joined to each other via single covalent bond only. They form the homologous series with a general formula C_nH_{2n+2}.



Name	*Molecular formula*	*Structural formula*	*State*	*m.p.* / °C	*b.p.* / °C	*density* / g cm^{-3}
methane	CH_4	CH_4	gas	–182	–164	0.424
ethane	C_2H_6	CH_3CH_3	gas	–183	–88	0.546
propane	C_3H_8	$CH_3CH_2CH_3$	gas	–190	–42	0.582
butane	C_4H_{10}	$CH_3(CH_2)_2CH_3$	gas	–138	–0.5	0.579
pentane	C_5H_{12}	$CH_3(CH_2)_3CH_3$	liquid	–130	36	0.626
hexane	C_6H_{14}	$CH_3(CH_2)_4CH_3$	liquid	–95	69	0.657
heptane	C_7H_{16}	$CH_3(CH_2)_5CH_3$	liquid	–90	98	0.684
octane	C_8H_{18}	$CH_3(CH_2)_6CH_3$	liquid	–57	126	0.703
nonane	C_9H_{20}	$CH_3(CH_2)_7CH_3$	liquid	–51	151	0.718
decane	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	liquid	–30	174	0.730
⋮						
eicosane	$C_{20}H_{42}$	$CH_3(CH_2)_{18}CH_3$	solid	37	344	0.785

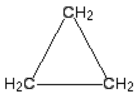
3) Physical properties of alkanes:
   i. Alkanes are **non-polar**, thus they are soluble in non-polar solvents like CCl_4. They are, in general, insoluble and less dense than water.

   ii. The boiling point of straight-chain alkanes **increases** with the size of molecule. This is because the number of electrons in each molecule increases, resulting in the increased strength of van der Waals'. Thus more energy is required to break these forces.

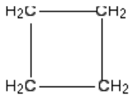
   iii. For a branched alkane, it is **more volatile** and its boiling point is **lower** than its counterpart with the same number of carbon atoms. This is because they are more spherical and have a lower surface area. Thus less temporary dipoles can be set up and the van der Waals' forces are weaker, less energy is required to overcome it.

   iv. The density of liquid alkanes **increases slightly**. The mass of each succeeding molecule increases but due to the increased strength of van der Waals' forces, the molecules are more closer together. This results in higher ratio of mass/volume.

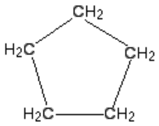
4) Cycloalkanes are alkanes that joined up as a **ring**. The smallest possible cycloalkane is cyclopropane. Cycloalkanes have two hydrogen less than the corresponding straight-chai alkanes.



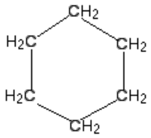
cyclopropane



cyclobutane



cyclopentane



cyclohexane

15.2 Reactions of Alkanes

Reactivity of alkanes

1) Alkanes are saturated and generally **unreactive** because they are non-polar, hence they are unattractive towards nucleophiles and electrophiles.

2) Alkanes will only react with non-polar reagents in the presence of heat or ultraviolet light.

Combustion

1) Alkanes undergo **complete combustion** under **excess oxygen** gas to give carbon dioxide and water. For example:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H^\circ = -890 \text{ kJ mol}^{-1}$$

2) In general,

$$C_xH_y + \left(x + \frac{y}{4}\right) O_2 \rightarrow xCO_2 + \left(\frac{y}{2}\right) H_2O$$

3) Larger alkanes are more difficult to ignite. This is because alkanes only burn in the gaseous state and larger alkanes have stronger van der Waals' forces that hold them together. Therefore more energy is required to vaporise it.

4) When the supply of oxygen is limited, alkanes undergo **incomplete combustion**. The possible products are carbon monoxide, carbon and water. For example,

$$2CH_4(g) + 3O_2(g) \rightarrow 2CO(g) + 4H_2O(g) \qquad \text{or}$$
$$CH_4(g) + O_2(g) \rightarrow C(s) + 2H_2O(g)$$

Halogenation

1) Alkanes undergo halogenation via **free-radical substitution** to give a range of products. In free-radical substitution, hydrogen atoms in the molecule are **gradually substituted** by halogen atoms.

2) **Reagent : Chlorine gas, Cl_2 or bromine gas, Br_2**
Condition : The presence of ultraviolet(UV) light or sunlight
Product : Halogenoalkanes (alkanes with halogens)

3) Free-radical substitution proceeds via a **chain reaction**. During a chain reaction, for every reactive species you start off with, a new one is generated at the end, and this keeps the process going.

4) i. When methane reacts with chlorine in sunlight, the greenish-yellow colour fades and steamy acidic fumes of hydrogen chloride can be observed.

$$CH_4 + Cl_2 \xrightarrow{u.v.} CH_3Cl + HCl$$

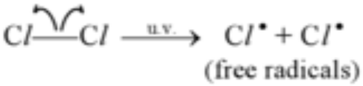
ii. However, this is a chain reaction and does not end here. More hydrogen atoms will be substituted as long as there are sufficient chlorine atoms.

$$\begin{aligned} CH_3Cl + Cl_2 &\rightarrow CH_2Cl_2 + HCl \\ CH_2Cl_2 + Cl_2 &\rightarrow CHCl_3 + HCl \\ CHCl_3 + Cl_2 &\rightarrow CCl_4 + HCl \end{aligned}$$

5) The mechanism of free-radical substitution:

i. *Step 1: Initiation step*

The reaction is initiated by the **homolytic fission** of chlorine molecule in the **presence of UV light**, forming chlorine free radicals.



$$Cl{-}Cl \xrightarrow{u.v.} \underbrace{Cl^\bullet + Cl^\bullet}_{\text{(free radicals)}}$$

ii. *Step 2: Propagation step*

The free radicals then **attack** the methane molecules, leading to a chain reaction.

$$\begin{aligned} CH_4 + Cl^\bullet &\longrightarrow CH_3^\bullet + HCl \\ CH_3^\bullet + Cl_2 &\longrightarrow CH_3Cl + Cl^\bullet \\ CH_3Cl + Cl^\bullet &\longrightarrow CH_2Cl^\bullet + HCl \\ CH_2Cl^\bullet + Cl_2 &\longrightarrow CH_2Cl_2 + Cl^\bullet \\ &\vdots \end{aligned}$$

iii. *Step 3: Termination step*

The reaction ends with the free radicals joining up with each other.

$$\boxed{\begin{aligned} Cl^{\bullet} + Cl^{\bullet} &\longrightarrow Cl_2 \\ CH_3^{\bullet} + Cl^{\bullet} &\longrightarrow CH_3Cl \\ CH_3^{\bullet} + CH_3^{\bullet} &\longrightarrow CH_3CH_3 \end{aligned}}$$

$$\begin{aligned} CH_3^{\bullet} + CH_2Cl^{\bullet} &\longrightarrow CH_3CH_2Cl \\ Cl^{\bullet} + CH_2Cl^{\bullet} &\longrightarrow CH_2Cl_2 \\ CH_2Cl^{\bullet} + CH_2Cl^{\bullet} &\longrightarrow CH_2ClCH_2Cl \\ &\vdots \end{aligned}$$

[Note: All other alkanes react in a similar manner but the reactions involved are getting more and more complicated.]

6) To produce mainly tetrachloromethane, an excess of chlorine gas is used so that all the hydrogen atoms eventually get substituted.

7) Bromine gas reacts in a similar manner but the reaction is slower.

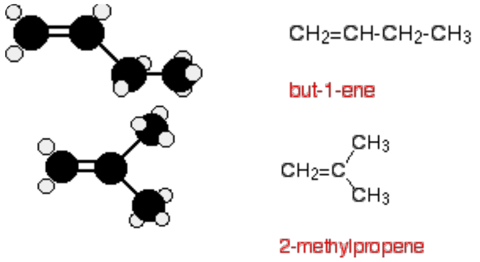
15.3 Introduction to Alkenes

What is an alkene?

1) Alkenes are **unsaturated hydrocarbons** which contain **at least one carbon-carbon double bond(C=C) bond**. They form the homologous series with the general formula of C_nH_{2n}.

2) The physical properties of alkenes are similar to that of alkanes.

3) Alkenes can exhibit **both structural and stereoisomerism**. This is due to the rotation-restricting double bond. The isomers of C_4H_8 are:

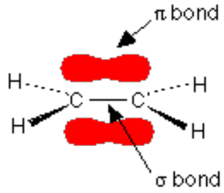


The structural isomers

The geometrical isomers

15.4 Reactions of Alkenes

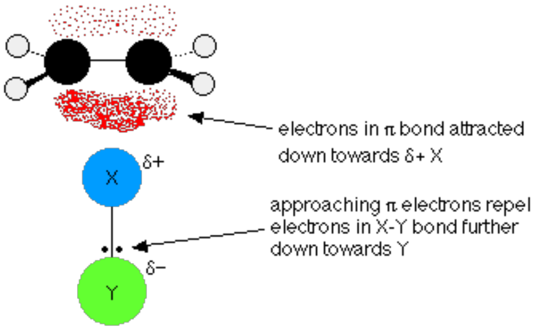
Electrophilic addition



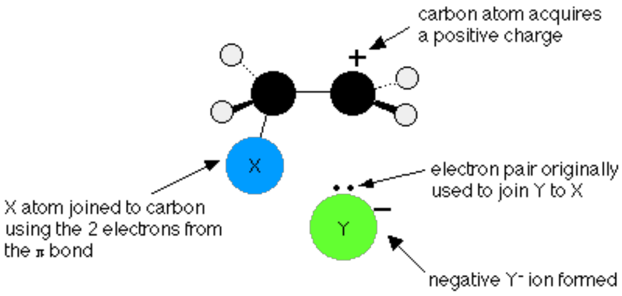
1) Unlike alkanes, alkenes are **more reactive** because they are unsaturated and contain a C=C bond. A C=C bond contains a σ bond and a π bond. A π bond is a **region of high density of electron** which is **open to attack** by something that carries an amount of positive charge, electrophiles.

2) Alkenes mainly undergo **electrophilic addition**. An electrophilic addition reaction is **the addition of an electrophile across the C=C bond**.

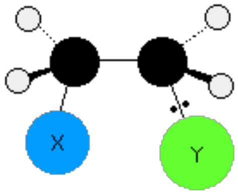
3) The general mechanism of electrophilic addition:
   i. The electronegativity difference in an electrophile, say, XY causes the molecule to be polar. Therefore it carries a δ+ and δ- end. The **δ+ end** of the molecule behaves as an electrophile.
   ii. The δ+ end is **attracted to the π bond**, a region with high electron density. As it approaches the π bond, the electrons in the X-Y bond are repelled further and further to the Y atom.



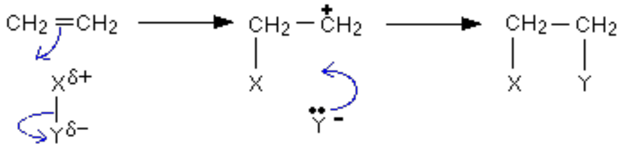
   iii. Eventually the electrons are donated to Y, forming Y^- ion. The X atom forms a single bond with carbon. The electrons needed for this bonding come from the π bond. As a result, the adjacent carbon atom will carry a positive charge because it has lost its π electron to the C-X bond.



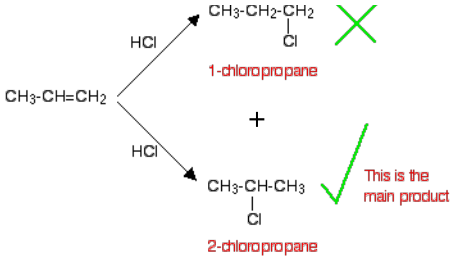
iv. The carbon-containing species which carries a positive charge is called **carbocation**. The carbocation is attracted to the negative Y^- ion. These two particles eventually bond together via a co-ordinate bond.



4) In the examination, the mechanism can be written like this. The curly arrows show the movement of electrons.



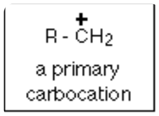
5) The addition of unsymmetrical alkenes follows **Markovnikov's rule**:
" In the addition of H-X to a C=C bond of an unsymmetrical alkene, the hydrogen atom attaches itself to the carbon atom <u>that holds the greatest number of hydrogen atoms</u>. "



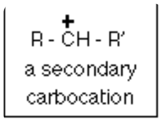
Minor product

Major product

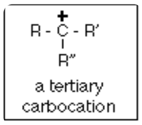
6) Hydrocarbons can be classified as primary, secondary or tertiary depending on the number of R groups attached to the positive carbon.



a primary carbocation



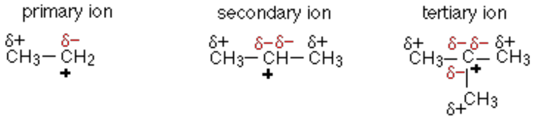
a secondary carbocation



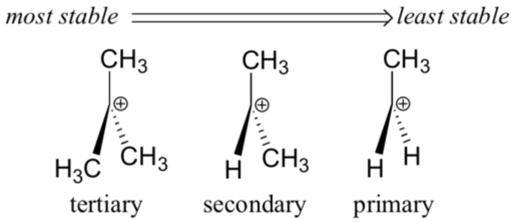
a tertiary carbocation

The Rs are alkyl groups, they can be the same or different. Carbocation is formed as an **intermediate** when the electrophile bonds with the carbon atom.

