

Fundamentals of Chemistry

Romain Elsaid



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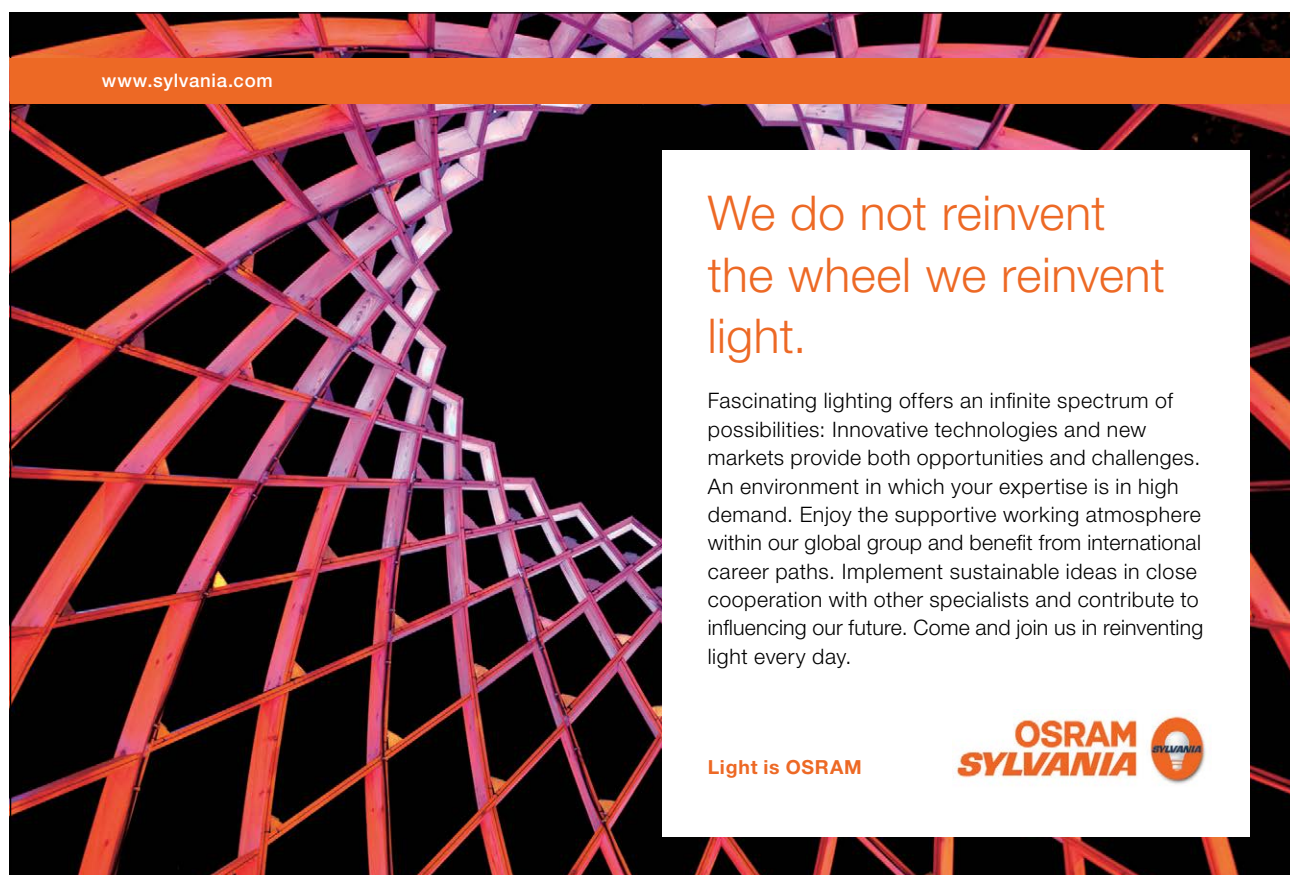
Romain Elsair

Fundamentals of Chemistry

Fundamentals of Chemistry
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Fundamentals of Chemistry

Aim of this Book

This book addresses first year students and aims at:

- Developing further knowledge and understanding of some core scientific concepts and principles
- Improving ability to understand and express scientific knowledge,
- Preparing for further study of specialist modules in physics, engineering, chemistry or biology, and
- Preparing for future undergraduate studies in Science or Engineering.

Scope of this Book

This book is mainly about Physical Chemistry and explains the basic concepts of gases, liquids and solids, the relation of properties to structure, the chemical changes, the trends and patterns in the Periodic Table.

Strong emphasis will be placed on chemical energy changes to finally provide an introduction to solutions and pH.

The fundamental properties of matter underlie all of Science and Engineering subjects, and will be needed, even if the student is not going to study more Chemistry.

General principles, methods of calculation and scientific thinking skills will be useful to all Science & Engineering subjects.

1 Substances and Reactions

1.1 Classifying Substances

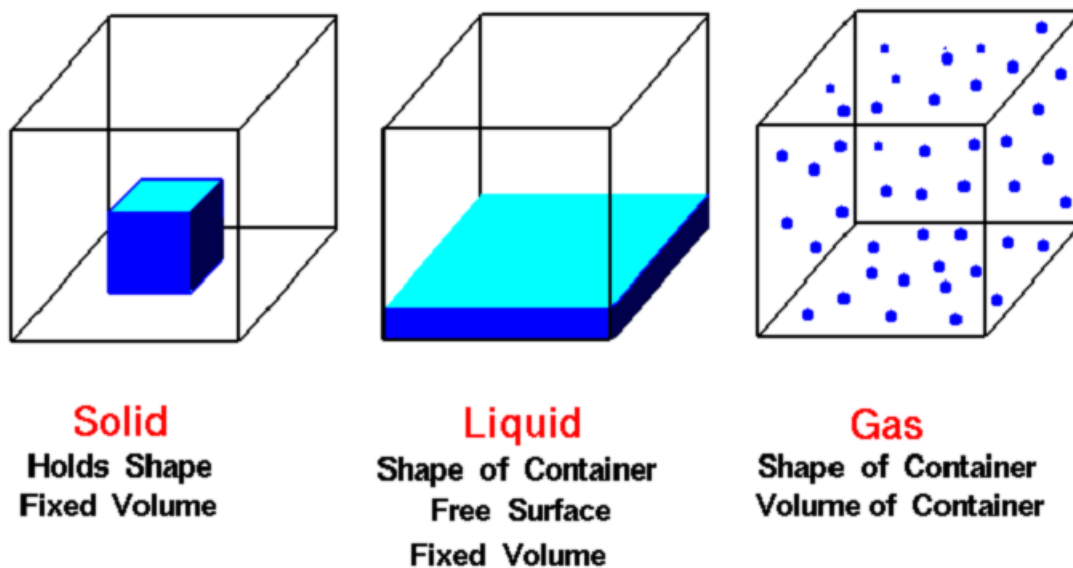
A substance is a pure form of matter. Substances can be classified or put into groups with similar substances.

Chemists have elaborated common ways of classifying:

- Solids, liquids and gases,
- Elements, mixtures, compounds, and
- Metals, non-metals, semi-metals.

1.2 Solids, Liquids and Gases

Solids have shape and volume. Liquids have volume but adopt the shape of their container. Gases occupy the shape and volume of their container.



1.2.1 Solids, Liquids and Gases. Changes of State

The three states of matter, solid, liquid and gas exist because each one has a different balance of kinetic and potential energy. If energy is added or removed from the substance, it changes its state.

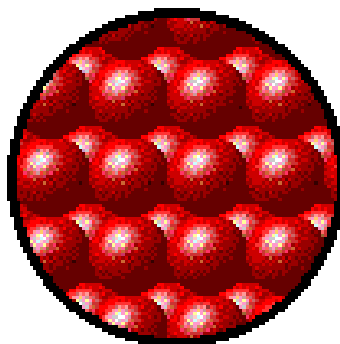
1.2.2 Kinetic Theory of matter

All matter is composed of particles (atoms, molecules, ions). The particles attract each other via interatomic forces. All the particles have kinetic energy (K.E.) which varies with temperature. The state of matter depends on balance between:

- K.E. of particles (tending to separate), and
- Attraction between particles (tending to pull together).

1.2.3 Solids

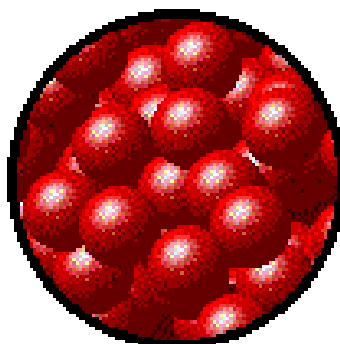
In a solid the atoms are close together, held in position by the strong interatomic electrostatic forces. They have some K.E., which makes them vibrate about an equilibrium position, but they cannot change places. This means that solids have a fixed shape and a fixed volume i.e. they are rigid.



Microscopic view of a Solid

1.2.4 Liquids

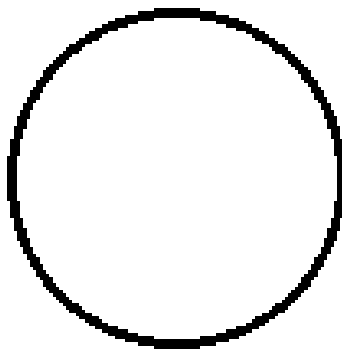
In a liquid the atoms are not much farther apart than in a solid. There are still quite strong interatomic bonds between the atoms. The atoms have more kinetic energy and are able to move randomly, changing places with their neighbours. There is less order than in a solid. Thus a liquid has no fixed shape but does occupy a fixed volume.



Microscopic view of a Liquid

1.2.5 Gases

In a gas the atoms move randomly at high speeds. They are much further apart than in solids or liquids. There are no interatomic forces between the atoms. Interaction only occurs when the atoms (or molecules) collide. The internal energy of a gas is entirely kinetic.



Microscopic view of a Gas

1.3 Changing state

When a substance changes state, it does not change into a new substance. Ice is still water – it is water in the solid state. Steam is still water – it is water in the gaseous state. The heat has not broken down the water into hydrogen and oxygen gases. Any substance can exist in any state, if it is cooled or heated enough.

E.g. If nitrogen gas is cooled to -195.79°C , it will change to a liquid. If this is cooled further to -210°C , the liquid nitrogen will solidify

E.g. Iron will melt to a liquid above 1538°C . This liquid iron will change to a gas above 2862°C .

The temperature at which a solid changes to a liquid is called the melting point. The temperature at which a liquid changes to a gas is called the boiling point.

1.4 Element

An element is a pure substance. It cannot be decomposed into simpler substances by chemical means. It contains only one type of atom. Over 100 known elements are listed in the Periodic Table. Sometimes found free but more often occur combined with other elements as compounds. Elements can be classified as metals, non-metals & semi-metals (metalloids). Recommended browsing at <http://www.webelements.com>

1.5 Metals & Non-metals

Metals

Metals have a shiny appearance, are good conductors of electricity and heat. They can be drawn into wires (ductile) and can be hammered into different shapes (malleable).

Non-metals

Non-metals have a dull appearance. They are poor conductors of electricity and heat. They cannot be drawn into wires or hammered into different shapes (brittle).

1.6 Chemical symbols

Traditionally, elements are represented by *symbols*.

1.6.1 Exercise

Write down the symbols for Sulphur, Silver, Sodium, and Silicon?

Write down the names of the elements represented by the symbols C; Ca; Cl; Co; Cu?

1.7 Compound

A compound is a pure substance made up of two or more elements combined in fixed proportions which contains more than one type of atom and can only be broken down to simpler substances by chemical means. A compound may contain charged particles (ions) or groups of atoms (molecules).

E.g. Sodium chloride is a naturally occurring compound quite different to its constituent elements



See images above at

Salt crystal: <http://www.scienceclarified.com/Co-Di/Crystal.html>

Salt lake in China: <http://www.historyforkids.org/learn/food/salt.htm>

1.8 Mixture

A mixture contains two or more substances; which could be elements or compounds and has variable composition. A mixture can be separated into its components by physical means.

E.g. sea water, on average has about 3.5% sodium chloride, but can be more or less in the same amount of water. The sea near a river mouth will be less salty, but the seawater in the Dead Sea is very salty. Also contains other substances such as magnesium, sulphur and iodine.

1.9 Physical separation

A mixture of two substances with differences in physical properties can be separated by physical means.

E.g. Salt and stones can be separated by adding to water, as the salt will dissolve, but the stones will not. Water can be separated from sea water by heating, as the water will boil at 100°C, but the salt and other dissolved minerals will not.

A compound can only be separated into its constituent elements by a chemical reaction. E.g. Iron can be extracted from iron oxide by reacting with carbon. The iron could not be extracted from the iron oxide by physical means such as heating, dissolving or with a magnet

1.10 Physical and chemical change

Physical change:

- Does not involve changing substances into different substances, and
- An element stays as an element when heated, although its shape or state may change.

Chemical change:

- Involves changing one or more substances into different substances, and
- A compound might break apart (decompose) into its elements, or into different compounds.



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Jane, Chinese architect

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1.11 Elements, mixtures or compounds?

Classify each of these as an element, a mixture or a compound:

- Aluminium
- Water
- Crisps
- Petrol
- Blood
- Oxygen
- Diamond
- Sugar (sucrose)
- Methane
- Gold

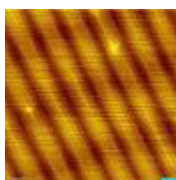
1.12 Atomic theory

All substances are made up of small particles. These particles can be:

- Atoms
- Molecules
- Ions

1.12. Atoms

An atom is the smallest part of an element that behaves like bulk sample. Each atom is $\sim 10^{-10}\text{m}$ in diameter. E.g. this scanning tunnelling microscope image clearly shows the individual atoms that make up this sheet of gold (Au) atoms.



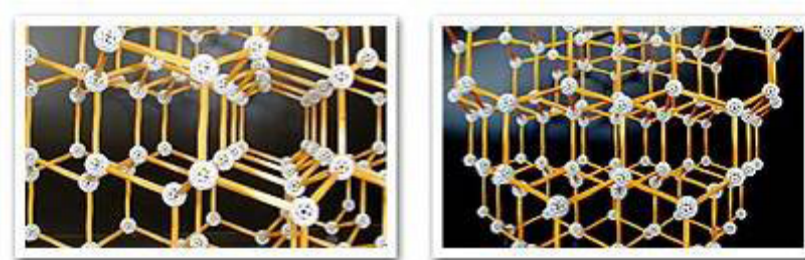
Gold atoms: Wikimedia Commons

1.12.2 Molecules

A few elements exist as individual atoms e.g. helium, neon, argon. Most exist as molecules. A molecule is a group of atoms bound together so they behave as a single particle. Molecules can consist of just two atoms (diatomic) or many atoms (polyatomic).

1.12.2.1 Giant molecules

Many elements exist as giant 3D arrangements of atoms e.g. metals, carbon (as diamond or graphite).

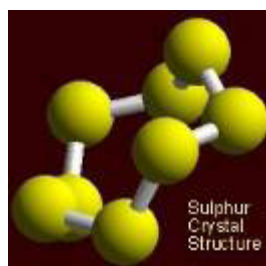


Diamond structure: <http://www.zometool.com/zomepro-spotlight.html>

1.12.2.2 Small molecules

Some elements exist as small molecules i.e. entities containing a few atoms only e.g. hydrogen, oxygen, nitrogen, phosphorus and sulphur. The molecules of a particular element always contain the same number of atoms.

E.g. structure of Sulphur molecule S_8



Sulphur molecule: <http://cnx.org/content/m34993/latest/?collection=col11124/latest>

1.12.2.3 Molecule

Compounds formed between atoms of different non-metals generally exist as molecules e.g. carbon dioxide, methane, aspirin ($C_9H_8HO_4$) and caffeine ($C_8H_{10}N_4O_2$). A molecule is the smallest particle of such a compound that behaves like bulk sample.

1.13 Chemical formulae

We can write a chemical formula for an element or compound which exists as a molecule. Using the chemical symbols, this shows how many of each type of atom the molecule contains.

E.g. the element oxygen exists as a diatomic molecule, so the formula is O_2 . The formula for methane is CH_4 .

If elements can combine to make groups containing different combinations of atoms joined together, these are different compounds, which have different chemical and physical properties. We write them with different formulae which show how many atoms are joined together.

Beware! Writing a formula does not mean that the compound necessarily exists.

E.g. there is no compound with the formula NO_4 . Theories about bonding can usually predict the most likely formula for a compound between two elements. The true formula can only be discovered by experiments.

1.14 Ion

An ion is a particle (an atom or group of atoms) carrying positive or negative charge. Ions with a positive charge are called Cations. Ions with a negative charge are called Anions.

Most elements only form one sort of ion. It is essential to learn the characteristic charges for the most common ions.



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Common Cations

Common Name	Formula
<i>Simple Cations</i>	
Aluminum	Al^{3+}
Hydrogen	H^+
Iron(II)	Fe^{2+}
Magnesium	Mg^{2+}
Sodium	Na^+
Zinc	Zn^{2+}
Iron(III)	Fe^{3+}
Calcium	Ca^{2+}

Polyatomic Cations

Ammonium	NH_4^+
Hydronium	H_3O^+

Common Anions

Formal Name	Formula
<i>Simple Anions</i>	
Chloride	Cl^-
Fluoride	F^-
Oxide	O^{2-}
Sulphide	S^{2-}
<i>Oxoanions</i>	
Carbonate	CO_3^{2-}
Hydroxide	OH^-
Permanganate	MnO_4^-
Sulphate	SO_4^{2-}
<i>Anions from Organic Acids</i>	
Acetate	$\text{C}_2\text{H}_3\text{O}_2^-$

1.14.1 Combining ions

Positive and negative ions combine together to form ionic compounds. Compounds must contain an equal number of positive and negative charges overall. Thus the charges on the ions will determine how many cations and anions will combine.

E.g. Na^+Cl^- not NaCl_2 or Na_2Cl or NaCl_3

1.14.2 Example - What is the formula of the compound formed between?

- Magnesium and Oxygen
 Mg^{2+} O^{2-} so MgO
- Calcium and Chlorine
 Ca^{2+} Cl^- so CaCl_2
- Sodium and Oxygen
 Na^+ O^{2-} so Na_2O
- Iron $^{2+}$ and Hydroxide ions
 Fe^{2+} OH^- so $\text{Fe}(\text{OH})_2$

1.14.3 Exercise - Write the formula for the following compounds:

- Calcium Carbonate
- Aluminium fluoride
- Potassium permanganate
- Zinc hydroxide
- Sodium carbonate
- Ammonium sulphate

1.14.4 Ionic compounds

If a compound is ionic it is not appropriate to use the term molecule, because many thousands of ions are joined together. The formula cannot show the number of atom. A chemical formula for an ionic compound shows the relative proportions of the different ions. The formula unit is the simplest formula for the compound and the smallest 'particle' that can exist.

E.g. NaCl (sodium chloride) and CaO (calcium oxide)

1.15 Naming Compounds

Ionic compounds are named with the metal (positive ion) first, then the non- metal (negative ion).

Note how the end of the non-metal changes to "ide" to show that it is a negative ion. If the ion contains oxygen as well, then the ending changes to "ate" or "ite".

2 Chemical Equations Subatomic Structure Relative Atomic Mass

2.1 Chemical equations

A chemical equation is a shorthand description of the changes that occur in a chemical reaction such as



It allows us to determine the quantitative relationships between reactants and products. To be valid, a chemical equation must be:

- Consistent with the experimental facts. Just because one can write an equation, it does not mean that it can really happen.
- Consistent with conservation of mass i.e. the total number of atoms of each element in the reactants must be equal to the total in the products. Atoms cannot disappear!
- Consistent with conservation of electric charge i.e. the net charge, before and after, must be the same

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To construct a chemical equation for a reaction:

- Write the names of the reactants on the left and products on the right side of the arrow,
- Replace the names with the correct chemical formulae,
- Balance the equation, and
- Write the state symbols after each substance: **(s) solid, (g) gas, (l) liquid** and **(aq) aqueous**.

2.1.1 Balancing chemical equations

Write the correct formulae for the reactants and products; reactants on left of arrow, products on right. Choose the most complicated compound that contains the greatest number of atoms, whether it is reactant or product. Start with the element in that compound that has the greatest number of atoms (not H or O or a polyatomic ion such as sulphate, nitrate, carbonate etc.). Balance the number of atoms in this compound with the corresponding atom on the other side by putting the appropriate numbers before the formulae. Repeat for other atoms. Next balance any polyatomic groups (such as SO_4 , NO_3 and CO_3) that appear on both sides of the equation. Finally check the numerical coefficients (the numbers before the formulae) to ensure they are whole numbers and in the lowest possible ratio. Include state symbols if required, in brackets, after the formulae.

E.g. Na(s) , $\text{H}_2\text{O(l)}$, $\text{N}_2\text{(g)}$, $\text{Cu}^{2+}\text{(aq)}$

Remember: it is not always possible to follow the guidelines in the previous slides exactly. Never change the formulae, only the numbers before the formulae (the coefficients). See examples below:

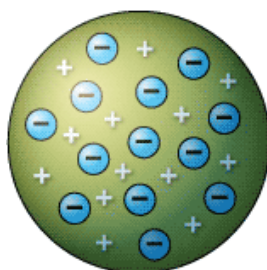
1. Chromium + Oxygen \rightarrow Chromium (III) oxide	Atom/group being balanced
$\text{Cr} + \text{O}_2 \rightarrow \text{Cr}_2\text{O}_3$	
$2\text{Cr} + \text{O}_2 \rightarrow \text{Cr}_2\text{O}_3$	Cr
$2\text{Cr} + 3\text{O}_2 \rightarrow 2\text{Cr}_2\text{O}_3$	O
$4\text{Cr (s)} + 3\text{O}_2\text{(g)} \rightarrow 2\text{Cr}_2\text{O}_3\text{(s)}$	Cr again
2. Iron + Steam \rightarrow tri-iron tetroxide + Hydrogen	
$\text{Fe} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$	
$3\text{Fe} + \text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$	Fe
$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$	O
$3\text{Fe (s)} + 4\text{H}_2\text{O (g)} \rightarrow \text{Fe}_3\text{O}_4\text{(s)} + 4\text{H}_2\text{(g)}$	H
3. Ammonia + Oxygen \rightarrow Nitrogen (II) oxide + Water	
$\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + \text{H}_2\text{O}$	H
$2\text{NH}_3 + \text{O}_2 \rightarrow \text{NO} + 3\text{H}_2\text{O}$	N
$2\text{NH}_3 + \text{O}_2 \rightarrow 2\text{NO} + 3\text{H}_2\text{O}$	O
$2\text{NH}_3 + 5/2\text{O}_2 \rightarrow 2\text{NO} + 3\text{H}_2\text{O}$	Whole
$4\text{NH}_3\text{(g)} + 5\text{O}_2\text{(g)} \rightarrow 4\text{NO(g)} + 6\text{H}_2\text{O(l)}$	coefficients

2.1.2 Exercise - Write balanced chemical equations for the following

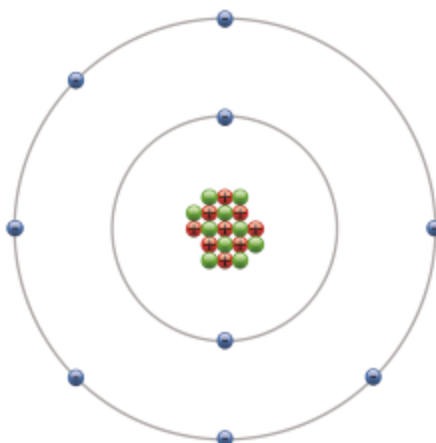
- Lead nitrate solution + potassium chloride solution \rightarrow Lead chloride solution + potassium nitrate solution
- Calcium + Oxygen \rightarrow Calcium Oxide

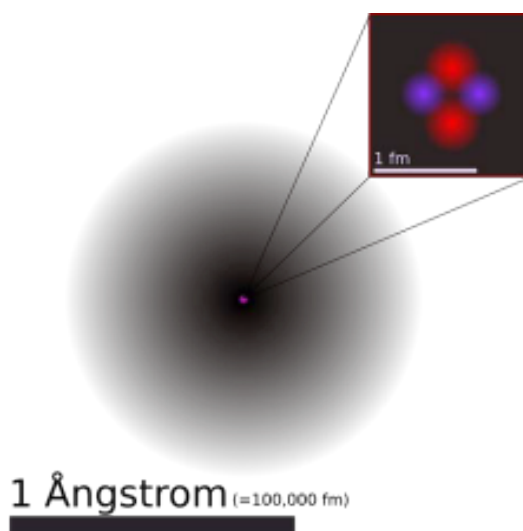
2.2 Atomic Structure

An atom was once thought to be the smallest part of something that could exist. In 1897, JJ Thompson discovered that by applying high voltage to gases at low pressure, he could produce tiny, negatively charged particles that he called electrons. These left behind the positively charged nucleus of the atom. So an atom must be made up of several different types of smaller particle. The first attempt to describe atomic structure was Dalton's 'Christmas pudding' model as shown below.




A more accurate understanding was revealed by a classic experiment carried out by Ernest Rutherford's students Geiger and Marsden. Their experiment disproved Dalton's model and revealed the following particles: electrons (blue and negative), protons (red and positive) and neutrons (green).





Helium atom: Wikimedia Commons

Protons and Neutrons are found at the centre of the atom in the Nucleus. The nucleus is extremely small but dense. Protons have positive charge, and neutrons have no charge, so the nucleus is positive. Most of atom is empty space. Nucleus is a $\sim 10^{-15}\text{m}$ diameter whereas atoms are $\sim 10^{-10}\text{m}$ in diameter.

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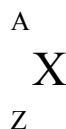
One generation's transformation is the next's status quo. In the near future, people may soon think it's strange that devices ever had to be "plugged in." To obtain that status, there needs to be "The Shift".



2.3 Fundamental subatomic particles

Particle	Relative Mass	Relative charge
Proton (p)	1	+1
Electron (e)	0.00055	-1
Neutron (n)	1	0

Electrons are only found outside the nucleus. We can say that the electron has a negligible mass because it is ~2000 times less heavy than both the proton and neutron. The atom is neutral therefore the number of protons is equal to the number of electrons which in turn is equal to the atomic number of atom. The Atomic Number is the number of protons (equal to the number of electrons). The Mass Number is the number of protons + neutrons. Neutrons do not change the way that an element behaves chemically. Different number of protons and electrons makes a different element; one which behaves in a different way chemically. Elements are typically represented in the following way: chemically. Elements are typically represented in the following way:



Where A is the Mass Number, Z the Atomic Number and X the symbol.

E.g.

23

Na This sodium atom contains 11 protons, 11 electrons and $23 - 11 = 12$ neutrons

11

2.3.1 Isotopes

Many elements have more than one type of atom. These atoms have the same number of protons but different numbers of neutrons. Atoms having different mass numbers but identical atomic numbers are called isotopes.

E.g. ^{35}Cl and ^{37}Cl

2.3.2 Atomic scale

Neutrons, protons (and electrons) have a definite mass, so atoms must have mass. It is convenient to define an atomic mass unit (written as amu or, simply, u) where $1\text{u} = 1.6605 \times 10^{-24}\text{ g}$. The atomic mass unit is defined with relation to a standard scale. It was originally defined as being equal to the mass of one H atom, but now a more precise scale is used - the carbon 12 scale. On this scale one atom of carbon 12 is assigned a mass of exactly 12u. 1u is exactly 1/12 of the mass of one atom of carbon isotope 12.

2.4 Chemical Masses

Symbol	Element or compound	Atomic Mass (amu)
H	Hydrogen	1
C	Carbon	12
N	Nitrogen	14
O	Oxygen	16
Cl	Chlorine	35
NaCl	Sodium chloride	58
C ₆ H ₁₂ O ₆	Glucose	180
C ₁₇ H ₂₁ NO ₄	Cocaine	303

2.4.1 Relative mass on the atomic scale

It is convenient to describe masses on a relative scale of numbers that has no units of 'u'. Relative mass of an entity is equal to the mass of that entity (u) is equal to 1/12 mass of a carbon 12 atom (1u), which in turn is also equal to a number with no units.

2.4.2 Relative mass of an isotope

These are very close to whole numbers and, for most purposes, are usually quoted as those whole numbers.

E.g.

$${}^1\text{H} = 1$$

$${}^2\text{H} = 2$$

$${}^{12}\text{C} = 12$$

$${}^{13}\text{C} = 13$$

$${}^{35}\text{Cl} = 35$$

$${}^{37}\text{Cl} = 37$$

2.4.3 Relative atomic mass

Naturally occurring elements exist as a mixture of different isotopes. The relative atomic mass of the element will be affected by the relative proportions of the different isotopes.

E.g. About 75% of naturally occurring chlorine is ${}^{35}\text{Cl}$ and 25% of ${}^{37}\text{Cl}$. Thus the relative atomic mass of Cl is $0.75 \times 35 + 0.25 \times 37 = 35.5$.

