Grammar Schools

Chemistry

GRADE

10

Express Publishing

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Contents

Introduction

For the student

Welcome to your new Chemistry textbook, *Grade 10 Chemistry*. Your textbook comes with a **Grade 10 Chemistry Student's Portfolio** and a range of *digital resources*. As well as deepening your understanding of key areas of Chemistry, this book aims to develop your learning skills in science. You will develop these skills in class, in laboratory practicals and whilst conducting research within and outside of class with your fellow students. An emphasis will be placed throughout this course on your ability to present core concepts, research and data effectively to others.

Glossary

A comprehensive glossary is included at the back of this book.

For the teacher

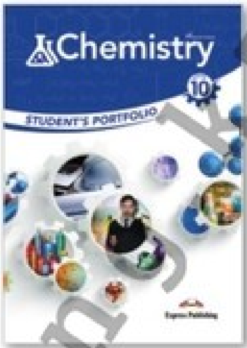
Written for the new Grade 10 Chemistry subject programme in Kazakhstan, *Grade 10 Chemistry* aims to meet the broad range of learning objectives set out in the Grade 10-11 Chemistry subject programme document. It focuses on developing learners' knowledge of and about science through the four content and skill strands outlined in the subject programme:

- Understanding of core subject areas in Chemistry
- Research and experimentation in science
- Communication in science
- Science and society

Key features of the textbook

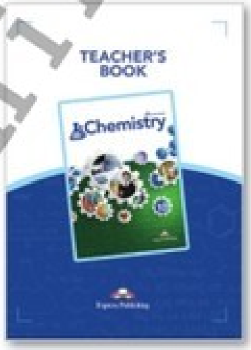
- **Learning outcomes** are clearly stated at the beginning of each module in student-friendly language
- **Activities** and practical demonstrations allow students to build on their knowledge through guided observation, laboratory practicals and research
- **Diagrams** have been fully labelled and are drawn in a simple style so that learners can replicate them easily
- **Questions** are interspersed within sections of the text to offer teachers the opportunity to use a range of teaching strategies. There are regular opportunities for learners to engage in group work and pair work, discussion, giving of presentations and online research.

Student's Portfolio



The student's Portfolio provides additional revision material and further tasks. The Portfolio enables learners to maintain a detailed record of laboratory practicals, giving them space to reflect on the processes and results of their work. In line with the textbook, it provides detailed sample workings of all stoichiometric calculations they are required to make.

Teacher´s Book



A Teacher's Book with full answers to all questions in both the Textbook and Student's Portfolio – giving detailed worked solutions for all calculations – is provided.

Digital resources

Grade 10 Chemistry **digital resources** for teachers will further enhance classroom learning. These resources work in conjunction with the Textbook and Student's Portfolio. The resources have been designed to fully integrate with the Textbook to compliment lesson content. Following the principles of the new national Chemistry subject programme, material is provided to suit a range of learner types and to encourage participation and engagement on the part of the learner.

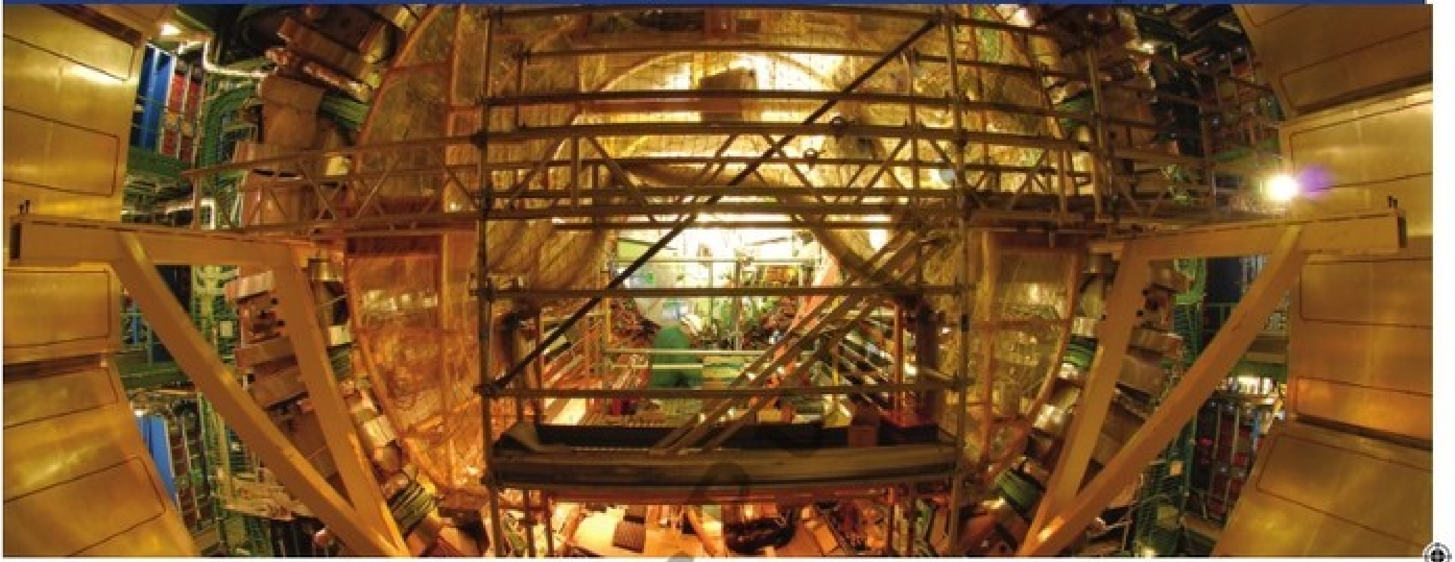
Answers to all questions in both the Textbook and Student's Portfolio and detailed **worked solutions** of all calculations is included.

A series of **videos** allow students to observe science in action across all modules. These videos will reinforce the topic at hand, promote discussion about scientific issues in society and enable teachers to bring a range of perspectives on topics in Chemistry into the classroom.

Further classroom discussion and participation is opened up through **PowerPoint presentations**, including a thematic presentation of information from the Textbook. **Experiment videos** allow for a visual review of laboratory activities and can be used for demonstration or summative plenary work.

Atomic Structure

MODULE 1



Learning objectives

- To explain main concepts of modern atomic theory 10.1.2.1
- To recognize the difference between shapes of s-, p-, d-, f- orbitals 10.1.2.2
- To name the characteristics and values of quantum numbers 10.1.3.1
- To apply the principle of minimum energy, Pauli principle and Hund's rule for electronic orbitals 10.1.3.2
- To write electronic configurations of the first 36 chemical elements 10.1.3.3

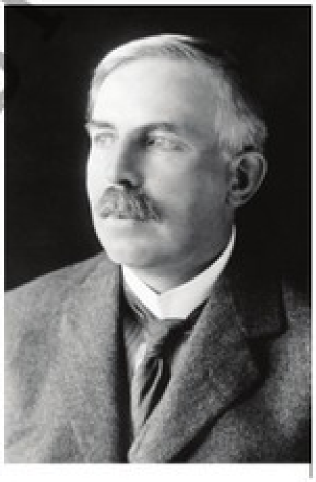
1.1 The Atom

Since atoms are extremely small, they are invisible to the naked eye, and until quite recently they could not be seen using even very powerful microscopes. It is only since the development of the scanning tunnelling microscope that direct evidence has been obtained that matter is made up of atoms.

It is generally accepted nowadays that matter is composed of minute particles, which may be atoms, molecules or ions. It is also known that atoms consist of electrons, protons and neutrons. The properties of these particles are well-known, as are their effects on the properties and behaviour of the atoms to which they belong. It is really only in the last one hundred and fifty years that most of this knowledge has been acquired. The seventy-year period from about 1870 was a particularly exciting time in the history of science, as a succession of outstanding chemists and physicists conducted painstaking work to develop and refine theories on the structure of the atom.

1.2 The Nucleus

The discovery of radioactivity gave Ernest Rutherford, a New Zealander, a new tool for probing inside atoms. In a very famous experiment, he directed his co-workers Geiger and Marsden to fire radioactive particles – alpha particles, which are positively charged – at very thin gold foil. They expected the alpha particles to pass straight through the gold foil, with only slight changes of direction.



Ernest Rutherford

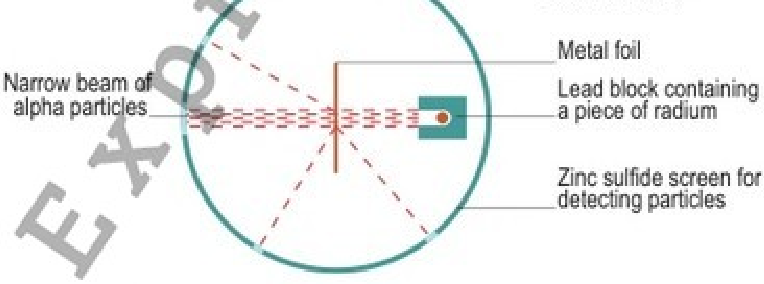


Figure 1.1
Alpha particle scattering by gold atoms

Geiger and Marsden made some unexpected observations:

- A very large number of the alpha particles were not deflected at all, showing that they had passed through essentially empty space.
- Many particles were deflected at small angles.
- A few particles in every 10,000 were deflected at angles greater than 90 °, and a very small number actually bounced back towards their source, repelled strongly by a dense concentration of positive charge.

Rutherford proposed a new model for the atom to explain the results of the Geiger–Marsden experiment. He believed that:

- The positive charge was not spread out in a cloud as in the plum pudding model, but concentrated into a very small, dense nucleus at the centre of the atom.
- If one of the positively charged alpha particles passed close to the positive mass of the nucleus it would be deflected, since like charges repel each other.
- If an alpha particle collided directly with the very dense nucleus of an atom, it would rebound.
- The rest of the atom is mostly empty space, occupied only by the electrons moving around in the atom's volume, balancing the positive charge of the nucleus and keeping the atom neutral.

QUESTIONS

1 Describe the gold foil experiment carried out by Rutherford's co-workers, Geiger and Marsden.

2 In the Geiger–Marsden experiment, what was the nature of the bombarding particles and from what material was the foil made?

3 What unexpected observations did Geiger and Marsden make?

4 Describe Rutherford's model of the atom.

1.3 Bohr Model of the Atom

With the acceptance that the atom was mostly empty space, with a dense positively charged nucleus and surrounding electrons, the Danish scientist **Niels Bohr** proposed his model of the atom in 1913. His initial work was based on the hydrogen atom. He proposed that its single electron travelled in a planetary-like orbit around the nucleus. He then extended his model to other atoms, proposing that the electrons were arranged in a series of concentric circular orbits at an increasing distance from the nucleus. These orbits had characteristic energy, so they were called **energy levels**. Bohr's model worked well for hydrogen, but less well for other atoms.

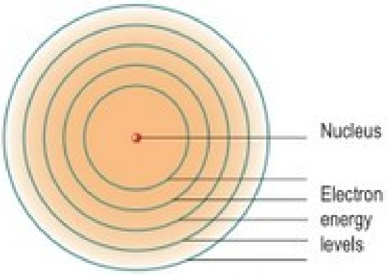


Figure 1.2
Bohr model of the atom

QUESTIONS

5 Describe Bohr's model of the atom.

6 Why were the Bohr orbits called energy levels?

1.4 The Protons

Rutherford did further experiments in which he bombarded six different elements with alpha particles. All of the elements bombarded gave out the same positively charged particle, which was identical to the nucleus of a hydrogen atom. He concluded that these hydrogen nuclei were produced in the break-up of the nuclei of the bombarded atoms. In 1920, Rutherford began calling these hydrogen nuclei **protons** and concluded that they made up the positive part of the nuclei of all atoms. The charge carried by the proton is of exactly the same size as that of the negative charge on the electron.
Rutherford could explain the charge on the nucleus in terms of the number of its protons. However, there were not enough protons to explain its mass. It was known that hydrogen had just one proton in its nucleus, and helium had two. However, the mass of helium was four times that of hydrogen. Rutherford suggested that the nucleus contained other particles of equal mass to protons, but with no charge.

1.5 James Chadwick and the Neutron

Because of the absence of charge, these neutral particles were difficult to detect. It was much later, in 1932, that one of Rutherford's co-workers, **James Chadwick**, produced the evidence for these particles, which were called **neutrons**. In his experiment, beryllium was bombarded with alpha particles. The alpha particles knocked neutrons out of beryllium atoms. The neutrons were not detected directly, but they knocked protons out of the atoms in paraffin wax. These protons were easily detected, because they were electrically charged (Figure 1.4).

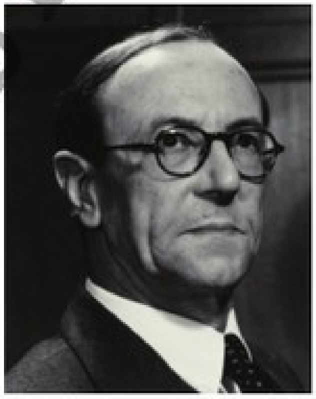


Figure 1.3 James Chadwick

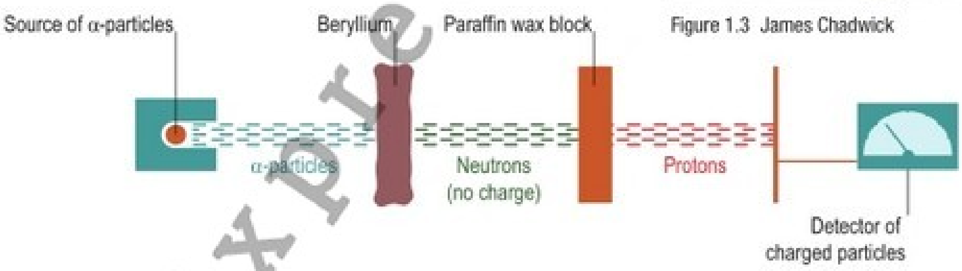


Figure 1.4
Chadwick's experiment

QUESTIONS

7 Describe how Rutherford discovered the existence of protons.

8 Name the scientist who discovered evidence for the existence of neutrons.

9 How did a comparison of the nuclei of hydrogen and helium lead to the suggestion that other nuclear particles existed?

1.6 Properties of Electrons, Protons and Neutrons

The masses and charges of electrons, protons and neutrons are now known very accurately. Since the values are extremely small, scientists use the ideas of relative mass and relative charge.

- The relative mass of a proton and of a neutron is approximately 1. The electron is much smaller, about 1/1836 of the mass of a proton.
- The relative charge of a proton is +1 and that of an electron is –1. The neutron has no charge, being neutral.

These properties, as well as the locations of the particles in the atom, are summarised in Table 1.1.

Particle	Relative Mass	Relative Charge	Location in the atom
Electron	1/1836	–1	Outside the nucleus
Proton	1	+1	In the nucleus
Neutron	1	0	In the nucleus

Table 1.1

QUESTIONS

10 What is the relative charge of (a) the electron (b) the proton (c) the neutron?

11 Which two particles found in the atom have approximately the same relative mass?

12 In what part of the atom are electrons found?

13 Name the particles found in the nucleus of the atom.

1.7 Atomic Number

All atoms are neutral, with the positive charge contributed by the protons balanced out by the negative charge contributed by the electrons. Since the size of the charge on the proton is the same as that on the electron, we can conclude that the number of protons is the same as the number of electrons. This number is called the **atomic number**. The fact that each element has its own particular atomic number was discovered by the English physicist, Henry Moseley. The atomic number is given the symbol **Z**.

The elements in the modern periodic table are arranged in order of atomic number. The atomic number gives three pieces of information about an element:

- The number of protons in the nucleus of an atom of the element.
- The number of electrons in an atom of the element.
- The position of the element in the modern periodic table.

The atomic number of an element is the number of protons in the nucleus of an atom of that element.

QUESTIONS

14 Define atomic number.

15 Name the scientist credited with introducing the idea of atomic number.

16 What pieces of information does the atomic number give about a particular element?

17 Why does the number of protons in an atom of an element define what element it is?

1.8 Mass Number

The mass number of an element is the sum of the number of protons and the number of neutrons in the nucleus of an atom of that element.

Neutrons have roughly the same mass as protons, so they contribute significantly to the mass of an atom. The **mass number** is given the symbol **A**.

Mass number = Number of protons + number of neutrons

The number of neutrons can be calculated by subtracting **Z** from **A**, i.e. number of neutrons = **A – Z**.

Information about an atom can now be written more fully by including the atomic number and the mass number. For example, potassium:

$${}^{39}_{19}\mathrm{K}$$

The subscript 19 is the atomic number, **Z**, and the superscript 39 is the mass number, **A**. The number of neutrons = A – Z = 39 – 19 = 20.

EXAMPLE 1.1

State the number of protons, neutrons and electrons for the argon atom,

$${}^{40}_{18}\mathrm{Ar}$$

Answer The atomic number Z = 18, so there are 18 protons and 18 electrons.
The mass number A = 40.
Number of neutrons = A – Z = 40 – 18 = 22.

Example 1.2

An atom of lithium has 3 protons and 4 neutrons. Indicate the mass number and atomic number for the atom.

Answer Since the number of protons is 3, the atomic number Z = 3. The periodic table indicates that the 3rd element is lithium, Li. There are 4 neutrons, so 4 = A – Z = A – 3. Thus the mass number A = 4 + 3 = 7. This information can be written as follows:

$^{7}_{3}\text{Li}$

Questions

18 Define mass number.

19 How may atomic number and mass number be used to calculate the number of neutrons in an atom of an element?

20 State the number of protons, electrons and neutrons for each of the following:

(a) $^{11}_{5}\text{B}$ (b) $^{28}_{14}\text{Si}$ (c) $^{24}_{12}\text{Mg}$ (d) $^{20}_{10}\text{Ne}$ (e) $^{19}_{9}\text{F}$

21 Indicate the mass number and atomic number for atoms which have (a) 19 protons and 20 neutrons (b) 6 protons and 6 neutrons (c) 4 protons and 5 neutrons.

1.9 Relative Atomic Mass (Ar)

The relative atomic mass (Ar) of an element is the average mass of an atom of the element relative to one-twelfth the mass of an atom of carbon-12.

Most elements exist naturally as two or more different isotopes. The mass of an element therefore depends on the relative abundances of all the isotopes present in the sample analysed. Relative atomic masses have no units; they represent the number of times heavier on average an atom of an element is than one-twelfth of a carbon-12 atom.

If a table of relative atomic masses is consulted, it will be seen that the values listed are not whole numbers e.g. 26.98 for aluminium. This is because the value is the average of all the element's naturally occurring isotopes, taking their relative abundance into account.

EXAMPLE 1.3

In a sample of carbon, 98.9% of the atoms are carbon-12 and 1.1% of them are carbon-13. Calculate to two decimal places the relative atomic mass, A_r, of carbon.

Answer The abundance of each isotope is multiplied by its mass, the sum of these products is calculated and the result divided by 100.

$A_r(C) = [(98.9 \times 12) + (1.1 \times 13)] / 100 = [1186.8 + 14.3] / 100 = 1201.1 / 100 = 12.01$

EXAMPLE 1.4

Calculate, to two decimal places, the relative atomic mass of silicon with the following isotopic composition: silicon-28 = 92.2%, silicon-29 = 4.7%, silicon-30 = 3.1%.

Answer

$A_r(Si) = [(92.2 \times 28) + (4.7 \times 29) + (3.1 \times 30)] / 100$

$= [2581.6 + 136.3 + 93] / 100$

$= 2810.9 / 100$

$= 28.11$

QUESTIONS

22 Define relative atomic mass.

23 Why are the relative atomic masses of elements not whole numbers?

24 Naturally occurring magnesium consists of 79% of magnesium-24, 10% of magnesium-25, and 11% of magnesium-26. Calculate the relative atomic mass, A_r, of magnesium.

25 Calculate the relative atomic mass of copper with the following isotopic composition: copper-63 = 69%, copper-65 = 31%.

26 In a sample of chlorine, 75% of the atoms are chlorine-35 and 25% of them are chlorine-37. Calculate the relative atomic mass, A_r, of chlorine.

1.10 Energy Levels in Atoms

An energy level is a region of definite energy within the atom that electrons can occupy.

Electrons in atoms occupy energy levels that are outside the nucleus. Different energy levels in atoms have different energy values, and have different capacities for electrons. The innermost energy level, the n = 1 level, can hold up to two electrons. The next level, the n = 2 level, can hold up to eight electrons. The third level, the n = 3 level, can hold up to 18 electrons, while the fourth level, the n = 4 level, can hold up to 32 electrons. Table 1.2 indicates how electrons are arranged in atoms of each of the first twenty elements in the Periodic table.

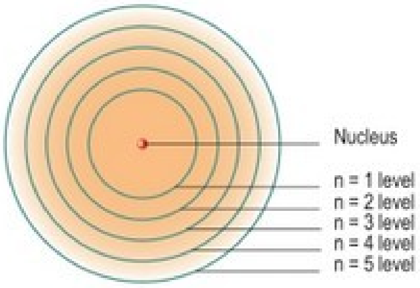


Figure 1.5
Energy levels in atoms

Element	Atomic Number	Electron Arrangement			
		n = 1	n = 2	n = 3	n = 4
Hydrogen	1	1			
Helium	2	2			
Lithium	3	2	1		
Beryllium	4	2	2		
Boron	5	2	3		
Carbon	6	2	4		
Nitrogen	7	2	5		
Oxygen	8	2	6		
Fluorine	9	2	7		
Neon	10	2	8		
Sodium	11	2	8	1	
Magnesium	12	2	8	2	
Aluminium	13	2	8	3	
Silicon	14	2	8	4	
Phosphorus	15	2	8	5	
Sulfur	16	2	8	6	
Chlorine	17	2	8	7	
Argon	18	2	8	8	
Potassium	19	2	8	8	1
Calcium	20	2	8	8	2

Table 1.2

The Group I elements lithium, sodium and potassium each have one electron in the outermost energy level of their atoms. There are two electrons in the outermost energy level of atoms of the Group II elements beryllium, magnesium and calcium respectively. There are seven electrons in the outermost energy level of atoms of the Group VII elements fluorine and chlorine respectively.

In general, elements in the same group of the periodic table have the same number of electrons in the outermost energy level of their atoms. The only exception to this is helium in Group 0; it has just two electrons in the outermost energy level of its atoms, unlike neon, argon and the other Group 0 elements which each have eight.

