

The Free High School Science Texts: A Textbook
for High School Students Studying Chemistry.

FHSST Authors¹

June 12, 2005

¹See <http://savannah.nongnu.org/projects/fhsst>

Copyright © 2003 “Free High School Science Texts”

Permission is granted to copy, distribute and/or modify this document under the terms of the GNU Free Documentation License, Version 1.2 or any later version published by the Free Software Foundation; with no Invariant Sections, no Front-Cover Texts, and no Back-Cover Texts. A copy of the license is included in the section entitled “GNU Free Documentation License”.

Contents

| | | |
|----------|---|-----------|
| I | MATTER AND MATERIALS | 1 |
| 1 | Classification of Materials (Grade 10) | 2 |
| 2 | What is matter made of? (Grade 10) | 3 |
| 3 | The Atom (Grade 10) | 4 |
| 3.1 | Models of the atom | 4 |
| 3.1.1 | The Plum Pudding Model | 4 |
| 3.1.2 | The Bohr Model | 5 |
| 3.1.3 | The Wave Model / Quantum Mechanical Model | 5 |
| 3.2 | Atomic Structure | 7 |
| 3.2.1 | The Electron | 7 |
| 3.2.2 | The Nucleus | 7 |
| 3.3 | Isotopes | 8 |
| 3.4 | Energy quantization and electron configuration | 9 |
| 3.5 | Periodicity of ionization energy to support atom arrangement in Periodic Table | 9 |
| 3.6 | Successive ionisation energies to provide evidence for arrangement of electrons into core and valence | 9 |
| 4 | Atomic combinations, Molecular structure, Chemical Bonding (Grade 11) | 10 |
| 4.1 | Chemical Bonding | 10 |
| 4.2 | What is a molecule? | 10 |
| 4.2.1 | Van Der Waals forces | 11 |
| 4.2.2 | Bonding and energy | 11 |
| 4.3 | Types of bonding | 11 |
| 4.3.1 | Covalent bonding | 11 |
| 4.3.2 | Ionic bonding | 12 |
| 4.3.3 | Metallic bonds | 15 |
| 4.4 | Representation of molecular structure | 16 |
| 5 | Atomic nuclei (Grade 11) | 17 |
| 5.1 | What is the atom made of? | 17 |
| 5.2 | Nucleus | 19 |
| 5.2.1 | Proton | 19 |
| 5.2.2 | Neutron | 19 |
| 5.2.3 | Isotopes | 20 |

| | | |
|----------|---|-----------|
| 5.3 | Nuclear force | 21 |
| 5.4 | Binding energy and nuclear masses | 22 |
| 5.4.1 | Binding energy | 22 |
| 5.4.2 | Nuclear energy units | 22 |
| 5.4.3 | Mass defect | 23 |
| 5.4.4 | Nuclear masses | 24 |
| 5.5 | Radioactivity | 26 |
| 5.5.1 | Discovery of radioactivity | 26 |
| 5.5.2 | Nuclear α , β , and γ rays | 26 |
| 5.5.3 | Danger of the ionizing radiation | 27 |
| 5.5.4 | Decay law | 28 |
| 5.5.5 | Radioactive dating | 29 |
| 5.6 | Nuclear reactions | 30 |
| 5.7 | Detectors | 31 |
| 5.7.1 | Geiger counter | 31 |
| 5.7.2 | Fluorescent screen | 32 |
| 5.7.3 | Photo-emulsion | 32 |
| 5.7.4 | Wilson's chamber | 32 |
| 5.7.5 | Bubble chamber | 32 |
| 5.7.6 | Spark chamber | 33 |
| 5.8 | Nuclear energy | 33 |
| 5.8.1 | Nuclear reactors | 34 |
| 5.8.2 | Fusion energy | 37 |
| 5.9 | Elementary particles | 42 |
| 5.9.1 | β decay | 42 |
| 5.9.2 | Particle physics | 43 |
| 5.9.3 | Quarks and leptons | 46 |
| 5.9.4 | Forces of nature | 46 |
| 5.10 | Origin of the universe | 47 |
| 6 | Thermal Properties & Ideal Gases (Grade 11) | 50 |
| 6.1 | Boyle's Law : Pressure and volume of an enclosed sample of gas . | 50 |
| 6.2 | Charles's Law: Volume and temperature of an enclosed sample of gas | 52 |
| 6.3 | Avogadro's Hypothesis: The link between number of gas particles and volume | 54 |
| 6.4 | Two General Equations | 55 |
| 6.5 | Overview of the Kinetic Theory of Matter | 56 |
| 7 | Organic Chemistry: Molecules (Grade 12) | 58 |
| 7.1 | Introduction | 58 |
| 7.1.1 | What is organic chemistry? | 58 |
| 7.1.2 | Unique properties of carbon | 58 |
| 7.1.3 | Special properties of organic compounds | 59 |
| 7.1.4 | Classification of organic compounds | 59 |
| 7.1.5 | Functional groups | 60 |
| 7.2 | Naming and Representation of Organic Compounds | 61 |
| 7.2.1 | Naming of organic compounds | 61 |
| 7.2.2 | Representation of organic compounds | 62 |
| 7.2.3 | Examples | 63 |

| | | |
|-----------|---|-----------|
| 7.3 | Hydrocarbons | 64 |
| 7.3.1 | Alkanes | 64 |
| 7.3.2 | Alkenes | 64 |
| 7.3.3 | Alkynes | 65 |
| 7.4 | Alcohols, carboxylic acids and esters | 65 |
| 7.4.1 | Alcohols | 65 |
| 7.4.2 | Oxidation reactions | 66 |
| 7.4.3 | Carboxylic acids | 66 |
| 7.4.4 | Esters | 66 |
| 8 | Organic Chemistry: Macromolecules (Grade 12) | 68 |
| II | CHEMICAL CHANGE | 69 |
| 9 | Physical and Chemical Change (Grade 10) | 70 |
| 10 | Representing Chemical Change (Grade 10) | 71 |
| 10.1 | Writing Chemical Equations | 71 |
| 10.2 | Balancing Chemical Equations | 72 |
| 11 | Quantitative Aspects of Chemical Change (Grade 11) | 76 |
| 12 | Energy and Chemical Change (Grade 11) | 77 |
| 13 | Reaction Types (Grade 11) | 78 |
| 13.1 | Chemical Reactions | 78 |
| 13.2 | Types of Chemical Reactions | 79 |
| 13.3 | Ionic reactions | 79 |
| 13.3.1 | What are ionic reactions? | 79 |
| 13.3.2 | Precipitation reactions | 79 |
| 13.3.3 | Formation of gases | 79 |
| 14 | Reaction Rates (Grade 12) | 80 |
| 14.0.4 | Factors affecting reaction rates | 81 |
| 14.1 | Energy changes in chemical reactions | 81 |
| 14.1.1 | Exothermic and endothermic reactions | 81 |
| 14.2 | Chemical equilibrium | 84 |
| 14.2.1 | Reversible reactions | 84 |
| 14.2.2 | Dynamic equilibrium | 84 |
| 14.2.3 | The equilibrium constant | 84 |
| 14.3 | The common ion effect | 86 |
| 14.3.1 | Equilibrium in solution | 88 |
| 14.3.2 | The solubility product | 88 |
| 15 | Electrochemical Reactions (Grade 12) | 89 |
| 15.1 | Reduction and Oxidation Reactions | 89 |
| 15.2 | Introduction | 89 |
| 15.2.1 | Oxidation and reduction | 89 |
| 15.2.2 | Redox reagents | 90 |
| 15.3 | Balancing redox reactions | 90 |

| | | |
|--------|---|-----|
| 15.3.1 | The ion-electron method | 91 |
| 15.4 | The Cu-Zn electrochemical cell | 93 |
| 15.4.1 | Direct electron transfer | 94 |
| 15.5 | Standard electrode potentials | 95 |
| 15.5.1 | The cell potential | 95 |
| 15.5.2 | The standard hydrogen electrode | 96 |
| 15.6 | Examples of electrochemical cells | 96 |
| 15.6.1 | The dry cell (Leclanche cell) | 97 |
| 15.6.2 | The alkaline dry cell | 97 |
| 15.6.3 | The lead-acid accumulator | 98 |
| 15.6.4 | The fuel cell | 98 |
| 15.7 | Electrolysis | 99 |
| 15.7.1 | The Chlor-alkali Process | 99 |
| 15.7.2 | The Downs process | 99 |
| 15.8 | Electrolysis of water | 99 |
| 15.9 | Extraction of Aluminium | 100 |
| 15.10 | Electro-refining of copper | 101 |
| 15.11 | Electroplating | 101 |
| 15.12 | Faraday's laws of electrolysis | 102 |

III CHEMICAL SYSTEMS 107

16 The Water Cycle (Grade 10) 108

17 The Nitrogen Cycle (Grade 10) 109

| | | |
|--------|---|-----|
| 17.1 | Nitrogen and Nitrogen Compounds | 109 |
| 17.2 | Nitrogen Gas (N_2) | 109 |
| 17.2.1 | Industrial Preparation of N_2 | 109 |
| 17.2.2 | Uses of Nitrogen | 110 |
| 17.3 | Ammonia (NH_3) | 110 |
| 17.3.1 | Laboratory Preparation | 110 |
| 17.3.2 | Industrial Preparation of NH_3 | 110 |
| 17.3.3 | Properties of NH_3 | 111 |
| 17.3.4 | Uses of NH_3 | 111 |
| 17.4 | Ammonium Salts | 112 |
| 17.4.1 | Preparation of Ammonium Salts | 112 |
| 17.4.2 | Properties of Ammonium Salts | 112 |
| 17.4.3 | Uses of Ammonium Salts | 112 |
| 17.5 | Nitrogen Dioxide (NO_2) | 112 |
| 17.5.1 | Laboratory Preparation: | 113 |
| 17.5.2 | Equilibrium between NO_2 and N_2O_4 | 113 |
| 17.6 | Nitric Acid (HNO_3) | 113 |
| 17.6.1 | Laboratory preparation of HNO_3 : | 114 |
| 17.6.2 | Industrial preparation of HNO_3 : | 114 |
| 17.6.3 | Reactions of Nitric Acid: | 114 |
| 17.6.4 | Uses of Nitric Acid: | 115 |
| 17.7 | Nitrates: | 115 |

18 The Hydrosphere (Grade 10) 116

| | |
|--|------------|
| 19 The Lithosphere: Exploiting the Earth's crust (Grade 11) | 117 |
| 20 The Atmosphere (Grade 11) | 118 |
| 21 The Chemical Industry: Resources, Needs and the Chemical Connection (Grade 12) | 119 |
| <i>Essay 1: Synthetic Polymers</i> | 120 |
| A GNU Free Documentation License | 123 |

Part I

**MATTER AND
MATERIALS**

Chapter 1

Classification of Materials (Grade 10)

Observing, describing, Classifying and using materials (a macroscopic view)

- The material(s) of which an object is composed
- Mixtures
 - Heterogeneous mixtures
 - Homogeneous mixtures
- Pure substances: elements and compounds
- Names and formulae of substances
- Metals, semimetals and nonmetals
- Electrical conductors, semiconductors and insulators
- Thermal conductors and insulators
- Magnetic and nonmagnetic materials

Chapter 2

What is matter made of? (Grade 10)

- Atoms and molecules (simple and giant)
- Material structures and properties: Linking macroscopic properties of materials to micro(particle) structure
- Intermolecular and intramolecular forces (chemical bonds). Physical state and density explained in terms of these forces. Particle kinetic energy and temperature. (NOTE TO SELF: (some is covered already but not all))

Chapter 3

The Atom (Grade 10)

- Energy quantization and electron configuration
- The Periodic Table of the Elements: Periodicity of ionization energy to support the arrangements of the atoms in the Periodic Table Successive ionization energies to provide evidence for the arrangement of electrons into core and valence electrons

Atoms are the building blocks of matter. They are the basis of all the structures and organisms in the universe. The planets, the sun, grass and trees, the air we breathe, and people are all made up of different combinations of atoms.

The idea of atoms was invented by two Greek philosophers, Democritus and Leucippus in the fifth century BC. The Greek word *ατομον* (atom) means *indivisible* because they believed that atoms could not be broken down into smaller pieces. However, the discovery of the fact that an atom is actually a complex system and can be broken into pieces was the most important step and pivoting point in the development of modern physics!

3.1 Models of the atom

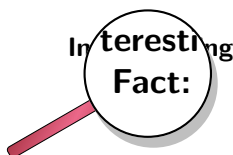
Nowadays, we know that atoms are made up of a *positively charged nucleus* in the centre surrounded by orbiting *negatively charged electrons*. However, in the past, before the structure of the atom had been discovered, scientists came up with lots of different *models* or *pictures* to describe what atoms look like.

3.1.1 The Plum Pudding Model

After the electron was discovered (by J.J. Thomson in 1897), people realised that atoms were made up of even smaller particles and the plum pudding model was proposed. In this picture, atoms are thought of as the negative electrons floating in a soup of positive charge like plums in a pudding or raisins in a fruit cake!

3.1.2 The Bohr Model

Some years later, it was discovered (by Rutherford in 1911) that atoms have a positively charged nucleus (centre) with the negative electrons moving around it. This proved that the plum pudding model was wrong and scientists then pictured the atom like a mini solar system where the electrons orbit the nucleus like planets orbiting around the sun. There were some problems with this model. For example it could not explain the very interesting observation that atoms only emit light at certain wavelengths or frequencies. Niels Bohr solved this problem by proposing that the electrons could only orbit the nucleus in certain special orbits with particular energies i.e. *energy levels*. The exact energies of the orbitals depends on the type of atom, for example Helium has different energy levels to Carbon. If an electron jumps down from a higher energy level (or orbital) to a lower energy level, then light is emitted from the atom. The energy of the light emitted is the same as the gap in the energy between the two energy levels!



Light has the properties of both a particle *and* a wave! Einstein discovered that light comes in energy packets which are called **photons**. When an electron in an atom changes energy levels, a photon of light is emitted. This photon has the same energy as the difference between the two electron energy levels!

Once an electron is in its lowest orbit, it cannot go down any further. Bohr calculated the size of the Hydrogen atom (nucleus plus one electron) by calculating the distance between the nucleus and the electron in its lowest energy level. This distance is known as the **Bohr radius**.

Definition: The **Bohr radius**, a_0 , is the radius of the lowest energy electron orbit in the Hydrogen atom.
 $a_0 = 5.29177210810^{-11}$ m

3.1.3 The Wave Model / Quantum Mechanical Model

The fact that Bohr's electron energy levels could only take certain energy values was a hint that some new physics was at play in the atom. Today we use what is called *quantum mechanics* or *wave mechanics* to describe the behaviour of very small particles at very small distances. In quantum mechanics, particles can be described as *waves* instead of little billiard balls. (We discussed earlier that light can be thought of as a wave, or as a particle called the *photon*.) Then the properties of the particle, for example its position or velocity, are described by probabilities.

Aside: Probabilities describe the *chance* of something happening or of being true. They usually have a value between 0 and 1 or 0% and 100% where 0 means no chance at all and 1 means definite. Probabilities are used when the state of something is uncertain. For example, probabilities are often used when predicting the weather e.g. there is a 50% (=0.5) chance of rain.

In the quantum mechanical model of the atom, you can imagine the electron as a wave. Then the electron does not move along a specific path in its orbit, but rather along *all* imaginable paths with different probabilities. If we were trying to catch this electron, after many attempts we would discover that the electron can be found *anywhere* around the nucleus, even very close to and very far from it. However, the probabilities of finding the electron at different distances from the nucleus would be different.

If you picture the electron as a cloud around the nucleus then in some places this cloud will be denser (thicker) while in other places it will be less dense (thinner). The density of the cloud corresponds to the probability of finding the electron in a particular place! Quantum mechanics is very useful because one can use it to calculate the probability of finding the electron at any point in space around the nucleus. The results of such a calculation for the hydrogen atom are shown in Fig. 5.1. On the y -axis is the probability of finding the electron and on the x -axis is the distance away from the center of the nucleus. You can see that the most likely distance (highest point on the curve) is the same as the Bohr radius!

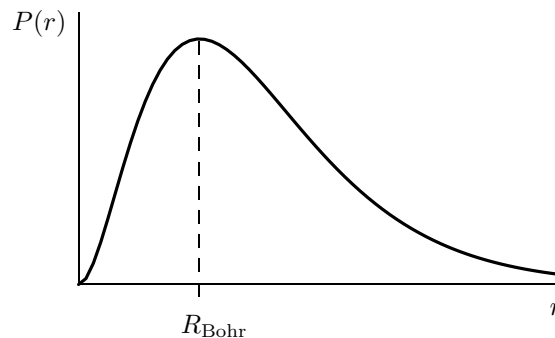


Figure 3.1: Probability density $P(r)$ for finding the electron at a distance r from the proton in the ground state of the hydrogen atom.

Its mass is very tiny compared to the total mass of the atom. This is because most of the mass of the atom is due to the nucleus! In the silicon atoms that are the main component of the rocks around us, all 14 electrons make up only 0.027% of the mass. When holding a heavy rock in your hand, you actually feel the collective weight of all the nuclei that are inside it!

3.2 Atomic Structure

So far, we have discussed that atoms are made up of a **nucleus** surrounded by one or more **electrons**.

3.2.1 The Electron

The electron is a very light particle. It has a mass of 9.11×10^{-31} kg! Currently, scientists believe that the electron can be treated as a *point particle* or *elementary particle* meaning that it cannot be broken down into anything smaller.

3.2.2 The Nucleus

Unlike the electron, the nucleus *can* be broken up into smaller building blocks: **protons** and **neutrons**. Collectively the protons and neutrons are called **nucleons**.

The Proton

In the early 1920's Rutherford and other physicists performed many experiments, changing one element into another by striking them with energetic helium nuclei. They noticed that every time hydrogen nuclei were emitted in the process. It was apparent that the hydrogen nucleus played a fundamental role in nuclear structure and was a constituent part of all other nuclei. By the late 1920's physicists were regularly referring to the hydrogen nucleus as the **proton**.

So it was established that atomic nuclei consisted of protons. Each proton carries a *positive charge* of +1. Therefore the total positive charge of a nucleus is equal to the number of protons in the nucleus! Since we know that atoms are *electrically neutral*, i.e. do not carry any extra charge, then the number of protons in an atom has to be the same as the number of electrons to balance out the positive and negative charge to zero!

The Neutron

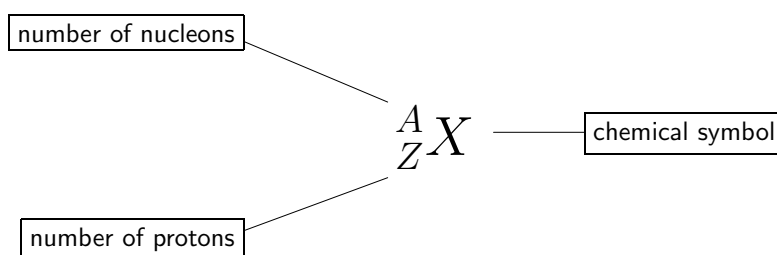
However, only having protons in the nucleus leads to some problems. For example, if there were only positively charged protons in the nucleus, then it should break into bits due to the repulsive electrostatic forces between the protons! Another problem was that the protons in the nucleus were not enough to account for the measured mass of different atoms! For example, if protons were the only particles in the nucleus, then a helium nucleus (atomic number 2) would have two protons and therefore only twice the mass of hydrogen. However, it is actually *four* times heavier than hydrogen. This suggests that there must be something else inside the nucleus in addition to protons.

Therefore Rutherford predicted (in 1920) that another kind of particle must be present in the nucleus along with the proton to help hold the nucleus together and add to its mass. To ensure the atom remains electrically neutral this particle had to be *neutral* itself. In 1932 James Chadwick discovered the **neutron** and measured its mass, which turned out to be almost the same, but slightly larger than that of the proton.

3.3 Isotopes

The chemical properties of an element are determined by the charge of its atomic nucleus, i.e. by the *number of protons*. This number is called the **atomic number** and is denoted by the letter Z . The mass of an atom depends on how many nucleons its nucleus contains. The number of nucleons, i.e. the total number of protons *plus* neutrons, is called the **atomic mass number** and is denoted by the letter A .

Standard notation shows the chemical symbol, the mass number and the atomic number as follows:



For example, the iron nucleus which has 26 protons and 30 neutrons, is denoted as



where the total nuclear charge is $Z = 26$ and the mass number $A = 56$. The number of neutrons is simply the difference $N = A - Z$. Since the type of element is linked directly to the number of protons in the nucleus (Z), the lower index is sometimes omitted and you may see notation like ${}^{56}\text{Fe}$.

If we add or remove a few neutrons from a nucleus, the chemical properties of the atom will remain the same because its charge is still the same. This means that such an atom should remain in the same place of the Periodic table. For example, no matter how many neutrons we add or subtract from a nucleus with 6 protons, that element will always be called carbon (see the Table of Elements). Atoms which have the same number of protons, but a different number of neutrons, are called **isotopes**.

Interesting Fact:

In Greek, "same place" reads as *ἴσος τόπος* (*isos topos*). This is why atoms which have the same number of protons, but different numbers of neutrons, are called *isotopes*!

The different isotopes of a given element have the same atomic number Z but different mass numbers A since they have different numbers of neutrons N . The chemical properties of the different isotopes of an element are identical, but they will often have great differences in nuclear stability. For stable isotopes of the light elements, the number of neutrons will be almost equal to the number

of protons, but for heavier elements, the number of neutrons is always greater than Z and the neutron excess tends to grow when Z increases. This is because neutrons are kind of glue that keeps repelling protons together. The greater the repelling charge, the more glue you need.

interesting fact: the neutrons and protons are *not* elementary particles. They are actually made up of even smaller particles called quarks. Both protons and neutrons are made of three quarks each. There are all sorts of other particles composed of quarks which nuclear physicists study using huge detectors - you can find out more about this by reading the essay in Chapter ??.

3.4 Energy quantization and electron configuration

3.5 Periodicity of ionization energy to support atom arrangement in Periodic Table

3.6 Successive ionisation energies to provide evidence for arrangement of electrons into core and valence

Chapter 4

Atomic combinations, Molecular structure, Chemical Bonding (Grade 11)

- A chemical bond as the net electrostatic force between two atoms sharing electrons.
- Oxidation number of atoms in molecules to explain their relative 'richness' in electrons.
- Multiple bonds
- Molecular shape as predicted using the Valence Shell Electron Pair Repulsion (VSEPR) theory

4.1 Chemical Bonding

4.2 What is a molecule?

All matter consists of atoms, the most basic element of life. When two or more atoms combine or bond they form a **molecule**. These molecules are neutral and behave as a unit in a chemical reaction.

e.g. two hydrogen atoms and one oxygen atom can combine to form one water molecule: $\text{H} + \text{H} + \text{O} = \text{H}_2\text{O}$

Most substances are composed of molecules. However, they can also be made up of atoms or ions. The noble gases (group VIII of the periodic table) are very stable and therefore prefer not to form bonds. So they are made up of a single atom and are sometimes called monatomic molecules. Most other gases, e.g. O_2 and Cl_2 , are diatomic molecules.

Neutral salts like NaCl consist of ions and don't have any formal bonds to make up a molecule. The ions make up a so-called **giant molecule**.

4.2.1 Van Der Waals forces

There are three types of intermolecular forces which are classified as Van Der Waals forces. These are ion-dipole, dipole-dipole and London forces.

Ion-dipole forces: These occur when an ionic substance dissolves in a polar liquid, e.g. KCl in H₂O. The positive and negative poles of the polar liquid attract the negative and positive ions of the ionic substance, respectively.

Dipole-dipole forces: These forces occur when polar molecules arrange themselves such that their oppositely charged ends can attract each other, e.g. H₂O and NaOH.

London forces: These occur between nonpolar molecules. The molecules are neutral but when two approach one another, the protons and electrons from different particles attract one another slightly. The electron clouds of these molecules then become distorted and result in a weak dipole. This is the weakest of the Van Der Waals forces and so all such substances have low melting points, e.g. CH₄ and CCl₄.

4.2.2 Bonding and energy

The potential energy of two atoms is zero when they are far apart since there is no attraction or repulsion between them. As the atoms approach each other, the negatively charged electron clouds and the positively charged nuclei repel each other. But the electron cloud and the nucleus of different atoms can also attract each other. The atoms move closer together until the lowest possible energy state is reached. **Bonding energy** has a negative value since energy is required to break a bond. The energy needed to break a bond is called **dissociation energy**.

4.3 Types of bonding

4.3.1 Covalent bonding

Covalent bonding occurs between atoms of nonmetals. Two half-filled orbitals of atoms overlap and an electron pair is shared between the atoms. The shared electrons must have opposite spins to comply with Pauli's Exclusion Principle.

Electronegativity is the extent to which an atom pulls a shared electron pair towards it. It is useful to remember that electronegativity increases from left to right across a period and from top to bottom down a group in the periodic table.

Polar and non-polar covalent bonds

Electronegativity can be used to explain the difference between two types of covalent bonds. **Non-polar covalent bonds** occur between two identical non-metal atoms, e.g. H₂, Cl₂ and O₂. Since the two atoms have the same electronegativity, the electron pair in the covalent bond is shared equally between them. However, if two different non-metal atoms bond then the shared electron pair will be pulled more strongly by the atom with the highest electronegativity.

This will result in the formation of a **polar covalent bond** in which one atom will have a slightly negative charge) and the other a slightly positive charge, e.g. H^+Cl^- .

Shape of molecules

Molecules with covalent bonds can exist in several shapes which depends on the number of atoms and whether there are lone pairs on these atoms.

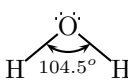
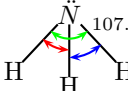
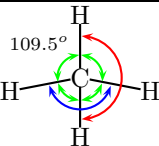
| Shape | Composition | Bond angle | Example |
|-------------|------------------------|---------------|---|
| Linear | 2 atoms | 180° | $\text{HBr} : \text{H} \text{---} \overset{\curvearrowright}{\text{Br}}$ 180° |
| Angular | 3 atoms : 2 lone pairs | 104.5° | $\text{H}_2\text{O} :$  |
| Pyramidal | 4 atoms : 1 lone pair | 107.3° | $\text{NH}_3 :$  |
| Tetrahedral | 5 atoms | 109.5° | $\text{CH}_4 :$  |

Table 4.1: Shapes of Molecules

Polar molecules

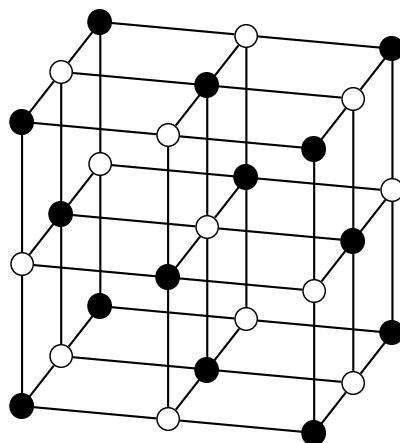
Some molecules with polar covalent bonds are **polar molecules**, e.g. H_2O . However, although CO_2 has two polar covalent bonds (between C^+ atom and the two O^- atoms), the molecule itself is not polar. The reason is that CO_2 is a linear molecule and is therefore symmetrical. So there is no difference in charge between the two ends of the molecule. So we can say that polar molecules must contain polar covalent bonds and they must be asymmetrical. The greater degree of polarity increases with the difference in electronegativity between two atoms.

4.3.2 Ionic bonding

Ionic bonding occurs between a metal and a non-metal atom. The difference in electronegativity of the atoms is more than 1.7 and so the electron pair is transferred from the metal electron donor to the non-metal electron acceptor. The metal will gain a positive charge and the non-metal a negative charge, resulting in an electrostatic force of attraction between the two atoms, e.g. Na^+Cl^- . The metal must have a **low ionisation energy** so that it can readily give up an electron pair. The non-metal must have a high **electron affinity** to readily accept the electron pair.

Ionic substances are actually a combination of lots of ions bonded together into a giant molecule. The arrangement of ions in a regular, geometric structure makes up a **crystal lattice**. The arrangement depends on the relative size of

the ions and also their charge. So in fact NaCl does not contain one Na and one Cl ion, but rather a lot of these two ions arranged in a crystal lattice where the ratio of Na to Cl ions is 1:1. The crystal lattice is shown in the figure below.



Energy involved in ionic bonding

Let us consider the example of a KBr molecule. There are several steps involved in the formation of the ionic bond between K and Br.

- Sublimation energy: this is the energy required for K metal to change to the gaseous state.
- Dissociation energy: this is the energy required for a Br_2 molecule to divide into separate Br atoms.
- Ionisation energy: this is the energy required for a K atom to donate an electron, resulting in the formation of a K^+ ion.
- Electron affinity: this is the energy released when a Br atom accepts an electron to form a Br^- ion.
- Lattice energy: this is the energy released when K^+ and Br^- ions arrange in a crystal lattice.

The difference between the energy required and the energy released during the bonding process is called the **bonding energy**.

Properties of ionic compounds

Ionic compounds usually have high bonding energies due to the strong forces between their ions. This means that the bonds are very strong and they have high melting and boiling points. Ionic compounds do not conduct electricity in the solid phase but they do in their molten phase. They are also hard and brittle.

Charge associated with ions and polyatomic ions

The charge on an ion is related to its group number in the periodic table. There are two general rules:

- Cations carry a maximum charge equal to their group number (*since the group number equals the number of valence electrons, this is the maximum number of electrons that the atoms can donate*)
- Anions carry a maximum charge equal to (8 - their group number) (*since the group number equals the number of valence electrons and the maximum number of electrons that an atom can be surrounded by is 8, the difference is the maximum number of electrons that the atom can receive*)

e.g.

Group I Li^+

Group II Ba^{2+}

Group III Al^{3+}

Group V N^{3-}

Group VI O^{2-}

Group VII Br^-

The overall charge of an ionic compound will always be zero and so the negative and positive charge must be of equal magnitude. It is therefore possible to determine the chemical formula of a compound knowing the charge on the individual ions.

e.g.