2.4.4 Relative atomic mass (R.A.M.) of an element

The relative atomic mass (R.A.M.) of an element is the average mass of the atoms in the naturally-occurring isotopic mixture of a carbon 12 atom (1u). It can be calculated from knowing the natural isotope abundance.

2.4.5 Calculating average Relative Atomic Mass

$$R.A.M. = \frac{(m_1P_1) + (m_2P_2) + (m_3P_3) + \dots}{100}$$

Where

- m_1, m_2, m_3 are the masses of the individual isotopes (use accurate values in u if they are given, or use the mass numbers of the isotopes)
- P_1, P_2, P_3 are the percentages of these isotopes in the naturally occurring mixture for this element

2.4.6 Exercise - Calculate the R.A.M. of Boron given the following data

Isotope	Isotopic mass (u)	Abundance (%)
^{10}B	10.0129	19.91
^{11}B	11.0093	80.09

R.A.M. of Boron = 10.81.



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R.A.M. values of elements are often expressed to the nearest whole number. E.g. H = 1, Li = 7, C = 12 and Na = 23. But sometimes more accurate values are needed, E.g. Cl = 35.45. Use the values provided on a Periodic Table.

2.4.7 Periodic Tables

Naturally occurring RAM values and atomic numbers for all elements can be found on a Periodic Table. Make sure you know which is which – some Periodic Tables have atomic number above element symbol, and some have it below. Atomic number is always less than RAM.

2.4.8 Masses of molecules

The mass of one molecule is obtained by adding up the atomic masses in that molecule.

E.g.

- N_2 : $2 \times \text{N} = 2 \times 14\text{u} = 28\text{u}$
- CH_4 (methane): $\text{C} + (4 \times \text{H}) = 12\text{u} + (4 \times 1\text{u}) = 16\text{u}$
- $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ (caffeine): $(8 \times \text{C}) + (10 \times \text{H}) + (4 \times \text{N}) + (2 \times \text{O}) = (8 \times 12\text{u}) + (10 \times 1\text{u}) + (4 \times 14\text{u}) + (2 \times 16\text{u}) = 194\text{u}$

2.4.9 Relative molecular mass

Relative molecular mass (R.M.M.) is obtained by dividing the masses by 1/12 of the mass of a Carbon 12 atom (i.e. by 1u). Therefore R.M.M. of methane = 16 and R.M.M. of caffeine = 194. Strictly, as ionic compounds do not exist as molecules, we should refer to the Relative Formula Mass (RFM) of an ionic compound, not the RMM. Calculate the RMM (or RFM) for the following compounds:

- Ethanol, $\text{C}_2\text{H}_5\text{OH}$
- Potassium bromide
- Magnesium chloride
- Copper sulphate
- Water

2.5 Mass spectrometer

How are relative masses determined experimentally? A mass spectrometer is used to determine the relative masses of different atoms or molecules.

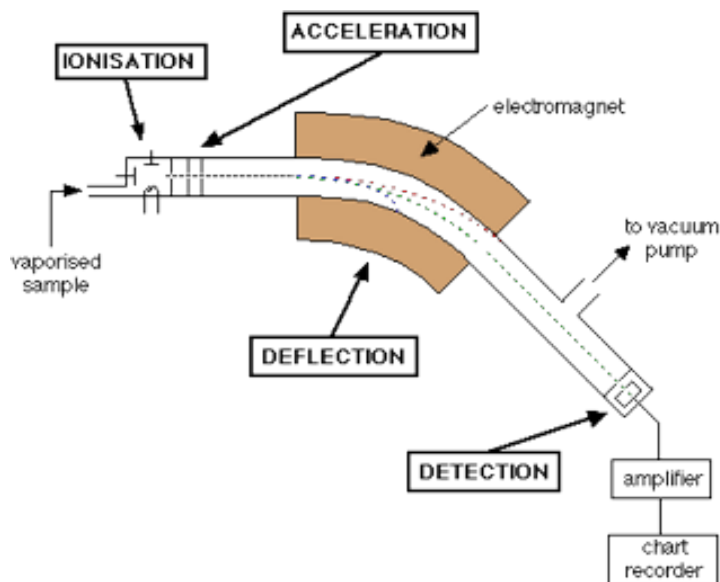
2.5.1 What is Mass Spectrometry?

Mass Spectrometry is a chemical analysis technique used to:

- Identify unknown samples, and
- Determine the amount of a chemical species in a sample.

Mass Spectrometry has an unparalleled combination of sensitivity, selectivity, and range of application (Astrophysics to Zoology). Most common areas of application are Chemistry and Biology.

2.5.2 Diagram of a simple mass spectrometer



<http://www.chemguide.co.uk/analysis/masspec/howitworks.html>

2.5.3 Vaporisation and Ionisation

Most of the mass spectrometer is pumped out to give a high vacuum. This is to give the ions a reasonable chance of travelling from one end of the instrument to the other without any hindrance from air molecules. The sample under investigation is heated and vaporised to a gas. The sample molecules are then ionized, because ions are easier to manipulate than neutral molecules.

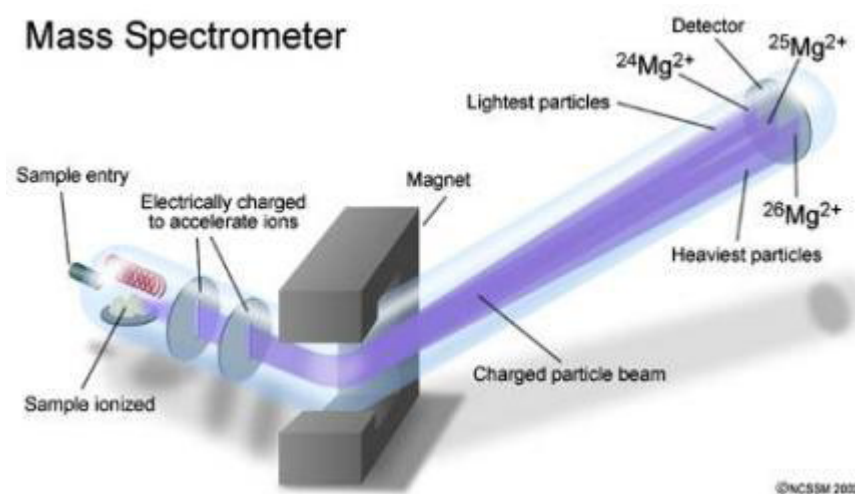
2.5.4 Ionisation

High energy electrons are fired at the gaseous sample. This knocks out electrons from the atoms or molecules of the sample to produce positive ions and high energy electron.

2.5.5 Acceleration of ions

Ions are accelerated by an electric field. Then they go through a magnetic field where they are separated according to their mass (m)-to-charge (e) ratios (m/e). Lighter ions are deflected more than heavier ions with the same charge.

2.5.6 Components of a mass spectrometer. Separation of the isotopes by magnets



Mass spectrometer: <http://MIIIW.dlt.ncssm.edu/TIGERIC>

2.5.7 Detection

As the magnetic field is gradually increased, the separated ions are detected and this signal sent to a data system where the m/e ratios are stored together with their relative abundance for presentation in the format of a spectrum.

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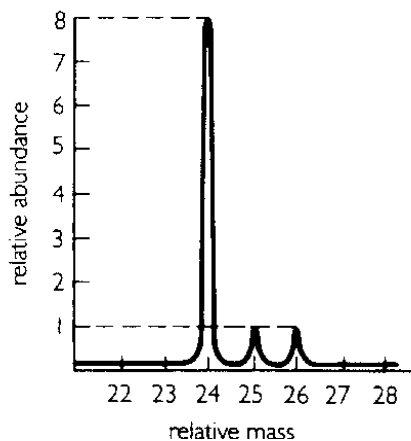
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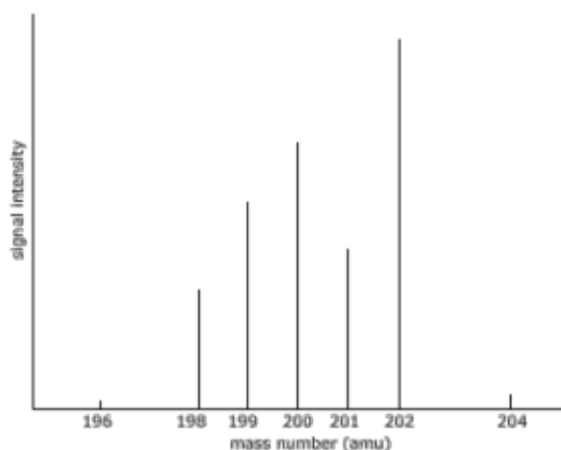
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Mass spectrum for magnesium



http://www.alevelchemistry.co.uk/Quizzes/images/mass_spectrometry_magnesium.gif

2.5.8 Exercise - A naturally occurring sample of mercury produces this mass spectrum



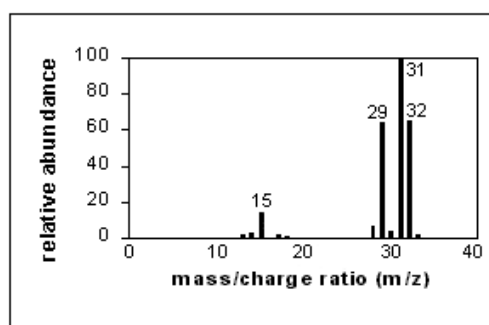
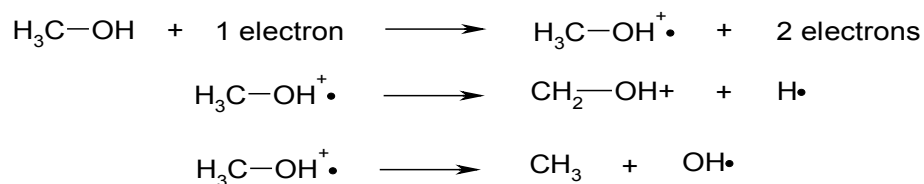
How many possible isotopes of mercury are there? Which isotope is most abundant? Estimate the RAM of naturally occurring mercury. Calculate the RAM accurately.

2.5.9 Molecules

Compounds can also be analysed in a mass spectrometer. The molecules are vaporised, ionised and accelerated. Electron ionisation causes fragmentation (break up) of the molecules in the sample. The lighter fragments are deflected more than the heavier ones.

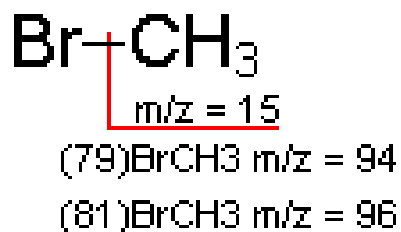
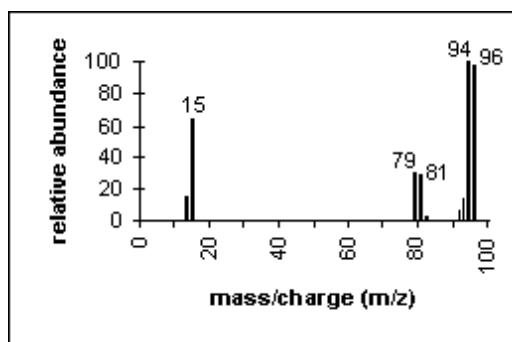
2.5.10 Example – Methanol CH_3OH

Each fragment gives rise to a separate peak. The heaviest fragment is usually the whole molecule, giving the RMM.



ions	m/z
$\text{CH}_3\text{OH}^{\bullet+}$	32
$\text{H}_2\text{C}=\text{OH}^+$	31
$\text{HC}\equiv\text{O}^+$	29
H_3C^+	15

2.5.11 Example – Bromomethane



As bromine has two isotopes, the mass spectrum shows more peaks.

3 The Mole

Introduction

For practical purposes, a microscopic (i.e. how many atoms) view of substances is not useful. We need to deal in macroscopic (e.g. how many grams) quantities of elements and compounds. To do this, we introduce the mole.

One mole of a substance is the amount of substance which contains a standard number of particles (atoms, ions or molecules). This standard number is defined as the same number of particles as there are Carbon atoms in 12g of the isotope Carbon-12. This is the Avogadro number 6.022×10^{23} particles.

So 12g of Carbon-12 represents one mole (written 1 mol) of Carbon-12. It contains 6.022×10^{23} Carbon atoms. Similarly one mole of sodium atoms contains 6.022×10^{23} sodium atoms. And half a mol of Neon atoms contains 3.011×10^{23} Neon atoms.

Because atoms of different elements do not have the same mass, one mole of sodium will not be as heavy as one mole of calcium. However, the mass of any substance can easily be related to the number of particles in it, as follows:

- R.A.M. of C = 12 and R.A.M. of He = 4
- 1 C atom is 3 times as heavy as 1 He atom
- 10 C atoms are 3 times as heavy as 10 He atoms
- 1000 C atoms are 3 times as heavy as 1000 He atoms
- 106 C atoms are 3 times as heavy as 106 He atoms

So if a sample of C has 3 times the mass of a sample of He, both samples must contain the same number of atoms.

3.1 Why is the mole useful?

If we express the R.A.M. of any element in grams, this must contain the same number of atoms (6.022×10^{23}). The R.A.M. of any element expressed in grams contains 1mol of that element. This is called the molar mass, and is given the symbol M.

For example, Beryllium (R.A.M. = 9); Argon (R.A.M. = 40). Therefore 9 g of Beryllium and 40 g of Argon contains the same number of atoms (6.022×10^{23}). Another example, Silicon (R.A.M. = 28), therefore the molar mass of Si is 28 g mol⁻¹ and is represented by M (Si).

3.2 Molecules

The mole concept is equally applicable to molecules. We introduce the relative molecular mass (R.M.M.) which is expressed in grams and represents one mole of the element or compound (i.e. 6.022×10^{23} molecules).

3.2.1 Example

Methane is CH_4 RMM of methane is $\text{RAM of C} + 4(\text{RAM H}) = 12 + 4 \times 1 = 16 \text{ g mol}^{-1} = \text{molar mass of methane}$

In 16g methane we can find one mole of methane. And 16g methane contains 6.022×10^{23} methane molecules.

3.2.2 Example

Caffeine ($\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$) and R.M.M. = $(8 \times 12) + (10 \times 1) + (4 \times 14) + (2 \times 16) = 194$

Therefore a mass of 194 g equals 1 mol of caffeine and 194 g mol^{-1} is the molar mass of caffeine.

3.2.3 Beware!

One mole of oxygen molecules (O_2) contains 6.022×10^{23} oxygen molecules which of course contains two moles of oxygen atoms! $M(\text{O}_2) = 16 + 16 = 32$

Therefore a mass of 32 equals 1 mol O_2 and 32 g mol^{-1} is the molar mass of O_2 represented by $M(\text{O}_2)$

3.2.4 Exercise

How many moles of calcium atoms are in 20 g calcium?

How many moles of bromine molecules are in 160 g bromine?

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What is the mass of 2 mol water molecules?

What is the mass of 0.25 moles chlorine molecules?

3.3 Ionic compounds

The mole concept is equally applicable to formula units and ions. A relative formula mass (R.F.M.) expressed in grams represents one mole of the compound (i.e. 6.022×10^{23} 'formula units').

For example, $M(\text{NaCl}) = 23 + 35.5 = 58.5$

Therefore, 58.5 g equals 1 mol of sodium chloride. In other words, 58.5 g mol^{-1} is the molar mass of NaCl.

3.3.1 Ions

For individual ions, it is common practice to use R.A.M. values

For example, 1 mol Na^+ equals 23g and 1 mol Cl^- equals 35.5g.

For polyatomic ions, add the RAM together.

3.3.2 Beware!

One mole of calcium chloride (CaCl_2) contains 1 mole of calcium ions, but two moles of chloride ions. Again, you must state clearly which particles you are referring to when giving the number of moles. How many moles of sodium ions are there in 1 mol sodium Carbonate? We find 2 moles of Na^+ ions in 1 mole of Na_2CO_3 .

3.4 Useful relationships involving the mole

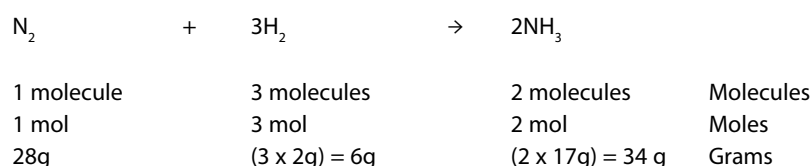
To convert amounts in grams to moles, divide by the molar mass (i.e. the R.A.M., R.M.M. or R.F.M. in grams). To convert moles to amounts in grams, multiply by the molar mass.

3.4.1 Equation to learn

Mass = No. of moles x Molar mass equivalent to Grams = moles x grams per mole or $(\text{g}) = (\text{mol}) \times (\text{g} \cdot \text{mol}^{-1})$

3.4.2 Mass relationships from equations

An equation like $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ can be interpreted on several levels:



Chemists tend to work in moles because one mole of any substance contains the same number of particles.

3.4.3 Mass relationship calculations

Write down the equation and do the working for a particular substance underneath its formula.

3.4.4 Sample question

For the reaction $C + 2H_2SO_4 \rightarrow CO_2 + 2SO_2 + 2H_2O$

- What mass of SO_2 would be produced from 4g of Carbon?
- How many moles of sulphuric acid would be needed to produce 50g of Carbon dioxide?
(R.A.M. values: H = 1, C = 12, O = 16, S = 32)

3.4.5 Answer



- So 12g of C corresponds to 2 x 64g of SO_2
So 1g of C corresponds to $2 \times 64 / 12$ of SO_2

So 4g of C corresponds to $2 \times 64 \times 4 / 12 \text{ g} = 42.7 \text{ g}$ of SO_2
- Similarly, 50g CO_2 corresponds to 1.14 mol CO_2
Now 2 mol H_2SO_4 produce 1 mol CO_2 , so to produce 1.14 mol CO_2 we need $2 \times 1.14 \text{ mol} = 2.28 \text{ mol}$ of H_2SO_4

3.5 Mass Percentage composition of elements in compounds

If we know the molar masses, we can calculate the percentage (by mass) of a particular element within a compound,

$$\% \text{ of element (by mass)} = \left[\frac{\text{molar mass of element} \times \text{number of atoms of the element in the formula of the compound}}{\text{molar mass of compound}} \right] \times 100$$

3.5.1 Example

What is % of Li in Li_2O (R.A.M's: Li = 7, O = 16)

$$\% \text{ Li} = (7 \times 2) / 30 \times 100\% = 46.7\%$$

3.5.2 Question

Calculate the % of Carbon in methane.

3.6 Empirical formulae of compounds

The Empirical formula is the simplest whole number ratio of atoms present. Divide % by mass of each element by its R.A.M. This gives the molar ratio of the elements present. Divide throughout by smallest number obtained to find the empirical formula. To obtain the molecular formula from the empirical formula we need to know R.M.M.

3.6.1 Question

A compound contains 26.7% C; 2.2% H and 71.1% O. The R.M.M. of the compound is 90. Calculate the empirical and molecular formula.

3.6.2 Question

Calculate the empirical formula of a compound which contains 63% Mn and 37% O.

3.7 Theoretical yield

The yield is the amount of product made in a reaction. Theoretical yield is the amount of product that would be made if there were no experimental errors in the experiment. A chemical equation expresses the ratio of the number of moles of reactants and products (the stoichiometry of the equation). So the expected (theoretical) yield of a reaction can be calculated.



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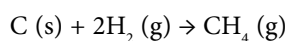
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3.7.1 Example

If 3g of Carbon is reacted with an excess of hydrogen what yield of methane will be produced?



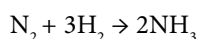
From the balanced equation we can see that 1 mole of C gives 1 mol of CH₄.

So 0.25 moles of C must give 0.25 moles of CH₄

The mass of 0.25 moles of CH₄ = moles x molar mass = 0.25 x 16 = 4g. The theoretical yield is 4g.

3.7.2 Question

What is the theoretical yield of ammonia if 21g of nitrogen is reacted with excess hydrogen?

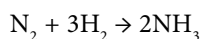


3.8 Percentage yield

Often, the actual yield is lower than predicted.

3.8.1 Example

What is the theoretical yield of ammonia if 21g of nitrogen is reacted with excess hydrogen?

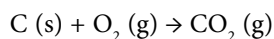


The actual (experimental) yield is 20.1g. What is the % yield?

Answer: % yield = $20.1/25.2 \times 100 = 78.8\%$

3.8.2 Question

10g of Carbon is burned in oxygen. The actual amount of Carbon dioxide that is made is 35g. What is the % yield?



3.9 Limiting reagent

If the reactants are not mixed in the same proportions as in the balanced reaction equation, there will still be excess of one reagent left when all the other has been used up. The limiting reagent will determine the maximum yield of the product.

3.9.1 Finding the limiting reagent

If 1mol each of Carbon and sulphuric acid are reacted together, which is limiting?



1mol C will react with 2mol H_2SO_4 but only 1 mol H_2SO_4 is available. So only 0.5mol of C can react; there is too much Carbon, therefore it is said to be in excess. So H_2SO_4 is the limiting reagent.

3.9.2 Question

If 10g of Carbon are burned with 20g of oxygen, which is the limiting reagent?

3.9.3 Question

These 3 calculations are often put together to make a single question.

For example: 5g of Carbon react with 20g of oxygen to form Carbon dioxide. The amount of Carbon dioxide formed is 17g. What is the % yield?

You need to follow these steps:

1. Determine which is the limiting reagent
2. Calculate the theoretical yield
3. Calculate the % yield

4 Solutions and Concentrations

Introduction

A Solution is a homogeneous mixture of two (or more) pure substances and typically consists of a solvent (the “dissolver”) which is generally present in the larger amount and a solute (the substance being dissolved) which is generally present in the smaller amount.

Usually we are talking about a solid that dissolves in a liquid, but we could mean a gas dissolved in a liquid, or a liquid dissolved in a liquid.

The liquid is most often water – e.g. copper sulphate solution, or instant coffee. The solvent could be other liquids – e.g. methanol or cyclohexane.

4.1 Dissolving

When a solution is made, the bonds between the solute particles are broken, and they spread out throughout the solvent. This is called *dissolving*. New bonds are formed between the solute and the solvent molecules.

E.g. H_2O and $\text{NaCl}(s)$ gives $\text{Na}^+(aq) + \text{Cl}^-(aq)$



“I studied English for 16 years but...
...I finally learned to speak it in just six lessons”
Jane, Chinese architect

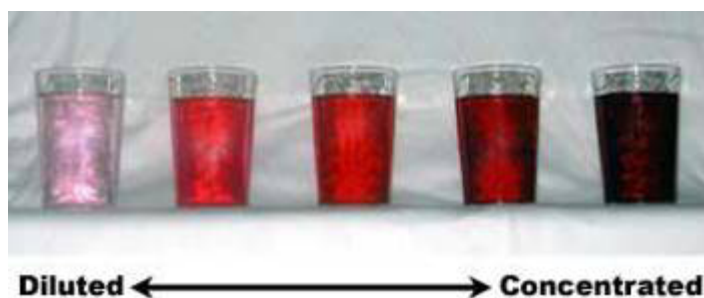
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4.2 Concentration

The concentration of a solution can be defined as the *amount of solute* dissolved in a particular *volume* of solution. Therefore a dilute solution contains a low concentration of solute and a concentrated solution contains a high concentration of solute.

Typically, “dilute” and “concentrated” are general terms. For accurate and quantitative work, more precision is necessary.



4.2.1 Common units of concentration

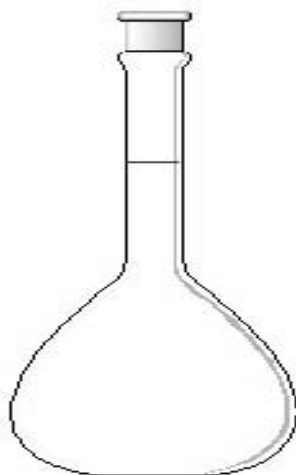
Chemists use grams per cubic decimetre. Remember that 1000 cubic centimetres (cm^3) equals 1 cubic decimetre (dm^3) also equals 1 litre (L).

We note that cm^3 are sometimes called *millilitres* (mL).

E.g. if 10g of glucose are dissolved in water and made up in a *volumetric flask* to 1000cm^3 , then the concentration of glucose in the flask is equal to 10 grams per cubic decimetre or $10\text{g}\cdot\text{dm}^{-3}$.

E.g. similarly if 10g of glucose are dissolved in water and made up to 100cm^3 , the concentration is 10g in 100cm^3 or $100\text{g}\cdot\text{dm}^{-3}$.

A volumetric flask is very accurate way to measure a volume, when filled exactly to line. It comes in different sizes.



4.2.2 Question

How much sodium chloride (in g) is contained in 200cm^3 of a $7.5\text{ g}\cdot\text{dm}^{-3}$ solution? Remember this is an amount, not a concentration.

4.3 Changing volume

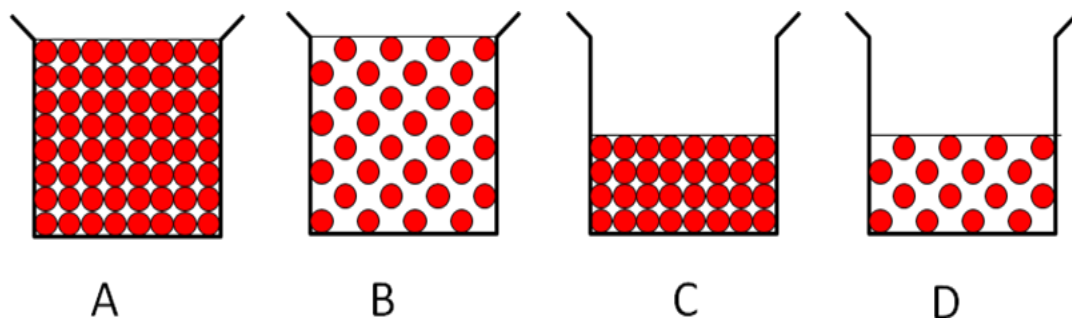
It may seem obvious but remember that, if you have a solution of concentration, say, $100\text{g}\cdot\text{dm}^{-3}$, you can have any volume of it.

A smaller volume will contain less solute, while a larger volume will contain more solute, but the *concentration* of both is the same.

4.3.1 Concentration

Which of these solutions have:

- Equal volume? A has same volume as B; C has same volume as D.
- Equal concentration? A has same concentration as C; B has same concentration as D.
- Equal number of moles of solute? B has same number of moles of solute as C.



4.4 Most useful unit of concentration - Molarity

The *number of moles* is always more important than the *mass* (as the reaction equations tell us how many moles will react together, not the number of grams). So the usual units for concentration are moles per cubic decimetre (mol dm^{-3}). This unit is also called molarity, with the symbol 'M' *i.e.* $0.1 \text{ mol dm}^{-3} = 0.1 \text{ M}$ (or "0.1 Molar"). You may still find the equivalent term moles per litre (mol L^{-1}) still used.

4.4.1 Unit conversion

To convert between concentrations expressed using the two different units, an important relationship is $\text{g dm}^{-3} / \text{g mol}^{-1}$ is equal to mol dm^{-3} (M) where g mol^{-1} is the molar mass.

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4.4.2 Example

90 g of glucose ($C_6H_{12}O_6$) are dissolved in water and made up to 1 dm^3 . What is the molarity?

RMM of $C_6H_{12}O_6 = 180$. Therefore $1\text{ mol} = 180\text{ g}$

As per equation above $90\text{ g dm}^{-3} = 90/180\text{ mol dm}^{-3} = 0.5\text{ mol dm}^{-3}$ (0.5M or 0.5 Molar).

4.4.3 Example

If 30 g of glucose ($C_6H_{12}O_6$) are dissolved in 250 cm^3 of solution, what is the molarity?

Molarity of glucose is 0.67 mol dm^{-3} (0.67M or 0.67 Molar).

4.5 Equation to learn

Concentration = Number of moles / Volume

The concentration (or molarity) is in mol.dm^{-3} , number of moles in mol and volume must be in dm^3 . You will often need to change from cm^3 . Remember – you may need to convert from grams to moles first.

4.6 Ionic Solutions

We can generally assume that salts dissociate completely into their ions when they dissolve in water. If you have a 0.1M solution of magnesium bromide ($Mg^{2+} 2Br^-$), the solution will be:

- 0.1M with respect to $MgBr_2$ (aq),
- 0.1M with respect of Mg^{2+} (aq), and
- 0.2M with respect to Br^- (aq).

4.6.1 Exercise

Use the following RAM values for the calculations:

What is the concentration, in mol.dm^{-3} of a solution containing

- 4.25g silver nitrate in 500 cm^3 of solution?
- 4.0g sodium hydroxide in 250 cm^3 solution?

What mass of solute is present in

- 50 cm^3 of 2.0 M sulphuric acid (H_2SO_4)?
- 250 cm^3 of 0.2 M sodium carbonate?