Lithium (2, 1) Sodium (2, 8, 1) Potassium (2, 8, 8, 1)

Figure 1.6
Arrangement of electrons in atoms of the Group I elements

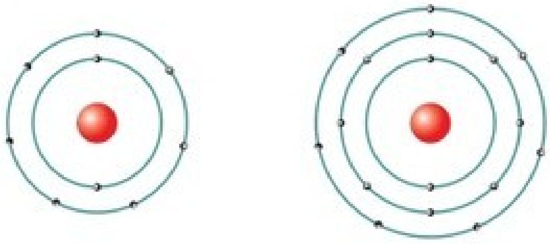


Figure 1.7
Arrangement of electrons in atoms of the Group VII elements

QUESTIONS

27 What are energy levels?

28 What is the arrangement of electrons in an atom of (a) silicon (b) calcium?

29 With regard to electron arrangement, what have the Group III elements got in common?

1.11 Atomic Orbitals

Louis de Broglie

In 1923, the French physicist **Louis de Broglie** stated that electrons, like light, have the properties of waves as well as of particles. This was confirmed by experiment four years later. This discovery, allied to the fact that the Bohr theory only worked well for simple atoms, led to the development of a more sophisticated theory of the atom.

Erwin Schrödinger

Because of the uncertainty with regard to the exact location of an electron in an atom, at any particular time, it is more meaningful to refer to the probability of finding the electron in a particular position within the atom. In calculating this probability, use is made of the fact that the electron has a wave nature. The probability is calculated using mathematical functions, which are found by solving the Schrödinger equation, developed by **Erwin Schrödinger**, a German physicist, in 1926.

For an electron in an atom, there are a number of different mathematical functions that can be used. Using any one of these, a boundary may be drawn within which there is a high probability of finding the electron. This region is called an **atomic orbital**.

An atomic orbital is a region in space where the probability of finding an electron is relatively high.

Quantum numbers

There are four quantum numbers that are used to completely describe the movement and trajectories of each electron within an atom. They are important in determining the electron configuration of an atom as well as the probable location of electrons in an atom. They are also used to determine other characteristics of atoms, such as ionization energy and atomic radius.

The first three quantum numbers: the principal (n), angular (ℓ), and magnetic (m) quantum numbers describe the size, shape, and orientation in space of the orbitals on an atom.

The **principal quantum number** (n) designates the principal electron shell. The larger the number, the further the electron is from the nucleus and the larger the size of the orbital. Electrons are attracted to the nucleus of an atom because of their opposite charge. An electron in an excited state absorbs energy and can jump, for example, from the first principal shell (n =1) to the second principal shell (= 2). This process is known as absorption. When electrons emit energy they move to lower principal shells in a process known as emission, moving, for example, from n = 3 to n = 2. The principal quantum number thus indirectly describes the energy of an orbital.

The **angular quantum number** (ℓ) determines the shape of an orbital. Orbitals have shapes which can be described as spherical (ℓ = 0), polar (ℓ = 1), or cloverleaf (ℓ = 2).

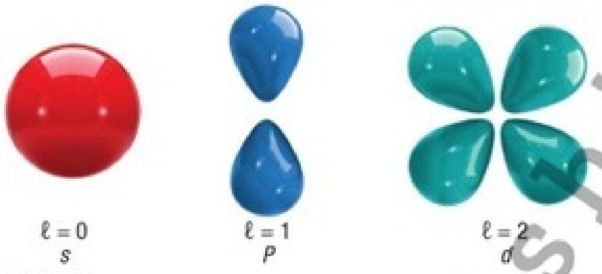


Figure 1.8a
s, p and d orbitals

A sphere (ℓ = 0) can only be oriented in space in one way. Orbitals that have polar (ℓ = 1) or cloverleaf (ℓ = 2) shapes can point in different directions and we thus have a third quantum number, **the magnetic quantum** (*m*) that indicates the orientation in space of a particular orbital.

The fourth quantum number, **the electron spin number** (*s*) designates the direction of the electron spin. The two electrons in an orbital are distinguished by an electron spin number designating one as + ½ and the other - ½ .

The rules of the first three quantum numbers allow us to define an orbital.

- Integers: 0, 1, 2, 3, 4 …. are used to describe quantum numbers (n, ℓ, m)
- The principal quantum number (*n*) cannot be zero. The allowed values of *n* are, therefore, 1, 2, 3, 4,….
- The value of the angular quantum number (ℓ) can be any integer between 0 and *n* - 1.
- The value of the magnetic quantum number (*m*) can be any integer between -ℓ and +ℓ.

The shell and subshell in which an orbital belongs is described using a two-character code e.g. 2p. The first character indicates the shell (n = 2) and the second identifies the subshell. The lowercase letters s, p, d, f are used to designate the different subshells corresponding to these ℓ values:

$$s: \ell = 0$$
$$p: \ell = 1$$
$$d: \ell = 2$$
$$f: \ell = 3$$

The rules of combination of the *n*, *l* and *m* quantum numbers mean that the number of subshells in a shell is equal to the principle quantum number for the shell.

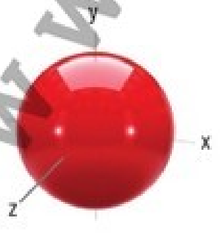


Figure 1.8b
s orbital

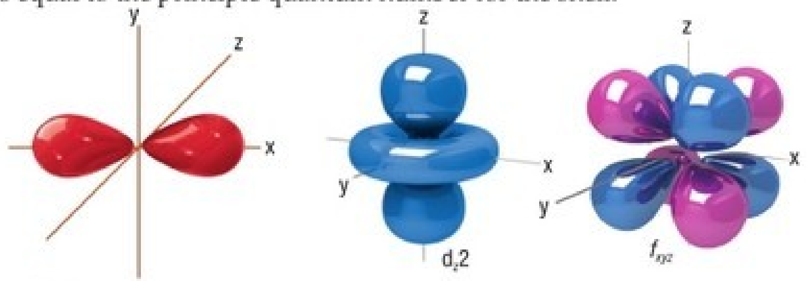


Figure 1.8c
p, d and f orbitals

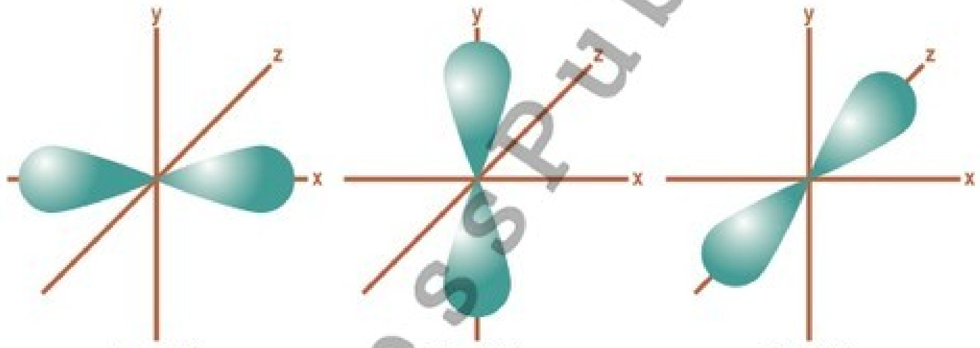
There are a number of different types of orbital:

- s orbitals are spherical (Figure 1.10b)
- p orbitals have a dumb-bell shape.
- d orbitals and f orbitals have more complex shapes. (Figure 1.10c)

All orbitals can hold two electrons. There are a number of different orbitals in each energy level in the atom, except in the n = 1 level (Table 1.3).

Energy level	Atomic orbital(s)	Relative energy	Orientation
n=1	1s		
n=2	2s; $2p_x$; $2p_y$; $2p_z$	$2p_x$, $2p_y$ and $2p_z$ are equal in energy; 2s of lower energy	$2p_x$, $2p_y$ and $2p_z$ are oriented at right angles to each other
n=3	3s; $3p_x$; $3p_y$; $3p_z$; five 3d orbitals	$3p_x$, $3p_y$ and $3p_z$ are equal in energy; 3s of lower energy and 3d of higher energy	$3p_x$, $3p_y$ and $3p_z$ are oriented at right angles to each other
n=4	4s; $4p_x$; $4p_y$; $4p_z$; five 4d orbitals; seven 4f orbitals	$4p_x$, $4p_y$ and $4p_z$ are equal in energy; 4s of lower energy, 4d of higher energy and 4f higher than 4d	$4p_x$, $4p_y$ and $4p_z$ are oriented at right angles to each other

Table 1.3



$2p_x$ orbital $2p_y$ orbital $2p_z$ orbital

Figure 1.9
The $2p_x$, $2p_y$ and $2p_z$ orbitals are oriented at right angles to each other

QUESTIONS

30 What is the maximum number of electrons that can be contained in (a) all the 3d orbitals (b) all the 2p orbitals (c) all the orbitals with n = 3 (d) all the 3p orbitals?

31 State three ways that s orbitals differ from p orbitals in the same energy level.

32 Make a sketch showing how the $3p_x$, $3p_y$ and $3p_z$ orbitals differ from each other.

33 How many electrons can be accommodated in the n = 4 energy level? How many orbitals are needed to accommodate these electrons?

1.12 Electronic Configurations of Atoms and Ions

An energy sublevel is a subdivision of an energy level containing one or more atomic orbitals, all of which have the same energy.

For example, the $2p_x$, $2p_y$ and $2p_z$ orbitals make up the 2p sublevel, while the five 3d orbitals make up the 3d sublevel. Different types of sublevel have different capacities, as indicated in Table 1.4.

Sublevel	Capacity
1s	2
2s	2
2p	6
3s	2
3p	6
3d	10
4s	2
4p	6
4d	10
4f	14

Table 1.4

To find out how electrons are arranged in different kinds of atoms, a diagram such as Figure 1.11, using energy values obtained from spectroscopic data, may be used. Note particularly that the 3d sublevel is of higher energy than the 4s sublevel. Simple rules are used in assigning electrons to the various sublevels and orbitals:

- The **aufbau principle**, which states that **electrons will occupy the lowest energy sublevel available**.
- **Hund's rule:**
  - every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied
  - all electrons in singly occupied orbitals have the same spin.
- **Pauli Principle:**
  - no two electrons in the same atom can be identified by the same set of quantum numbers
  - no more than two electrons can occupy the same orbital
  - two electrons in the same orbital must have different spins

Klechovsky's rule

The order in which these orbitals are filled is given by the $n+\ell$ rule, known as Klechkowsky's rule. Those orbitals with a lower $n+\ell$ value are filled before those with higher $n+\ell$ values.

In the case of $n+\ell$ values being equal, the orbital with a lower n value is filled first.

Klechkowsky's rule is typically represented visually thus:

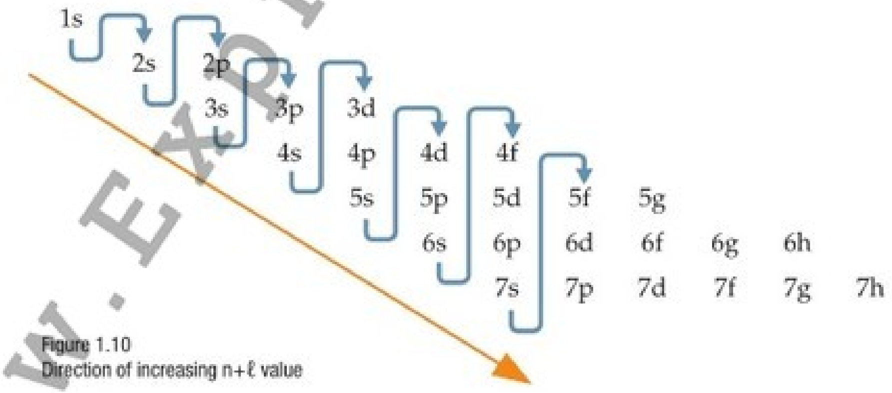


Figure 1.10
Direction of increasing $n+\ell$ value

In working out the electronic configuration of an atom, electrons are allocated to the sublevel of lowest energy until this is full. Then electrons are placed in the sublevel of next lowest energy, and the process is repeated until all of the electrons are accounted for.

The hydrogen atom has one electron, which will occupy the sublevel of lowest energy, the 1s. The electronic configuration of hydrogen is written as $1s^1$, where the superscript denotes the number of electrons in the 1s sublevel. Helium, having two electrons, will have both of these in the 1s sublevel, and its electronic configuration is written as $1s^2$. Lithium, with three electrons, will have two of these in the 1s sublevel, which is then full. The third electron goes into the 2s sublevel. The electronic configuration of lithium is written as $1s^22s^1$.

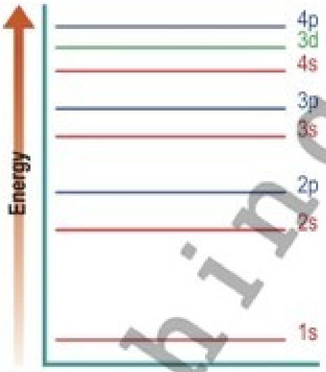


Figure 1.11
Order of filling of energy sublevels

Using this approach, the electronic configuration of sodium (atomic number = 11) is found to be $1s^22s^22p^63s^1$, while the electronic configuration of potassium (atomic number = 19) is $1s^22s^22p^63s^23p^64s^1$. Note that potassium has a similar outer electronic configuration to that of lithium and sodium, consistent with the fact that they have similar chemical properties and are in the same group of the periodic table.

EXAMPLE 1.5

What is the electronic configuration of magnesium?

Answer Magnesium has 12 electrons. Using the order of filling energy sublevels shown in Figure 1.12 the electronic configuration of magnesium is $1s^22s^22p^63s^2$.

All elements in Groups I and II of the periodic table have the outermost electrons in their atoms occupying an s sublevel. It is for that reason that this region of the periodic table is referred to as the s-block.

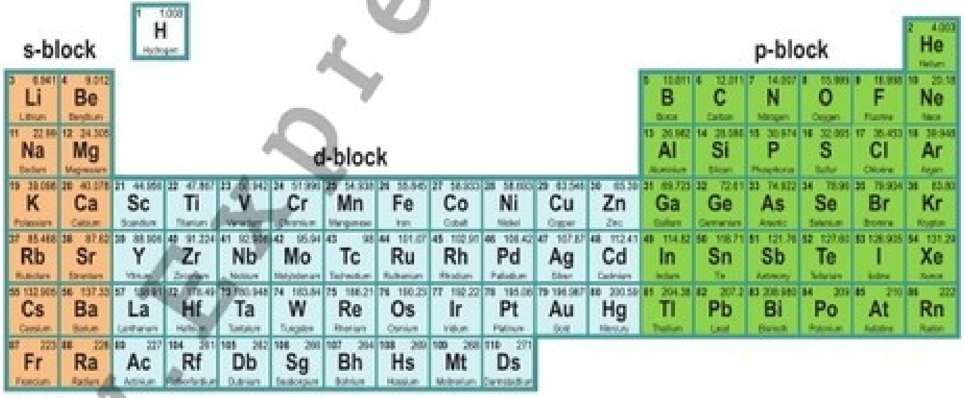


Figure 1.12

EXAMPLE 1.6

What is the electronic configuration of fluorine?

Answer Fluorine has 9 electrons. Using the order of filling energy sublevels shown in Figure 1.12 the electronic configuration of fluorine is $1s^22s^22p^5$.

EXAMPLE 1.7

What is the electronic configuration of silicon?

Answer Silicon has 14 electrons. Using the order of filling energy sublevels shown in Figure 1.12 the electronic configuration of silicon is $1s^2 2s^2 2p^6 3s^2 3p^2$.

Fluorine and silicon can be referred to as p-block elements. This is because, like all elements that are members of one of the following groups in the periodic table: III, IV, V, VI, VII and 0, they have the outermost electrons in their atoms occupying a p sublevel.

EXAMPLE 1.8

What is the electronic configuration of iron?

Answer Iron has 26 electrons. Using the order of filling energy sublevels shown in Figure 1.12 the electronic configuration of iron is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$.

This approach to working out electronic configurations works for all but two of the first 36 elements. The electronic configurations of two of the d-block elements are exceptional, as indicated in Table 1.5.

Element	'Expected' configuration	Actual electronic configuration
Copper	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
Chromium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Table 1.5

These unexpected configurations are due to the extra stability in the case of chromium of a structure with half-filled 3d and 4s sublevels, and in the case of copper of a structure with a full 3d and a half-filled 4s sublevel.

Electronic configurations of ions

The electronic configurations of ions of s-block and p-block elements are worked out in a similar way to that used for the electronic configuration of atoms.

EXAMPLE 1.9

What is the electronic configuration of Mg^{2+}?

Answer A magnesium atom has 12 electrons. This means that a magnesium ion (Mg^{2+}) has 10 electrons. The electronic configuration of Mg^{2+} is $[1s^2 2s^2 2p^6]^{2+}$.

EXAMPLE 1.10

What is the electronic configuration of Cl^-?

Answer A chlorine atom has 17 electrons. This means that a chloride ion (Cl^-) has 18 electrons. The electronic configuration of Cl^- is $[1s^2 2s^2 2p^6 3s^2 3p^6]^-$.

Arrangement of electrons in individual orbitals

How are electrons allocated when there are orbitals of equal energy available? Consider the electronic configurations of carbon, nitrogen and oxygen (Figure 1.13).

Electrons tend to occupy orbitals of equal energy singly where possible, as in the cases of carbon and nitrogen. In an atom such as the oxygen atom, pairing is necessary in the $2p_x$ orbital, but the other 2p electrons occupy the $2p_y$ and $2p_z$ orbitals singly, instead of occupying the same orbital.

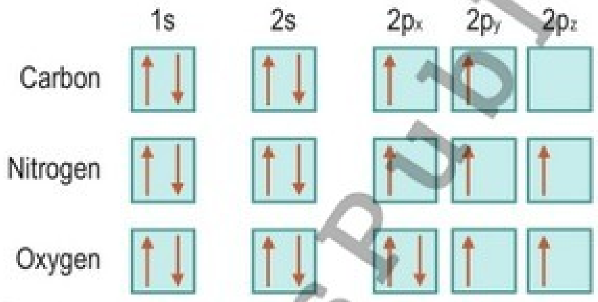


Figure 1.13
The arrangement of electrons in orbitals in carbon, nitrogen and oxygen

EXAMPLE 1.11

What is the arrangement of electrons in individual orbitals in a sulfur atom?

Answer Sulfur has 16 electrons. Using the order of filling energy sublevels shown in Figure 1.14 the electronic configuration of sulfur is $1s^2 2s^2 2p^6 3s^2 3p^4$.

Each 2p orbital is full, and so the 2p electrons are arranged as follows: $2p_x^2 2p_y^2 2p_z^2$.
In the 3p sublevel, there are four electrons available. Two of these fill the 3px orbital, and the other two are distributed between the 3py and the 3pz: $3p_x^2 3p_y^1 3p_z^1$.
Thus the expanded electronic configuration of sulfur is $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2 3s^2 3p_x^2 3p_y^1 3p_z^1$.

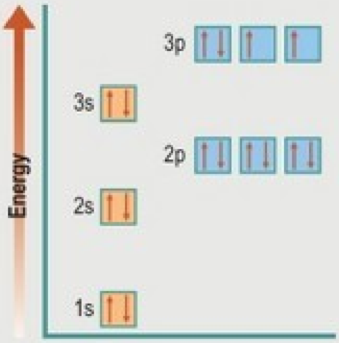


Figure 1.14
The electronic configuration of sulfur

QUESTIONS

34 Write the electronic configurations (s, p, d) for each of the following: Be, N, C, Co, Ni, Zn, Br, Ca.

35 Which atoms have the following electronic configurations? (a) $1s^2 2s^2 2p^6 3s^2 3p^3$ (b) $1s^2 2s^2 2p^3$ (c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$ (d) $1s^2 2s^2 2p^6 3s^2$.

36 Which ions have the following electronic configurations? (a) $[1s^2]^+$ (b) $[1s^2 2s^2 2p^6]^-$ (c) $[1s^2 2s^2 2p^6 3s^2 3p^6]^{2-}$ (d) $[1s^2 2s^2 2p^6 3s^2 3p^6]^{2+}$

37 Write down the total number of (a) s electrons (b) p electrons in a chromium atom. Where are the remaining electrons in this atom accommodated?

1.13 Isotopes

Isotopes are atoms with the same number of protons but different numbers of neutrons.

Atoms of the same element always have the same number of protons, but may have different numbers of neutrons. Isotopes have the same atomic number, Z, but different mass numbers, A.

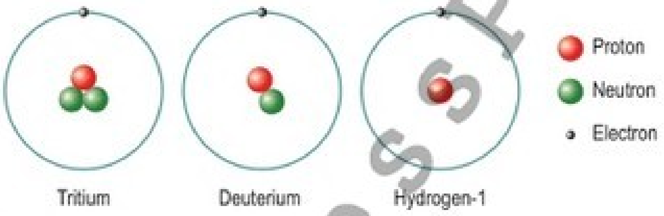


Figure 1.15
The isotopes of hydrogen

Naturally occurring hydrogen consists of three isotopes, ^1H (1 proton and no neutron), ^2H (1 proton and 1 neutron), known as deuterium, and ^3H (1 proton and 2 neutrons), known as tritium. The ^1H isotope, which may also be written as hydrogen-1, is the only atom of any element without any neutron in the nucleus. It is by far the most abundant isotope of hydrogen.

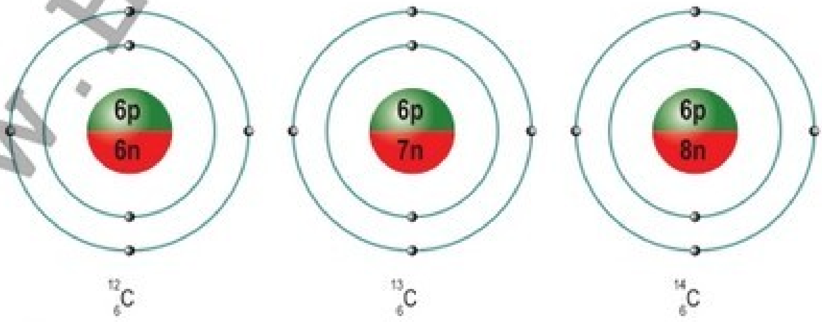


Figure 1.16
The isotopes of carbon

Naturally occurring carbon consists of three isotopes, carbon-12 (i.e. ^{12}C, with 6 protons and 6 neutrons), carbon-13 (i.e. ^{13}C, with 6 protons and 7 neutrons) and carbon-14 (i.e. ^{14}C, with 6 protons and 8 neutrons). Carbon-12 is the most abundant isotope.

The chemical properties of an element depend on the number and arrangement of the electrons. Isotopes of an element have the same chemical properties since they have the same number and arrangement of electrons. However, there may be slight differences in physical properties because of the difference in mass. In addition, some isotopes have unstable nuclei, for example ^{14}C, and such isotopes are said to be radioactive.

QUESTIONS

38 Define isotopes.

39 Explain isotopes in terms of numbers of protons and neutrons.

40 Explain isotopes in terms of atomic number and mass number.

41 For the three isotopes of hydrogen, indicate the mass number and atomic number, and state the numbers of protons, neutrons and electrons.