7) The alkyl groups have an **electron-pushing effect**, they tend to push the electrons towards the carbon atom which carries a positive charge.



8) It follows that **tertiary carbocation is the most stable** because the positive charge is neutralised by the negative charges. The charge density on the carbon atom is the least.



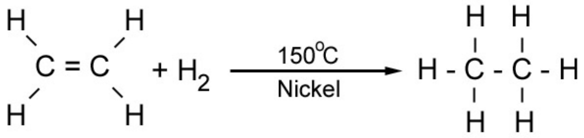
9) Therefore, if the electrophile is bonded in such a way that a tertiary carbocation is produced, the stability of the intermediate formed can be increased. This can only happen if the hydrogen attaches itself with the carbon with most hydrogen atom(normally at the ends of the molecule). Therefore Markovnikov's rule is obeyed.

10) Reactions that alkenes undergo:
  i. Addition of hydrogen, H_2 (Hydrogenation)
  ii. Addition of steam, H_2O (Hydration)
  iii. Addition of halogen, X_2 (Halogenation) where X = A halogen
  iv. Addition of hydrogen halide, HX where X = A halogen
  v. Oxidation by cold and hot potassium manganate(VII), $KMnO_4$
  vi. Addition polymerisation

Addition of hydrogen, H_2 (Hydrogenation)

1) **Reagent : Hydrogen gas, H_2**
Condition : Heat in the presence of nickel, Ni catalyst at 150 °C
Product : Alkanes

2) In hydrogenation of ethene, two hydrogen atoms are added across the C=C double bond. Ethane is produced.

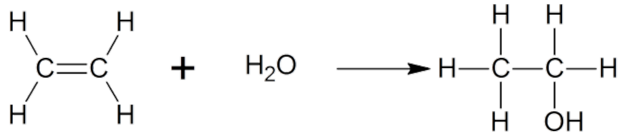


3) In this case, although hydrogen molecule has no polarity, it is still able to behave as an electrophile. This is because as the hydrogen molecule approaches the double bond, **a dipole is induced** due to the repulsion between the two bond pair of electrons(one from the C=C bond, another from the H-H bond).

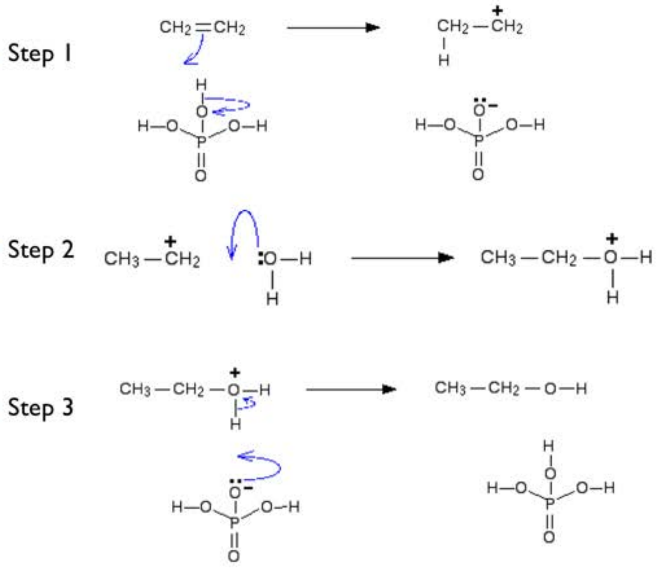
Addition of steam, H_2O (Hydration)

1) **Reagent : Steam, H_2O**
Condition : Heat the gaseous alkene at 330 °C and 60 atm in the presence of phosphoric(V) acid, H_3PO_4 as catalyst
Product : Alcohols (compounds that -OH group)

2) In the hydration of alkene, steam, H-OH is added across the double bond. Ethanol is produced.

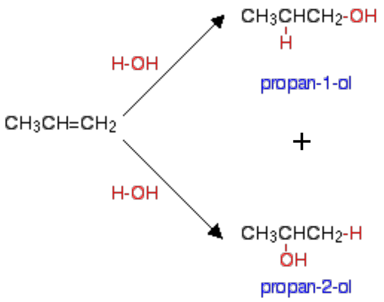


3) The detailed mechanism of the reaction is as follow:



The only way oxygen can have 3 bonds is by having a positive charge.

4) The addition of unsymmetrical alkene is as follow. Take propene as an example:



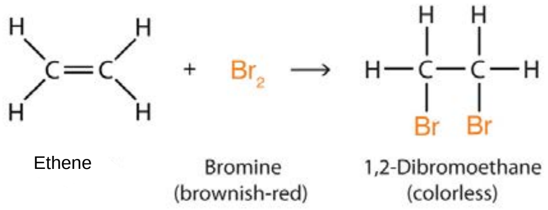
Minor product

Major product

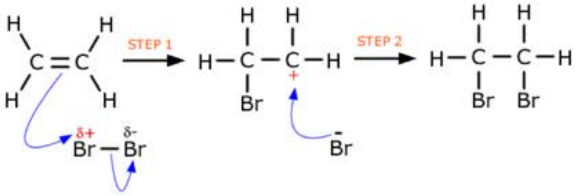
Addition of halogen, X_2 (Halogenation)

1) **Reagent : Halogen, X_2 (in tetrachloromethane or aqueous)**
Condition : Room temperature in dark
Product : Halogenoalkanes (alkanes with halogens)

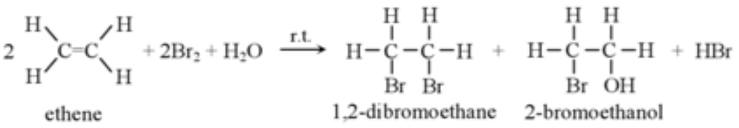
2) When ethene is bubbled into **Br_2 in CC$_4$** at room temperature in dark, Br-Br is added across the C=C bond. The brown colour of bromine is decolourised. 1,2-dibromoethane is produced.



3) The mechanism of this reaction is as follow:



4) When ethene is bubbled into **aqueous Br_2** at room temperature in dark, two products are obtained:

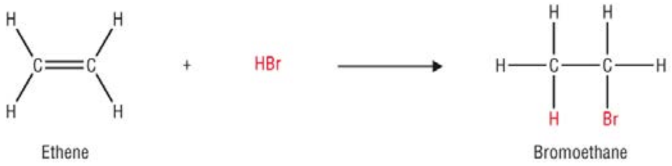


5) Br_2 in CCl_4 is used as **a test to differentiate alkanes and alkenes** as they both are colourless. **Alkene will decolourise the brown colour of bromine** whereas alkane will not.

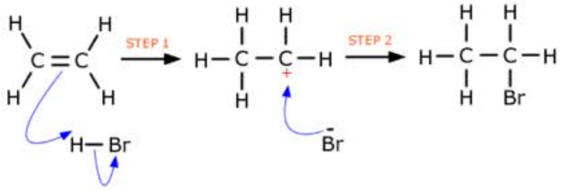
Addition of hydrogen halide, H*X*

1) **Reagent : Hydrogen halide, H*X*(g)**
Condition : Room temperature
Product : Halogenoalkanes (alkanes with halogens)

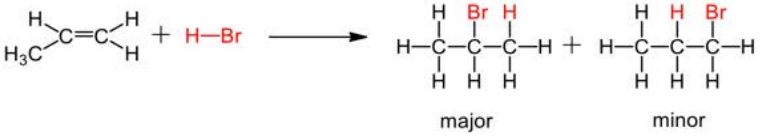
2) When ethene reacts with hydrogen bromide, 1-bromoethane, a halogenoalkane is produced.



3) The mechanism of this reaction is as follow:



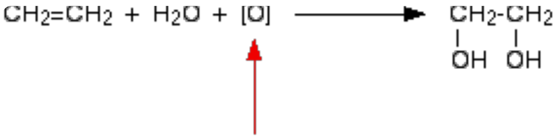
4) The addition of unsymmetrical alkene is as follow. Take propene as an example:



Oxidation by cold and dilute potassium manganate(VII) solution, $KMnO_4$

1) **Reagent : Cold and dilute potassium manganate(VII) solution, $KMnO_4$**
Condition : Room temperature
Product : Alcohols(diols)

2) When ethene is reacted with cold, dilute acidified $KMnO_4$ solution, the purple colour of $KMnO_4$ is decolourised. Ethane-1,2-diol is produced.



$$CH_2{=}CH_2 + H_2O + [O] \longrightarrow \underset{OH}{CH_2}\text{-}\underset{OH}{CH_2}$$

oxygen from the oxidising agent

3) This is a redox reaction, the carbon species is oxidised while the oxidising agent is reduced.

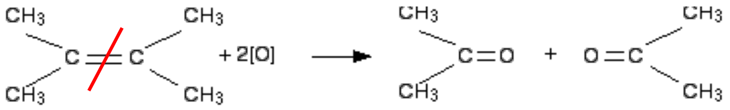
4) This is **another test used to differentiate alkanes and alkenes**. **Only alkene will decolourise the purple colour of $KMnO_4$** whereas alkane will not.

Oxidation by hot and concentrated potassium manganate(VII) solution, $KMnO_4$

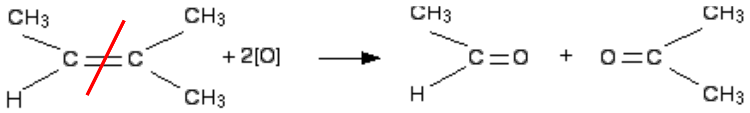
1) **Reagent : Hot and concentrated acidified potassium manganate(VII) solution, $KMnO_4$**
Condition : Room temperature
Product : Carbon dioxide/carboxylic acids/ketones

2) When an alkene is reacted with hot and concentrated acidified $KMnO_4$ solution, the **C=C bond in the alkene ruptures**. The purple colour of $KMnO_4$ is also decolourised. The product formed will differ according to the position of the C=C bond.

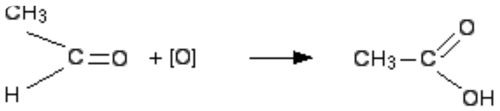
3) i. If there are two alkyl groups at one end of the bond, that part of the molecule will give a **ketone**. For example:



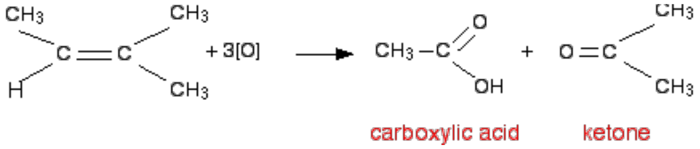
ii. If there are one alkyl group and one hydrogen at one end of the bond, that part of the molecule will give a **carboxylic acid**. For example:



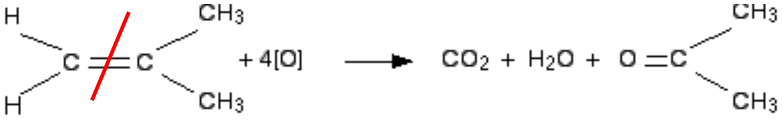
Ethanal(an aldehyde) is further oxidised to ethanoic acid(a carboxylic acid)



The net effect is as such:



iii. If there are two hydrogens at one end of the bond, that part of the molecule will give **carbon dioxide and water**. For example:

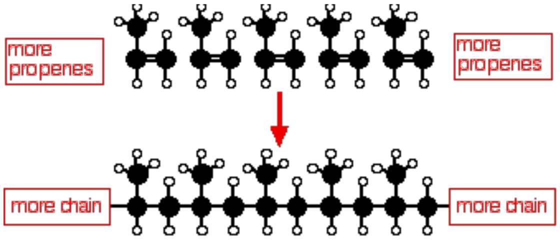


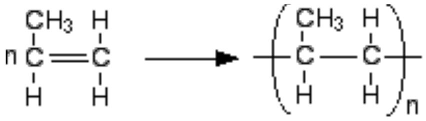
4) This reaction is useful in determining the position of C=C bond in an alkene molecule. This can be done by examining the product(s) formed.

Addition polymerisation

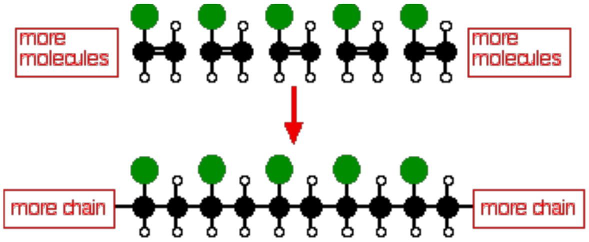
1) Alkenes can open up its C=C bond and join with each other in a long chain to form a polymer. A *polymer* is a long-chain molecule made of repeating units called monomers.