PbO Pb^{2+} (Group II)... 2+ charge and O^{2-} (Group VI)... 2- charge one Pb^{2+} ion and one O^{2-} ion are needed to make up a neutral PbO molecule

CaCl₂ Ca^{2+} (Group II)... 2+ charge and Cl^- (Group VII)... 1- charge one Ca^{2+} ion and two Cl^- ions are needed to make up a neutral CaCl₂ molecule

K₂O K^+ (Group I)... 1+ charge and O^{2-} (Group VI)... 2- charge two K^+ ions and one O^{2-} ions are needed to make up a neutral K₂O molecule

Na₃N Na^+ (Group I)... 1+ charge and N^{3-} (Group V)... 3- charge three Na^+ ions and one N^{3-} ions are needed to make up a neutral Na₃N molecule

Al₂S₃ Al^{3+} (Group III)... 3+ charge and S^{2-} (Group VI)... 2- charge two Al^{3+} ions and three S^{2-} ions are needed to make up a neutral Al₂S₃ molecule

Some groups of atoms behave as a unit and therefore we need to learn the charge associated with these ion groups.

More examples of ionic formulae:

BaCO_3 , $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2\text{SO}_4$, $\text{Ca}_3(\text{PO}_4)_2$

| Negative Ions | | | | Positive Ions | |
|---------------------------|---------------------|------------------------------|--------------|------------------------|----------|
| ClO_3^- | Chlorate | CO_3^{2-} | Carbonate | NH_4^+ | Ammonium |
| CN^- | Cyanide | CrO_4^{2-} | Chromate | H_3O^+ | Oxonium |
| CH_3COO^- | Ethanoate (acetate) | $\text{Cr}_2\text{O}_7^{2-}$ | Dichromate | | |
| HCO_3^- | Hydrogen carbonate | MnO_4^{2-} | Manganate | | |
| HSO_4^- | Hydrogen sulphate | SO_4^{2-} | Sulphate | | |
| OH^- | Hydroxide | SO_3^{2-} | Sulphite | | |
| IO_3^- | Iodate | SiO_3^{2-} | Silicate | | |
| NO_3^- | Nitrate | $\text{S}_2\text{O}_3^{2-}$ | Thiosulphate | | |
| NO_2^- | Nitrite | | | | |
| MnO_4^- | Permanganate | | | | |
| CNS^- | Thiocyanate | | | | |

Table 4.2: Ions

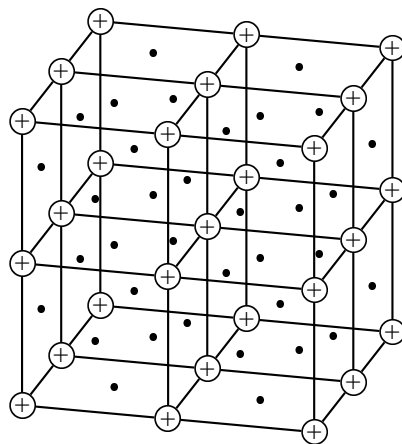
4.3.3 Metallic bonds

All metals have crystal structures and are arranged in a lattice structure (similar to ionic compounds). The valence electrons are delocalised, leaving behind positively charged metal ions also referred to as the atomic kernel. These are surrounded by a sea of delocalised electrons which are electrostatically attracted to the atomic kernels this constitutes a **metallic bond**. The arrangement of metals in a crystal lattice is only determined by the size of the atoms.

Metals have several unique properties as a result of this arrangement:

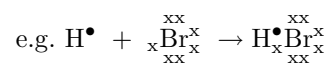
- Good electrical and thermal conductors: electrons are loosely bound and are able to move from areas of high potential/temperature to low potential/temperature
- Malleable and ductile: bonds are not spatially directed so atoms can easily slide over one another, making metals easy to shape and mould or draw into threads
- High density: atoms are packed closely together and therefore metals are dense
Metallic luster: loosely bound electrons are able to absorb light energy and reflect light at all frequencies, giving metals a highly polished appearance

The figure below shows the arrangement of the atomic kernel and the sea of delocalised electrons in a crystal lattice.

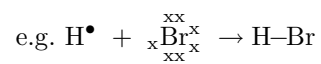


4.4 Representation of molecular structure

There are two forms of notation used to represent covalent bonding. **Lewis notation** uses dots and crosses to represent electrons on different atoms.



Only the electrons involved in the bond between H and Br are shown with **Couper notation** but these are shown with a line (one for each covalent bond) instead of dots and crosses.



Chapter 5

Atomic nuclei (Grade 11)

- nuclear structure and stability
- radioactivity
- ionising radiation
- fission and fusion and their consequences
- nucleosynthesis - the sun and stars
- age determination in geology and archaeology

Amazingly enough, human mind that is kind of contained inside a couple of liters of human's brain, is able to deal with extremely large as well as extremely small objects such as the whole universe and its smallest building blocks. So, what are these building blocks? As we already know, the universe consists of galaxies, which consist of stars with planets moving around. The planets are made of molecules, which are bound groups (chemical compounds) of atoms.

There are more than 10^{20} stars in the universe. Currently, scientists know over 12 million chemical compounds i.e. 12 million different molecules. All this variety of molecules is made of only a hundred of different atoms. For those who believe in beauty and harmony of nature, this number is still too large. They would expect to have just few different things from which all other substances are made. In this chapter, we are going to find out what these elementary things are.

5.1 What is the atom made of?

The Greek word *ατομον* (atom) means indivisible. The discovery of the fact that an atom is actually a complex system and can be broken in pieces was the most important step and pivoting point in the development of modern physics.

It was discovered (by Rutherford in 1911) that an atom consists of a positively charged nucleus and negative electrons moving around it. At first, people

tried to visualize an atom as a microscopic analog of our solar system where planets move around the sun. This naive planetary model assumes that in the world of very small objects the Newton laws of classical mechanics are valid. This, however, is not the case.

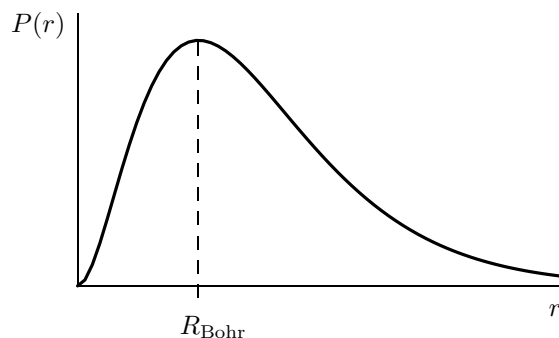


Figure 5.1: Probability density $P(r)$ for finding the electron at a distance r from the proton in the ground state of hydrogen atom.

The microscopic world is governed by quantum mechanics which does not have such notion as trajectory. Instead, it describes the dynamics of particles in terms of quantum states that are characterized by probability distributions of various observable quantities.

For example, an electron in the atom is not moving along a certain trajectory but rather along all imaginable trajectories with different probabilities. If we were trying to catch this electron, after many such attempts we would discover that the electron can be found anywhere around the nucleus, even very close to and very far from it. However, the probabilities of finding the electron at different distances from the nucleus would be different. What is amazing: the most probable distance corresponds to the classical trajectory!

You can visualize the electron inside an atom as moving around the nucleus chaotically and extremely fast so that for our “mental eyes” it forms a cloud. In some places this cloud is more dense while in other places more thin. The density of the cloud corresponds to the probability of finding the electron in a particular place. Space distribution of this density (probability) is what we can calculate using quantum mechanics. Results of such calculation for hydrogen atom are shown in Fig. 5.1. As was mentioned above, the most probable distance (maximum of the curve) coincides with the Bohr radius.

Quantum mechanical equation for any bound system (like an atom) can have solutions only at a discrete set of energies $E_1, E_2, E_3 \dots$, etc. There are simply no solutions for the energies E in between these values, such as, for instance, $E_1 < E < E_2$. This is why a bound system of microscopic particles cannot have an arbitrary energy and can only be in one of the quantum states. Each of such

states has certain energy and certain space configuration, i.e. distribution of the probability.

A bound quantum system can make transitions from one quantum state to another either spontaneously or as a result of interaction with other systems. The energy conservation law is one of the most fundamental and is valid in quantum world as well as in classical world. This means that any transition between the states with energies E_i and E_j is accompanied with either emission or absorption of the energy $\Delta E = |E_i - E_j|$. This is how an atom emits light.

Electron is a very light particle. Its mass is negligible as compared to the total mass of the atom. For example, in the lightest of all atoms, hydrogen, the electron constitutes only 0.054% of the atomic mass. In the silicon atoms that are the main component of the rocks around us, all 14 electrons make up only 0.027% of the mass. Thus, when holding a heavy rock in your hand, you actually feel the collective weight of all the nuclei that are inside it.

5.2 Nucleus

Is the nucleus a solid body? Is it an elementary building block of nature? No and no! Although it is very small, a nucleus consists of something even smaller.

5.2.1 Proton

The only way to do experiments with such small objects as atoms and nuclei, is to collide them with each other and watch what happens. Perhaps you think that this is a barbaric way, like colliding a “Mercedes” and “Toyota” in order to learn what is under their bonnets. But with microscopic particles nothing else can be done.

In the early 1920’s Rutherford and other physicists made many experiments, changing one element into another by striking them with energetic helium nuclei. They noticed that all the time hydrogen nuclei were emitted in the process. It was apparent that the hydrogen nucleus played a fundamental role in nuclear structure and was a constituent part of all other nuclei. By the late 1920’s physicists were regularly referring to hydrogen nucleus as *proton*. The term “proton” seems to have been coined by Rutherford, and first appears in print in 1920.

5.2.2 Neutron

Thus it was established that atomic nuclei consist of protons. Number of protons in a nucleus is such that makes up its positive charge. This number, therefore, coincides with the atomic number of the element in the Mendeleev’s table.

This sounded nice and logical, but serious questions remained. Indeed, how can positively charged protons stay together in a nucleus? Repelling each other by electric force, they should fly away in different directions. Who keeps them

together?

Furthermore, the proton mass is not enough to account for the nuclear masses. For example, if the protons were the only particles in the nucleus, then a helium nucleus (atomic number 2) would have two protons and therefore only twice the mass of hydrogen. However, it actually is four times heavier than hydrogen. This suggests that it must be something else inside nuclei in addition to protons.

These additional particles that kind of “glue” the protons and make up the nuclear mass, apparently, are electrically neutral. They were therefore called *neutrons*. Rutherford predicted the existence of the neutron in 1920. Twelve years later, in 1932, his assistant James Chadwick found it and measured its mass, which turned out to be almost the same but slightly larger than that of the proton.

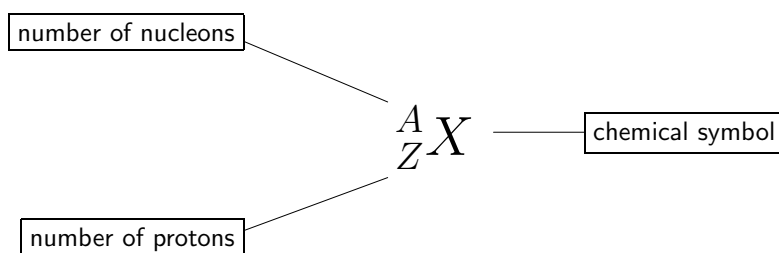
5.2.3 Isotopes

Thus, in the early 1930’s it was finally proved that atomic nucleus consists of two types of particles, the protons and neutrons. The protons are positively charged while the neutrons are electrically neutral. The proton charge is exactly equal but opposite to that of an electron. The masses of proton and neutron are almost the same, approximately 1836 and 1839 electron masses, respectively.

Apart from the electric charge, the proton and neutron have almost the same properties. This is why there is a common name for them: *nucleon*. Both the proton and neutron are nucleons, like the man and woman are both humans. In the literature, the proton is denoted by letter p and the neutron by n . Sometimes, when the difference between them is unimportant, it is used the letter N meaning nucleon (in the same sense as using the word person instead of man or woman).

Chemical properties of an element are determined by the charge of its atomic nucleus, i.e. by the number of protons. This number is called the *atomic number* and is denoted by letter Z . The mass of an atom depends on how many nucleons its nucleus contains. The number of nucleons, i.e. total number of protons and neutrons, is called the *atomic mass number* and is denoted by letter A .

Standard nuclear notation shows the chemical symbol, the mass number and the atomic number of the isotope.



For example, the iron nucleus (26-th place in the Mendeleev's periodic table of the elements) with 26 protons and 30 neutrons is denoted as



where the total nuclear charge is $Z = 26$ and the mass number $A = 56$. The number of neutrons is simply the difference $N = A - Z$ (here it is used the same letter N as for nucleon, but this should not cause any confusion). Chemical symbol is inseparably linked with Z . This is why the lower index is sometimes omitted and you may encounter the simplified notation like ${}^{56}\text{Fe}$.

If we add or remove few neutrons from a nucleus, the chemical properties of the atom remain the same because its charge is the same. This means that such atom should remain in the same place of the Periodic table. In Greek, "same place" reads *ισος τὸπος* (*isos topos*). The nuclei, having the same number of protons, but different number of neutrons, are called therefore *isotopes*.

The different isotopes of a given element have the same atomic number Z but different mass numbers A since they have different numbers of neutrons N . The chemical properties of the different isotopes of an element are identical, but they will often have great differences in nuclear stability. For stable isotopes of the light elements, the number of neutrons will be almost equal to the number of protons, but for heavier elements, the number of neutrons is always greater than Z and the neutron excess tends to grow when Z increases. This is because neutrons are kind of glue that keeps repelling protons together. The greater the repelling charge, the more glue you need.

5.3 Nuclear force

Since atomic nuclei are very stable, the protons and neutrons must be kept inside them by some force and this force must be rather strong. What is this force? All of modern particle physics was discovered in the effort to understand this force!

Trying to answer this question at the beginning of the XX-th century, physicists found that all they knew before, was inadequate. Actually, by that time they knew only gravitational and electromagnetic forces. It was clear that the forces holding nucleons were not electromagnetic. Indeed, the protons, being positively charged, repel each other and all nuclei would decay in a split of a second if some other forces would not hold them together. On the other hand, it was also clear that they were not gravitational, which would be too weak for the task.

The simple conclusion was that nucleons are able to attract each other by yet unknown *nuclear forces*, which are stronger than the electromagnetic ones. Further studies showed that this hypothesis was correct.

Nuclear force has rather unusual properties. Firstly, it is charge independent. This means that in all pairs nn , pp , and np nuclear forces are the same. Secondly, at distances $\sim 10^{-13}$ cm, the nuclear force is attractive and very strong, ~ 100

times stronger than the electromagnetic repulsion. Thirdly, the nuclear force is of a very short range. If the nucleons move away from each other for more than few *fermi* (1 fm=10⁻¹³ cm) the nuclear attraction practically disappears. Therefore the nuclear force looks like a “strong man with very short hands”.

5.4 Binding energy and nuclear masses

5.4.1 Binding energy

When a system of particles is bound, you have to spend certain energy to disintegrate it, i.e. to separate the particles. The easiest way to do it is to strike the system with a moving particle that carries kinetic energy, like we can destroy a glass bottle with a bullet or a stone. If our bullet-particle moves too slow (i.e. does not have enough kinetic energy) it cannot disintegrate the system. On the other hand, if its kinetic energy is too high, the system is not only disintegrated but the separated particles acquire some kinetic energy, i.e. move away with some speed. There is an intermediate value of the energy which is just enough to destroy the system without giving its particles any speed. This minimal energy needed to break up a bound system is called *binding energy* of this system. It is usually denoted by letter *B*.

5.4.2 Nuclear energy units

The standart unit of energy, *Joule*, is too large to measure the energies associated with individual nuclei. This is why in nuclear physics it is more convenient to use a much smaller unit called Mega-electron-Volt (MeV). This is the amount of energy that acquires an electron passing between two charged plates with the potential difference (voltage) of one million Volts. Sounds very huge, isn't it? But look at this relation

$$1 \text{ MeV} = 1.602 \times 10^{-13} \text{ J}$$

and think again. In the units of MeV, most of the energies in nuclear world can be expressed by values with only few digits before decimal point and without ten to the power of something. For example, the binding energy of proton and neutron (which is the simplest nuclear system and is called *deuteron*) is

$$B_{pn} = 2.225 \text{ MeV} .$$

The simplicity of the numbers is not the only advantage of using the unit MeV. Another, more important advantage, comes from the fact that most of experiments in nuclear physics are collision experiments, where particles are accelerated by electric field and collide with other particles. From the above value of B_{pn} , for instance, we immediately know that in order to break up deuterons, we need to bombard them with a flux of electrons accelerated through a voltage not less than 2.225 million Volts. No calculation is needed! On the other hand, if we know that a charged particle (with a unit charge) passes through a voltage, say, 5 million Volts, we can, without any calculation, say that it acquires the energy of 5 MeV. It is very convenient. Isn't it?

5.4.3 Mass defect

Comparing the masses of atomic nuclei with the masses of the nucleons that constitute them, we encounter a surprising fact: Total mass of the nucleons is greater than mass of the nucleus! For example, for the deuteron we have

$$m_d < m_p + m_n ,$$

where m_d , m_p , and m_n are the masses of deuteron, proton, and neutron, respectively. The difference is rather small,

$$(m_p + m_n) - m_d = 3.968 \times 10^{-30} \text{ kg} ,$$

but on the nuclear scale is noticeable since the mass of proton, for example,

$$m_p = 1672.623 \times 10^{-30} \text{ kg}$$

is also very small. This phenomenon was called “*mass defect*”. Where the mass disappears to, when nucleons are bound?

To answer this question, we notice that the energy of a bound state is lower than the energy of free particles. Indeed, to liberate them from a bound complex, we have to give them some energy. Thinking in the opposite direction, we conclude that, when forming a bound state, the particles have to get rid of the energy excess, which is exactly equal to the binding energy. This is observed experimentally: When a proton captures a neutron to form a deuteron, the excess energy of 2.225 MeV is emitted via electromagnetic radiation.

A logical conclusion from the above comes by itself: When proton and neutron are bounding, some part of their mass disappears together with the energy that is carried away by the radiation. And in the opposite process, when we break up the deuteron, we give it the energy, some part of which makes up the lost mass.

Albert Einstein came to the idea of the equivalence between the mass and energy long before any experimental evidences were found. In his theory of relativity, he showed that total energy E of a moving body with mass m is

$$E = \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}} , \quad (5.1)$$

where v is its velocity and c the speed of light. Applying this equation to a not moving body ($v = 0$), we conclude that it possesses the *rest* energy

$$E_0 = mc^2 \quad (5.2)$$

simply because has mass. As you will see, this very formula is the basis for making nuclear bombs and nuclear power stations!

All the development of physics and chemistry, preceding the theory of relativity, was based on the assumption that the mass and energy of a closed system

are conserving in all possible processes and they are conserved separately. In reality, it turned out that the conserving quantity is the *mass-energy*,

$$E_{\text{kin}} + E_{\text{pot}} + E_{\text{rad}} + mc^2 = \text{const} ,$$

i.e. the sum of kinetic energy, potential energy, the energy of radiation, and the mass of the system.

In chemical reactions the fraction of the mass that transforms into other forms of energy (and vice versa), is so small that it is not detectable even in most precise measurements. In nuclear processes, however, the energy release is very often millions times higher and therefore is observable.

You should not think that mutual transformations of mass and energy are the features of only nuclear and atomic processes. If you break up a piece of rubber or chewing gum, for example, in two parts, then the sum of masses of these parts will be slightly larger than the mass of the whole piece. Of course we will not be able to detect this “mass defect” with our scales. But we can calculate it, using the Einstein formula (5.2). For this, we would need to measure somehow the mechanical work A used to break up the whole piece (i.e. the amount of energy supplied to it). This can be done by measuring the force and displacement in the breaking process. Then, according to Eq. (5.2), the mass defect is

$$\Delta m = \frac{A}{c^2} .$$

To estimate possible effect, let us assume that we need to stretch a piece of rubber in 10 cm before it breaks, and the average force needed for this is 10 N (approximately 1 kg). Then

$$A = 10 \text{ N} \times 0.1 \text{ m} = 1 \text{ J} ,$$

and hence

$$\Delta m = \frac{1 \text{ J}}{(299792458 \text{ m/s})^2} \approx 1.1 \times 10^{-17} \text{ kg} .$$

This is very small value for measuring with a scale, but huge as compared to typical masses of atoms and nuclei.

5.4.4 Nuclear masses

Apparently, an individual nucleus cannot be put on a scale to measure its mass. Then how can nuclear masses be measured?

This is done with the help of the devices called *mass spectrometers*. In them, a flux of identical nuclei, accelerated to a certain energy, is directed to a screen where it makes a visible mark. Before striking the screen, this flux passes through magnetic field, which is perpendicular to velocity of the nuclei. As a result, the flux is deflected to certain angle. The greater the mass, the smaller is the angle (because of inertia). Thus, measuring the displacement of the mark from the center of the screen, we can find the deflection angle and then calculate the mass.

| particle | number of protons | number of neutrons | mass (MeV) |
|-------------------------|-------------------|--------------------|------------|
| e | 0 | 0 | 0.511 |
| p | 1 | 0 | 938.272 |
| n | 0 | 1 | 939.566 |
| ${}^2_1\text{H}$ | 1 | 1 | 1875.613 |
| ${}^3_1\text{H}$ | 1 | 2 | 2808.920 |
| ${}^3_2\text{He}$ | 2 | 1 | 2808.391 |
| ${}^4_2\text{He}$ | 2 | 2 | 3727.378 |
| ${}^7_3\text{Li}$ | 3 | 4 | 6533.832 |
| ${}^9_4\text{Be}$ | 4 | 5 | 8392.748 |
| ${}^{12}_6\text{C}$ | 6 | 6 | 11174.860 |
| ${}^{16}_8\text{O}$ | 8 | 6 | 14895.077 |
| ${}^{238}_{92}\text{U}$ | 92 | 146 | 221695.831 |

Table 5.1: Masses of electron, nucleons, and some nuclei.

Since mass and energy are equivalent, in nuclear physics it is customary to measure masses of all particles in the units of energy, namely, in MeV. Examples of masses of subatomic particles are given in Table 5.1. The values given in this table, are the energies to which the nuclear masses are equivalent via the Einstein formula (5.2).

There are several advantages of using the units of MeV to measure particle masses. First of all, like with nuclear energies, we avoid handling very small numbers that involve ten to the power of something. For example, if we were measuring masses in kg, the electron mass would be $m_e = 9.1093897 \times 10^{-31}$ kg. When masses are given in the equivalent energy units, it is very easy to calculate the mass defect. Indeed, adding the masses of proton and neutron, given in the second and third rows of Table 5.1, and subtracting the mass of ${}^2_1\text{H}$, we obtain the binding energy 2.225 MeV of the deuteron without further ado. One more advantage comes from particle physics. In collisions of very fast moving particles new particles (like electrons) can be created from vacuum, i.e. kinetic energy directly transforms into mass. If the mass is expressed in the energy units, we know how much energy is needed to create this or that particle, without calculations.

5.5 Radioactivity

As was said before, the nucleus experiences the intense struggle between the electric repulsion of protons and nuclear attraction of the nucleons to each other. It therefore should not be surprising that there are many nuclei that are unstable. They can spontaneously (i.e. without an external push) break in pieces. When the fragments reach the distances where the short range nuclear attraction disappears, they fiercely push each other away by the electric forces. Thus accelerated, they move in different directions like small bullets making destruction on their way. This is an example of nuclear radioactivity but there are several other varieties of radioactive decay.

5.5.1 Discovery of radioactivity

Nuclear radioactivity was discovered by Antoine Henri Becquerel in 1896. Following Wilhelm Roentgen who discovered the X-rays, Becquerel pursued his own investigations of these mysterious rays.

The material Becquerel chose to work with contained uranium. He found that the crystals containing uranium and exposed to sunlight, made images on photographic plates even wrapped in black paper. He mistakenly concluded that the sun's energy was being absorbed by the uranium which then emitted X-rays. The truth was revealed thanks to bad weather.

On the 26th and 27th of February 1896 the skies over Paris were overcast and the uranium crystals Becquerel intended to expose to the sun were returned to a drawer and put over the photographic plates. On the first of March, Becquerel developed the plates and to his surprise, found that the images on them were clear and strong. Therefore the uranium emitted radiation without an external source of energy such as the sun. This was the first observation of the nuclear radioactivity.

Later, Becquerel demonstrated that the uranium radiation was similar to the X-rays but, unlike them, could be deflected by a magnetic field and therefore must consist of charged particles. For his discovery of radioactivity, Becquerel was awarded the 1903 Nobel Prize for physics.

5.5.2 Nuclear α , β , and γ rays

Classical experiment that revealed complex content of the nuclear radiation, was done as follows. The radium crystals (another radioactive element) were put at the bottom of a narrow straight channel made in a thick piece of lead and open at one side. The lead absorbed everything except the particles moving along the channel. This device therefore produced a flux of particles moving in one direction like bullets from a machine gun. In front of the channel was a photoplate that could register the particles.

Without the magnetic field, the image on the plate was in the form of one single dot. When the device was immersed into a perpendicular magnetic field,

the flux of particles was split in three fluxes, which was reflected by three dots on the photographic plate.

One of the three fluxes was straight, while two others were deflected in opposite directions. This showed that the initial flux contained positive, negative, and neutral particles. They were named respectively the α , β , and γ particles.

The α -rays were found to be the ${}^4\text{He}$ nuclei, two protons and two neutrons bound together. They have weak penetrating ability, a few centimeters of air or a few sheets of paper can effectively block them. The β -rays proved to be electrons. They have a greater penetrating power than the α -particles and can penetrate 3 mm of aluminum. The γ -rays are not deflected because they are high energy photons. They have the same nature as the radio waves, visible light, and the X-rays, but have much shorter wavelength and therefore are much more energetic. Among the three, the γ -rays have the greatest penetrating power being able to pass through several centimeters of lead and still be detected on the other side.

5.5.3 Danger of the ionizing radiation

The α , β , and γ particles moving through matter, collide with atoms and knock out electrons from them, i.e. make positive ions out of the atoms. This is why these rays are called *ionizing radiation*.

Apart from ionizing the atoms, this radiation destroys molecules. For humans and all other organisms, this is the most dangerous feature of the radiation. Imagine thousands of tiny tiny bullets passing through your body and making destruction on their way. The nuclear radiation harms the cells of the body and thus can make people sick or even kill them. Illness can strike people years after their exposure to nuclear radiation. For example, because the ionizing particles can randomly modify the DNA (long organic molecules that store all the information on how a particular cell should function in the body). As a result, some cells with wrong DNA may become cancer cells.

Fortunately, our body is able to repair some damages caused by radiation. Indeed, we are constantly bombarded by the radiation coming from the outer space as well as from the inner parts of our own planet and still survive. However, if the number of damages becomes too large, the body will not cope with them anymore.

There are established norms and acceptable limits for the radiation that are considered safe for human body. If you are going to work in contact with radioactive materials or near them, make sure that the exposure dose is monitored and the limits are adhered to.

You should understand that no costume can protect you from γ -rays! Only a thick wall of concrete or metal can stop them. The special costumes and masks that people wear when handling radioactive materials, protect them not from the rays but from contamination with that materials. Imagine if few specks of radioactive dirt stain your everyday clothes or if you inhale radioactive atoms.

They will remain with you all the time and will shoot the “bullets” at you even when you are sleeping.

In many cases, a very effective way of protecting yourself from the radiation is to keep certain distance. Radiation from nuclear sources is distributed equally in all directions. Therefore the number n of dangerous particles passing every second through a unit area (say 1 cm^2) is the total number N of particles emitted during 1 second, divided by the surface of a sphere

$$n = \frac{N}{4\pi r^2} ,$$

where r is the distance at which we make the observation. From this simple formula, it is seen that the radiation intensity falls down with increasing distance quadratically. In other words, if you increase the distance by a factor of 2, your exposure to the radiation will be decreased by a factor of 4.

5.5.4 Decay law

Unstable nuclei decay spontaneously. A given nucleus can decay next moment, next day or even next century. Nobody can predict when it is going to happen. Despite this seemingly chaotic and “unscientific” situation, there is a strict order in all this.

Atomic nuclei, being microscopic objects, are ruled by quantum probabilistic laws. Although we cannot predict the exact moment of its decay, we can calculate the probability that a nucleus will decay within this or that time interval. Nuclei decay because of their internal dynamics and not because they become “old” or somehow “rotten”.

To illustrate this, let us imagine that yesterday morning we found that a certain nucleus was going to decay within 24 hours with the probability of 50%. However, this morning we found that it is still “alive”. This fact does not mean that the decay probability for another 24 hours increased. Not at all! It remains the same, 50%, because the nucleus remains the same, nothing wrong happened to it. This can go on and on for centuries.

Actually, we never deal with individual nuclei but rather with huge numbers of identical nuclei. For such collections (ensembles) of quantum objects, the probabilistic laws becomes statistical laws. Let us assume that in the above example we had 1 million identical nuclei instead of only one. Then by this morning only half of these nuclei would survive because the decay probability for 24 hours was 50%. Among the remaining 500000 nuclei, 250000 will decay by tomorrow morning, then after another 24 hours only 125000 will remain and so on.

The number of unstable nuclei that are still “alive” continuously decreases with time according to the curve shown in Fig. 5.2. If initially, at time $t = 0$, their number is N_0 , then after certain time interval $T_{1/2}$ only half of these nuclei will remain, namely, $\frac{1}{2}N_0$. Another one half of the remaining half will decay during another such interval. So, after the time $2T_{1/2}$, we will have only one

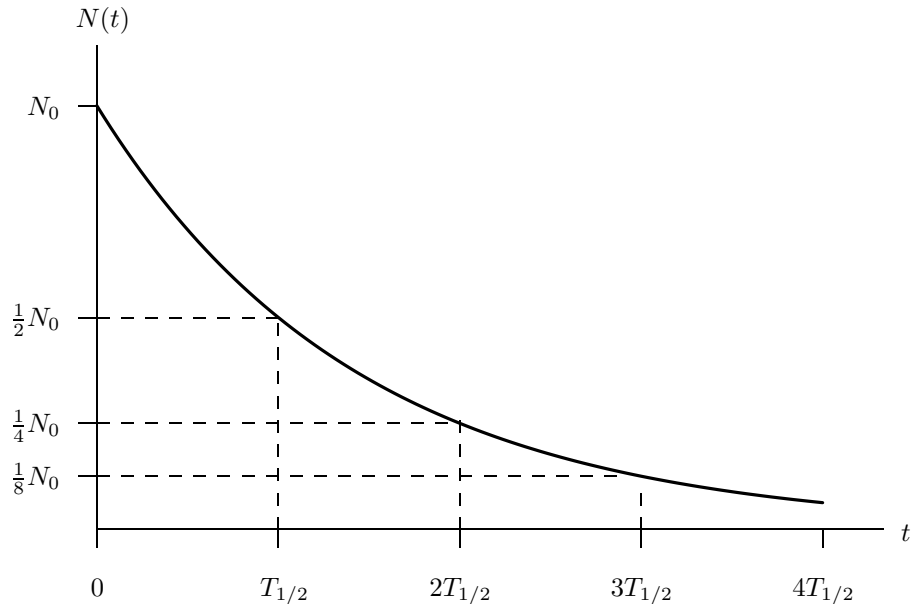


Figure 5.2: The time $T_{1/2}$ during which one half of the initial amount of unstable particles decay, is called their half-life time.

quarter of the initial amount, and so on. The time interval $T_{1/2}$, during which one half of unstable nuclei decay, is called their *half-life time*. It is specific for each unstable nucleus and vary from a fraction of a second to thousands and millions of years. Few examples of such lifetimes are given in Table 5.2

5.5.5 Radioactive dating

Examining the amounts of the decay products makes possible radioactive dating. The most famous is the *Carbon dating*, a variety of radioactive dating which is applicable only to matter which was once living and presumed to be in equilibrium with the atmosphere, taking in carbon dioxide from the air for photosynthesis.