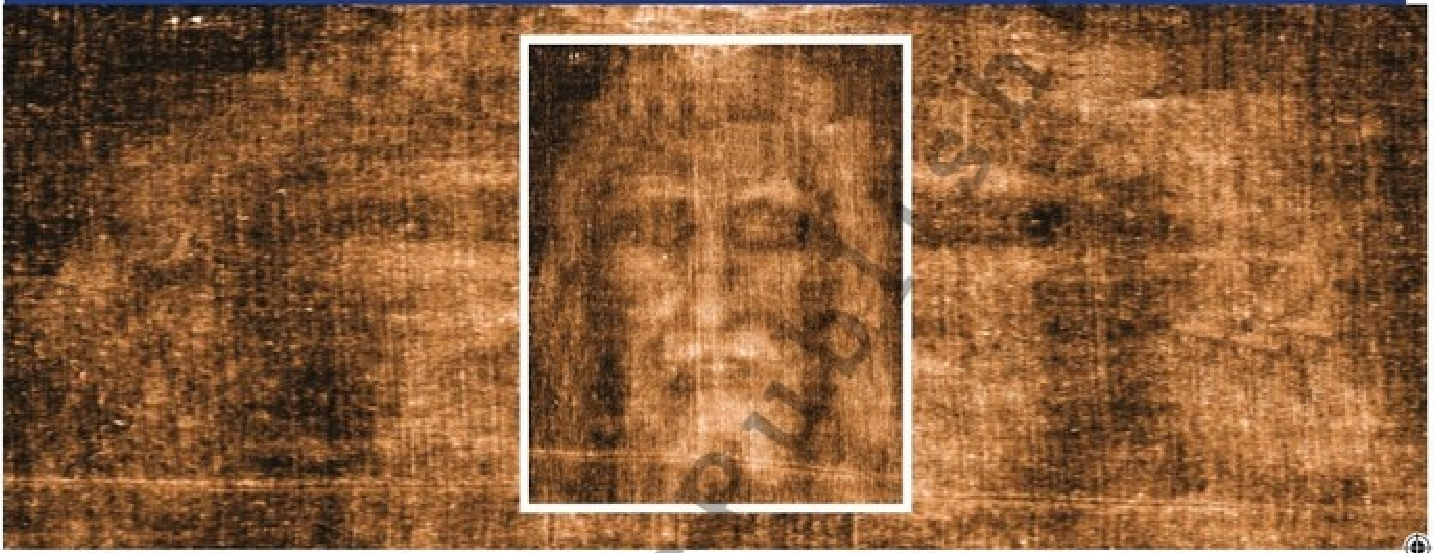
42 What name is given to a hydrogen atom of mass 2?

43 What is tritium?

44 What is the nuclide configuration of the three isotopes of carbon?

Radioactivity

MODULE 2



Learning objectives

- To explain the nature of radioactivity and the use of radioactive isotopes 10.1.2.3
- To find the chemical formula of a compound from analytical data 10.1.1.1
- To define the notion of a radioactive compound 10.2.1.8
- To name the kinds of radioactive radiation, complete the nuclear equations (α, β^-, β^+ decay, γ rays) 10.2.1.9
- To understand the significance of nuclear equations for Kazakhstan's industry 10.2.1.10

2.1 Radioactivity

The nuclei of atoms of every element except the simplest isotope of hydrogen contain neutrons as well as protons. For the nucleus to be stable, it must contain a suitable ratio of protons to neutrons. If this ratio is not suitable, the nucleus disintegrates, throwing out fragments and/or energy in an effort to achieve a stable ratio.

Radioactivity is defined as the spontaneous breaking up of certain unstable nuclei, accompanied by the emission of radiation.

2.2 Types of Radiation

There are three types of radiation emitted by radioactive isotopes:

- α particles, which have a positive charge
- β particles, which have a negative charge
- γ rays, which are neutral.

The **Geiger–Müller tube** is one of the devices that may be used to detect radioactivity. In a Geiger–Müller tube, a gas is ionised by alpha, beta or gamma radiation, and the resulting electric current is amplified and detected.

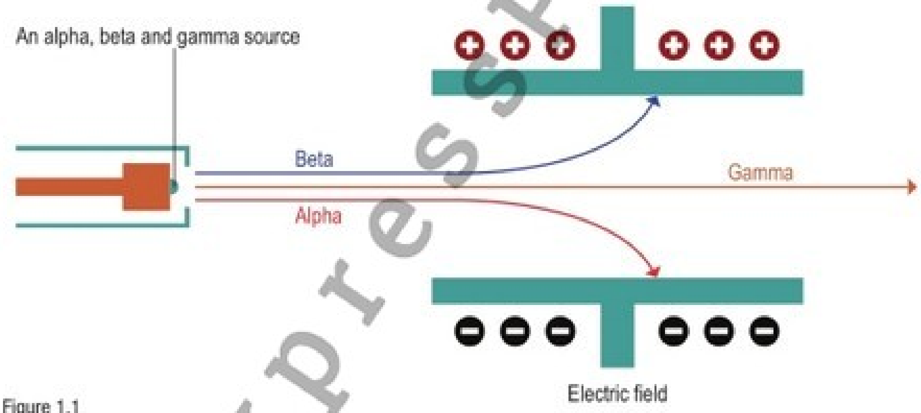


Figure 1.1
The effect of an electric field on alpha, beta and gamma radiation

α particles (alpha particles)

These particles consist of two protons and two neutrons, i.e. they are helium nuclei. They move relatively slowly and are stopped quite easily, e.g. by human skin or by a few sheets of paper. However, they are strongly ionising and extremely hazardous if they get into the body through the mouth or the nose. The molecules in a living cell may be damaged or destroyed, perhaps leading to cancer, if penetrated by ionising radiation. Many radioactive isotopes emit alpha particles. An example of an α emitter is americium-241, which is used in many smoke detectors. It decays according to the following equation:

$$^{241}_{95}\mathrm{Am} \rightarrow {}^{237}_{93}\mathrm{Np} + {}^{4}_{2}\mathrm{He} + \text{energy}$$

The new element formed is neptunium.

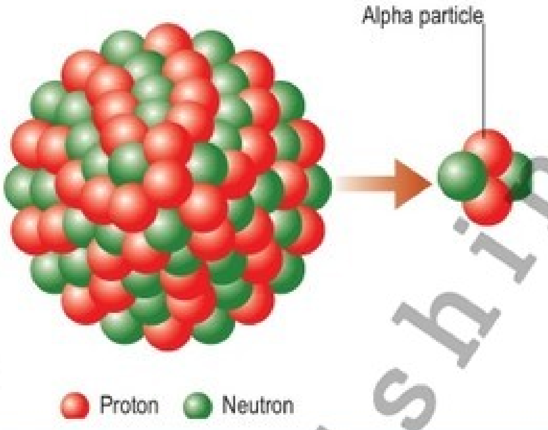


Figure 1.2
Diagram showing alpha decay

Alpha particles are helium nuclei, with a positive charge and little penetrating ability.

β particles (beta particles)

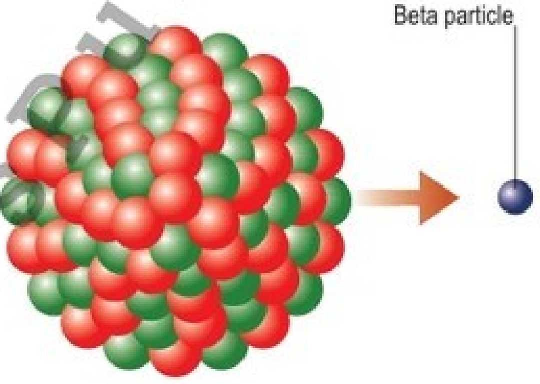


Figure 1.3
Diagram showing beta decay

In some radioactive atoms, neutrons disintegrate into protons and electrons. The electrons – β particles – are emitted from the nucleus in a fast-moving stream. They are more penetrative than α particles. The β particles can be stopped by a 5 mm thickness of aluminium. β particles are capable of penetrating deep into the body and are potentially very damaging – they could cause cancer. The proton formed by the disintegration remains in the nucleus. As a result, there is no change in the mass number, but the atomic number increases by one. This means that a new element has been formed.

Carbon-14, which is used for age determination, is an example of a β emitter. It decays according to the following equation:

$$^{14}_{6}\mathrm{C} \rightarrow \, ^{14}_{7}\mathrm{N} + \, ^{0}_{-1}\mathrm{e} + \text{energy}$$

The new element formed is nitrogen.

Beta particles are electrons, with a negative charge and greater penetrating ability than alpha particles.

γ rays (gamma rays)

The third type of radioactivity emitted by radioactive isotopes is a form of energy called γ rays. These rays have no mass or charge. Unlike α and β radiation, they are not particles. They move very quickly and have much greater penetration than α or β radiation. Thick shields of concrete or lead can stop them. Gamma rays can be very damaging to the human body. They could cause cancer.

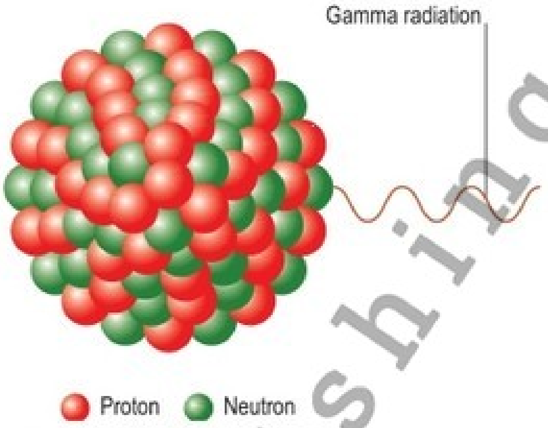


Figure 1.4
Diagram showing gamma decay

Gamma rays are high-energy electromagnetic radiation, with greater penetrating ability than beta particles.

An example of a γ emitter is cobalt-60, which is used for cancer treatment and for food irradiation.

$$^{60}_{27}\text{Co} \rightarrow ^{60}_{27}\text{Co} + \text{energy}$$

The equation shows that no new element is formed, but energy is emitted.

Type of radiation	Properties
Alpha particles	○ Positive charge ○ Poor penetrating ability ○ Deflected by electrical and magnetic fields ○ Damaging to human cells
Beta particles	○ Negative charge ○ Moderate penetrating ability ○ Deflected by electrical and magnetic fields ○ Damaging to human cells
Gamma rays	○ No charge ○ Very high penetrating ability ○ Not deflected by electrical and magnetic fields ○ Damaging to human cells

Table 1.1

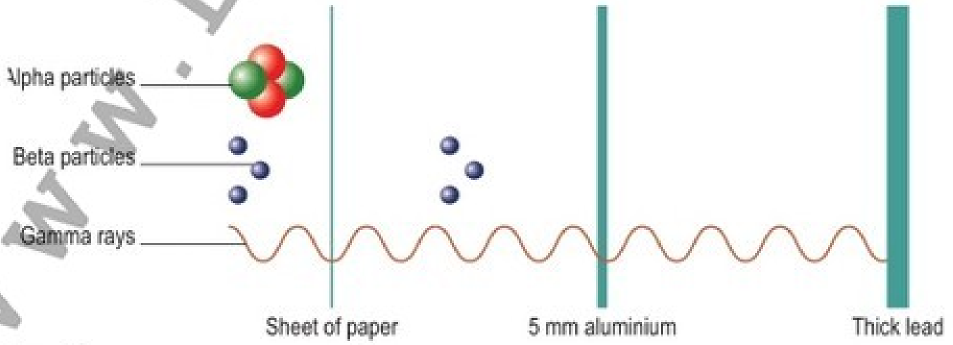


Figure 1.5
The relative penetrating properties of alpha, beta and gamma radiation

QUESTIONS

1 What is radioactivity?
2 Name the three kinds of radioactive radiation.
3 Name an instrument that can be used to detect radioactivity.
4 Alpha particles can be stopped by a piece of ________________.
5 Beta particles can be stopped by a sheet of ________________.
6 Gamma rays can be stopped by a block of ________________.
7 What electric charge does (a) an alpha particle (b) a beta particle (c) a gamma ray have?
8 What changes occur in the nucleus of an atom that undergoes beta emission?

2.3 Distinction between Chemical and Nuclear Reactions

The alpha decay of americium-241

$$^{241}_{95}\text{Am} \rightarrow {}^{237}_{93}\text{Np} + {}^{4}_{2}\text{He} + \text{energy}$$

and the beta decay of carbon-14

$$^{14}_{6}\text{C} \rightarrow {}^{14}_{7}\text{N} + {}^{0}_{-1}\text{e} + \text{energy}$$

are examples of nuclear reactions. They involve changes in the nucleus involving protons and neutrons. **They cause elements to change into other elements**.

In contrast, chemical reactions only involve changes in the distribution of electrons, usually those in the outer shells of the bonding atoms. Chemical reactions **cannot** change one element into another element.

When an isotope undergoes beta decay, its atomic number increases by 1, while its mass number remains unchanged.

EXAMPLE 2.1

Write an equation for the beta decay of the radioactive isotope

$$^{19}_{8}\text{O}$$

Answer When the ^{19}O isotope undergoes beta decay, its atomic number increases by 1, while its mass number remains unchanged.

$$^{19}_{8}\text{O} \rightarrow {}^{19}_{9}\text{F} + {}^{0}_{-1}\text{e}$$

When an isotope undergoes alpha decay, its atomic number decreases by 2, while its mass number decreases by 4.

EXAMPLE 2.2

Write an equation for the alpha decay of the radioactive isotope

$^{202}_{82}Pb$

Answer When the ^{202}Pb isotope undergoes alpha decay, its atomic number decreases by 2, while its mass number decreases by 4.

$$^{202}_{82}Pb \rightarrow {}^{198}_{80}Hg + {}^{4}_{2}He$$

QUESTIONS

9 State one difference between a nuclear reaction and a chemical reaction.

10 Complete the following nuclear equations:

(a) $^{238}_{92}U \rightarrow \_\_ + {}^{4}_{2}e$	(d) $^{32}_{15}P \rightarrow \_\_ + {}^{0}_{-1}e$
(b) $^{3}_{1}H \rightarrow \_\_ + {}^{0}_{-1}e$	(e) $^{212}_{84}Po \rightarrow \_\_ + {}^{4}_{2}He$
(c) $^{239}_{94}Pu \rightarrow \_\_ + {}^{4}_{2}He$	

11 Write an equation for the beta decay of carbon-14.

2.4 Radioisotopes and Half-life

Most naturally occurring elements have isotopes, some stable and some unstable. Carbon-12, for example, is stable, whereas carbon-14 is radioactive. Unstable, radioactive isotopes are called **radioisotopes**. All isotopes of atomic number greater than 83 are naturally radioactive. However, almost every element with an atomic number below 84 has at least one stable isotope.

In a sample of radioactive material, it cannot be predicted when a particular atom will disintegrate, because radioactive decay is a random process. However, it is possible to predict how many atoms will decay in a given time. Radioactive atoms decay in such a way that the number of them present is halved after some fixed interval of time. This interval of time is called the **half-life** of the sample. Some radioisotopes decay very quickly and have short half-lives. Others do so more slowly and have long half-lives. Half-lives vary from fractions of seconds to billions of years. Radium-214, for example, has a half-life of 20 minutes while uranium-238 has a half-life of 4.5 billion years.

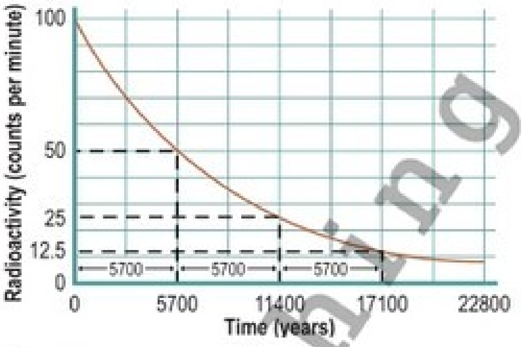


Figure 1.6
The radioactive decay of carbon-14

The slow decrease of radioactivity in isotopes of long half-life, and the difficulty of disposing of nuclear waste, convince many people that nuclear power stations are unacceptably dangerous. However the problems associated with the use of fossil fuels, including their involvement in global warming and their decreasing availability, have forced governments and scientists to consider alternatives. Nuclear power is now being looked at more favourably than in the recent past, and is seen in some quarters as the lesser of two evils compared with fossil fuels.

The half-life of a radioactive isotope is the time taken for half of the atoms in a sample of the isotope to decay.

QUESTIONS

12 What is a radioisotope?
13 What is meant by the half-life of a radioisotope?
14 Why are radioisotopes with long half-lives a problem?
15 Why is nuclear power being considered more favourably than in the recent past?

2.5 Uses of Radioisotopes

Radioisotopes have many uses and are particularly important in archaeology, in medicine and in food preservation. An important household use of radioisotopes is in smoke alarms.

Archaeology

Carbon dating is an important method used for estimating the age of objects that contain carbon, such as paintings, fabrics and wood. Carbon-14 is a radioisotope emitting beta particles and it has a half-life of 5730 years. When an animal or plant is alive, it will have carbon-12 and carbon-14 in the same ratio as is present in the air. After the death of the organism, the unstable carbon-14 decays, while the stable carbon-12 remains unchanged. By measuring the changed ratio, and taking into account the half life of carbon-14, the age of the object can be estimated.

Medicine

Cobalt-60, a gamma-ray emitter, is used in the treatment of cancer with radiation, i.e. radiotherapy. Ionising radiation damages human cells, but cancerous cells are more susceptible to damage than normal cells. The gamma rays from the cobalt-60 are directed onto the tumour.


Patient receiving radiotherapy using a cobalt-60 source

Food preservation

Cobalt-60 is also used in preserving food by irradiation. The γ rays kill micro-organisms and insects present in food that could cause the food to deteriorate quickly.

Smoke alarms

Americium-241 is an alpha emitter which is used in many smoke detectors. It is safe to use, as the radiation it emits is not very penetrating. The battery in a smoke alarm has to be replaced at intervals, but the americium does not, since it has a long half-life (over 400 years).

QUESTIONS

16 Why is cobalt-60 useful in cancer treatment?

17 Carbon-14 dating is confined to objects containing ________________.

18 Explain how the carbon-14 isotope allows certain archaeological artefacts to be dated.

19 Why is cobalt-60 useful in food preservation?

2.6 Nuclear Industry in Kazakhstan

Kazakhstan has around 12% of the world's uranium resources and since 2009 has been the world's leading uranium producer, providing around a third of the world's uranium. Although the only ever nuclear power reactor operated in Kazakhstan in Aktau closed in 1999, Kazakhstan has a major nuclear facility for making nuclear fuel pellets in Ust-Kamenogorsk.

Most of the world's nuclear power reactors require 'enriched' uranium fuel in which the proportion of the uranium-235 isotope is increased from the natural level of 0.7% to around 3.5% to 5%. To undergo the enrichment process the uranium recovered from mines in the form of uranium oxide in processed into a gaseous form: uranium hexafluoride. Enrichment plants like the one in Ust-Kamenogorsk concentrate the useful uranium-235 in uranium hexafluoride and convert it into nuclear fuel pellets. These pellets of enriched uranium are used in the majority of the world's light water reactors which produce electricity.

In 2017 the Ust-Kamenogorsk plant which produces low enriched uranium [LEU] became the site of the world's first LEU bank run by the International Atomic Energy Authority. This bank now holds around 90 metric tons of low enriched uranium which can be drawn on by other countries under the supervision of the IAEA when their supplies of nuclear fuel are disrupted. The initiative is seen as an important one in assuring countries a guaranteed supply of nuclear fuel and helping to limit nuclear proliferation around the world.

The Periodic Table and Periodicity

MODULE 3

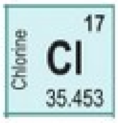
Learning objectives

- To explain the meaning of the Periodic Law 10.2.1.1
- To explain the meaning of valency and oxidation numbers 10.2.1.2
- To explain regularities in changes of properties of atoms of chemical elements: radius, ionisation energy, electron affinity, electronegativity and the degree of oxidation 10.2.1.3
- To explain the trends in changes of acidic-basic properties of oxides, hydroxides and hydrogen compounds of chemical elements across periods and groups 10.2.1.4
- To predict properties of chemical elements and their compounds according to their location in the periodic table 10.2.1.5
- To identify scientific developments associated with the discovery of periodic law 10.2.1.6

3.1 The Periodic Table of the Elements

In the periodic table of the elements, elements with similar chemical properties are grouped together. This makes the study of chemistry very much easier than it would be otherwise.

In the periodic table, elements are arranged in order of increasing atomic number. Elements that have similar chemical properties (for example, sodium and potassium) are placed in vertical columns, called **groups**. There are eight main groups, designated I, II, III, IV, V, VI, VII and 0 respectively. The elements between groups II and III are known as the **d-block** elements. Each vertical group in this region of the table is known as a subgroup; for example, copper, silver and gold make up the copper subgroup.



Directly above the symbol of each element in the periodic table is written its atomic number. The **relative atomic mass** (formerly known as the **atomic weight**) is written underneath the symbol. For example, chlorine (Cl) can be seen to have an atomic number of 17 and a relative atomic mass of 35.453.

Chlorine is in Group VII and has chemical properties that are similar to the other Group VII elements fluorine, bromine, iodine and astatine.

A horizontal row of elements in the periodic table is called a **period**. The first period contains two elements, hydrogen and helium. There are eight elements in the second period, starting with lithium and ending with neon.

There are also eight elements in the third period, starting with sodium and ending with argon. There are eighteen elements in the fourth period, starting with potassium and ending with krypton.

The stepped line shown in Figure 3.1 divides the metallic elements from the elements that are non-metals. The elements on the left-hand side of the line are metals, while those on the right are non-metals. Some of the elements next to the stepped line, for example silicon and germanium, have some properties similar to metals and other properties similar to non-metals.

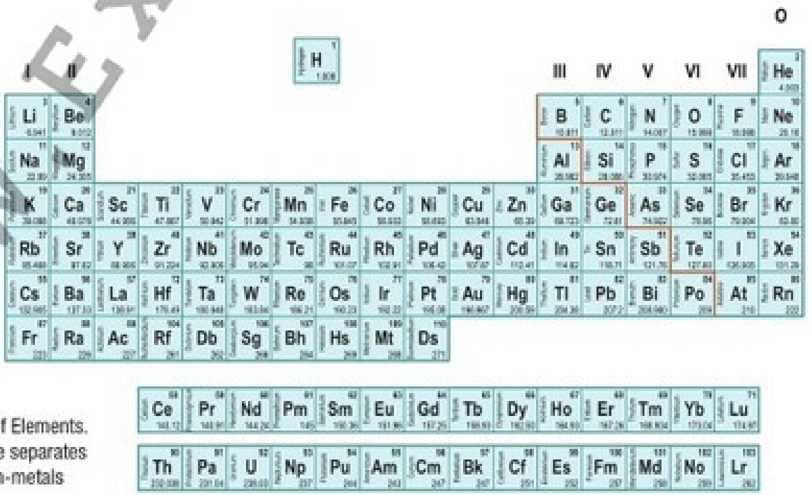


Figure 3.1
Periodic Table of Elements.
The stepped line separates metals from non-metals

3.2 Valency

The valency of an element is the number of bonds an atom of the element forms when it reacts.