4.6.2 Exercise

Now use the most accurate values for the RAMs that you can find. Quote your answer to an appropriate number of significant figures.

If 2.80 g of potassium hydroxide is dissolved in 500 cm³ solution, what is the molarity of the resulting solution?

- Molar mass KOH = 39.098 + 15.999 + 1.008 = 56.105.
- Number of moles = mass/molar mass = 2.80/56.105 = 0.0499 moles.
- Concentration = moles/volume = 0.0499/0.500.0 = 0.998 M

4.7 Diluting Solutions

Often, in analytical work, it is necessary to know how to prepare a more dilute solution from a more concentrated one. This process is called Dilution. To dilute a solution, water must be added. When extra water (the solvent) is added, the number of moles of solute *does not* change, but the volume of the solution *does* change, hence the concentration changes.

For example, solution A has been diluted twice. Which of these quantities remain constant:

- volume,
- concentration,
- number of moles?

A very useful equation is: $C_{\text{original}} \times V_{\text{original}} = C_{\text{diluted}} \times V_{\text{diluted}}$

Where:

- C_{original} and V_{original} are the concentration and volume of original solution,
- C_{diluted} and V_{diluted} are the concentration and volume of diluted solution

Often written as $C_1 \times V_1 = C_2 \times V_2$. When using this equation, the units of concentration and volume must be the same on both sides.

Different quantities can then of course, be taken from the diluted solution – here, some of solution C has been removed into a smaller container. Which of these quantities remain constant:

- Volume,
- Concentration,
- Number of moles?

4.7.1 Example

If you have a solution containing 10 g.L^{-1} of hydrochloric acid, how would you prepare 100 cm^3 of a 0.1M solution? (R.A.M. H = 1.0, Cl = 35.5)

Part 1: calculate the molarity of the original solution:

R.M.M. of HCl = 36.5 g mol^{-1} so concentration of original solution = 0.274 M

Part 2: the dilution

$C_{\text{original}} \times V_{\text{original}} = C_{\text{dilute}} \times V_{\text{dilute}}$

$0.274 \times V_{\text{original}} = 0.1 \times 100$

$V_{\text{original}} = 0.1 \times 100 / 0.274 = 36.5 \text{ cm}^3$

So measure carefully 36.5 cm^3 of the original solution into a 100 cm^3 volumetric flask and make it up to 100 cm^3 with distilled water.

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4.7.2 Exercise

Commercial concentrated hydrochloric acid is 12.4 M. How many cm^3 of this acid would you dilute to prepare 1.5 dm^3 of 0.50 M hydrochloric acid? (Remember to quote answers to the correct number of significant figures).

- $C_1V_1 = C_2V_2$ so $12.4 \times V_1 = 1.5 \times 0.5$
- $V_1 = 1.5 \times 0.5 / 12.4 = 0.060 \text{ dm}^3 = 0.060 \times 1000 \text{ cm}^3 = 60 \text{ cm}^3$

4.8 The pH scale

The strength of acids or alkalis is directly related to the concentration of H^+ ions. Typical concentrations are:

- strong acids: 0.1 mol dm^{-3}
- weak acids: $10^{-6} \text{ mol dm}^{-3}$

The pH scale is used to express this concentration as a small, more easily useable number. H^+ ions have big impact on chemical reactions and the amount of H^+ ions present determines whether a solution is acid or alkaline (basic).

4.8.1 Definition of pH

$$\text{pH} = -\log_{10} [\text{H}^+]$$

Where $[\text{H}^+]$ = concentration of H^+ in mol dm^{-3} .

Definition of log:

$$\text{if } a = b^c, \text{ then } \log_b a = c$$

Converting the number to a logarithm compresses values ranging from 1 to 10^{-14} into a scale of 1 – 14.

4.8.2 The pH scale

On this scale,

- pH of pure water = 7
- pH < 7 for acidic solutions and
- pH > 7 for alkaline solutions

Remember, a *small* pH means a *high* concentration of H^+ ions and a *high* pH means a *low* concentration of H^+ ions.

4.8.3 Example

What is the pH of 0.05M HCl?

HCl is a strong acid i.e. it is completely ionised to H^+ and Cl^- in water. Thus, $[\text{H}^+] = 0.05 \text{ M}$ then $\text{pH} = -\log 0.05 = -(-1.3) = 1.3$

4.8.4 Exercise

A Cola drink is found to have a pH of 2.6. What is the $[\text{H}^+]$?

4.9 Other units for concentration

Many other units are used for measuring concentration in industry, or in specialist applications. You need to be aware of these.

4.9.1 Units for very low concentrations

Concentrations of pollutants in water, or of drugs in the bloodstream are so small that molarity concentrations are not very useful.

Parts per million (ppm) are used instead where concentration of ion (in ppm) = (mass of substance / mass of solution) $\times 10^6$

4.9.2 Example

A sample of tap water contains 0.15mg of Fe^{3+} per dm^3 . What is its concentration in ppm?

The density of water is 1.0g per cm^3 then mass of 1 dm^3 water is 1000g = 1×10^6 mg and therefore concentration = 0.15 ppm.

4.9.3 Parts per billion

For extremely small quantities, the units can be expressed as parts per *billion* (ppb). Calculated as for ppm except multiplying factor is now 10^9 thus 1 ppm = 10^3 ppb.

4.9.4 Other units for very low concentrations

- By volume (for gas mixtures) (volume of substance / volume of sample) $\times 10^6$
- By mass/volume (for aqueous solutions) [(mass of substance (g) / volume of solution (cm^3))] $\times 10^6$

4.9.5 Concentration as percentage (%)

This is often used for *solutions* in the commerce or industry

- % by mass (w/w) = (mass of solute / mass of solution) $\times 100$
- % by volume (v/v) = (volume of liquid solute / volume of solution) $\times 100$

4.9.6 Concentration as mole fraction

Mole Fraction = moles of substance / total moles present. This has no units to this measurement as it is a ratio and value varies between 0 and 1.

5 Electromagnetic Radiation and Spectroscopy

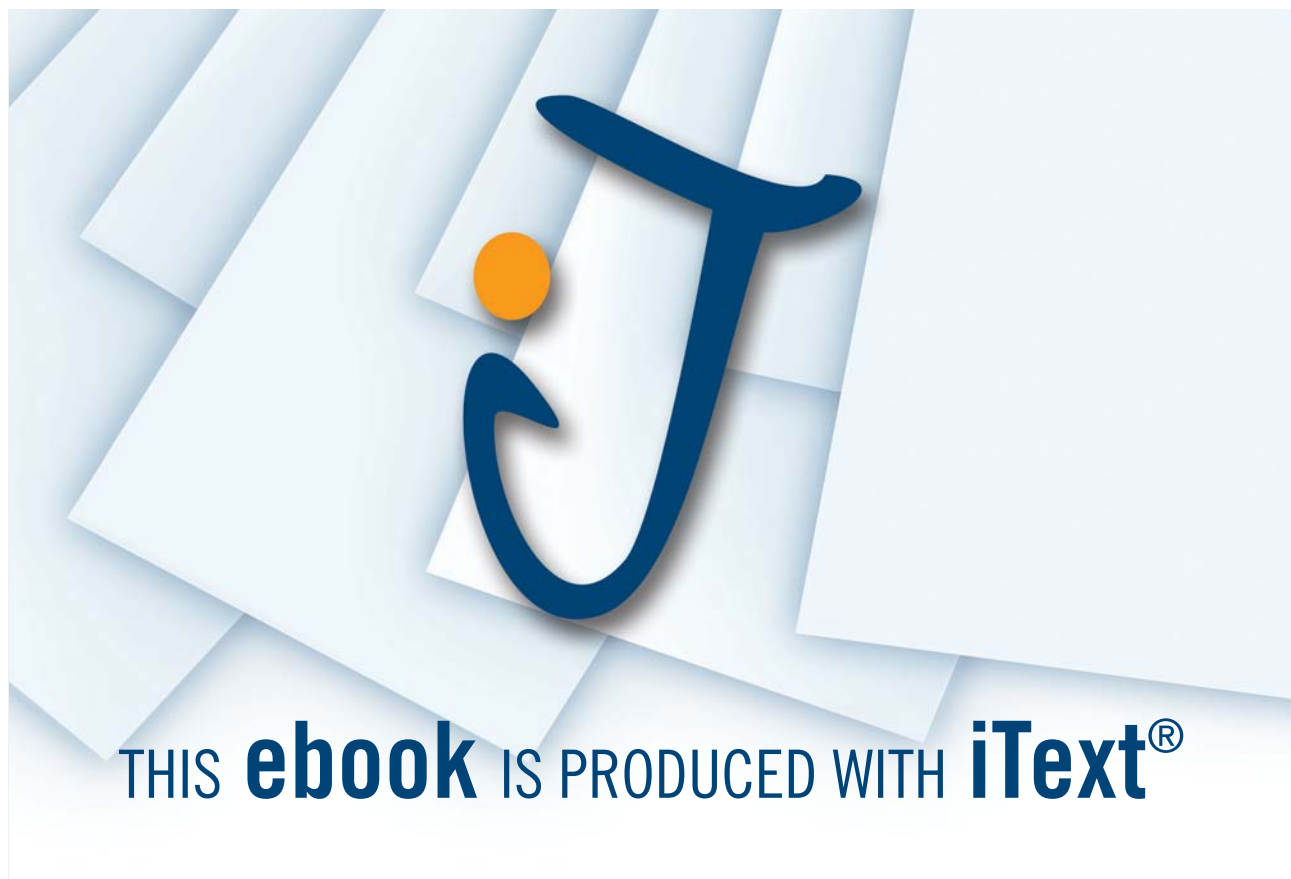
5.1 Electromagnetic Spectrum

Isaac Newton studied radiation from Sun; what we call white light. He found sunlight was made up of many colours when he passed sunlight through a prism. We call this the visible spectrum.

5.1.1 Radiation

Light is made up of electromagnetic waves which carry energy. Each colour of light corresponds to a different wavelength. There is also radiation at wavelengths our eyes can't see

- Ultraviolet: shorter wavelengths than visible
- Infrared: longer wavelengths than visible

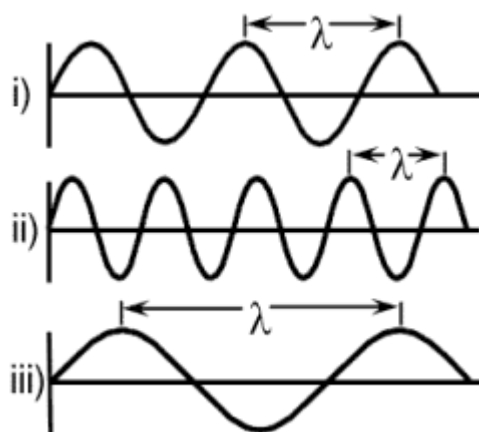


5.1.2 Electromagnetic Radiation

Radiation always travels at $3.0 \times 10^8 \text{ m s}^{-1}$ and this speed is given the symbol 'c'.

Radiation has

- A wavelength (symbol lambda, λ) measured in metres (m) and this the distance from crest to crest.
- A frequency (symbol nu, ν) is measured in Hertz (Hz) and $1 \text{ Hz} = 1 \text{ s}^{-1}$



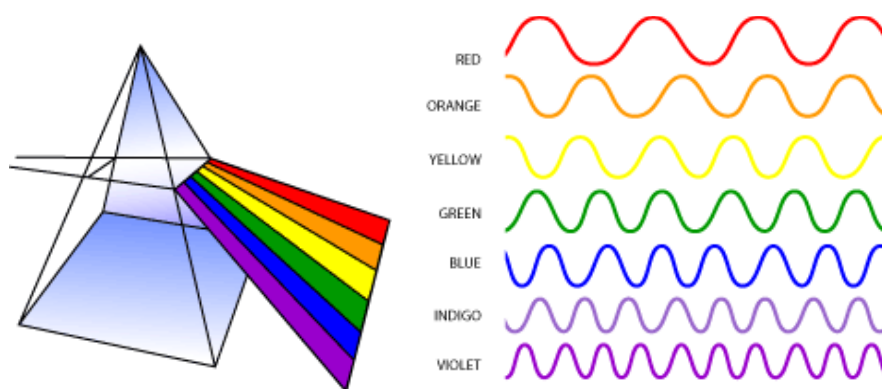
5.1.3 Equation to learn

$$c = \lambda \nu \text{ or } \nu = c / \lambda$$

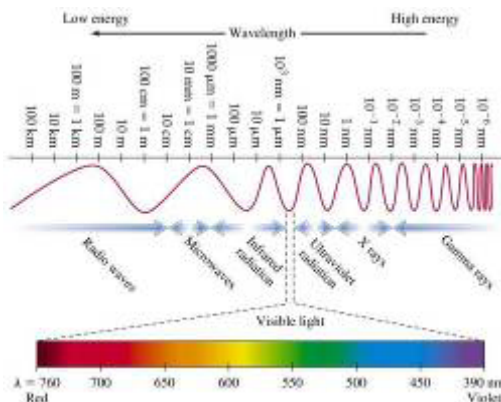
Radiation with a high frequency has a short (low) wavelength. Similarly, radiation with a low frequency has a long (high) Wavelength

5.1.4 Electromagnetic Spectrum

The visible region constitutes a small part of the overall spectrum



Many different types of radiation make up the whole electromagnetic spectrum



5.2 Definition of Electromagnetic Radiation (EMR)

Electromagnetic radiation consists of energy transported through space in the form of periodic disturbances of electric and magnetic fields – a wave.

5.2.1 Properties of Electromagnetic Radiation (EMR).

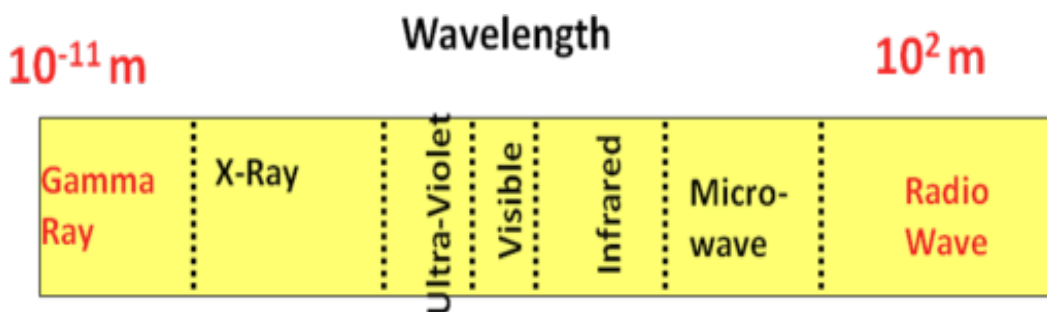
EMR has a “dual” nature wave form “particle” or photon form. Quantum theory regards radiation as consisting of “packets of energy” (quanta) called photons. The energy of a photon is given by $E = h\nu$ where ‘h’ is Planck’s constant and Planck’s constant is $6.626 \times 10^{-34} \text{ J s}$.

5.3 Energy of Light

$$E = h\nu = \frac{hc}{\lambda}$$

Thus radiation from different regions of the electromagnetic spectrum has different energies. The amount of energy (in Joules) can be determined by this equation where:

Let’s compare the energy of two forms of light at opposite ends of the spectrum, gamma rays and radio waves.



The shorter the wavelength the more energy light has. The energy of one mole of photons is obtained by multiplying by Avogadro's number (N_A) and $N^A = 6.022 \times 10^{23} \text{ mol}^{-1}$

So per mole = $h \times N_A = 6.626 \times 10^{-34} \times 6.022 \times 10^{23} = 3.99 \times 10^{-10} \text{ J s mol}^{-1}$

5.3.1 Exercise

Calculate the energy, in J mol^{-1} , corresponding to a wavelength of 620 nm.

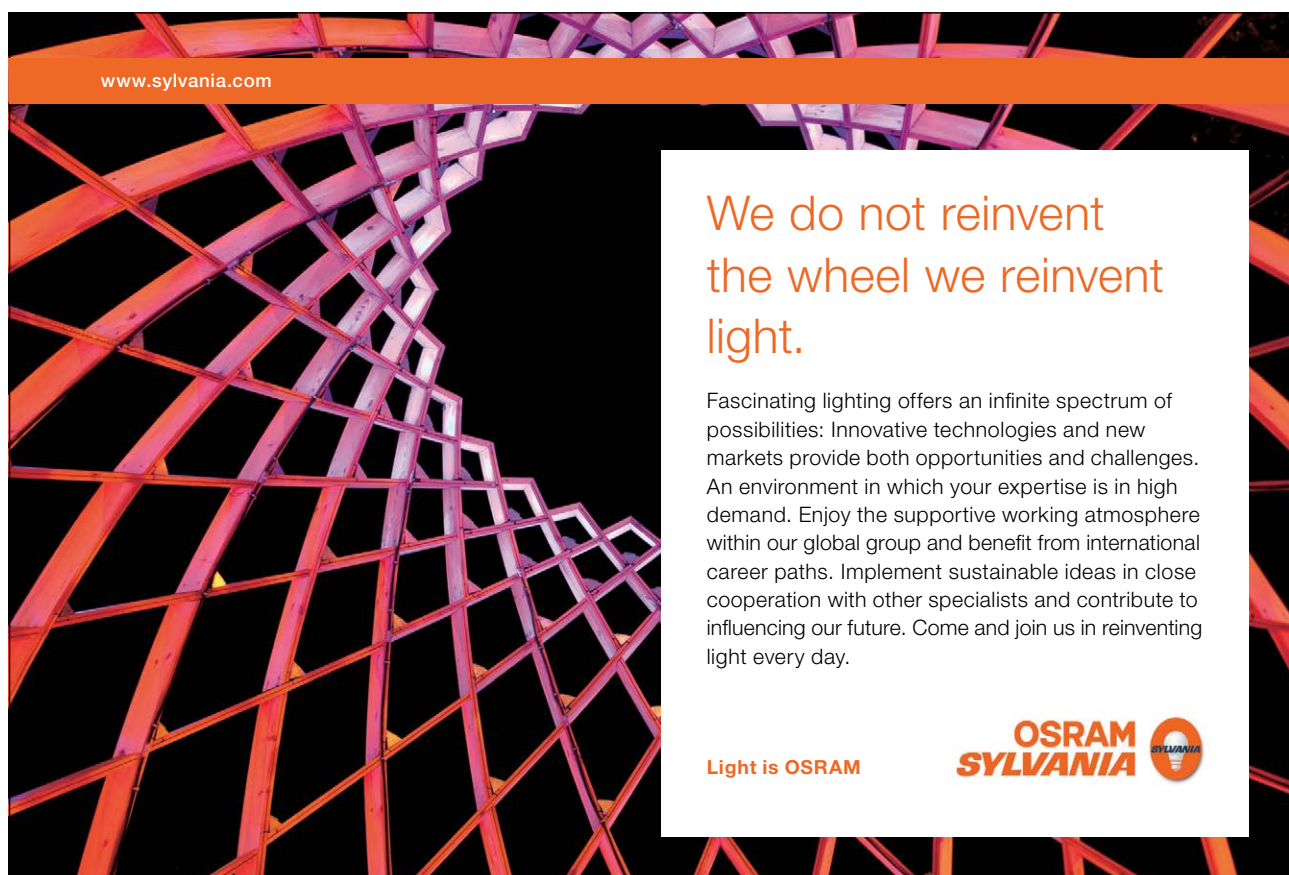
$$\lambda = 620 \text{ nm} = 620 \times 10^{-9} \text{ m}$$

$$E = 6.626 \times 10^{-34} \times 6.022 \times 10^{23} \times 3.0 \times 10^8 / 620 \times 10^{-9} = 193125 \text{ J mol}^{-1} = 193.1 \text{ kJ mol}^{-1}$$

Note that calculations of this nature are often quoted with the units kJ mol^{-1} , even though J mol^{-1} are strictly the SI units. Planck's constant can be quoted using kJ s or J s , so make sure you are using units consistently.

5.4 Emission Spectra

When a gas at low pressure has a voltage applied to it, or when a substance is burnt, it emits light characteristic of the element. When the emitted light is analysed with a spectrometer, a series of discrete bright lines is observed. Each line has a different wavelength and colour. This series of lines is called an emission spectrum.




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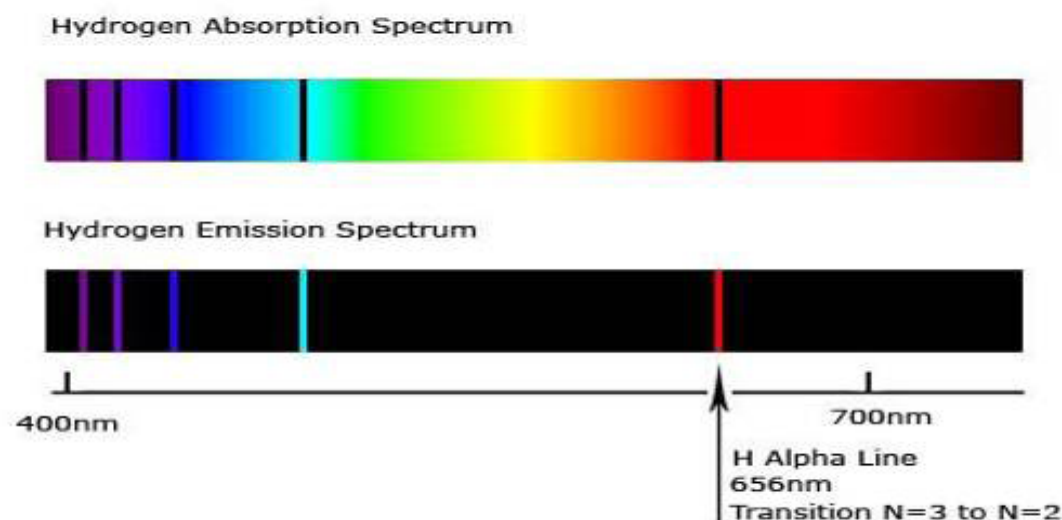




Different elements have different emission spectra.

5.5 Absorption Spectra

An element can also absorb light at specific wavelengths. An absorption spectrum can be obtained by passing a continuous radiation spectrum (white light) through a vapour of the gas. The absorption spectrum consists of a series of dark lines superimposed on the otherwise continuous spectrum (like the rainbow). The dark lines of the absorption spectrum coincide with the bright lines of the emission spectrum.



5.5.1 Absorption Spectra in Astronomy

Most stellar spectra are absorption spectra. Hot, high density objects give off a continuous spectrum. If this light then passes through a low density gas, photons of certain wavelengths can be absorbed – if the light is observed after it has passed through the gas, you will see an absorption spectrum. The continuous spectrum emitted by the Sun passes through the cooler gases of the Sun's atmosphere:

- The various absorption lines can be used to identify elements in the solar atmosphere, and
- This led to the discovery of helium (named after Helios, god of the sun).

5.6 Uses of spectroscopy

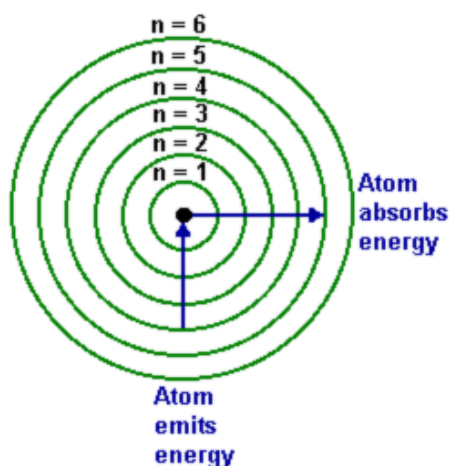
By looking at a star or planet's absorption spectrum we can learn about its composition. E.g. Sodium is only atom to produce 2 absorption lines in yellow part of the visible spectrum with wavelengths 589 and 589.6nm. The same is true for any chemical we heat up. Spectroscopy is an important technique for the quantitative analysis of many elements, particularly metals.

5.7 Quantum theory

Emission and absorption spectra are evidence that the electrons within an atom have quantised energies i.e. an electron cannot possess a continuous range of values for energy, but must have specific values called energy levels. The lowest energy level is called the ground state (E_0). Any higher energy level is called an excited state.

5.7.1 Bohr model

In 1913 Niels Bohr (1885-1962) developed a theory to explain light emission and absorption. The Bohr model of the atom pictures electrons circling the nucleus at a fixed radius – in an energy shell. Bohr's theory works well for the one-electron hydrogen atom, but note that more sophisticated theories are needed to explain multi-electron atoms.

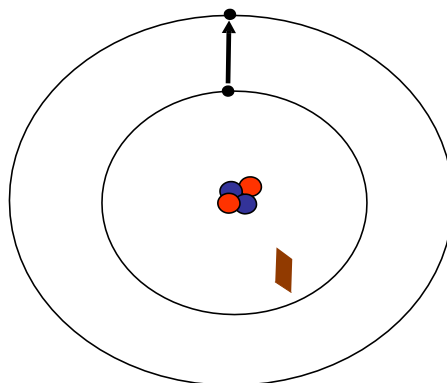


The energy shells are labelled with a principal quantum number; $n=1$, $n=2$ etc. The closer the electron's orbit is to the nucleus, the stronger the attractive force. The lowest energy electrons are those nearest the nucleus in the $n = 1$ shell. Extra energy would need to be added to enable them to pull away from the nuclear attraction into an excited state.

5.7.2 Moving electrons

Moving an electron between a lower and higher energy level can only be achieved if it absorbs energy of a particular amount; this could be from a particular wavelength of light. Conversely if an electron moves down from a higher energy level to a lower one it will emit light of a particular wavelength equivalent to the difference in energy.

As electrons absorb sufficient energy from heat or other energy source they move up from the ground state to an excited state. To absorb a photon, the photon must have exactly the correct amount of energy (or in other words the correct wavelength).



As electrons cool down they lose the energy they gained and fall back to a lower or ground state.



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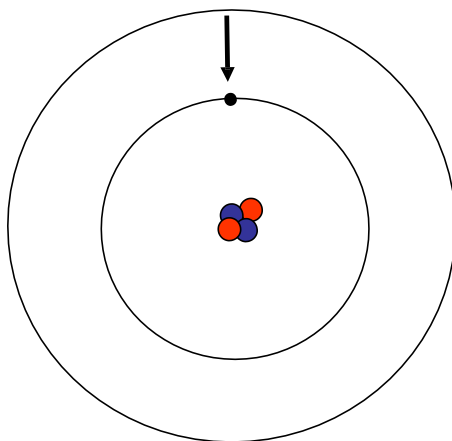
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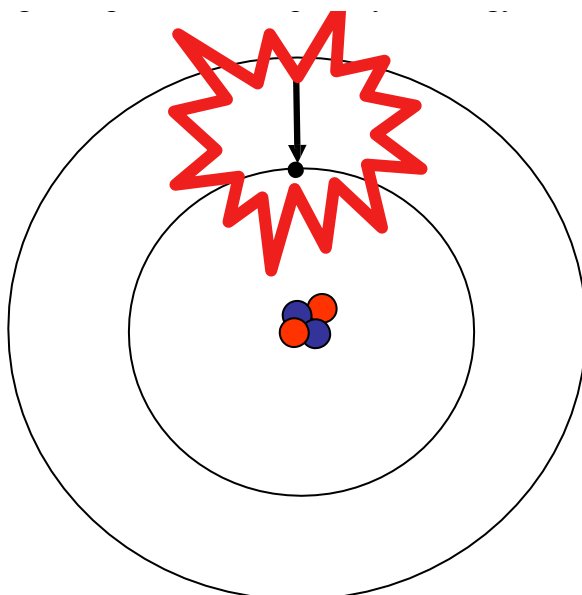
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- During this fall visible light is emitted. The colour of light is specific to the quantity of energy lost and it contributes to the spectra of an element.

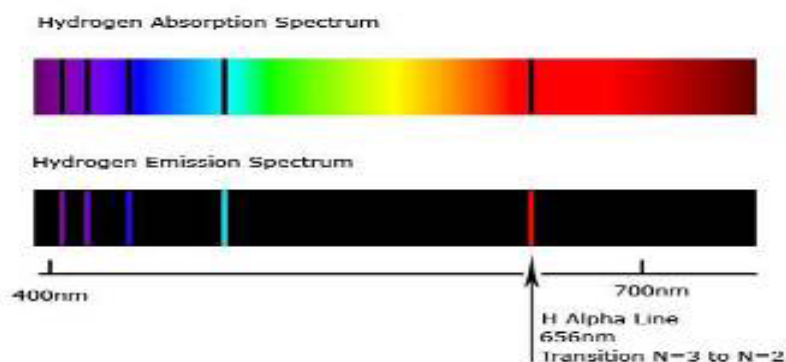


5.8 Interpreting electronic spectra

The simplest spectra to study are those of H, as it only has one electron. These contain sets of lines which can be related to the energy levels. The Lyman series (in the ultra-violet) correspond to transitions to or from the ground state, i.e. $n=1$.