Cosmic ray protons blast nuclei in the upper atmosphere, producing neutrons which in turn bombard nitrogen, the major constituent of the atmosphere. This neutron bombardment produces the radioactive isotope $^{14}_6\text{C}$. The radioactive carbon-14 combines with oxygen to form carbon dioxide and is incorporated into the cycle of living things.

The isotope $^{14}_6\text{C}$ decays (see Table 5.2) inside living bodies but is replenished from the air and food. Therefore, while an organism is alive, the concentration of this isotope in the body remains constant. After death, the replenishment from the breath and food stops, but the isotopes that are in the dead body

| isotope | $T_{1/2}$ | decay mode |
|--------------------------|---------------------------------|-------------------|
| ${}^{214}_{84}\text{Po}$ | $1.64 \times 10^{-4} \text{ s}$ | α, γ |
| ${}^{89}_{36}\text{Kr}$ | 3.16 min | β^-, γ |
| ${}^{222}_{86}\text{Rn}$ | 3.83 days | α, γ |
| ${}^{90}_{38}\text{Sr}$ | 28.5 years | β^- |
| ${}^{226}_{88}\text{Ra}$ | 1.6×10^3 years | α, γ |
| ${}^{14}_6\text{C}$ | 5.73×10^3 years | β^- |
| ${}^{238}_{92}\text{U}$ | 4.47×10^9 years | α, γ |
| ${}^{115}_{49}\text{In}$ | 4.41×10^{14} years | β^- |

Table 5.2: Half-life times of several unstable isotopes.

continue to decay. As a result the concentration of ${}^{14}_6\text{C}$ in it gradually decreases according to the curve shown in Fig. 5.2. The time $t = 0$ on this Figure corresponds to the moment of death, and N_0 is the equilibrium concentration of ${}^{14}_6\text{C}$ in living organisms.

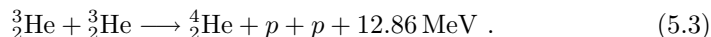
Therefore, by measuring the radioactive emissions from once-living matter and comparing its activity with the equilibrium level of emissions from things living today, an estimation of the time elapsed can be made. For example, if the rate of the radioactive emissions from a piece of wood, caused by the decay of ${}^{14}_6\text{C}$, is one-half lower than from alive trees, then we can conclude that we are at the point $t = T_{1/2}$ on the curve 5.2, i.e. it is elapsed exactly one half-life-time period. According to the Table 5.2), this means that the tree, from which this piece of wood was made, was cut approximately 5730 years ago. This is how physicists help archaeologists to assign dates to various organic materials.

5.6 Nuclear reactions

Those of you who studied chemistry, are familiar with the notion of chemical reaction, which, in essence, is just regrouping of atoms that constitute molecules. As a result, reagent chemical compounds are transformed into product compounds.

In the world of nuclear particles, similar processes are possible. When nuclei are close to each other, nucleons from one nucleus can “jump” into another one. This happens because there are attractive and repulsive forces between the nucleons. The complicated interplay of these forces may cause their regrouping. As a result, the reagent particles are transformed into product particles. Such processes are called *nuclear reactions*.

For example, when two isotopes ${}^3_2\text{He}$ collide, the six nucleons constituting them, can rearrange in such a way that the isotope ${}^4_2\text{He}$ is formed and two protons are liberated. Similarly to chemical reactions, this process is denoted as



The same as in chemical reactions, nuclear reactions can also be either exothermic (i.e. releasing energy) or endothermic (i.e. requiring an energy input). The above reaction releases 12.86 MeV of energy. This is because the total mass on the left hand side of Eq. (5.3) is in 12.86 MeV greater than the total mass of the products on the right hand side (you can check this using Table 5.1).

Thus, when considering a particular nuclear reaction, we can always learn if it releases or absorbs energy. For this, we only need to compare total masses on the left and right hand sides of the equation. Now, you can understand why it is very convenient to express masses in the units of energy.

Composing equations like (5.3), we should always check the superscripts and subscripts of the nuclei in order to have the same number of nucleons and the same charge on both sides of the equation. In the above example, we have six nucleons and the charge +4 in both the initial and final states of the reaction. To make the checking of nucleon number and charge conservation easier, sometimes the proton and neutron are denoted with superscripts and subscripts as well, namely, 1_1p and 1_0n . In this case, all we need is to check that sum of superscripts and sum of subscripts are the same on both sides of the equation.

5.7 Detectors

How can we observe such tiny tiny things as protons and α -particles? There is no microscope that would be able to discern them. From the very beginning of the sub-atomic era, scientists have been working on the development of special instruments that are called particle detectors. These devices enable us either to register the mere fact that certain particle has passed through certain point in space or to observe the trace of its path (the trajectory). Actually, this is as good as watching the particle. Although the particle sizes are awfully small, when passing through some substances, they leave behind visible traces of tens of centimeters in length. By measuring the curvature of the trajectory of a particle deflected in electric or magnetic field, a physicist can determine the charge and mass of the particle and thus can identify it.

5.7.1 Geiger counter

The most familiar device for registering charged particles is the Geiger counter. It cannot tell you anything about the particle except the fact that it has passed through the counter. The counter consists of a thin metal cylinder filled with gas. A wire electrode runs along the center of the tube and is kept at a high voltage ($\sim 2000 \text{ V}$) relative to the cylinder. When a particle passes through the tube, it causes ionization of the gas atoms and thus an electric discharge between

the cylinder and the wire. The electric pulse can be counted by a computer or made to produce a “click” in a loudspeaker. The number of counts per second tells us about intensity of the radiation.

5.7.2 Fluorescent screen

The very first detector was the fluorescent screen. When a charged particle hits the screen, a human eye can discern a flash of light at the point of impact. In fact, we all use this kind of detectors every day when watching TV or looking at a computer (if it does not have an LCD screen of course). Indeed, the images on the screens of their electron-ray tubes are formed by the accelerated electrons.

5.7.3 Photo-emulsion

Another type of particle detector, dating back to Becquerel, is the nuclear photographic emulsion. Passage of charged particles is recorded in the emulsion in the same way that ordinary black and white photographic film records a picture. The only difference is that nuclear photoemulsion is made rather thick in order to catch a significant part of the particle path. After the developing, a permanent record of the charged particle trajectory is available.

5.7.4 Wilson’s chamber

In the fields of sub-atomic physics and nuclear physics, Wilson’s cloud chamber is the most fundamental device to observe the trajectories of particles. Its basic principle was discovered by C. T. R. Wilson (UK, 1869 - 1959) in 1897, and it was put to the practical use in 1911.

The top and the side of the chamber is covered by glasses, and of a diameter of several centimeters. At the bottom of the chamber, a piston is placed. The air filled in the chamber is saturated with vapor of water. When pulling down the piston quickly, the volume of the chamber would be expanded and the temperature goes down, and then the air inside would be supersaturated with the vapor. If a charged particle enters into such a supersaturated state to form ions, the vapor of water would condense along the line of the ions, which is the path of the charge. Thus we can observe the trace, and also take a photograph. To make clear the trace, a light is sometimes illuminated from the side. When placing the cloud chamber in a magnetic field, we can obtain various informations about the charged particle by measuring the curvature of the trace and other data. The bubble chamber and the spark chamber have taken place of the cloud chamber which is nowadays used only for the educational purposes. Wilson’s cloud chamber has however played a very important role in the history of physics.

5.7.5 Bubble chamber

Bubble chamber is a particle detector of major importance during the initial years of high-energy physics. The bubble chamber has produced a wealth of physics from about 1955 well into the 1970s. It is based on the principle of bubble formation in a liquid heated above its boiling point, which is then suddenly

expanded, starting boiling where passing charged particles have ionized the atoms of the liquid. The technique was honoured by the Nobel prize award to D. Glaser in 1960. Even today, bubble chamber photographs provide the aesthetically most appealing visualization of subnuclear collisions.

5.7.6 Spark chamber

Spark chamber is a historic device using electric discharges over a gap between two electrodes with large potential difference, to render passing particles visible. Sparks occurred where the gas had been ionized. Most often, multiple short gaps were used, but wide-gap chambers with gaps up to 40 cm were also built. The spark chamber is still of great scientific value in that it remains relatively simple and cheap to build as well as enabling an observer to view the paths of charged particles.

5.8 Nuclear energy

Nuclei can produce energy via two different types of reactions, namely, *fission* and *fusion* reactions. Fission is a break up of a nucleus in two or more pieces (smaller nuclei). Fusion is the opposite process: Formation of a bigger nucleus from two small nuclei.

A question may arise: How two opposite processes can both produce energy? Can we make an inexhaustible source of energy by breaking up and then fusing the same nuclei? Of course not! The energy conservation law cannot be circumvented in no way. When speaking about fusion and fission, we speak about different ranges of nuclei. Energy can only be released when either light nuclei fuse or heavy nuclei fission.

To understand why this is so, let us recollect that for releasing energy the mass of initial nuclei must be greater than the mass of the products of a nuclear reaction. The mass difference is transformed into the released energy. And why the product nuclei can lose some mass as compared to the initial nuclei? Because they are more tightly bound, i.e. their binding energies are larger.

Fig. 5.3 shows the dependence of the binding energy B per nucleon on the number A of nucleons constituting a nucleus. As you see, the curve reaches the maximum value of ~ 9 MeV per nucleon at around $A \sim 50$. The nuclei with such number of nucleons cannot produce energy neither through fusion nor through fission. They are kind of “ashes” and cannot serve as a fuel. In contrast to them, very light nuclei, when fused with each other, make more tightly bound products as well as very heavy nuclei do when split up in lighter fragments.

In fission processes, which were discovered and used first, a heavy nucleus like, for example, uranium or plutonium, splits up in two fragments which are both positively charged. These fragments repel each other by an electric force and move apart at a high speed, distributing their kinetic energy in the surrounding material.

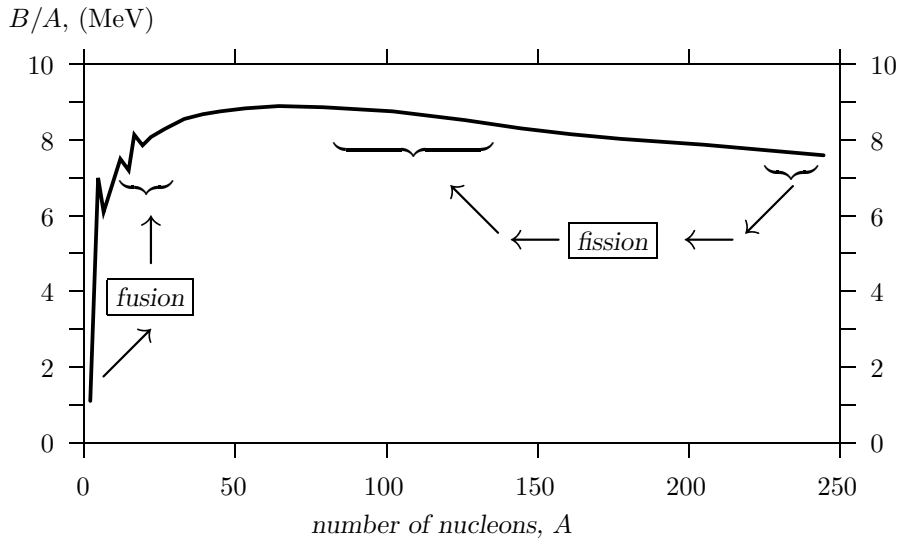


Figure 5.3: Binding energy per nucleon.

In fusion reactions everything goes in the opposite direction. Very light nuclei, like hydrogen or helium isotopes, when approaching each other to a distance of a few fm ($1 \text{ fm} = 10^{-13} \text{ cm}$), experience strong attraction which overpowers their Coulomb (that is electric) repulsion. As a result the two nuclei fuse into a single nucleus. They collapse with extremely high speeds towards each other. To form a stable nucleus they must get rid of the excessive energy. This energy is emitted by ejecting a neutron or a photon.

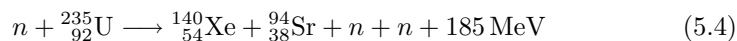
5.8.1 Nuclear reactors

Since the discovery of radioactivity it was known that heavy nuclei release energy in the processes of spontaneous decay. This process, however, is rather slow and cannot be influenced (speed up or slow down) by humans and therefore could not be effectively used for large-scale energy production. Nonetheless, it is ideal for feeding the devices that must work autonomously in remote places for a long time and do not require much energy. For this, heat from the spontaneous-decays can be converted into electric power in a radioisotope thermoelectric generator. These generators have been used to power space probes and some lighthouses built by Russia. Much more effective way of using nuclear energy is based on another type of nuclear decay which is considered next.

Chain reaction

The discovery that opened up the era of nuclear energy was made in 1939 by German physicists O. Hahn, L. Meitner, F Strassmann, and O. Frisch. They found that a uranium nucleus, after absorbing a neutron, splits into two frag-

ments. This was not a spontaneous but induced fission



that released $\sim 185 \text{ MeV}$ of energy as well as two neutrons which could cause similar reactions on surrounding nuclei. The fact that instead of one initial neutron, in the reaction (5.4) we obtain two neutrons, is crucial. This gives us the possibility to make the so-called *chain reaction* schematically shown in Fig. 5.4.

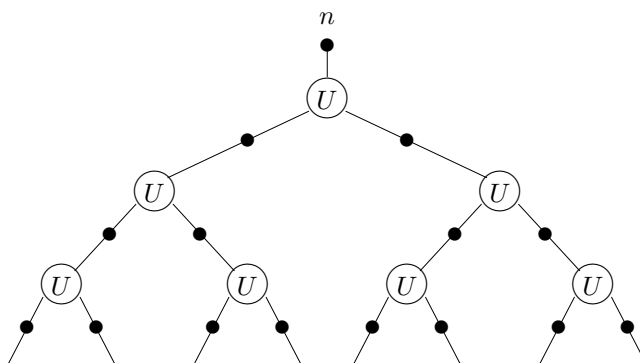


Figure 5.4: Chain reaction on uranium nuclei.

In such process, one neutron breaks one heavy nucleus, the two released neutrons break two more heavy nuclei and produce four neutrons which, in turn, can break another four nuclei and so on. This process develops extremely fast. In a split of a second a huge amount of energy can be released, which means explosion. In fact, this is how the so-called atomic bomb works.

Can we control the development of the chain reaction? Yes we can! This is done in nuclear reactors that produce energy for our use. How can it be done?

Critical mass

First of all, if the piece of material containing fissile nuclei is too small, some neutrons may reach its surface and escape without causing further fissions. For each type of fissile material there is therefore a minimal mass of a sample that can support explosive chain reaction. It is called the *critical mass*. For example, the critical mass of ${}^{235}_{92}\text{U}$ is approximately 50 kg. If the mass is below the critical value, nuclear explosion is not possible, but the energy is still released and the sample becomes hot. The closer mass is to its critical value, the more energy is released and more intensive is the neutron radiation from the sample.

The criticality of a sample (i.e. its closeness to the critical state) can be reduced by changing its geometry (making its surface bigger) or by putting inside it some other material (boron or cadmium) that is able to absorb neutrons. On

the other hand, the criticality can be increased by putting neutron reflectors around the sample. These reflectors work like mirrors from which the escaped neutrons bounce back into the sample. Thus, moving in and out the absorbing material and reflectors, we can keep the sample close to the critical state.

How a nuclear reactor works

In a typical nuclear reactor, the fuel is not in one piece, but in the form of several hundred vertical rods, like a brush. Another system of rods that contain a neutron absorbing material (control rods) can move up and down in between the fuel rods. When totally in, the control rods absorb so many neutrons, that the reactor is shut down. To start the reactor, operator gradually moves the control rods up. In an emergency situation they are dropped down automatically.

To collect the energy, water flows through the reactor core. It becomes extremely hot and goes to a steam generator. There, the heat passes to water in a secondary circuit that becomes steam for use outside the reactor enclosure for rotating turbines that generate electricity.

Nuclear power in South Africa

By 2004 South Africa had only one commercial nuclear reactor supplying power into the national grid. It works in Koeberg located 30 km north of Cape Town. A small research reactor was also operated at Pelindaba as part of the nuclear weapons program, but was dismantled.

Koeberg Nuclear Power station is a uranium Pressurized Water Reactor (PWR). In such a reactor, the primary coolant loop is pressurised so the water does not boil, and heat exchangers, called steam generators, are used to transmit heat to a secondary coolant which is allowed to boil to produce steam. To remove as much heat as possible, the water temperature in the primary loop is allowed to rise up to about 300 °C which requires the pressure of 150 atmospheres (to keep water from boiling).

The Koeberg power station has the largest turbine generators in the southern hemisphere and produces ~10000 MWh of electric energy. Construction of Koeberg began in 1976 and two of its Units were commissioned in 1984-1985. Since then, the plant has been in more or less continuous operation and there have been no serious incidents.

Eskom that operates this power station, may be the current technology leader. It is developing a new type of nuclear reactor, a modular pebble-bed reactor (PBMR). In contrast to traditional nuclear reactors, in this new type of reactors the fuel is not assembled in the form of rods. The uranium, thorium or plutonium fuels are in oxides (ceramic form) contained within spherical pebbles made of pyrolytic graphite. The pebbles, having a size of a tennis ball, are in a bin or can. An inert gas, helium, nitrogen or carbon dioxide, circulates through the spaces between the fuel pebbles. This carries heat away from the reactor.

Ideally, the heated gas is run directly through a turbine. However since the gas from the primary coolant can be made radioactive by the neutrons in the reactor, usually it is brought to a heat exchanger, where it heats another gas, or steam.

The primary advantage of pebble-bed reactors is that they can be designed to be inherently safe. When a pebble-bed reactor gets hotter, the more rapid motion of the atoms in the fuel increases the probability of neutron capture by $^{238}_{92}\text{U}$ isotopes through an effect known as Doppler broadening. This isotope does not split up after capturing a neutron. This reduces the number of neutrons available to cause $^{235}_{92}\text{U}$ fission, reducing the power output by the reactor. This natural negative feedback places an inherent upper limit on the temperature of the fuel without any operator intervention.

The reactor is cooled by an inert, fireproof gas, so it cannot have a steam explosion as a water reactor can.

A pebble-bed reactor thus can have all of its supporting machinery fail, and the reactor will not crack, melt, explode or spew hazardous wastes. It simply goes up to a designed "idle" temperature, and stays there. In that state, the reactor vessel radiates heat, but the vessel and fuel spheres remain intact and undamaged. The machinery can be repaired or the fuel can be removed.

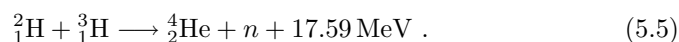
A large advantage of the pebble bed reactor over a conventional water reactor is that they operate at higher temperatures. The reactor can directly heat fluids for low pressure gas turbines. The high temperatures permit systems to get more mechanical energy from the same amount of thermal energy.

Another advantage is that fuel pebbles for different fuels might be used in the same basic design of reactor (though perhaps not at the same time). Proponents claim that some kinds of pebble-bed reactors should be able to use thorium, plutonium and natural unenriched Uranium, as well as the customary enriched uranium. One of the projects in progress is to develop pebbles and reactors that use the plutonium from surplus or expired nuclear explosives.

On June 25, 2003, the South African Republic's Department of Environmental Affairs and Tourism approved Eskom's prototype 110 MW pebble-bed modular reactor for Koeberg. Eskom also has approval for a pebble-bed fuel production plant in Pelindaba. The uranium for this fuel is to be imported from Russia. If the trial is successful, Eskom says it will build up to ten local PBMR plants on South Africa's seacoast. Eskom also wants to export up to 20 PBMR plants per year. The estimated export revenue is 8 billion rand a year, and could employ about 57000 people.

5.8.2 Fusion energy

For a given mass of fuel, a fusion reactions like



yield several times more energy than a fission reaction. This is clear from the curve given in Fig. 5.3. Indeed, a change of the binding energy (per nucleon nucleon) is much more significant for a fusion reaction than for a fission reaction. Fusion is, therefore, a much more powerful source of energy. For example, 10 g of Deuterium which can be extracted from 500 litres of water and 15 g of Tritium produced from 30 g of Lithium would give enough fuel for the lifetime electricity needs of an average person in an industrialised country.

But this is not the only reason why fusion attracted so much attention from physicists. Another, more fundamental, reason is that the fusion reactions were responsible for the synthesis of the initial amount of light elements at primordial times when the universe was created. Furthermore, the synthesis of nuclei continues inside the stars where the fusion reactions produce all the energy which reaches us in the form of light.

Thermonuclear reactions

If fusion is so advantageous, why it is not used instead of fission reactors? The problem is in the electric repulsion of the nuclei. Before the nuclei on the left hand side of Eq. (5.5) can fuse, we have to bring them somehow close to each other to a distance of $\sim 10^{-13}$ cm. This is not an easy task! They both are positively charged and “refuse” to approach each other.

What we can do is to make a mixture of the atoms containing such nuclei and heat it up. At high temperatures, the atoms move very fast. They fiercely collide and loose all the electrons. The mixture becomes *plasma*, i.e. a mixture of bare nuclei and free moving electrons. If the temperature is high enough, the colliding nuclei can overcome the electric repulsion and approach each other to a fusion distance.

When the nuclei fuse, they release much more energy than was spent to heat up the plasma. Thus the initial energy “investment” pays off. The typical temperature needed to ignite the reaction of the type (5.5) is extremely high. In fact, it is the same temperature that our sun has in its center, namely, ~ 15 million degrees. This is why the reactions (5.3), (5.5), and the like are called *thermonuclear reactions*.

Human-made thermonuclear reactions

The same as with fission reactions, the first application of thermonuclear reactions was in weapons, namely, in the hydrogen bomb, where fusion is ignited by the explosion of an ordinary (fission) plutonium bomb which heats up the fuel to solar temperatures.

In an attempt to make a controllable fusion, people encounter the problem of holding the plasma. It is relatively easy to achieve a high temperature (with laser pulses, for example). But as soon as plasma touches the walls of the container, it immediately cools down. To keep it from touching the walls, various ingenious methods are tried, such as strong magnetic field and laser beams di-

rected to plasma from all sides. In spite of all efforts and ingenious tricks, all such attempts till now have failed. Most probably this straightforward approach to controllable fusion is doomed because one has to hold in hands a “piece of burning sun”.

Cold fusion

To visualize the struggle of the nuclei approaching each other, imagine yourself pushing a metallic ball towards the top of a slope shown in Fig. 5.5. The more kinetic energy you give to the ball, the higher it can clime. Your purpose is to make it fall into the narrow well that is behind the barrier.

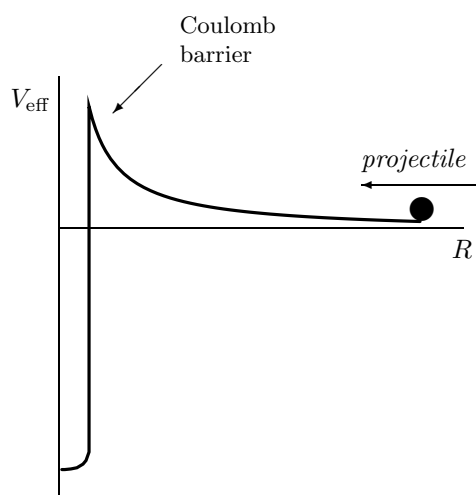


Figure 5.5: Effective nucleus–nucleus potential as a function of the separation between the nuclei.

In fact, the curve in Fig. 5.5 shows the dependence of relative potential energy V_{eff} between two nuclei on the distance R separating them. The deep narrow well corresponds to the strong short-range attraction, and the $\sim 1/R$ barrier represents the Coulomb (electric) repulsion. The nuclei need to overcome this barrier in order to “touch” each other and fuse, i.e. to fall into the narrow and deep potential well. One way to achieve this is to give them enough kinetic energy, which means to rise the temperature. However, there is another way based on the quantum laws.

As you remember, when discussing the motion of the electron inside an atom (see Sec. 5.1), we said that it formed a “cloud” of probability around the nucleus. The density of this cloud diminishes at very short and very long distances but never disappears completely. This means that we can find the electron even inside the nucleus though with a rather small probability.

The nuclei moving towards each other, being microscopic objects, obey the quantum laws as well. The probability density for finding one nucleus at a distance R from another one also forms a cloud. This density is non-zero even under the barrier and on the other side of the barrier. This means that, in contrast to classical objects, quantum particles, like nuclei, can penetrate through potential barriers even if they do not have enough energy to go over it! This is called the *tunneling effect*.

The tunneling probability strongly depends on thickness of the barrier. Therefore, instead of lifting the nuclei against the barrier (which means rising the temperature), we can try to make the barrier itself thinner or to keep them close to the barrier for such a long time that even a low penetration probability would be realized.

How can this be done? The idea is to put the nuclei we want to fuse, inside a molecule where they can stay close to each other for a long time. Furthermore, in a molecule, the Coulomb barrier becomes thinner because of electron screening. In this way fusion may proceed even at room temperature.

This idea of *cold fusion* was originally (in 1947) discussed by F. C. Frank and (in 1948) put forward by A. D. Sakharov, the “father” of Russian hydrogen bomb, who at the latest stages of his career was worldwide known as a prominent human rights activist and a winner of the Nobel Prize for Peace. When working on the bomb project, he initiated research into peaceful applications of nuclear energy and suggested the fusion of two hydrogen isotopes via the reaction (5.5) by forming a molecule of them where one of the electrons is replaced by a muon.

The muon is an elementary particle (see Sec. 5.9), which has the same characteristics as an electron. The only difference between them is that the muon is 200 times heavier than the electron. In other words, a muon is a heavy electron. What will happen if we make a muonic atom of hydrogen, that is a bound state of a proton and a muon? Due to its large mass the muon would be very close to the proton and the size of such atom would be 200 times smaller than that of an ordinary atom. This is clearly seen from the formula for the atomic Bohr radius

$$R_{\text{Bohr}} = \frac{\hbar^2}{me^2} ,$$

where the mass is in the denominator.

Now, what happens if we make a muonic molecule? It will also be 200 times smaller than an ordinary molecule. The Coulomb barrier will be 200 times thinner and the nuclei 200 times closer to each other. This is just what we need! Speaking in terms of the effective nucleus–nucleus potential shown in Fig. 5.5, we can say that the muon modifies this potential in such a way that a second minimum appears. Such a modified potential is (schematically) shown in Fig. 5.6.

The molecule is a bound state in the shallow but wide minimum of this potential. Most of the time, the nuclei are at the distance corresponding to

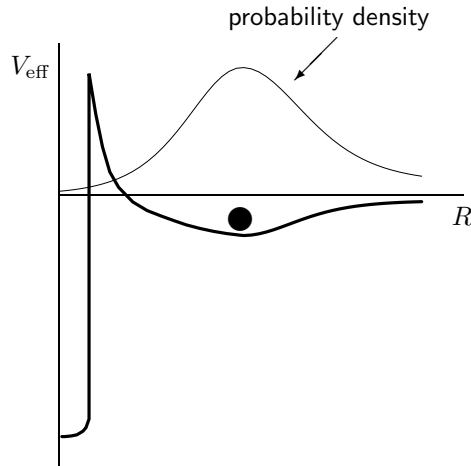


Figure 5.6: Effective nucleus–nucleus potential (thick curve) for nuclei confined in a molecule. Thin curve shows the corresponding distribution of the probability for finding the nuclei at a given distance from each other.

the maximum of the probability density distribution (shown by the thin curve). Observe that this density, though is rather small, is not zero under the barrier and even at $R = 0$. This means that the system can (with a small probability) jump from the shallow well into the deep well through the barrier, i.e. can tunnel and fuse.

Unfortunately, the muon is not a stable particle. Its lifetime is only $\sim 10^{-6}$ sec. This means that a muonic molecule cannot exist longer than 1 microsecond. As a matter of fact, from a quantum mechanical point of view, this is quite a long interval.

The quantum mechanical wave function (that describes the probability density) oscillates with a frequency which is proportional to the energy of the system. With a typical binding energy of a muonic molecule of 300 eV this frequency is $\sim 10^{17} \text{ s}^{-1}$. This means that the particle hits the barrier with this frequency and during 1 microsecond it makes 10^{11} attempts to jump through it. The calculations show that the penetration probability is $\sim 10^{-7}$. Therefore, during 1 microsecond nuclei can penetrate through the barrier 10000 times and fusion can happen much faster than the decay rate of the muon.

Cold fusion via the formation of muonic molecules was done in many laboratories, but unfortunately, it cannot solve the problem of energy production for our needs. The obstacle is the negative efficiency, *i.e.* to make muonic cold fusion we have to spend more energy than it produces. The reason is that muons do not exist like protons or electrons. We have to produce them in accelerators. This takes a lot of energy.

Actually, the muon serves as a catalyst for the fusion reaction. After helping one pair of nuclei to fuse, the muon is liberated from the molecule and can form another molecule, and so on. It was estimated that the efficiency of the energy production would be positive only if each muon ignited at least 1000 fusion events. Experimentalists tried their best, but by now the record number is only 150 fusion events per muon. This is too few. The main reason why the muon does not catalyze more reactions is that it is eventually trapped by a ${}^4\text{He}$ nucleus which is a by-product of fusion. Helium captures the muon into an atomic orbit with large binding energy, and it cannot escape.