Valency gives a measure of the combining power of an atom. It is defined as **the number of bonds an atom forms when it reacts.** For example, carbon forms four bonds when it reacts, so it has a valency of four.

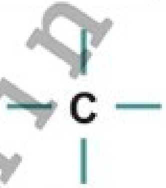


Figure 3.2

The valency of an element can usually be worked out by calculating the number of electrons that its atoms would need to lose, gain or share to attain a stable electronic structure such as that of the nearest noble gas in the periodic table.

- Atoms of Group I elements (e.g. Li, Na, K), which each have one electron in the outer level, reach noble gas structure by losing this one outer electron. Thus these elements have a valency of one.
- Atoms of Group II elements (e.g. Mg, Ca) reach noble gas structure by losing their two outer electrons. Thus these elements have a valency of two.
- Atoms of Group III elements (e.g. Al, Ga) reach noble gas structure by losing their three outer electrons. Thus these elements have a valency of three. (Boron also has a valency of three. However, although it forms three bonds, it does so by sharing electrons, and does not attain noble gas structure).
- Atoms of Group IV elements (e.g. C, Si, Ge) tend to bond by gaining a share in four electrons from atoms of other elements. Thus Group IV elements have a valency of four.
- Atoms of Group V elements (e.g. N, P, As) tend to bond by gaining a share of three electrons from atoms of other elements. Thus Group V elements usually have a valency of three.
- Atoms of Group VI elements (e.g. O, S, Se) tend to bond by gaining two electrons, or a share of two electrons, from atoms of other elements. Thus Group VI elements have a valency of two.
- Atoms of Group VII elements (e.g. F, Cl, Br) tend to bond either by gaining an electron, or a share of an electron, from atoms of other elements. Thus Group VII elements have a valency of one.

The valencies of s-block and p-block elements are summarised in Table 3.1.

Group number	I	II	III	IV	V	VI	VII	0
Valency	1	2	3	4	3	2	1	0

Table 3.1

Transition elements have variable valencies, some of which are shown in Table 3.2:

Element	Valency
Chromium	2, 3, 6
Manganese	2, 3, 4, 6, 7
Iron	2, 3, 6
Copper	1, 2

Table 3.2

Figure 3.3
Valencies of group VI atoms

EXAMPLE 3.1

What is the formula of ammonia, a compound containing nitrogen and hydrogen only?

Answer Nitrogen has a valency of 3, while hydrogen has a valency of 1. A nitrogen atom will therefore form three bonds, and hydrogen will form one bond. Three hydrogen atoms are therefore required to bond with one atom of nitrogen.

Thus the formula of ammonia is NH_3.

Figure 3.4

EXAMPLE 3.2

What is the formula of aluminium oxide?

Answer Aluminium has a valency of 3, and oxygen has a valency of 2. An aluminium atom forms three bonds on reaction, while an oxygen atom forms two. Three oxygen atoms will therefore be needed to bond with two aluminium atoms, to enable all atoms to form the correct number of bonds.

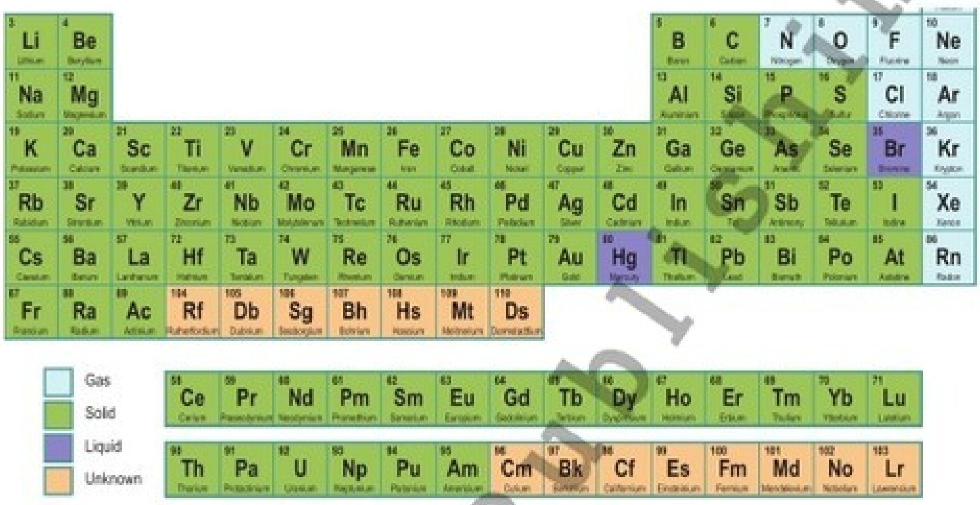
Thus the formula of aluminium oxide is Al_2O_3.

QUESTIONS

1. What is the valency of each of the following elements: sodium, hydrogen, lithium, fluorine, magnesium, sulfur, iodine, aluminium, bromine, oxygen, potassium, nitrogen, arsenic, boron, silicon?
2. Using valencies, write the formula of each of the following compounds: (a) beryllium chloride (b) hydrogen fluoride (c) calcium chloride (d) hydrogen sulfide.

3.3 The Periodic Groups

At room temperature, most of the elements are solids, two are liquids (mercury and bromine) and 11 are gases (hydrogen, nitrogen, oxygen, fluorine, chlorine and all of the Group 0 elements). Most of the solid elements are metals.



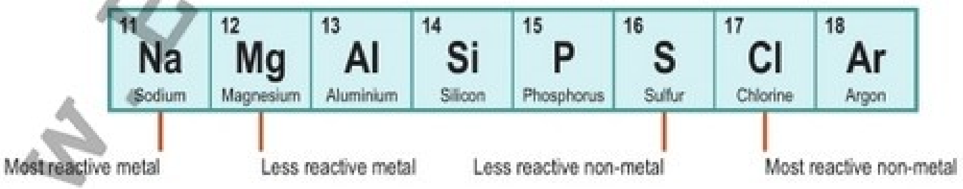
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds								

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 3.5
Periodic table of the elements showing physical states

Elements show great variety in their chemical properties. Within a group, however, there are similarities in the chemical properties of the elements. The most reactive elements are the Group I elements and the Group VII elements.

Elements between the Group I elements (the most reactive metals) and the Group VII elements (the most reactive non-metals) have properties that lie between these two extremes. For example, on going across the third period, from magnesium to sulfur, we observe a gradual change in properties. Magnesium and aluminium are metals which are less reactive than sodium, while silicon, phosphorus and sulfur are non-metals which are less reactive than chlorine.



11	12	13	14	15	16	17	18
Na	Mg	Al	Si	P	S	Cl	Ar
Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulfur	Chlorine	Argon

Figure 3.6
The third period elements

The Alkali Metals

The Group I elements are called the **alkali metals**. **They are all very reactive metals, increasing in reactivity down the group**.

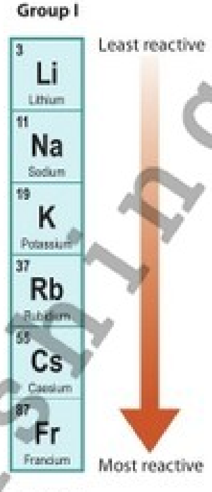


Figure 3.7
Reactivity trend in Group I

Physical properties

- They are soft metals – they can be cut with a knife.
- They have low densities – lithium, sodium and potassium each float in water.

Chemical properties

- When they are freshly cut, they have a metallic shine, but this disappears rapidly due to reaction of the exposed metal surface with oxygen in the air. The metal oxide is formed, as it is when the alkali metals burn in air. The following **word equation** shows how sodium reacts with oxygen:

  Sodium + oxygen → sodium oxide

- They react vigorously with water, forming a basic solution and hydrogen. For example sodium reacts as follows:

  Sodium + water → sodium hydroxide + hydrogen

  $$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

(In the above **chemical equation**, **chemical formulas** are used, and the subscripts following each formula give information about the physical states of reactants and products: (s) = solid; (l) = liquid; (aq) = dissolved in water [aqueous solution]; (g) = gas.)

Alkali metals are stored in oil to prevent reactions with water and with atmospheric oxygen.

3.1 PRACTICAL DEMONSTRATION

The reaction of alkali metals with water

The chemical equations for the reactions between alkali metals and water in this demonstration are as follows:

$$2Li_{(s)} + 2H_2O_{(l)} \rightarrow 2LiOH_{(aq)} + H_{2(g)}$$
$$2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$
$$2K_{(s)} + 2H_2O_{(l)} \rightarrow 2KOH_{(aq)} + H_{2(g)}$$

Chemicals needed	**Equipment needed**
Lithium	Trough
Sodium	Knife
Potassium	
Water	
Litmus paper	

Procedure

NB: Wear your safety glasses

Figure 3.8

3. Place a small piece of lithium in a trough of water. Describe and explain what happens.
4. Dip a piece of red litmus paper into the trough. Describe and explain what happens.
5. Place a small piece of sodium in a trough of water. Describe and explain what happens.
6. Dip a piece of red litmus paper into the trough. Describe and explain what happens.
7. Place a small piece of potassium in a trough of water. Describe and explain what happens.
8. Dip a piece of red litmus paper into the trough. Describe and explain what happens.
9. What metal shows the most energetic reaction?
10. What metal shows the least energetic reaction?

The Alkaline Earth Elements

The Group II elements are called the **alkaline earth elements. They are all reactive elements, with reactivity increasing down the group**. Some properties that magnesium and calcium have in common are as follows:

Physical properties

- They are metals which are harder than the alkali metals.

Chemical properties

- They are less reactive than the corresponding alkali metals. For example, magnesium reacts very slowly with water. Calcium reacts more quickly, but less vigorously than the corresponding alkali metal:

  Calcium + water → calcium hydroxide + hydrogen

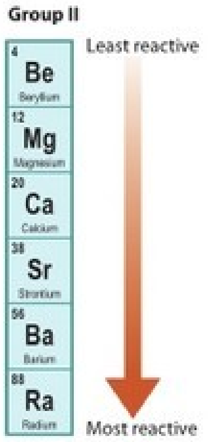


Figure 3.9
Reactivity trend in Group II

The Halogens

The Group VII elements are called the **halogens. They are very reactive non-metals, decreasing in reactivity down the group**.

Physical properties

- They have low melting and boiling points. At room temperature, fluorine and chlorine are yellow-green gases, bromine is a red liquid and iodine is a dark solid.

Chemical properties

- They react with hydrogen to form compounds which dissolve in water to form acidic solutions. For example, in the case of chlorine:

  Hydrogen + chlorine → hydrogen chloride gas

  $H_{2(g)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

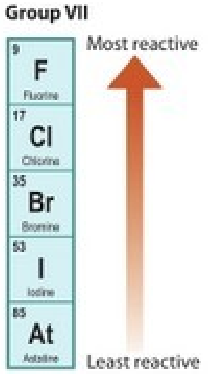


Figure 3.10
Reactivity trend in Group VII

Hydrogen chloride gas + water → hydrochloric acid solution
$HCl_{(g)} + H_2O_{(l)} \rightarrow HCl_{(aq)}$

- They react vigorously with sodium (and the other alkali metals), forming white salts, for example:

Sodium + chlorine → sodium chloride

The Noble Gases

The Group 0 elements are called the **noble gases**. The main properties that these elements have in common are as follows:

Physical properties

- They are all gases at room temperature. The boiling point and density increase going down the group.

Chemical properties

- They are the least reactive of all elements. Over 50 years elapsed between the discovery of the noble gases in the late nineteenth century and the synthesis of the first compound of a noble gas.

QUESTIONS

3 Name six elements that are gases at room temperature.

4 Name six elements that are solids at room temperature.

5 Name two elements that are liquids at room temperature.

6 What are the most reactive groups of elements in the periodic table?

7 What is the least reactive group of elements?

8 Using one of the words acid, base or salt in each case, state what is formed when (a) lithium reacts with water (b) fluorine reacts with hydrogen (c) potassium reacts with chlorine.

9 List (a) two physical properties (b) two chemical properties of the alkali metals.

10 List (a) one physical property (b) one chemical property of the alkaline earth elements.

11 List (a) one physical property (b) two chemical properties of the halogens.

12 What chemical properties would you expect caesium (atomic number = 55) to have?

13 (a) Nine substances that are now recognised as elements were known to the ancients. Seven of these were metals, and two were non-metals. Name as many of these elements as you can.
(b) Four more elements were known to the medieval alchemists. They included bismuth, antimony and two other elements, X and Z. X is a metal now widely used in the galvanising of iron. Z is a very poisonous non-metal. Identify X and Z.

14 Which two elements are most abundant in the sun?

s-block and p-block Elements

The elements in Groups I and II form a block of reactive metals, called the **s-block elements**. They have lower densities, lower melting points and lower boiling points, and are more reactive, than most other metals.

The elements in Groups III, IV, V, VI, VII and 0 are called the **p-block elements**. These are mainly non-metals, but the lower members of some of these groups, for example tin and lead in Group IV, are metals.

QUESTIONS

15 Name (a) an alkali metal (b) a noble gas (c) a halogen (d) an s-block element (e) a p-block element (f) a d-block element.

16 Discuss the following statement: 'The alkaline earth elements are less reactive than the alkali metals.' Talk to your partner about the chemical properties of both of these groups of elements.

17 Discuss the following statement: 'The most reactive non-metals are the halogens, while the least reactive non-metals are the noble gases.' Talk to your partner about the chemical properties of both of these groups of elements.

3.4 Periodicity

Periodicity a fundamental aspect of the **periodic table** of the elements. It concerns the recurring trends that are seen in element properties going down or across the periodic table. It was such trends that became apparent to Mendeleev as he undertook the task of arranging the elements in order of increasing mass.

In the modern periodic table, elements are ordered by increasing **atomic number**, which reflects **the number of protons** in an atom. The basic periodic properties the table reflects are:

- ionization energy
- atomic radius
- electronegativity
- electron affinity

QUESTIONS

18 Match each of the properties above to their definition.
(A) measure of the ability of an atom to attract a pair of electrons towards it
(B) half the distance between the centres of two atoms that are touching each other
(C) energy required to remove an electron from an ion or gaseous atom
(D) ability of an atom to accept an electron

PERIODICITY Trends

Figure 3.11 show the trends relating to these periodic properties moving across a row or period of the periodic table or moving down a column or group.

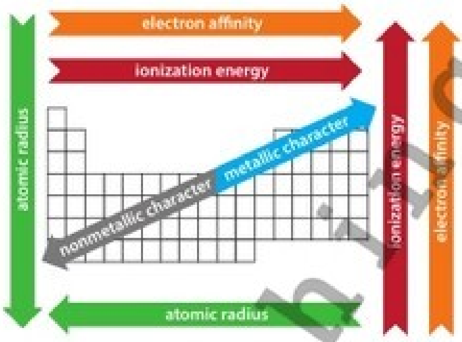


Figure 3.11
electronegativity

3.5 Atomic Radius and Periodicity

The atomic radius of an element is half the distance between the nuclei of two atoms of the element that are joined together by a single covalent bond.

The size of an atom is not easy to define, because the probability of finding an electron at a point does not become zero even at great distances from the nucleus. Therefore, the selection of the position of the boundary of the atom is rather arbitrary.

Values for the atomic radii of the elements, measured in nm, are given in Figure 3.12. These values can be measured using X-rays.

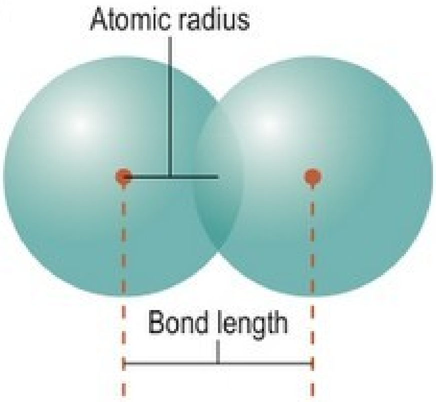
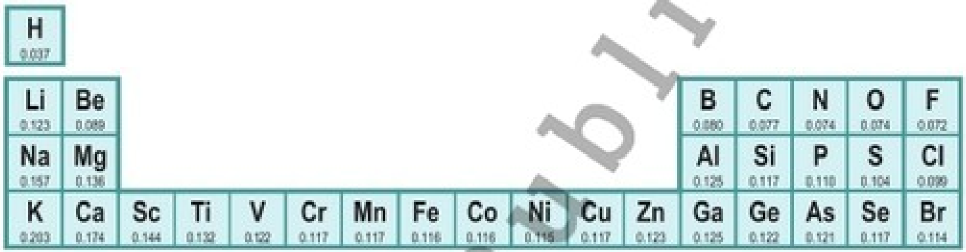


Figure 3.12
The atomic radius is equal to half the distance between the nuclei of the two atoms

Trends in the size of the atomic radius on going **down a group** depend on:

- number of energy levels occupied
- screening effect.

In atoms with an atomic number greater than 2, electrons in inner levels partially neutralise the attractive force of the nucleus by repelling the outer electrons. The effect of screening is most marked on going down a group in the periodic table. In Group I, for example, on going from lithium to sodium, an extra level is added. The **effective nuclear charge** experienced by the outermost electron is much less than the full nuclear charge. The atomic radius **increases** on going down a group, because of the addition of extra energy levels, and the resultant extra screening by inner levels.



H 0.037																
Li 0.123	Be 0.089											B 0.080	C 0.077	N 0.074	O 0.074	F 0.072
Na 0.157	Mg 0.136											Al 0.125	Si 0.117	P 0.110	S 0.104	Cl 0.099
K 0.203	Ca 0.174	Sc 0.144	Ti 0.132	V 0.122	Cr 0.117	Mn 0.117	Fe 0.116	Co 0.116	Ni 0.115	Cu 0.117	Zn 0.123	Ga 0.125	Ge 0.122	As 0.121	Se 0.117	Br 0.114

Figure 3.13
The table of atomic radii for the first 36 elements

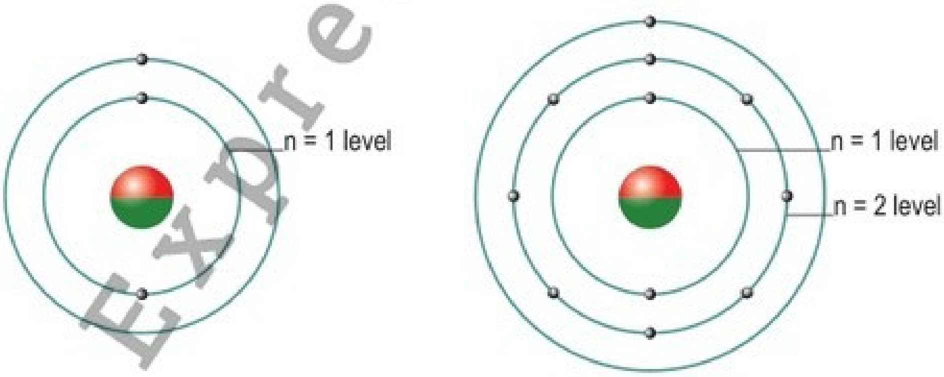


Figure 3.14
The outer electron of a lithium atom is screened by electrons in the n=1 energy level only. The outer electron in a sodium atom is screened by electrons in both the n=1 and n=2 energy levels

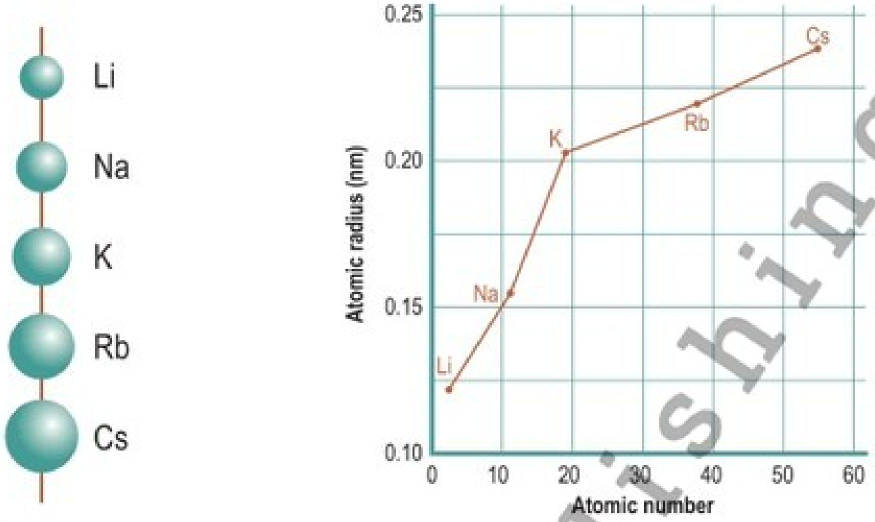
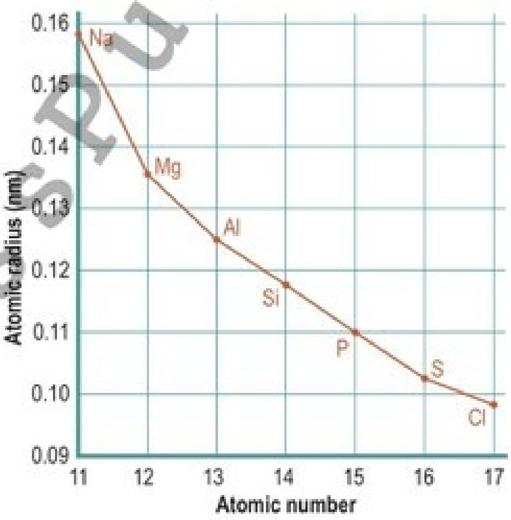


Figure 3.15
The increase in atomic radius values down Group I

Trends in the size of the atomic radius on going **across a period** depend on a number of factors:

- Nuclear charge
  The atomic radius **decreases** on going from left to right across a period, because of the increasing nuclear charge, which exerts a greater attractive force on the outer electrons.
- Screening effect
  Within the same energy level, the screening effect by inner levels is the same, because there is the same number of inner levels.



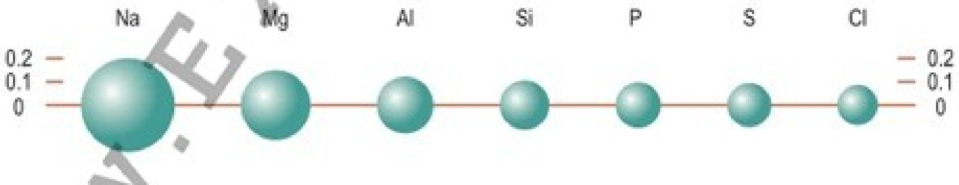


Figure 3.16
The downward trend in atomic radius values across the third period

QUESTIONS

19 What happens to the atomic radius on going from left to right across a period in the periodic table? Explain your answer.