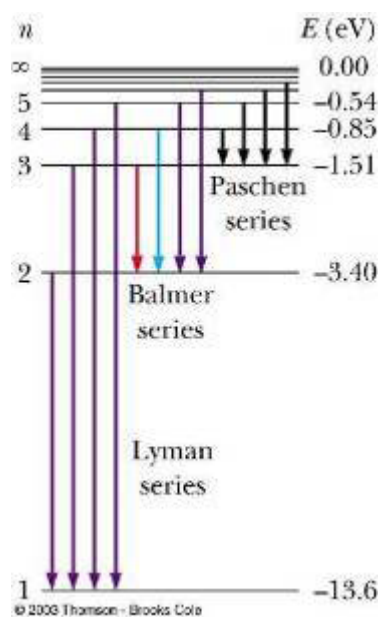
5.8.1 Balmer series

A second set of lines, in the visible region are called the Balmer series. They correspond to transitions involving excitation from the second energy level, $n=2$. Further series correspond to transitions involving higher energy shells.



5.8.2 Energy Level Diagram

The diagram shows transitions between energy levels. An electron moves up from one energy level to another when it absorbs a particular wavelength. An electron moves down from one energy level to another when it emits a particular wavelength.



5.8.3 Interpreting electronic spectra

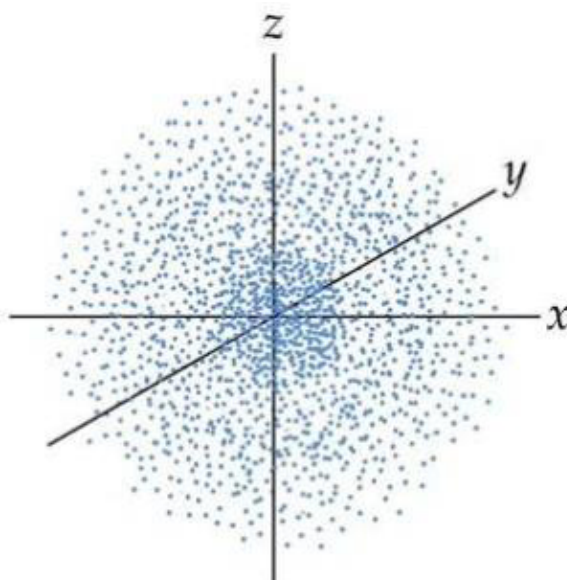
Careful study of absorption or emission spectra reveals the permitted electronic energy levels within an atom. The amount of energy needed to remove an electron completely from an atom is called the ionisation energy. This is equivalent to an electron in the ground state absorbing enough energy to move up to the infinite energy level.

5.9 Quantum-Mechanical Model

Bohr's theory was a start but it only explained the hydrogen atom (one electron as a particle orbiting around a nucleus). The Quantum-Mechanical (QM) model, first developed by Erwin Schrödinger in 1926 describes electrons mathematically as both waves and particles. Schrödinger replaced Bohr's orbits by complex 3-dimensional mathematical wave equations.

5.9.1 Orbitals

Orbitals are probability 'maps' because electrons do not have predictable positions. Heisenberg's Uncertainty Principle – this states that the exact location and momentum of an electron is impossible to know at the same time. Whilst the value of one is known the value of the other remains unknown. For an electron in a particular energy level, the atomic orbitals can be imagined as specific locations (volumes of space) in which there is a high probability (>90% chance) of finding the electron. Each orbital can hold a maximum of 2 electrons. Orbitals describe the most likely place electrons will be found around the nucleus. We call this a probability density.



5.9.2 Quantum Mechanical Model

Each electron in an atom can be uniquely described by four quantum numbers. A number, n , the Principal Quantum Number, is used to identify the main energy level in which the electrons are located, where $n = 1$, $n = 2$, $n = 3$ etc

5.10 Sublevels

Emission spectra confirm that within each main energy level, except the lowest ($n = 1$), there are sub-levels. There are four types of sublevel known as s, p, d and f. each of which contains one or more orbitals. The sublevels within a level have different energies, increasing $s \rightarrow p \rightarrow d \rightarrow f$.

5.10.1 Angular momentum Quantum number l

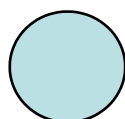
The sub-levels (s, p, d, f) are defined mathematically by the angular momentum quantum number, l . This is related to the shape of the orbital and has values from 0 to $(n-1)$. So, for e.g. $n = 3$, l can be 0, 1 or 2 i.e. there are 3s, 3p and 3d orbitals, but not 3f.

5.10.2 Sublevels

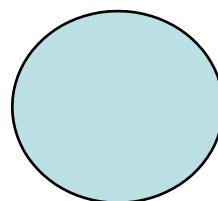
Main Energy level Principal quantum number n	Angular momentum quantum number, l	Energy sub-level
1	0	1s
2	0	2s
	1	2p
3	0	3s
	1	3p
	2	3d
4	0	4s
	1	4p
	2	4d
	3	4f

5.11 s orbitals

The simplest orbital is the s orbital. This has a spherical shape



1s



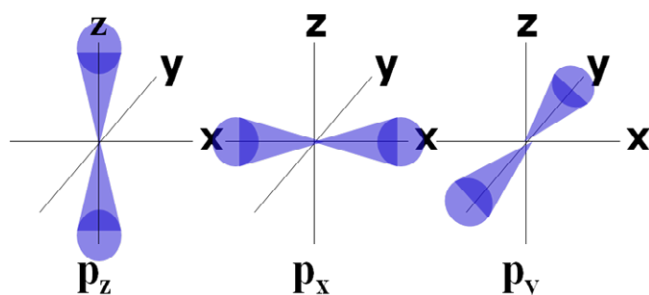
2s

Each type of sub-level apart from s (i.e. p, d, or f) has more than one orbital of equivalent energy. The differences between these orbitals are described mathematically by the Magnetic quantum number m_L . This is related to the orientation of the orbital and has values from -1 to +1 (including 0).

	Type of energy sub-level	Number of orbitals	Number of electrons	Possible values of m_l
0	s	One s orbital	2	0
1	p	Three p orbitals	6	-1, 0, +1
2	d	Five d orbitals	10	-2, -1, 0, 1, 2
3	f	Seven f orbitals	14	-3, -2, -1, 0, 1, 2, 3

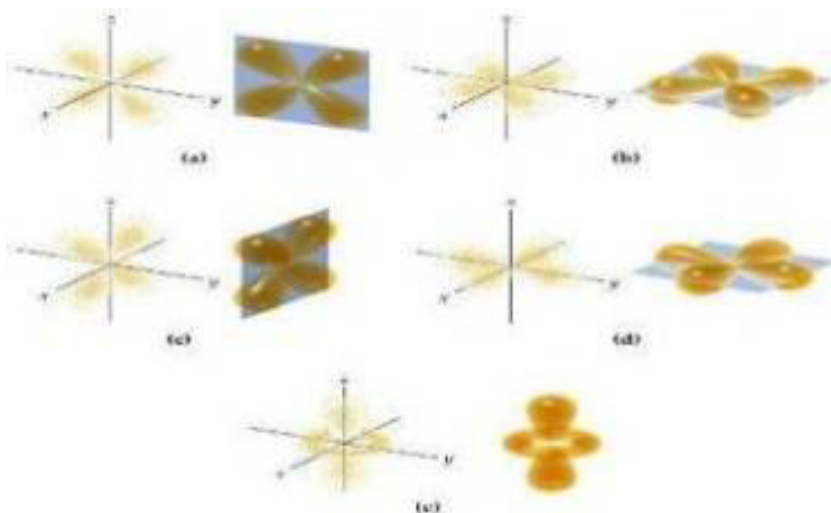
Each orbital can contain up to 2 electrons. So, for example $l = 1$, m_l can be -1, 0, or 1 i.e. there are three different p orbitals, which are similar in shape, but differently orientated. They are degenerate (i.e. of equal energy). As each main energy level (except $n=1$) can have $l = 1$, there will be three p orbitals of equal energy for each of $n = 2$, $n = 3$, $n = 4$ etc.

5.12 p orbitals



5.13 d orbitals

There are 5 degenerate d orbitals. Some are similar to the p orbital but orientated in space differently. Other d orbitals have a totally different shape.



5.13.1 Spin Magnetic Quantum number m_s

Each orbital can contain up to 2 electrons. Each electron has a Quantum Mechanical property called spin with an associated quantum number m_s , which can have values of $+\frac{1}{2}$ or $-\frac{1}{2}$. Note that “spin” is a misleading old-fashioned name – the electron is not spinning round! It represents a property which describes how the electron interacts with a magnetic field.



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5.14 Quantum Numbers

<u>Name</u>	<u>Description</u>
• Principal ($n = \text{Shell}$)	• Orbital size/energy
• Angular momentum ($l = \text{subshell}$)	• Shape of orbital
• Magnetic (m_l)	• Orientation in space of orbital
• Spin (m_s)	• Direction of spin of electron

5.14.1 The Four Quantum Numbers

If values for the four quantum numbers, n , l , m_l and m_s are given, it is possible to define any single electron in an atom in terms of its energy and likely location.

E.g. if $n = 3$, $l = 2$, $m_l = 1$ and $m_s = +\frac{1}{2}$, this describes an electron in a particular 3d orbital with an “up” spin.

5.14.2 Exercise

State which of the following sets of quantum numbers would be possible and which impossible for an electron in an atom

n	l	m_l	m_s
0	0	0	$+\frac{1}{2}$
1	1	0	$+\frac{1}{2}$
1	0	0	$-\frac{1}{2}$
2	1	-2	$+\frac{1}{2}$
2	1	-1	$+\frac{1}{2}$

5.15 The Pauli Exclusion Principle

This principle states that no two electrons in any one atom can have the same set of four quantum numbers. Which means:

- There is a maximum of 2 electrons in any one orbital.
- If there are 2 electrons in an orbital, then they must have opposite spins - either “up” or “down”

5.16 Electronic Configuration

The electronic configuration of an atom describes which orbitals the electrons occupy in the ground state. The simplest is the “Bohr” notation, which only states how many electrons are in each of the main energy levels. E.g. Na 2.8. There are two main ways in which the more detailed electronic configurations of atoms can be expressed.

A. Spectroscopic Notation

A hydrogen atom has one electron, which will occupy the 1s orbital. This can be expressed as 1s¹. Helium will have both its electrons in the 1s orbital and this can be written as 1s².

5.16.1 Ways of Writing Electronic Configurations

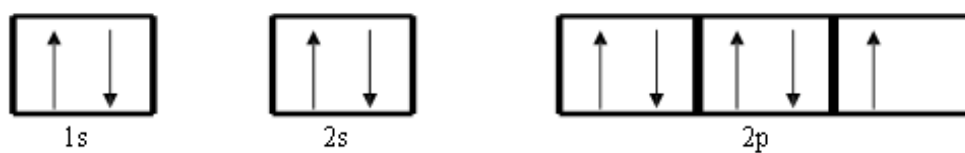
Element	Simple shell configuration	Simple orbital configuration	Detailed orbital configuration
H	1	1s ¹	1s ¹
Li	2.1	1s ² .2s ¹	1s ² .2s ¹
B	2.3	1s ² .2s ² 2p ¹	1s ² .2s ² 2p ^{x1}
N	2.5	1s ² .2s ² 2p ³	1s ² .2s ² 2p ^{x1} 2p ^{y1} 2p ^{z1}
F	2.7	1s ² .2s ² 2p ⁵	1s ² .2s ² 2p ^{x2} 2p ^{y2} 2p ^{z1}
Ne	2.8	1s ² .2s ² 2p ⁶	1s ² .2s ² 2p ^{x2} 2p ^{y2} 2p ^{z2}
Na	2.8.1	1s ² .2s ² 2p ⁶ .3s ¹	1s ² .2s ² 2p ^{x2} 2p ^{y2} 2p ^{z2} .3s ¹

5.16.2 Exercise - Write simple Bohr notation (E.g. 2,8,1) and the detailed orbital configuration (e.g. 1s²2s²) for

- Si
- S
- Ar
- K

B. Orbital box notation

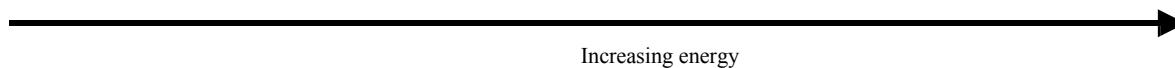
Another way is to show the orbitals as boxes. The electrons are shown as arrows. Those with parallel spins are shown pointing in the same direction. Paired spins have the arrows facing in the opposite direction e.g. the electron configuration for Fluorine



5.17 The Aufbau Principle

Before we can write the electronic configuration for more complicated multi- electron atoms, we need to know the order in which the various orbitals are filled. The Aufbau Principle states that the orbitals of the lowest energy levels are always filled first:

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s 4f 5d 6p 7s 5f 6d 7p



5.18 Hund's Rule

Hund's Rule of Maximum Multiplicity states that when electrons occupy degenerate orbitals (i.e. orbitals of the same energy levels) the electrons fill each orbital singly, keeping their spins parallel before spin pairing occurs.

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5.18.1 Exercise - Using both spectroscopic and orbital box notations write down the electronic configurations for:

A. Lithium

B. Argon

C. Fluoride F^- ionD. Sulphide S^{2-} ion**5.19 Summary**

Electromagnetic radiation can be described in terms of wavelength, frequency and energy. These parameters are related using the relationships: Emission and absorption spectroscopy can be used to identify and quantify unknown samples. The electronic configuration of atoms is based on spectroscopic evidence and quantum theory. The shapes and relative energies of atomic orbitals for the first 40 elements can be described. These can be related to the four quantum numbers n , l , m_l and m_s . The electronic configuration of atoms can be predicted by the Aufbau principle, Pauli principle and Hund's rule.

6 Electron Configuration Bonding Redox equations

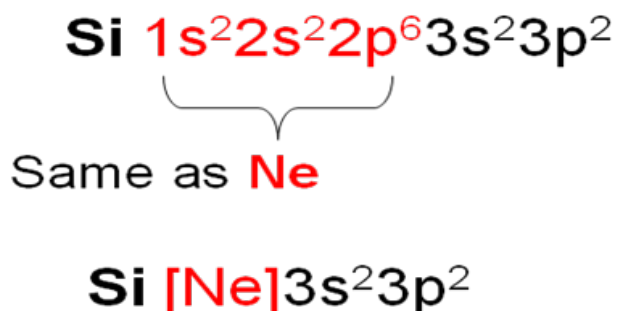
6.1 Valence Electrons and Bonding

Electrons can either be core electrons or valence electrons. The valence electrons are the outermost electrons of an atom.



Core Valence

As orbitals are filled, core electrons are part of the inner electronic configuration. This can be used to write electronic configuration in short hand notation.



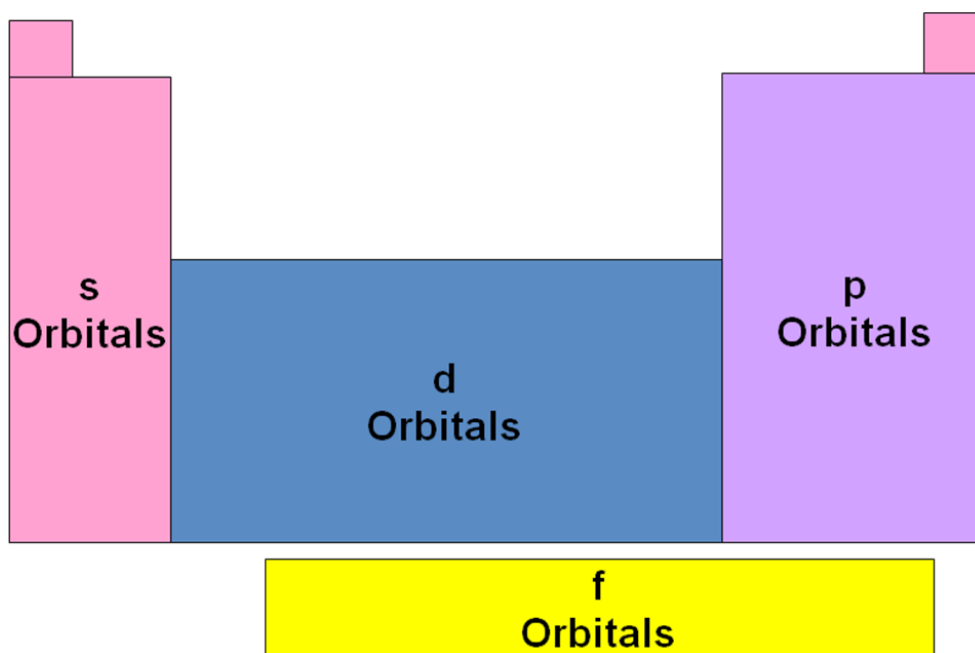
6.2 Valence electrons

Valence electrons occupy the highest energy (outer) shell. They are the electrons most affected by the approach of another atom. They are the electrons most likely to be involved when bonding occurs.

6.2.1 Quantum Numbers and the Periodic Table

The number of valence electrons dictates the way an element reacts, so the Periodic Table relates electronic configuration to chemical properties. Elements with the same number of electrons in the outer shell will have similar chemical properties, and are arranged underneath one another in Groups. The number of electrons permitted in each atomic orbital underlies the layout of the Periodic Table. The 7 horizontal rows on the Periodic Table correspond to the main energy levels. Each row (called a Period) represents a value of n – the Principal Quantum Number.

6.2.1.1 Periodic Variation of Electronic Configuration



As each successive element adds one more electron, the Aufbau principle means that the energy sub-levels will be filled in order of increasing energy. Thus for each new value of n , the first two elements will add electrons that will fill the s orbital. These are the elements in Group 1 & 2 – the “ s block”. Then the next six elements will each add an extra electron into the p orbitals. These are the elements in Groups 13 – 18 – the “ p block”. From the $n = 4$ Period, the order of the energy levels (shown by the Aufbau Principle) has to be studied carefully. After the $4s$ sub-level, the $3d$ orbital is filled next. This holds up to 10 electrons. These elements are the first row of Transition Metals – the “ d block”. Eventually, the f orbitals are filled as well – these elements in the “ f block” are sometimes called the Inner Transition Metals.

6.2.2 Example

For example, fluorine has a configuration $1s^2 2s^2 2p^5$. Its outermost electrons are in the $2p$ orbital, so fluorine can be found in the p block. F behaves like other Group 17 elements and is reactive because of its almost complete p sub-shell.

6.3 Bonding

Only with the noble gases (Group 18 or 0) do elements occur as free atoms. Atoms of other elements occur in a combined form i.e. bonded to other atoms. Why do atoms combine?

- To go to a more stable electronic energy state, and
- Energy is normally given out or evolved when bonds are formed.

6.3.1 Noble Gases

Noble gases are He, Ne, Ar, Kr, Xe, Rn. Helium has a filled shell of 2 electrons. All the rest have 8 electrons in their highest energy shells. The noble gases are either unreactive or of very low reactivity. They used to be called ‘inert gases’.

6.3.2 Bonding using the Octet Rule

The stability of the Noble gases is attributed to an outer energy shell arrangement of eight electrons (except He, with two). When other atoms combine, they often behave as if they are seeking to achieve an outer octet of electrons - like the noble gases. An outer shell of eight electrons is an extremely stable electronic arrangement.

6.3.3 Octet rule or 'rule of eight'

Atoms can achieve an outer shell of eight electrons by either:

- Transferring electrons from one to another to produce ions. This is ionic bonding (or electrovalency), or
- Sharing electrons between one another.

This is called covalent bonding (or covalency).

6.3.4 Octet/duet rule states atoms want electronic configuration like that of a noble gas

Metals tend to lose electrons to fulfill octet rule.

For example, $\text{Li} \rightarrow \text{Li}^+$ cation i.e. $1s^2 2s^1$ loses one electron $\rightarrow 1s^2$

Non-metals tend to gain electrons to fulfill octet rule.

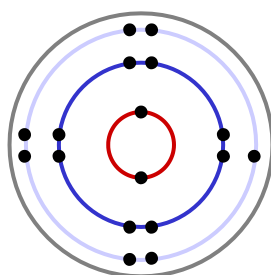
For example, $\text{F} \rightarrow \text{F}^-$ anion i.e. $1s^2 2s^2 2p^5$ gains one electron $\rightarrow 1s^2 2s^2 2p^6$

Only (outer) valence electrons are lost or gained.

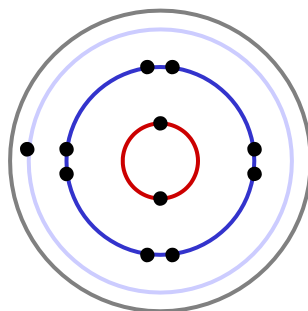
6.3.5 Ionic bonding

Typically involves metals from Groups 1 & 2 combining with non-metals from Groups 16 & 17. The metals lose electrons to form positively-charged cations (oxidation). The non-metals gain electrons to form negatively charged anions (reduction). The maximum number of electrons lost or gained is usually 2 (occasionally 3).

6.3.5.1 Ionic Formation of Sodium Chloride



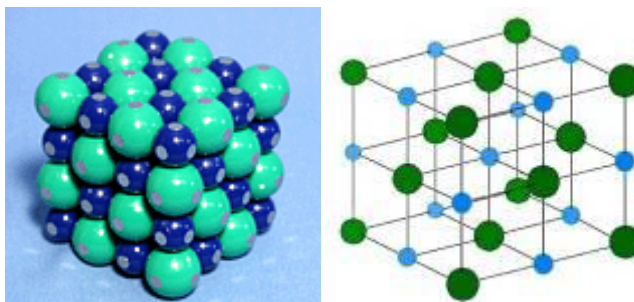
A Chlorine atom has 17 electrons. A Chloride ion (Cl^-) has 18 electrons.



A Sodium ion (Na^+) has 10 electrons. A Sodium atom has 11 electrons.

The oppositely-charged cations and anions are held together by electrostatic attraction. The smallest unit of an ionic compound is the formula unit e.g. Na^+Cl^- (sodium chloride), $\text{Mg}^{2+}\text{O}^{2-}$ (magnesium oxide), $\text{Ca}^{2+}\text{F}^{2-}$ (calcium fluoride).

6.3.5.2 Structure of Sodium Chloride



Sodium Chloride: Wikimedia Commons

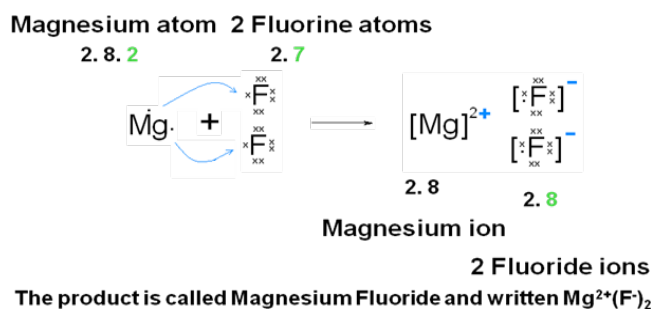
6.4 Lewis diagrams

Drawing atoms and ions with all the orbits or orbitals is time consuming. We usually draw Lewis diagrams to represent the way that electrons form bonds. These are simpler and quicker.

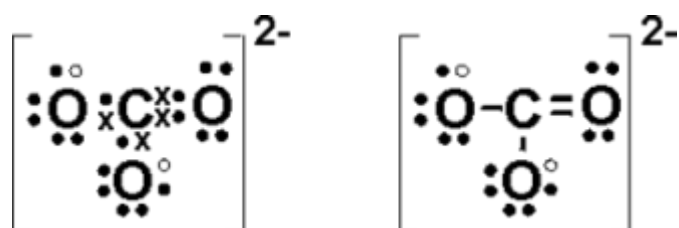
6.4.1 Rules for drawing Lewis diagrams

Count the number of valence electrons each atom brings into the molecule. For ions, the charge must be taken into account. Write the symbol for the element at the centre. Draw a dot or a cross for each electron around the symbol – use dots for one element, and crosses for the other, to show which atoms the electrons have come from (although once the bond has been made, they are indistinguishable).

6.4.2 Lewis diagram for the formation of ionic compound



For polyatomic ions, the overall charge must be taken into account.



Open circles represent two extra electrons from 2- charge.

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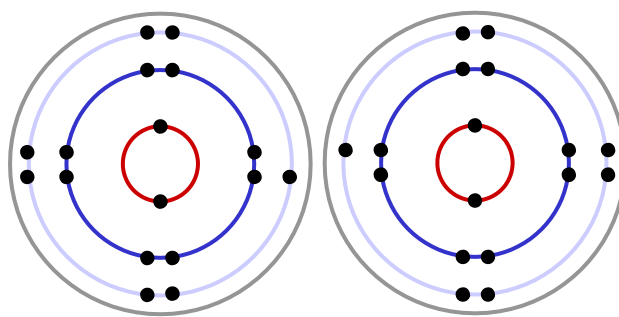
6.4.3 Exercise - Draw Lewis structures to show

- A bromide ion
- The formation of magnesium oxide
- Lithium oxide

6.5 Covalent bonding

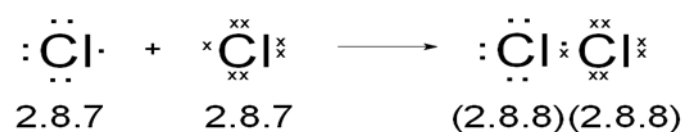
Covalent bonding occurs when too many electrons (typically 3 or more) have to be transferred for ionic bonding to be energetically favourable. Outer octet achieved by electron sharing. Commonly occurs in bonding between the non-metallic elements in Groups 13 – 17. Covalent is found in both elements (e.g. H₂, Cl₂) and compounds (e.g. CH₄, SiCl₄). Covalent bonding produces molecules (individual and giant). The shared electrons are attracted to both nuclei of the combining atoms, 'glueing' them together.

6.5.1 Formation of a covalent bond between two chlorine atoms



Each Chlorine atom has 17 electrons

6.5.2 Lewis diagram for formation of covalent compound

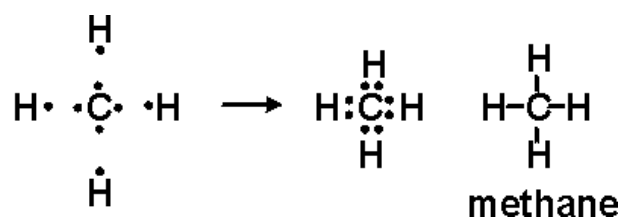


written as Cl—Cl or Cl₂

6.5.3 Rules for drawing Lewis diagrams

Lewis diagrams of covalent molecules: Put electron pairs about each atom such that there are 8 electrons around each atom (octet rule) (with the exception of H, which is only surrounded by 2 electrons).

6.5.4 Some other example



6.5.5 Exercise - Draw Lewis structures to show

- H_2S
- PBr_3
- C_2H_6

6.6 Single and multiple covalent bonds

Sometimes more than one pair of electrons is shared as follows:

- 1 pair of shared electrons = SINGLE covalent bond
- 2 pairs of shared electrons = DOUBLE covalent bond
- 3 pairs of shared electrons = TRIPLE covalent bond

Only C, N, O and S will form multiple bonds.

6.7 Redox reactions

Many chemical reactions involve the transfer of electrons from one element or compound to another. These are called REDOX reactions.

6.7.1 Oxidation and Reduction

Old definitions:

- Oxidation – gain of O; loss of H
- Reduction – loss of O; gain of H

But these descriptions proved too narrow. Modern definitions:

- Oxidation – loss of electrons
- Reduction – gain of electrons

6.7.2 Oxidation Number

Changes in electron distribution are best described using Oxidation Numbers. Oxidation Number (O.N.) is a way of describing how the electron density around an atom within a compound compares to that around the isolated atom. O.N. can be used for ionic or covalently bonded compounds.

6.7.3 Oxidation number of an atom

The Oxidation Number is the modern replacement for 'valency'. It reflects the 'combining capacity' of an element in a compound. The Oxidation Number may be positive or negative. Change in oxidation number reflects whether an atom has been oxidised or reduced as such:

- Positive change = oxidation
- Negative change = reduction

Oxidation numbers do not tell us anything about the type of bonding in a compound. Many elements, particularly non-metals can show more than one O.N.

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6.7.4 Rules for assigning O.N.

O.N. of an element in the free or uncombined state is zero. Sum of O.N.s in a neutral molecule or formula unit is zero. In ionic compounds, the O.N. of each element is the charge on its ion. The sum of the O.N.s in a polyatomic ion is equal to the ionic charge of the ion.

Hydrogen normally has O.N. = +1 (except in metal hydrides). Oxygen normally has O.N. = -2 (except in peroxides and compounds with fluorine). Generally elements in Group 1 have O.N. +1; and those in Group 2 an O.N. = +2. Chlorine has O.N. = -1 (except in compounds with O and F).