Nonetheless, the research in the field of cold fusion continues. There are some other ideas how to keep nuclei close to each other. One of them is to put the nuclei inside a crystal. Another way out is to increase the penetration probability by using molecules with special properties, namely, those that have quantum states with almost the same energies as the excited states on the compound nucleus. Scientists try all possibilities since the energy demands of mankind grow continuously and therefore the stakes in this quest are high.

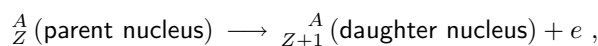
5.9 Elementary particles

In our quest for the elementary building blocks of the universe, we delved inside atomic nucleus and found that it is composed of protons and neutrons. Are the three particles, e , p , and n , the blocks we are looking for? The answer is “no”. Even before the structure of the atom was understood, Becquerel discovered the radioactivity (see Sec. 5.5.1) that afterwards puzzled physicists and forced them to look deeper, i.e. inside protons and neutrons.

5.9.1 β decay

Among the three types of radioactivity, the α and γ rays were easily explained. The emission of α particle is kind of fission reaction, when an initial nucleus spontaneously decays in two fragments one of which is the nucleus ${}^4_2\text{He}$ (i.e. α particle). The γ rays are just electromagnetic quanta emitted by a nuclear system when it transits from one quantum state to another (the same like an atom emits light).

The β rays posed the puzzle. On one hand, they are just electrons and you may think that it looks simple. But on the other hand, they are not the electrons from the atomic shell. It was found that they come from inside the nucleus! After the β -decay, the charge of the nucleus increases in one unit,



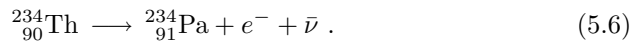
which is in accordance with the charge conservation law.

There was another puzzle associated with the β decay: The emitted electrons did not have a certain energy. Measuring their kinetic energies, you could find very fast and very slow electrons as well as the electrons with all intermediate speeds. How could identical parent nuclei, after losing different amount of energy, become identical daughter nuclei. Maybe energy is not conserving in the

quantum world? The fact was so astonishing that even Niels Bohr put forward the idea of statistical nature of the energy conservation law.

To explain the first puzzle, it was naively suggested that neutron is a bound state of proton and electron. At that time, physicists believed that if something is emitted from an object, this something must be present inside that object before the emission. They could not imagine that a particle could be created from vacuum.

The naive (pe) model of the neutron contradicted the facts. Indeed, it was known already that the pe bound state is the hydrogen atom. Neutron is much smaller than the atom. Therefore, it would be unusually tight binding, and perhaps with something else involved that keeps the size small. By the way, this “something else” could also save the energy conservation law. In 1930, Wolfgang Pauli suggested that in addition to the electron, the β decay involves another particle, ν , that is emitted along with the electron and carries away part of the energy. For example,



This additional particle was called *neutrino* (in Italian the word “neutrino” means small neutron). The neutrino is electrically neutral, has extremely small mass (may be even zero, which is still a question in 2004) and very weakly interacts with matter. This is why it was not detected experimentally till 1956. The “bar” over ν in Eq. (5.6) means that in this reaction actually the anti-neutrino is emitted (see the discussion on anti-particles further down in Sec. 5.9.2).

5.9.2 Particle physics

In an attempt to explain the β decay and to understand internal structure of the neutron a new branch of physics was born, the *particle physics*. The only way to explore the structure of sub-atomic particles is to strike them with other particles in order to knock out their “constituent” parts. The simple logic says: The more powerful the impact, the smaller parts can be knocked out.

At the beginning the only source of energetic particles to strike other particles were the cosmic rays. Earth is constantly bombarded by all sort of particles coming from the outer space. Atmosphere protects us from most of them, but many still reach the ground.

Antiparticles

In 1932, studying the cosmic rays with a bubble chamber, Carl Anderson made a photograph of two symmetrical tracks of charged particles. The measurements showed that one track belonged to an electron and the other was made by a particle having the same mass and equal but positive charge. These particles were created when a cosmic γ quantum of a high energy collided with a nucleus.

The discovered particle was called *positron* and denoted as e^+ to distinguish it from the electron, which sometimes is denoted as e^- . It was the first antiparticle discovered. Later, it was found that every particle has its “mirror reflection”, the antiparticle. It is used “bar” over a particle symbol to denote an antiparticle. For example, \bar{p} is the anti-proton, which has the same mass as an ordinary proton but a negative charge.

When a particle collides with its “mirror reflection” they annihilate, i.e. they burn out completely. In this collision, all their mass is transformed into electromagnetic energy in the form of γ quanta. For example, if an electron collides with a positron, the following reaction may take place

$$e^- + e^+ \longrightarrow \gamma + \gamma, \quad (5.7)$$

where two photons are needed to conserve the total momentum of the system.

In principle, stable antimatter can exist. For example, the pair of \bar{p} and e^+ can form an atom of anti-hydrogen with exactly the same energy states as the ordinary hydrogen. Experimentally, atoms of anti-helium were obtained. The problem with them is that surrounded by ordinary matter, they cannot live long. Colliding with ordinary atoms, they annihilate very fast.

There are speculations that our universe should be symmetric with respect to particles and antiparticles. Indeed, why should preference be given to matter and not to anti-matter? This implies that somewhere very far it must be equal amount of anti-matter, i.e. anti-universe. Can you imagine what happens if they meet?

Muon, mesons, and the others

In yet another cosmic-ray experiment a particle having the same properties as the electron but ~ 207 times heavier, was discovered in 1935. It was given the name *muon* and the symbol μ . For a long time it remained “unnecessary” particle in the picture of the world. Only the modern theories harmonically included the muon as a constituent part of the matter (see Sec 5.9.3).

The same inexhaustible cosmic rays revealed the π and K mesons in 1947. The π mesons (or simply *pions*) were theoretically predicted twelve years before by Yukawa, as the mediators of the strong forces between nucleons. The K mesons, however, were unexpected. Furthermore, they showed very strange behaviour. They were easily created only in pairs. The probability of the inverse process (i.e. their decay) was 10_{13} times lower than the probability of their creation.

It was suggested that these particles possess a new type of charge, the *strangeness*, which is conserving in the strong interactions. When a pair of such particles is created, one of them has strangeness $+1$ and the other -1 , so the total strangeness remains zero. When decaying, they act individually and therefore the strangeness is not conserving. According to the suggestion, this is only possible through the weak interactions that are much weaker than the

strong interactions (see Sec. 5.9.4) and thus the decay probability is much lower.

The golden age of particle physics began in 1950-s with the advent of particle accelerators, the machines that produced beams of electrons or protons with high kinetic energy. Having such beams available, experimentalists can plan the experiment and repeat it, while with the cosmic rays they were at the mercy of chance. When the accelerators became the main tool of exploration, the particle physics acquired its second name, the *high energy physics*.

During the last half a century, experimentalists discovered so many new particles (few of them are listed in Table 5.3) that it became obvious that they cannot all be elementary. When colliding with each other, they produce some other particles. Mutual transformations of the particles is their main property.

| family | particle | symbol | mass (MeV) | Lifetime $T_{1/2}$ (s) |
|---------|-------------------|----------------------|------------|------------------------|
| photon | photon | γ | 0 | stable |
| leptons | electron | e^-, e^+ | 0.511 | stable |
| | muon | μ^-, μ^+ | 105.7 | 2.2×10^{-6} |
| | tau | τ^-, τ^+ | 1777 | 10^{-13} |
| | electron neutrino | ν_e | ~ 0 | stable |
| | muon neutrino | ν_μ | ~ 0 | stable |
| | tau neutrino | ν_τ | ~ 0 | stable |
| hadrons | pion | π^+, π^- | 139.6 | 2.6×10^{-8} |
| | pion | π^0 | 135.0 | 0.8×10^{-16} |
| | kaon | K^+, K^- | 493.7 | 1.2×10^{-8} |
| | kaon | K_S^0 | 497.7 | 0.9×10^{-10} |
| | kaon | K_L^0 | 497.7 | 5.2×10^{-8} |
| | eta meson | η^0 | 548.8 | 10^{-18} |
| | proton | p | 938.3 | stable |
| | neutron | n | 939.6 | 900 |
| | lambda | Λ^0 | 1116 | 2.6×10^{-10} |
| | sigma | Σ^+ | 1189 | 0.8×10^{-10} |
| | sigma | Σ^0 | 1192 | 6×10^{-20} |
| | sigma | Σ^- | 1197 | 1.5×10^{-10} |
| | omega | Ω^-, Ω^+ | 1672 | 0.8×10^{-10} |

Table 5.3: Few representatives of different particle families.

Physicists faced the problem of particle classification similar to the problems of classification of animals, plants, and chemical elements. The first approach was very simple. The particles were divided in four groups according to their mass: *leptons* (light particles, like electron), *mesons* (intermediate mass, like pion), *barions* (heavy particles, like proton or neutron), and *hyperons* (very heavy particles).

Then it was realized that it would be more logical to divide the particles in three families according to their ability to interact via weak, electromagnetic, and strong forces (all particles experience gravitational attraction towards each

other). Except for the gravitational interaction, the photon (γ quantum) participates only in electromagnetic interactions, the leptons take part in both weak and electromagnetic interactions, and *hadrons* are able to interact via all forces of nature (see Sec. 5.9.4).

In addition to conservation of the strangeness, it were discovered several other conservation laws. For example, number of leptons is conserving. This is why in the reaction (5.6) we have an electron (lepton number +1) and anti-neutrino (lepton number -1) in the final state. Similarly, the number of baryons is conserving in all reactions.

The quest for the constituent parts of the neutron has led us to something unexpected. We found that there are a hundred of different particles that can be “knocked out” of the neutron but none of them are its parts. Actually, the neutron itself can be knocked out of some of them! What a mess! Further efforts of experimentalists could not find an order, which was finally discovered by theoreticians who introduced the notion of *quarks*.

5.9.3 Quarks and leptons

While experimentalists seemed to be lost in the maze, the theoreticians groped for the way out. Using an extremely complicated mathematical technique, they managed to group the hadrons in such families which implied that all known (and yet unknown) hadrons are build of only six types of particles with fractional charges. The main credit for this (in the form of Nobel Prize) was given to M. Gell-Mann and G. Zweig.

At first, they considered a subset of the hadrons and developed a theory with only three types of such truly elementary particles. When Murray Gell-Mann thought of the name for them, he came across the book “Finnegan’s Wake” by James Joyce. The line “Three quarks for Mister Mark...” appeared in that fanciful book (in German, the word “quark” means cottage cheese). He needed a name for three particles and this was the answer. Thus the term *quark* was coined.

Later, the theory was generalized to include all known particles, which required six types of quarks. Modern theories require also that the number of different leptons should be the same as the number of different quark types. Thus, the world is constructed of just twelve types of elementary building blocks that are given in Table 5.4. Amazingly enough, the electron that was discovered before all other particles, more than a century ago, turned out to be one of them!

5.9.4 Forces of nature

The interactions in the Universe are governed by four forces (strong, weak, electromagnetic and gravitational).

| family | elementary particle | symbol | charge | mass (MeV) |
|---------|---------------------|------------|--------|------------|
| leptons | electron | e^- | -1 | 0.511 |
| | muon | μ^- | -1 | 105.7 |
| | tau | τ^- | -1 | 1777 |
| | electron neutrino | ν_e | 0 | ~ 0 |
| | muon neutrino | ν_μ | 0 | ~ 0 |
| | tau neutrino | ν_τ | 0 | ~ 0 |
| quarks | up | u | +2/3 | 360 |
| | down | d | -1/3 | 360 |
| | strange | s | -1/3 | 1500 |
| | charmed | c | +2/3 | 540 |
| | top | t | +2/3 | 174000 |
| | bottom | b | -1/3 | 5000 |

Table 5.4: Elementary building blocks of the universe.

| Force | Relative Strength | Range |
|-----------------|-------------------|------------|
| Strong | 1 | Short |
| Electromagnetic | 0.0073 | Long |
| Weak | 10^{-9} | Very Short |
| Gravitational | 10^{-38} | Long |

Physicists are trying to find one theory that would describe all the forces in nature as a single law. So far they have succeeded in producing a single theory that describes the weak and electromagnetic forces (called electroweak force). The strong and gravitational forces are not yet described by this theory.

Grand unification

5.10 Origin of the universe

Nowadays, the most popular theory, describing the history of the universe, is the so-called *Big-Bang* model. The diagram given in Fig. 5.7, shows the sequence of events which led to the creation of matter in its present form.

Nobody knows what was before the Big Bang and why it happened, but it is assumed that just after this enigmatic cataclysm, the universe was so dense and hot that all four forces of nature (strong, electromagnetic, weak, and gravitational) were indistinguishable and therefore gravity was governed by quantum laws, like the other three types of interactions. A complete theory of quantum gravity has not been constructed yet, and this very first “epoch” of our history remains as enigmatic as the Big Bang itself.

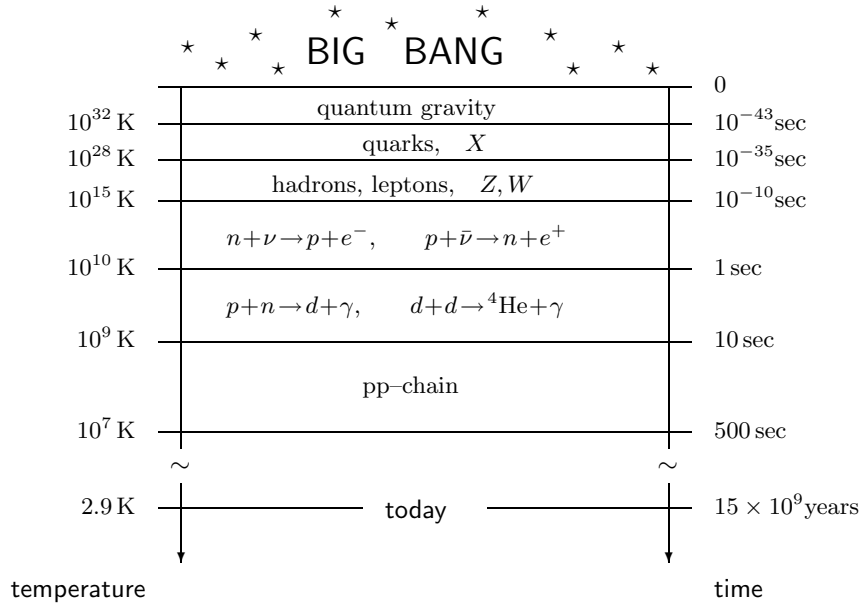


Figure 5.7: Schematic “history” of the universe.

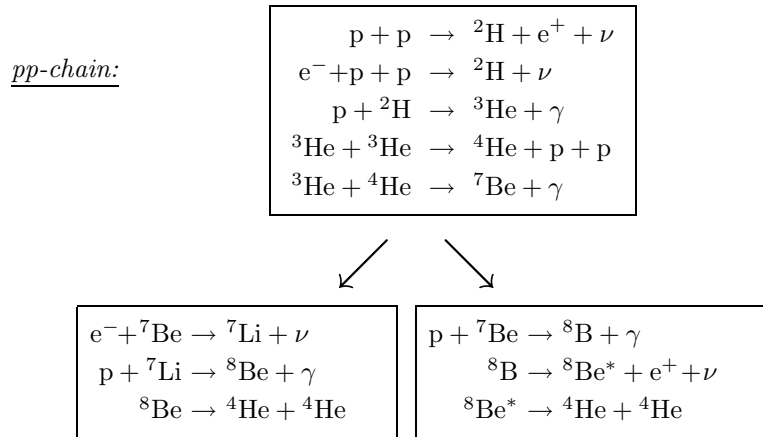
The ideal “democracy” (equality) among the forces lasted only a small fraction of a second. By the time $t \sim 10^{-43}$ sec the universe cooled down to $\sim 10^{32}$ K and the gravity separated. The other three forces, however, remained unified into one universal interaction mediated by an extremely heavy particle, the so-called X boson, which could transform leptons into quarks and vice versa.

When at $t \sim 10^{-35}$ sec most of the X bosons decayed, the quarks combined in trios and pairs to form nucleons, mesons, and other hadrons. The only symmetry which lasted up to $\sim 10^{-10}$ sec, was between the electromagnetic and weak forces mediated by the Z and W particles. From the moment when this last symmetry was broken ($\sim 10^{-10}$ sec) until the universe was about a second old, neutrinos played the most significant role by mediating the neutron-proton transmutations and therefore fixing their balance (neutron to proton ratio).

Already in few seconds after the Big Bang nuclear reactions started to occur. The protons and neutrons combined very rapidly to form deuterium and then helium. During the very first seconds there were too many very energetic photons around which destroyed these nuclei immediately after their creation. Very soon, however, the continuing expansion of the universe changed the conditions in favour of these newly born nuclei. The density decreased and the photons could not destroy them that fast anymore.

During a short period of cosmic history, between about 10 and 500 seconds, the entire universe behaved as a giant nuclear fusion reactor burning hydrogen. This burning took place via a chain of nuclear reactions, which is called the *pp-chain* because the first reaction in this sequence is the proton-proton collision leading to the formation of a deuteron. But how do we know that the scenario

was like this? In other words, how can we check the Big-Bang theory? Is it possible to prove something which happened 15 billion years ago and in such a short time? Yes, it is! The pp-chain fusion is the key for such a proof.



As soon as the nucleosynthesis started, the amount of deuterons, helium isotopes, and other light nuclei started to increase. This is shown in Fig. 5.8 for ${}^2\text{H}$ and ${}^4\text{He}$. The temperature and the density, however, continued to de-

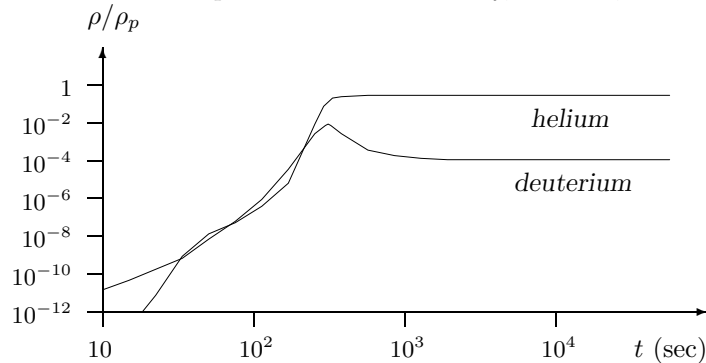


Figure 5.8: Mass fractions (relative to hydrogen) of primordial deuterium and helium versus the time elapsed since the Big Bang.

crease. After a few minutes the temperature dropped to such a level that the fusion practically stopped because the kinetic energy of the nuclei was not sufficient to overcome the electric repulsion between nuclei anymore. Therefore the abundances of light elements in the cosmos were fixed (we call them the *primordial abundances*). Since then, they practically remain unchanged, like a photograph of the past events, and astronomers can measure them. Comparing the measurements with the predictions of the theory, we can check whether our assumptions about the first seconds of the universe are correct or not.

Chapter 6

Thermal Properties & Ideal Gases (Grade 11)

- Motion of particles
- Kinetic theory of gases
- Temperature, Heat and Pressure
- Ideal Gas Law

Our interest in this chapter is to describe the behaviour of gases and to develop a simple mathematical model that allows us to predict and calculate how they behave.

We begin this development looking at the classic laws of gas behaviour, **Boyles Law**, **Charless Law** and **Avogadros Hypothesis**. Unfortunately, these laws only give accurate predictions in a small range of physical situations. We look at how these *macroscopic* laws (i.e. laws that relate to everyday human scale) are linked to the *microscopic* world of atoms and molecules. Using this approach we then develop the so-called Ideal Gas Model of gases. We then try to explain why these laws do not work in all situations.

6.1 Boyle's Law : Pressure and volume of an enclosed sample of gas

If you have ever tried to force in the plunger of a syringe or a bicycle pump while sealing the opening with a finger you will know that there is some sort of inverse relationship between the force you apply and how far in you can push it. Greater and greater forces are needed to push the plunger further and further in. In other words, the smaller you make the volume of the enclosed air, the bigger the pressure of that enclosed air.

Scientific progress is closely related to technological development : they feed and support each other. No real progress could be made in the study of gases until the 17th century when the first effective vacuum pumps were developed. An Englishman named Robert Boyle designed some excellent vacuum pumps

which allowed him to take very accurate measurements over a good range of pressures and volumes. He discovered the startlingly simple fact that the pressure and volume are not just vaguely inversely related, but are exactly inversely proportional.

Definition: Boyle's Law: The pressure of a fixed quantity of gas is inversely proportional to the volume it occupies so long as the temperature remains constant.

The standard modern laboratory version of his apparatus consists of a vertical glass tube sealed at the top end, with the other end filled up to a certain point with oil. This end is attached to an oil reservoir, which in turn has a layer of air above it (which the oil keeps separate from the trapped air.) The air trapped in the tube by oil is then subjected to various pressures (usually a bicycle pump is used to pump in air through a non-return valve) which are registered by a Bourdon gauge. As the air pressure above the oil inside the reservoir is increased, the pressure of the oil on the trapped air increases. The change in volume of the air in the tube can be read off on a scale next to it. (NOTE TO SELF: Include a diagram here!!!)

We may write this symbolically as

$$p \propto 1/V$$

which becomes the equation

$$p = a/V$$

where a is a proportionality constant. These two relations can be interpreted in two ways:

1. $p \propto 1/V$ and $pV = a$

Here we relate p and V and view the relationship between them as inverse proportion : p is inversely proportional to V ; this yields a hyperbolic graph if we plot p against V

2. $p \propto 1/V$ and $p = a(1/V)$

Here we relate p and $1/V$ and view the relationship between them as direct proportion : p is directly proportional to $1/V$; this yields a straight line (through the origin) of gradient a if we plot values of p against values of $1/V$.

Note that the law requires two conditions. First that the amount of gas stay constant. Clearly, if you let a little of the air escape from the syringe, the force you need to apply to push the plunger in further suddenly becomes less, and the inverse proportion is broken. Second, the temperature must stay constant. Cooling or heating matter generally causes it to contract or expand. If you were to heat up the gas in the syringe, it would expand and force you to apply a greater force to keep the plunger at a given position, and again the proportionality would be broken. (The idea of temperature was not well understood in Boyles time, and in any case he did not include this condition; however, his results were still very good because his apparatus stayed at a more-or-less constant room temperature.)

The parameter a (a parameter is a variable constant i.e. it is constant in a particular set of situations, but in two different sets of situations it has different constant values) is therefore clearly a function of temperature and amount of gas (moles of gas). These two factors are covered by the other two laws.

Worked Example 1 : Ideal Gas Laws I

Question: A sample of helium occupies 160 cm^3 at 100 kPa and 25 C . What volume will it occupy if the pressure is adjusted to 80 kPa and if the temperature remains unchanged ?

Answer:

1. Since T and n are fixed, the conditions for Boyles Law are met. Thus $p \propto 1/V$. Since the pressure has changed by a factor of $80/100 = 0.8$, volume must change by a factor of $1/0.8 = 1.25$. Thus the new volume must be $1.25 \cdot 160 \text{ cm}^3 = 200 \text{ cm}^3$.
2. Since $pV = a$ where a is constant (it depends on T and n , and is thus constant), we have

$$p_2 V_2 = p_1 V_1$$

(where 1 and 2 represent the initial and final states of the gas).

Thus,

$$\begin{aligned}(80) \cdot V_2 &= (100) \cdot (160) \\ V_2 &= 100 \cdot 160 / 80 \\ &= 200 \text{ cm}^3\end{aligned}$$

Note that SI units were not used, but that this is allowed here, because the conversion factor cancels out. The first method uses the meaning of inverse proportion directly, while the second sets up an equation that links the two states of the gas (before and after the change has been made.)

Assignment:

Here are some of Boyles original data. Plot graphs of p versus V and of p versus $1/V$. Does the law follow from these data ?

Note that the volume is given in terms of arbitrary marks (evenly made), and that the pressure is measured using a mercury manometer, in which the enclosed air supports a column of mercury. A gas at STP (standard temperature and pressure) can support a column of mercury that is 76 cm long i.e. 101.325 kPa is equivalent to 760 mm mercury (sometimes this is given the unit *torr* after Torricelli, a 17th century Italian Physicist and Mathematician.) Can you prove that the pressure is directly proportional to the length of the column of mercury ? (Hint : $p = F/A$)

6.2 Charles's Law: Volume and temperature of an enclosed sample of gas

About a hundred and fifty years after Boyles discovery, the Frenchman Jacques Alexandre Charles found the Law that carries his name :

| Volume (graduation mark) | Pressure (inches mercury) | Volume (graduation mark) | Pressure (inches mercury) |
|-----------------------------|------------------------------|-----------------------------|------------------------------|
| 48 | 29 2/16 | 23 | 61 5/16 |
| 46 | 30 9/16 | 22 | 64 1/16 |
| 44 | 31 15/16 | 21 | 67 1/16 |
| 42 | 33 8/16 | 20 | 70 11/16 |
| 40 | 35 5/16 | 19 | 74 2/16 |
| 38 | 37 | 18 | 77 14/16 |
| 36 | 39 5/16 | 17 | 82 12/16 |
| 34 | 41 10/16 | 16 | 87 14/16 |
| 32 | 44 3/16 | 15 | 93 1/16 |
| 30 | 47 1/16 | 14 | 100 7/16 |
| 28 | 50 5/16 | 13 | 107 13/16 |
| 26 | 54 5/16 | 12 | 117 9/16 |
| 24 | 58 13/16 | | |

Table 6.1:

Definition: Charless Law : The volume of an enclosed sample of gas is directly proportional to its absolute temperature provided the pressure is kept constant.

In symbols :

$$V \propto T$$

or

$$V = bT$$

which yields a straight line graph through the origin with a gradient of b. Now, b is a function of the two parameters of pressure (p) and molarity (n).

Again, you can imagine the apparatus to be a gas syringe containing a certain amount of air that is linked to a Bourdon gauge via a rubber pipe. However, now the plunger must be able to move freely in and out as you heat or cool the syringe in a water bath (with a thermometer in it.) In this way you can take pressure and temperature readings.

**Interesting
Fact:**

Charless Law is also known as Gay-Lussacs Law. This is because Charles did not publish his discovery, and it was rediscovered independently by another French Chemist Joseph Louis Gay-Lussac some years later.

Worked Example 2 : Ideal Gas Laws II

Question: Ammonium chloride and calcium hydroxide are allowed to react. The released ammonia is collected in a gas syringe and sealed in. This is allowed to come to room temperature which is 32°C. The volume of the ammonia is found to be 122 ml. It is now placed in a water bath set at 7°C. What will be the volume reading after the syringe has been left in the bath for a good while (assume the plunger moves completely freely) ?

Answer:

1. Since $V = bT$ and b is fixed (since it depends on p and n , both of which are constant here) we have that

$$V_2/T_2 = V_1/T_1$$

Thus

$$\begin{aligned} V_2/280 &= 122/305 \\ V_2 &= 112ml. \end{aligned}$$

2. Since

$$V \propto T$$

(p and n are constant, therefore Charles Law holds) and since the temperature changes by a factor of 280/305, it follows that the volume must change by the same factor. Therefore the new volume must be:

$$122(280/305) = 112ml$$

Note that here the temperature must be converted to Kelvin (SI) since the change from degrees Celcius involves addition, not multiplication by a fixed conversion ratio (as is the case with pressure and volume.)

6.3 Avogadro's Hypothesis: The link between number of gas particles and volume

Around the same time Charles younger Italian contemporary Amedeo Avogadro hypothesized that if you have samples of different gases, of the same volume, at a fixed temperature and pressure, then the samples must contain the same number of freely moving particles (i.e. atoms or molecules). His proposal came a few years after Daltons ground-breaking insights into the atomic nature of matter (until the early 19th century atoms were not at all understood in the way we do now.)

Definition: Avogadros Hypothesis: Equal volumes of gases kept at the same pressure and temperature contain the same number of independent units.

This essentially states that the volume occupied by any kind of gas is directly proportional to the number of gas atoms or molecules. Symbolically we can write this as

$$V \propto n$$

for p and T constant. As an equation we have

$$V = cn$$

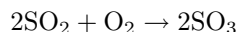
where c is a parameter depending on p and T .

Calculations very similar to the previous worked examples can be done. Heres a more advanced application :

Worked Example 3 : Ideal Gas Laws III

Question: Suppose 5 dm^3 of oxygen at a certain pressure and temperature reacts completely with excess sulphur dioxide. The resulting sulphur trioxide is allowed to return to the initial pressure and temperature conditions (assume these to be such that the sulphur trioxide is gaseous.) What volume will it occupy?

Answer: The balanced reaction equation is :



Thus 1 mol of oxygen produces 2 mol of sulphur trioxide. Since Avogadro's Hypothesis holds, the volume must change by the same factor as the number of moles yielding $25\text{dm}^3 = 10\text{dm}^3$.

6.4 Two General Equations

The three laws we have done can be summarized as follows :

$p \propto 1/V$ i.e. $pV = a$ for n and T constant

$V \propto T$ i.e. $V = bT$ for p and n constant

$V \propto n$ i.e. $V = cn$ or p and T constant

We can combine these three relations into one as

$$pV \propto nT$$

or as an equation :

$$pV = nRT$$

R is called the universal gas constant and has the value of $8.3143 \text{ J.K.mol}^{-1}$. This is essentially a constant for all gases within a certain range of physical situations. It is also sometimes written as

$$pV = mRT/M$$

using $n = m/M$.

Note that any of the three laws can be obtained from this equation by keeping two of p , V , n or T constant. For example, if n and T are kept constant then

$$pV = nRT = a.$$

A forth relation emerges if we keep V and n constant:

$$\begin{aligned} p &= (nR/V)T \\ &= dT \end{aligned}$$

where d is a constant yielding $p \propto T$. This would be quite easy to test practically. Can you come up with a design for a set of apparatus for this purpose ?

One other important equation emerges. If only n is kept constant i.e. if you have a fixed amount of gas which can change p , V or T then you have

$$pV = kT$$

or as a proportionality

$$pV \propto T.$$

Now you can relate two states by saying that

$$p_1V_1/T_1 = p_2V_2/T_2.$$

Worked Example 4 : Ideal Gas Laws IV

Question: Calculate the number of air particles in a 10 m by 7 m by 2 m classroom on a day when the temperature is 23^oC and the air pressure is 98 kPa.