20 What happens to the atomic radius on going down a group in the periodic table? Explain your answer.

21 Why does an increase in nuclear charge tend to decrease the atomic radius?

22 How does the presence of extra occupied energy levels in an atom affect its atomic radius? Explain your answer.

3.6 Periodicity and Ionisation energies

In an atom with many electrons, the electrons occupy different sublevels of distinct energy values. Since the electrons have different energies, different amounts of energy will be needed to remove different electrons from an atom.

The first ionisation energy of an element is the minimum energy in kilojoules required to remove the most loosely bound electron from each isolated atom in a mole of the element in its ground state.

The first ionisation energy for an element X is represented by the following equation:

$$X_{(g)} \rightarrow X^{+}_{(g)} + e^{-}$$

The first ionisation energy of an element is measured in kilojoules per mole.

Li 519	Be 900											B 799	C 1090	N 1400	O 1310	F 1680	Ne 2080
Na 494	Mg 736											Al 577	Si 786	P 1060	S 1000	Cl 1260	Ar 1520
K 418	Ca 590	Sc 632	Ti 661	V 648	Cr 653	Mn 716	Fe 762	Co 757	Ni 736	Cu 745	Zn 908	Ga 577	Ge 762	As 966	Se 941	Br 1140	Kr 1350

Figure 3.17
Table of first ionisation energy values for the first 36 elements

Figure 3.17 gives values for the first ionisation energies of the elements. These values **generally increase** on going from left to right **across a period**. This is due to:

- The increase in nuclear charge, caused by an increase in the number of protons in each successive element. The electrons are held more tightly, which makes them more difficult to remove from an atom.
- The decrease in atomic radius, which has the same effect. In each period, the element in Group 0, having a full outer level, will have the highest first ionisation energy value.

On going **down a group**, the values of the first ionisation energies **decrease**. This is due to:

- The increase in atomic radius, which makes it easier to remove an electron from an atom despite the increased nuclear charge
- The screening effect of inner energy levels, which results in the effective nuclear charge experienced by the outermost electron being much less than the full nuclear charge.

Exceptions to the trend across a period

On going across the second period from left to right, first ionisation energy values generally increase.

- However, beryllium has a higher first ionisation energy value than the next element, boron. The electronic configuration of beryllium is $1s^22s^2$, while that of boron is $1s^22s^22p_x^1$. The extra electron in boron is added to the $2p_x$ orbital, which is of higher energy than the 2s orbital. This electron is more readily removed than the 2s electron in beryllium. The beryllium atom, having a **full outer sublevel**, is particularly stable.

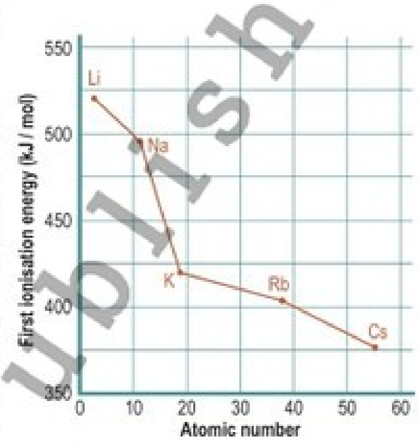


Figure 3.18
The decrease in first ionisation energy values down Group I, due to the increase of the screening effect and in the atomic radius

Another exception in the second period to the general trend occurs between nitrogen and oxygen.

- The first ionisation energy of nitrogen (electronic configuration $1s^22s^22p_x^12p_y^12p_z^1$) is greater than that of oxygen (electronic configuration $1s^22s^22p_x^22p_y^12p_z^1$). In oxygen the two electrons in the 2px orbital repel each other, making the outermost electron easier to remove. As a result, the value of the first ionisation energy is lower than that of nitrogen. The nitrogen atom, having a **half-full outer p sublevel**, is particularly stable.

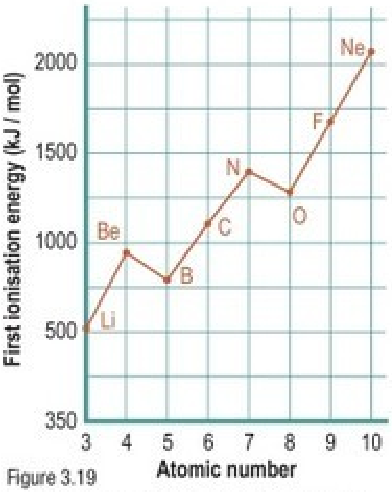


Figure 3.19
The general increase in first ionisation energy values across the second period, due to the increase in the nuclear charge and the decrease in the atomic radius. Note the exceptions to the general trend

Similar exceptions to the general trend occur between Groups II and III and between Groups V and VI in other periods, for similar reasons. Otherwise, for the s- and p- block elements, the general trend holds.

3.7. Periodicity and Redox reactions

Oxidation potential follows the same trends as ionization energy. An oxidation reaction is one that involves the loss of an electron and smaller ionization energies make it easier to remove an electron.

Reduction potentials, on the other hand, follow the same trend as electron affinity. A reduction reaction is one that involves gaining an electron and larger electron affinities make it easier to give an electron.

3.8 Periodicity and acid and base trends

The arrows indicate the relative acid and base strength of compounds such as hydrides or oxides of the elements moving across periods and down groups in the table.
The trend in hydrides – compounds formed between hydrogen and any other element – can be seen by looking across period 3.

Period 3	NaH	MgH_2	AlH_3	SiH_4	PH_3	H_2S	HCl
	Strong base	Weak base	Amphoteric Substance	No acid-base properties	Weak base	Weak acid	Strong acid

Figure 3.20
Hydroxide trends across period 3.

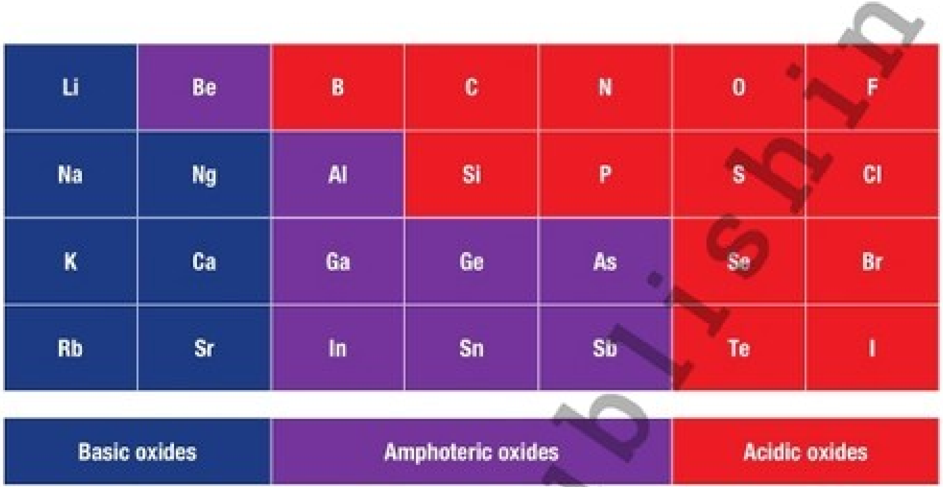
The more strongly basic hydrides [metal hydrides] are on the left of the table
NaH = basic hydride:

$$Na^+_{(aq)} + H^-_{(aq)} + H_2O_{(l)} \rightarrow H_{2(g)} + Na^+_{(aq)} + OH^-_{(aq)}$$

and the more strongly acidic hydrides [non-metal hydrides] to the right
HCl = acidic hydride:

$$H^+_{(aq)} + Cl^-_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Generally speaking, the determining factor in whether an oxide will be acidic or basic is the electropositive character of the central atom of the oxide. The more electropositive elements to the left of the table form basic oxides, whereas the more electronegative elements to the right of the table form acidic oxides. The oxides in-between are often amphoteric as shown in the table below.



Li	Be	B	C	N	O	F
Na	Ng	Al	Si	P	S	Cl
K	Ca	Ga	Ge	As	Se	Br
Rb	Sr	In	Sn	Sb	Te	I

🟦	🟪	🟥
Basic oxides	Amphoteric oxides	Acidic oxides

Figure 3.21
Periodic trends of oxides

QUESTIONS

23 What factors influence the value of the first ionisation energy?

24 What is the trend in values of the first ionisation energy on going from left to right across a period in the periodic table? Give reasons for this.

25 List the exceptions among the first eighteen elements to the trend in first ionisation energy values going across a period, and explain why they occur.

26 What is the trend in values of the first ionisation energy on going down a group in the periodic table? Explain your answer.

27 What type of ion – positive or negative – will an atom such as sodium, which has a low first ionisation energy value, tend to form?

28 Prepare a short presentation on trends in the periodic table in one of the following areas (a) metallic/non-metallic character of elements (b) oxidation states. Think about the ideas discussed in 3.5, 3.6 and 3.7.

Ionic and Covalent Bonding

MODULE 4

Learning objectives

- To explain the formation of covalent bonds by sharing and donor-acceptor mechanisms 10.1.4.1
- To describe the properties of covalent bonds 10.1.4.2
- To draw dots-and-crosses diagrams for following compounds H_2, Cl_2, O_2, N_2, HCl, NH_3 10.1.4.3
- To recognise the difference between types of orbital hybridization 10.1.4.4
- To explain the relationship between structure and properties of following substances BF_3, CH_4, NH_3, H_2O, $BeCl_2$ 10.1.4.5
- To explain the principle of atom electronegativity and predict the type of chemical bond related to it 10.1.4.6
- To understand that ionic bonds are formed as a result of electrostatic attraction of opposite charged ions 10.1.4.7
- To make dots-and-crosses diagrams for following compounds NaCl, CaO, MgF_2, KH 10.1.4.8
- To explain the nature of metallic bonds and their effects on the physical properties of metals 10.1.4.9
- To explain the mechanism of hydrogen bond formation 10.1.4.10
- To predict properties of compounds according to type of bonds and crystal lattice 10.1.4.11

4.1 Chemical Compounds

A chemical **compound** is formed when two or more elements combine in a chemical reaction. For example, if hydrogen gas is burned in oxygen gas, water, a compound, is formed.

$$2H_2(g) + O_{2(g)} \rightarrow 2H_2O_{(l)}$$

Unlike elements, compounds can be broken down chemically into simpler substances, and in many cases directly to their elements. If an electric current is passed through water, the compound breaks up into its constituent elements, hydrogen and oxygen.

$$2H_2O_{(l)} \rightarrow 2H_{2(g)} + O_{2(g)}$$

Each compound has a fixed composition and it can be represented by a chemical formula. Water always contains two parts hydrogen to one part oxygen. This is shown by its chemical formula, H_2O. The formula of a compound tells us what elements make up the compound and in what relative proportions.

Sulfuric acid is an example of a compound made up of three elements. Its formula, H_2SO_4, indicates that it is made up of two parts hydrogen, one part sulfur, and four parts oxygen.

Crystals of hydrated copper sulfate $CuSO_4 \times 5H_2O$

Washing soda

Hydrated substances contain molecules of water in definite proportions, usually locked into a crystal structure. Washing soda, hydrated sodium carbonate, is an example. It contains 10 parts of water to one part of sodium carbonate, so its formula is $Na_2CO_3 \times 10H_2O$. It has two parts sodium, one part carbon, three parts oxygen and ten parts water. In cases of this type, the water is regarded as a unit within the formula. Water bound in this way is described as **water of crystallisation**; it can be driven off by heating to give the corresponding **anhydrous** compound.

$$Na_2CO_3 \times 10H_2O_{(s)} \rightarrow Na_2CO_{3(s)} + 10H_2O_{(l)}$$

Water of crystallisation is water chemically combined in definite proportions in a crystalline compound.

QUESTIONS

1 The compounds in the following list are encountered in everyday life: (a) sodium chloride, NaCl; (b) ethanoic acid, CH_3COOH; (c) magnesium hydroxide, $Mg(OH)_2$; (d) heptane, C_7H_{16}; (e) sodium hypochlorite, NaOCl; (f) calcium carbonate, $CaCO_3$; (g) carbon dioxide, CO_2.
In each case name the elements that constitute the compound and the proportion in which they are present.

4.2 Noble Gas Electron Configuration

The elements of Group 0 of the periodic table, the noble gases, are found to be very stable and unreactive compared with most other elements. This is because they have very stable outer electronic configurations. The first two elements in the group, helium and neon, are so unreactive that they do not form any compounds.

Atom	Electron arrangement
Helium (He)	2
Neon (Ne)	2, 8
Argon (Ar)	2, 8, 8
Krypton (Kr)	2, 8, 18, 8

Table 4.1

Table 4.1 shows the distribution of electrons in the main energy levels of noble gas atoms.

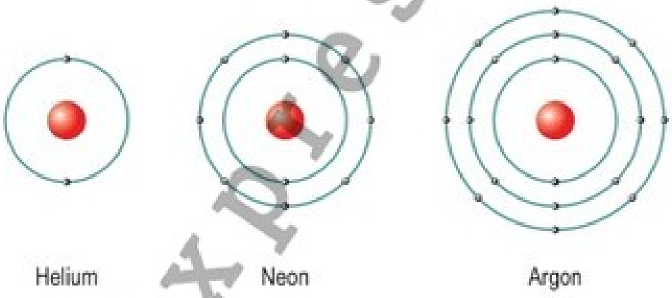


Figure 4.1
Arrangement of electrons in noble gas atoms

Electric light bulbs are filled with argon

Apart from helium, whose outer level (and only occupied level) is full, each of the other noble gases has eight electrons – an octet – in its outer level. Given the relative unreactivity of the Group 0 elements, it is clear that having eight electrons in the outer level, or having a filled outer level, is a stable arrangement of electrons.

The uses of helium and argon are related to their chemical unreactivity. Helium is a much safer alternative to hydrogen for use in weather balloons and blimps. Both gases have very low densities, but unlike hydrogen, helium is not flammable. Electric light bulbs are filled with argon to prevent the tungsten filament from evaporating or reacting. Incandescent light bulbs are being replaced by energy-saving bulbs throughout the EU.

Helium is used in blimps

Noble gas	Use
Helium	In weather balloons and blimps
Argon	In light bulbs

QUESTIONS

2 In what way are the noble gases different to most other elements?

3 Why is helium more suitable for use in weather balloons than the less dense hydrogen?

4 To what feature of their electronic structures is the stability of the noble gases due?

4.3 Octet Rule

When atoms of different elements combine together to form compounds, there is a change in the arrangement of the electrons in the outermost energy level of each atom. Some of these electrons form links called **chemical bonds** between the atoms. Usually the new arrangement is more stable than the original situation.

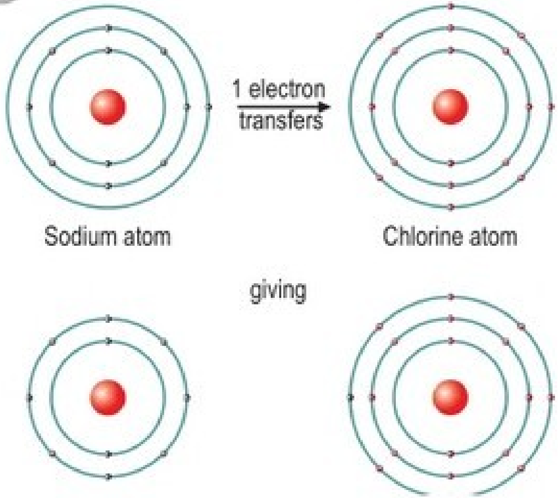


Figure 4.2

Elements achieve stable noble gas configurations by losing, gaining or sharing electrons when they react to form compounds. This idea forms the basis of the electronic theory of chemical bonding. The idea is usually expressed as the **octet rule**, which states that **atoms on reaction tend to reach an electron arrangement with eight electrons in the outermost energy level**.

For example, in the formation of sodium chloride from sodium, the sodium atom, whose electron arrangement is 2, 8, 1, loses an electron to chlorine, ending up as the sodium ion Na+ with an arrangement of 2, 8.

On the other hand, the chlorine atom gains an electron from sodium and its electron arrangement goes from 2, 8, 7 in the neutral atom to 2, 8, 8 in the chloride ion. In other words, both elements obey the octet rule and end up with eight electrons in the outer level.

EXAMPLE 4.1

Use the octet rule and the electronic structures of calcium and fluorine to predict the formula of calcium fluoride.

Answer The electronic structure of calcium is: Ca 2, 8, 8, 2

The electronic structure of fluorine is: F 2, 7

To obey the octet rule and end up with eight electrons in the outer level, calcium loses two electrons to form the calcium ion Ca^{2+}, and fluorine gains one electron to form the fluoride ion, F^-. So that the total charge is zero, two fluorine atoms are required, gaining one electron each. Consequently the formula of calcium fluoride is CaF_2.

While the octet rule does not work in all cases, it is nonetheless a useful aid in using the electronic structure of atoms to predict the ions formed in ionic bonding and the consequent chemical formulas of compounds.

A similar method is used to predict the formulas of compounds of complex ions. It is not possible to use the octet rule to work out the charges on such ions. The information required is shown in Table 4.2.

Anion	Formula
Hydroxide	OH^-
Carbonate	CO_3^{2-}
Nitrate	NO_3^-
Hydrogencarbonate	HCO_3^-
Sulfite	SO_3^{2-}
Sulfate	SO_4^{2-}
Phosphate	PO_4^{3-}
Dichromate(VI)	$Cr_2O_7^{2-}$
Ethanoate	CH_3COO^-
Ammonium	NH_4^+
Manganate(VII)	MnO_4^-

Table 4.2
Formulas of complex ions

EXAMPLE 4.2

What is the formula of potassium carbonate?

Answer The electronic structure of potassium is: K 2, 8, 8, 1

The potassium ion is K^+ and the carbonate ion is CO_3^{2-}. Two potassium ions and one carbonate ion are required so that the total charge is zero. Thus the formula is K_2CO_3.

EXAMPLE 4.3

What is the formula of magnesium hydroxide?

Answer The electronic structure of magnesium is: Mg 2, 8, 2

The magnesium ion is Mg^{2+} and the hydroxide ion is OH^-. One magnesium ion and two hydroxide ions are required so that the total charge is zero. Thus the formula is $Mg(OH)_2$.

QUESTIONS

5 Write the formula of each of the following compounds: (a) sodium chloride (b) potassium oxide (c) magnesium bromide (d) calcium oxide (e) aluminium oxide.

6 Write the formula of each of the following compounds: (a) aluminium hydroxide (b) calcium carbonate (c) magnesium nitrate (d) sodium hydrogen carbonate (e) potassium sulfite (f) aluminium sulfate.

4.4 Exceptions to the Octet Rule

There are several exceptions to the octet rule:

- Beryllium and boron atoms have few electrons in their outer levels, so they cannot gain enough electrons to reach eight in the outer level.
- The d-block elements do not usually obey the octet rule.
- The rule works in some cases for sulfur and phosphorus, but not in others.
- Hydrogen and lithium atoms tend to reach the electronic structure of helium, but they are unable to gain the large number of electrons required to attain an octet.

4.5 Covalent Bonding

When atoms combine chemically other than by ionic bonding, **molecules** are formed. These may consist of atoms of the same element, such as the hydrogen molecule, H_2, or of atoms of different elements, such as the sulfuric acid molecule, H_2SO_4. Most molecules consist of a small number of atoms. Consequently, molecules – like atoms – are of extremely minute sizes. They are too small to be seen under the most powerful optical microscopes, but can be seen under scanning electron microscopes.

Atoms can gain the stability of a noble gas configuration by **sharing** electron pairs in their outer levels. Each shared pair of electrons is regarded as one **covalent bond**. Shared electrons count as part of the outer level of both atoms of the bond.

A covalent bond is formed when two atoms share a pair of electrons.

The simplest example of this type of bonding is the hydrogen molecule, H_2. The dot and cross diagram for the H_2 molecule is shown in Figure 4.3.

Figure 4.3

A hydrogen atom has one electron. In order to obtain a full outer level, and gain the electronic structure of the nearest noble gas (helium), the atomic orbital containing its single electron overlaps with that of another hydrogen atom. Each atom now has a share in a pair of electrons, and a covalent bond is formed. The nuclei of the atoms are attracted to the shared pair of electrons, and are thus held close to each other in a molecule. Since there is just one shared pair of electrons, this is a **single bond**.

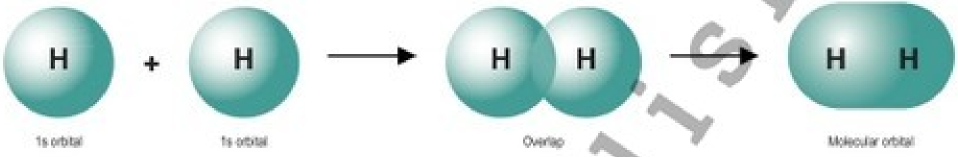


Figure 4.4

EXAMPLE 4.4

Draw a dot and cross diagram of the chlorine molecule, Cl_2.

Answer The chlorine molecule, Cl_2, is another example of a single covalent bond between two atoms of the same element. The dot and cross diagram is shown in Figure 4.5.

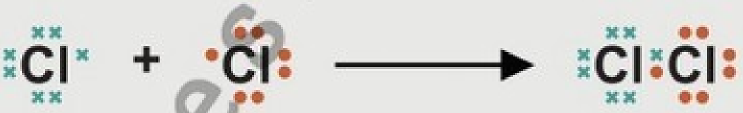


Figure 4.5

Since chlorine atoms have seven electrons in their outer levels, this time the octet rule is obeyed and each atom gains the electronic structure of argon.

EXAMPLE 4.5

Draw a dot and cross diagram of the hydrogen chloride molecule, HCl.

Answer The hydrogen chloride molecule, HCl, is an example of a single covalent bond between atoms of different elements, hydrogen and chlorine. The dot and cross diagram is shown in Figure 4.6.

Hydrogen gains the electronic structure of helium, and chlorine gains the electronic structure of argon.

Figure 4.6

EXAMPLE 4.6

Draw a dot and cross diagram of the water molecule, H_2O.

Answer Water is an example of a molecule with three atoms, each hydrogen being bonded to the oxygen. The dot and cross diagram is shown in Figure 4.7.

Since the oxygen atom has six electrons in its outer level, it needs to gain two electrons to reach the electronic structure of neon. It does this by sharing electrons with each of two hydrogen atoms. The hydrogen atoms reach the configuration of helium in the process. The resultant water molecule has two single covalent bonds.