In covalent compounds, one element must be given a positive O.N. and the other a negative one. The negative O.N. is assigned to the more non-metallic (more electronegative) atom. It is the hypothetical charge that would result if the electrons in each bond were given to the more electronegative atom.

6.7.5 Examples

HCl	O.N. of H = +1
	O.N. of Cl = -1
H ₂ O	O.N. of H = +1
	O.N. of O = -2
SiO ₂	O.N. of Si = +4
	O.N. of O = -2
Mn ₂ O ₇	O.N. of Mn = +7
	O.N. of O = -2

6.7.6 Exercise - Assign oxidation numbers to the underlined atoms in the following examples:

<u>S</u> O ₂	<u>N</u> H ₃	<u>S</u> ₈
<u>Cr</u> Cl ₅	<u>N</u> O ₃ ⁻	<u>Xe</u> F ₂
Ca (<u>S</u> O ₄)	<u>Bi</u> O ₃ ⁻	<u>Cr</u> ₂ O ₇ ²⁻

6.7.7 Oxidation and reduction

In many reactions, one substance transfers electrons to another. This type of reaction is called a REDOX reaction because both Reduction and Oxidation occur at the same time.

An easy way to remember about redox is OILRIG

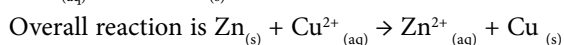
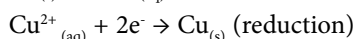
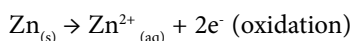
- Oxidation is loss (of electrons)
- Reduction is gain (of electrons)

An oxidising agent is a substance that accepts electrons in a reaction i.e. it oxidises something else but gets reduced itself. A reducing agent is a substance that provides (loses) electrons in a reaction i.e. it reduces something else but gets oxidised itself.

6.7.8 Writing and balancing redox equations

Need to construct two half-equations – an oxidation half-equation and a reduction half-equation. The balanced redox equation is obtained by adding these two half- equations together so that the electrons lost and gained are balanced.

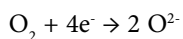
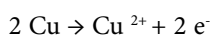
Example - Zinc metal reduces copper ions in copper sulphate solution



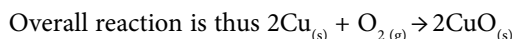
We note that the equation doesn't need to include spectator ions such as sulphate which just remain in solution and are not changed during the reaction.

6.7.9 Example - Copper reacts with oxygen to produce copper oxide.

Write the half equations for both oxidation and reduction. Then write the overall equation.



The second half equation needs 4 electrons, so the first half equation needs to be doubled.



6.7.10 Exercise - Calcium reacts with bromine to produce calcium bromide

Write the half equations for both oxidation and reduction. Then write the overall equation.

And do the same for the reaction of zinc with silver nitrate solution.

6.7.11 More complicated redox equations

Most reactions will occur in neutral or acidic solution. Some half-equations need careful balancing first:

- Balance the atoms of the element being oxidised or reduced,
- Balance O atoms with H_2O ,
- Balance H atoms with H^+ , and
- Add electrons (e^-) to balance the charges.

6.7.12 Example - Reduction of dichromate (VI) to chromium (III)

	What is being balanced
$\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$	
$\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+}$	Cr
$\text{Cr}_2\text{O}_7^{2-} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	O
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	H
Overall charge + 12 overall charge + 6	

Need to add electrons to balance the charge $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{e}^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$

So the balanced redox half-equation is: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$

6.8 Summary

The structure of the Periodic Table is dependent on the electronic configuration of atoms. When electrons are transferred or shared between atoms, bonds are formed. These bonds can be ionic or covalent. When atoms combine to make compounds, the electronic configuration of the valence electrons usually obeys the octet rule. The loss or gain of electrons can be represented by a change in the Oxidation Number. Reactions in which electrons are transferred are known as REDOX reactions.

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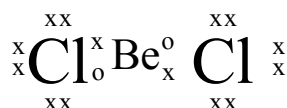
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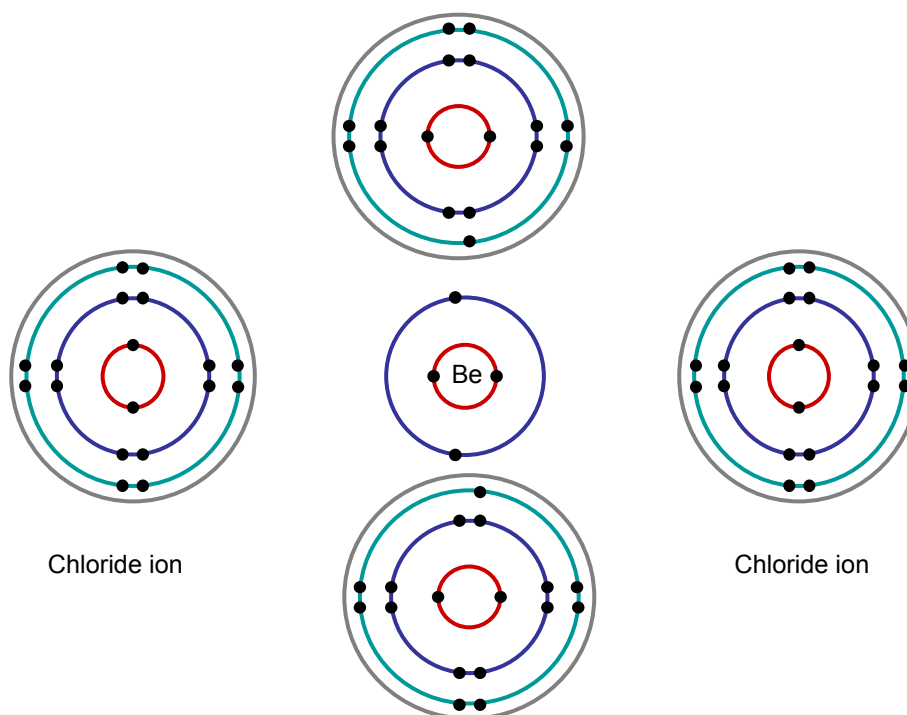
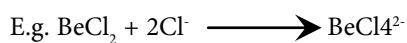
7 Shapes of Molecules

7.1 Exceptions to the octet rule

Sometimes covalently-bonded atoms have a share in fewer than 8 electrons e.g. Be in BeCl_2 , B in BH_3 . Be and B have very high ionisation energies, and so do not form ionic compounds easily. But, they do not have enough electrons to form sufficient covalent bonds to make an octet.



Semi-stable compounds can be formed if all the available electrons are shared. Atoms with less than a complete octet can readily accept electron pairs to 'complete their octets.' So, they react easily with other substances which have an electron pair available for forming co-ordinate bonds.



7.2 Exceptions to the octet rule

Sometimes covalently-bonded atoms have a share in more than 8 electrons.

E.g. P in PCl_5 and S in SF_6

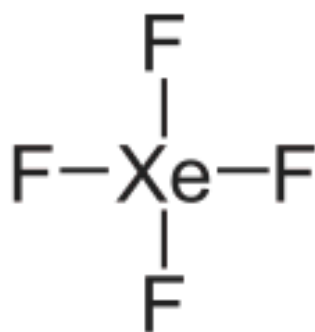
How can the octet rule be violated? The octet rule arises because the s and p orbitals can take up to 8 electrons. However, once we reach the third row of elements in the periodic table we also have d-orbitals, and these help take the extra electrons.

7.3 Limitations of Lewis structures

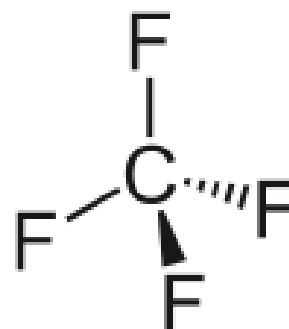
The Lewis dot structure approach gives a good idea of how the electrons are distributed within a molecule when different atoms bond together. However, it cannot tell us the shape of the molecule will be.

7.4 Shapes of covalent molecules

For example, why do XeF_4 and CF_4 have different shapes even though the central atom is surrounded by four Fluorine atoms in both cases?



Square planar



Tetrahedral

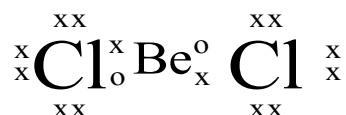
The shape of any molecule can be predicted by using the Valence Shell Electron Pair Repulsion theory (VSEPR theory). This assumes that bonding electron pairs will be spaced as far apart as possible.

7.4.1 Using VSEPR Theory

Draw Lewis structure first. Then count the number of electron pairs around the central atom. These electron pairs will repel each other, and hence arrange themselves as far apart as possible. Select the appropriate geometry for this number of electron pairs.

7.4.2 VSEPR Theory 2 electron pairs: Linear

E.g.



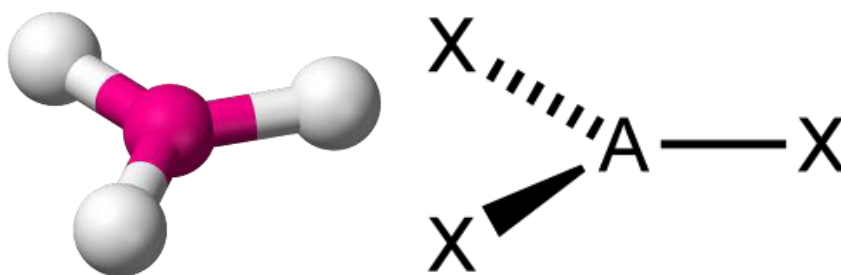
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There are only two pairs of electrons around Be. The arrangement that puts the bonding electron pairs as far apart as possible is a linear arrangement:



e.g. BeCl_2

7.4.3 VSEPR Theory – 3 electron pairs: Trigonal Planar



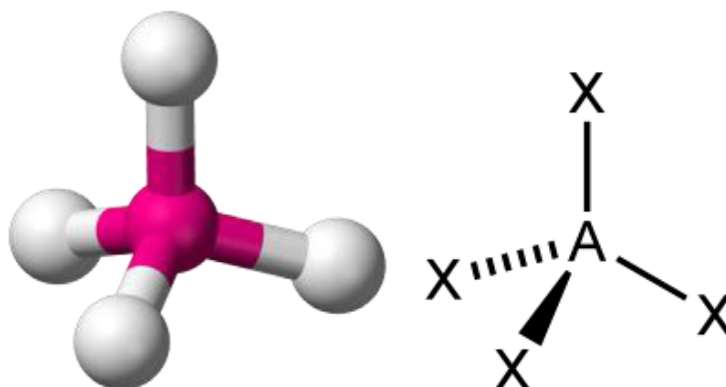
e.g. BCl_3

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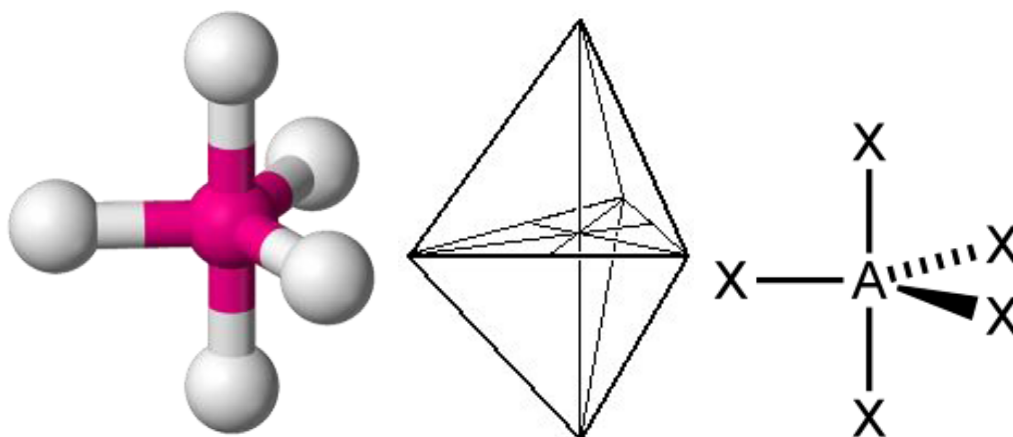
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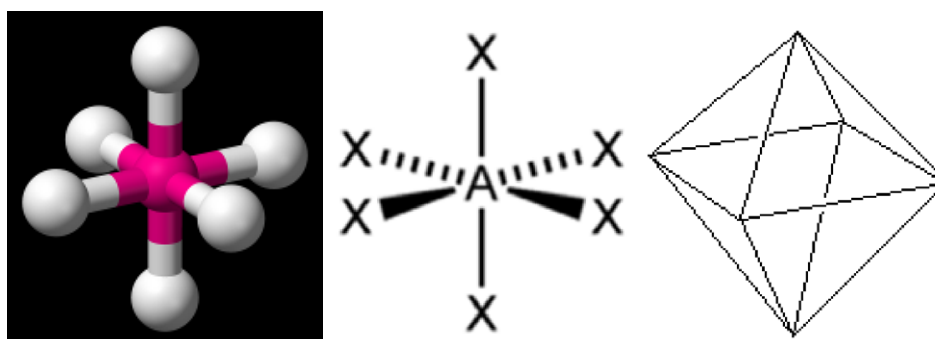
7.4.4 VSEPR Theory – 4 electron pairs: Tetrahedral

e.g. CH_4

7.4.5 VSEPR Theory – 5 electron pairs: Trigonal bipyramid

e.g. PF_5

7.4.6 VSEPR Theory 6 electron pairs: Octahedral

e.g. SF_6

7.4.7 Using VSEPR Theory

You need to be able to draw the shapes in three dimensions. To show a bond coming forward from the page, draw a thick, slightly triangular line. To draw a bond going backwards, draw a dotted line. Learn names of all of the shapes. Add to your vocabulary book. Treat multiple bonds like single bonds e.g. Ethyne and Sulphur dioxide.

7.4.8 Electron pair and molecular shape table

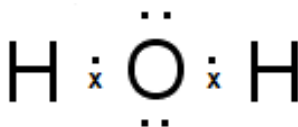
Number of Electron Pairs	Shape	Bond Angle	Example
2	Linear	180°	BeCl ₂
3	Trigonal planar	120°	BF ₃
4	Tetrahedral	109.5°	CH ₄
5	Trigonal bipyramid	90°, 120°, 180°	PCl ₅
6	Octahedral	90	SF ₆

7.5 Molecules with lone pairs

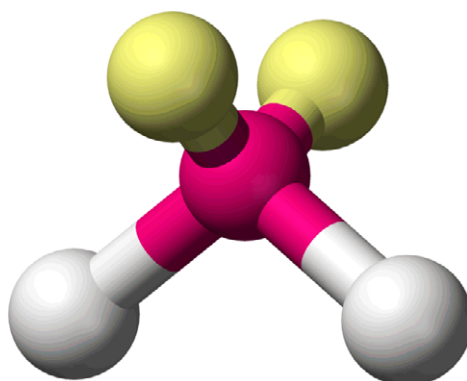
If some of the electron pairs are not bonding pairs but non-bonding lone pairs, then they will still affect the shape, but not be seen in the resulting molecule. Draw the Lewis structure, and count the total number of electrons around the central atom. Divide by two to get the total number of electron pairs.

Select the appropriate shape for this number of electron pairs as before. Decide where the lone pairs will go, and where the bonding pairs will go. Record the resulting molecule shape – i.e. with only the bonding pairs of electrons being seen.

E.g. Water

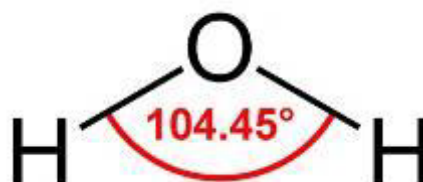


Water has two bonding pairs and two lone pairs. So the shape will be tetrahedral. However, we will only “see” the bonding pairs – a bent shape. Molecule is a Bent shape.



7.6 Distorted shapes

Lone-pairs of electrons repel more than bonding pairs; this leads to distorted shapes and bond angles. Normal tetrahedral angle is 109.5° . In a water molecule, the bond angle is slightly smaller due to the stronger repulsion of the lone pairs.



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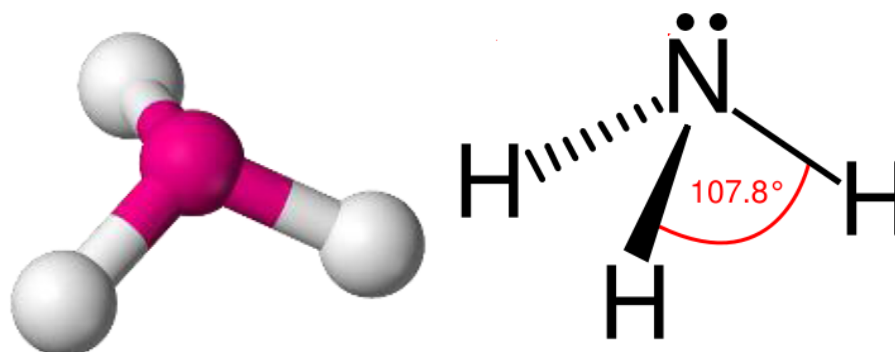
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7.7 Exercise - What shape is an ammonia molecule?

Draw the Lewis structure. Count the number of electron pairs. Select the correct structure. How many are bonding pairs and how many are lone pairs? What shape will we see for the ammonia molecule? How will the lone pair distort this shape?

7.7.1 Ammonia



Lone pair repels bonding pairs more, reducing the bond angle.

7.8 Non-equivalent positions

For some of the molecule shapes, not all the positions are equivalent. In the trigonal bipyramid shape, the axial positions and the equatorial positions are different. Write down the angles between the different bonds.



7.8.1 Minimise repulsions

If more than one structure is possible, then you need to select the structure which minimises repulsions according to these rules:

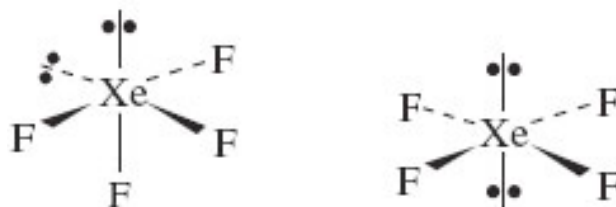
$$180^\circ \text{ repulsions} < 120^\circ \text{ repulsions} < 90^\circ \text{ repulsions.}$$

Remember: lone pairs are closer in to the nucleus than bonding pairs, so are generally closer to each other, giving stronger repulsion.

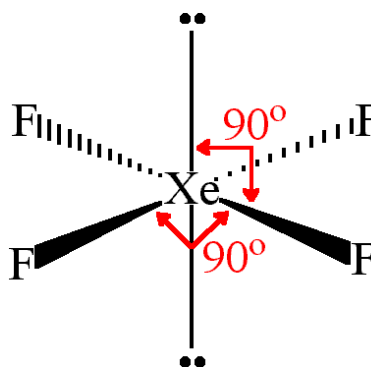
Bonding Pair repulsions-Bonding Pair repulsions < Bonding Pair repulsions-Lone Pair repulsions < Lone Pair repulsions-Lone Pair repulsions or B.P - B.P repulsions at 90° < B.P - L.P repulsions at 90° < L.P - L.P repulsions at 90°

7.8.2 Example - What is the structure of XeF₄?

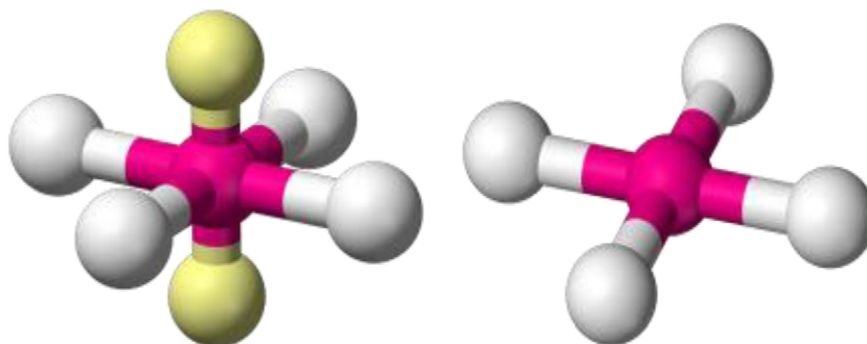
First draw Lewis structure. Xenon is surrounded by 6 electron pairs therefore it is an octahedral shape.



There are two possible arrangements of the electron pairs/bonding pairs in the octahedron. B is better, since A has a 90° lone pair-lone pair repulsions, and B has 180° L.P.-L.P. repulsions.



Lone pairs are invisible, so the shape we see is square planar.



7.9 Molecules with lone pairs

The shapes of any molecule or polyatomic ions (e.g. NH_4^+) can be predicted from the number of bonding electron pairs and the number of non-bonding electron pairs (lone pairs).

7.9.1 Exercise - What is the shape of

- PCl_5 ? Trigonal bipyramid
- PCl_3 ? Trigonal pyramidal (tetrahedral with one lone pair)
- CO_2 ? Linear
- BrF_3 ? T-shaped (trigonal bipyramid with two lone pairs occupying equatorial positions)
- BrF_5 ? Square pyramidal (octahedral with one lone pair)

7.10 Limitations with Lewis structures

Lewis structures are very useful to predict whether ionic or covalent bonds will form between certain elements; and in what ratio they will combine. VSEPR predicts molecular shape well. However, they assume that pairs of electrons are all localised into bonds. Occasionally the true shape of a molecule (discovered by X-ray crystallography) shows that some electrons must be delocalised over more atoms.

7.10.1 Resonance Structures

Sometimes a molecule or ion cannot be accurately represented by one electron-sharing Lewis diagram. E.g. carbonate ion CO_3^{2-} .

Two or more resonance structures can be drawn, the true structure being a resonance hybrid (an imagined blending) of the different, non-existent resonance structures. X ray crystallography shows that all three bonds are the same length.

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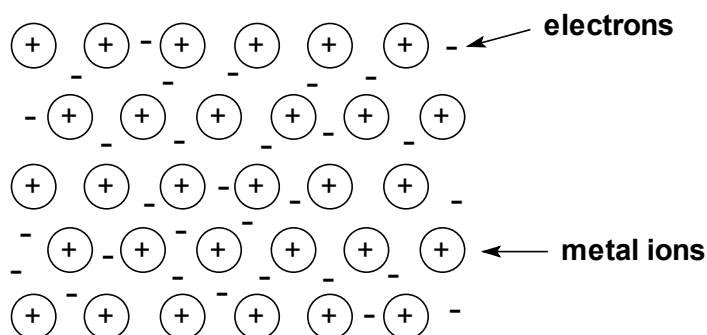
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7.11 Metallic bonding

The bonding in metals cannot be represented by Lewis structures. A simple picture of the structure of metals is of a regular array of positive ions with a “cloud” of delocalised valence electrons spread throughout. Metallic bonding is the strong, electrostatic attraction between each of the positive ions and the negative electron cloud.



7.12 Ionic and Covalent

Lewis structures assume that electrons are either entirely located on one atom (in ionic compounds) or shared equally between two atoms (covalent bonding). Ionic bonding and perfect covalency (perfect sharing) are two extremes. Most compounds are neither perfectly ionic nor perfectly covalent, but somewhere in between. Small highly charged cations (e.g. Mg^{2+} , Al^{3+}) can polarise the electrons in large anions giving covalent nature to some ionic compounds.

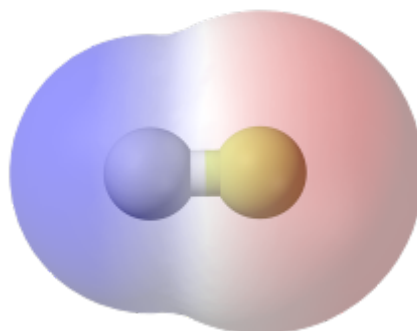
7.13 Electronegativity

The degree of ionic character in a covalent bond is determined by the electronegativity difference between the two elements bonded together. Electronegativity is the ability of an atom in a bond to attract electrons towards itself. It increases from left to right across a Period and it increases up a Group. Electronegativity difference between covalently bonded atoms produces polar bonds and molecular dipoles.

E.g. H-Cl

7.14 Polar bonds

Hydrogen fluoride has a polar bond. F is very electronegative, so attracts more of the electron cloud than H.



The H end has a slightly positive charge, and the F end a slightly negative charge – this charge separation is called a dipole.

7.14.1 Polar and non-polar molecules

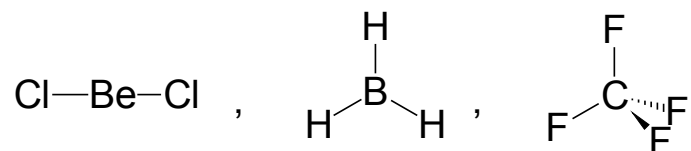
To decide whether a molecule has an overall dipole or not, ask the following

- Does the molecule contain polar bonds?
- What is the shape of the molecule?
- Is the molecule symmetrical?

7.14.2 Non-polar molecules

A molecule will not have an overall dipole (i.e. will be non-polar) if:

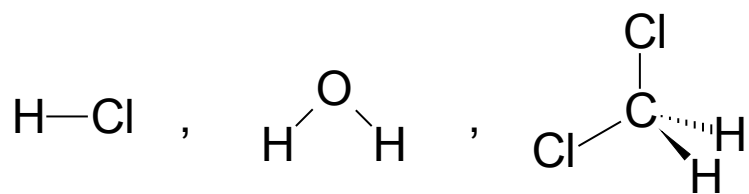
- It has no polar bonds
- It does have polar bonds but the overall shape and symmetry of the molecule causes the dipoles to cancel



7.14.3 Polar molecules

A molecule will have an overall dipole (i.e. be polar) if:

- It has polar bonds
- The overall shape of the molecules is such that the individual dipoles do not cancel



7.15 Intermolecular forces

Attractive forces between separate molecules (sometimes known as Van der Waals forces). For polar molecules, attractive forces are:

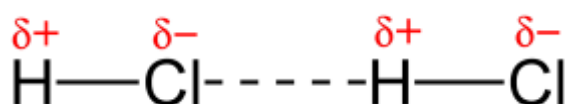
- Dipole-dipole attractions
- Hydrogen bonding (H-bonding)
- London dispersion forces (very weak)

For non-polar molecules, attractive forces are London dispersion forces only.

The greater the attractive forces between molecules, the more difficult it is to separate them and the higher the melting and boiling points. Intermolecular forces are much weaker than the covalent bonds inside the individual molecules (intramolecular).

7.15.1 Dipole-dipole attractions

Any molecule with a dipole will be attracted to other polar molecules.



The δ^+ end of each molecule will be attracted to the δ^- end of a neighbouring molecule.

7.15.2 Hydrogen bonding

H has the lowest electronegativity of any of the non-metals, so all bonds involving H are very polar. Thus compounds with O-H, N-H or F-H will show significant dipole-dipole attraction. These are known as hydrogen bonds. Remember though that these intermolecular forces are still much weaker than full covalent bonds.



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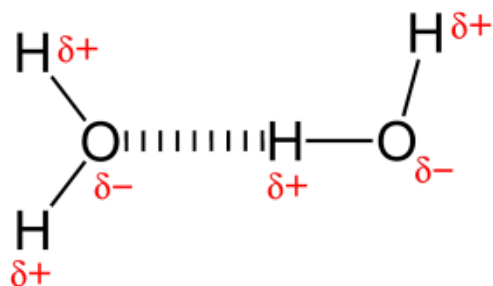
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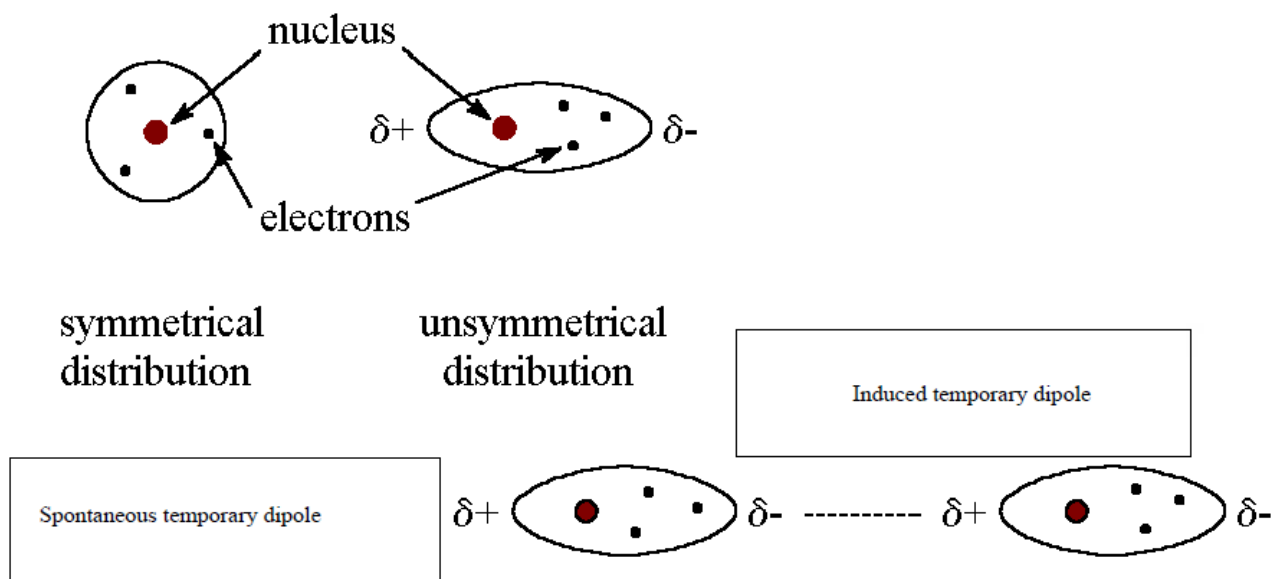
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7.15.3 London dispersion forces

Although non-polar molecules have no permanent dipole, it is possible to have a small temporary dipole for an instant when the electron cloud happens to be more to one side of the molecule than the other. This temporary dipole can attract or repel the electron cloud of a neighbouring atom, and induce another temporary dipole there. These temporary dipoles will spread continually throughout any substance. These cause weak attractive intermolecular forces known as London dispersion forces. The size of these forces increases for larger molecules with more electrons, or as the molecules get closer together- i.e. at low temperatures or high pressures.