Answer: The volume of the classroom is $10 \times 7 \times 2 = 140 \text{ m}^3$. The absolute temperature is 296 K. The pressure in SI is $98000 = 9.8 \times 10^4 \text{ Pa}$. Thus we can calculate the number of moles of air particles : $(9.8 \times 10^4) \cdot (140) = n \cdot (8.31) \cdot (296)$ which yields $n = 5.6 \times 10^3 \text{ mol}$. Then the number is given by $N = nN_A = (5.6 \times 10^3) \cdot (6.022 \times 10^{23}) = 3.37 \times 10^{27}$.

Worked Example 5 : Ideal Gas Laws V

Question: Calculate the molar volume of a gas at STP.

Answer: You should know at this stage that one mole of a gas at STP occupies 22.4 dm³. It is easy to show

$$\begin{aligned} V_m &= V/n \\ &= RT/p \\ &= (8.314) \cdot (273) / (1.013105) \\ &= 22.410 - \text{dm}^3. \end{aligned}$$

6.5 Overview of the Kinetic Theory of Matter

There are two very basic postulates (assumptions) that underlie the Kinetic Theory :

1. The particles of matter are in continuous motion i.e. they have kinetic energy. This motion is apparent to us as heat : when matter gains heat energy, the average speed of the particles increases and vice-versa.

2. There are forces of attraction and repulsion between the particles

This model allows us to explain phase changes for instance. In the solid phase the particles mostly vibrate about fixed points. Most have too little kinetic energy to loosen from the lattice. As the temperature increases, they vibrate faster and faster until most have enough E_k to overcome the forces of attraction keeping them in the lattice : the solid begins to melt and they now move about each other, but most still have too little E_k to separate from the liquid. Only when the temperature becomes high enough (at boiling point) do most begin to separate to form a gas. In fact absolute temperature is defined as being directly proportional to the average kinetic energy of the particles in an object :

$$T \propto E_{k_{average}} \propto v_{average}^2$$

since $E_k = \frac{1}{2}mv^2$ Also, it allows us to explain what is meant by pressure of a fluid (a gas or liquid). Pressure is a ratio of force to area

$$p = F/A$$

and each collision applies a small force to the walls of the container. If there are more collisions (when volume is made smaller), or if the collisions are more powerful (when the temperature is higher) then the pressure must increase.

THE IDEAL GAS MODEL :

Chapter 7

Organic Chemistry: Molecules (Grade 12)

- Organic molecular structures functional groups saturated and unsaturated structures, isomers
- systematic naming and formulae, structure physical property relationships
- substitution, addition and elimination reactions

(NOTE TO SELF: NOTE: I have changed the headings given in your chapter outline.)

7.1 Introduction

7.1.1 What is organic chemistry?

Organic substances all contain carbon atoms and organic chemistry can therefore be thought of as the chemistry of carbon compounds. All organic compounds also contain hydrogen. Compounds that contain only $C-C$ and $C-H$ bonds are also called hydrocarbons. In addition to carbon and hydrogen, organic compounds can also contain oxygen, nitrogen, sulphur, phosphorus and halogen atoms. The main sources of carbon, and therefore organic compounds, are fuels such as coal, petroleum and natural gas. (NOTE: If you're going to have an essay, this fact could go in the essay and be left out here.)

7.1.2 Unique properties of carbon

Carbon has some unique properties that are important to the understanding of organic chemistry.

- Carbon has four valence electrons and is therefore found in Group IV of the periodic table. Carbon forms mainly covalent bonds which means that most organic compounds are non-polar in nature. In fact, the difference in electronegativity between carbon (2.5) and hydrogen (2.1) is so small that C-H bonds are almost purely covalent.

- Carbon atoms can form up to four covalent bonds with other carbon atoms. This means that long chain structures and also ring structures may be formed. The chain structures can either be (a) straight or (b) branched:

INSERT INSERT

(a) (b)

7.1.3 Special properties of organic compounds

There are several interesting properties of organic compounds which will help explain their reactions.

- Organic compounds can have the same molecular formula but different structural formula. These substances are called structural isomers and they have different names and chemical properties.

Worked example 1: Draw two structural isomers with the molecular formula C₄H₁₀. (You won't know how to name these compounds yet, but remember to come back later and name the isomers.) INSERT

- Most organic compounds are non-polar and so there won't be many collisions between compounds. So according to the collision theory, the rates of reactions will be slow and therefore the yields of organic reactions are usually quite low.
- Since most organic compounds are non-polar, they are usually insoluble or only slightly soluble in water.
- The majority of organic compounds are gases or liquids which implies that their intermolecular forces are not very strong.
- Most organic reactions are non-stoichiometric. This means that the mass of the reactants will not equal the mass of the products and it can be explained by the poor yields of organic reactions described above.
- Two or more of the same molecule can bond together to form a long chain or polymer. The type of reaction is called polymerisation.

Worked example 2: List the dimer (two molecules) and polymer of the monomer ethene (C₂H₄).

Monomer: $H_2C = CH_2$ (ethene)

Dimer: $CH_3CH_2CH = CH_2$

Polymer: $CH_3CH_2(CH_2CH_2)_nCH = CH_2$ (polythene, where n is the number of ethene molecules)

7.1.4 Classification of organic compounds

There are so many organic compounds, due to the ability of carbon to bond to itself, that it is necessary to subdivide organic compounds into categories and give names to compounds with particular properties. Organic compounds

that contain only single bonds are called saturated (e.g. alkanes). Compounds that contain at least one double (e.g. alkenes) or triple bond (e.g. alkynes) are called unsaturated. The unsaturated compounds may also contain single bonds.

Hydrocarbons can be divided into two main categories.

- Aliphatic hydrocarbons have mainly long chain structures (it is possible for aliphatics to have ring structures too but we will not consider these here; they will have similar properties to the long chain structures though). The acyclic aliphatic compounds can be further subdivided into alkanes, alkenes and alkynes, as shown in the diagram below.
- Aromatic hydrocarbons all have unsaturated ring structures. An example of such a compound is benzene, but we will not consider aromatics in this syllabus.

Hydrocarbons

Aliphatic Aromatic (not part of syllabus)

Alkanes Alkenes Alkynes

7.1.5 Functional groups

All organic compounds have a particular bond or group of atoms which we call its functional group. This group is important in determining the reactivity of the compound and also the way in which it is named. A series of compounds with the same functional group is called a homologous series.

A few letters in the name of the examples has been written in bold. This shows the name ending which is used for a particular functional group (this will be more clear when you read the next section on naming of compounds).

INSERT FIGURES IN TABLE Homologous series Functional group Simplest example

Alkane

methane

Halo-alkane

X = F, Cl, Br, I

bromomethane

Alkene

ethene

Alkyne

ethyne

Alcohol

methanol

Aldehyde

methanal

Ketone

propanone

Carboxylic acid

methanoic acid

Ester
(R=alkyl group; eg. CH₃)
methyl methanoate

7.2 Naming and Representation of Organic Compounds

7.2.1 Naming of organic compounds

A lot of rules have been drawn up to allow us to name the many organic compounds. Before we consider all of these rules, there are two important things that you must learn.

1. You must learn how to recognise a compound's functional group. We have already discussed this in the previous section.

2. You must learn the prefixes that we use to indicate the number of carbon atoms in a main or branched chain. If the carbon atoms are in a main chain, the prefix will get an ending which shows the compound's functional group (eg. methane). If the carbon atoms form part of a branched group, then the prefix will be given the ending "yl" (eg. methyl).

No. of carbons Alkanes Alkenes Alkynes Substituents
1 methane methene methyne methyl
2 ethane ethene ethyne ethyl
3 propane propene propyne propyl
4 butane butene butyne butyl
5 pentane pentene pentyne pentyl
6 hexane hexene hexyne hexyl
7 heptane heptene heptyne heptyl
8 octane octene octyne octyl
9 nonane nonene nonyne nonyl
10 decane decene decyne decyl

Now we are ready to consider the rules for naming of organic compounds. The rules are drawn up by an organisation of chemists called IUPAC and so we sometimes refer to the IUPAC nomenclature for a compound.

We will concentrate on the naming of hydrocarbons. The rules below will be illustrated with the following example:

INSERT

1. Identify the functional group of the compound. This will determine the ending of the name.

Example: The compound is an alkene so the ending will be "ene".

2. Find the longest continuous carbon chain (it won't necessarily be a straight chain) and think of the prefix for this number of carbon atoms. If there is a double or triple bond, this must be part of the longest chain.

Example: The longest chain has 9 carbons (in this example they are in a straight line). We use the prefix "non" for nine carbon atoms.

3. Number the longest carbon chain. If there are double or triple bonds, start numbering so that these have the lowest possible number. If there are only single bonds, start at the end nearest the first branched group. The branched

groups should have the lowest numbers possible but this does not take priority over the number of the double or triple bond.

Example: The numbering must begin closest to the double bond. This means that the double bond is at carbon 2 and the compound name will end with "2-ene".

4. Name the branched groups according to the number of carbon atoms that they contain, and give them a number according to their position along the longest carbon chain.

Example: There is a branched group at carbon number 2 which has one carbon atom (methyl). There are 2 branched groups attached to carbon number 5 and they both have 3 carbon atoms (propyl).

5. Use the prefixes di-, tri-, tetra- and penta- to show the presence of 2, 3, 4 or 5 identical branched groups, or identical double and triple bonds.

Example: There are 2 propyl branched groups so they will be listed as "dipropyl".

6. Arrange the names of the branched groups alphabetically. Separate numbers and letters by hyphens and separate numbers by commas. When listing the branched groups in alphabetical order, ignore the prefixes di-, tri-, tetra- and penta-.

Example: The branched groups will be listed as: 2-methyl-5-dipropyl.

7. Combine the elements of the name into a single word in the following order: branched groups, prefix, name ending according to the functional group and its position along the longest carbon chain.

Example: The name of the compound is: 2-methyl-5,5-dipropylnon-2-ene.

Note: Although the above rules have been illustrated for hydrocarbons, the same rules will apply to other organic compounds. The main difference will be the ending of the name, which will depend on the functional group (see the table in section 18.1.5).

7.2.2 Representation of organic compounds

There are several ways to represent organic compounds. You should be familiar with all of these as you may be given any one of them and asked to name the compound.

The example 2methylpropane will be used to illustrate the three representations.

- Molecular formula: list the number of each atom as a subscript following the atomic symbol, e.g. C_4H_{10}
- Structural formula: all of the bonds between atoms must be shown, e.g. INSERT
- Condensed structural formula: each carbon atom and the hydrogens bonded directly to it are listed as a molecular formula, followed by a similar molec-

ular formula for the neighbouring carbon atom, etc; branched groups are shown in brackets after the carbon atom to which they are bonded, e.g. $CH_3CH(CH_3)CH_3$. Sometimes you may see a combination of the structural and condensed structural formula used, as it is more convenient not to show all of the $C - H$ bonds, e.g.

INSERT

7.2.3 Examples

INSERT FIGURES BELOW

Worked Example 1

Naming Organic Compounds

Question: Name the following compounds according to the IUPAC nomenclature:

- a) f)
- b) g)
- c) h)
- d) i)
- e)

Answer: a) 2-chloro-3-methylbutane;
b) 6-ethyl-4-methylnon-2-ene;
c) butan-2-ol;
d) 3-methylpentanoic acid;
e) 4,4-bromochlorohexan-2-ol;
f) 3-methylbutan-2-one;
g) ethanal;
h) 2,2-dichloro-3-methylpentanol;
i) 1,2,3-propantriol

Worked Example 2

More

Question: Give three representations for each of the following compounds. a) 1,2-dibromoethane, b) hex-2-yne, c) 1,3-pentadiene, d) 2-butanol

Answer: Compound Molecular formula Structural formula Condensed structural formula a

b

c
d

7.3 Hydrocarbons

7.3.1 Alkanes

These hydrocarbons have only single covalent bonds. This means that they are saturated which makes them quite unreactive. The general formula for an alkane is C_nH_{2n+2} where n is the number of carbon atoms.

Here are the first three alkanes in the series:

- ? methane - CH_4 or $C(1)H_2(1)+2$ H-C-H INSERT
- ? ethane - C_2H_6 or $C(2)H_2(2)+2$ H-C-C-H INSERT
- ? propane - C_3H_8 or $C(3)H_2(3)+2$ H-C-C-C-H INSERT

Substitution reactions

Substitution reactions involve the removal of a hydrogen atom which is replaced by a halogen atom (*F*, *Cl*, *Br* or *I*). The product is therefore called a halo-alkane. Since alkanes are not very reactive, heat (Δ) or light (hf) is needed to start the reaction.

?/ hf e.g. $CH_4 + Br_2 \rightarrow CH_3Br + HBr$? CH_2Br_2 ? $CHBr_3$? CBr_4

Oxidation reactions

When alkanes are burnt in air, they react with the oxygen in the air and heat is produced. This is called an oxidation or combustion reaction. Carbon dioxide and water are given off as products. Heat is also given off which tells us that these reactions are exothermic (and the heat of enthalpy ΔH will be negative).

e.g. $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{heat}$

7.3.2 Alkenes

Alkenes have the general formula C_nH_{2n} . They contain at least one double bond and since these are less stable than single bonds, alkenes are more reactive than alkanes.

Here are the first three alkenes in the series:

- ? ethene - C_2H_4 or $C(2)H_2(2)$ C=C INSERT
- ? propene - C_3H_6 or $C(3)H_2(3)$ C=C-C-H INSERT
- ? butene - C_4H_8 or $C(4)H_2(4)$ C=C-C-C-H INSERT

If the position of the double bond is not specified in the IUPAC name of the compound, then you can assume that it is at carbon number 1. These are the structures that have been shown above. However, another structural isomer is possible for the molecular formula C_4H_8 :



Addition reactions

Alkenes can undergo additional reactions since they are unsaturated. They readily react with hydrogen, water and halogens. The double bond is broken and a single, saturated bond is formed. A new group is then added to one or both of the carbon atoms that previously made up the double bond.

H_2 /Pt e.g. $H_2C=CH_2 \rightarrow H_3C-CH_3$ (hydrogenation reaction; a catalyst such as Pt is needed) $HBr \rightarrow H_3C-CH_2Br$ (halogenation reaction) $H_2O \rightarrow H_3C-CH_2OH$

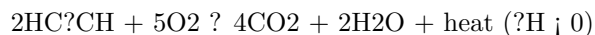
7.3.3 Alkynes

Alkyne compounds have a triple covalent bond and they are unsaturated. Triple bonds are weaker than double bonds which makes alkynes highly reactive. The general formula for alkynes is C_nH_{2n-2} . We will only consider the reactions of ethyne for the syllabus. Ethyne is prepared by dripping water onto calcium carbide, the source of the 2 carbon atoms in ethyne:



Oxidation reaction

When ethyne is burnt, it reacts with the oxygen in the air and produces carbon dioxide and water. As for the oxidation of alkanes, the reaction is exothermic.

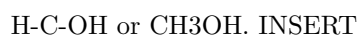


7.4 Alcohols, carboxylic acids and esters

7.4.1 Alcohols

Alcohols (or alkanols) are hydroxyl derivatives of hydrocarbons. This means that they are hydrocarbons which have an OH group in place of a H or alkyl group. The presence of the OH group makes alcohols polar and so they are soluble in water.

The simplest example of an alcohol is methanol:



7.4.2 Oxidation reactions

Alcohols can easily be oxidized by $KMnO_4$ or $K_2Cr_2O_7$ which act as oxidizing agents. The product will be an aldehyde. If an excess of the oxidizing agent is added, then a carboxylic acid is formed.

e.g. $5CH_3-CH_2-OH + MnO_4^- + 3H^+ \rightarrow 5CH_3-CHO + Mn^{2+} + 4H_2O$
ethanol (purple) ethanal (colourless)

$5CH_3-CH_2-OH + 4MnO_4^- + 12H^+ \rightarrow 5CH_3-COOH + 4Mn^{2+} + 11H_2O$
ethanol ethanoic acid

If $K_2Cr_2O_7$ is used as the oxidizing agent, then the orange colour of $Cr_2O_7^{2-}$ changes to green with the formation of Cr^{3+} ions.

7.4.3 Carboxylic acids

Carboxylic acids all contain a $COOH$ group, also called a carboxyl group. They are weak acids which is shown by their low K_a values (ionisation constants). So carboxylic acids only ionise partially in water as shown below and the equilibrium will lie far to the left:

e.g. $H_3C-COOH + H_2O \rightleftharpoons H_3C-COO^- + H_3O^+$

The simplest carboxylic acids are methanoic acid and ethanoic acid:

H-C-OH H-C-C-OH INSERT

7.4.4 Esters

Esters are the products of a reaction between an alcohol and a carboxylic acid. They all contain the functional group $COOR$ where R can be any alkyl group (e.g. CH_3 or CH_2CH_3).

The simplest example of an ester is methyl methanoate. But since this is already shown in the table of functional groups (section 18.1.5), here we will show you the reaction to produce ethyl methanoate:

$H_3C-CH_2-OH + H-C-OH \rightarrow H_3C-C-O-C-H + H_2O$ INSERT

ethanol methanoic acid ethyl methanoate

Notice that when naming an ester, the prefix of the name is derived from the alcohol and the suffix is derived from the name of the carboxylic acid.

More Worked Examples

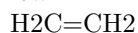
Here are some more examples to help you test your knowledge of organic chemistry.

Worked Example 3

More

Question: 1. Write down the full and condensed structural formula for:

- a) 2,4-dimethylhex-2-ene b) 3-ethylpentanoic acid.
2. Answer the following questions with regard to the compound below.



- a) Name the homologous series to which the compound belongs.
b) Give the general formula for this homologous series.
c) Give the product of the above compound with water.
d) Name the type of reaction described in (c).
e) With reference to the above compound and the product in (c), state whether the two compounds are saturated or unsaturated.
3. Write a balanced equation for the oxidation of propane.
4. a) Name the two organic compounds which, when reacted with each other, will produce the ester ethyl propanoate.
b) Give structural formulae for the two reactants and the ester product.
5. Give structural formula and names for the structural isomers of C_4H_8 .

Answer: INSERT

- 1a) b)
 $\text{H}-\text{C}-\text{C}=\text{C}-\text{C}-\text{C}-\text{C}-\text{H}$ $\text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{OH}$
 $\text{CH}_3\text{C}(\text{CH}_3)\text{CHCH}(\text{CH}_3)\text{CH}_2\text{CH}_3$ $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{COOH}$
2a) alkenes d) addition reaction b) C_nH_{2n} e) alkene is unsaturated;
c) compound (c) is saturated $\text{H}-\text{C}-\text{C}-\text{OH}$
3) $\text{C}_3\text{H}_8 + 5\text{O}_2 \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$
4a) ethanol and propanoic acid b)
 $\text{H}-\text{C}-\text{C}-\text{OH}$ $\text{H}-\text{C}-\text{C}-\text{C}-\text{OH}$ $\text{H}-\text{C}-\text{C}-\text{O}-\text{C}-\text{C}-\text{H}$
5) From the molecular formula, we can tell that this compound is an alkene since the number of carbons and hydrogens agree with the formula C_nH_{2n} . This is helpful in determining the possible structures, the most obvious of which should be butene.
but-1-ene but-2-ene 2-methylprop-1-ene

Chapter 8

Organic Chemistry: Macromolecules (Grade 12)

8.1 Plastics and Polymers

- thermoplastic and thermoset

8.2 Biological Macromolecules

These substances are natural polymers much the same as synthetic plastics are. Both are composed of long molecular chains, the links of which can either be one chemical or several different chemicals. If several chemicals make up the macromolecule, the entire chain can be used to encode information, based on the sequence of the links. The general term for natural or synthetic macromolecules is the term **polymer**, the links of the chain are known as **monomers**.

8.2.1 Polysaccharides

These are the simplest of the biological macromolecules, most are composed of only 1 kind of chemical link, a sugar. There are a number of different sugars but the two most important are *glucose* and *fructose*. Sugars are known as **carbohydrates**, the general chemical formula is (CH_2O) and most of them form five or six member rings. Single sugar molecules are known as *monosaccharides*; linking two together results in a *disaccharide*. The most common disaccharide is ordinary white sugar, known chemically as sucrose. It is a combination of glucose and fructose. Linking three or more sugars results in a polysaccharide and the most important ones are all based on the sugar glucose.

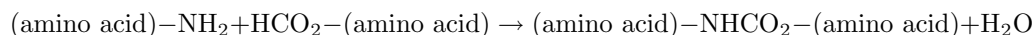
Animals use polysaccharides as an energy source and store glucose in the form of the polysaccharide glycogen. Plants polymerize glycogen further into starch. The most important polysaccharide is cellulose which plants use as a building material. Cellulose is indigestible to most animals due to the way it is polymerized by plants. In the carbohydrate chain, every other molecule of glucose is inverted. Fungi and some protozoa can metabolize cellulose however, and many larger animals such as termites and cows use these protozoa to break down cellulose into glucose. The metabolism of glucose is known as respiration.

In aerobic respiration, oxygen is used to break sugars down into carbon dioxide and water. In anaerobic respiration, sugars are broken down into alcohols in environments without oxygen. Plants use the energy of sunlight to turn carbon dioxide and water back into carbohydrates, a process known as photosynthesis. Plants thus recycle carbon dioxide and manufacture food for animals.

8.2.2 Polypeptides

These are the most complex of biological macromolecules, and in fact act like tiny machines. The polypeptide chains are composed of substances known as **amino acids**. There are around 20 different kinds of amino acids but they all are composed of a central carbon atom with an *amine* group, a *carboxylate* group, a hydrogen and one of 20 different chemical groups. Because this carbon atom has four different chemical groups attached to it it is known as a "chiral center" and amino acids all have what are known as "stereo isomers". A stereoisomer is rather like a pair of hands. Each is nearly identical except they are mirror images of one another. The importance of this is that all life on earth can only metabolize amino acids with an "L" configuration. Likewise, it can only metabolize glucose with a "D" configuration.

Amino acids are linked together by combining the amine group on one end with the carboxylate group on the other amino acid.



The chain still has an amine group on one end and a carboxyl ate group on the other end and thus, can be polymerized further. As the chain grows in size, it begins to twist into a spiral structure. This is held together by weak attachments known as "hydrogen bonds" which form between hydrogen atoms and atoms such as oxygen or nitrogen. The chain itself is known as the protein's primary structure. The spiral is called an "alpha helix" and is known as the "secondary structure" of the protein. Finally, the helix itself can bend and twist into a particular three-dimensional shape known as the protein's tertiary structure.

Proteins can be used in a number of ways. Structural proteins perform what cellulose did in plant cells, giving animal cells strength and protection. Keratin is a very common structural protein found in the animal kingdom. It is what horns, hooves, hair and scales are composed of. Natural silk is another example of this class of proteins. When proteins are used as chemical catalysts, they are known as enzymes. A catalyst is a chemical which speeds up a chemical reaction, but remains unchanged itself. Enzymes are essentially what makes cells alive. These proteins are responsible for all the chemical reactions which result in cellular functions like respiration, photosynthesis and reproduction. Enzymes are composed entirely of amino acids, but most enzymes have another non-protein compound known as a coenzyme. The coenzyme is frequently an organic compound containing a metal atom like iron, magnesium or zinc. In the enzyme hemoglobin, heme is the coenzyme and contains iron.

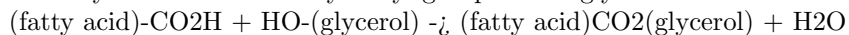
8.2.3 Polynucleotides

This polymer is known chemically as deoxyribonucleic acid and it has 4 different chemicals which form the links in its chain. Each link is known chemically as a nucleotide. Like proteins, the chain is twisted into an alpha helix but each DNA molecule is composed of two chains held together by hydrogen bonds. The outer part of the chain is composed of simple sugars and phosphate groups. To this chain are attached one of four ring like structures containing nitrogen atoms. Hydrogen atoms from the ring on the opposite helix form hydrogen bonds, and each type of ring pairs only with another particular type of ring. In DNA the ring structures are known as adenine ('A'), thiamine ('T'), cytosine ('C'), and guanine ('G'). Adenine only pairs with thiamine and cytosine only pairs with guanine. The order of ring structures along the DNA chain is used by cells to encode information regarding the sequence of amino acids in proteins. Every three links encode a single type of amino acid. The order of the links therefore is precisely correlated to the structure of proteins. Unlike proteins however, DNA can replicate itself. To do so, the two chains of DNA come apart and two new chains are created. Since each ring structure only bonds to 1 of the other three structures (both form what are known as "base pairs"), the result is two identical molecules of DNA. Since DNA can contain billions of base pairs, sometimes mistakes are made during replication. This is known as a "mutation". Most mutations are fatal, but sometimes they can be beneficial. Beneficial mutations accumulate over time and this is how new species evolve.

Simple organisms like bacteria have a single strand of DNA in a loop structure. Multicelled animals and plants have their DNA compacted into structures known as "chromosomes". When new enzymes need to be made, a section of a chromosome opens up, exposing its DNA. This is known as gene "activation". In multicelled animals and plants, the DNA is contained in a special area of the cell known as the nucleus. This protects the DNA from being damaged. Actual protein synthesis is accomplished by another polynucleotide known as RNA, or ribonucleic acid. It contains the sugar ribose and has a ring structure known as uracil instead of thiamine. The enzyme RNA polymerase copies sections of RNA from the DNA chain in the cell nucleus. The RNA then travels out of the nucleus to a structure known as a ribosome. The RNA strand and ribosome then assemble protein chains using amino acids. RNA is used this way because if it is damaged it can easily be replaced. It is possible to replace RNA and defective proteins, but if the DNA itself is damaged, it is impossible to repair.

8.2.4 Fats and Waxes

These are the smallest biological macromolecules, consisting primarily of long hydrocarbon chains. Fats are composed of fatty acids, three of which are attached to a molecule of a carbohydrate known as glycerin. The carboxylic group on the fatty acid links to the hydroxyl group on the glycerol:



The combination of a carboxylic acid and the hydroxyl group of an alcohol is known as esterification, the result being an "ester". Unlike polysaccharides, polypeptides and polynucleotides, fats don't necessarily polymerize any further once they become esters. Fats with especially long hydrocarbon chains are known as waxes. The presence of double bonds in the hydrocarbon chain is used

to classify fats. "Saturated fats" have few, if any double bonds. "Polyunsaturated fats" have many double bonds. Fats are important to cells as components of the cell membrane. This barrier functions as the cell's skin, protecting its interior from harmful chemicals. When used as a membrane, one or more phosphate groups are linked to the glycerin, forming a "phospholipid". Phospholipids are polar molecules, the phosphate attracting water and the long hydrocarbon chain repelling it. The cell membrane is composed of a double layer of phospholipid molecules, their hydrocarbon tails pointing inwards and their polar heads pointing outward. Polar molecules like water are attracted to the outside of the cell, but cannot penetrate the non-polar hydrocarbon barrier. Floating in this layer of phospholipids are large proteins known as surface enzymes. Half the enzyme is outside the cell and the other half inside. Some of these enzymes are hollow, but functioning like machines, allow only certain molecules to enter the cell. Because of this, the cell is said to have a "semipermeable membrane". Other surface enzymes are more sophisticated. When encountering a specific molecule outside the cell, the enzyme changes its shape and this triggers a chain of chemical reactions inside the cell which can involve the cell's DNA, activating genes. This is how a living cell reacts to its environment and is responsible for things such as cell differentiation in multicelled animals, and also primarily how the immune system functions.

Thus, it is seen how important biological macromolecules are to life and how large structures are sequentially built up from smaller molecules. Most biological macromolecules are composed primarily of hydrogen, oxygen, carbon and nitrogen, the chemical elements themselves being recycled with energy supplied either from the sun or as heat from the earth.

Part II

CHEMICAL CHANGE

Chapter 9

Physical and Chemical Change (Grade 10)

- Microscopic interpretation of macroscopic changes (for example changes in conductivity and temperature)
- Separation of particles in decomposition and synthesis reactions
- Conservation of atoms and mass
- Law of constant composition
- Conservation of energy
- Volume relationships in gaseous reactions

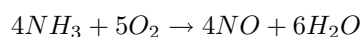
Chapter 10

Representing Chemical Change (Grade 10)

10.1 Writing Chemical Equations

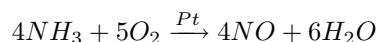
A chemical equation is an equation that expresses a chemical reaction using symbolic representation of the chemical formulae. Simply put: a chemical equation represents a chemical reaction and each molecule is represented by a chemical formula e.g. H_2O represents water.

The first equations of the Oswald Process will be used to explain how to read a chemical equation. This equation is written as:

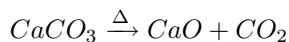


As stated earlier each compound represents a different molecule e.g. NH_3 represents Ammonia, O_2 represents oxygen, NO represents nitrogen oxide H_2O represents water. Compounds on the left of the arrow are called the reactants and the compounds on the right are called the products. A reactant is a compound that is needed for the reaction to occur, in this case the reactants are NH_3 and O_2 . What is formed from the reaction is called a product. The products in this reaction are NO and H_2O . The coefficients for each of the molecules represent the relative number of reactants needed and products formed. In this case four ammonium molecules will react with five oxygen molecules to form four nitrogen oxide molecules and six water molecules.

Occasionally a catalyst is added to the reaction. A catalyst is a substance that speeds up the reaction without undergoing any net change to itself. This is represented in the chemical equation by placing the chemical formula of the catalyst above the arrow. In this example, platinum is added as the catalyst and the equation then becomes:



To show that heat was required for the reaction to take place, a Greek delta (Δ) is placed above the arrow in the same way as that of a catalyst. For example, when calcium carbonate is heated, it decomposes to form calcium oxide and carbon dioxide as shown in the following equation.



The state of the compounds can also be expressed in the chemical equation. This is done by placing the correct label on the right hand side of the formula. There are only four labels that can be used, these are:

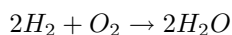
1. (g) for gaseous compounds,
2. (l) for liquid compounds,
3. (s) for solid compounds, and
4. (aq) for aqueous (water) solution.

The decomposition of calcium carbonate can now be written as:



10.2 Balancing Chemical Equations

In a chemical reaction no elements are created or destroyed, they are merely rearranged. Hence, for an equation to be balanced, the elements of each atom on the left hand side of the arrow are equal to the elements of each atom on the right hand side. Consider the production of water from hydrogen and oxygen:



One oxygen molecule (O₂) contains two O atoms. Thus the left hand side of the equation has two O atoms. Water (H₂O) contains one O atom. However, there are two water atoms on the right hand side. Thus there are two O atoms on the right hand side. The O atoms are now balanced on both sides. Hydrogen (H₂) consists of two H atoms and since there are two hydrogen molecules, there are four H atoms on the left hand side. Using the same method, there are four H atoms on the right hand side. Since all elements are equal on both sides, the chemical equation is said to be balanced.