Figure 4.7

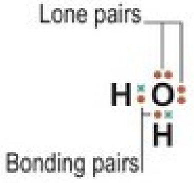


Figure 4.8

Figure 4.9

Shared electron pairs that form covalent bonds are called **bonding pairs**. Pairs of electrons not involved in bonding are called **lone pairs** or non-bonding pairs. A water molecule (Figure 4.8) has two bonding pairs of electrons and two lone pairs of electrons. An ammonia molecule (Figure 4.9) has three bonding pairs and one lone pair.

QUESTIONS

7 What is a molecule?

8 What does a covalent bond consist of?

9 How many electron pairs are there in a single covalent bond?

10 Draw dot and cross diagrams of the following molecules: (a) fluorine, F_2 (b) hydrogen bromide, HBr (c) hydrogen sulfide, H_2S (d) ammonia, NH_3 (e) methane, CH_4 (f) phosphorous trichloride, PCl_3.

11 What is the difference between a lone pair of electrons and a bonding pair of electrons? Using your answers to question 10, state (a) the number of lone pairs (b) the number of bonding pairs in each of the following molecules: F_2, HBr, H_2S, NH_3, CH_4, PCl_3.

Co-ordinate covalent bonding

A different type of covalent bond, which is known as the coordinate or dative covalent bond, involves the unequal sharing of an electron pair by two atoms in a donor-acceptor relationship. Whereas in ordinary covalent bonding a bond forms from the interaction of two electrons from different atoms, in co-ordinate covalent bonding a bond forms as a result of a pair of electrons from one atom [the donor] bonding to an unfilled orbital from another atom [the acceptor].

A typical example of co-ordinate covalent bonding is the ammonium ion, NH_4^+. In the reaction of **ammonia and hydrogen chloride**:

$$NH_3 + HCl \rightarrow NH_4Cl_)$$

ammonium ions, NH_4^+ form when the hydrogen ion from the hydrogen chloride transfers to the lone pair of electrons on the ammonia molecule.

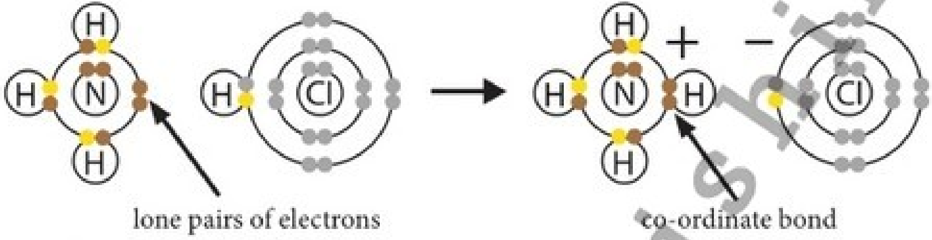


Figure 4.10

The resulting ammonium ion, NH_4^+, has a positive charge because only the hydrogen nucleus transfers. The hydrogen leaves its electron behind and the negatively charged chloride ion is formed.

The donor-acceptor relationship of the co-ordinate covalent bond is shown diagrammatically by the use of an arrow in diagrams like this:

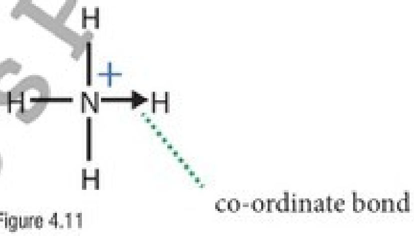


Figure 4.11

The arrow points from the (donor) atom that donates the pair of electrons to the (acceptor) atom that accepts them.

The complete compound [NH_4Cl] that is formed in this reaction thus results from three types of bonding: covalency in the formation of NH_3; co-ordinate bonding in the formation of NH_4^+; and electrovalency in the formation of NH_4Cl

Another example of co-ordinate bonding is the Hydronium ion, H_3O^+. In this case the water molecule, H_2O, donates a lone pair of electrons to the vacant s orbital of hydrogen ion,

$$H^+ . H_2O(l) + H^+_{(aq)} \rightarrow H_3O^+_{(aq)}$$

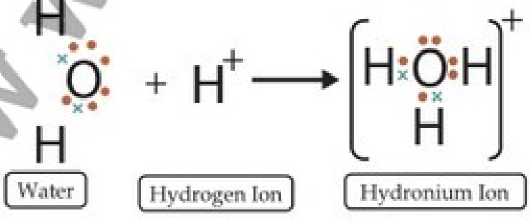


Figure 4.12

This is the type of bonding that occurs when hydrochloric acid, for example, is dissolved in water.

$H_2O + HCl \rightarrow H_3O^+ + Cl^-$

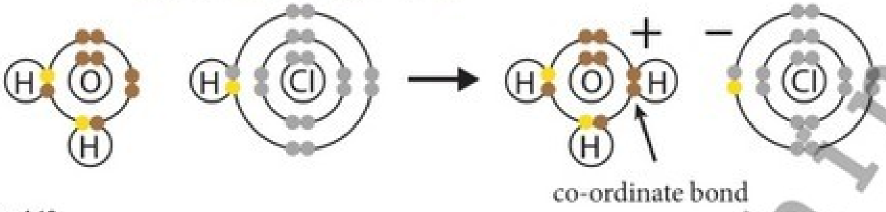


Figure 4.13

Once a co-ordinate bond is formed, it is not distinguishable from the other hydrogen bonds in the ion. Thus, when the hydronium ion subsequently reacts any of the three hydrogen ions can break away.

QUESTIONS

12 State two differences between a regular covalent bond and a coordinate covalent bond.

13 Explain what features of the water molecule enable it to form co-ordinate bonds.

14 Draw dots-and-crosses diagrams to show the bonding in the ammonium ion and the hydronium ion. Distinguish between the ordinary covalent bonds and co-ordinate bonds.

4.6 Double and Triple Covalent Bonds

Some atoms form covalent bonds by sharing two pairs of electrons. An example of a molecule with two pairs of electrons shared between two atoms is the oxygen molecule, O_2. Since an oxygen atom has six electrons in the outer level, it needs to gain two electrons, or a share of two electrons, to reach the electronic structure of neon. Two oxygen atoms share two pairs of electrons to reach the octet. A **double** covalent bond is formed.

EXAMPLE 4.7

Draw a dot and cross diagram of the oxygen molecule, O_2.

Answer A double covalent bond is formed in which two pairs of electrons are shared.

Figure 4.14

The double bond in the oxygen molecule can also be represented as O=O.

When three electron pairs are shared to form a bond, a **triple** covalent bond is formed. The nitrogen molecule is an example in which this type of bonding is found. Since a nitrogen atom has five electrons in the outer level, it needs to gain a share of three more electrons to reach the electronic structure of neon. Two nitrogen atoms share three electrons each to reach the octet.

EXAMPLE 4.8

Draw a dot and cross diagram of the nitrogen molecule, N_2.

Answer A triple covalent bond is formed in which three pairs of electrons are shared.

Figure 4.15

The triple bond in the nitrogen molecule can also be represented as N≡N.

The strengths of covalent bonds can be studied by measuring the energy needed to break bonds. These bond dissociation energies show that a double bond is stronger than a single bond between the same two atoms, but not twice as strong. A triple bond is found to be stronger still than a double bond between the same two atoms, but not three times as strong as a single bond. This indicates that not all the bonds in a multiple bond are equally strong.

When a single covalent bond is formed between two atoms, atomic orbitals containing a single electron from each atom overlap. The new molecular orbital formed contains a pair of electrons which constitute a single covalent bond. This bond is called a σ **(sigma) bond** when it involves two s orbitals, an s and a p orbital, or two p orbitals which overlap **end-on** to each other. A σ bond is always formed between two atoms in a molecule if they are covalently bonded.

Figure 4.16
Sigma bonding by end-on overlap of p orbitals

In double or triple bonds, sideways overlap is possible between two p atomic orbitals, each containing one electron. In this case, a π **(pi)** bond is formed.

An example of a π bond is found in the oxygen molecule, O_2. The O=O double bond, like all double bonds, consists of one σ bond and one π bond. Triple bonds, such as that in the nitrogen molecule, N≡N, consist of one σ bond and two π bonds. σ bonds are stronger than π bonds.

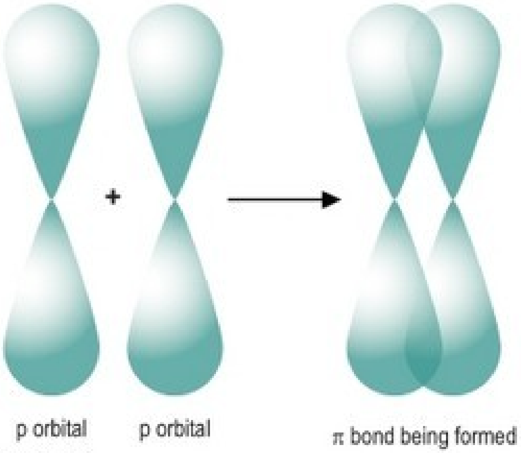


Figure 4.17
Pi bonding between two p orbitals

QUESTIONS

15 How many shared pairs of electrons are there in a (a) single (b) double (c) triple covalent bond?

16 Draw a dot and cross diagram to represent the covalent bonds in a molecule of carbon dioxide,
O=C=O.

17 Draw a dot and cross diagram to represent the covalent bonds in a molecule of ethene (Figure 4.18)

18 Draw a dot and cross diagram to represent the covalent bonds in a molecule of ethyne (Figure 4.19)

19 Explain the difference between a σ bond and a π bond.

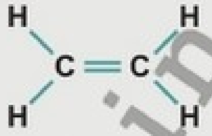


Figure 4.18

Figure 4.19

4.7 Polar and Non-polar Covalent Bonding

The atoms in a covalent bond share one or more pairs of electrons. When a molecule such as hydrogen, H_2, contains only one type of atom the nuclei of the atoms attract the shared electrons in the covalent bond equally. Because of this, the electrons are equally shared. The bond is a pure covalent bond and is said to be **non-polar**. Oxygen (O_2), nitrogen (N_2), chlorine (Cl_2) and bromine (Br_2) are other examples of molecules containing non-polar covalent bonds.

However, most covalent bonds are formed between atoms that are quite different from each other. For example, a hydrogen chloride molecule is formed from a hydrogen atom and a chlorine atom. Two factors dictate the extent to which the shared electrons are attracted by different nuclei: the size of the atom and the nuclear charge.

- Smaller atoms have a stronger attraction than larger atoms with a similar charge because they can get closer to the shared pair of electrons.
- Atoms with a bigger charge in the nucleus will have a greater attraction for the shared electrons than atoms of a similar size with a smaller charge.

When electrons are shared unequally, **polar covalent** bonds are formed. Usually, different types of atom will attract the electrons unequally in a covalent bond. The atom with the lesser share of electrons will become slightly positively charged, and this partial charge is indicated by δ+. The other atom will become slightly negatively charged, and this partial charge is indicated by δ−. In the hydrogen chloride molecule, HCl, for example, the chlorine atom has a greater attraction for the shared pair of electrons than the hydrogen atom. Consequently the molecule is represented as follows:

$$H^{\delta+} - Cl^{\delta-}$$

Other examples of polar covalent bonds are the $O^{\delta-}{-}H^{\delta+}$ bond in water, the $N^{\delta-}{-}H^{\delta+}$ bond in ammonia and the $H^{\delta+}{-}F^{\delta-}$ bond in hydrogen fluoride.

QUESTIONS

20 State whether the bonds in each of the following molecules are polar or non-polar:
(a) fluorine, F_2 (b) iodine, I_2 (c) oxygen, O_2 (d) hydrogen bromide, HBr (e) water, H_2O
(f) methane, CH_4.

21 Name the factors that affect the extent to which atoms attract electrons in a covalent bond.

22 How are the partial charges on atoms in a covalent bond represented? Use the hydrogen chloride molecule, HCl, to illustrate your answer.

4.8 Characteristics of Covalent Substances

The characteristic properties of covalent substances are caused by the fact that while the covalent bonds within molecules – the intramolecular forces – are strong, the forces between molecules – the intermolecular forces – are weak.

- Since the intermolecular forces are weak, most molecular substances are liquids or gases at room temperature. Those that are solids have low melting and boiling points.
- In general they do not conduct electricity when in the liquid state or in solution. This is because they consist of neutral molecules rather than electrically charged particles such as ions. However, some molecules such as HCl react with water to form ions and the solution formed can then conduct electricity.
- Most covalent substances do not dissolve readily in water. However polar covalent compounds have some ionic character and are more likely to form aqueous solutions.

4.9 Electronegativity

Different types of atom attract the shared electrons unequally in a polar covalent bond. The ability of an atom in a covalent bond to attract the shared electrons to itself is given by the atom's **electronegativity** value.

Electronegativity is the relative attraction of an atom for shared pairs of electrons in a covalent bond.

The most commonly used scale of electronegativity is the Pauling scale, devised by Linus Pauling. On this scale, which runs from 0 to 4, the higher the electronegativity value an atom has, the better it is at attracting the shared electrons towards itself. As can be seen in the table, electronegativities increase from left to right across a period, and decrease from the top to the bottom of a group.

Three factors are responsible for the variations in electronegativity values in atoms of different elements:

- The nuclear charge, that is, the positive attraction of the nucleus for the electrons

- The atomic radius, that is, the distar
- The screening effect by which inne from the full force of the nuclear ch

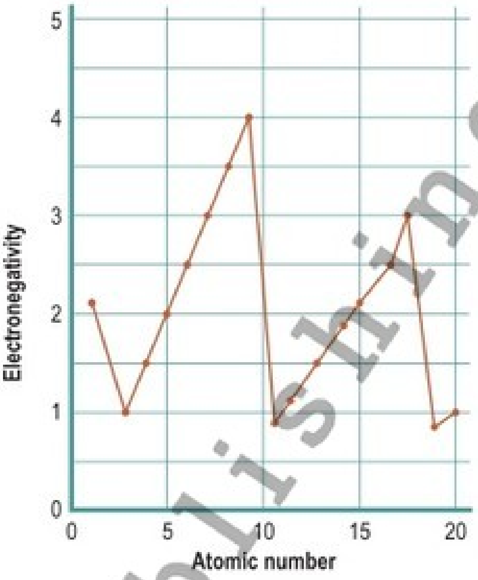


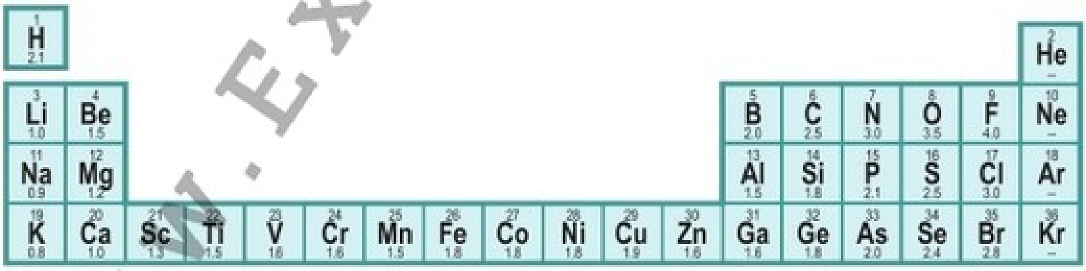
Figure 4.20
Variation in electronegativities among the first 20 elements

Electronegativity increases across a period.

- As the atomic number – the number of protons in the nucleus – increases, the nuclear charge increases
- The extra electrons in atoms of each successive element across the period are added to the same (outer) shell, with no change in screening by inner shell electrons. The increased nuclear charge pulls the electrons in more tightly and atomic radius decreases.
- The larger the nuclear charge and the smaller the atomic radius, the greater the attraction for the electron pair in a covalent bond, resulting in an increase in electronegativity.
-

Electronegativity decreases down a group

- On going down a group, the addition of extra levels of electrons shields the outer electrons from the nucleus
- These extra levels also cause an increase in atomic radius
- Even though the nuclear charge is increasing, the electrons are not attracted as strongly.
- The combination of greater screening and increased atomic radius reduces the attraction for the electron pair in a covalent bond, resulting in a decrease in electronegativity.



1 H 2.1																	2 He –
3 Li 1.0	4 Be 1.5											5 B 2.0	6 C 2.5	7 N 3.0	8 O 3.5	9 F 4.0	10 Ne –
11 Na 0.9	12 Mg 1.2											13 Al 1.5	14 Si 1.8	15 P 2.1	16 S 2.5	17 Cl 3.0	18 Ar –
19 K 0.8	20 Ca 1.0	21 Sc 1.3	22 Ti 1.5	23 V 1.6	24 Cr 1.6	25 Mn 1.5	26 Fe 1.8	27 Co 1.8	28 Ni 1.8	29 Cu 1.9	30 Zn 1.6	31 Ga 1.6	32 Ge 1.8	33 As 2.0	34 Se 2.4	35 Br 2.8	36 Kr –

Figure 4.21
Electronegativities of the elements

Predicting the nature of bonds

Compounds with pure ionic bonds or pure (non-polar) covalent bonds are extreme types. Most compounds are somewhere between the two, with some degree of polarity.

The greater the difference in electronegativity values between the two bonding atoms, the greater the degree of polarity.

Carbon and sulfur each have an electronegativity value of 2.5, and so the electronegativity difference between the two is zero. A carbon–sulfur bond in carbon disulfide, CS_2, is thus a non-polar covalent bond.

Potassium has an electronegativity value of 0.8 and fluorine – the most electronegative element – has a value of 4.0. The difference of 3.2 is extremely high. In this case the fluorine has such a strong attraction for the electrons that the electron pair resides solely on the fluorine. In other words, a negatively charged fluoride ion, F^-, is formed. The potassium atom has lost an electron to fluorine, so what remains is a potassium ion, K^+. Since electron transfer has occurred, the bond is ionic.

Electronegativity differences can be used to predict the type of bond between two atoms.

- If the electronegativity difference is zero or very small, the bond can be regarded as being non-polar covalent; for example, the H–H bond in the hydrogen molecule, H_2, and the C–S bond in carbon disulfide, CS_2, are both non-polar.
- In cases where the electronegativity difference is greater than 1.7, the degree of ionic character is greater than the degree of covalent character so the bond is predicted to be ionic. For example, the bond in sodium chloride, NaCl, where the electronegativity difference is $3.0 - 0.9 = 2.1$, is ionic.
- The bond is predicted to be polar covalent if the electronegativity difference is less than 1.7, unless the difference is very small indeed. For example, the bond in hydrogen chloride, HCl, is predicted to be polar covalent because the electronegativity difference is $3.0 - 2.1 = 0.9$.

EXAMPLE 4.9

Use electronegativity values to predict the type of bond in (a) NaBr (b) CO (c) NH_3 (d) N_2 (e) CH_4.

Answer

(a) The electronegativity difference between sodium and bromine is $2.8 - 0.9 = 1.9$, which is > 1.7.
The bonding in NaBr is predicted to be ionic.

(b) The electronegativity difference between carbon and oxygen is $3.5 - 2.5 = 1.0$, which is < 1.7 but > 0.
The bonding in CO is predicted to be polar covalent.

(c) The electronegativity difference between nitrogen and hydrogen is $3.0 - 2.1 = 0.9$, which is < 1.7 but > 0.
The bonding in NH_3 is predicted to be polar covalent.

(d) Since both atoms are of the same element, nitrogen, the electronegativity difference is $3.0 - 3.0 = 0$.
The bond is predicted to be non-polar covalent.

(e) The electronegativity difference between carbon and hydrogen is $2.5 - 2.1 = 0.4$, which is < 1.7 but > 0.
The bonding in CH_4 is predicted to be weakly polar covalent.

QUESTIONS

23 Define electronegativity.

24 How do electronegativity values change (a) across a period (b) down a group?

25 Explain how electronegativity values are used to predict the nature of chemical bonds.

26 Use electronegativity values to predict the type of bonding, whether non-polar covalent, polar covalent or ionic in
   - (a) CH_4
   - (b) SiO_2
   - (c) KI
   - (d) HF
   - (e) HBr
   - (f) LiCl
   - (g) PH_3
   - (h) H_2O
   - (i) MgO
   - (j) SO_2.

4.10 Shapes of Molecules

Molecules are formed when atoms are joined together by covalent bonds. The arrangement in space of the atoms dictates the shape of the molecule.
The simplest possible molecule is diatomic, i.e. consisting of just two atoms.
Given that there are just two atoms, they can be connected by a straight line, so the shape is said to be **linear**.

Examples of diatomic molecules are oxygen, O_2, hydrogen, H_2, and hydrogen chloride, HCl. It is also possible for molecules with more than two atoms to be linear e.g. beryllium chloride, $BeCl_2$.

If a molecule with three atoms is not linear like beryllium chloride, each atom must be out of line with the other two. Such molecules are angular or **V-shaped**. Water, H_2O, is an example. (Note that all linear and V-shaped molecules are also planar.)

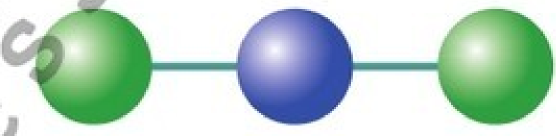


Figure 4.22
Beryllium chloride molecules are linear

Two possibilities arise with molecules which contain four atoms, where one is the central atom to which the other three are bonded.

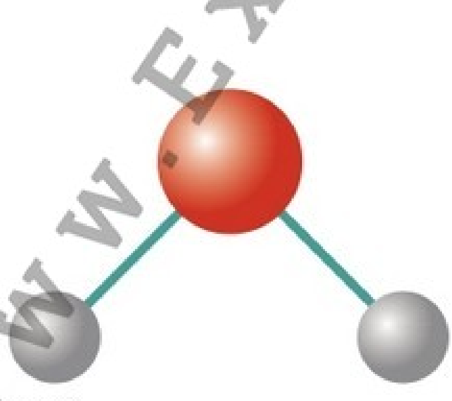


Figure 4.23
Water molecules are V-shaped

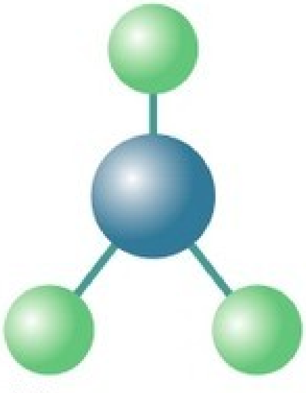


Figure 4.24
Boron trifluoride molecules are trigonal planar

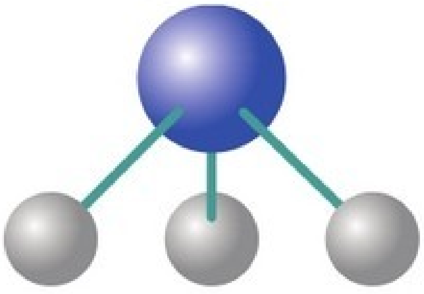


Figure 4.25
Ammonia molecules are pyramidal

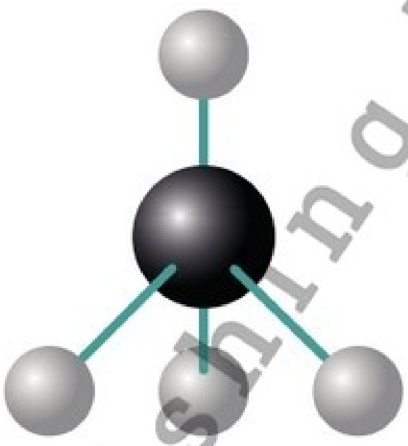


Figure 4.26
Methane molecules are tetrahedral

The first case has the four atoms lying in the same plane with the three outlying atoms pointing towards the vertices of an equilateral triangle. This shape is **trigonal planar**, and an example is boron trifluoride, BF_3.