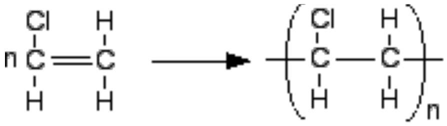
2) i. Polymer : Poly(propene)
Monomer : Propene



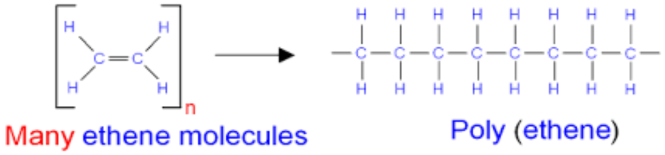


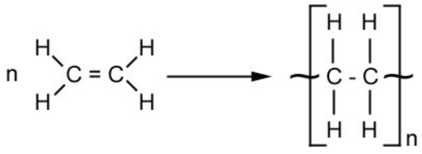
ii. Polymer : Poly(chloroethene) (polyvinyl chloride or PVC)
Monomet : Chloroethane





iii. Polymer : Poly(ethene) (polythene or polyethylene)
Monomer : Ethene
The conditions required for this to happen are as follow:
Temperature - about 60°C
Pressure - a few atmospheres
Catalyst - Ziegler-Natta catalysts or other metal compounds





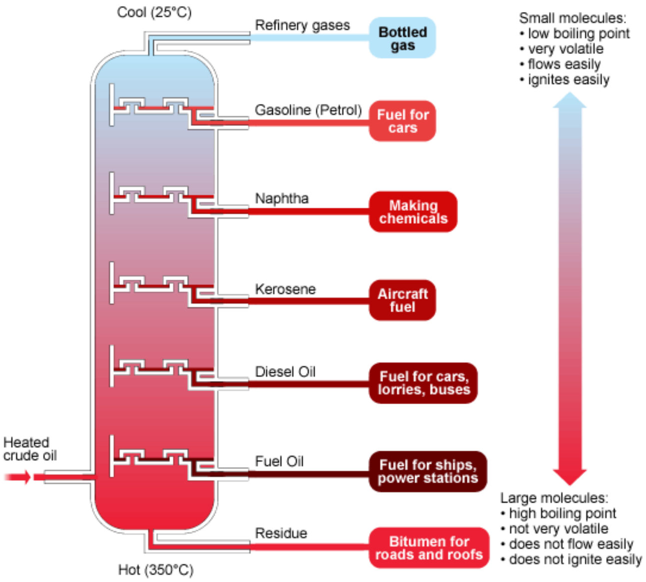
15.5 Uses of Hydrocarbons

Sources of hydrocarbons

1) **Crude oil** is the main source of hydrocarbons, it is found trapped in layers beneath the surface of the earth. Crude oil is a **complex mixture of hydrocarbons - alkanes, cycloalkanes and aromatic compounds**.
[Note: Aromatic compounds are compounds which have a benzene ring attached to it]

2) These substances can be separated by a technique called **fractional distillation**. *Fractional distillation* is the separation of compounds by their boiling points.

3) Different hydrocarbons have different molar masses, and so they have different boiling points.



4) Crude oil enters the bottom of the fractionating column as liquid and vapour. The liquids(less volatile hydrocarbons) are drawn off at the bottom while less volatile ones rise up the column. They condense at different levels as the temperature gradually falls and are collected as liquids.

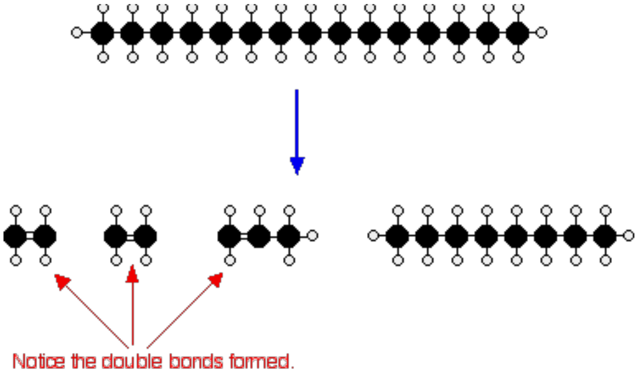
5) The most volatile short-chain hydrocarbons, which are methane and butane, leave the top as gases.

Catalytic cracking

1) After the hydrocarbons are separated, oil companies found that hydrocarbons from lighter fractions(such as gasoline) are in higher demand compared to the ones from heavier fractions.

2) Therefore something must be done to convert those heavier hydrocarbons into the more useful, lighter ones. This is done by **cracking**.

3) Cracking breaks less useful hydrocarbons(normally long-chain) into smaller and more useful ones. Alkenes are normally produced as they are more industrially useful. This is because starting from alkenes, a wide range of organic compounds can be produced.



4) The larger hydrocarbons are fed into a chamber which contains no oxygen, so combustion does not take place. The larger hydrocarbons are heated at **high temperature(about 500 °C)** and passed over **zeolite catalyst**.

5) Cracking of a hydrocarbon is **not unique**, different molecules of hydrocarbons can be broken in different ways, giving rise to different products. One possible reaction of involving $C_{15}H_{32}$ is as follow:

$$C_{15}H_{32} \longrightarrow 2C_2H_4 + C_3H_6 + C_8H_{18}$$

ethene propene octane

Environmental consequences of using hydrocarbons

1) Alkanes are often used as **fuels**. This is because the combustion of alkanes is an exothermic process and produces a lot heat energy. Alkanes are also readily available and relatively cheap. The main uses of alkanes as fuels are:

- To generate electricity.
- To heat domestic houses and cook foods.
- To provide energy needed in industrial processes.
- To provide power for ships, aeroplanes, trains, lorries, buses, cars and motorbikes.

2) However, the combustion of alkanes can produce some poisonous gases which can act as pollutants.

3) One such example is **carbon monoxide, CO** which arises from the incomplete combustion of alkane. Carbon monoxide is a toxic gas that will bind readily to the haemoglobin molecules in the blood. This causes oxygen cannot be transported to cells and the victim will die.

4) The **carbon dioxide, CO_2** produced from the complete combustion of alkane can also act as a **greenhouse gas**. The increasing amount of these greenhouse gases enhances **global warming**.

5) Burning fuels in car engines will also oxidise the nitrogen gas in air to produce **oxides of nitrogen(nitrogen monoxide, NO or nitrogen dioxide, NO_2)**. These oxides of nitrogen is believed to contribute in the formation of acid rain. (For more details, refer Chapter 13)

6) Catalytic converters can be installed to remove carbon monoxide and the oxides of nitrogen. More details about catalytic converters can be found in Chapter 13.

CHAPTER 16: Halogen Derivatives

__Learning outcomes:__

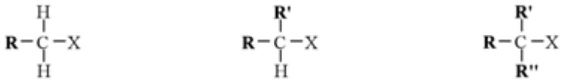
- *(a) recall the chemistry of halogenoalkanes as exemplified by*
  - *(i) the following nucleophilic substitution reactions of bromoethane: hydrolysis, formation of nitriles, formation of primary amines by reaction with ammonia.*
  - *(ii) the elimination of hydrogen bromide from 2-bromopropane.*
- *(b) describe the mechanism of nucleophilic substitution (by both* S_N1 *and* S_N2 *mechanisms) in halogenoalkanes.*
- *(c) interpret the different reactivities of halogenoalkanes(with particular reference to hydrolysis and to the relative strengths of the C-Hal bonds).*
- *(d) explain the uses of fluoroalkanes and fluorohalogenoalkanes in terms of their relative chemical inertness.*
- *(e) recognise the concern about the effect of chlorofluoroalkanes on the ozone layer.*

16.1 Introduction to Halogenoalkaes

What are halogenoalkanes?

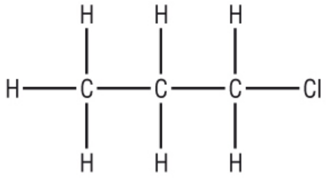
1) *Halogenoalkanes*(or alkyl halides) are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine or iodine).

2) Halogenoalkanes can be classified as **primary**, **secondary** or **tertiary** depending on the number of alkyl groups(R groups) attached to the carbon atom holding the halogen atom.

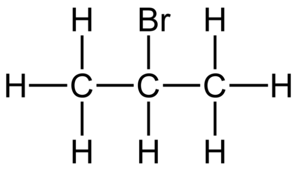


primary (1°) (1 R group or 2 H atoms) *secondary* (2°) (2 R groups or 1 H atom) *tertiary* (3°) (3 R groups or no H atoms)

3) Some examples of halogenoalkanes:



Chloropropane, $CH_3CH_2CH_2Cl$

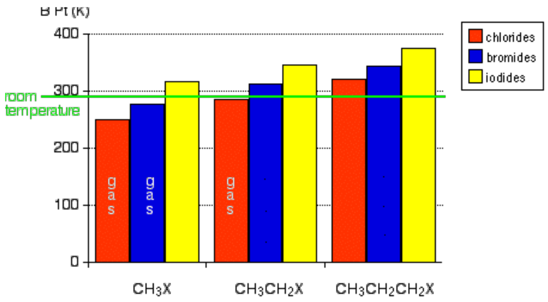


2-bromopropane, $CH_3CHBrCH_3$

1,2-diiodoethane, ICH_2CH_2I

Physical properties of halogenoalkanes

1) i. Boiling point of the halogenoalkanes increases as the molecular size increases. This is because there are **more electrons** in larger molecules and **more temporary dipoles** can be set up, resulting in stronger van der Waal's forces.



ii. Primary halogenoalkanes have higher boiling point compared to secondary and tertiary halogenoalkanes of the same molecular weight. This is because the **surface area of primary halogenoalkanes is higher**, more temporary dipoles can be set up, resulting in stronger van der Waal's forces.

2) i. Halogenoalkanes are **insoluble in water but soluble in organic solvents**.

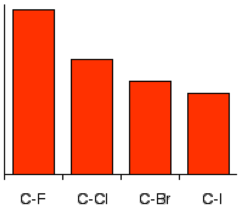
ii. This is because when dissolved in water(polar solvents), the energy needed to break the hydrogen bonds between water molecules is too high. The energy released when halogenoalkane-water attraction is set up is not enough to compensate it. This makes the structure to gain energy overall, making it less stable.

iii. While when it is dissolved in organic solvents, the halogenoalkane-solvent attraction is strong enough to compensate the energy needed to break the weak van der Waal's forces between organic molecules.

16.2 Reactions of Halogenoalkanes

Chemical reactivity of halgenoalkanes

1) **Fluoroalkanes are the least reactive while iodoalkanes are the most reactive**. This is because the carbon-halogen bond strength decreases from fluorine to iodine as the size of the halogen atoms increases.

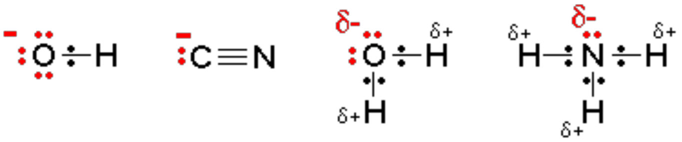


2) Since reactions of halogenoalkanes involve the breaking of the carbon-halogen bond, it follows that carbon-iodine bonds are the easiest to break, making them the easiest to react.

Nucleophilic substitution

1) The signature reaction of halogenoalkanes is **nucleophilic substitution**. Nucleophilic substitution is the **substitution of an atom by a nucleophile**.

2) A nucleophile is a species(an ion or a molecule) which is strongly attracted to a region of positive charge in something else. It normally carries **either a partial or fully negative charge on the molecule**. Some example of nucleophiles are shown below:



3) Nucleophilic substitution is possible due to **polarity of the carbon-halogen bond**. Halogens are more electronegative than carbon, therefore the electron pair in the carbon-halogen bond will be attracted towards the halogen end, leaving the halogen slightly negative and the carbon slightly positive.

4) Since nucleophiles are negative, it is attracted to the positive carbon and this initiates the substitution to occur.

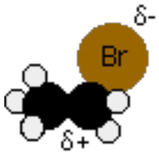
5) For carbon-iodine bond, although there is no polarity, it is still possible because the nucleophile can induce a dipole in the bond due to the electrons repelling each other.

6) Nucleophilic substitution is done via two mechanisms, the **S_N1 or S_N2** mechanism.
-Primary halogenoalkanes will use S_N2.
-Tertiary halogenoalkans will use S_N1.
-Secondary halogenoalkanes will use both.

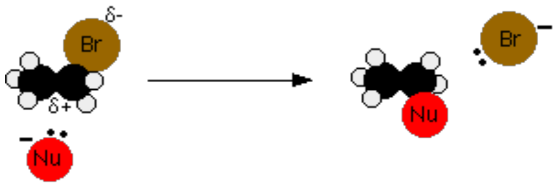
The S_N2 mechanism

1) In S_N2 mechanism, the 'S' stands for substitution, the 'N' stands for nucleophilic and the '2' stands for the **initial step(rate-determining step) involves two species(the halogenoalkane and the nucleophile)**.