Worked Example 6 : Balancing Chemical Equations I

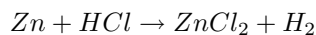
Question: Solid zinc metal reacts with aqueous hydrochloric acid to form an aqueous solution of zinc chloride and hydrogen gas. Write a balanced equation.

Answer:

Step 1 : Identify the reactants and products and their chemical formula:

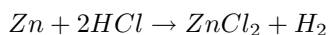
The reactants are zinc (Zn) and hydrochloric acid (HCl). The products are zinc chloride (ZnCl₂) and hydrogen (H₂).

Step 2 : Place the reactants on the left hand side and the products on the right hand side of the arrow:



Step 3 : Balance the equation:

You will notice that the zinc atoms balance but the chloride and hydrogen atoms do not. Since there are two chloride atoms on the right and only one on the left, we will give HCl a coefficient of two so that there would be two chloride atoms on each side of the equation.

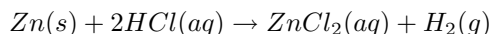


Step 4 : Recheck the balancing of the equation:

By re-examing the equation you will notice that all the atoms are now balanced.

Step 5 : Ensure all detail was added:

We were told initially that Zinc was a metal, hydrochloric acid and zinc chloride were in aqueous solutions and hydrogen was a gas.



Worked Example 7 : Balancing Chemical Equations II - The first reaction of the Oswald process

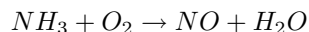
Question: You are told that ammonia reacts with oxygen over a platinum catalyst to produce nitrogen oxide and water. Produce a balanced equation.

Answer:

Step 1 : Identify the reactants and products and their chemical formula:

The reactants of this equation are ammonia (NH_3) and oxygen (O_2). The products are nitrogen oxide (NO) and water (H_2O).

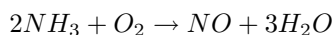
Step 2 : Place the reactants on the left hand side and the products on the right hand side of the arrow:



Step 3 : Balance the equation:

You can start balancing any atom you choose, but all the atoms have to be balanced. Usually it is best to start with atoms that appear only once on each side, in this case that will be the N and H atoms. Starting with the N atoms, there is one on the left hand side and one on the right hand side. The N atoms are balanced.

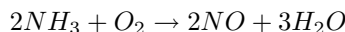
There are three H atoms on the left and only two on the right. The H atoms are not balanced. To balance the equation we will have to give NH_3 a coefficient of two and H_2O a coefficient of three. This will give six H atoms on both sides of the arrow. The equation now looks like this:



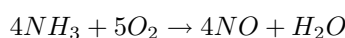
Step 4 : Recheck the balancing of the equation:

We now know that the H atoms balance, but on closer examination you will notice that the N atoms now do not balance. There are two on the left and only one on the right. **It is important to**

note that when any change has been made to the equation all atoms have to be rechecked to ensure that they still balance. To balance the N atoms, the NO molecule will have to be given a coefficient of two, hence:



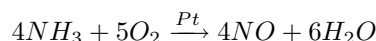
Count each of the elements again, the N and H atoms balance but the O atoms do not. There are two O atoms on the left and five on the right. To balance the equation, O₂ will need a coefficient of 2. However, since we do not like working with fractions, all molecules will be multiplied by two.



Again we have to check each of the atoms individually in the same manner as earlier. After doing this, you will notice that each of the atoms are balanced.

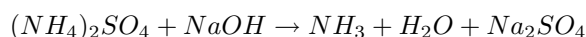
Step 5 : Ensure all detail was added:

We were told that platinum was used as a catalyst, we add *Pt* (symbol for platinum) to the reaction above the arrow.



Worked Example 8 : Balancing Chemical Equations III - Complex reaction

Question: Balance the following equation:

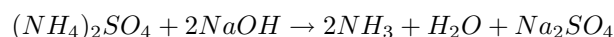


In this example steps one and two are not necessary as the reactants and products have already been given.

Answer:

Step 1 : Balance the equation:

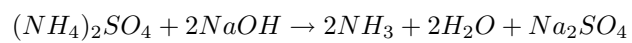
With a complex equation it is always best to start with atoms that appear only once on each side i.e. Na, N and S atoms. Since the S atoms already balance, we will start with Na and N atoms. There are two Na atoms on the right and one on the left. We will add a second Na atom by giving NaOH a coefficient of two. There are two N atoms on the left and one on the right. To balance the N atoms NH₃ will be given a coefficient of two. The equation will now look as follows:



Step 2 : Recheck the balancing of the equation:

N, Na and S atoms balance, but O and H atoms do not. There are six O atoms and ten H atoms on the left and five O atoms and eight H atoms on the right. We need to add one O atom and two H atoms

on the right to balance the equation. This is done by adding another H₂O molecule on the right hand side. Now we need to recheck the balance again.



On re-examination of the equation we see that all atoms balance!

Chapter 11

Quantitative Aspects of Chemical Change (Grade 11)

- Atomic weights
- molecular and formula weights
- determining the composition of substances
- amount of substance (mole) molar volume of gases, concentration
- stoichiometric calculations (in progress)

Chapter 12

Energy and Chemical Change (Grade 11)

- energy changes in reactions related to bond energy changes
- exothermic and endothermic reactions
- activation energy

Chapter 13

Reaction Types (Grade 11)

- acid-base and redox reactions
- substitution, addition, and elimination
- Reactions (needs some work)
- Acids and Bases (in progress)

13.1 Chemical Reactions

Chemical reactions are also known as chemical changes. This refers to the changes in the structure of molecules. Such reactions can result in molecules attaching to each other to form larger molecules, molecules breaking apart to form two or more smaller molecules, or rearrangements of atoms within molecules. Chemical reactions usually involve the making or breaking of chemical bonds. A chemical reaction does not involve or change the nucleus of the atom in any way. Only the electron clouds around the atoms, involved in the reaction, interact.

A chemical reaction can result in:

- molecules attaching to each other to form larger molecules
- molecules breaking apart to form two or more smaller molecules
- rearrangements of atoms within molecules

A chemical reaction almost always involves a change in energy, conveniently measured in terms of heat. The energy difference between the "before" and "after" states of a chemical reaction can be calculated theoretically using tables of data (or a computer). For example, consider the reaction $\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}$ (combustion of methane in oxygen). By calculating the amounts of energy required to break all the bonds on the left ("before") and right ("after") sides of the equation, we can calculate the energy difference between the reactants and the products. This is referred to as ΔH , where Δ (Delta) means difference, and H stands for enthalpy, a measure of energy which is equal to the heat transferred at constant pressure. ΔH is usually given in units of kJ (thousands of joules) or in kcal (kilocalories). If ΔH is negative for the reaction, then energy has been released. This type of reaction is referred to as exothermic

(literally, outside heat, or throwing off heat). An exothermic reaction is more favourable and thus more likely to occur. Our example reaction is exothermic, which we already know from everyday experience, since burning gas in air gives off heat.

A reaction may have a positive ΔH . This means that, to proceed, the reaction requires an input of energy from outside. This type of reaction is called endothermic (literally, inside heat, or absorbing heat).

13.2 Types of Chemical Reactions

There are various types of chemical reactions that can occur. The main groups of reactions are:

- acid-base
- redox - REDuction and Oxidation
- substitution, addition and elimination

13.3 Ionic reactions

13.3.1 What are ionic reactions?

Ionic reactions are based on the idea that opposites attract. An ionic reaction occurs when two ions, a negatively charged anion and a positively charged cation combine to form a neutral compound. Ionic reactions usually take place in a solution where the element or compound with the higher electronegativity loses an electron to become a cation and an element or compound with a high electron affinity captures the free electron to become an anion.

Ions can be single atoms, as in common table salt (sodium chloride), or more complex groups such as calcium carbonate. But to be considered ions, they must carry a positive or negative charge due to an imbalance in the ratio of protons to electrons.

Ionic reactions occurs between metals and non-metals. The atom that loses electron(s) is usually a metal whilst the atom that gains is usually a non-metal.

Some examples of cations and anions $Li^+ + F^- \rightarrow Li^+F^-$

13.3.2 Precipitation reactions

When some soluble element or compound react in water, an insoluble salt is formed. These insoluble salts are known as precipitates.

13.3.3 Formation of gases

In some reactions, the product is not a salt or a precipitate but a gas, which escapes from the solution.

Chapter 14

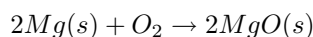
Reaction Rates (Grade 12)

- measuring rates of reaction
- mechanism of reaction and of catalysis
- application of equilibrium principles

Chemical reactions proceed at different speeds depending, for example, on the temperature or the nature of the substances which are reacting with each other. We call the substances which are undergoing the reaction, the **reactants**. The substances which are formed as a result of the reaction are called the **products**.

Definition: The *reaction rate* of a reaction describes how quickly *reactants* are used up or *products* are formed.
The units are: mols/second

For example:



This reaction rate depends on the rate at which the reactants, solid magnesium and oxygen gas, are used up, or the rate at which the product magnesium oxide is formed.

The average rate of a reaction is expressed in terms of the number of mols of reactant or product divided by the total reaction time. Using the same magnesium reaction as shown above:

$$\begin{aligned} \text{Ave rate} &= \text{mols Mg/reaction time(s)} \\ &\textit{or} \\ \text{Ave rate} &= \text{mols O}_2/\text{reaction time(s)} \\ &\textit{or} \\ \text{Ave rate} &= \text{mols MgO/reaction time(s)}. \end{aligned}$$

14.0.4 Factors affecting reaction rates

Several factors affect the rate of a reaction. It is important to know these factors so that reaction rates can be controlled, e.g. to improve product yields and efficiency in industrial processes:

1. **nature of reactants:** substances have different chemical properties and therefore react differently and at different rates
2. **concentration** (or **pressure** in the case of gases): as the concentration of reactants increases, so does the reaction rate
3. **temperature:** depending on the type of reaction (i.e. endothermic or exothermic) increasing the temperature can speed up (endothermic) or slow down (exothermic) the reaction rate
4. **catalyst:** adding a catalyst will increase the reaction rate
5. **surface area of solid reactants:** increasing the surface area of the reactants (e.g. if a solid reactant is finely broken up) will increase the reaction rate because there is more area for the reactants to touch and react with each other

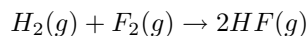
14.1 Energy changes in chemical reactions

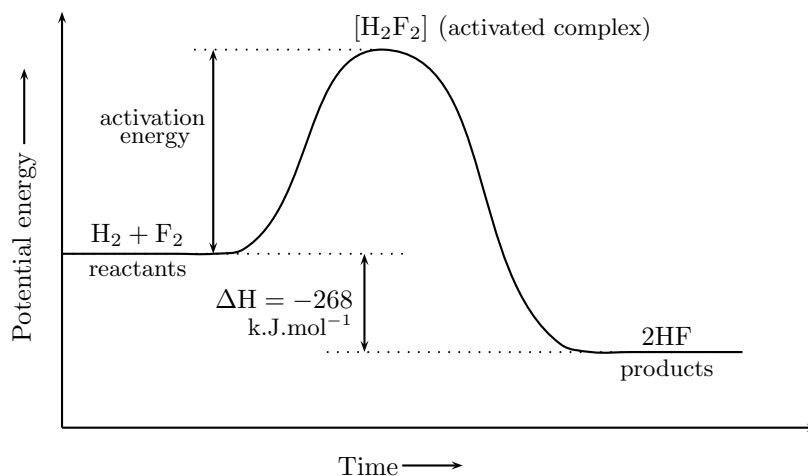
14.1.1 Exothermic and endothermic reactions

Energy changes occur during a chemical reaction. In some cases, heat energy is used up during the reaction and so the solution will cool down (**endothermic reaction**). In other reactions, heat energy is given off and the solution of products will be hot (**exothermic reaction**). If a reaction doesn't happen spontaneously, energy (e.g. heat or light) may need to be added. The difference in energy between the reactants and the products is known as the **heat of the reaction** and is represented by the symbol ΔH , where:

$$\Delta H = E_{prod} - E_{react}$$

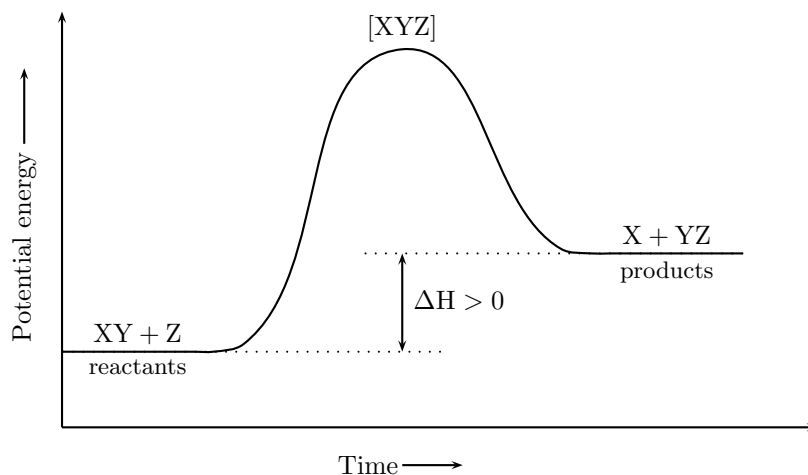
It is possible to draw an energy diagram to show energy changes that take place during a particular reaction. Let's consider an example:



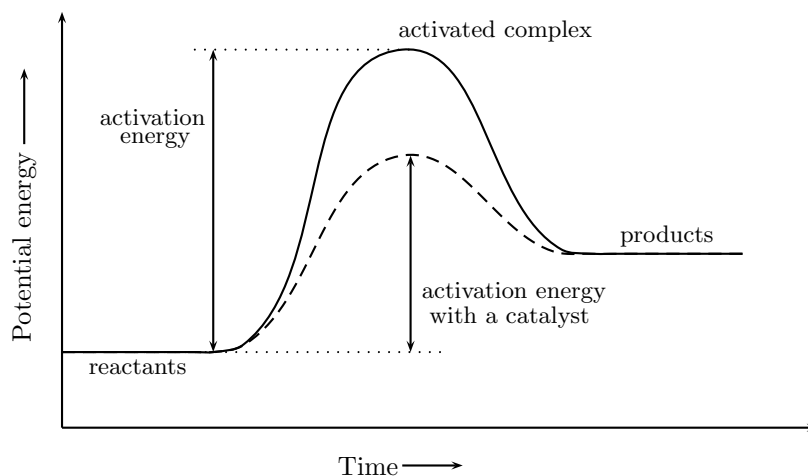


The reaction between $\text{H}_2(g)$ and $\text{F}_2(g)$ needs energy in order to proceed, called **activation energy**. An in-between, temporary state is then reached in which the two reactants combine to give H_2F_2 - this compound is called the **activated complex**. The final product is HF and it has a lower energy than the reactants. Thus ΔH is negative and the reaction is exothermic.

In an endothermic reaction, the products have a higher energy than the reactants. An energy diagram is shown below for the endothermic reaction $\text{XY} + \text{Z} \rightarrow \text{X} + \text{YZ}$.



Energy diagrams are useful to illustrate the effect of a **catalyst** on reaction rates. Catalysts decrease the activation energy required for a reaction to proceed (shown by the smaller “hump” on the energy diagram below), and therefore decrease the reaction rate. When the activated complex H_2F_2 decomposes to form the final product, the catalyst is released unchanged. Therefore the catalyst affects the reaction rate but not whether the reaction will occur.



Worked Example 9 : Reaction Rates I

Question: $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ and $\Delta H > 0$ How will the rate of the reverse reaction be affected by:

1. a decrease in temperature?
2. the addition of a catalyst?
3. the addition of more NO gas?

Answer:

1. The rate of the reverse reaction will decrease since temperature is directly proportional to the reaction rate. So will the forward reaction since temperature affects both directions.
2. The rate of the reverse (and the forward) reaction will increase.
3. The rate of the reverse (and the forward) reaction will increase since the pressure of a substance is directly proportional to the reaction rate.

Worked Example 10 : Reaction Rates II

Question:

1. Write a balanced equation of the exothermic reaction between Zn(s) and HCl.
2. Name 3 ways to increase the reaction rate between hydrochloric acid and zinc metal.

Answer:

1. $Zn(s) + 2HCl(aq) \rightleftharpoons ZnCl_2(aq) + H_2(g)$
2. A catalyst could be added, the zinc solid could be ground into a fine powder to increase its surface area, the HCl concentration could be increased or the reaction temperature could be increased.

14.2 Chemical equilibrium

14.2.1 Reversible reactions

Some reactions can take place in two directions. In one direction the reactants combine to form the products - called the forward reaction. In the other, the products react to regenerate the reactants - called the reverse reaction. A special kind of double-headed arrow is used to indicate this type of **reversible reaction**: $XY + Z \rightleftharpoons X + YZ$

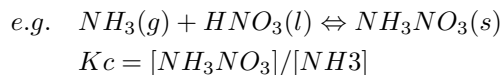
14.2.2 Dynamic equilibrium

When the rate of the forward reaction ($XY + Z \rightarrow X + YZ$) and the reverse reaction ($X + YZ \rightarrow XY + Z$) are equal, the system is said to be in **equilibrium**. Macroscopic changes do not occur at this point, but the forward and reverse reactions continue to take place and so microscopic changes occur in the system. This state is called **dynamic equilibrium**.

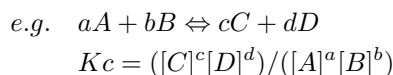
14.2.3 The equilibrium constant

An **equilibrium constant**, shown by K_c , can be computed for a reversible reaction in a closed system at a constant temperature. Consider the following reaction: $A + B \rightleftharpoons C + D$. Then, $K_c = ([C][D])/([A][B])$ where the concentrations are in $mol.dm^{-3}$.

In the case of a gas, pressure is used instead of concentration in the above formula. Solids and liquids do not affect K_c .



If the equation requires balancing, you will need to take into account the molar ratios of reactants and products.



So it is important to first balance an equation before calculating K_c .

Significance of K_c values

The formula for K_c has the concentration of the products in the numerator and concentration of reactants in the denominator. So a high K_c value means that the concentration of products is high and the reaction had a high yield. We can also say that the equilibrium lies far to the right. The opposite is true for a low K_c value. This implies a low yield and that the equilibrium lies far to the left.

Factors that affect equilibrium

Three factors can influence which direction the equilibrium of a reaction lies. These are:

1. temperature

2. concentration

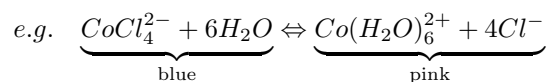
3. pressure

A catalyst can influence how quickly equilibrium is reached (since it influences the reaction rate) but not the state of equilibrium. So if we wanted to increase the yield of an important chemical process, we could force the forward reaction to be favoured by manipulating reaction conditions.

Le Chatelier's principle

Le Chatelier's Principle helps to predict what a change in temperature, concentration or pressure will have on the position of the equilibrium in a chemical reaction. It states: When the equilibrium of a closed system is disturbed, the equilibrium will shift to cause the opposite effect and so cancel the change. In other words the system will try to get back to equilibrium.

Concentration: If the concentration of a substance is increased, the equilibrium will shift so that this concentration decreases. Since K_c is fixed for a reaction at a particular temperature, if [reactant] were increased then Le Chatelier would want to shift the equilibrium to decrease [reactant].

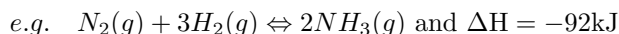


(NOTE TO SELF: Get colours here - check original)

Observation: If we add water, the solution will turn pink. However, if we add hydrochloric acid (which contain Cl^- ions) then the solution will turn blue.

Explanation: If water is added, the equilibrium will shift to use up water and therefore the forward reaction will be favoured. So the solution will turn pink. Addition of excess Cl^- ions will favour the reverse reaction in which Cl^- ions are used up. Therefore the solution will turn blue.

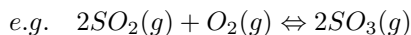
Temperature: If the temperature of a reaction mixture is increased, the equilibrium will shift to decrease the temperature. So it will favour the reaction which will "use up" heat energy, namely the endothermic reaction. The opposite is true if we decrease the temperature, namely the exothermic reaction will be favoured.



Observation: If we increase the temperature then the yield of NH_3 will decrease.

Explanation: The above reaction is exothermic, so heat is given off in the forward direction. Heat is used up in the reverse direction. So an increase in temperature will favour the endothermic reverse reaction. Since this reaction uses up NH_3 , its yield will decrease.

Pressure: in the case of gases, we refer to pressure instead of concentration. A similar principle applies as that described before for concentration.

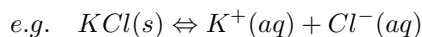


Observation: If we increase the pressure on the closed system, more SO_3 will be produced.

Explanation: The equilibrium will shift to decrease the pressure and since pressure is directly proportional to the number of moles (because $pV = nRT$), it will shift in the direction of the least number of moles of gas. The RHS contains 2 mols of gas compared with 3 mols of gas on the LHS. So the forward reaction will be favoured and more SO_3 will be produced.

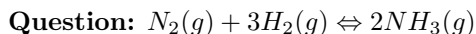
14.3 The common ion effect

A decrease in solubility of a substance when a solute containing a common ion is added is called the **common ion effect**. It can be explained using Le Chatelier's Principle.



If we add a few drops of HCl (which contains Cl^- ions) the equilibrium will shift to the left to use up the excess Cl^- ions. So more KCl solid will be produced and its solubility therefore decreases.

Worked Example 11 :

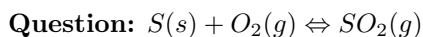


1. Write an equation for the equilibrium constant.
2. Calculate the equilibrium constant if the equilibrium concentrations are: $[NH_3] = 0.03 \text{ mol.dm}^{-3}$, $[N_2] = 0.40 \text{ mol.dm}^{-3}$, $[H_2] = 0.5 \text{ mol.dm}^{-3}$.

Answer:

1. $K_c = [NH_3]^2 / ([N_2][H_2]^3)$
2. $K_c = 0.03 / (0.4 \times 0.5^3) = 0.15$

Worked Example 12 :



1. Write an equation for the equilibrium constant.
2. Calculate the equilibrium concentration of O_2 if $K_c = 6$ and $[SO_2] = 3 \text{ mol.dm}^{-3}$ at equilibrium.

Answer:

1. $K_c = [SO_2] / [O_2]$

$$2. \quad 6 = 3 \times [O_2]$$

$$\therefore [O_2] = 2 \text{ mol} \cdot \text{dm}^{-3}$$

Worked Example 13 :

Question: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

When 0.496 mol H_2 and 0.181 mol I_2 are heated at 450°C , the equilibrium mixture is found to contain 0.00749 mol I_2 . Calculate the equilibrium constant for the reaction at 450°C .

Answer:

| | $H_2(g)$ | $I_2(g)$ | $2HI(g)$ |
|------------|----------|----------|----------|
| Mols start | 0.496 | 0.181 | |
| Mols used | 0.17351 | 0.17351 | |
| Mols eqm | 0.32249 | 0.00749 | 0.34702 |

1.

Worked Example 14 :

Question: $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$ and $\Delta H > 0$

1. State how the following changes would affect the amount of NO_2 at equilibrium:
 - (a) Increase in temperature
 - (b) Increase in pressure
 - (c) More NO is added
 - (d) Catalyst is added.
2. Explain your answer to (1a) using Le Chatelier's Principle.

Answer:

1. (a) decrease
 (b) increase
 (c) increase
 (d) no effect
2. The forward reaction will be favoured since it is endothermic and will therefore use up the heat energy and lower the temperature. Thus the equilibrium will shift to the right and the amount of NO_2 will decrease.

Worked Example 15 :

Question: How could NH_4Cl and KOH be separated in solution?

Answer: Add hydrochloric acid which has a common ion to NH_4Cl , namely Cl^- ions. This will decrease the solubility of NH_4Cl and thus

it will precipitate out of the solution and can then be separated from KOH by filtration.

14.3.1 Equilibrium in solution

14.3.2 The solubility product

Chapter 15

Electrochemical Reactions (Grade 12)

- relation of current and potential to rate and equilibrium
- understanding of the processes and redox reactions taking place in cells
standard electrode potentials

15.1 Reduction and Oxidation Reactions

15.2 Introduction

(Grade 10) Chemical reactions involve the exchange of electrons between two or more atoms or molecules. The species involved, exchange electrons which, leads to a change in the charge of both of the atoms of that species. This change in the charges of atoms (change in the atom's oxidation number) by means of electron exchange is defined as a Reduction-Oxidation (Redox) reaction.

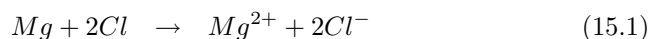
15.2.1 Oxidation and reduction

Oxidation

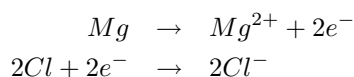
Definition: The *oxidation number* of an atom is the indicator as to what the atom's charge is. The oxidation number of Mg^{2+} is +2 whereas the oxidation number of Cl^{-} is -1.

Definition: *Oxidation* is defined as the process whereby an atom experiences an *increase* in its oxidation number.

The process whereby the atom involved loses electrons, is called *Oxidation*. Electrons have negative charges and thus the atom attains a more positive charge. An atom of magnesium is oxidized when it reacts with chlorine, i.e



can be written as 2 half reactions:



In the process of exchange of electrons when the two species react, the magnesium becomes oxidized.

Reduction

Definition: *Reduction* is defined as the process in which an atom experiences a *decrease* in its oxidation number.

The other species involved in the Redox reaction with the magnesium, is the chlorine. The chlorine atoms each gain an electron and in so doing, get a negative charge. This process of ‘accepting’ or *gaining electrons* is known as *reduction*.

15.2.2 Redox reagents

In the reaction 15.1 above, the magnesium is being oxidized by the chlorine, and the chlorine is being reduced by the magnesium. The magnesium undergoes oxidation and the chlorine undergoes reduction.

Therefore Chlorine is the **Oxidizing agent!** An *oxidizing agent* causes the other species with which it is reacting to be oxidized. In this process, the oxidizing agent *accepts electrons* and thus becomes reduced.

Magnesium is the **Reducing agent!** A *Reducing agent* causes the other species with which it is reacting to be reduced. In this process, the reducing agent *donates electrons* and thus becomes oxidized.

To summarise, magnesium is a reducing agent and in the reaction, it is oxidized because it donates its electrons and increases its oxidation number (it becomes more positive). Chlorine is an oxidizing agent and in the reaction, it is reduced because it accepts electrons and decreases its oxidation number (it becomes more negative).

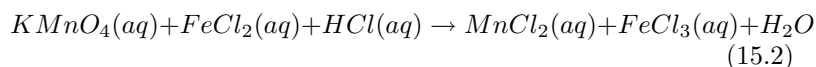
15.3 Balancing redox reactions

(Grade 12) The reaction of species involves the transfer of electrons and involves numerous steps and perhaps more than two atoms. The ion-electron method can be used successfully to balance multi-atomic redox reactions involving numerous electron transfers.

15.3.1 The ion-electron method

Worked Example 16 : Ion-electron I

The following process shows the ion-electron method which makes use of the oxidation and reduction half reactions to attain a balanced Redox reaction. We will perform this using the following reaction :-A redox reaction between potassium permanganate and iron chloride in HCl.



Step 1 : (*NOTE TO SELF: step is deprecated, use westep instead.*)

Balancing the Oxidation half reaction:

The first step in balancing this equation is to consider what species are being oxidized or reduced. This involves splitting the reaction into 2 half reactions.



The above equation involves the oxidation of the ferric ion (Fe^{2+}) to the ferrous ion (Fe^{3+}). The loss of the negatively charged electron leads to an increase in the oxidation number and a more positive charge. The addition of the electron to the right side of the equation balances out the charges.

Step 2 : (*NOTE TO SELF: step is deprecated, use westep instead.*)

Balancing the Reduction half reaction:



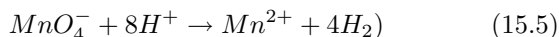
This reaction is an incomplete half reaction involving the reduction of manganese.

1. Balancing Oxygen atoms with water:

The presence of the oxygen on the left needs to be balanced on the right by adding 4 water molecules. See equation 15.2, the reaction takes place in water (aqueous = in water).

2. Balancing Hydrogen atoms with H^+ ions:

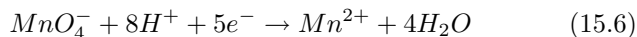
This means that the hydrogen atoms on the right have to be balanced as well:



It can be seen that the hydrogen, manganese and oxygen balance but the left side has a net charge of +7 and the right has a charge of +2.

3. Balancing charge with electrons:

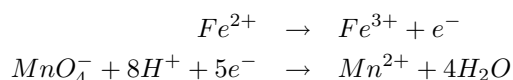
This unbalanced charge can be balanced by adding 5 negatively charged electrons to the left hand side of the equation:



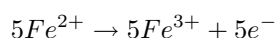
Step 3 : (*NOTE TO SELF: step is deprecated, use westep instead.*)

Combination and balancing of 2 half reactions:

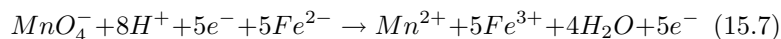
The two balanced half reactions are, 15.3 and 15.6. When combined they are as follows:



To balance the electrons for both equations when combined, the equation 15.3 needs a factor of 5 by which it must be multiplied to balance the electrons:

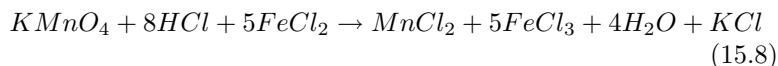


Combining both of the equations the resultant is as follows:



The two sides both have 5 electrons and these can be taken out to simplify the equation. The *spectator ions* can also be added into the final equation to complete the reaction.

Spectator Ions are those ions/species that do not take part in the Redox reaction. They do not change their oxidation number, e.g. the chloride ion Cl^{-} stays as is and only swaps cations after the redox reaction is complete. The same can be said for the potassium ion K^{+} which swaps its anions.



Step 4 : (*NOTE TO SELF: step is deprecated, use westep instead.*)

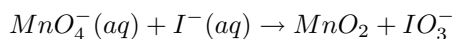
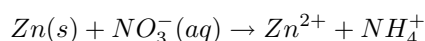
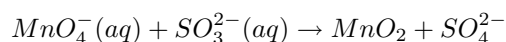
The final species check:

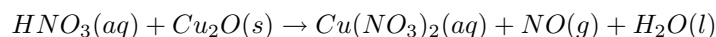
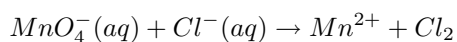
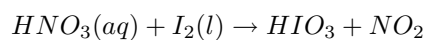
The final check is to see if all species balance on both sides of the equation.