The second possibility has the central atom above the plane of the other three, but is otherwise similar. The shape is now **pyramidal**, and an example is ammonia, NH_3.

Molecules such as methane, CH_4, have four atoms joined to a central atom. The four outlying atoms are arranged as far from each other as possible, and are directed towards the corners of a regular tetrahedron. This shape is **tetrahedral**.

A tetrahedral arrangement is particularly important in molecules containing carbon.

Hybridization of orbitals

Hybridisation is the term used to describe the combination of s and p orbitals belonging to the same atom during covalent bonding to form new hybrid orbitals. The newly formed orbitals will all have equal energies and identical geometric shape. Hybrid orbitals are denoted as sp^x. The s and p indicate the orbitals that are combined in the hybridisation process, and the value of ^{x} [from 1 to 3] indicates the number of p orbitals involved. The number of hybrid orbitals produced is equal to the number of atomic orbitals combined.

The different characteristics of sp, sp^2 and sp^3 orbitals are described below.

sp hybridization occurs where one s and one p orbital combine to produce two new hybrid orbitals. The axes of the new hybrid orbitals form an angle of 180 degrees.

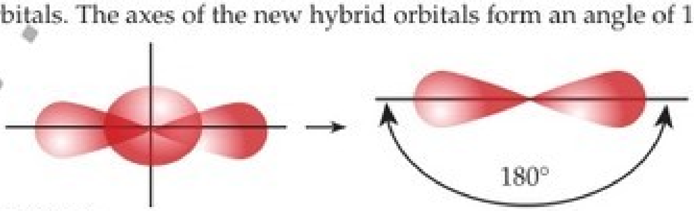


Figure 4.27
sp hybridization

Examples of sp hybridisation include all compounds of carbon containing a triple bond such as C_2H_2 and compounds of beryllium such as BeH_2 and BeF_2.

Molecules which are formed by sp-hybrid atoms are linear in shape **sp_2 hybridisation** occurs where one s and two p orbitals combine to form three new hybrid orbitals:

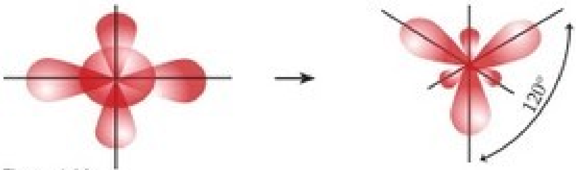


Figure 4.28
sp^2 hybridization

The new hybrid molecules have a flat structure with the axes forming a 120° angle. Examples of sp_2 hybridization include compounds such as aluminium chloride $AlCl_3$ and ethylene C_2H_4.

sp^3 hybridization occurs when one s-orbital and three p-orbitals combine to form four hybrid orbitals. The new hybrid orbitals have a tetrahedral shape, with the axes of the orbitals forming angles of 109°28′.

Figure 4.29
sp^3 hybridization

Examples of sp^3 hybridization include compounds such as ammonia NH_3 and methane CH_4

ammonia

methane

Figure 4.30
Shape of ammonia and methane molecules

QUESTIONS

27 What is the hybridization of the molecular bonds NH_3?

28 Which of these molecules has an atom with sp^2 hybridization? (a) H_2O (b) C_2H_4 (c) CH_4

29 Match the type of hybridization to its shape:

(a) tetrahedral (i) sp
(b) linear (ii) sp^2
(c) trigonal planar (iii) sp^3

30 Work out the type of hybridisation in these two compounds:

(a)

(b) H : C ⋮⋮ C : H

Activity

Models of molecules with the shapes described above can be made using balloons, or plasticine and matchsticks. Alternatively, various types of models can be purchased, such as the ball and stick models illustrated.

QUESTIONS

31 Predict the bond type formed between each of the elements below

Elements	Electronegativity calculation	Difference	Bond type prediction
Oxygen and itself			
H and O			
H and C			
Na and Cl			
H and Cl			
N and O			

32 Sketch the shape of each of the following molecules: CH_4, BF_3, H_2O, $BeCl_2$, NH_3, H_2 and HCl. Write the name of each shape underneath the sketch.

4.11 Electron Pair Repulsion Theory

The electron pair repulsion theory may be used to explain the shapes of simple molecules that consist of atoms bonded to a central atom. According to the theory:

- **The electron pairs in the valence (outer) shell of the central atom repel each other and end up as far apart as is geometrically possible.**
- **Lone pairs (that is, pairs not involved in bonding) have a greater repelling effect than bonding pairs.**

The orientation of the electron pairs relative to each other depends on their number, so by counting the electron pairs their arrangement can be predicted or explained.

Molecules with only bonding pairs around the central atom

If all of the electron pairs are bonding pairs, that is, constituting covalent bonds, then the term used to describe the arrangement of the electron pairs is also used to describe the shape of the molecule. For example, the electron pairs in a methane molecule (in which there are four bonding pairs) have a tetrahedral arrangement, and the methane molecule has a tetrahedral shape.

Beryllium hydride

- The beryllium hydride molecule, BeH_2, has two hydrogen atoms bonded to the central beryllium atom. Beryllium has just two electrons in its valence shell, and with each hydrogen contributing its sole electron, the electronic structure of the molecule is 

Figure 4.31

- There are thus two bonding pairs of electrons in the valence shell of the beryllium atom in beryllium hydride. These electron pairs repel each other so as to get as far apart as possible, causing them to be located on either side of the beryllium atom. The result is a linear arrangement of electron pairs.
- Thus the molecule has a **linear** shape.
- The bond angle (∠HBeH) is 180°.

Other molecules with the central atom surrounded by two bonding pairs **only**, such as $BeCl_2$, also have a linear shape.

Boron trifluoride

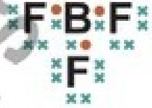


Figure 4.32

- The electronic structure of the boron trifluoride molecule is as shown in Figure 4.32.
- There are three bonding pairs in the valence shell of the boron atom in boron trifluoride. The furthest apart that three electron pairs can be arranged is when they are directed towards the vertices of an equilateral triangle. The result is a trigonal arrangement of electron pairs.
- Thus the molecule has a **trigonal planar** shape.
- Each bond angle (∠FBF) is 120°.

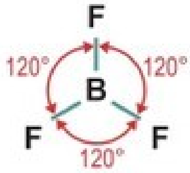


Figure 4.33

Other molecules in which the central atom is surrounded by three bonding pairs **only**, such as BCl_3, also have a trigonal planar shape.

Methane

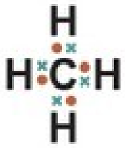


Figure 4.34

- The electronic structure of the methane molecule is as shown in Figure 4.34.
- There are four bonding pairs in the valence shell of the carbon atom in methane. The mutual repulsion causes them to have a tetrahedral arrangement.
- Thus the methane molecule has a **tetrahedral** shape.
- Each bond angle (∠HCH) is 109.5°.

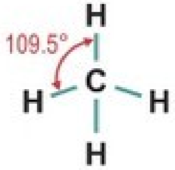


Figure 4.35

Other molecules in which the central atom is surrounded by four bonding pairs **only**, such as $SiCl_4$, also have a tetrahedral shape.

In all molecules containing 2, 3 or 4 bonding pairs only, the arrangement of the electron pairs can be predicted or explained by counting the number of these pairs.

Number of electron pairs	Arrangement of electron pairs	Bond angle	Example
2	Linear	180°	BeH_2
3	Trigonal planar	120°	BF_3
4	Tetrahedral	109.5°	CH_4

Table 4.3

Provided that all of the electron pairs are bonding pairs, the shape of the molecule is the same as the arrangement in space of the electron pairs.

Molecules with lone pairs and bonding pairs around the central atom

In molecules such as water and ammonia, not all of the electron pairs in the valence shell are bonding pairs.

In ammonia, the nitrogen atom has one lone pair in its valence shell, while the oxygen atom in water has two. **Since lone pairs are closer to the nucleus of the central atom, they are closer to each other, and so their mutual repulsion is greater than the mutual repulsion between bonding pairs**. The repulsion between a lone pair and a bonding pair is intermediate in strength. The order of strength of these repulsions is as follows: **lone pair: lone pair > lone pair : bonding pair > bonding pair: bonding pair.**

The consequence of this is that where both lone pairs and bonding pairs occur in the valence shell of the central atom, distortion in the expected arrangement is found, and the bond angles are a little different to what might otherwise be expected.

Ammonia

- The electronic structure of the ammonia molecule is shown in Figure 4.36.
- In ammonia, NH_3, the valence shell of nitrogen contains four electron pairs – three bonding pairs and one lone pair. The presence of four electron pairs indicates a tetrahedral arrangement. However the presence of the lone pair with its increased repulsion of the bonding pairs causes the bonding pairs to be pushed a little closer to each other than normal, and the bond angle is about 107° rather than the expected 109.5°. Thus the arrangement of the electron pairs is that of a distorted tetrahedron.
- Since a lone pair rather than an atom occupies one of the corners of the tetrahedron, the shape of the molecule is **pyramidal**.

Figure 4.36 Ammonia

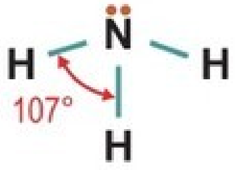


Figure 4.37

Other molecules in which the central atom is surrounded by three bonding pairs and one lone pair, such as the PCl_3 molecule, have similar shapes.

Water

- The electronic structure of the water molecule is shown in Figure 4.38.
- In the water molecule, there are two bonding pairs and two lone pairs in the valence shell of the central oxygen atom. The distortion due to repulsion by lone pairs is thus greater than in the case of ammonia, and the bonds are pushed even more closely together, resulting in a bond angle of 104.5°.
- Since lone pairs rather than atoms occupy two of the corners of the tetrahedron, the shape of the molecule is **V-shaped**.

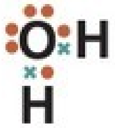


Figure 4.38 Water

Figure 4.39

Other molecules in which the central atom is surrounded by two bonding pairs and two lone pairs, such as the H_2S molecule, are also V-shaped.

Molecule	Number of electron pairs	Number of lone pairs	Arrangement of electron pairs	Bond angle	Shape of molecule
NH_3	4	1	Distorted tetrahedral	107°	Pyramidal
H_2O	4	2	Distorted tetrahedral	104.5°	V-shaped

Table 4.4

QUESTIONS

33 Explain why the BeH_2 molecule has a linear shape.

34 Explain why the BF_3 molecule has a trigonal planar shape.

35 Explain why the CH_4 molecule has a tetrahedral shape.

36 Explain why the H_2O molecule is V-shaped.

37 Explain why the NH_3 molecule is pyramidal.

38 What is the electronic structure of each of the following molecules: H_2S, PH_3, SiH_4 and BCl_3? Use the electron pair repulsion theory to predict the shape of each of these molecules.

4.12 Relationship between Symmetry and Polarity in a Molecule

A polar molecule must have two characteristics. The molecule must contain polar covalent bonds, and it must not be symmetrical.

Centres of positive and negative charge coinciding

Sometimes, a molecule can be non-polar overall even though the individual bonds are polar. This occurs when the molecule has a high degree of symmetry, with a geometric centre.

In the beryllium hydride molecule (Figure 4.46), the beryllium atom is the centre of positive charge, since beryllium is less electronegative than hydrogen. Being midway between the two hydrogen atoms, it is also the centre of negative charge. Thus both centres of charge coincide and the molecule is non-polar overall.

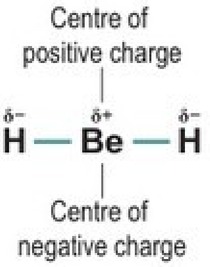


Figure 4.40

In the boron trifluoride molecule (Figure 4.41), the boron atom is the centre of positive charge. The centre of negative charge is at the geometric centre of the vertices of the equilateral triangle formed by the three fluorine atoms i.e. the boron atom.

Once again the centres of positive and negative charge coincide so the molecule is non-polar overall.

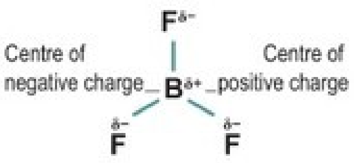


Figure 4.41

The methane molecule has a perfect tetrahedral shape with the carbon atom at the centre, and the four hydrogen atoms at the corners of a regular tetrahedron. As carbon is slightly more electronegative than hydrogen, each bond is slightly polar, with the carbon atom having a partial negative charge and each hydrogen a partial positive charge.

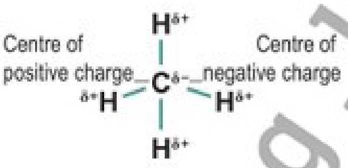


Figure 4.42

The only negative charge is located on the carbon atom, so it is said to be the centre of negative charge. Each hydrogen atom has a partial positive charge, so the centre of positive charge will be at the geometric centre of the tetrahedron, i.e. on the carbon atom. Thus the centre of positive charge coincides with the centre of negative charge, and the molecule is non-polar.

Separated centres of positive and negative charge

Molecules of water and ammonia, which contain polar covalent bonds, do not contain the same degree of symmetry as the molecules considered above. Consequently the centres of positive and negative charge do not coincide (that is, permanent dipoles exist), and the molecules overall are polar. Indeed water and ammonia both exhibit a high degree of polarity.

In the case of the ammonia molecule, which has a pyramidal shape, the nitrogen atom at the apex of the pyramid is the centre of negative charge. The centre of positive charge is at the geometrical centre of the three hydrogen atoms that form an equilateral triangle at the base of the pyramid. Thus the centres of positive and negative charge are separated, resulting in a polar molecule (Figure 4.43).

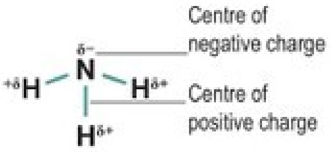


Figure 4.43

The water molecule is V-shaped, with the centre of negative charge on the oxygen at the apex of the V. The centre of positive charge is midway between the two hydrogen atoms, and separated from the centre of negative charge. As a result the water molecule is polar overall (Figure 4.44).

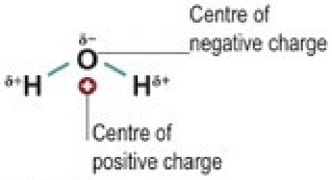


Figure 4.44

QUESTIONS

39 Why is a water molecule polar?

40 Why is a beryllium hydride molecule non-polar?

41 Why are the bonds in the PH_3 molecule non-polar?

4.13 Intramolecular Bonding and Intermolecular Forces

The prefix intra- means 'within' or on the inside. Thus **intramolecular bonding** means the bonding within the molecule that holds the atoms together. The pure covalent bond holding the two atoms of hydrogen together in a molecule of hydrogen gas is an example of an intramolecular bond. So also is the polar covalent bond in a molecule of hydrogen chloride.
The prefix inter- means 'between'. Thus **intermolecular forces** means forces between molecules. These forces, which include van der Waals' forces, dipole–dipole interactions, and hydrogen bonding, are much weaker than covalent bonds but have a significant effect on physical properties such as the boiling point of the substance. The presence of these attractive forces means that the molecules are more difficult to separate than would otherwise be the case, as a greater amount of heat has to be provided to allow molecules to escape from the main bulk of liquid. The stronger the attractive forces, the higher the boiling point of the liquid.

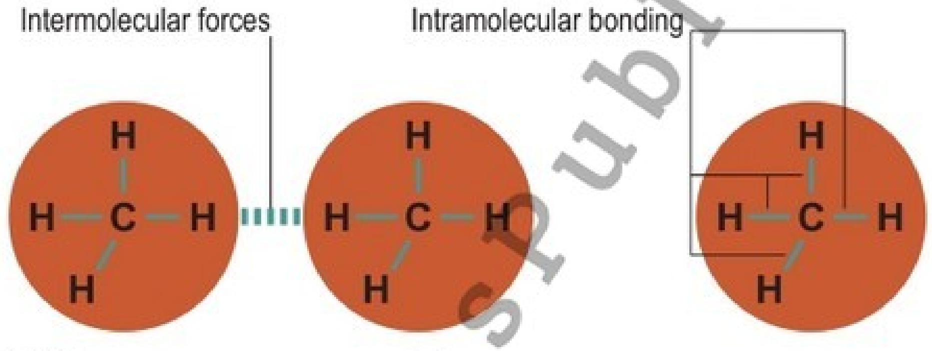


Figure 4.45
Methane: intermolecular forces and intramolecular bonding

4.14 van der Waals' Forces

The fact that non-polar gases such as hydrogen and oxygen can be liquefied indicates that some attractive forces exist between the molecules. These attractive forces are called **van der Waals' forces**, after the Dutch scientist Johannes van der Waals, whose work on gases led to the discovery that such forces existed.

These forces are much weaker than covalent bonds, and can themselves vary in strength. The boiling point of oxygen gas, for example, is 90.2 K, while that of hydrogen gas is only 20.5 K. This indicates that the intermolecular van der Waals' forces in oxygen are considerably stronger than those in hydrogen.

Van der Waals' forces are weak attractive forces caused by the movement of electrons within a molecule. The hydrogen molecule, H_2, for example, is a non-polar molecule, with a pure covalent bond. The only pair of electrons present is shared equally between the two hydrogen atoms. The electrons move randomly within the bond, so at a particular point in time they may both be nearer to one atom than the other. This creates a temporary polarity – called a **temporary dipole** - in the molecule.

$H^{\delta+} – H^{\delta-}$

If two molecules with similar temporary dipoles happen to be orientated with opposite charges directed at each other, an attractive force will exist between the two molecules.

$$H^{\delta+} - H^{\delta-} \text{ - - - - - - - - } H^{\delta+} - H^{\delta-}$$

Another possibility is that a temporary dipole in one molecule will induce a similar dipole in a neighbouring molecule, with a result similar to the above. The combined effect of these temporary and induced dipoles is to produce weak attractive forces between neighbouring molecules, resulting in increased boiling points.

The greater the number of electrons in a molecule, the greater are the number of possible temporary dipoles. Consequently the extent of the intermolecular attraction is greater. This explains why oxygen gas (with 16 electrons per molecule) has a higher boiling point than hydrogen (with only 2 electrons per molecule).

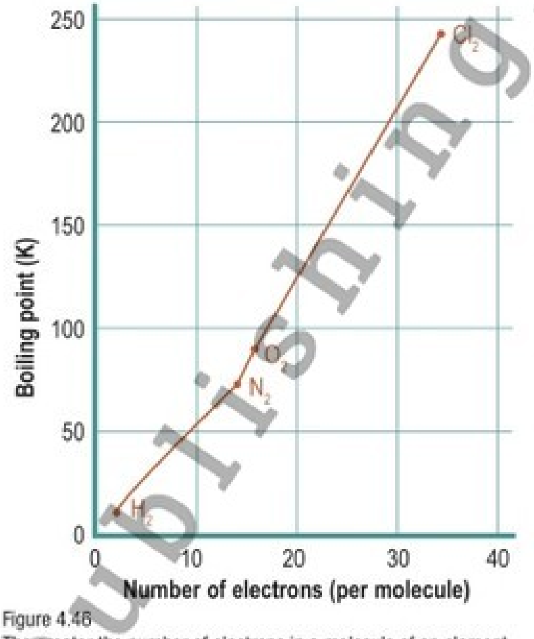


Figure 4.46
The greater the number of electrons in a molecule of an element, the stronger the van der Waals' forces between molecules of that element

4.15 Dipole–Dipole Interactions between Polar Molecules

Dipole–dipole interactions between polar molecules are another example of intermolecular forces. They are similar to van der Waals' forces in that the negative end of one dipole is attracted to the positive end of another, but they differ in that the dipoles are permanent due to the polarity in the molecule. Because they are permanent, they are stronger than van der Waals' forces.

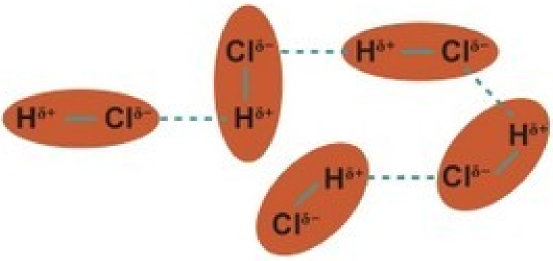


Figure 4.47
Dipole–dipole interactions between hydrogen chloride molecules

Figure 4.48

Ethene, C_2H_4, (M_r = 28) and methanal, HCHO (M_r =30) would be expected to have similar boiling points owing to the similar size of their relative molecular masses. This would be the case if there were only van der Waals' forces between their respective molecules. However ethene boils at 169 K, while methanal boils at 252 K. The difference arises because of methanal's stronger intermolecular forces.

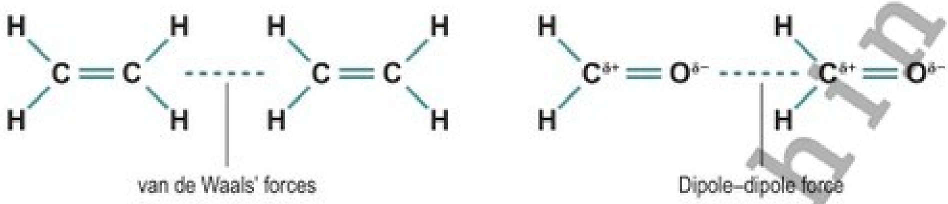


Figure 4.49
The intermolecular forces between ethene molecules are weaker than those between methanal molecules

Like all aldehydes, methanal contains a carbonyl group, a carbon–oxygen double bond. The bond is quite polar (electronegativity difference of 1.0), with the more electronegative oxygen carrying the negative charge. In other words, a permanent dipole exists. The negative oxygen of one molecule is attracted by the positive carbon of another molecule.

$$C^{\delta+} = O^{\delta-} \text{ - - - - - - - - } C^{\delta+} = O^{\delta-}$$

These dipole–dipole attractions must be overcome when liquid methanal boils.

4.16 Ionic Bonding

Ionic bonds are usually found in compounds that contain metals combined with non-metals. The word **ion** is used to describe any chemical species that has unequal numbers of protons and electrons, and so carries an electric charge. Like atoms, ions are extremely small.