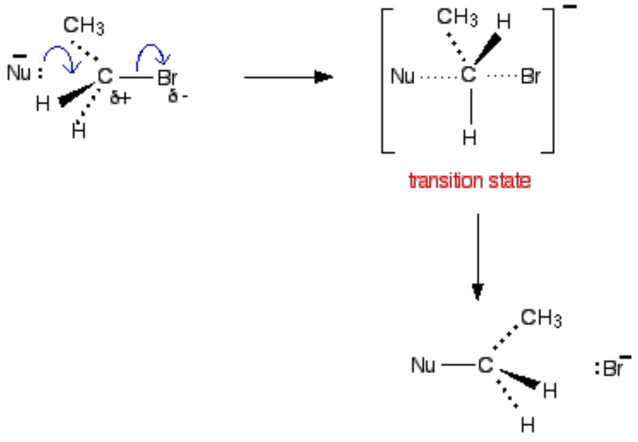
2) The general mechanism of an S_N2 reaction, using bromoethane, CH_3CH_2Br as a typical primary halogenoalkane and Nu^- as a general nucleophile:
   i. The carbon-bromine bond in bromoethane is polarised due to the electronegativity difference between the two atoms. Carbon carries a partial positive charge while bromine carries a partial negative charge.



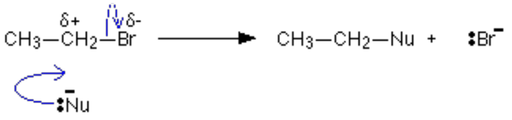
   ii. The nucleophile, **Nu^- is attracted towards the positive carbon**, beginning to form a co-ordinate bond with it. Meanwhile, the negative bromine atom is **repelled further** due to the approaching nucleophile.
   iii. Eventually, there is a state, called the **transition state** where the carbon-bromine bond is just at the point of breaking and the carbon-nucleophile bond is just at the point of forming. The transition state has **five groups** attached to the central carbon atom.
   iii. The movement goes on until the Nu^- is firmly attached to the carbon, and the bromine has been expelled as a Br^- ion. The nucleophile has substituted the bromine.



3) In the examination, the mechanism can be written like this:



....or a more simplified version:

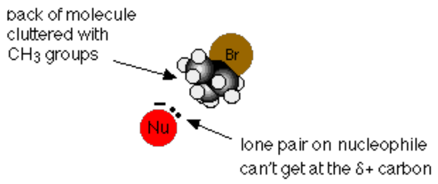


4) Note:

i. When the nucleophile approaches the halogenoalkane, it approaches **from the opposite side of bromine** because the negative bromine hinders the attack from its side.

ii. It is crucial to get the orientation of the atoms right, the molecule has been inverted at the end of the reaction. This is called the **inversion of configuration**(product has a configuration opposite to the reactant).

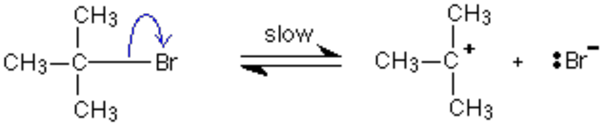
5) It is unlikely for tertiary halogenoalkanes to react by S_N2 mechanism. This is because S_N2 mechanism involves the nucleophile approaching and forming bond from the opposite side of the halogen. In the case of tertiary halogenoalkane, it is unlikely because the opposite of the halogen is cluttered with CH_3 group(s).



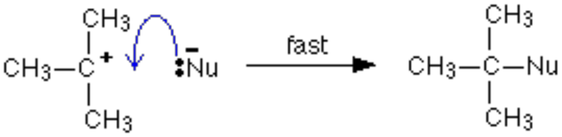
The S_N1 mechanism

1) In S_N1 mechanism, the '1' stands for the **initial step(rate-determining step) involves one species only(the halogenoalkane)**. The overall rate of reaction is governed by the rate of the first step.

2) The general mechanism of an S_N2 reaction, using 2-bromo-2-methylpropane, $(CH_3)_3Br$ as a typical tertiary halogenoalkane and Nu^- as a general nucleophile:
   i. The reaction happens in two stages. In the first stage, a small proportion of the halogenoalkane **ionises to give a carbocation and a bromide ion**.



   ii. Once the carbocation is formed, it will **react immediately** when it comes into contact with a nucleophile, Nu^-. The lone pair of the nucleophile is **strongly attracted** towards the positive carbon, and moves towards it to create a new bond.



3) Tertiary halogenoalkanes react via S_N1 because the **tertiary carbocation intermediate formed is relatively stable**. If primary halogenoalkanes were to react in the same manner, the primary carbocation formed would be relatively unstable, resulting in high activation energy of the reaction.

4) Secondary halogenoalkanes can react using **both S_N1 and S_N2** mechanisms because:
   i. The opposite of the halogen is not cluttered by CH_3 group(s).
   ii. The secondary carbocation formed is more stable than primary carbocation.

Summary of reactions that halogenoalkanes undergo

1) i. Substitution with hydroxide ions, OH^-.
   ii. Substitution with cyanide ions, CN^-.
   iii. Substitution with ammonia, NH_3.
   iv. Elimination

Substitution with hydroxide ions, OH^- (Hydrolysis)

1) **Reagent : Aqueous sodium hydroxide, NaOH or water**
Condition : Heat under reflux
Product : Alcohols

2) When aqueous sodium hydroxide, NaOH is heated with bromoethane under reflux, the bromine is substituted by hydroxide ion, OH. Ethanol is produced.

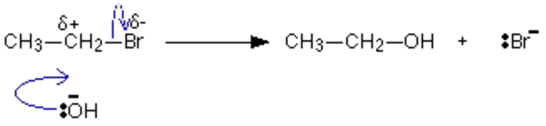
$$CH_3CH_2Br + NaOH \rightarrow CH_3CH_2OH + NaBr$$

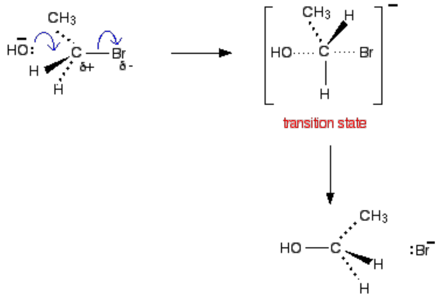
...or the ionic equation:

$$CH_3CH_2Br + OH^- \rightarrow CH_3CH_2OH + Br^-$$

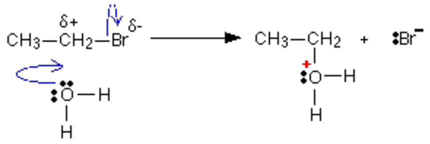
3) Heating under reflux means heating with a condenser placed vertically in the flask to prevent loss of volatile substances from the mixture.

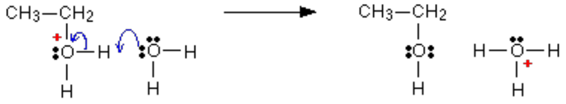
4) The mechanism of this reaction is the same as the ones mentioned before for primary halogenoalkanes, the nucleophile here is hydroxide ion, OH^-.





5) Water can also be used as the nucleophile in this reaction. However, hydrolysis using water occurs much slower. This is because the negatively-charged OH^- is a more effective nucleophile than water. The mechanism is as shown:





6) For a particular alkyl group R, the rate of hydrolysis decreases in the order:

R–I > R–Br > R–Cl > R–F
most reactive ... least reactive

...as the strength of carbon-halogen increases progressively from iodine to fluorine. In fact, the carbon-fluorine bond is so strong that fluoroalkanes do not undergo hydrolysis.

Substitution with cyanide ions, CN^-

1) **Reagent : Potassium cyanide, KCN <u>in ethanol</u>**
   Condition : Heat under reflux
   Product : Nitriles

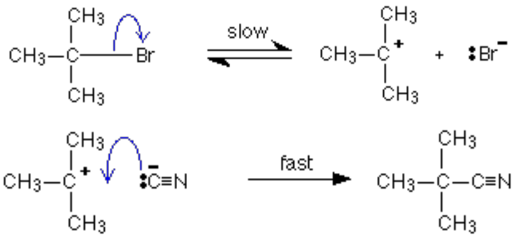
2) When ethanolic potassium cyanide, KCN is heated with 2-bromo-2-methylpentane under reflux, the bromine is substituted by cyanide ion, CN^-. 2-methyl-2-propanenitrile is produced.

$$(CH_3)_3Br + KCN \rightarrow (CH_3)_3CN + KBr$$

...or the ionic equation:

$$(CH_3)_3Br + CN^- \rightarrow (CH_3)_3CN + Br^-$$

3) The mechanism of this reaction is the same as the ones mentioned before for tertiary halogenoalkanes, the nucleophile here is cyanide ion, CN^-.


Step 1: Ionisation of the halogenoalkane

Step 2: Rapid attack by CN^-

4) This is a very useful reaction in organic synthesis.
   i. It serves as a means of **increasing the length of carbon chain**(a step-up reation).
   ii. The nitrile produced can be converted to carboxylic acid by heating under reflux with acid or alkali(hydrolysis reaction)

$$(CH_3)_3CN + 2H_2O + H^+ \rightarrow (CH_3)_3COOH + NH_4^+ \quad ;\text{ acidic hydrolysis}$$
$$(CH_3)_3CN + H_2O + OH^- \rightarrow (CH_3)_3COO^- + NH_3 \quad ;\text{ alkaline hydrolysis}$$

Substitution with ammonia, NH_3

1) **Reagent : Excess ammonia, NH_3 <u>in ethanol</u>**
   Condition : Heat in sealed tube
   Product : Amines

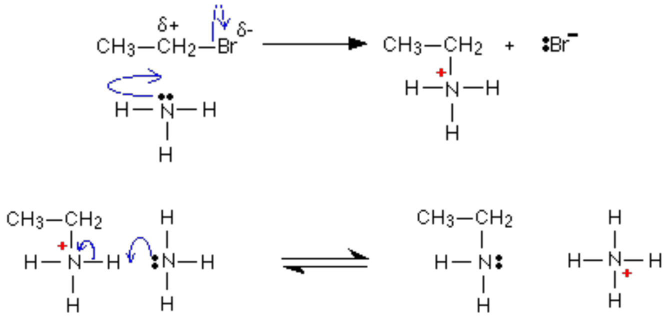
2) When ethanolic ammonia, NH_3 is heated with bromoethane in a sealed tube, the bromine is substituted by amine group, $-NH_2$. The reaction occurs in two stages. In the first stage, a salt is, ethylammonium bromide is formed.

$$CH_3CH_2Br + NH_3 \rightarrow CH_3CH_2NH_3^+Br^-$$

...In the second stage, a reversible reaction occurs between this salt and the excess ammonia. Ethylamine, a primary amine is formed.

$$CH_3CH_2NH_3^+Br^- + NH_3 \rightleftharpoons CH_3CH_2NH_2 + NH_4Br$$

3) The mechanism of the reaction is shown below, ammonia is behaving as a nucleophile.

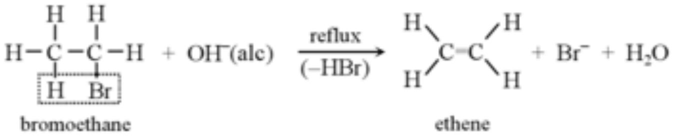


4) If the ammonia used is not in excess, a complicated mixture containing secondary and tertiary amine is obtained. This is because ethylamine is a good nucleophile and it can attack the unreacted bromoethane.

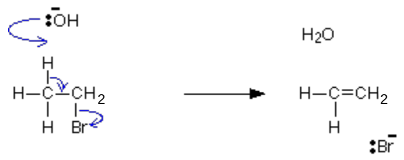
Elimination

1) **Reagent : Sodium hydroxide, NaOH in ethanol**
Condition : Heat under reflux
Product : Alkenes

2) In this alcoholic condition, the hydroxide ion, OH^- acts as a **base** rather than a nucleophile. Hence it will accept a proton(hydrogen ion) from the carbon atom next door to the one holding the bromine. The resulting re-arrangement of the electrons expels the bromine as a bromide ion and produces ethene.



3) The mechanism of the reaction is shown below:



4) In unsymmetrical halogenoalkanes, a mixture of products of different isomers is produced due to the choice of hydrogen being removed.

16.3 Uses of Halogenoalkanes

The use of CFCs

1) CFCs are chlorofluorocarbons, compounds containing carbon with chlorine and fluorine atoms attached. Two common CFCs are CFC-11(CCl_3F) and CFC-12(CCl_2F_2).