Note: If the redox reaction occurs in a basic solution, the H^{+} ions can be substituted with OH^{-} ions to balance the equations.

Worked Example 17 : Electron-Ion 2

Question: Try a few examples with the following reactions:



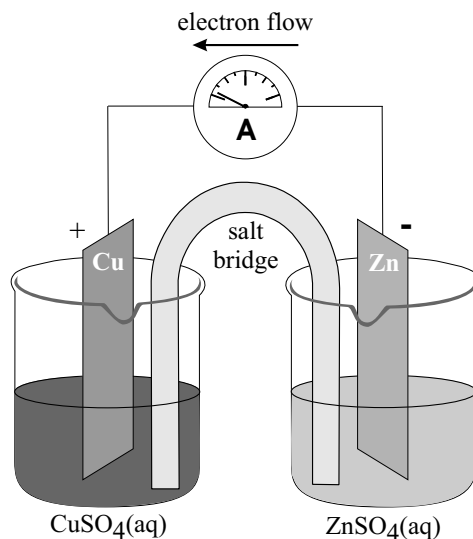


15.4 The Cu-Zn electrochemical cell

(Grades 10,12) The copper-zinc Daniel electrochemical cell is a perfect practical example to illustrate the redox reactions that occur between two different metals in ionic solutions due to their differing electrode potentials.

Definition: An *electrochemical cell* is a system comprised of electrodes dipped into an electrolyte where a chemical reaction either uses or generates electric current.

Definition: A *voltaic/galvanic cell* is an electrochemical cell that uses a chemical reaction between two dissimilar electrodes dipped in electrolyte to generate an electric current. See the diagram below.



Note that the salt bridge acts as a transfer medium that allows ions to flow through without allowing the different solutions to mix and react. The salt bridge normally is a gel medium containing electrolyte species (usually aqueous K^+ and Cl^- ions).

Due to the different oxidation potentials of the two metals, the copper metal is precipitated at the cathode as it collects the electrons donated by the zinc anode. The zinc donates its electrons and in so doing, dissolves into solution.

The result is an increased concentration of $ZnSO_4$ and a weaker solution of $CuSO_4$.

The transfer of electrons between the connected electrodes is seen as a flow of electric current. The electrons flow from the Zn anode to the Cu cathode.

The standard notation used for all voltaic/galvanic cells is:



For the typical Daniel Cell configuration:

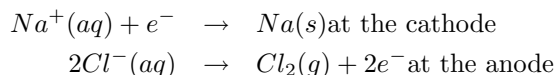


where



Definition: *An electrolytic cell* An electrolytic cell is an electrochemical cell that makes use of electricity to drive an otherwise unspontaneous chemical reaction.

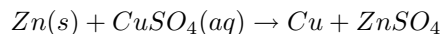
An example of this would be the electrolysis of brine (aqueous $NaCl$) to produce chlorine gas. The direct electric current is used to drive the electrochemical breakup of $NaCl$ and provides the mechanism where the chloride ions (Cl^-) are able to donate their electrons at the anode and the electrons then are provided to the Na^+ cations which deposit on the cathode. The two half reactions are as follows:



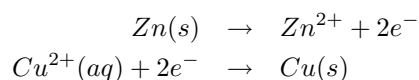
The direct current battery drives this unspontaneous reaction by providing an electro-motive force (EMF).

15.4.1 Direct electron transfer

Direct electron transfer is the mechanism by which a Redox reaction occurs between two species at the same site. For example, if a piece of metal zinc is added to a solution of copper sulphate, the following reaction occurs:



This overall reaction comprises of 2 half reactions:



The copper oxidizes the zinc and in so doing deposits itself on the zinc metal as the zinc dissolves. The result is solid copper and a solution of zinc sulphate. Zinc loses its electrons more readily than copper and thus is oxidized.

Anodes and Cathodes

The following table explains the definitions of anode and cathode:

15.5 Standard electrode potentials

(Grade 12)

15.5.1 The cell potential

The electrochemical cell is comprised of two electrodes dipped in electrolyte solutions, which due to the difference in oxidizing/reducing strength of the cell electrodes, allows for a current to pass through the cell.

The cell has an Electromotive Force with is defined as the following:

Definition: The *Electromotive Force (EMF)* of a cell is defined as the maximum *potential difference* between two electrodes or half cells of a voltaic cell. EMF is the electrical driving force of the cell reaction or any redox reaction. i.e. the *higher* the EMF, the *stronger* the reaction.

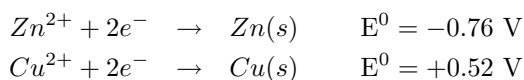
Definition: The *Standard EMF* (E_{cell}^0) is the EMF of a voltaic cell operating under standard state conditions (solute concentrations = 1M), gas pressures = 1 atm, and temperatures = 298K. The symbol 0 denotes standard-state conditions.

$$\begin{aligned} E_{cell}^0 &= \text{oxidation potential for half rxn} + \text{reduction potential for other half rxn} \\ &= E_{cathode} - E_{anode} \end{aligned}$$

Thus for a Daniel cell: (*Zn* and *Cu*)

$$\begin{aligned} E_{cell}^0 &= E_{Cu} + (-E_{Zn}) \\ E_{cell}^0 &= E_{Cu} - E_{Zn} \end{aligned}$$

From the redox reaction tables:



Thus the redox reaction of copper and zinc in a Daniel Cell will have a standard EMF

$$\begin{aligned} E_{cell}^0 &= E_{Cu} - E_{Zn} \\ E_{cell}^0 &= 0.52 + (-0.76) \\ E_{cell}^0 &= -0.24 \text{ V} \end{aligned}$$

Definition: *Potential difference* is the difference in electric potential (electric pressure to move electrons) between two points. It is measured in the S.I. units of Volts (V).

Definition: An *electrode potential* is one of the 'half' potentials which comprise the EMF. In a Daniel cell (*Zn/Cu*), the EMF of the cell is comprised of the electrode potentials of both the *Zn* and *Cu* electrodes.

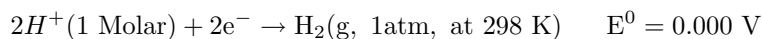
The anode of a voltaic cell has a higher negative potential than the cathode and electrons flow from the anode to the cathode.

Because only the complete cell (EMF) can be measured (Any reduction must have an oxidation reaction), the half-cell electrode potentials have to be measured against a standard or reference point. Thus the decision was made to create a standard reference electrode.

15.5.2 The standard hydrogen electrode

Standard Reference Electrode

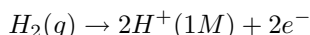
The reference point used to determine the electrode potentials of substances is the hydrogen cell. It is set up under the following standard temperature and pressure conditions. (T = 298K, Pressure = 1atm, Solute concentration = 1 Molar)



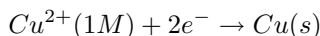
Using this standard, the various substances are linked up in a cell arrangement with the hydrogen cell and the measured EMF gives the standard electrode potential of the tested substance. The EMF measured under standard conditions is labeled as: E^0 .

As an example, the electrode potential of copper in acidic conditions is measured as follows:

At the anode: (At S.T.P. conditions)



At the cathode:



The combined reaction is as follows and the measured EMF of the hydrogen/copper voltaic cell is as follows $E_{cell} = 0.337V$. Thus it can be concluded that the Standard electrode potential of copper is $E^0 = 0.337V$.

There are lists available for many of the standard electrode potentials of substances/metals. They are measured either in acidic conditions (pH = 0, $[H^+] = 1M$) or under alkaline (pH=14, $[OH^-] = 1M$) conditions.

The table of Standard Electrode Potentials is at the end of the chapter.

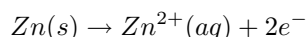
15.6 Examples of electrochemical cells

(Grades 10,12)

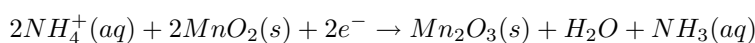
15.6.1 The dry cell (Leclanche cell)

The Leclanche cell is a Zinc-Carbon dry cell battery used commercially as a source of electrical power to drive radios, torches and walkmen. The battery is set up so that the *anode* is the Zinc can, which act as the container (Outer ‘shell’) and the *cathode* is the graphite rod, which is immediately surrounded by a paste of MnO_2 and graphite carbon (carbon black). The rest of the Zinc can is filled with a $ZnCl_2$ and NH_4Cl paste.

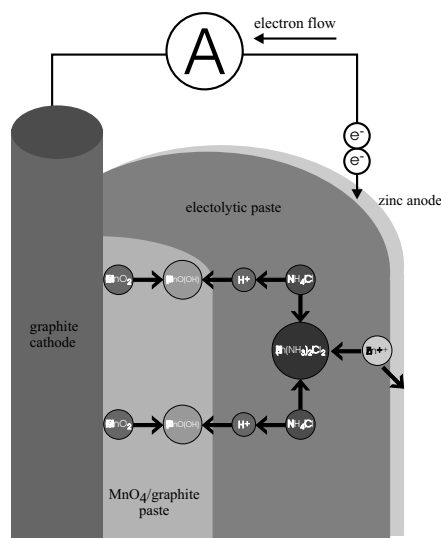
The following reactions occur in this cell: At the anode:



At the cathode:



The carbon acts as an electrode transfer point and allows the current to flow between the Zn anode and the MnO_2 /Chloride cathode.

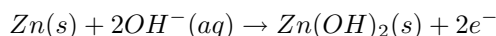


15.6.2 The alkaline dry cell

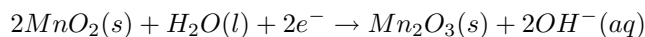
The alkaline dry cell is similar to the Leclanche cell. The difference is that the ammonium chloride (NH_4Cl) is replaced with potassium hydroxide (KOH). It performs better under low temperature conditions, has a longer shelf life and performs better under high current drain.

It isn't exactly 'dry', because it contains aqueous paste solutions as follows: The anode is Zinc powder and KOH paste surrounding a brass current collector. The cathode is a paste of MnO_2 and graphite carbon (carbon black).

The following reactions occur in this cell: At the anode:



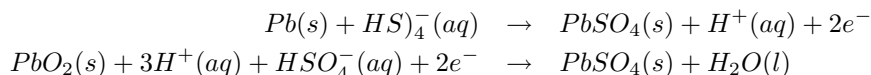
At the cathode:



15.6.3 The lead-acid accumulator

The lead-acid battery is commonly known the 12 Volt car battery. The battery is set up as follows: It consists of lead alloy grids bathed in a H_2SO_4 solution. The *anode* consists of spongy lead and the *cathode* consists of lead dioxide.

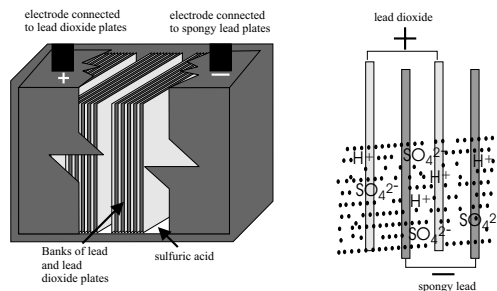
The following reactions occur in the cell:



Both electrodes are coated with a white $PbSO_4$ as the battery is used. The cells each give a 2V EMF and thus 6 are combined to give a battery of 12V.

This battery can be recharged by means of electric currents which reverse the above half reactions. In the recharging process, hydrogen and oxygen are produced and thus water needs to be periodically added to the battery to maintain a supply of water which is vital in the operation of the battery.

The recharged battery allows for replacement of the PbO_2 and Pb metal and removes the $PbSO_4$ covering. This reversal of the processes is termed **electrolytic reversal**, ie electric current is used in the electrolytic cell, which promotes the reverse reactions.

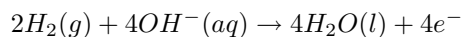


15.6.4 The fuel cell

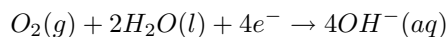
The fuel cell is essentially a battery but makes use of a continuous supply of energetic reactants. The fuel cell facilitates the oxidation of a fuel by means of air and uses the oxidation thereof to create an electric current.

For a hydrogen fuel cell (Hydrocarbon fuel cells are also in development) the following reactions occur:

Hydrogen Oxidation:(anode)



Oxygen Reduction:(cathode)



The fuel cells normally use solid catalysts to facilitate the oxidation reaction. The common catalysts are Platinum, Palladium and Silver. The expensive raw materials and problems with handling potentially explosive hydrogen, has meant that the technology has taken time to take off and become economically viable.

15.7 Electrolysis

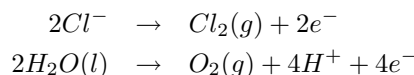
(Grade 10) As discussed in section 15.4, an electrolytic cell is an electrochemical cell that makes use of electricity to drive an otherwise unspontaneous chemical reaction (bring about chemical change to species).

Industrial examples of electrolysis being used is the production of chlorine gas from brine/sea water ($NaCl$) and the production of sodium metal by the 'Downs' process.

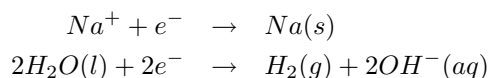
15.7.1 The Chlor-alkali Process

In the Chlor-alkali process, the electrolysis of aqueous brine takes place to produce chlorine gas and hydrogen. This takes place by means of the following reactions:

At the *anode* two reactions can occur:



whereas at the *cathode*, the following happens:

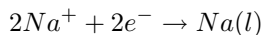
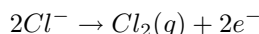


When the chloride concentration is high, the chloride oxidation is favoured but in low concentration brines, the oxidation of water is favoured. The potential products of this process, chlorine, hydrogen, sodium, $NaOH$ and oxygen, are all valuable industrial raw materials for other processes.

15.7.2 The Downs process

In the 'Downs' process, electric current is passed through molten $NaCl$ salt (at $\pm 900^\circ C$) and the resistive heating keeps the salt molten. The electric current facilitates the production of sodium metal and chlorine gas. The redox reactions are as follows:

At the anode:



The electric current acts as a driving force for the redox reactions to occur.

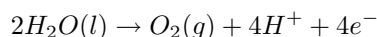
15.8 Electrolysis of water

The electrolysis of water to produce hydrogen gas is practiced in regions where electricity is cheap. This process is very energy intensive and requires large amounts of electricity.

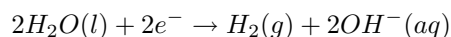
The process involves passing an electric current through a current carrying ionic solution of water and $NaOH$ or H_2SO_4 . The dissolved ions act as current

carriers and facilitate the breakup of water to produce Hydrogen and Oxygen. The following redox reactions occur:

At the anode:



At the cathode:



15.9 Extraction of Aluminium

Aluminum metal is a commonly used metal in industrial uses where its light / strong properties can be utilized. It is used in the manufacture of aeroplanes, motor cars etc. The metal is present in deposits of bauxite which is a mixture of silicas, iron oxides and hydrated alumina ($Al_2O_3 \cdot xH_2O$).

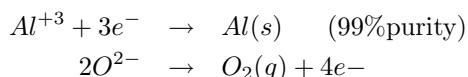
Aluminum extraction makes use of the 'Bayer' process. This involves the following steps:

1. Bauxite is digested in hot sodium hydroxide under pressure
2. This forms Tetrahydroxoaluminate, $Na[Al(OH)_4]$ and leads to the precipitation of SiO_2 in complex forms.
3. The iron oxides are insoluble and are filtered from the solution.
4. The pregnant alumina carrying solution is then diluted with water and cooled.
5. The $Al(OH)_3$ is then precipitated out and filtered.
6. Heat is then applied to drive off the water, leaving anhydrous Al_2O_3 .

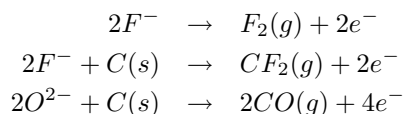
Another method uses electrolysis for the extraction of Aluminum. The 'Hall' process makes of the following process for extraction and produces 99% pure aluminum:

1. Aluminum is melted along with cryolite (Na_3AlF_6) which acts as the electrolyte.
2. The *anode* carbon rods provide sites for the oxidation of O^{2-} and F^- ions. Oxygen and fluorine gas are given off at the anodes and also lead to anode consumption.
3. At the *cathode* cell lining, the Al^{3+} ions are reduced and metal aluminum deposits on the lining.
4. The AlF_6^{3-} electrolyte is stable and remains in its molten state.

The basic electrolytic reactions involved are as follows: At the *cathode*:



At the *anode*:



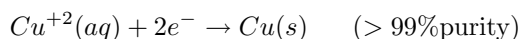
15.10 Electro-refining of copper

Copper plays a major role in the electrical reticulation industry as it is very conductive and is used in electric cables. One of the problems faced are that the copper must be pure if it is to be an effective current carrier.

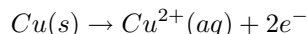
One of the methods used to purify copper, is electro-winning. The copper electro-winning process is as follows:

1. Bars of crude (impure) copper containing other metallic impurities is placed on the *anodes*.
2. The *cathodes* are made up of pure copper with little impurities.
3. The electrolyte is a solution of aqueous $CuSO_4$ and H_2SO_4 .
4. areful control of the voltage and current allows the favorable electro-winning and deposition of pure copper onto the *cathodes* as the copper in the anodes slowly *dissolves*.
5. The other metal impurities (Zn, Au, Ag, Fe and Pb) do not dissolve and form a solids sludge at the bottom of the tank or remain in solution in the electrolyte.

he reactions occur as follows: At the *anode*:



At the *cathode*:



15.11 Electroplating

The most common industrial use of electroplating is the galvanizing of iron and steel to protect it from the oxidizing atmosphere and to provide it with cathodic protection . The most common galvanizing agent is zinc.

The process of zinc electroplating (Galvanising) is as follows:

1. A zinc salt is dissolved in an aqueous bath.
2. Prior to the electroplating, the steel structure is dipped in acid (usually HCl) to pickle the metal and remove oxides that may prevent a good electroplating finish.
3. The steel is then dried of the acid and then dipped in the zinc salt bath.
4. An electric current is provided to oxidize the zinc ions, which are reduced and deposit on the steel structure.
5. The *cathode* half reaction is as follows:
At the cathode: $Zn^{2+}(aq) + 2e^{-} \rightarrow Zn(s)$
the solid zinc deposits onto the steel as a covering.

15.12 Faraday's laws of electrolysis

The British chemist, Michael Faraday discovered the relationship of electric current flow due to electron movement and the amount of substance that is consumed/deposited at the electrodes of an electrochemical cell. Some examples:

1. In the electroplating of zinc, every atom of zinc deposited onto the steel structure, requires 2 electrons to be donated to form an atom of deposited zinc.
2. The same concept can be used when determining how many electrons will be given off by the chloride ions at the anode in the Chlor-alkali process to produce chlorine gas.

Definition: *Faradays laws for Electrolysis:*

1. The quantity of a substance liberated is directly proportional to the quantity of electric charge that has flowed in the circuit.
2. For a given quantity of charge, the amount of metal that is deposited is proportional to its equivalent weight (Equivalent weight = Atomic Weight/Charge of metal ion)

Some more definitions to learn:

- **Coulomb (C):** A coulomb is the S.I. unit for electric charge. An electron has the charge of 1.6022×10^{-19} Coulombs.
- **Mole:** 1 mole is equivalent to the number of atoms in 12g of carbon. 1 mole = Avogadro's Number (6.022×10^{23} atoms).
- **Faraday (F):** A faraday is the charge contained in 1 mole of electrons.

$$\begin{aligned} 1 \text{ Faraday} &= \text{Avogadro's Number} \times \text{Charge of 1 electron} \\ &= 6.0220 \times 10^{23} \times 1.6022 \times 10^{-19} \\ &= 9.6485 \times 10^4 \text{ Coulombs/mole } e^{-} \end{aligned}$$

- **Ampere (A):** The ampere is the S.I. unit for current. It is defined as follows:

$$\begin{aligned} 1 \text{ Ampere} &= \frac{1 \text{ Coulomb}}{1 \text{ second}} \\ 1 \text{ A} &= 1 \text{ C s}^{-1} \end{aligned}$$

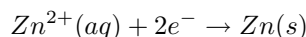
Therefore, if 1 ampere of current travels in a conductor for 1 second, 1 coulomb of charge has passed.

Worked Example 18 : Faraday's Laws:

Question: In Zinc electroplating the following example will help to show the concept of the Faraday laws.

Step 1 : (NOTE TO SELF: step is deprecated, use westep instead.)

The cathode half reaction is:



Thus for every atom of Zinc deposited, 2 electrons are required. For 1 mole of zinc to be deposited, the number of electrons required is:

= Number of atoms in 1 mole of zinc x 2

= Avogadro's No x 2 = 1.2044×10^{24} electrons.

Step 2 : (NOTE TO SELF: step is deprecated, use westep instead.)

The charge to be passed to deposit 1 mole of zinc is:

= 1.2044×10^{24} e-/mole Zn x Charge of one electron

= 1.2044×10^{24} e-/mole Zn x 1.6022×10^{-19} C/e-

= 1.9297×10^5 C

= 2 Farads (1 Farad = 9.6485×10^4 C)

Step 3 : (NOTE TO SELF: step is deprecated, use westep instead.)

If 3 Amperes flow for 30s, the number of Zinc atoms deposited is: 1

A = 1 Coulomb/second

Thus 3A for 30s = 90 Coulombs

For 1 mole of zinc to be deposited, 1.9297×10^5 Coulombs must be passed.

Therefore in that 30 seconds, ($90 \text{ C} / 1.9297 \times 10^5 \text{ C/mol Zn}$) moles of zinc are deposited.

= 4.6639×10^{-4} moles are deposited

But 1 mole zinc = 6.0220×10^{23} atoms.

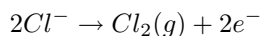
Therefore:- The number of zinc atoms deposited is:

= $4.6639 \times 10^{-4} \times 6.0220 \times 10^{23}$

= 2.8086×10^{20}

Worked Example 19 : Faradays Laws II

Question: Chlorine gas is given off at the *anode* in the Chlor-alkali process as follows:



The complete half reaction shows that 2 electrons are required to be removed from the anode for every molecule of chlorine gas generated. If a current of 100 kA runs for 2 hours, what mass of gas is generated at the anode?

Answer:

Step 1 : (NOTE TO SELF: step is deprecated, use westep instead.)

1 mole Chlorine gas (Cl_2) requires 2 moles of e^{-} to be deposited at the anode. The charge deposited per mole of chlorine generated is:

= No electrons per mole Cl_2 x Charge of 1 mole of electrons

= 2 x 1 Farad

= 2 X 9.6485×10^4 C

$$= 1.9297 \times 10^5 \text{ C/ mole } Cl_2$$

Step 2 : (NOTE TO SELF: step is deprecated, use westep instead.)

The charge discharged when the current was operating is as follows:

$$100 \text{ kA} = 100 \times 1000 \text{ A}$$

$$100 \text{ kA} = 10^5 \text{ A}$$

$$2 \text{ hours} = 2 \times 60 \text{ minutes/hour} \times 60 \text{ seconds/minute} = 7200 \text{ seconds}$$

$$1 \text{ ampere} = 1 \text{Coulomb / second}$$

Therefore 100kA running for 7200 s is:

$$= 7200 \text{ s} \times 10^5 \text{ C}$$

$$= 7.2 \times 10^8 \text{ C}$$

Step 3 : (NOTE TO SELF: step is deprecated, use westep instead.)

Thus the number of moles of chlorine generated is:

Charge discharged by current flow / (Charge deposited per mole of Cl_2)

$$= (7.2 \times 10^8 \text{ C}) / (1.9297 \times 10^5 \text{ C/mole } Cl_2)$$

$$= 7.2 \times 10^8 / 1.9297 \times 10^5$$

$$= 3.73 \times 10^3 \text{ moles of Chlorine}$$

| Properties | Anode | Cathode |
|-----------------------------------|--|---|
| Reduction / Oxidation | Oxidation | Reduction |
| Ionic behaviour | Anions (Cl^- or SO_4^{2-}) migrate to anode in solution of cell: e.g. Zn donates easily | Cations (K^+ or Na^+) migrate to cathode in solution of cell: e.g. Cu^{2+} receives e^- from cathode |
| Electron flow | Electrons leave (donated-dissolve) | Electrons enter (deposits) |
| Charge (Voltaic cell) | Negative | Positive |
| Charge (Electrolytic cell) | Positive | Negative |

Table 15.1: Properties of anodes and cathodes

| Half-Reaction | E^0V |
|---|-------------|
| $Li^+ + e^- \rightleftharpoons Li$ | -3.04 |
| $K^+ + e^- \rightleftharpoons K$ | -2.92 |
| $Ba^{2+} + 2e^- \rightleftharpoons Ba$ | -2.90 |
| $Ca^{2+} + 2e^- \rightleftharpoons Ca$ | -2.87 |
| $Na^+ + e^- \rightleftharpoons Na$ | -2.71 |
| $Mg^{2+} + 2e^- \rightleftharpoons Mg$ | -2.37 |
| $Mn^{2+} + 2e^- \rightleftharpoons Mn$ | -1.18 |
| $2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$ | -0.83 |
| $Zn^{2+} + 2e^- \rightleftharpoons Zn$ | -0.76 |
| $Cr^{2+} + 2e^- \rightleftharpoons Cr$ | -0.74 |
| $Fe^{2+} + 2e^- \rightleftharpoons Fe$ | -0.44 |
| $Cr^{3+} + 3e^- \rightleftharpoons Cr$ | -0.41 |
| $Cd^{2+} + 2e^- \rightleftharpoons Cd$ | -0.40 |
| $Co^{2+} + 2e^- \rightleftharpoons Co$ | -0.28 |
| $Ni^{2+} + 2e^- \rightleftharpoons Ni$ | -0.25 |
| $Sn^{2+} + 2e^- \rightleftharpoons Sn$ | -0.14 |
| $Pb^{2+} + 2e^- \rightleftharpoons Pb$ | -0.13 |
| $Fe^{3+} + 3e^- \rightleftharpoons Fe$ | -0.04 |
| $2H^+ + 2e^- \rightleftharpoons H_2(g)$ | 0.00 |
| $S + 2H^+ + 2e^- \rightleftharpoons H_2S(g)$ | 0.14 |
| $Sn^{4+} + 2e^- \rightleftharpoons Sn^{2+}$ | 0.15 |
| $Cu^{2+} + e^- \rightleftharpoons Cu^+$ | 0.16 |
| $SO_4^{2-} + 4H^+ + 2e^- \rightleftharpoons SO_2(g) + 2H_2O$ | 0.17 |
| $Cu^{2+} + 2e^- \rightleftharpoons Cu$ | 0.34 |
| $2H_2O + O_2 + 4e^- \rightleftharpoons 4OH^-$ | 0.40 |
| $Cu^+ + e^- \rightleftharpoons Cu$ | 0.52 |
| $I_2 + 2e^- \rightleftharpoons 2I^-$ | 0.54 |
| $O_2(g) + 2H^+ + 2e^- \rightleftharpoons H_2O_2$ | 0.68 |
| $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ | 0.77 |
| $NO_3^- + 2H^+ + e^- \rightleftharpoons NO_2(g) + H_2O$ | 0.78 |
| $Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$ | 0.78 |
| $Ag^+ + e^- \rightleftharpoons Ag$ | 0.80 |
| $NO_3^- + 4H^+ + 3e^- \rightleftharpoons NO(g) + 2H_2O$ | 0.96 |
| $Br_2 + 2e^- \rightleftharpoons 2Br^-$ | 1.06 |
| $O_2(g) + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ | 1.23 |
| $MnO_2 + 4H^+ + 2e^- \rightleftharpoons Mn^{2+} + 2H_2O$ | 1.28 |
| $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$ | 1.33 |
| $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$ | 1.36 |
| $Au^{3+} + 3e^- \rightleftharpoons Au$ | 1.50 |
| $MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$ | 1.52 |
| $Co^{3+} + e^- \rightleftharpoons Co^{2+}$ | 1.82 |
| $F_2 + 2e^- \rightleftharpoons 2F^-$ | 2.87 |

Table 15.2: Standard Electrode Potentials

Part III

CHEMICAL SYSTEMS

Chapter 16

The Water Cycle (Grade 10)

- Physical changes and energy transfers: The movement of water from the ocean and land surfaces as controlled by energy in sunlight. Reservoirs for water on earth.
- Macroscopic properties of the three phases of water related to their microscopic structure

Chapter 17

The Nitrogen Cycle (Grade 10)

- Chemical changes and energy transfers: The movement of nitrogen between interrelated biological and geological systems
- Industrial fixation of nitrogen
- Nitrogen and Nitrogen Compounds (in progress)

17.1 Nitrogen and Nitrogen Compounds

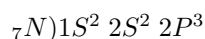
17.2 Nitrogen Gas (N_2)

Nitrogen is a colourless and odourless gas which constitutes about 78% of the atmosphere. It is slightly soluble in water, and less dense than air. Nitrogen gas occurs as diatomic molecules (N_2), with a Lewis structure as follows:

(NOTE TO SELF: fill in electrons and bonds)

N N or N N

The Sp notation of nitrogen is:



With three covalent bonds the molecule is stable and therefore nitrogen is not very reactive.

17.2.1 Industrial Preparation of N_2

Nitrogen gas is prepared by the fractional distillation of liquid air. Purified air is liquefied at a very low temperature (below $-200^\circ C$) and under very high pressure. The temperature is then raised and as nitrogen has the lowest boiling

point (bp= -196°C) it is the first to boil off, it then cools and condenses and is collected for storage. The liquid oxygen (bp= -183°C) and liquid argon (bp= -186°C) are left behind.

17.2.2 Uses of Nitrogen

- Liquid nitrogen is used for quick freezing food.
- Liquid nitrogen is used in medicine for the freezing of superficial skin tumours and growths.
- Nitrogen is used in the manufacture of ammonia (using the Haber process) which is used in cleaning agents and fertilizers
- All proteins are made of nitrogen and therefore it is necessary for life.

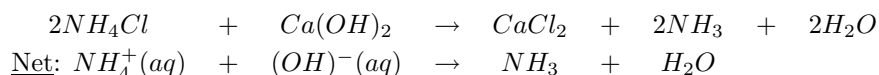
17.3 Ammonia (NH_3)

Ammonia is a gas which is lighter than air, has a characteristic smell which takes one's breath away and is highly soluble in water. It has a pyramidal structure and is therefore a polar molecule.