The evidence for London forces is that even elements that are monatomic or consist of diatomic molecules (in which there can be no permanent dipole) do liquify at cold enough temperatures – so there must be some attractive forces between them.



8 Chemical Bonding and Solid Structures

Introduction

The atoms, molecules or ions that make up different materials can be found in four types of solid structures:

- Giant metallic,
- Giant ionic,
- Simple molecular, and
- Giant covalent.

The type of structure and the strength of the bonding affect the following physical properties:

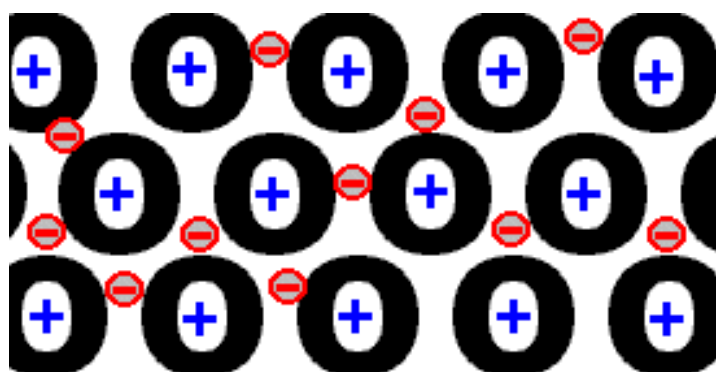
- Melting Point,
- Boiling Point,
- Hardness,
- Behaviour when hit,
- Density,
- Electrical conductivity,
- Thermal conductivity, and
- Solubility.

8.1 Giant metallic structures and their properties

8.1.1 Metal structure

Metal atoms are arranged in layers. The atoms are as close together as possible – a “close-packed” crystal structure. This close-packing explains the high density of metals.

The structure of metals consists of ions surrounded by a ‘sea of electrons’. The outer electrons (negatively charged) from the original metal atoms are free to move around between the positive metal ions (+).



8.1.2 Properties of Metals

There is a strong attractive force between all the delocalised electrons and all the positively charged metal ions. Pulling the metal apart requires breaking these strong bonds, and takes a large amount of energy. Thus metals have high melting and boiling points.

If a strong force is applied to the metal (see diagram below), one layer of atoms can slide over another, and then settle into their close packed positions again.

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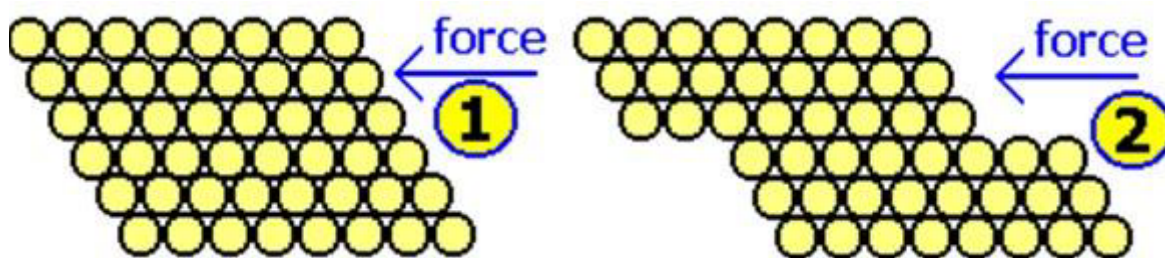
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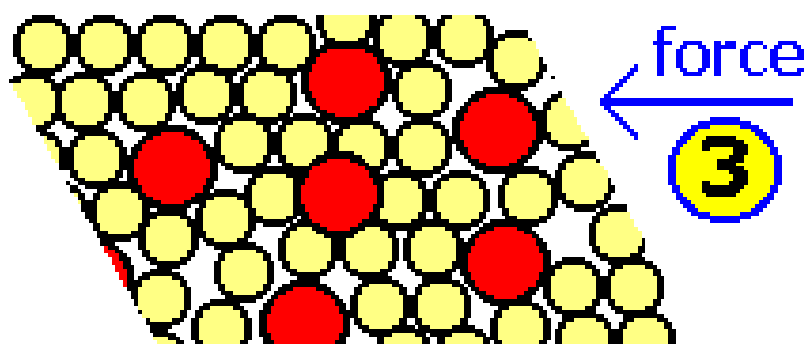
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Because the attractive forces are the same in all these positions, the metal stays bonded together. This makes the metal: malleable (can be hammered into different shapes) and ductile (can be pulled out into wires).

If some atoms of a different metal are introduced, then the regular arrangement of the atoms is disrupted, as seen in diagram below. The different size of the new atoms means that the layers cannot slide as easily over each other.



The distortion of the regular close packed structure by differently sized atoms explains the fact that alloys, such as steel, are harder, and much less malleable than pure metals such as iron.

8.1.3 Conductivity of Metals

Because the electrons are free to move around the metal lattice, they can easily move through the metal when a potential difference is applied – i.e. an electric current can flow through the metal. The free electrons are the reason why solid metals are good electrical conductors.

8.1.4 Thermal conductivity of Metals

When a metal is heated, the heat energy is transferred to the electrons. As these are delocalised, they can move easily throughout the metal, the heat is transferred easily as well. Thus metals are good thermal conductors.

8.1.5 Appearance of Metals

Light falling on metal surface can excite the electrons in the 'sea' into a higher energy level. When the electrons then return to a lower energy state, light is then re-emitted. This gives metals a shiny appearance.

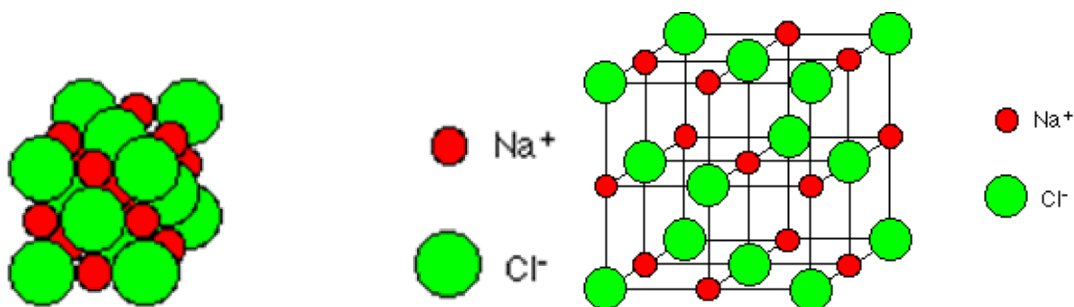
8.2 Giant ionic structures and their properties

8.2.1 Ionic Compounds

Ionic compounds are crystalline solids. A crystal has a regular shape with flat sides (“faces”), and consistent angles between the faces. This is because the atoms are arranged in an orderly repeating pattern.

8.2.2 Structure of Ionic Compounds

Ionic compounds contain positive and negative ions. The ions in the crystal are arranged in a ‘giant’ 3- dimensional structure called an ionic lattice.



The lattice is held together by electrostatic attraction between the cations and anions. Remember that ionic structures are only found in compounds (i.e. between atoms of different elements).

8.2.3 Crystal structure

An X-ray analysis shows that the ions in solids are arranged in different patterns. The exact arrangement of the ions in an ionic lattice varies according to the particular ions. In an ionic lattice the positive and negative ions may have similar sizes or may be quite different in size. The relative sizes of the ions influence the numbers which can pack together and this dictates the geometry of the crystal.

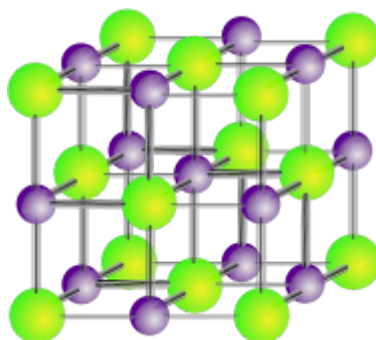
8.2.4 Using X-Ray crystallography

The ions in an ionic crystal lattice are closely packed together in a basic repeating building block called a Unit cell. The Unit cell, determined by X-ray crystallography, contains all the structural information about a crystal. The whole crystal (in theory) could be constructed from sticking lots of these units together.

8.2.5 Types of crystal structures

8.2.5.1 Face-centred cubic lattice

Sodium chloride is a face-centred cubic lattice as seen below.



In sodium chloride each Na^+ ion is surrounded by six Cl^- ions and vice versa. This is known as 6:6 coordination. The number of nearest neighbours to a particular ion is called its coordination number. The sodium chloride lattice structure has a face-centred cubic arrangement. The ionic radius of Na^+ is 95 pm and that of Cl^- is 181 pm. This structure is generally adopted by other ionic compounds in which the anion is somewhat bigger than the cation. This optimum arrangement is a compromise between maximum attraction of oppositely charged ions and minimum repulsion of ions of the same charge.

8.2.5.2 Body-centred cubic lattice

When the positive and negative ions have similar sizes, the crystalline structure adopted is more likely to be that of cesium chloride which has 8:8 coordination. The ionic radius for Cs^+ is 174 pm, which is fairly similar to that of Cl^- (181 pm).

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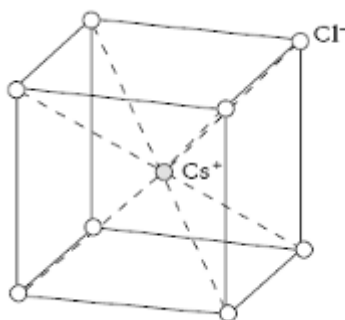
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8.2.5.3 Summary

The key points to remember are:

- Body-centred and face-centred cubic lattices are two common crystal structures, and
- The type of crystal structure is dependent on the relative radii of the positive and negative ions.

8.2.5.4 Exercise

Which structure, that of NaCl or CsCl, is likely to be adopted by the following ionic compounds?(a) NiO (b) MgO (c) CsBr (d) CaO

Compound	Cation radius (pm)	Anion radius (pm)	Radius ratio
NaCl	95.0	181	0.525
CsCl	169	181	0.933
(a) NiO	78.0	140	0.557
(b) MgO	65.0	140	0.464
(c) CsBr	169	195	0.867
(d) CaO	100	140	0.714

8.2.6 Other crystal structures

As well as the sodium chloride and cesium chloride lattices there are other types of ionic crystalline structures. Different structures are found in compounds where the ratio of positive to negative ions is not 1:1.

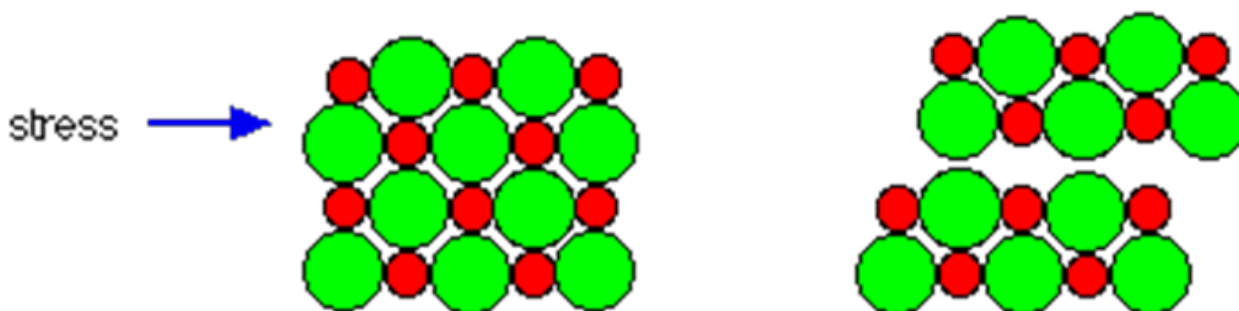
For example, in rutile, TiO_2 , each titanium ion is surrounded by six oxide ions and each oxide ion is surrounded by three titanium ions and so the rutile structure has 6:3 co-ordination.

8.2.7 Properties of ionic solids

In ionic solids, there are strong, electrostatic attractive forces between the positive and negative ions. To melt the solid, these very strong forces must be overcome. Thus all ionic compounds are solids at room temperature and generally they have very high melting and boiling points.

E.g. MgF_2 has a melting point of 1261°C and a boiling point of 2239°C

The strong forces between the ions are hard to break, and this also explains the fact that crystals of ionic compounds are hard. However, if a force is applied suddenly to the crystal, the layers of ions slip over each other:



Now, instead of a positive ion being over a negative one, it is over another positive one – which causes the layers to repel one another. So when a crystal is hit, it breaks apart very easily – it shatters. Thus ionic crystals are brittle.

8.2.8 Conductivity of ionic solids

Ionic solids have no free electrons. Any charged particles (including ions) can carry electric current, but in an ionic solid the ions are trapped in the lattice, and cannot move away from their fixed positions. Solid ionic compounds do not conduct electricity.

In the liquid state the charged ions are able to move around. The positive ions move towards the negative terminal, and the negative ions move towards the positive terminal. Thus the current is carried through the liquid, and the compound is able to conduct electricity. Molten ionic compounds do conduct electricity.

When ionic solids are put in water, the polar water molecules attract the ions in the lattice, and pull them into solution. The attractive forces from the water molecules are enough to break down the strong ionic bonds, and so most ionic compounds dissolve in water easily. The charged ions can move freely around the water, so dissolved ionic solids can conduct electricity well.

8.3 Molecular structures and their properties

8.3.1 Covalently-bonded substances

Whereas ionic bonds are only found in compounds, covalent bonding is found in both elements (e.g. H_2 , Cl_2) and compounds (e.g. H_2O , CH_4). Covalent bonding always produces molecules but these can vary greatly in complexity. The size and type of molecule affects the properties. The size of molecules is typically defined as follows:

- Small molecules (H_2 , H_2O)
- Larger molecules ($C_9H_8O_4$ aspirin, $C_8H_9N_4O_2$ caffeine)
- Very large molecules (plastics, proteins)
- ‘Giant’ molecules (infinite assemblies of atoms) including diamond (C atoms), Silica (Si and O atoms, 1:2) and Carborundum (Si and C atoms, 1:1).

8.4 Giant Covalent structures and their properties

8.4.1 Giant covalent structures

Some elements (such as carbon and silicon) are most stable when each atom forms several covalent bonds to other atoms. This means that some of the molecules have very large, three dimensional structures made up of millions of atoms. For example, the pure element carbon can exist as several allotropes (different forms) with different structures and different properties.



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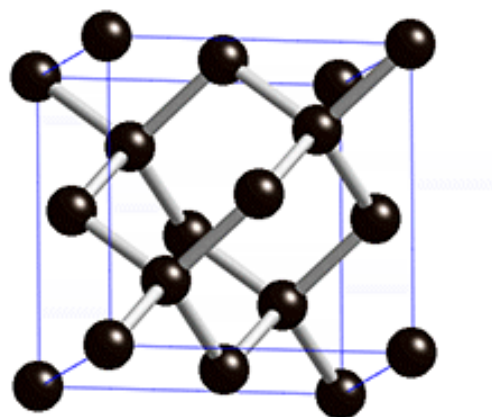
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8.4.2 Diamond

One form of carbon is diamond. This has a very strong three dimensional structure like this, in which every carbon is joined to four others by covalent bonds. This giant molecule can contain billions of atoms. The very regular way that the ions are packed leads to the distinctive regular crystal shape with flat surfaces at fixed angles.

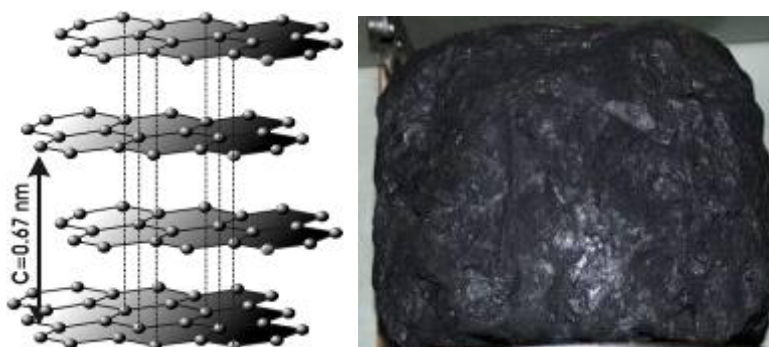


8.4.3 Properties of Diamond

The strong covalent bonds mean that diamond has a very high melting point of 3800°C. The strong bonds and rigid structure makes diamond hard. As the atoms are not arranged in layers, they cannot slide over each other, so diamonds are not malleable or ductile. There are no free electrons, so diamond does not conduct electricity.

8.4.4 Graphite

Graphite (the “lead” inside pencils) is another allotrope of carbon. Each carbon atom is joined with strong covalent bonds to three others, forming sheets of atoms arranged in hexagon patterns. There are only weak London forces between the layers.



8.4.5 Properties of graphite

The strong covalent bonds between the atoms give graphite a very high melting point of 3600°C. The bonds between the layers are longer and weaker than the other bonds. This makes graphite less dense than diamond.

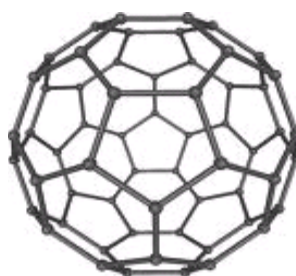
The strong bonds within the layers make graphite very strong in the direction perpendicular to the layers. The weak bonds between the layers mean that graphite can be split easily in the direction parallel to the layers. The graphite layers can also slide over each other easily, and break off. This is what happens when a pencil is rubbed over paper, leaving a mark. The slippery nature of graphite also makes it suitable for use as a lubricant in engine oils.

8.4.6 Conductivity of graphite

While three electrons from each carbon are used in covalent bonds, the fourth electron is delocalized over all the atoms in its layer. These free electrons mean that graphite will conduct electricity and heat. The conductivity parallel to the layers is much greater than in a perpendicular direction. Graphite is often used as one of the terminals in batteries.

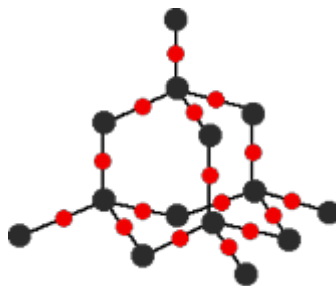
8.4.7 Fullerenes

Fullerenes are a recently discovered family of carbon allotropes in the form of spheres, tubes or flat planes with unusual and potentially useful properties. The first to be discovered in 1985 was Buckminsterfullerene. The structure is a little like graphite, but instead of never-ending sheets, the hexagons curve round to form a complete sphere - a C_{60} molecule.



8.4.8 Giant covalent molecules

Some compounds can form giant covalent structures as well. E.g. Silica, SiO_2 (the structure is similar to diamond – black atoms are Si, red atoms are O) as shown below:



8.5 Simple molecular structures and their properties

8.5.1 Simple molecules

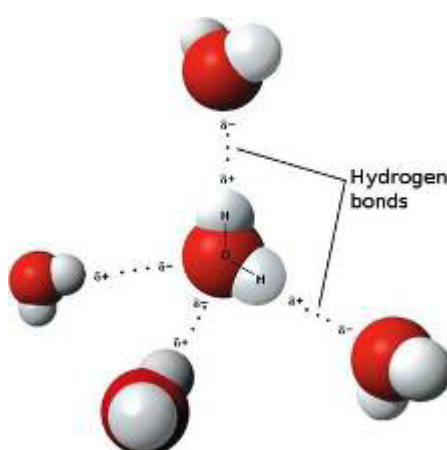
Most covalently bonded substances exist as simple small or medium sized molecules, rather than as giant structures. When simple molecules are heated moderately, the atoms do not get enough kinetic energy to break the strong covalent bonds, and so most molecules do not break apart (decompose) on heating.

The forces between molecules – London dispersion or dipole-dipole are much weaker than the covalent bonds. Just a little heat gives enough kinetic energy to separate each molecule from neighbouring molecules. When a molecular substance melts, only the weak intermolecular bonds are broken.

The size of the molecule affects the melting and boiling points, as larger, heavier molecules are more difficult to separate. Small molecules (H_2 , H_2O) have low melting and boiling points, are gases or liquids at room temperature. Larger molecules ($C_9H_8O_4$ aspirin, $C_8H_9N_4O_2$ caffeine) have higher melting points (but still \ll ionic) and are solids at room temperature.

8.5.2 Simple molecules (2)

Stronger intermolecular forces (such as dipole-dipole or hydrogen bonding) are more difficult to break. Polar molecules such as water have higher melting and boiling points than non-polar molecules such as methane of similar size.



8.5.3 Properties of simple molecules

Intermolecular forces are weak, so the molecules are not pulled very close together. More space between the molecules means that solid simple molecular compounds have low density. Weak bonds between the molecules are easily broken, so the solids are soft, and the liquids have low viscosity.

Weak intermolecular bonds are easily broken, so small covalent molecules can dissolve in similar non-polar solvents. If they have no dipole, they will not dissolve in polar solvents like water. There are no charged particles or free electrons within the simple molecules. Therefore they generally display poor thermal and electrical conductivity.

8.5.4 Bonding, Structure and Properties

Follow this sequence to determine the physical properties of any substance:

- Electronic structure
- Type of Bonding
- Type of structure
- Properties.



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8.5.5 Summary

Write down the detailed electronic configuration of each element involved. Use this to determine the type of bonding: either Ionic, Covalent or Metallic.

What sort of bonding is found in pure elements? Metallic bonding – most elements in the Periodic Table are metals. Covalent bonding – found in non-metals and also in giant molecules. Ionic bonding is not found in pure elements.

What sort of bonding is found in compounds between different elements? Ionic bonding is generally formed between metals and non-metals. Covalent bonding is generally formed between non-metals. Metallic bonding is not found in compounds, only in mixtures – in alloys of different metals, e.g. brass (copper and zinc), bronze (copper and tin).

The type of bonding will determine the type of structure; and the structure type will determine the properties. You need to be able to recognise or quote the usual properties for each kind of structure:

- Giant metallic
- Giant ionic
- Simple molecular (including effect of intermolecular forces)
- Giant covalent

8.5.6 Summary: Properties of Metals

- High Melting and Boiling Points
- Malleable and Ductile
- Good conductors of heat and electricity
- Shiny
- Hard
- Dense
- Insoluble in polar or non-polar solvents

8.5.7 Summary: Properties of Giant Ionic Structures

- High Melting and Boiling Points
- Brittle
- Non-conductors of heat and electricity when solid
- Good conductors of heat and electricity when molten or in solution.
- Hard
- Soluble only in polar solvents

8.5.8 Summary: Properties of Giant Covalent Structures

- High Melting and Boiling Points
- Brittle

- Non-conductors of heat and electricity (apart from graphite)
- Hard
- Insoluble in polar or non-polar solvents

8.5.9 Summary: Properties of Simple Covalent Structures

- Low Melting and Boiling Points
- Brittle; Soft
- Low density
- Non-conductors of heat and electricity
- Soluble in similar solvents only
- non-polar molecules in non-polar solvents
- polar molecules in polar solvents

8.5.10 Keywords

DELOCALISED ELECTRONS - the electrons are free to move around

ELECTROSTATIC ATTRACTION - attraction between positive and negative charges

ELECTRONEGATIVITY - a measure of the attraction an atom has for a pair of shared electrons

INTERMOLECULAR ATTRACTION - attraction between molecules or atoms (includes Van Der Waals, dipole-dipole and hydrogen bonding)

DIPOLE - a molecule with opposite charges at each end

INDUCED DIPOLE - polarisation of a molecule that results from the approach of an already polar molecule

LONDON DISPERSION FORCES - the weak attraction between a temporary dipole and an induced temporary dipole

DIPOLE-DIPOLE ATTRACTIONS - attractions between polar molecules

HYDROGEN BONDS - attractions between polar molecules where hydrogen is one of the atoms involved

9 Trends in the Periodic Table

9.1 Historical trends

Where does the modern layout of the Periodic Table come from?

- Dobereiner's "triads" (1829) where groups of three similar elements were made such as Li, Na, K ; Ca, Sr, Ba; or Cl, Br, I. This was the forerunner of the idea of Groups.
- Newlands "law of octaves" (1865) where around 60 known elements have been arranged in increasing R.A.M. Elements had similar properties to those 8 places before them and 8 places after them. This was the forerunner of the idea of Periods and led to the name Periodic Table.

9.2 Mendeleev's table (1869)

Mendeleev arranged known elements in order of increasing R.A.M. but placed elements with similar properties underneath each other. Elements were arranged "periodically". However he left gaps where elements still to be discovered and predicted their properties.

9.2.1 Mendeleev's predictions for Germanium

Property	Predicted by Mendeleev (1871)	Observed on Discovery (1886)
R.A.M.	72	72.3
Density (gcm ⁻³)	5.5	5.47
Colour	dirty grey	greyish white
Heating in air gives	EO ₂	GeO ₂ formed

Predictions:

- "eka-aluminium", discovered in 1875 and given the name Gallium
- "eka-boron", discovered in 1879 and given the name Scandium
- "eka-silicon", discovered in 1886 and given the name Germanium

Mendeleev also put elements in the "right place" e.g. Tellurium has greater R.A.M. than Iodine but Mendeleev realised I must come after Te and under Br.

9.3 Modern Periodic Table

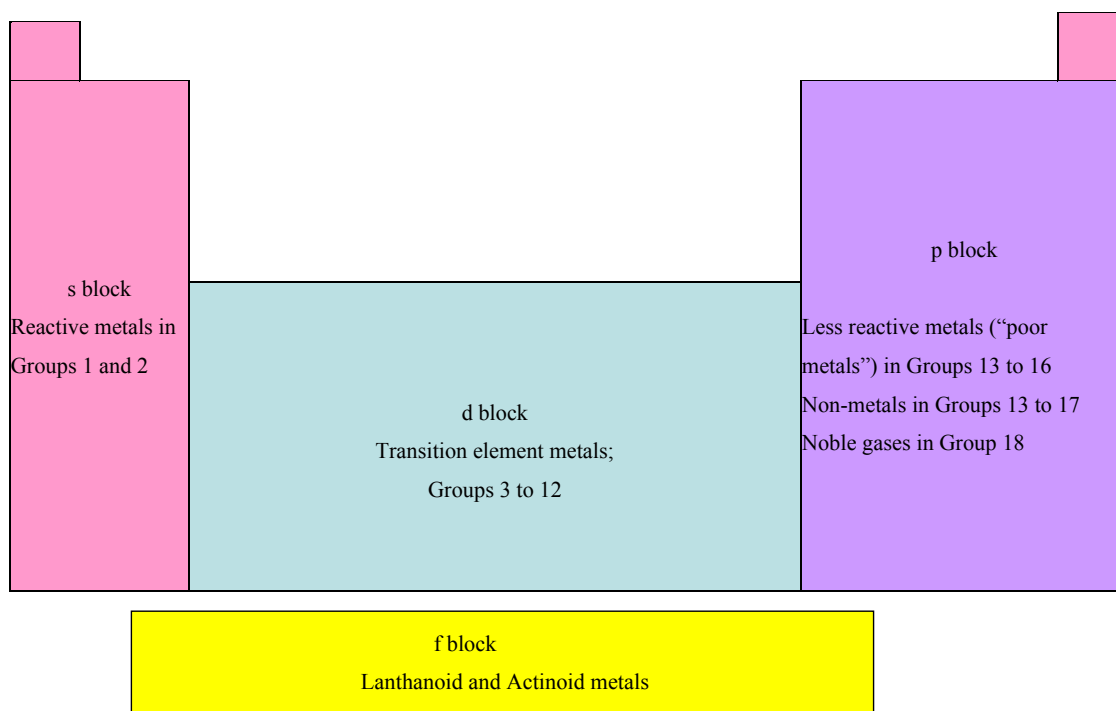
In a modern Periodic Table the elements are written in order of increasing atomic number, not increasing R.A.M. This leads to Periodic law which states that "the properties of the elements are a periodic function of their atomic numbers".