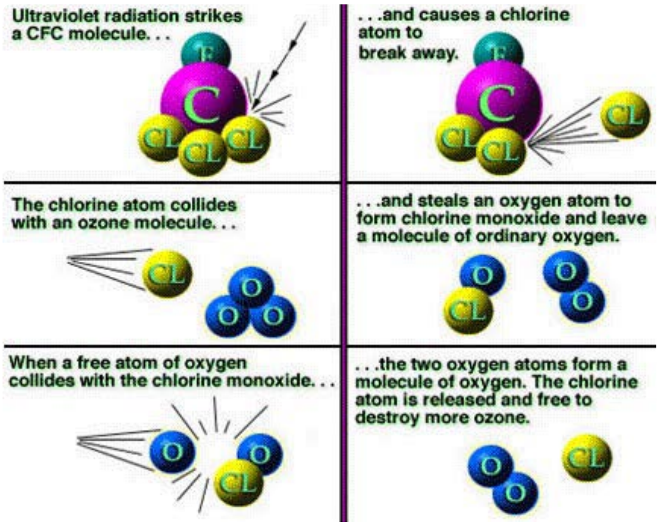
2) Some properties and uses of CFCs:

***Properties of* CFCs**	***Uses of* CFCs**
➢ chemically unreactive or inert. ➢ non-flammable. ➢ low toxicity. ➢ odourless, tasteless. ➢ volatile (low boiling point).	➢ as *refrigerants* (cooling fluids), e.g. in refrigerators and air-conditioners. ➢ as *aerosol propellants*, e.g. in perfume and insecticide sprays. ➢ as *foam-blowing agents*, e.g. to make expanded polystyrene packaging. ➢ as *cleaning agent* (solvent) in electronic industries. ➢ as *flame retardant* in fire extinguisher, e.g. $CClBrF_2$.

CFCs and the environment

1) CFCs have many uses in our daily life. However, due to their stability and inertness, they are also large responsible for the **destruction of the ozone layer**. Ozone layer prevents harmful ultraviolet radiation from reaching us.

2) Destruction of the ozone layer involves the **conversion of ozone molecule, O_3 to oxygen molecule, O_2**. The detailed mechanism is as shown below:



3) Possible solutions to protect the ozone layer:
   i. Reduce the use of CFCs. For example, replace aerosol spray with manual pump spray.
   ii. Collect and recycle CFCs for future use.
   iii. Find alternatives for CFCs.

4) Possible alternatives for CFCs:
   i. Use HCFCs(CFCs with at least one hydrogen atom, for example, CF_3CHCl_2)
      - HCFCs have smaller effect on ozone depletion because they are more readily destroyed in the troposphere.
      - However, a disadvantage of using it is, it is flammable. Also, it could potentially form toxic chemicals in the troposphere.
   ii. Use LPG(liquid petroleum gas) as propellant in aerosol sprays.
   iii. Use air-blowing agent in packaging and building industries.
   iv. Use water-based cleaning system in electronic industries.

CHAPTER 17: Hydroxy Compounds

17.1 Introduction to Alcohols
17.2 Reactions of Alcohols

Learning outcomes:

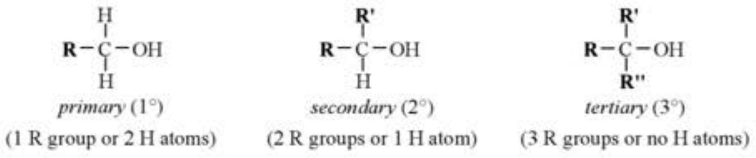
- *(a) recall the chemistry of alcohols, exemplified by ethanol:*
  - *(i) combustion.*
  - *(ii) substitution to give halogenoalkanes.*
  - *(iii) reaction with sodium.*
  - *(iv) oxidation to carbonyl compounds and carboxylic acids.*
  - *(v) dehydration to alkenes.*
  - *(vi) formation of esters by esterification with carboxylic acids.*
- *(b) (i) classify hydroxy compounds into primary, secondary and tertiary alcohols.*
  - *(ii) suggest characteristic distinguishing reactions, e.g. mild oxidation.*

17.1 Introduction to Alcohols

What are alcohols?

1) *Alcohols* are compounds in which one or more hydrogen atoms in an alkane have been replaced by an -OH group.

2) Alcohols can be classified as **primary**, **secondary** or **tertiary** depending on the number of alkyl groups(R groups) attached to the carbon atom holding the -OH group.

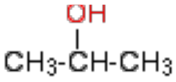


primary (1°) (1 R group or 2 H atoms)
secondary (2°) (2 R groups or 1 H atom)
tertiary (3°) (3 R groups or no H atoms)

3) Some examples of alcohols:

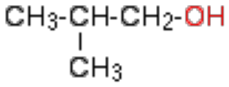
CH_3-CH_2-OH

ethanol



$CH_3-\overset{OH}{\overset{|}{C}}H-CH_3$

propan-2-ol

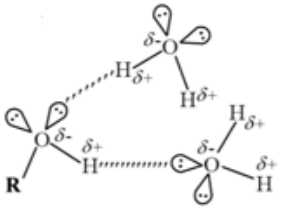


$CH_3-\underset{CH_3}{\underset{|}{C}}H-CH_2-OH$

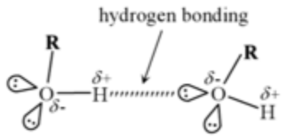
2-methylpropan-1-ol

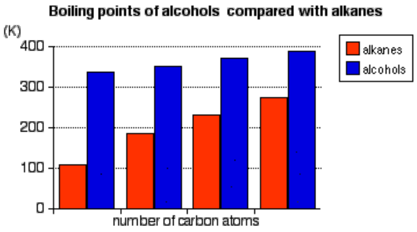
Physical properties of alcohols

1) i. Alcohols are **soluble in water** because they can form **hydrogen bonds** with water molecules.
   ii. However, the solubility decreases as the number of carbon atoms increases. This is because the presence of long hydrocarbon tail disrupts the effectiveness of hydrogen bonding.



2) i. Alcohols have **higher boiling points** than the alkanes with similar M_r due to the presence of **intermolecular hydrogen bonding** in addition of van der Waals' forces of attraction.
   ii. The boiling point increases as the number of carbon atoms increases. This is because there are more electrons, hence more temporary dipoles can be set up. More energy is required to overcome these forces.





17.2 Reactions of Alcohols

Summary

1) Summary of reactions that alcohols undergo:
   i. Combustion.
   ii. Dehydration to give alkenes.
   iii. Reaction with sodium.
   iv. Substitution to give halogenoalkanes.
   iv. Oxidation.
   v. Esterification.

Combustion

1) **Reagent : Oxygen supply**
   Condition : Heat
   Product : Carbon dioxide(and carbon monoxide) and water

2) Alcohols undergo complete combustion under **excess oxygen** to give carbon dioxide and water. Example:

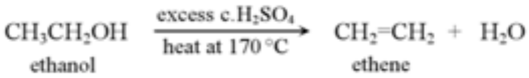
$$C_2H_5OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$$

3) When oxygen is limited, carbon monoxide and carbon soot might be formed.

Dehydration

1) **Reagent/ Catalyst : Excess concentrated sulfuric acid, H_2SO_4 or hot aluminium oxide, Al_2O_3**
   Condition : Heat at about 170 °C
   Product : Alkenes

2) When ethanol is heated with concentrated sulfuric acid, the alcohol is dehydrated, a water molecule is removed from the alcohol. Ethene is produced.

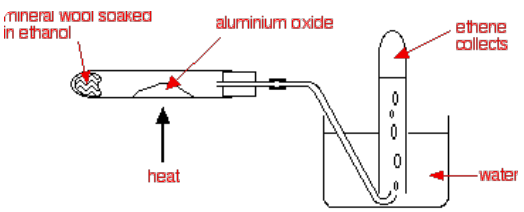


$$\underset{\text{ethanol}}{CH_3CH_2OH} \xrightarrow[\text{heat at 170 °C}]{\text{excess c.}H_2SO_4} \underset{\text{ethene}}{CH_2{=}CH_2} + H_2O$$

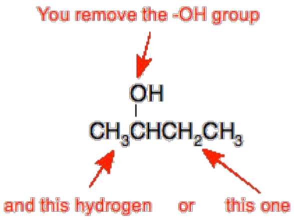
3) During dehydration, the **-OH group gets removed together with a hydrogen atom from the next-door carbon atom**.

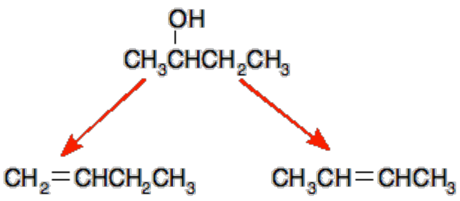
4) i. Alternatively, dehydration can be carried out by passing ethene through **hot aluminium oxide**. The ethene gas produced is collected over water.

ii. At the end of the reaction, the apparatus is left to cool with the delivery tube out of water. This is done so that the cold water would not be sucked back into the hot delivery tube, cracking it eventually.



5) For more complicated alcohols, be careful of the possibility of **more than one product being formed** and also the possibility of **geometric isomers in the alkenes**. This is due to a different hydrogen being removed from the alcohol. An example is butan-2-ol.





Reaction with sodium metal, Na

1) **Reagent : Sodium metal, Na**
Condition : Room temperature
Product : Alkoxides and hydrogen gas

2) Acids react with metals to produce hydrogen gas and a salt. Alcohols are **very weak acids**, so they undergo this reaction as well.

3) When sodium metal is added to ethanol, the sodium metal sinks and bubbles of hydrogen gas are released. The salt formed is sodium ethoxide, a white solid.

$$2CH_3CH_2OH + 2Na \rightarrow 2CH_3H_2O^-Na^+ + H_2$$

4) This reaction can be used as **a test for hydroxy, -OH group**. Bubbles of hydrogen gas is released if a hydroxy group is present.

5) Remember, in order to produce a hydrogen gas molecule, H_2, two hydrogens from two molecules of alcohols must be used.

Substitution to give halogenoalkanes

1) The -OH group of the alcohol can be substituted by a halogen to produce a halogenoalkane. The halogen can be obtained from three sources:
   i. Hydrogen halide, H*X* ; where *X* = Cl/Br/I
   ii. Phosphorus halide, PCl_5 or PBr_3 or PI_3
   iii. Thionyl chloride(or sulfur dichloride oxide), $SOCl_2$

2) With **hydrogen halide, H*X***:
   i. The alcohol is refluxed with sodium halide, Na*X* and concentrated sulfuric acid, H_2SO_4 to produce the hydrogen halide, H*X*.
   $$NaX + H_2SO_4 \rightarrow HX + NaHSO_4 \quad ; \text{where } X = Cl/Br$$
   For iodine, phosphoric(V) acid, H_3PO_4 is used instead of sulfuric acid.
   ii. The hydrogen halide, H*X* is the reacted with the alcohol. Take ethanol as an example:
   $$CH_3CH_2OH + HX \rightarrow CH_3CH_2X + H_2O \quad ; \text{where } X = Cl/Br/I$$

3) With **phosphorus halide, $PCl_5/PCl_3/PBr_3/PI_3$**:
   i. Alcohols react with phosphorus(V) chloride, to produce a halogenoalkane, **white fumes of hydrogen chloride gas** is also observed. Take ethanol as an example:
   $$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$$
   ii. This can be used as **a test for the hydroxy, -OH group**. White fumes of hydrogen chloride gas is observed if hydroxy group is present.
   iii. For phosphorus(III) halides, a halogenoalkane is also obtained. The phosphorus halides are prepared *in situ* by mixing red phosphorus and the halogen.
   $$3CH_3CH_2OH + PX_3 \rightarrow 3CH_3CH_2X + H_3PO_4 \quad ; \text{where } X = Cl/Br/I$$

4) With **thionyl chloride, $SOCl_2$**:
   i. Alcohols react with thionyl chloride to produce a halogenoalkane. Sulfur dioxide and hydrogen chloride are are given off as well.
   $$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2X + SO_2 + HCl \quad ; \text{where } X = Cl/Br/I$$
   ii. This reaction is useful in obtaining pure halogenoalkane. This is because the other two products are gases, and they can be separated from the mixture easily.

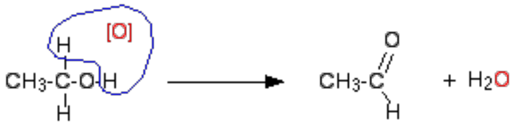
Oxidation

1) **Reagent : Acidified potassium dichromate(VI), $K_2Cr_2O_7$ or acidified potassium manganate(VI), $KMnO_4$**
Condition : Heat under reflux
Product : Primary alcohol - Aldehydes and carboxylic acids
Secondary alcohol - Ketones
Tertiary alcohol - Will not be oxidised

2) Different class of alcohols(primary, secondary or tertiary) will behave differently during oxidation. Therefore, it is a very useful test to distinguish them.

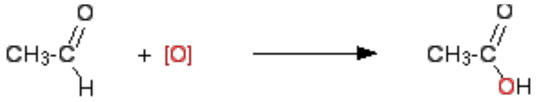
3) i. For **primary alcohols**, if the **alcohol used is in excess** and the **product formed is distilled off as soon as possible**, **aldehydes are formed**. Take ethanol as an example, ethanal is formed.

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$



ii. If the **alcohol used is limited** and **heated under reflux**, the primary alcohol will be oxidised **to aldehyde then to carboxylic acid**. Take ethanol as an example, from the aldehyde formed, ethanoic acid is formed.

$$CH_3CHO + [O] \rightarrow CH_3COOH$$

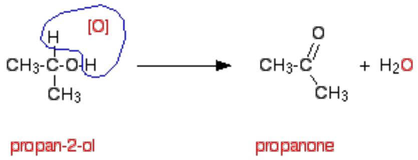


...or the full equation from ethanol to ethanoic acid:

$$CH_3CH_2OH + 2[O] \rightarrow CH_3COOH + H_2O$$

4) For **secondary alcohols**, the secondary alcohol **will be oxidised to a ketone**. Take propan-2-ol as an example, propanone is formed.