(NOTE TO SELF: insert figure here)

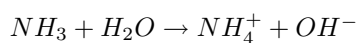
17.3.1 Laboratory Preparation

Ammonia can be prepared by heating any ammonium salt with a stable base, in this case calcium hydroxide. The gas is collected by the downward displacement of air.



The gas jar in which the ammonia is collected is seen to be full when wet indicator paper held at the mouth indicates the presence of an alkali (basic solution), i.e. damp litmus paper will be turned blue.

This is seen in the reaction:



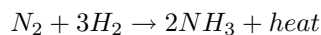
Note: It is the OH^- which causes the indicator to change colour.

17.3.2 Industrial Preparation of NH_3

The industrial preparation of ammonia is known as the 'Haber Process' or 'Haber-Bosch Process'.

At a high pressure and a temperature of about 500°C and in the presence of a suitable catalyst, nitrogen and hydrogen produce ammonia in a reversible reaction.

(NOTE TO SELF: in equation below replace arrow with equilibrium arrow)



Four considerations according to Le Chateliers principle:

- Decrease temperature: forward reaction is favoured to generate heat and more ammonia is produced (decrease to $450^\circ C$)
- Increase pressure: forward reaction is favoured to decrease pressure ($4mol \rightarrow 2mol$)
- Change concentration of the gases: If NH_3 is removed as it is formed, the forward reaction is favoured to make up for the decrease in NH_3 concentration and more NH_3 is formed.
- Catalyst: iron or iron oxide can be used to change the rate of the reaction, not the amount of product formed.

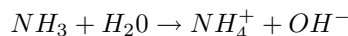
17.3.3 Properties of NH_3

NH_3 is extremely soluble in water and ionizes to form an alkaline solution due to the formation of OH^- ions).

This can be demonstrated by the fountain experiment. The bromothymol blue turns blue as a result of the basic property of ammonia.

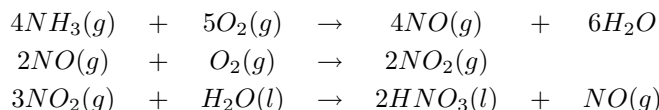
(Insert diagram 1)

An example of an ionization reaction:



17.3.4 Uses of NH_3

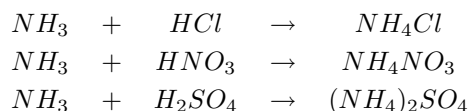
- Preparation of fertilizers like $(NH_4)_2SO_4$ and urea
- In cleansing and washing agents
- In cooling installations
- Preparation of wood pulp for preparation of paper
- The preparation of HNO_3 (nitric acid) by the catalytic oxidation of ammonia. This occurs in the presence of heated platinum or copper. (See nitric acid section for details of the process)



17.4 Ammonium Salts

17.4.1 Preparation of Ammonium Salts

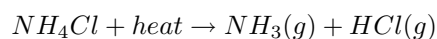
Ammonium salts are formed when ammonia reacts with a strong acid. Below are some examples of these reactions:



An ammonium ion is NH_4^+

17.4.2 Properties of Ammonium Salts

- They are soluble in water and give off ammonia when heated with $Ca(OH)_2$.
- They are thermally unstable (i.e. they decompose upon heating). An example of this is as follows:



(Insert diagram no 2)

Note: The NH_4Cl sublimes on heating, i.e. it changes directly from a solid to a gas.

17.4.3 Uses of Ammonium Salts

- NH_4Cl is used to clean metal surfaces before soldering and as an electrolyte in dry cells
- $(NH_4)_2SO_4$ is used as a fertilizer.
- NH_4NO_3 is used as a fertilizer, as an explosive and in the preparation of laughing gas.

17.5 Nitrogen Dioxide (NO_2)

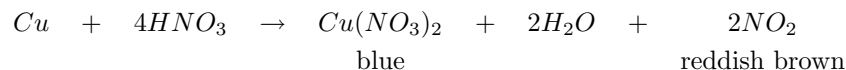
Nitrogen Dioxide is a reddish brown gas.

Interesting
Fact:

NO_2 is the culprit of smog as it creates a brown haze

17.5.1 Laboratory Preparation:

The laboratory preparation of nitrogen dioxide involves the reaction of concentrated nitric acid (HNO_3) with copper. The gas can be collected by the upward displacement of air or by liquefying the gas at a low temperature.



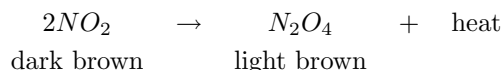
(Insert diagram 3)

The liquefied gas (NO_2) is a light yellow liquid.

17.5.2 Equilibrium between NO_2 and N_2O_4

NO_2 is nitrogen dioxide and dark, reddish brown in colour. N_2O_4 is dinitrogen tetroxide and is light, yellowy brown in colour. So:

(NOTE TO SELF: in the reaction below replace the arrow with an equilibrium arrow)



Effect of change of temperature:

The forward reaction is exothermic, i.e. it releases heat, and the reverse reaction is endothermic, i.e. it consumes heat. Heating favours both reactions, but the endothermic reaction is favoured more (as the excess heat will be used up). Therefore an increase in temperature will lead to the formation of more of the reddish brown nitrogen dioxide.

Cooling slows down both reactions, but the endothermic reaction is slowed down more. Therefore cooling favours the formation of more yellowy brown N_2O_4 .

Effect of change of pressure:

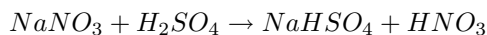
An increase in pressure (decreasing the volume) leads to the formation of less molecules. Therefore the forward reaction is favoured and leads to the formation of more N_2O_4 . A decrease in pressure (increase in volume) favours the reaction leading to more molecules. This favours the reverse reaction forming more NO_2 .

17.6 Nitric Acid (HNO_3)

Nitric acid is a colourless liquid which decomposes slowly at room temperature giving off brown vapours of NO_2 . The NO_2 dissolves in the acid giving it a yellow colour. HNO_3 is an important industrial acid which 'fumes' strongly in air and has a choking smell. It mixes well with water causing an increase in temperature. It is highly corrosive when concentrated and must be treated with caution.

17.6.1 Laboratory preparation of HNO_3 :

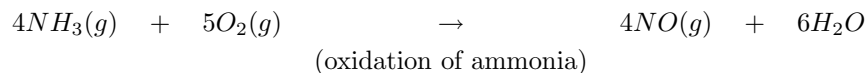
Nitric acid is prepared in the laboratory by the action of concentrated H_2SO_4 on a nitrate.



17.6.2 Industrial preparation of HNO_3 :

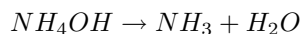
The industrial preparation of nitric acid involves the catalytic oxidation of ammonia (NH_3) and is known as the **Ostwald Process**:

- A stream of pure NH_3 and filtered air are passed over heated platinum gauze which is a contact catalyst. This occurs at about $800^\circ C$ as the reaction is very slow at room temperature.



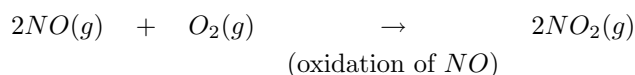
The NH_3 is obtained when NH_4OH is heated and decomposes releasing NH_3 and water.

(NOTE TO SELF: triangle on arrow below)

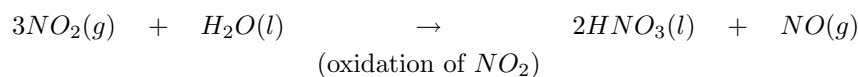


The NH_3 then mixes with O_2 and the reaction proceeds.

- The NO formed acts with the excess of atmospheric oxygen to form NO_2



- The gases are cooled and led to absorption towers where the NO_2 reacts with H_2O .

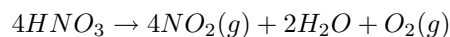


17.6.3 Reactions of Nitric Acid:

Reaction upon heating

Nitric acid is thermally unstable and heating causes it to decompose forming reddish brown NO_2 .

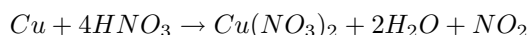
(NOTE TO SELF: triangle on arrow below)



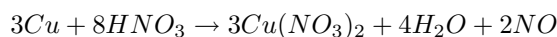
This reaction takes place slowly at normal room temperature hence the yellow-brown colour of the nitric acid. This is also the reason that nitric acid is stored in brown bottles in the laboratory, the dark colour of the glass keeps out the sunlight avoiding decomposition.

Reactions with Copper

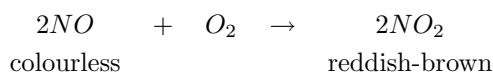
a. React copper with concentrated nitric acid



b. React copper with dilute nitric acid (HG only)



The colourless NO turns brown on contact with air



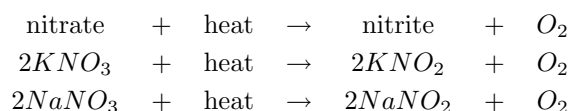
In both these reactions with copper HNO_3 is acting as an oxidizing agent.

17.6.4 Uses of Nitric Acid:

- Preparation of explosives, for example T.N.T (trinitro-toluene) and nitro-glycerine.
- Preparation of fertilizers, for example ammonium nitrate (NH_4NO_3).
- Preparation of pigments.
- In the plastics industry nitric acid is used for the manufacture of basic materials for the preparation of plastic articles.
- Preparation of nitrates for medicinal and industrial use.

17.7 Nitrates:

- All nitrates are soluble in water.
- Nitrates decompose on heating to form a nitrite and oxygen



Chapter 18

The Hydrosphere (Grade 10)

- composition and interaction with other global systems
- Ions in aqueous solution: their interaction and effects
 - Electrolytes and extent of ionisation as measured by conductivity
 - Precipitation reactions

Chapter 19

The Lithosphere: Exploiting the Earth's crust (Grade 11)

- Mining and mineral processing gold, iron, phosphate (South Africa's strengths), environmental impact of these activities
- Energy resources and their use

Chapter 20

The Atmosphere (Grade 11)

- Atmospheric chemistry
- Global warming and the environmental impact of population growth

Chapter 21

The Chemical Industry: Resources, Needs and the Chemical Connection (Grade 12)

Essay 1: Synthetic Polymers

Author: Dean Govender

Dean Govender holds a Bachelor of Science degree (with honours) in Chemical Engineering from the University of Natal, South Africa. He is currently employed as a process engineer by Sasol and works in the Operations, Profitability and Improvement division. Moreover, he is responsible for business innovation, technology optimisation and engineering support. Dean is currently pursuing a Bachelor of Physiology and Biochemistry degree

Synthetic Polymers

Scientists throughout the world are constantly developing and searching for compounds or materials that will add value to our everyday lives. Synthetic (laboratory-made or man-made) polymers have made the biggest inroad into our modern day living and today polymer chemistry has given rise to a multibillion-rand industry. Pens, plastic bottles, food wrap, clothes, photographic film and toys are just some of the diverse items that are made from synthetic polymers.

What is a polymer? A polymer is a macromolecule (large molecule) that is formed by linking together many monomers (smaller and identical molecules or units). The process of linking these molecules together is called polymerisation. Imagine joining together identical paperclips to form a long chain. The chain would represent the polymer and each paperclip would represent the monomer.

Polyethylene, a type of plastic that has many uses, is an example of a simple polymer. Ethylene ($\text{CH}_2=\text{CH}_2$) is the monomer that makes up the many repeating units of polyethylene $[-\text{CH}_2-\text{CH}_2-]_n$ (n is the number of times that the monomer is repeated in the polymer).

The applications of polymers are endless and you can probably see these applications by exploring your house or shopping mall. Some of these applications are listed below:

Consumer goods

Polyethylene, poly(vinyl chloride) and polypropylene are just some of the many polymers that are used in the manufacture of everyday products such as film, squeeze bottles and toys respectively. Packaging, food containers and hot drink cups are made from polystyrene while Teflon provides non-stick surfaces for dishes and clothes. Synthetic polymers are also used in the manufacture of carpets, blankets and clothing.

Medicine

In addition to artificial joints, heart valves and surgical gowns synthetic polymers have also played a major role in tissue engineering.

Industry

Many of the parts found in trucks and cars are made from synthetic polymers. Poly(vinyl chloride) is used in the fabrication of piping that is used extensively in industry. Further, polymers have also been used in space shuttle nose cones and in components found on aircrafts.

Sport

Synthetic polymers possess incredible strength and heat resistance and are used in the manufacture of many types of sporting equipment such as tennis racquets and hi-tech bicycles. Nylon is not only used in the clothing industry but is also used to make fishing line and ropes. Kevlar is used in the manufacture of skis. In addition, the strength of Kevlar is greater than steel and is used in bullet-proof vests, flame-resistant clothing and helmets.

Sir Isaac Newton (a very famous scientist) once said, If I have seen further it is by standing on the shoulders of giants. The pioneers of polymer chemistry and their revolutionary work and discoveries paved the way for future scientists to make many astonishing discoveries and inventions of their own. Today, polymer chemistry has become a sophisticated science that designs macromolecules for almost every conceivable use.

Lets look at some of the major developments of polymer chemistry:

- **1839:** Charles Goodyear discovered the process of vulcanization by serendipity (an accidental discovery). He accidentally spilled a mixture of rubber (a polymer) and sulphur on a stove. The resulting mixture had better and improved properties than natural rubber. Goodyear named the process after Vulcan, the Roman god of fire.
- **1887:** Rayon, the first synthetic fibre, was developed by Count Hilaire de Chardonnet.
- **1909:** Leo Baekeland becomes the first person to develop the first synthetic plastic called Bakelite.
- **1920:** Hermann Staudinger proposes that polymers are actually long chains that are made up of repeating units. Staudinger later received the Nobel Prize for his research. X-ray crystallography later proved that polymers are indeed made from smaller units called monomers.
- **1920:** During the late 1920s Wallace Carothers and a team of scientists at the Du Pont company in America began to synthesise many polymers including nylon.
- **1939:** The industrial production of polyethylene began.
- **1971:** The production of Kevlar began.

Nowadays, making bigger and better polymers have become the norm. However, there are many scientists that have turned their attention to alleviating environmental pollution. One such attempt is the production of polymers that will degrade over time when subjected to ultraviolet light or when buried in the soil.

The polymer industry generates huge turnovers in many countries and South Africa is no exception. Sasol Polymers, a division of Sasols chemical business, is South Africas leading producer of monomers and polymers. By 2006, Sasol Polymers will be will be producing more than 1.5 million tons of polymers a year and marketing these to a growing base of customers in Africa, Europe and Asia. The

two main polymer/monomer producing plants are based in Sasolburg and Secunda and are responsible for the production of ethylene, propylene, low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE), polypropylene, vinyl chloride monomer (VCM) and polyvinyl chloride (PVC), as well as other miscellaneous chemicals.

Together with joint venture partners, Sasol Polymers manages investments in two large plants in Malaysia and are currently developing an integrated ethylene and polyethylene production facility in Iran. In order to remain cost-competitive and consistently reliable, Sasol Polymers have invested substantially in upgrading their technologies, including their catalysts, and the manner in which they modify and refine their polymerisation reactors. Further, they have setup a Polymers Technology Centre, which will play a key role in demonstrating Sasol Polymers drive for continuing improvement in product and service output. At the centre, the polymers undergo several tests to determine their suitability for certain end-products and conversion processes. In addition, the centre will also help improve plant technology, operational efficiencies and new product offerings.

Sasol Polymers is truly a remarkable company as many of their products are utilised in a vast array of applications such as: woven cloth, furniture, automotive components, domestic ware, cable sheathing for electrical, electronic and telecommunication applications, cling wrap, personal-care products, floor tiles, piping, credit cards, smart cards, computer housing, footwear, wallpaper, blood and transfusion sets and many other applications.

The future of polymer chemistry is very promising. Perhaps one day you will become a famous scientist that discovers a new material that will revolutionise our lives!

Chapter Sections:

- SASOL, fuels, monomers and polymers, polymerisation
- the Chloralkali industry (soap, PVC, etc)
- Fertiliser industry (NPK)
- Batteries, torch car etc.

Appendix A

GNU Free Documentation License

Version 1.2, November 2002

Copyright © 2000,2001,2002 Free Software Foundation, Inc.

59 Temple Place, Suite 330, Boston, MA 02111-1307 USA

Everyone is permitted to copy and distribute verbatim copies of this license document, but changing it is not allowed.

PREAMBLE

The purpose of this License is to make a manual, textbook, or other functional and useful document “free” in the sense of freedom: to assure everyone the effective freedom to copy and redistribute it, with or without modifying it, either commercially or non-commercially. Secondly, this License preserves for the author and publisher a way to get credit for their work, while not being considered responsible for modifications made by others.

This License is a kind of “copyleft”, which means that derivative works of the document must themselves be free in the same sense. It complements the GNU General Public License, which is a copyleft license designed for free software.

We have designed this License in order to use it for manuals for free software, because free software needs free documentation: a free program should come with manuals providing the same freedoms that the software does. But this License is not limited to software manuals; it can be used for any textual work, regardless of subject matter or whether it is published as a printed book. We recommend this License principally for works whose purpose is instruction or reference.

APPLICABILITY AND DEFINITIONS

This License applies to any manual or other work, in any medium, that contains a notice placed by the copyright holder saying it can be distributed under the terms of this License. Such a notice grants a world-wide, royalty-free license, unlimited in duration, to use that work under the conditions stated herein.

The “Document”, below, refers to any such manual or work. Any member of the public is a licensee, and is addressed as “you”. You accept the license if you copy, modify or distribute the work in a way requiring permission under copyright law.

A “Modified Version” of the Document means any work containing the Document or a portion of it, either copied verbatim, or with modifications and/or translated into another language.

A “Secondary Section” is a named appendix or a front-matter section of the Document that deals exclusively with the relationship of the publishers or authors of the Document to the Document’s overall subject (or to related matters) and contains nothing that could fall directly within that overall subject. (Thus, if the Document is in part a textbook of mathematics, a Secondary Section may not explain any mathematics.) The relationship could be a matter of historical connection with the subject or with related matters, or of legal, commercial, philosophical, ethical or political position regarding them.

The “Invariant Sections” are certain Secondary Sections whose titles are designated, as being those of Invariant Sections, in the notice that says that the Document is released under this License. If a section does not fit the above definition of Secondary then it is not allowed to be designated as Invariant. The Document may contain zero Invariant Sections. If the Document does not identify any Invariant Sections then there are none.

The “Cover Texts” are certain short passages of text that are listed, as Front-Cover Texts or Back-Cover Texts, in the notice that says that the Document is released under this License. A Front-Cover Text may be at most 5 words, and a Back-Cover Text may be at most 25 words.

A “Transparent” copy of the Document means a machine-readable copy, represented in a format whose specification is available to the general public, that is suitable for revising the document straightforwardly with generic text editors or (for images composed of pixels) generic paint programs or (for drawings) some widely available drawing editor, and that is suitable for input to text formatters or for automatic translation to a variety of formats suitable for input to text formatters. A copy made in an otherwise Transparent file format whose markup, or absence of markup, has been arranged to thwart or discourage subsequent modification by readers is not Transparent. An image format is not Transparent if used for any substantial amount of text. A copy that is not “Transparent” is called “Opaque”.

Examples of suitable formats for Transparent copies include plain ASCII without markup, Texinfo input format, L^AT_EX input format, SGML or XML using a publicly available DTD and standard-conforming simple HTML, PostScript or PDF designed for human modification. Examples of transparent image formats include PNG, XCF and JPG. Opaque formats include proprietary formats that can be read and edited only by proprietary word processors, SGML or XML for which the DTD and/or processing tools are not generally available, and the machine-generated HTML, PostScript or PDF produced by some word processors for output purposes only.

The “Title Page” means, for a printed book, the title page itself, plus such following pages as are needed to hold, legibly, the material this License requires to appear in the title page. For works in formats which do not have any title page as such, “Title Page” means the text near the most prominent appearance of the work’s title, preceding the beginning of the body of the text.

A section “Entitled XYZ” means a named subunit of the Document whose title either is precisely XYZ or contains XYZ in parentheses following text that translates XYZ in another language. (Here XYZ stands for a specific section name mentioned below, such as “Acknowledgements”, “Dedications”, “Endorsements”, or “History”.) To “Preserve the Title” of such a section when you modify the Document means that it remains a section “Entitled XYZ” according to this definition.

The Document may include Warranty Disclaimers next to the notice which states that this License applies to the Document. These Warranty Disclaimers are considered to be included by reference in this License, but only as regards disclaiming warranties: any other implication that these Warranty Disclaimers may have is void and has no effect on the meaning of this License.

VERBATIM COPYING

You may copy and distribute the Document in any medium, either commercially or non-commercially, provided that this License, the copyright notices, and the license notice saying this License applies to the Document are reproduced in all copies, and that you add no other conditions whatsoever to those of this License. You may not use technical measures to obstruct or control the reading or further copying of the copies you make or distribute. However, you may accept compensation in exchange for copies. If you distribute a large enough number of copies you must also follow the conditions in section A.

You may also lend copies, under the same conditions stated above, and you may publicly display copies.

COPYING IN QUANTITY

If you publish printed copies (or copies in media that commonly have printed covers) of the Document, numbering more than 100, and the Document’s license notice requires Cover Texts, you must enclose the copies in covers that carry, clearly and legibly, all these Cover Texts: Front-Cover Texts on the front cover, and Back-Cover Texts on the back cover. Both covers must also clearly and legibly identify you as the publisher of these copies. The front cover must present the full title with all words of the title equally prominent and visible. You may add other material on the covers in addition. Copying with changes limited to the covers, as long as they preserve the title of the Document and satisfy these conditions, can be treated as verbatim copying in other respects.

If the required texts for either cover are too voluminous to fit legibly, you should put the first ones listed (as many as fit reasonably) on the actual cover, and continue the rest onto adjacent pages.

If you publish or distribute Opaque copies of the Document numbering more than 100, you must either include a machine-readable Transparent copy along with each Opaque copy, or state in or with each Opaque copy a computer-network location from which the general network-using public has access to download using public-standard network protocols a complete Transparent copy of the Document, free of added material. If you use the latter option, you must take reasonably prudent steps, when you begin distribution of Opaque copies

in quantity, to ensure that this Transparent copy will remain thus accessible at the stated location until at least one year after the last time you distribute an Opaque copy (directly or through your agents or retailers) of that edition to the public.

It is requested, but not required, that you contact the authors of the Document well before redistributing any large number of copies, to give them a chance to provide you with an updated version of the Document.

MODIFICATIONS

You may copy and distribute a Modified Version of the Document under the conditions of sections A and A above, provided that you release the Modified Version under precisely this License, with the Modified Version filling the role of the Document, thus licensing distribution and modification of the Modified Version to whoever possesses a copy of it. In addition, you must do these things in the Modified Version:

1. Use in the Title Page (and on the covers, if any) a title distinct from that of the Document, and from those of previous versions (which should, if there were any, be listed in the History section of the Document). You may use the same title as a previous version if the original publisher of that version gives permission.
2. List on the Title Page, as authors, one or more persons or entities responsible for authorship of the modifications in the Modified Version, together with at least five of the principal authors of the Document (all of its principal authors, if it has fewer than five), unless they release you from this requirement.
3. State on the Title page the name of the publisher of the Modified Version, as the publisher.
4. Preserve all the copyright notices of the Document.
5. Add an appropriate copyright notice for your modifications adjacent to the other copyright notices.
6. Include, immediately after the copyright notices, a license notice giving the public permission to use the Modified Version under the terms of this License, in the form shown in the Addendum below.
7. Preserve in that license notice the full lists of Invariant Sections and required Cover Texts given in the Document's license notice.
8. Include an unaltered copy of this License.
9. Preserve the section Entitled "History", Preserve its Title, and add to it an item stating at least the title, year, new authors, and publisher of the Modified Version as given on the Title Page. If there is no section Entitled "History" in the Document, create one stating the title, year, authors, and publisher of the Document as given on its Title Page, then add an item describing the Modified Version as stated in the previous sentence.

10. Preserve the network location, if any, given in the Document for public access to a Transparent copy of the Document, and likewise the network locations given in the Document for previous versions it was based on. These may be placed in the “History” section. You may omit a network location for a work that was published at least four years before the Document itself, or if the original publisher of the version it refers to gives permission.
11. For any section Entitled “Acknowledgements” or “Dedications”, Preserve the Title of the section, and preserve in the section all the substance and tone of each of the contributor acknowledgements and/or dedications given therein.
12. Preserve all the Invariant Sections of the Document, unaltered in their text and in their titles. Section numbers or the equivalent are not considered part of the section titles.
13. Delete any section Entitled “Endorsements”. Such a section may not be included in the Modified Version.
14. Do not re-title any existing section to be Entitled “Endorsements” or to conflict in title with any Invariant Section.
15. Preserve any Warranty Disclaimers.

If the Modified Version includes new front-matter sections or appendices that qualify as Secondary Sections and contain no material copied from the Document, you may at your option designate some or all of these sections as invariant. To do this, add their titles to the list of Invariant Sections in the Modified Version’s license notice. These titles must be distinct from any other section titles.

You may add a section Entitled “Endorsements”, provided it contains nothing but endorsements of your Modified Version by various parties—for example, statements of peer review or that the text has been approved by an organisation as the authoritative definition of a standard.

You may add a passage of up to five words as a Front-Cover Text, and a passage of up to 25 words as a Back-Cover Text, to the end of the list of Cover Texts in the Modified Version. Only one passage of Front-Cover Text and one of Back-Cover Text may be added by (or through arrangements made by) any one entity. If the Document already includes a cover text for the same cover, previously added by you or by arrangement made by the same entity you are acting on behalf of, you may not add another; but you may replace the old one, on explicit permission from the previous publisher that added the old one.

The author(s) and publisher(s) of the Document do not by this License give permission to use their names for publicity for or to assert or imply endorsement of any Modified Version.

COMBINING DOCUMENTS

You may combine the Document with other documents released under this License, under the terms defined in section A above for modified versions, provided

that you include in the combination all of the Invariant Sections of all of the original documents, unmodified, and list them all as Invariant Sections of your combined work in its license notice, and that you preserve all their Warranty Disclaimers.

The combined work need only contain one copy of this License, and multiple identical Invariant Sections may be replaced with a single copy. If there are multiple Invariant Sections with the same name but different contents, make the title of each such section unique by adding at the end of it, in parentheses, the name of the original author or publisher of that section if known, or else a unique number. Make the same adjustment to the section titles in the list of Invariant Sections in the license notice of the combined work.

In the combination, you must combine any sections Entitled “History” in the various original documents, forming one section Entitled “History”; likewise combine any sections Entitled “Acknowledgements”, and any sections Entitled “Dedications”. You must delete all sections Entitled “Endorsements”.

COLLECTIONS OF DOCUMENTS

You may make a collection consisting of the Document and other documents released under this License, and replace the individual copies of this License in the various documents with a single copy that is included in the collection, provided that you follow the rules of this License for verbatim copying of each of the documents in all other respects.

You may extract a single document from such a collection, and distribute it individually under this License, provided you insert a copy of this License into the extracted document, and follow this License in all other respects regarding verbatim copying of that document.

AGGREGATION WITH INDEPENDENT WORKS

A compilation of the Document or its derivatives with other separate and independent documents or works, in or on a volume of a storage or distribution medium, is called an “aggregate” if the copyright resulting from the compilation is not used to limit the legal rights of the compilation’s users beyond what the individual works permit. When the Document is included an aggregate, this License does not apply to the other works in the aggregate which are not themselves derivative works of the Document.

If the Cover Text requirement of section A is applicable to these copies of the Document, then if the Document is less than one half of the entire aggregate, the Document’s Cover Texts may be placed on covers that bracket the Document within the aggregate, or the electronic equivalent of covers if the Document is in electronic form. Otherwise they must appear on printed covers that bracket the whole aggregate.

TRANSLATION

Translation is considered a kind of modification, so you may distribute translations of the Document under the terms of section A. Replacing Invariant Sec-

tions with translations requires special permission from their copyright holders, but you may include translations of some or all Invariant Sections in addition to the original versions of these Invariant Sections. You may include a translation of this License, and all the license notices in the Document, and any Warranty Disclaimers, provided that you also include the original English version of this License and the original versions of those notices and disclaimers. In case of a disagreement between the translation and the original version of this License or a notice or disclaimer, the original version will prevail.

If a section in the Document is Entitled “Acknowledgements”, “Dedications”, or “History”, the requirement (section A) to Preserve its Title (section A) will typically require changing the actual title.

TERMINATION

You may not copy, modify, sub-license, or distribute the Document except as expressly provided for under this License. Any other attempt to copy, modify, sub-license or distribute the Document is void, and will automatically terminate your rights under this License. However, parties who have received copies, or rights, from you under this License will not have their licenses terminated so long as such parties remain in full compliance.

FUTURE REVISIONS OF THIS LICENSE

The Free Software Foundation may publish new, revised versions of the GNU Free Documentation License from time to time. Such new versions will be similar in spirit to the present version, but may differ in detail to address new problems or concerns. See <http://www.gnu.org/copyleft/>.

Each version of the License is given a distinguishing version number. If the Document specifies that a particular numbered version of this License “or any later version” applies to it, you have the option of following the terms and conditions either of that specified version or of any later version that has been published (not as a draft) by the Free Software Foundation. If the Document does not specify a version number of this License, you may choose any version ever published (not as a draft) by the Free Software Foundation.

ADDENDUM: How to use this License for your documents

To use this License in a document you have written, include a copy of the License in the document and put the following copyright and license notices just after the title page:

Copyright © YEAR YOUR NAME. Permission is granted to copy, distribute and/or modify this document under the terms of the GNU Free Documentation License, Version 1.2 or any later version published by the Free Software Foundation; with no Invariant Sections,

no Front-Cover Texts, and no Back-Cover Texts. A copy of the license is included in the section entitled “GNU Free Documentation License”.

If you have Invariant Sections, Front-Cover Texts and Back-Cover Texts, replace the “with...Texts.” line with this:

with the Invariant Sections being LIST THEIR TITLES, with the Front-Cover Texts being LIST, and with the Back-Cover Texts being LIST.

If you have Invariant Sections without Cover Texts, or some other combination of the three, merge those two alternatives to suit the situation.

If your document contains nontrivial examples of program code, we recommend releasing these examples in parallel under your choice of free software license, such as the GNU General Public License, to permit their use in free software.