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A group is a column, down the periodic table. In other words, vertical columns in the Table are called Groups. Elements in the same Group have similar properties. Elements in the same group generally have the same number of valence electrons in the highest energy level of their atoms. Groups are numbered from 1 to 18 and Groups 1, 2 and 13 to 18 are the Main Groups.

A period is a row, across the periodic table. In other words, horizontal rows in the Table are called Periods. Periods are numbered from 1 to 7. Each Period corresponds to a new value of n , the principal quantum number. The nature and properties of the elements change in a similar manner across each period.

It is useful to split the Periodic Table into blocks of similar elements with similar structure and properties.

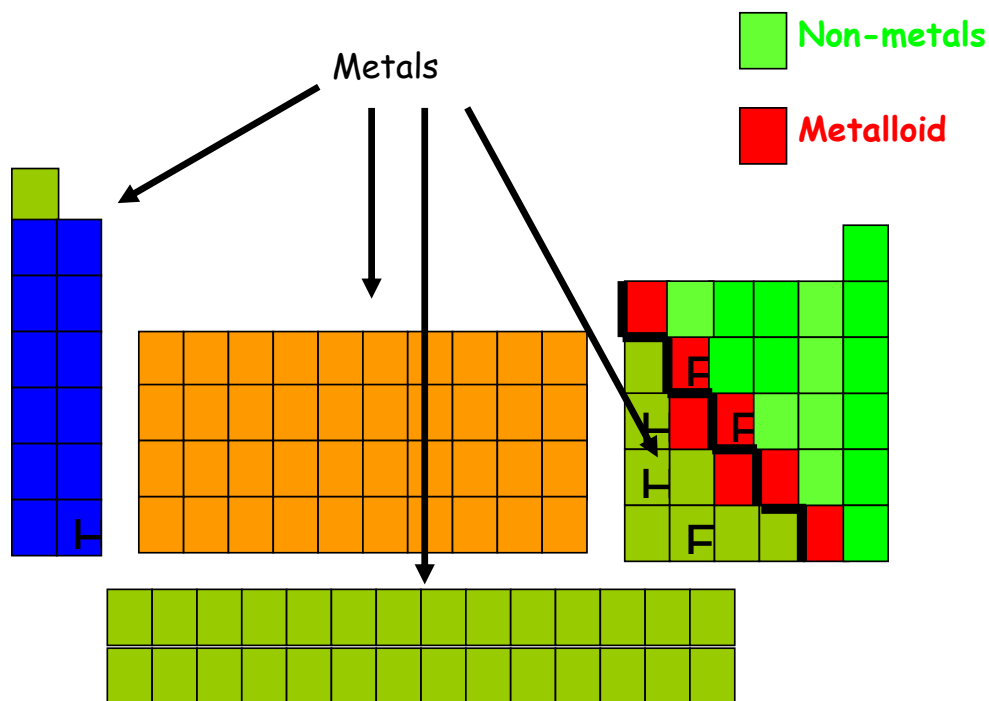


9.4 Metals / non-metals

Reactive metals can be found in Groups 1 and 2 and less reactive metals ("poor metals") in Groups 13 to 16.

Non-metals are found in Groups 13 to 17 and Noble gases in Group 18.

9.4.1 The Periodic table



What do you want to do?

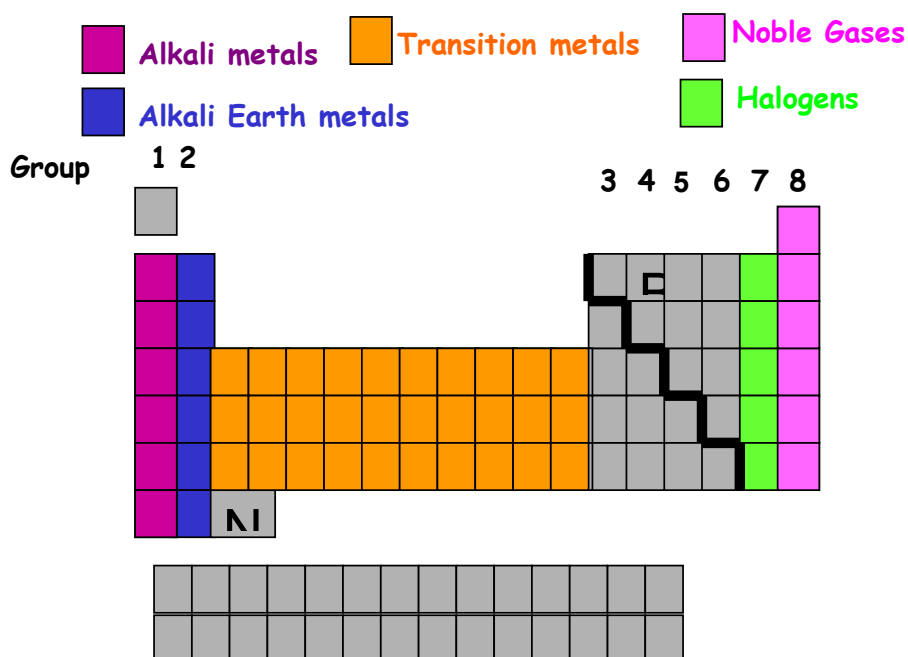
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9.4.2 The Blocks of Elements in the Periodic Table



9.4.3 Modern Periodic Table

The chemical properties and physical properties of an element arise from the electronic structure as suggested below:

- s-block elements have s-orbital electrons in their outer shells,
- p-block elements have p-orbital electrons in their outer shells, and
- d-block elements are gradually filling up their d-orbitals with electrons.

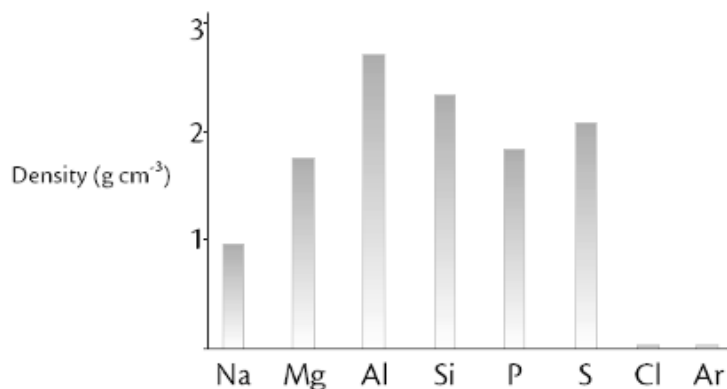
9.5 Physical Properties

In the following section, we will discuss how physical properties of atoms evolve in the Periodic table. We will focus on the five following physical properties:

- Density,
- Melting points and boiling points,
- Atomic size,
- Ionisation enthalpy, and
- Electronegativity.

9.5.1 Density

The density of a substance is its mass per unit volume, usually measured in g cm^{-3} . The graph below shows the variation in density (at room temperature) across Period 3.



Na, Mg and Al have metallic bonding which is the attraction between the delocalised outer shell electrons and the fixed positive ions. The greater the number of outer shell electrons the greater the charge on the positive ion and so the greater the attraction. This means as we go from Na to Mg to Al the metallic bonding becomes stronger and the ions are pulled more closely together, leading to an increase in density.

Phosphorus and sulphur atoms are heavier than silicon atoms so we might expect their densities to be higher. However silicon is a giant covalent network of tightly packed atoms whereas the P₄ and S₈ molecules are only loosely held by Van Der Waals forces, so they are further apart.

Chlorine and argon are gases at room temperature. The chlorine molecules and argon atoms are well spread out so their densities are very low.

9.5.2 Melting and boiling points

H -259 -253 gas							1 He -270 -269 gas				
Li 180 1340 solid		Be 1280 2500 solid	B 2030 3700 solid		C 3500 3900 solid	2 N -210 -196 gas		O -219 -183 gas	F -220 -188 gas	Ne -249 -246 gas	
Na 98 883 solid		Mg 650 1110 solid	Al 660 2400 solid		Si 1410 2500 solid	3 P 44 280 solid		S 119 445 solid	Cl -101 -34 gas		Ar -189 -186 gas
K 63 760 solid		5 Ca 850 1440 solid		4							

Key: symbol, m.pt. (°C), b.pt. (°C), state

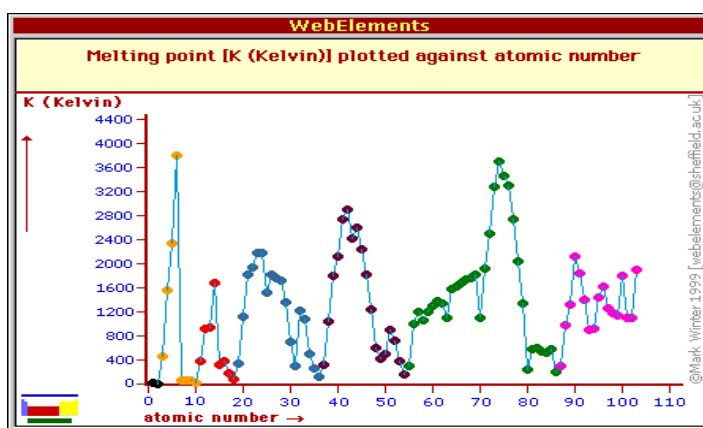
The melting and boiling points of elements give an indication of the intermolecular forces that hold the atoms or molecules together. Typically we say that the higher the melting and boiling point the stronger the forces. The trend is similar for both melting and boiling points.

9.5.3 Melting points

The melting point starts off low, gradually increases to a peak (at group 14) then gradually decreases to a very low value (at group 0 or 18). How can we explain this trend? Think about the strength of the forces between the molecules.

In group 1 the atoms are held together by metallic bonds. In group 14 the atoms are held together by many very strong covalent bonds (giant covalent network). In group 18 the atoms are held together by very weak bonds (monatomic gases).

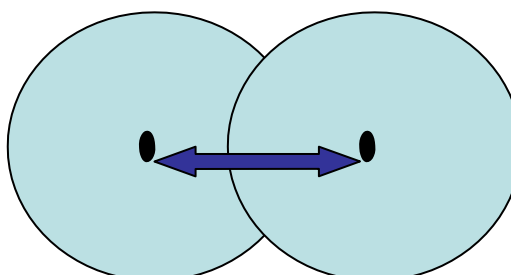
By studying the bonding in each group of elements we can explain the range of melting points. The melting point temperature of a solid is a measure of the amount of energy needed to break the bonds which hold the basic particles (atoms or molecules) together. So high melting points indicate strong bonds are being broken



The graph of melting point against atomic number has a similar shape to the density graph, as the strength of the interatomic bonds affects both properties in a similar way.

9.5.4 Atomic Size

The atomic size is just like it sounds the size of an atom. The covalent radius is defined as half the distance between the centres of covalently bonded atoms.



The size of an atom will depend on two parameters:

- The number of energy levels, and
- The nuclear charge pulling the electrons in.

Down a group the atomic size increases from top to bottom. Across a period the atomic size decreases from left to right. Down a group there is an increase in the number of energy levels surrounding the nucleus. Across a period an increasing nuclear charge (+) pulls the outer electrons (-) closer in towards the nucleus.

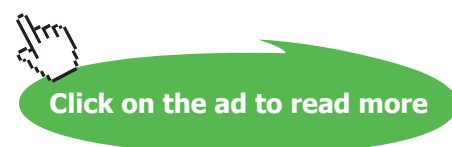
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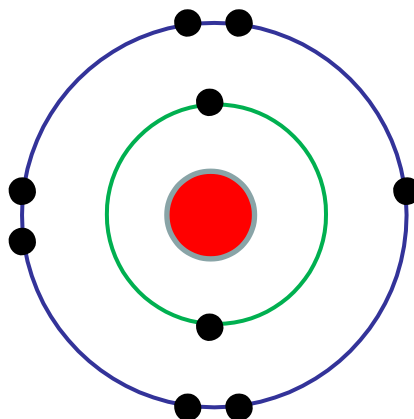
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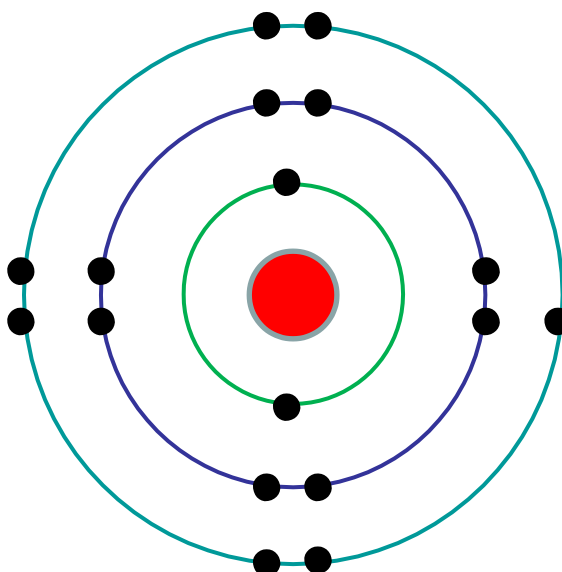
Li	2, 1	123
Na	2, 8, 1	157
K	2, 8, 8, 1	203
Rb	2, 8, 18, 8, 1	216
Cs	2, 8, 18, 18, 8, 1	235



As we go down a group each member has an extra “shell” of electrons so the atomic radius increases. The positive charge on the nucleus does increase down a group (which tends to pull the electrons closer) but the effect of adding an extra energy level has more effect than this, so the size increases.

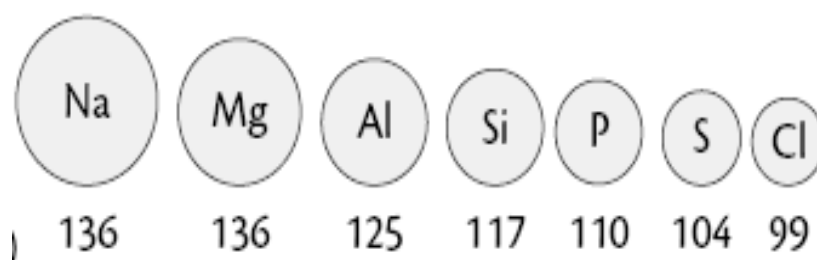


A Fluorine atom has its outer electrons in the $n = 2$ energy level



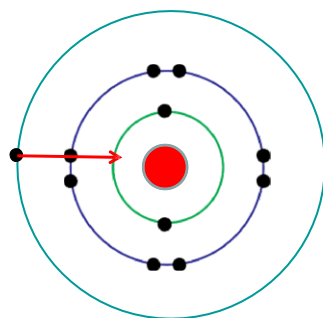
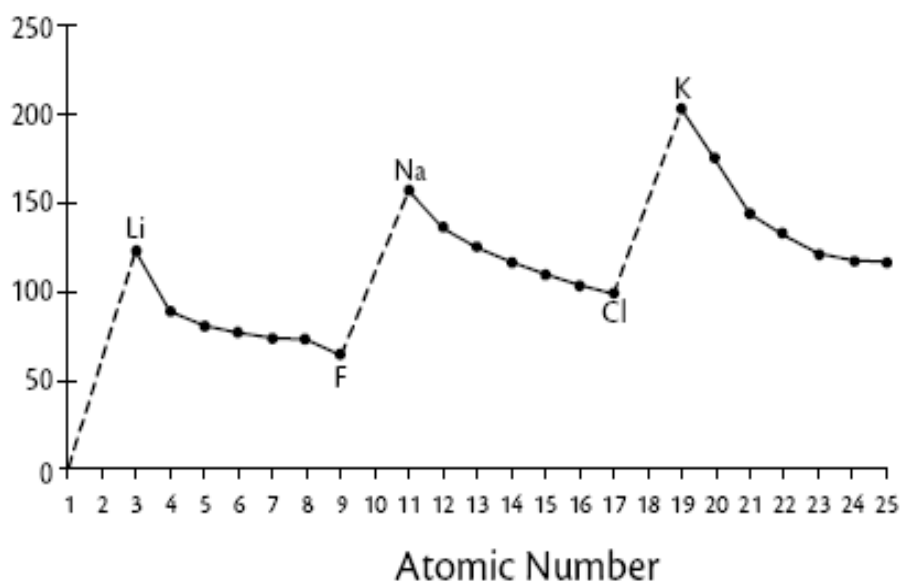
A Chlorine atom has its outer electrons in the larger $n = 3$ energy level

Therefore Fluorine is smaller than Chlorine.

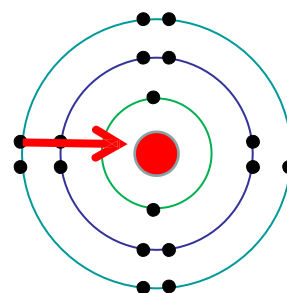


As we go across a period electrons are being added to the same “shell” while protons are being added to the nucleus. This increasing positive charge pulls in the outer electrons more closely so the radius decreases.

The graph shows how Atomic Radius varies with Atomic Number



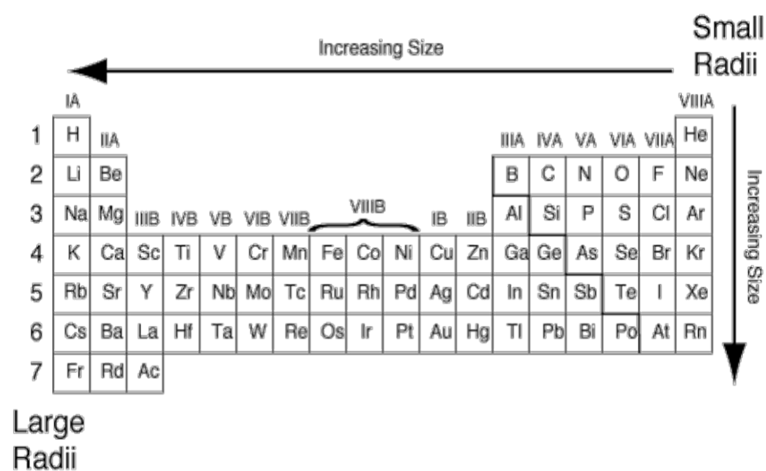
A Sodium atom has 11 protons attracting each outer electron



A Chlorine atom has 17 protons attracting each outer electron

Therefore Sodium is larger than Chlorine.

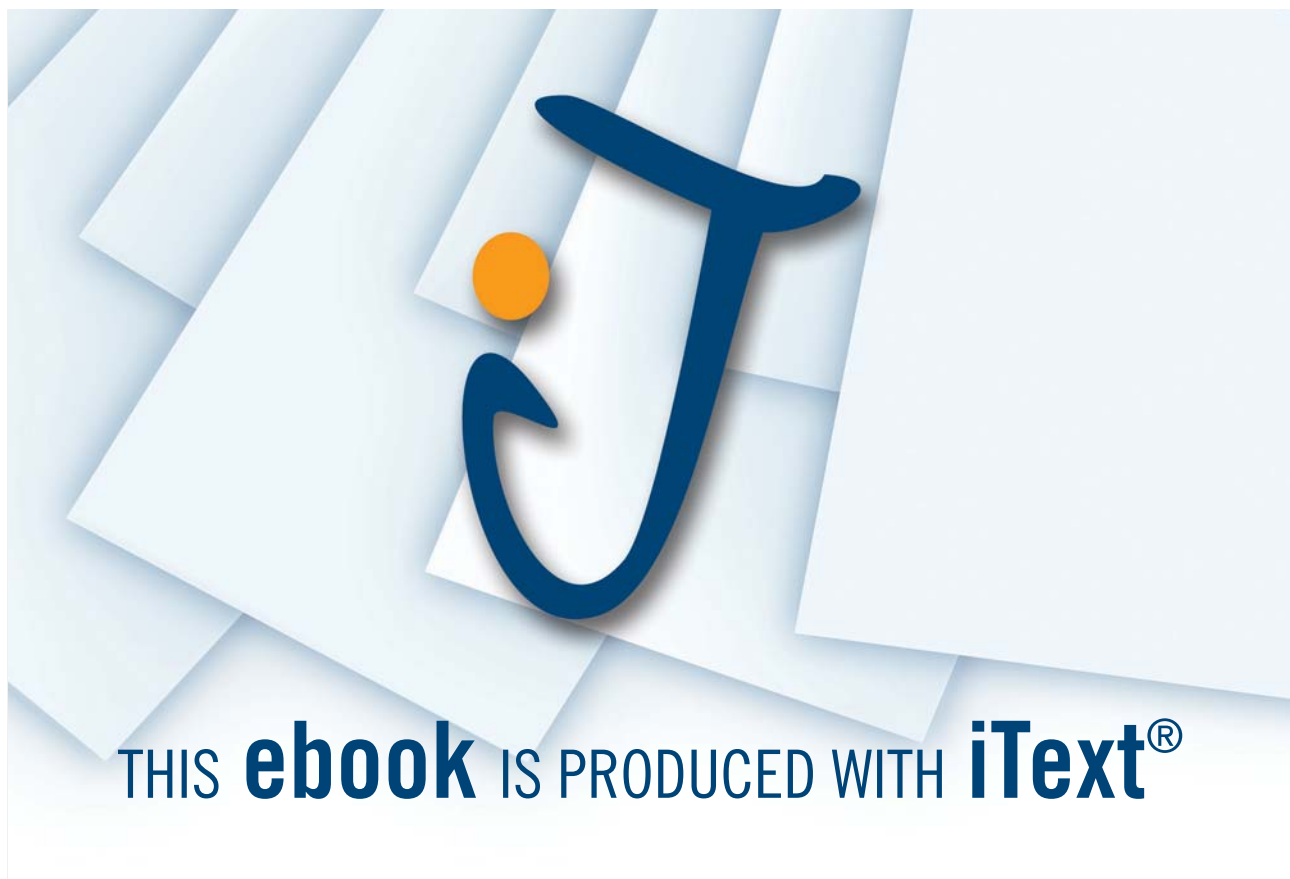
The atomic size in the Periodic Table varies as shown in the graph below:



9.5.5 Ionisation Enthalpy

Ionisation enthalpy is the energy required to remove a mole of electrons from a mole of free gaseous atoms i.e. the energy required to remove an electron from an atom e.g. $\text{Mg (g)} \rightarrow \text{Mg}^+ \text{(g)} + e^-$

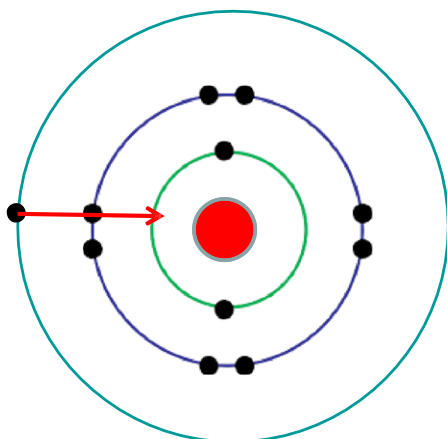
This is known as the 1st Ionisation Enthalpy. What would affect the ionisation enthalpy? The degree of attraction the outer electrons feel from the nucleus.



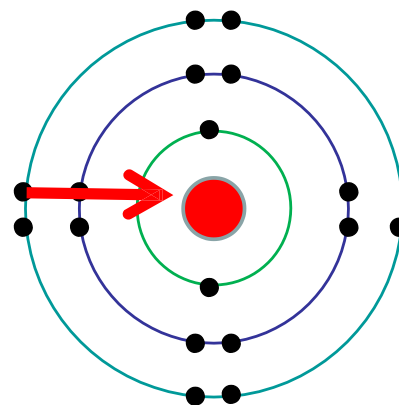
9.5.6 First Ionisation Enthalpy

Across a period the ionisation enthalpy increases from left to right. Down a group the first ionisation enthalpy decreases from top to bottom. What affects how much nuclear charge an electron feels? Across a period increase in nuclear charge and decrease of atomic size makes it more difficult to remove an electron. Down a group there is a shielding effect from the extra energy levels, and increased distance from the nucleus makes it easier to remove an electron.

The outermost electron in Sodium is further away from the nucleus than in Chlorine, so is more easily pulled away.

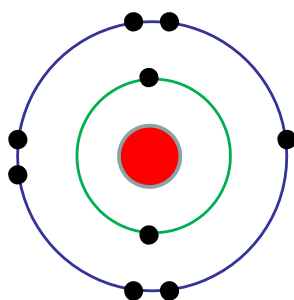


A Sodium atom has an atomic radius of 157pm

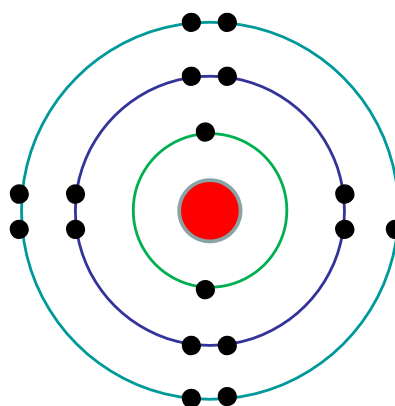


A Chlorine atom has an atomic radius of 99pm.

The increased shielding from an extra “shell” of electrons means that the outer electrons experience the same effective nuclear charge. However the extra distance reduces the attractive force. Therefore, Fluorine has a higher first ionisation enthalpy than Chlorine.

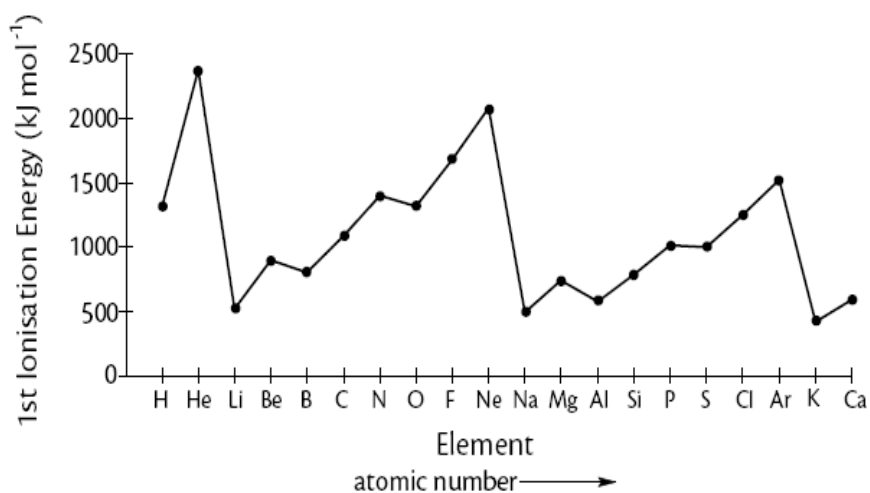
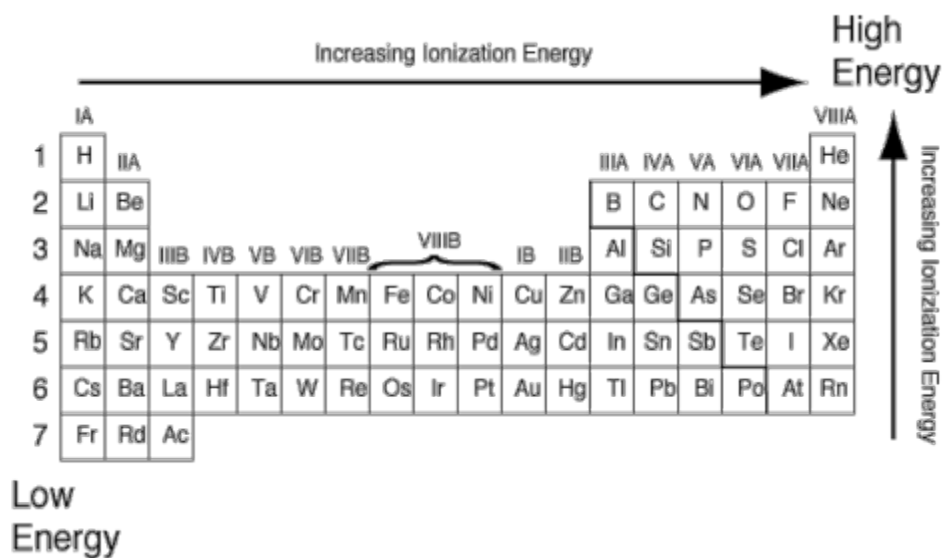


The outer electrons of a Fluorine atom feel an effective nuclear charge of $9 - 2 = 7$



The outer electrons of a Chlorine atom feel an effective nuclear charge of $17 - 10 = 7$

The first ionisation enthalpy in the Periodic Table varies as shown in the figures below:



Peaks correspond to Noble gases (group 8) and Troughs to Alkali metals (group 1).