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$



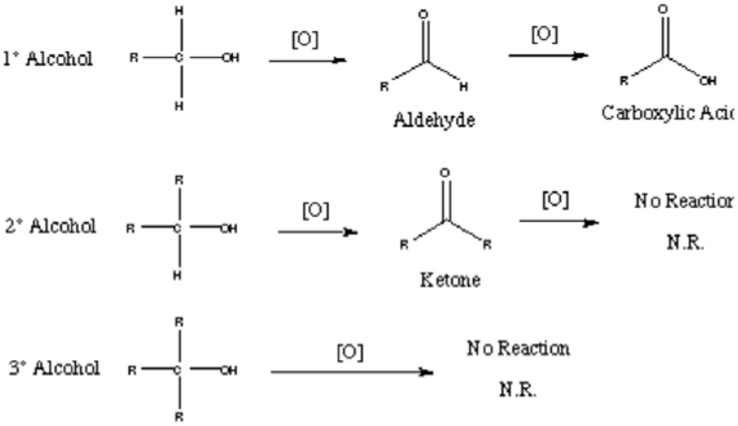
5) For **tertiary alcohols**, they will **not be oxidised**. This is because there is no hydrogen atom from the carbon atom holding the -OH group can be removed.

6) For observation:

i. If $K_2Cr_2O_7$ is used as oxidising agent: colour of solution changes from **orange** to **green**.

ii. If $KMnO_4$ is used as oxidising agent : colour of solution changes from **purple** to **colourless**.

7) Summary:



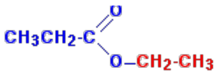
Esterification

1) **Reagent : Carboxylic acid**

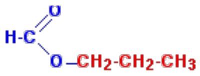
Conditions : Heat under reflux with concentrated sulfuric acid, H_2SO_4 as catalyst

Product : Esters

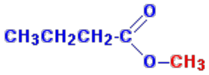
2) Esters are derivatives of carboxylic acids. In an ester, the hydrogen from the -COOH group of carboxylic acid is replaced by an alkyl group. The alkyl group came from the alcohol. Some common esters and their naming:



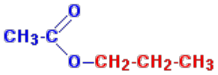
ethyl propanoate



propyl methanoate



methyl butanoate

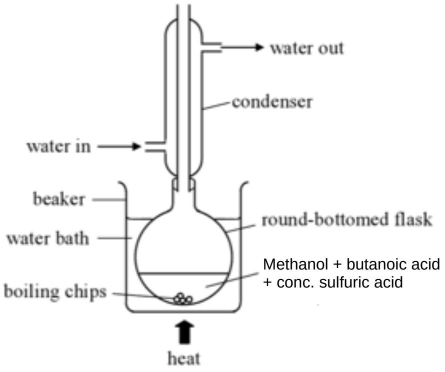


propyl ethanoate

4) Note that the name of an ester is **'alcohol + carboxylic acid'**.

5) For example, to make methyl butanoate, methanol and butanoic acid are used. Both of them are heated under reflux with the presence of catalyst. Esters can be detected from a **sweet-smelling odour**.

$$CH_3OH + CH_3CH_2CH_2COOH \rightleftharpoons CH_3CH_2CH_2COOCH_3 + H_2O$$



Note:

1) To find out more about aldehydes and ketones, refer Chapter 18.
2) To find out more about carboxylic acids and esters, refer Chapter 19.

CHAPTER 18: Carbonyl Compounds

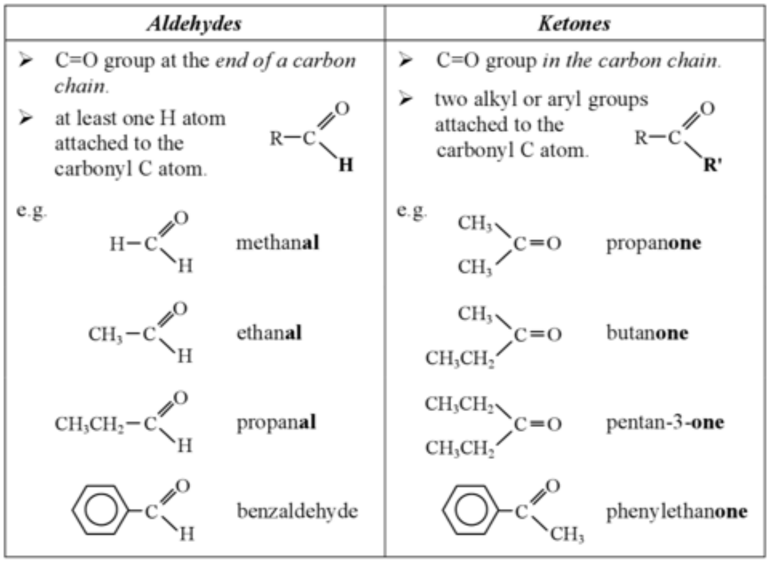
Learning outcomes:

(a) describe:
  (i) the formation of aldehydes and ketones from primary and secondary alcohols respectively using $Cr_2O_7^{2-}/H^+$.
  (ii) the reduction of aldehydes and ketones, e.g. using $NaBH_4$ *or* $LiAlH_4$.
  (iii) the reaction of aldehydes and ketones with HCN and NaCN.
(b) describe the mechanism of the nucleophilic addition reactions of hydrogen cyanide with aldehydes and ketones.
(c) describe the use of 2,4-dinitrophenylhydrazine (2,4-DNPH) reagent to detect the presence of carbonyl compounds.
(d) deduce the nature (aldehyde or ketone) of an unknown carbonyl compound from the results of simple tests (i.e. Fehling's and Tollens' reagents; ease of oxidation).

18.1 Introduction to Aldehydes and Ketones

What are carbonyl compounds?

1) Carbonyl compounds are compounds that contain the C=O(carbonyl) group. Examples are aldehydes and ketones.



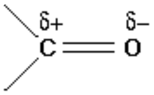
Aldehydes		*Ketones*	
➢ C=O group at the *end of a carbon chain.* ➢ at least one H atom attached to the carbonyl C atom.	$R-C(=O)$**H**	➢ C=O group *in the carbon chain.* ➢ two alkyl or aryl groups attached to the carbonyl C atom.	$R-C(=O)$**R'**
e.g. $H-C(=O)H$	methan**al**	e.g. $(CH_3)(CH_3)C=O$	propan**one**
$CH_3-C(=O)H$	ethan**al**	$(CH_3)(CH_3CH_2)C=O$	butan**one**
$CH_3CH_2-C(=O)H$	propan**al**	$(CH_3CH_2)(CH_3CH_2)C=O$	pentan-3-**one**
	benzaldehyde		phenylethan**one**

Physical properties of carbonyl compounds

1) i. The boiling point of carbonyl compounds is higher than the alkanes with similar M_r.

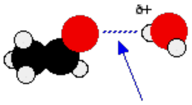
ii. The boiling point increases with increasing number of carbon atom. This is because there are more electrons, hence more temporary dipoles can be set up. More energy is required to overcome these forces.

ii. Besides temporary dipoles, permanent dipole-dipole forces are also present due to carbonyl compounds being polar.



iii. Methanal and ethanal are gases at room temperature, while others are liquids.

2) i. Carbonyl compounds are soluble in water. This is because they are able to form hydrogen bond with water molecules.



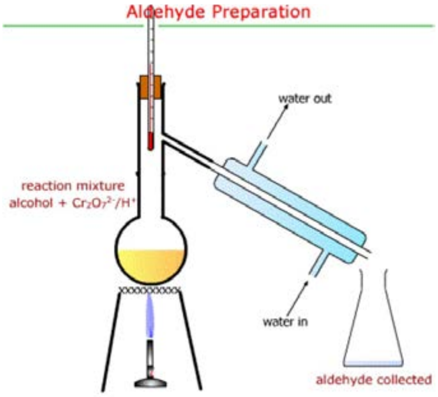
Hydrogen bond between a slightly positive hydrogen and a lone pair on the oxygen in the carbonyl group

ii. The solubility decreases with increasing number of carbon atoms. This is because the long hydrocarbon chain disrupts the hydrogen bonding.

Preparation of aldehydes and ketones

1) Aldehydes and ketones can be made by **oxidising primary and secondary alcohol respectively**. The oxidising agent used is either acidified potassium dichromate(VI), $K_2Cr_2O_7$ or acidified potassium manganate(VII), $KMnO_4$.

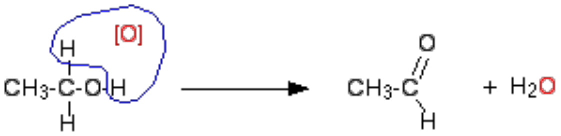
2) To make an **aldehyde**:



   i. The primary alcohol used must be in excess and heated under reflux with acidified $K_2Cr_2O_7/KMnO_4$. The aldehyde formed **must be distilled off as soon as possible**.

   ii. Under these conditions, a primary alcohol is oxidised to an aldehyde. Take ethanol as an example, ethanal is produced.

$$CH_3CH_2OH + [O] \rightarrow CH_3CHO + H_2O$$

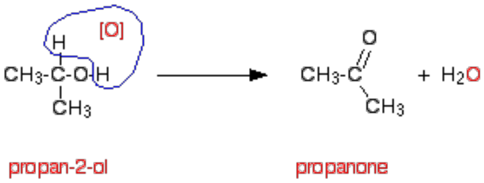


3) To make a **ketone**:

   i. The secondary alcohol is heated under reflux with acidified $K_2Cr_2O_7/KMnO_4$.

   ii. Under these conditions, a secondary alcohol is oxidised to a ketone. Take propan-2-ol an an example:

$$CH_3CH(OH)CH_3 + [O] \rightarrow CH_3COCH_3 + H_2O$$



18.2 Reactions of Aldehydes and Ketones

Reactivity of carbonyl compounds

1) The C=O bond of the carbonyl group is highly polarised due to oxygen atom being more electronegative.

2) This causes the slightly positive carbon atom to be susceptible to nucleophilic attacks. Nucleophiles are something that carries a negative charge.

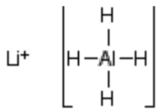
3) Therefore, carbonyl compounds will undergo **nucleophilic addition**.

4) Summary of reactions carbonyl compounds undergo:
   i. Reduction.
   ii. Oxidation.
   iii. Reaction with hydrogen cyanide, HCN.

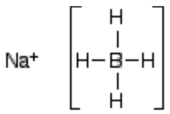
Reduction

1) **Reagent : Lithium tetrahydridoaluminate, $LiAlH_4$ or sodium tetrahydridoborate, $NaBH_4$**
   Condition : For $LiAlH_4$ - in dry ether
   For $NaBH_4$ - in aqueous alcoholic solution
   Product : Aldehyde - primary alcohol
   Ketone - secondary alcohol

2) $LiAlH_4$ and $NaBH_4$ are acting as reducing agents as well as providing the nucleophile, H^-. This is a redox reaction as well as a nucleophilic addition reaction.

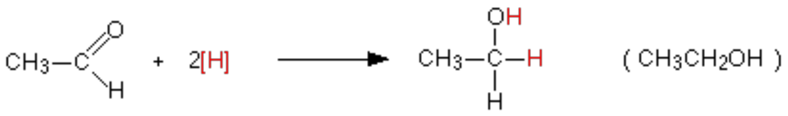


lithium tetrahydridoaluminate

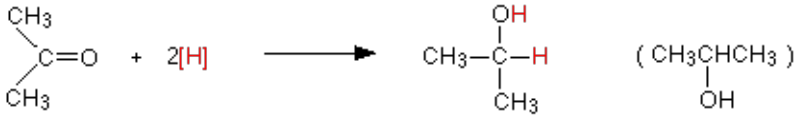


sodium tetrahydridoborate

3) For aldehydes, **primary alcohols** are formed upon reduction. Take ethanal as an example:



4) For ketones, **secondary alcohols** are formed upon reduction. Take propanone as an example:



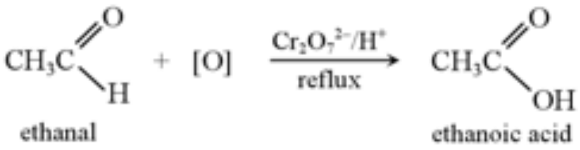
5) Note:

i. Due to the reactivity of $LiAlH_4$, it cannot be used in the presence of water or alcohol. It must be carried out in solution in a carefully dried ether such as ethoxyethane(diethyl ether).

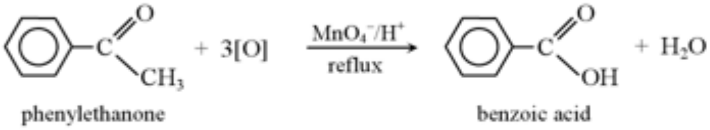
Oxidation

1) **Reagent : Acidified potassium dichromate(VI), $K_2Cr_2O_7$ or acidified potassium manganate(VI), $KMnO_4$**
Condition : Heat under reflux
Product : Aldehyde - Carboxylic acid
Ketone - Will not be oxidised.

2) Aldehydes will be oxidised to **carboxylic acids**. Take ethanal as an example:



3) Ketones **will not be oxidised** by acidified $K_2Cr_2O_7$ or $KMnO_4$. The only exception is phenylethanone.



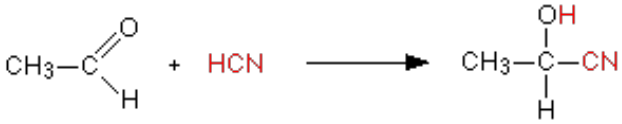
Reaction with hydrogen cyanide, HCN

1) **Reagent : Sodium/potassium cyanide, NaCN and a little sulfuric acid, H_2SO_4**
Condition : Room temperature
Product : Hydroxynitriles

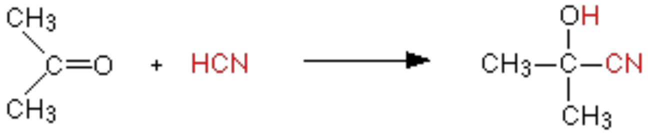
2) Hydrogen cyanide is not used alone because it is a poisonous gas. Instead, it is produced from the reaction between sodium/potassium cyanide and sulfuric acid. The solution will contain hydrogen cyanide and some free cyanide ions.

3) For both aldehydes and ketones, **hydroxynitriles** are produced.

i. For aldehydes, take ethanal as an example, 2-hydroxypropanenitrile is produced.

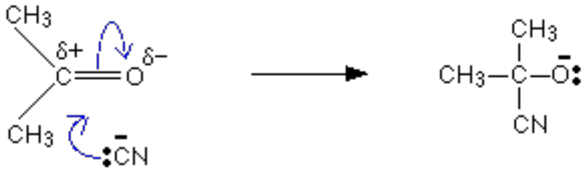


ii. For ketones, take propanone as an example, 2-hydroxy-2-methylpropanenitrile is produced.



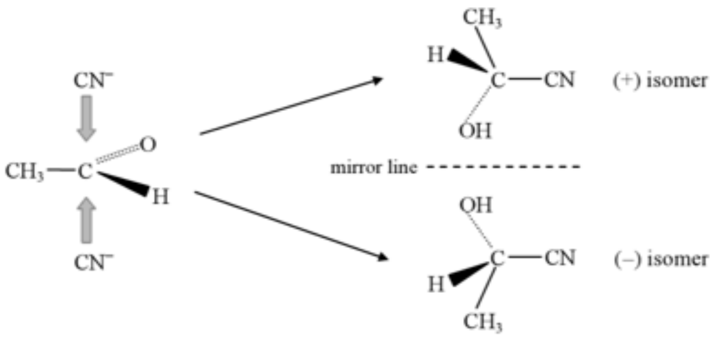
4) The mechanism of this reaction - **nucleophilic addition**:

i. The electron-deficient carbon atom is attacked by the nucleophile, CN^-.



ii. The negative ion formed then picks up a hydrogen ion from hydrogen cyanide, or from the water

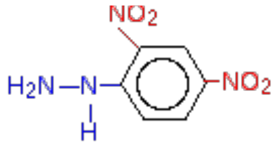
5) Such a reaction will produce a mixture of different isomers. This is because carbonyl compounds are planar and the cyanide ion has equal chance of attacking from above or below the plane of the molecule.



18.3 Tests for Aldehydes and Ketones

Test for carbonyl group using 2,4-dinitrophenylhydrazine(2,4-DNPH)

1) 2,4-dinitrophenylhydrazine or 2,4-DNPH can be used **to detect the presence of carbonyl group, C=O**. The structure of 2,4-DNPH is shown below:

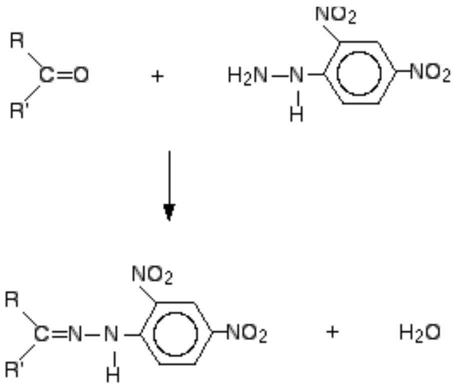


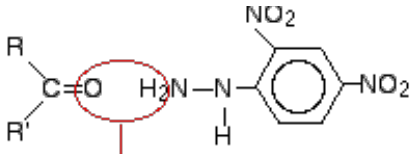
2,4-dinitrophenyl**hydrazine**

2) This test is usually carried out using Brady's reagent, that is, a solution of the 2,4-dinitrophenylhydrazine in methanol and sulfuric acid.

3) When a little aldehyde or ketone is added to the Brady's reagent, an **orange-yellow precipitate** is formed.

4) A **condensation reaction** occurs when a carbonyl compound is added to 2,4-DNPH. During this reaction, a water molecule is lost. The final compound is seen as orange-yellow precipitate.





This gets lost as water, and the other two bits just join together.

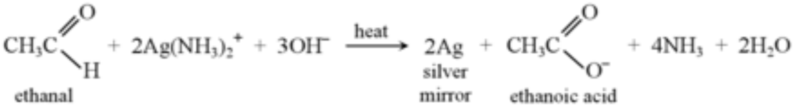
Test for aldehydes using Tollens' reagent(silver mirror test)

1) Tollens' reagent contains **diamminesilver(I) ions, $[Ag(NH_3)_2]^+$**. Aldehydes will reduce the diamminesilver(I) ions to metallic silver, aldehyde itself is oxidised to a salt of carboxylic acid.

2) Since ketones will not be oxidised, it will not reduce it to metallic silver.

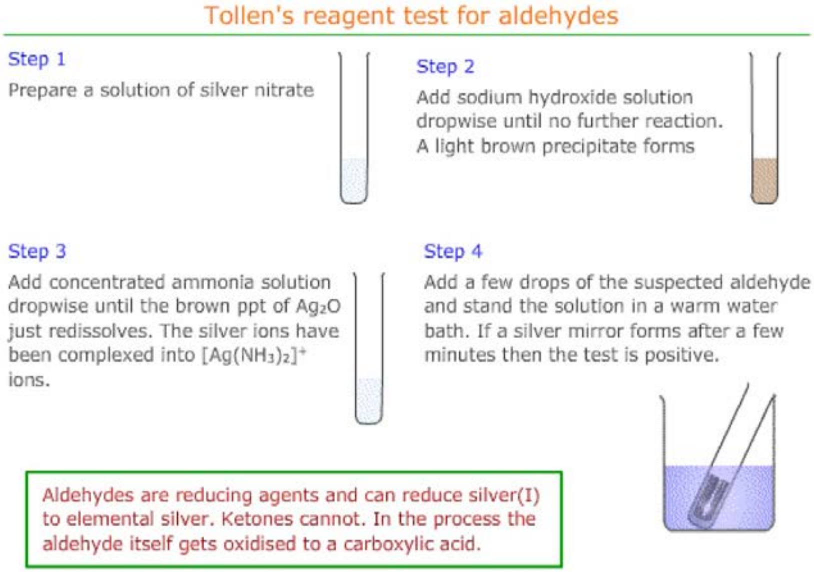
3) Therefore, when a few drops of aldehyde is added to the freshly prepared Tollens' reagent, and warmed in a water bath for a few minutes, **a grey precipitate or a silver mirror** is observed only if aldehyde is present.

4) Take ethanal as an example, the equation is:



$$CH_3CHO + 2Ag(NH_3)_2^+ + 3OH^- \xrightarrow{heat} 2Ag + CH_3COO^- + 4NH_3 + 2H_2O$$

5) The details on the preparation of Tollens' reagent are as shown below.



Tollen's reagent test for aldehydes

Step 1

Prepare a solution of silver nitrate

Step 2

Add sodium hydroxide solution dropwise until no further reaction. A light brown precipitate forms

Step 3

Add concentrated ammonia solution dropwise until the brown ppt of Ag_2O just redissolves. The silver ions have been complexed into $[Ag(NH_3)_2]^+$ ions.

Step 4

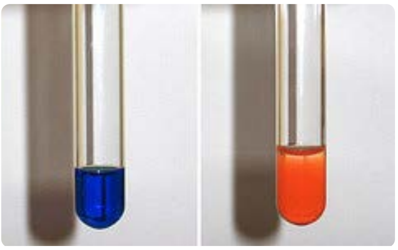
Add a few drops of the suspected aldehyde and stand the solution in a warm water bath. If a silver mirror forms after a few minutes then the test is positive.

Aldehydes are reducing agents and can reduce silver(I) to elemental silver. Ketones cannot. In the process the aldehyde itself gets oxidised to a carboxylic acid.

Test for aldehydes using Fehling's solution

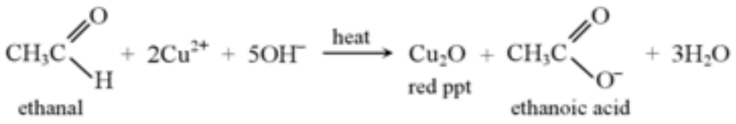
1) Fehling's solution contains **copper(II) ions complexed with tartrate ions** in sodium hydroxide solution. Complexing the copper(II) ions with tartrate ions prevents precipitation of copper(II) hydroxide. It is a blue solution.

2) Only aldehydes will reduce the complexed copper(II) ion to copper(I) oxide. Because the solution is alkaline, the aldehyde itself is oxidised to a salt of the corresponding carboxylic acid.

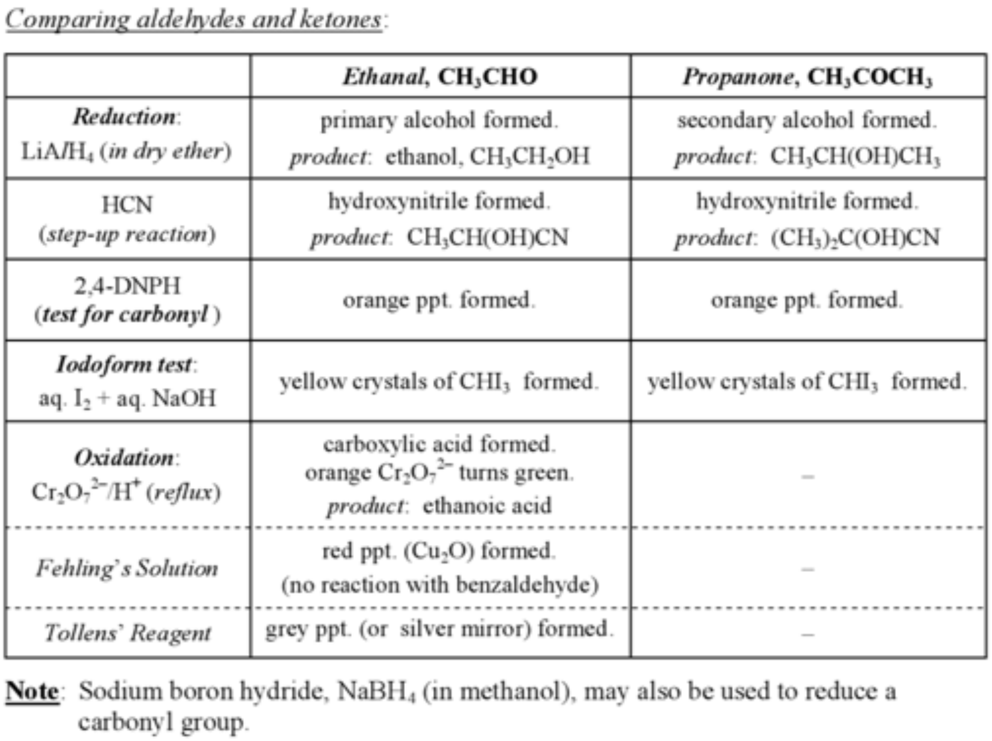


3) When a few drops of the aldehyde is added to the reagent, and the mixture is warmed gently in a hot water bath for a few minutes, a **red precipitate** is observed only if aldehydes present.

4) Take ethanal as an example, the equation is:



Summary



Comparing aldehydes and ketones:

	Ethanal, **CH_3CHO**	***Propanone***, **CH_3COCH_3**
Reduction: $LiAlH_4$ (*in dry ether*)	primary alcohol formed. *product*: ethanol, CH_3CH_2OH	secondary alcohol formed. *product*: $CH_3CH(OH)CH_3$
HCN (*step-up reaction*)	hydroxynitrile formed. *product*: $CH_3CH(OH)CN$	hydroxynitrile formed. *product*: $(CH_3)_2C(OH)CN$
2,4-DNPH (***test for carbonyl***)	orange ppt. formed.	orange ppt. formed.
Iodoform test: aq. I_2 + aq. NaOH	yellow crystals of CHI_3 formed.	yellow crystals of CHI_3 formed.
Oxidation: $Cr_2O_7^{2-}/H^+$ (*reflux*)	carboxylic acid formed. orange $Cr_2O_7^{2-}$ turns green. *product*: ethanoic acid	–
Fehling's Solution	red ppt. (Cu_2O) formed. (no reaction with benzaldehyde)	–
Tollens' Reagent	grey ppt. (or silver mirror) formed.	–

Note: Sodium boron hydride, $NaBH_4$ (in methanol), may also be used to reduce a carbonyl group.