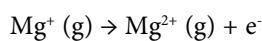
The increase in first ionisation energy is not regular but has a zigzag appearance. This irregularity is due to extra stability being associated with filled and half-filled as shown below:

- Be $2s^2$
- N $2s^2 2p^3$
- Mg $3s^2$
- P $3s^2 3p^3$

The first ionisation enthalpy is large for noble gases - it requires considerably more energy to remove an electron from a completely full energy level (very stable), which is nearer the nucleus.

9.5.7 Second Ionisation Enthalpy

The second Ionisation Enthalpy of an element is the energy required to remove the second mole of electrons as for example:



So the total energy to remove 2 moles of electrons from an atom is the sum of the first and second Ionisation Enthalpies. The second Ionisation energy of an atom is always larger than the first because it involves removing an electron from a species that is already positively charged.

Element	Symbol	Ionisation Energies (kJ mol ⁻¹)			
		First	Second	Third	Fourth
lithium	Li	526	7310	11800	—
beryllium	Be	905	1770	14800	—
boron	B	807	2440	3660	25000
carbon	C	1090	2360	4640	6220
nitrogen	N	1410	2860	4580	7470
oxygen	O	1320	3400	5320	7470
fluorine	F	1690	3380	6060	8410
neon	Ne	2090	3960	6140	9360



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Notes:

- The large increase from the first to second ionisation energy of sodium. The 1st ionisation energy removes the single valence electron from the sodium atom so the 2nd ionisation energy involves breaking into a stable octet of electrons. This requires a lot of energy.
- With magnesium the large increase in ionisation energy comes once the two valence electrons of the magnesium atom have been removed.
- The third ionisation energy breaks into a stable octet.

9.6 Electronegativity

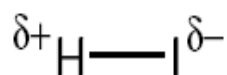
Different elements have different attractions for bonding electrons (valency electrons). The relative ability of an element to attract electrons in a covalent bond is called its Electronegativity. Those elements that require just one or two electrons to fill an energy level can attract electrons more easily. The smaller the atom the easier it is to capture an electron since they will experience a greater “pull” from the nucleus.

Electronegativity values increase across a period. Electronegativity values decrease down a group. Therefore the most electronegative element is F.

9.6.1 Electronegativity & Bonding

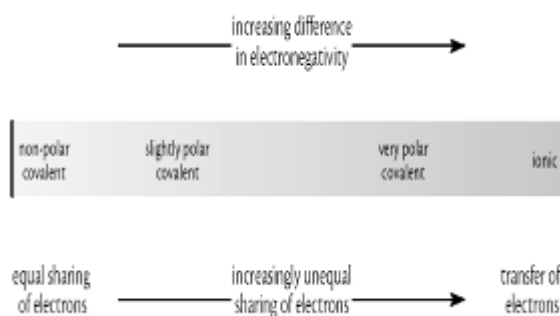
Electronegativity values are useful in predicting how electrons will be shared. Electronegativity is a measure of the attraction an atom involved in a covalent bond has for the electrons of the bond. In hydrogen iodide, HI, the iodine atom is more electronegative than the hydrogen so the iodine has the greater attraction for the shared electrons.

This means the shared pair are attracted nearer to iodine, which as a result becomes slightly negatively charged, δ^- . The hydrogen becomes slightly positive, δ^+ because the shared electrons have moved nearer the iodine. When the sharing of the bonding electrons is unequal we call it a polar covalent bond.



In hydrogen fluoride, HF, the difference in electronegativities is greater so this covalent bond is more polar. In some compounds one atom is so much more electronegative than the other that there is no sharing of electrons at all. E.g. in Lithium fluoride the electronegativities are ^{1.0} Li and F ^{4.0}. This difference is so great that the bonding electron originally belonging to lithium is transferred to the fluorine. This forms two ions of opposite charge, Li⁺ and F⁻. These are attracted to each other. This electrostatic attraction is called the ionic bond. Don't think of non-polar covalent, polar covalent and ionic as three completely separate types of bonding. Rather think of them as being on a continuous scale. At one end is non-polar covalent with its equal sharing of electrons, moving on to progressively more and more polar covalent. Eventually the sharing is so unequal that an electron is effectively transferred from one atom to the other forming ions, and therefore ionic bonding.

9.6.2 Range of bonding



9.6.3 Electronegativity & Bonding

The difference in the ability of elements to attract electrons (Electronegativity) tells us about the type of bonding we can expect between them:

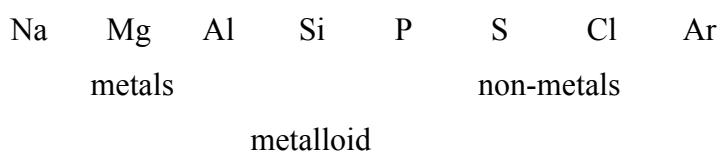
- No difference corresponds to a pure covalent bonding,
- Small difference (< 1.7) corresponds to a polar covalent bonding, and
- Large difference (> 1.7) corresponds to an ionic bonding.

9.7 Trends across a Period

Atomic size (radius) decreases across a Period. The first ionisation energy) shows a general increase across a Period. The elements become more electronegative. Elements become weaker reducing agents and better oxidising agents.

The elements change from metal to non metal via metalloid as shown below:

E.g.



9.8 Trends down a Group

As a summary, we can say that down a Group:

- Atomic “size” (radius) increases,
- Elements become less electronegative,
- First ionisation energy decreases and
- Elements become more metallic e.g. group 14.

Easier electron loss means greater reducing power so the elements become increasingly strong reducing agents down a Group (particularly noticeable in Groups 1, 2, 13, 14). The opposite is true – elements become increasingly weak oxidising agents down a Group (which is particularly noticeable in Groups 15-17).

Reactivity of s-block metals increases (easier loss of electrons) illustrated by greater reducing ability as shown on <http://www.youtube.com/watch?v=Ft4E1eCUItI>

The reactivity of the non-metals in the p-block (particularly Groups 16 and 17) decreases down the Group which is illustrated by a weaker oxidising ability.



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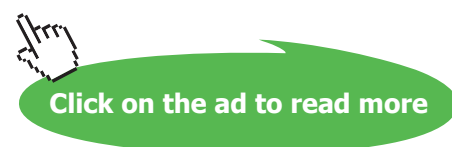
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10 Thermochemistry

Introduction

Thermodynamics is the science of the relationship between heat and other forms of energy.

Thermochemistry is the area of Thermodynamics related to the heat changes involved in chemical reactions.

10.1 Forms of Energy

Energy is defined as the capacity to move matter. The units of energy are Joules (J). Energy can be in many forms:

- Radiant Energy such as Light,
- Thermal Energy such as Heat,
- Energy stored within a compressed spring, and
- Sound Energy.

There are three main types of energy:

- Kinetic Energy is the energy associated with the movement of an object,
- Potential Energy is the stored energy an object has because of its position (e.g. gravitational, magnetic or electrostatic),
- Internal Energy is the sum of the kinetic and potential energies of the particles making up a substance.

10.1.1 Kinetic Energy

An object of mass m and speed or velocity v has a kinetic energy E_k equals to $0.5 m v^2$.

10.1.2 Potential Energy

This energy depends on the “position” (such as height) in a “field of force” (such as gravity or the compression of a spring). For example, a ball of a given mass m at the top of a mountain is at a relatively high “position” h in the “gravitational field” g of the earth. Its potential energy E_p is given by $E_p = m g h$ where m = mass, g = gravity and h = height.

Potential energy is not just “height” energy. Other situations where energy is stored include:

- A compressed spring,
- Two magnets held near together, and
- Charged particles near together.

10.1.3 Internal Energy

The internal energy is the energy of the particles (the electrons, protons and neutrons) making up a substance. The internal energy includes the kinetic energy of the electrons and nuclei; and the potential energy related to the electronic energy levels, electrostatic attractions etc.

10.1.4 Total Energy

The Total Energy (E_{tot}) of a system is the sum of its kinetic energy (E_k), potential energy (E_p), and internal energy, U .

10.2 Energy and Chemical Reactions

All chemical reactions obey the First Law of Thermodynamics (also known as The Law of Conservation of Energy). This law states that the “Energy may be converted from one form to another, but the total quantities of energy remain constant”.

When a chemical reaction happens:

- Energy is required to break bonds, and
- Energy is released when bonds are formed.

Usually in a lab experiment, the substance is not moving, so it has no kinetic energy. Also, there is no change in potential energy as the reaction vessel is not moved. Therefore all the energy released or absorbed relates to changes in the Internal Energy of the substances. In chemical reactions, energy is often transferred from the “system” to its “surroundings,” or vice versa. The substance or mixture of substances under study in which a change occurs is called the thermodynamic system (or simply system.). The surroundings are everything outside the thermodynamic system.

10.2.1 Heat Energy and Chemical Reactions

Heat can be defined as the energy that flows into or out of a system because of a difference in temperature between the system and its surroundings. The Heat energy is transferred from a region of higher temperature to one of lower temperature; once the temperatures become equal, heat flow stops.

10.2.2 Temperature

Remember, heat is not the same as temperature. Temperature is directly related to the average kinetic energy of the particles. The temperature change when a certain quantity of heat is transferred will depend on the amount of substance present. The Temperature of the system can also change if the volume or pressure are changed.

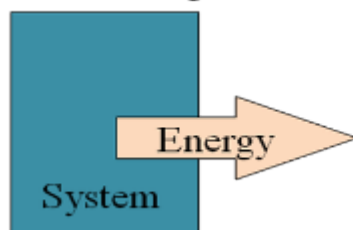
10.2.3 Heat and Chemical Reactions

In equations Heat is denoted by the symbol q and is positive if heat is absorbed by the system. On the other hand, q is negative if heat is evolved by the system.

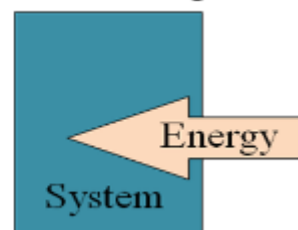
Exothermic ($q < 0$)
Heat “out of” a system

Endothermic ($q > 0$)
Heat “into” a system

Surroundings



Surroundings



10.2.4 Heat and Work

Part of the energy released can be used to move something (“do work”).

E.g. if a gas is produced during the reaction the volume changes, and work has to be done to push back the atmosphere. This amount of work is $P\Delta V$, which subsequently changes the internal energy U .

10.3 Enthalpy, H

The heat absorbed or evolved by a reaction depends on the conditions under which it occurs, such as pressure. Thus instead of the term “heat”, scientists prefer to refer to a related absolute property: Enthalpy. The symbol used for enthalpy is H .

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10.3.1 Enthalpy and Enthalpy Change

When a reaction happens, reactants change into products. The reactants have a particular enthalpy (energy) and the products have a different enthalpy (energy). The difference between these two energies is the “heat of reaction” or “enthalpy of the reaction” and typically $\Delta H = H_{\text{products}} - H_{\text{reactants}}$.

10.3.2 Enthalpy, H

Often, reactions take place in an open vessel, and therefore at the constant pressure of the atmosphere. The enthalpy change is equal to the heat energy change at constant pressure, q_p , i.e. $\Delta H = q_p$.

Strictly, $H = U + PV$ where U = internal energy, P = Pressure, and V = Volume.

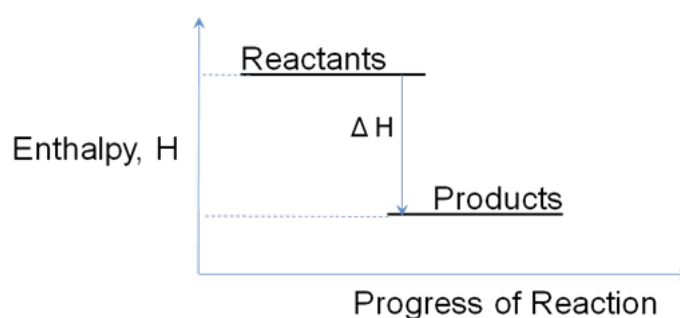
Enthalpy is an extensive property of substances (i.e. it depends on the amount of substance, as do mass and volume). It is a state function i.e. the value of any enthalpy change does not depend on how any change was made, but only on the initial and final state of the system.

10.4 Heat Energy and Chemical Reactions

If a reaction does work, then $\Delta H = \Delta U + P\Delta V$. $P\Delta V$ is usually much smaller than ΔU , so, at constant pressure, the change in enthalpy can be taken to represent the changes in kinetic or potential energy within the atoms – usually changes in the bonding.

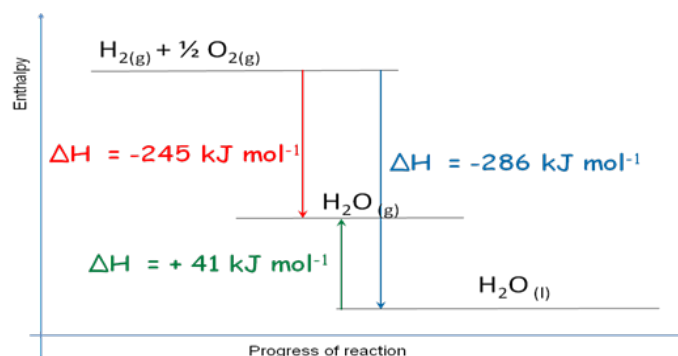
10.5 Enthalpy and Enthalpy Change

There is no way of measuring the enthalpy of any single substance directly. For this reason we can only discuss enthalpy changes in a reaction and this can be measured as an amount of heat given out (exothermic reaction) or taken in (endothermic reaction). We can represent the level of enthalpy possessed by reactants and products on an “Enthalpy Diagram” as seen below.

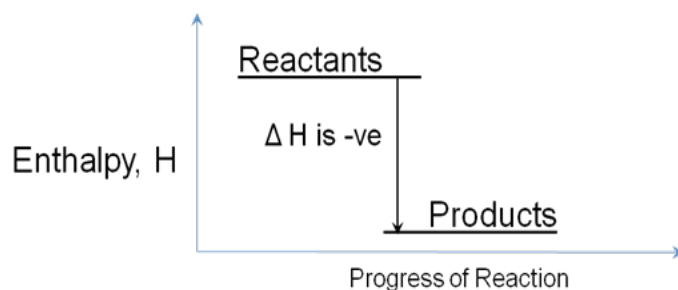


10.5.1 Enthalpy diagrams

Enthalpy diagrams are a representation of the relative internal energy of a system before and after a reaction. Horizontal lines are drawn to show the energy of the system at a particular time. The nature of the system which has that energy is written on the line. The formulae of all the elements or compounds present in the system including their state: solid, liquid or gas. There is no scale on the y axis, as absolute enthalpy cannot be measured. A line at a higher level merely shows that the enthalpy of the system has increased due to the addition of heat from the surroundings, which has caused a physical change (e.g. melting) or chemical change (i.e. a reaction) in the system. The x axis can be labelled progress of reaction.



10.5.2 Exothermic reactions



If the potential energy diagram shows that the energy of the reactants is higher than that of the products, the reaction will release energy. ΔH is negative. It will be an exothermic reaction.

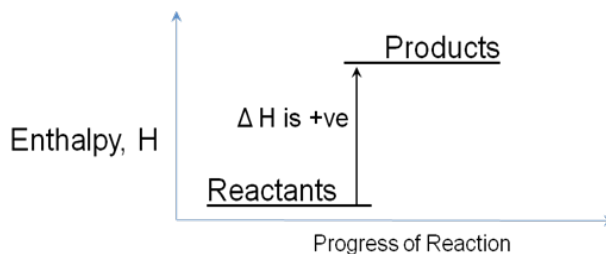
10.5.3 Example

When concrete is mixed, the main reaction is between calcium oxide and water $\text{CaO (s)} + \text{H}_2\text{O (l)} \rightarrow \text{Ca(OH)}_2\text{(s)}$ $\Delta H = -65.2 \text{ kJ mol}^{-1}$

This reaction gives out a large amount of heat – so much that when building a large concrete structure such as a dam, cooling pipes must be included to carry away the heat.

10.6 Endothermic reactions

If the potential energy diagram shows that the energy of the reactants is lower than that of the products, the reaction will take in energy. ΔH is positive. It will be an endothermic reaction.



10.6.1 Example

One example of an endothermic reaction is: $2\text{NH}_4\text{NO}_3(\text{s}) + \text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}(\text{s}) + 2\text{NH}_3(\text{g}) + 10\text{H}_2\text{O}(\text{l}) + \text{Ba}(\text{NO}_3)_2(\text{aq})$, $\Delta H = +17.44 \text{ kJ mol}^{-1}$. Watch this at: <http://www.youtube.com/watch?v=GmiZ0huvZzs>

10.7 Enthalpy and Enthalpy Change

Obviously, these amounts of heat energy released or absorbed must be dependent on the quantity of substances reacting so we must define the enthalpy changes in terms of energy changes (kilojoules) per amount of substance (mole). Therefore, the units of enthalpy and enthalpy change are kJ mol^{-1} .

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10.8 Thermochemical equations

It is important to give the exact reaction equation when quoting the associated energy change. $2\text{Mg (s)} + \text{O}_2 \text{(g)} \rightarrow 2\text{MgO (s)}$, $\Delta H = -1204 \text{ kJ mol}^{-1}$. For example, if no reaction equation was stated, ΔH for this reaction is $-1204 \text{ kJ mol}^{-1}$ of O_2 , but only 602 kJ mol^{-1} of Mg.

Note: Always give the states of the reactants and products when quoting H for a reaction.

E.g. $\text{Pb (s)} + \text{Cl}_2 \text{(g)} \rightarrow \text{PbCl}_2 \text{(s)}$, $H = -359 \text{ kJ mol}^{-1}$ There would be a large extra energy change needed to change Pb (s) into Pb (g)!

10.9 Standard State Enthalpy Changes

In order that chemists worldwide can compare notes on thermochemical experiments, a series of special conditions have been agreed. The term “standard state enthalpy” refers to an enthalpy change for a reaction in which reactants and products are considered to be in their standard states (most stable state of the substance) at a specified temperature of 298 K and pressure of 1 atmosphere.

10.10 Standard State Enthalpies

The enthalpy change for a reaction in which reactants are in their standard states is denoted as; ΔH° (“delta H zero” or “delta H nought”).

10.10.1 Measuring the Enthalpy changes in chemical reactions

Enthalpy changes are measured by measuring the heat required to raise the temperature of a surrounding substance (usually water), because a thermochemical measurement is based on the relationship between heat and temperature change. The heat required to raise the temperature of a substance is its heat capacity.

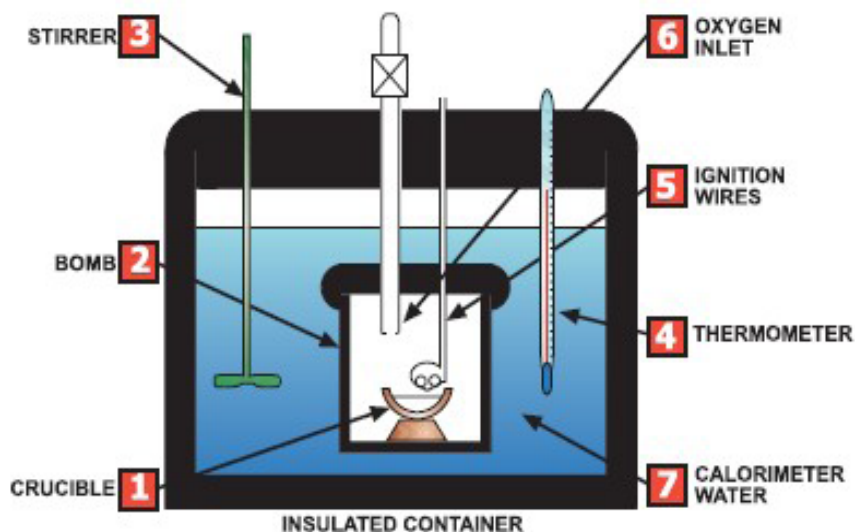
10.11 Specific heat capacity

The specific heat capacity, c , of a substance is the amount of heat needed to raise the temperature of one gram of a substance by one degree. Some values of specific heat capacity are shown in the table below.

Substance	Specific heat capacity ($\text{J g}^{-1} \cdot \text{K}^{-1}$)
Aluminium	0.901
Iron	0.449
Water	4.18

10.11.1 Measuring Enthalpy Changes: Calorimetry

A calorimeter is a device used to measure the heat absorbed or released during a physical or chemical change. Everything inside the bomb is the system. The water is the surroundings. The sample is ignited, and the heat absorbed by the calorimeter and its contents is the negative of the heat of reaction. A calorimeter is represented in the figure below.



10.11.2 Measuring the Enthalpy change

Allow the reaction to heat (or cool) a known mass of water, measure the temperature change of the water then calculate the energy required using the formula; $\Delta H = -c m \Delta T$

Where:

- ΔH = the enthalpy change for the reaction,
- ΔT = the temperature change (in C or K) (the final temperature – initial temperature),
- m = mass of water (in kg), and
- c = specific heat capacity of water (4.18kJK⁻¹.kg⁻¹).

10.11.3 Example

0.253g of ethanol is burned in a calorimeter. The temperature of the surrounding 150g of water rises 10K. Calculate the enthalpy of combustion of ethanol.

$$\text{Heat absorbed by water} = c m \Delta T = (4.18 \times 0.15 \times 10) \text{ kJ} = 6.27 \text{ kJ}$$

$$\text{Molar mass of ethanol} = 46\text{g} \text{ therefore moles of ethanol used} = 0.253/46 = 0.0055 \text{ moles}$$

Assuming all the heat produced by the combustion was absorbed by the water: 0.0055 moles of ethanol burns to give 6.27kJ of heat. Therefore 1 mole of ethanol burns to give $(6.27 \times 1/0.0055) \text{ kJ} = 1140 \text{ kJ}$ of heat.

Estimated enthalpy of combustion ($\Delta H_{\text{combustion}}$) = - 1140 kJ mol⁻¹

10.11.4 Exercise

Enthalpy changes are not just for combustion (burning) reactions – the heat evolved when a substance dissolves can be measured this way too. Calculate the enthalpy of solution for dissolving 0.80 g of Sodium Hydroxide in 25cm³ of water if the temperature rise observed is 5.2°C.

Note that the density of water = 1g cm⁻³

10.12 Standard State Enthalpies

There are a number of enthalpies which we need to be able to calculate and use such as:

- Enthalpy of Formation,
- Enthalpy of Combustion,
- Enthalpy of Solution, and
- Enthalpy of Neutralisation.

10.12.1 Enthalpy of Formation ΔH_f°

The enthalpy of formation, written ΔH_f° is the enthalpy change when “one mole of a substance in its standard state is formed (made) from its component elements in their standard state”.



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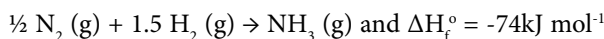
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Note: The standard enthalpy of formation for a pure element in its standard state is zero.

E.g. ΔH_f° of CH_4 is the enthalpy change for one mole of carbon (as graphite, which is the standard reference form) and two moles of hydrogen gas molecule in the reaction:



E.g. ΔH_f° of NH_3 is the enthalpy change for this reaction:

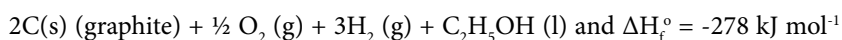


Note that to make one mole of ammonia; the equation must refer to half a mole of nitrogen and one and a half moles of hydrogen.

Note that although ΔH_f° can be measured experimentally for many reactions, direct measurement may not be possible. ΔH_f° can be calculated indirectly instead. It is still defined in the same way, whether or not the elements actually react together to form the product.

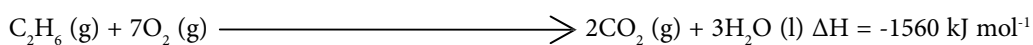
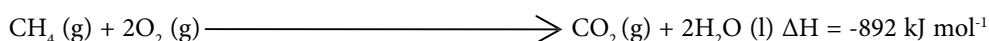
10.12.2 Exercise

The standard heat of formation of ethanol, $\text{C}_2\text{H}_5\text{OH} = -278 \text{ kJ mol}^{-1}$. Write a thermochemical equation that expresses this.



10.12.3 Enthalpy of Combustion ΔH_c°

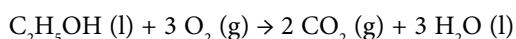
The enthalpy of combustion, written ΔH_c° is the enthalpy change when: "1 mole of a substance completely burns in excess oxygen". All equations must be written and balanced with the balancing number of the substance burned being one,



N.B. In tables of values of heats of combustion the negative sign is often missed out because they are always exothermic!

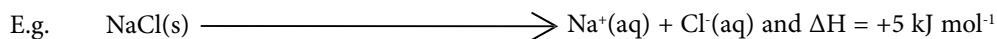
10.12.4 Exercise

The standard heat of combustion of ethanol, $\Delta H = 111 \text{ kJ mol}^{-1}$. Write a thermochemical equation which expresses this.

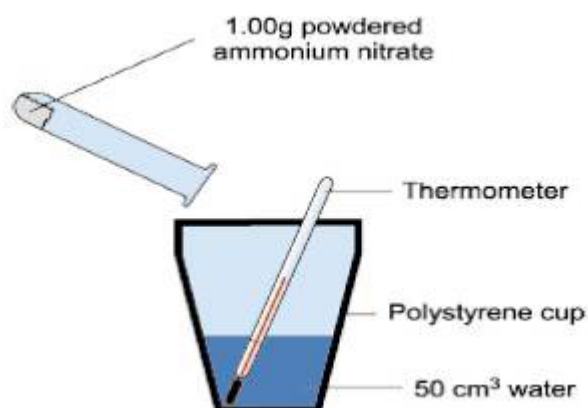


10.12.5 Enthalpy of Solution ΔH_s°

The enthalpy of solution is the enthalpy change when: “1 mole of solute is dissolved in a quantity of water”. In other words, the enthalpy of solution is the enthalpy change when 1 mole of solute is completely dissolved.

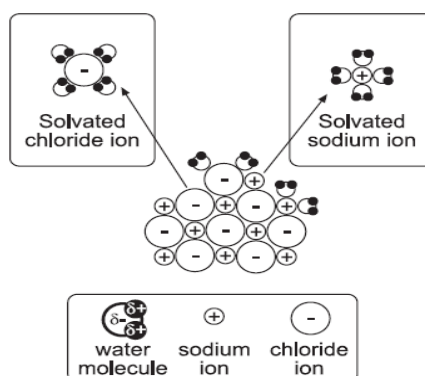


To determine the enthalpy of solution of a substance in water, a known weight of it is dissolved in a known volume of water. The temperature change is noted when the substance has dissolved. The experiment is carried out under conditions where the system (substance plus water) is thermally insulated from the surroundings. Although it is the solution (rather than pure water) whose temperature is raised, the specific heat capacity can be taken to be that of water.



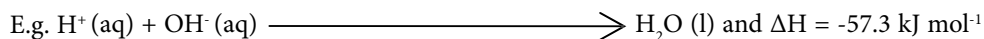
For simple, practical purposes polystyrene cups are very useful - they have good insulation and themselves have a very low specific heat capacity.

What is happening to the ions? They become surrounded by water molecules as shown below:

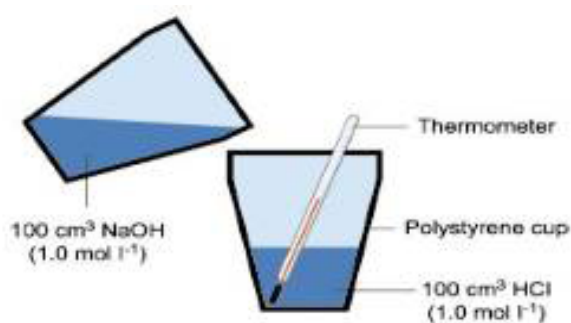
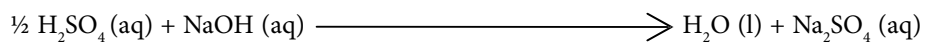


10.12.6 Enthalpy of Neutralisation ΔH_n°

The Enthalpy of neutralisation is the enthalpy change involved when: "1 mole of water is formed by neutralisation of an acid with a base". This always involves the reaction of a mole of H^+ (aq) with one mole of OH^- (aq).



Again, select the reaction equation carefully to refer to one mole of product (water)



Enthalpy changes for this reaction can be also obtained by using polystyrene cups to reduce heat loss to a minimum when a known volume of alkali is added to an equivalent amount of acid and the temperature change noted.

10.13 Summary

- Laboratory methods for determining the enthalpy of combustion, enthalpy of solution and enthalpy of neutralisation are described.
- These use the equation: energy transferred $Q = c m \Delta T$.
- The enthalpy of formation is the energy change when 1 mole of an element is formed from its elements.
- The enthalpy of combustion is the energy change when 1 mole of a substance is completely burned in oxygen.
- The enthalpy of solution is the energy change when 1 mole of a substance dissolves in water.
- The enthalpy of neutralisation of an acid is the energy change when the acid is neutralised by an alkali to produce 1 mole of water.