CHAPTER 19: Carboxylic Acids and Derivatives I

Learning outcomes:

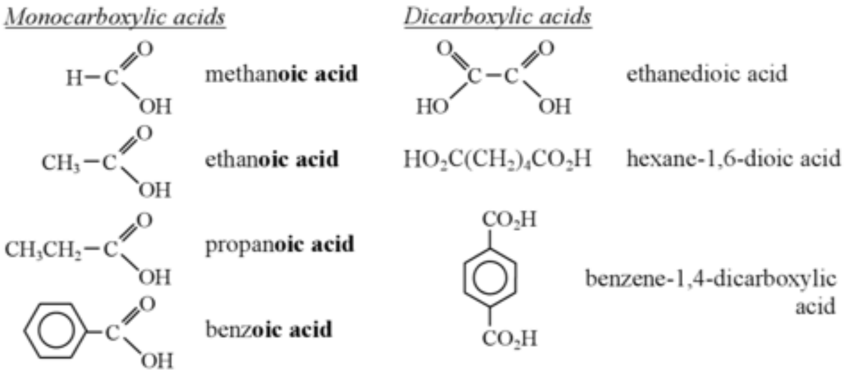
(a) describe the formation of carboxylic acids from alcohols, aldehydes and nitriles.
(b) describe the reactions of carboxylic acids in the formation of:
  (i) salts, by the use of reactive metals, alkalis or carbonates.
  (ii) esters.
  (iii) acyl chlorides.
(c) describe the formation of esters from carboxylic acids, using ethyl ethanoate as an example.
(d) describe the acid and base hydrolysis of esters.
(e) state the major commercial uses of esters, e.g. solvents, perfumes, flavourings.

19.1 Carboxylic Acids

Introduction to carboxylic acids

1) Carboxylic acids are compounds that contain the **-COOH group**.

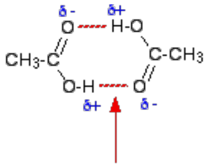
2) Examples of carboxylic acids:



3) Salts of carboxylic acids are called carboxylate salts. The formation of carboxylate salts shows that carboxylic acids are acidic. A carboxylate salt is formed upon the removal of H^+ from -COOH group, leaving $-COO^-$.

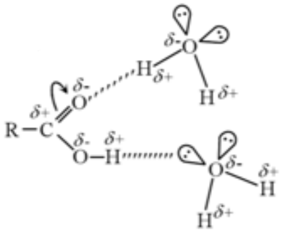
Physical properties of carboxylic acids

1) Carboxylic acids have **higher melting and boiling points** than the corresponding alcohols.
   i. This is because in a pure carboxylic acid, **hydrogen bonding** can occur between two molecules of acid to produce a **dimer**.
   ii. This **doubles the size of the molecule**, making the van der Waals' forces stronger.
   iii. Hence more energy is required to overcome these forces of attraction.



Hydrogen bond between the fairly positive hydrogen atom and a lone pair on the fairly negative oxygen atom.

2) **Small carboxylic acids are soluble in water.**
   i. This is because carboxylic acid is capable of forming hydrogen bond with water molecule.
   ii. However, the solubility decreases as the number of carbon atoms increases. This is because the presence of long hydrocarbon tail disrupts the effectiveness of hydrogen bonding.



Preparation of carboxylic acids

1) There are **three ways to produce carboxylic acids**:
   - i. Oxidation of primary alcohol.
   - ii. Oxidation of aldehyde.
   - iii. Acidic/alkaline hydrolysis of nitrile.

2) For oxidation of primary alcohol and aldehyde, refer back previous chapters.

3) **Acidic hydrolysis of nitrile**:
   - i. When nitrile is **heated under reflux** with a dilute acid such as dilute hydrochloric acid, **carboxylic acid will be formed**.
   - ii. Using ethanenitrile as an example, ethanoic acid is formed.

$$CH_3CN + 2H_2O + H^+ \rightarrow CH_3COOH + NH_4^+$$

4) **Alkaline hydrolysis of nitrile**:
   - i. When nitrile is **heated under reflux** with an alkali such as sodium hydroxide, **salt of carboxylic acid(carboxylate salt) is produced**. Using ethanenitrile as an example, ethanoate ion is formed.

$$CH_3CN + 2H_2O + OH^- \rightarrow CH_3COO^- + NH_3$$

   - ii. Ethanoate ion can be converted to ethanoic acid by the **addition of acid**.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

19.2 Reactions of Carboxylic Acids

Acidity of carboxylic acids

1) **Carboxylic acids are acidic** because they can donate a proton to form carboxylate ion and hydroxonium ion. The presence of hydroxonium ions makes the solution acidic.

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

2) However, **carboxylic acids are only weak acids**. For instance ethanoic acid has a pH of about 2-3.

Reaction with bases

1) Since carboxylic acids are acids, **they will react with a base** such as sodium hydroxide **to produce a carboxylate salt and water**. This is a simple neutralisation reaction.

2) Take ethanoic acid and sodium hydroxide as an example:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

...and the ionic equation is:

$$H^+ + OH^- \rightarrow H_2O$$

Reaction with metals

1) Carboxylic acids **will react with reactive metals** such as sodium **to produce a carboxylate salt and hydrogen gas**.

2) Take ethanoic acid and sodium metal as an example:

$$2CH_3COOH + 2Na \rightarrow 2CH_3COONa + H_2$$

Reaction with carbonates and hydrogencarbonates

1) Carboxylic acids **will react with carbonates and hydrogencarbonates to produce a carboxylate salt, carbon dioxide gas and water**.

2) Take ethanoic acid and sodium carbonate as an example:

$$2CH_3COOH + Na_2CO_3 \rightarrow 2CH_3COONa + CO_2 + H_2O$$

...and the ionic equation is:

$$2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$$

3) Take ethanoic acid and sodium hydrogencarbonate as an example:

$$CH_3COOH + NaHCO_3 \rightarrow CH_3COONa + CO_2 + H_2O$$

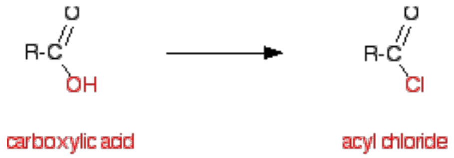
...and the ionic equation is:

$$H^+ + HCO_3^- \rightarrow CO_2 + H_2O$$

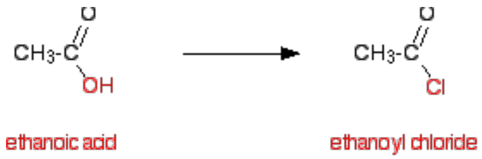
4) This is a useful **test to distinguish carboxylic acids from alcohols and phenols**. This is because alcohols and phenols are not acidic enough to react with these.

Converting carboxylic acids to acyl chlorides

1) Acyl chlorides have the -OH in the -COOH group of the carboxylic acid replaced by chlorine.



2) Take ethanoic acid as an example, ethanoyl chloride is produced.



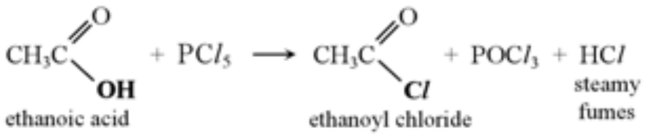
3) Acyl chlorides are very reactive and can be used to produce a range of other organic compounds.

4) There are **three methods to produce acyl chlorides** from carboxylic acids:
   i. Reaction with **phosphorus(III) chloride, PCl_3**.
      - Take ethanoic acid as an example, the equation is:

$$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_4$$

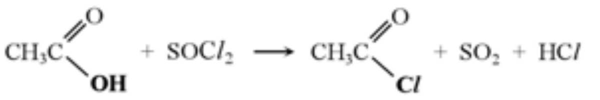
   ii. Reaction with **phosphorus(V) chloride, PCl_5**.
      - Take ethanoic acid as an example, the equation is:

$$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$$



   iii. Reaction with **thionyl chloride, $SOCl_2$**.
      - Take ethanoic acid as an example, the equation is:

$$CH_3COOH + SOCl_2 \rightarrow CH_3COCl + SO_2 + HCl$$

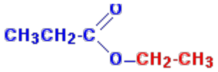


      - This method is generally preferred because SO_2 and HCl are both gases, and can be separated from the mixture easily.

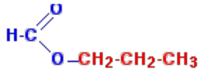
19.3 Esters

Introduction to esters

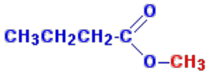
1) Esters are derivatives of carboxylic acids. In an ester, the hydrogen from the -COOH group of carboxylic acid is replaced by an alkyl group. The alkyl group came from the alcohol/phenol. Some common esters and their naming:



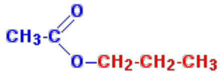
ethyl propanoate



propyl methanoate



methyl butanoate



propyl ethanoate

2) Note that the name of an ester is **'alcohol + carboxylic acid'**.

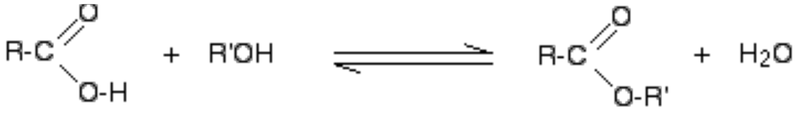
3) Physical properties of esters:
   i. Esters have **lower melting and boiling points than carboxylic acids**. This is because they are not capable of forming intermolecular hydrogen bonding.
   ii. Esters are **insoluble in water** and often identified by their **strong fruity smell**.

4) Unlike carboxylic acids, **esters are neutral**. This is because they cannot donate or accept a proton.

Preparation of esters

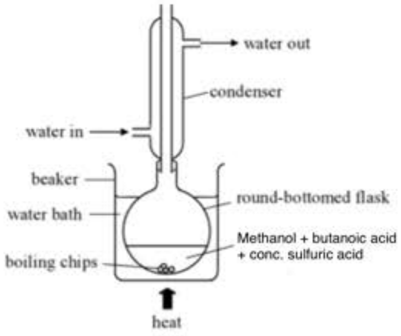
1) Esters can be prepared from the **reaction between alcohol and carboxylic acid(AS)**.

2) Between alcohol and carboxylic acid:
   i. To prepare an ester from carboxylic acid and alcohol, both them are heated under reflux in the presence of concentrated sulfuric acid as catalyst. Esters can be detected from a **sweet-smelling odour**. The general equation:



ii. For example, to make methyl butanoate, methanol and butanoic acid are used.

$$CH_3OH + CH_3CH_2CH_2COOH \rightleftharpoons CH_3CH_2CH_2COOCH_3 + H_2O$$



ii. This reaction cannot be used to produce esters when the -OH group is attached to a benzene ring, also known as phenol. In other words, **carboxylic acid cannot react with phenol to produce ester**.

Hydrolysis of esters

1) **Acidic hydrolysis of esters**:

i. When ester is **heated under reflux** with a dilute acid such as dilute hydrochloric acid, **the corresponding carboxylic acid and alcohol will be formed**.

ii. Using methyl propanoate as an example, propanoic acid and methanol is formed.

$$\underset{\text{methyl propanoate}}{CH_3CH_2COOCH_3} + H_2O \xrightleftharpoons{H^+(aq)} \underset{\text{propanoic acid}}{CH_3CH_2COOH} + \underset{\text{methanol}}{CH_3OH}$$

iii. This is just the reverse process of esterification.

2) **Alkaline hydrolysis of esters**:

i. When ester is **heated under reflux** with a base such as sodium hydroxide solution, **the corresponding carboxylate salt and alcohol will be formed**.

ii. Using methyl propanoate as example, sodium propanoate and methanol is formed.

$$\underset{\text{methyl propanoate}}{CH_3CH_2COOCH_3} + NaOH \longrightarrow \underset{\text{sodium propanoate}}{CH_3CH_2COONa} + \underset{\text{methanol}}{CH_3OH}$$

iii. The sodium propanoate can be converted to propanoic acid by adding dilute acid.

Uses of esters

1) **As solvents**:
   i. Small esters such as methyl ethanoate, ethyl ethanoate and butyl ethanoate are very widely used as solvents.

2) **As perfumes and flavourings**:
   i. The smell and taste of fruits such as oranges, apples, pears, raspberries, strawberries, and so on, are due to naturally occurring esters. Many foods will have those same esters added to them to simulate the smell and taste of real fruit.
   ii. Flower and other smells are also produced by naturally occurring esters.
   iii. Perfumes will have the same esters added. Benzyl ethanoate, for example, is used to produce jasmine or gardenia fragrances.