Metal atoms, when they react, lose one or more electrons and become positively charged ions or **cations**. For example, a sodium atom has 11 protons and 11 electrons, and so is electrically neutral. A sodium ion, Na^+, is formed when a sodium atom loses one electron. The ion has an overall charge of +1 because it has 11 protons but only 10 electrons. In terms of electronic structure, the change is:

$$\text{Na } 2, 8, 1 - 1e^- \rightarrow \text{Na}^+ \ 2, 8$$

The sodium ion is smaller than the sodium atom. In general, a cation is smaller than the corresponding atom.

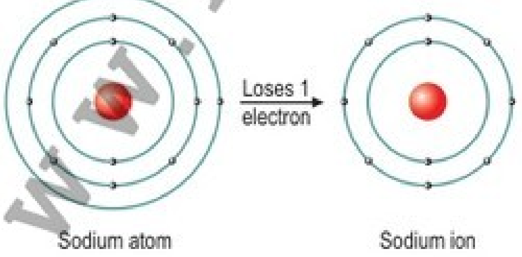


Figure 4.50a

Non-metal atoms, when they react, gain one or more electrons and become negatively charged ions or **anions**. For example, a chlorine atom has 17 protons and 17 electrons and so is electrically neutral. A chloride ion, Cl^-, is formed when a chlorine atom gains one electron. The ion has an overall charge of –1 because it has 17 protons and 18 electrons. In terms of electronic structure, the change is:

$$\text{Cl } 2, 8, 7 + 1e^- \rightarrow \text{Cl}^- \ 2, 8, 8$$

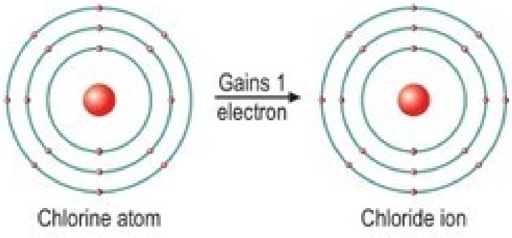


Figure 4.50b

The chloride ion is larger than the chlorine atom. In general, an anion is larger than the corresponding atom.

In order that an ionic bond can be formed, as between sodium and chlorine, electrons are **transferred** from the metal atoms to the non-metal atoms during the chemical reaction. The cations and anions formed by the transfer of electrons usually have noble gas electronic structures. They are held together by an electrostatic force of attraction (i.e. the attraction of opposite charges), which acts in all directions around the ions. This attraction is the ionic bond.

An ionic bond is the electrostatic force of attraction between oppositely charged ions.

Ionic bonds are represented by using dot and cross diagrams that show the electron arrangement in the neutral atoms and in the ions. The electrons are represented by dots for one atom and crosses for the other. It is usual to show only the outer level of electrons in these diagrams.

EXAMPLE 4.10

Draw a dot and cross diagram to show the formation of an ionic bond between sodium and chlorine.

Answer The charges on the sodium and chloride ions are equal but opposite. They balance each other and the resulting formula of sodium chloride is NaCl.

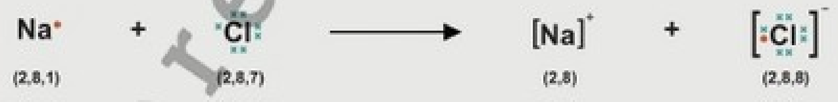


Figure 4.51

EXAMPLE 4.11

Draw a dot and cross diagram to show the ionic bonding between calcium and fluorine.

Answer Calcium obtains a full outer level by losing two electrons. These are transferred, one to each of the fluorine atoms. Since the calcium ion has a charge of +2, two fluoride ions, each of charge –1, are needed so that the charges are balanced. The compound formed is calcium fluoride, CaF_2.

Figure 4.52

QUESTIONS

42 Draw dot and cross diagrams to represent the ionic bonds in: (a) potassium fluoride (b) magnesium chloride (c) lithium bromide (d) aluminium chloride (e) calcium oxide (f) sodium oxide.

43 What is (a) an ion (b) a cation (c) an anion?

44 What is the type of charge on (a) a cation (b) an anion?

45 In terms of electrons, what happens when an ionic bond is formed?

4.17 Crystal Structure

Ionic bonding does not result in the formation of molecules. The oppositely charged ions attract each other to form a rigid three-dimensional lattice. Each ion in the lattice is surrounded by others of opposite charge.

The structure of crystal lattices is determined by an X-ray technique. Figure 4.53 shows the structure of a small part of a single sodium chloride crystal. Many millions of sodium and chloride ions are arranged in this way in a single crystal of sodium chloride to make up a giant ionic structure. It may be deduced that ions are extremely small in size.

Study of Figure 4.53 or examination of a model of the NaCl crystal shows that each sodium ion in the lattice is surrounded by six chloride ions, and each chloride ion is surrounded by six sodium ions. However not all ionic substances have the same crystalline structure as sodium chloride.

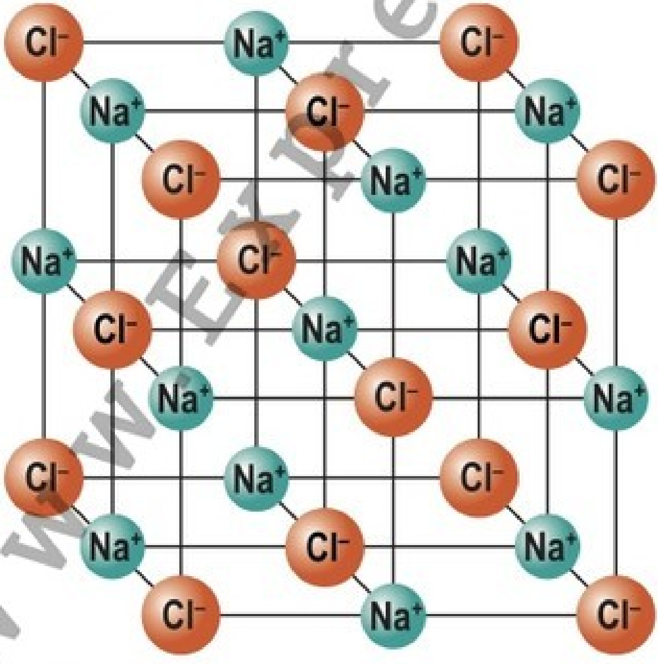


Figure 4.53

QUESTIONS

46 Explain how an ionic crystal lattice is formed.

47 Draw a two-dimensional diagram to show how the ions in a crystal of lithium bromide are arranged. Indicate the charge on the ions (lithium bromide has the same crystalline structure as sodium chloride).

48 Are the ions in a crystal of sodium chloride likely to number hundreds, thousands or millions? Explain your answer.

4.18 Characteristics of Ionic Substances

Ionic substances have characteristic properties caused by the nature both of the particles involved and of the forces of attraction holding the ions together in a crystal.

- The strong forces of attraction between the ions mean that a lot of energy is needed to break up the lattice and allow the ions to move. This means that ionic substances have high melting points, and are hard solids at room temperature.
- They cannot conduct electricity in the solid state because the ions are held tightly in the crystal and are not free to move.
- Most ionic substances dissolve in water to some extent. Water molecules, which are polar, are attracted to the charge of the ions. The water molecules surround the ions, pulling them apart and breaking up the lattice.
- Ionic substances conduct electricity when molten or in aqueous solution – they are electrolytes. Since the ions have been freed from their fixed positions in the crystal they are able to move. Thus an electric current can pass through when a voltage is applied between two electrodes dipped into the ionic melt or solution.

4.19 Ionic Materials in Everyday Life

Many ionic materials are found in everyday life.

- Salt tablets are taken to replace salt lost from the body by sweating.
- Brine, a solution of sodium chloride, has long been used for curing bacon, in effect a preservation process.
- Fluoridation of water supplies to prevent tooth decay is carried out by adding a salt of fluorine such as sodium fluoride, NaF, or sodium fluorosilicate, Na_2SiF_6.

Toothpaste sometimes contains sodium fluoride

4.20 Hydrogen Bonding

Hydrogen bonding is a specific type of dipole–dipole interaction. It occurs when hydrogen is bonded to small highly electronegative atoms – O, N or F. It is stronger than other types of dipole–dipole interactions.

Hydrogen bonding is a special type of dipole–dipole interaction, which occurs when hydrogen is bonded to small, highly electronegative atoms such as O, N, or F.

Hydrogen bonding in water

In water molecules, the O–H bond is highly polar owing to the large electronegativity difference between oxygen and hydrogen. Oxygen carries a partial negative charge and hydrogen carries a partial positive charge. Consequently, an oxygen atom in a water molecule will have a strong attraction for hydrogen atoms in neighbouring molecules, and vice versa.

These strong intermolecular forces cause a much higher than expected boiling point in water, 373 K. Hydrogen bonding is also the main intermolecular force that holds molecules of water together in ice crystals.

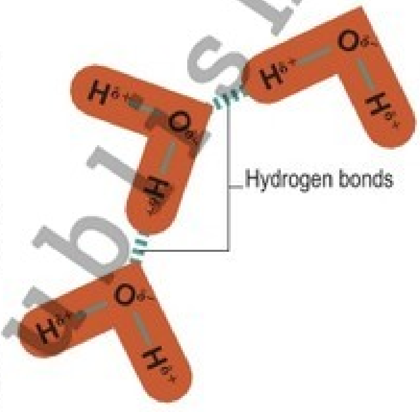


Figure 4.54
Hydrogen bonding between water molecules

Comparison between water and hydrogen sulfide

Hydrogen sulfide, H_2S, might be expected to have a higher boiling point than water owing to its greater relative molecular mass. However, it actually boils at 211 K.

The reason for this is:

- The H–S bond is much less polar than the O–H bond in water.
- In addition, the partial negative charge is more diffuse, and thus less effective, on the large sulfur atom than on the smaller oxygen atom.
- Thus there is no hydrogen bonding between the H_2S molecules, and the dipole–dipole interactions are much weaker. The large difference in boiling point is indicative of the strength of the hydrogen bonding in water.

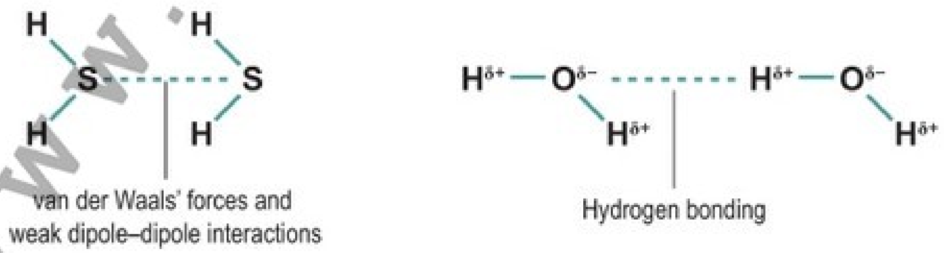


Figure 4.55
The intermolecular forces between hydrogen sulfide molecules are weaker than those between water molecules

Comparison between water and hydrides of elements in groups IV and VI

The boiling points of a number of hydrides of elements in groups IV and VI are shown in Figure 4.56. The group IV hydrides, CH_4, SiH_4, GeH_4 and SnH_4 are non-polar molecules, and show the normal trend among such molecules of boiling point increasing with increasing relative molecular mass. Three of the group VI hydrides, H_2S, H_2Se and H_2Te, show a similar trend of boiling point increasing with increasing relative molecular mass. The diagram clearly shows that the other group VI hydride, H_2O, has an exceptionally high boiling point. This is because there is hydrogen bonding between its molecules.

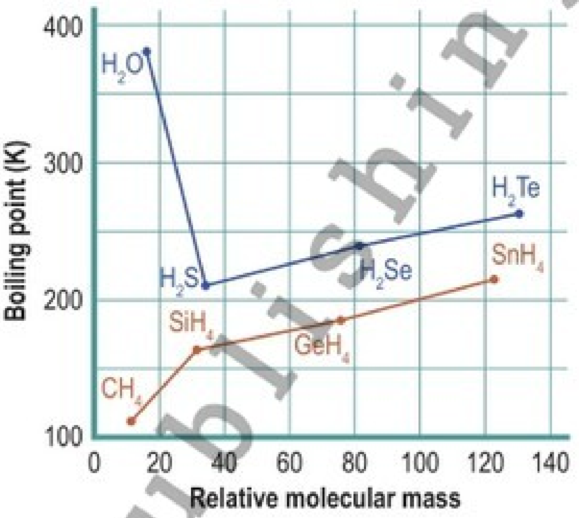


Figure 4.56
The boiling points of some hydrides

Hydrogen bonding in ammonia and hydrogen fluoride

Hydrogen bonding is also evident in ammonia and in hydrogen fluoride. The high solubility of each of these compounds in water is partly explained by hydrogen bonding which occurs between the water and the solute.

The boiling point of water (100°C) is much higher than that of ammonia (−33°C), even though each ammonia molecule could form one more hydrogen bond than could a water molecule. The greater electronegativity of oxygen compared with nitrogen is the significant factor, making the hydrogen bonds in water stronger than those in ammonia.

The boiling point of water is also higher than that of hydrogen fluoride (19.5°C).

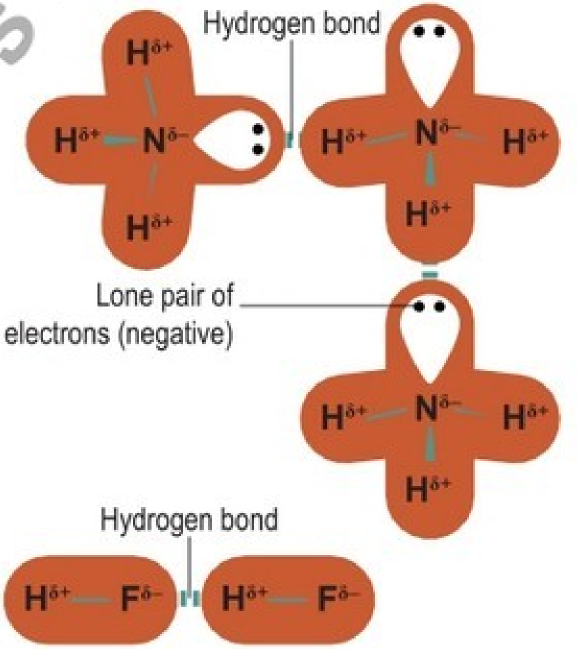


Figure 4.57
Hydrogen bonding between molecules of ammonia and between molecules of hydrogen fluoride

This time the greater number of possible hydrogen bonds for each water molecule is a more significant factor than the stronger hydrogen bonds in hydrogen fluoride brought about by fluorine's greater electronegativity.

There is no evidence of hydrogen bonding in hydrogen chloride despite the sizeable electronegativity difference. This is due to the large size of the chlorine atom and the consequent diffuse negative charge on the atom.

Small electronegative atoms form hydrogen bonds

Why is it that only atoms which are both small and electronegative, such as F, O and N, can form hydrogen bonds? When a hydrogen atom is bonded to a very electronegative small atom, its share of the bonding pair of electrons is very small, so that it is little more than a bare proton. It will then be readily attracted to another electronegative atom. If this atom has a lone pair of electrons, in a small orbital, so that the negative charge is concentrated, it can share this pair with the hydrogen atom. Because the hydrogen atom is so small, only two atoms can bond to it at one time, one by a hydrogen bond, the other by a covalent bond.

Hydrogen bonds are usually many times weaker than covalent bonds, but many times stronger than other dipole–dipole attractions.

Table 4.5 indicates the types of intermolecular force found in different types of substance.

Type of substance	Intermolecular forces
Non-polar	van der Waals' forces
Containing N-H, O-H or H-F bonds	Hydrogen bonding and van der Waals' forces
Polar (but not containing N-H, O-H or H-F bonds)	Dipole–dipole interactions and van der Waals' forces

Table 4.5

QUESTIONS

49 What is the difference between intramolecular bonding and intermolecular forces?

50 Explain how van der Waals' forces between hydrogen molecules arise.

51 Explain why methanal has a higher boiling point than ethene.

52 Explain how hydrogen bonding between water molecules arises.

53 Between what types of molecule are there dipole–dipole interactions?

54 Between what types of molecule are there van der Waals' forces?

4.21 Crystals

A crystal is a solid in which the atoms, ions or molecules of which it is composed are arranged in a regular three-dimensional structure.

The particles of which a crystal is made may be packed in different ways in crystals of different substances. The ordered way in which the particles are packed is called the crystal structure or crystal lattice. The regular outside appearance of the crystal is the direct result of the ordered way in which the particles are arranged inside the crystal.

- Ionic compounds, such as sodium chloride, form **ionic crystals**.
- Covalent compounds, such as water, and elements like iodine that are composed of small molecules, form **molecular crystals**.

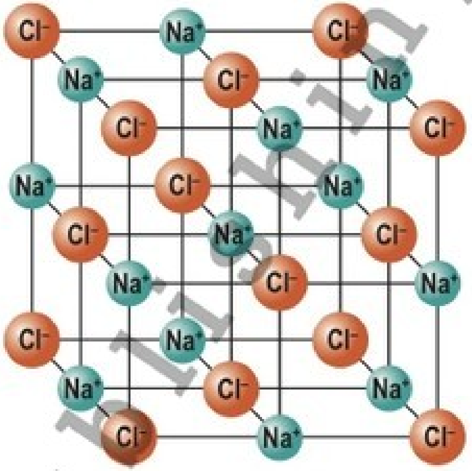


Figure 4.58
The sodium chloride crystal with the lattice points occupied by sodium or chloride ions

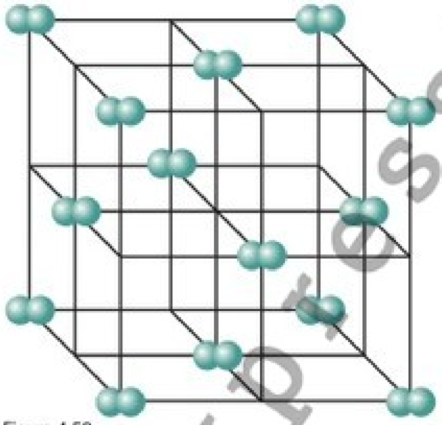


Figure 4.59
The iodine crystal with the lattice points occupied by molecules of iodine

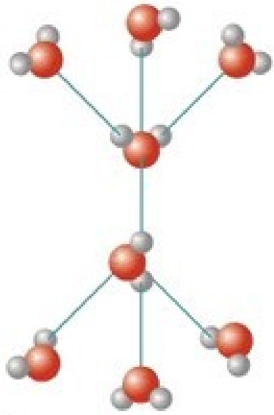


Figure 4.60
Water molecules held in position by hydrogen bonds in an ice crystal

- In **covalent macromolecular crystals,** such as diamond and quartz, atoms occupy the lattice points. Covalent bonding holds the atoms together. Like other crystal types, there is a regular three-dimensional structure. In diamond, for example, each carbon atom is bonded to four other carbon atoms in a tetrahedral arrangement.

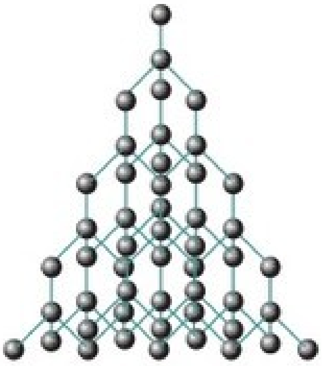


Figure 4.61
The structure of diamond

Different types of crystal are summarised in Table 4.6.

Crystal type	Species occupying lattice points	Binding forces	Examples
Ionic	Positive and negative ions	Ionic bonds	Sodium chloride
Molecular (non-polar)	Molecules	van der Waals' forces	Iodine
Molecular (polar)	Molecules	van der Waals' forces and dipole–dipole attractions or hydrogen bonds	Ice
Metallic	Positive ions	Metallic bond	Sodium
Covalent macromolecular	Atoms	Covalent bonds (sometimes with van der Waals' forces)	Diamond, graphite

Table 4.6

4.22 Properties of Crystals

The physical properties of crystals are related to the binding forces in the crystal. The properties of different types of crystal are summarised in Table 4.7.

Type of crystal	Strength	Melting points	Electrical conductivity	Solubility
Ionic	Hard, but brittle	High	Conducts when molten or in solution	Usually dissolves in polar solvents
Molecular	Relatively weak	Low	Non-conductor	Depends on the type of molecule
Covalent macromolecular	Usually hard	High	Non-conductor (apart from graphite)	Insoluble
Metallic	Most are hard, though malleable and ductile	Variable	Good conductors	Insoluble except in mercury

Table 4.7

- The solubility of **molecular crystals** in different solvents depends on the nature of individual molecules in the crystal. Those crystals consisting of non-polar molecules such as iodine, I_2, are soluble in non-polar solvents like cyclohexane. On the other hand, crystals consisting of polar molecules such as solid hydrogen chloride dissolve in polar solvents such as water.

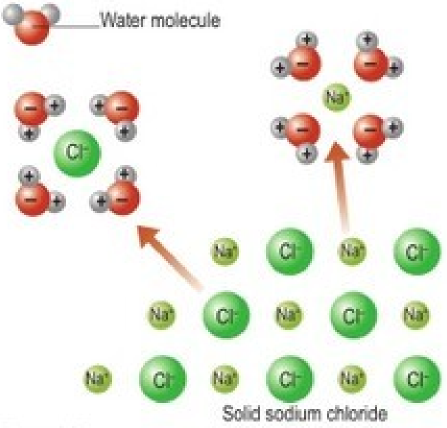


Figure 4.62
How sodium chloride dissolves in water

- Materials such as diamond and quartz which are composed of very large molecules form **covalent macromolecular crystals**. The giant interlocking structures of these crystals mean that they are usually very hard and have very high melting points. For example, the hardness and high melting point of diamond are due to the atoms in the crystal being tetrahedrally arranged and covalently bonded. Covalent macromolecular crystals are usually poor conductors of electricity, since electrons cannot easily move from one atom to another. The crystals do not dissolve in polar or non-polar solvents, because of the stability of their structures.
- Graphite, like diamond, is an allotrope of carbon, that is, they are different physical forms of the same element. Graphite forms macromolecular crystals, but has a number of properties that are very different from those of diamond. Graphite is made up of giant two-dimensional molecules, which are held together by van der Waals' forces. These forces are strong enough to hold the molecules to each other, but are too weak to prevent them from sliding over each other if a force is applied. As a result, graphite is soft, and can be used as a lubricant for machinery, and as pencil lead. Each carbon atom, within the planar molecules, uses three of its valence electrons to form covalent (sigma) bonds with each of three neighbouring carbon atoms. The remaining electrons are used to form delocalised pi bonds and are free to move if a voltage is applied. Consequently graphite is a conductor of electricity.

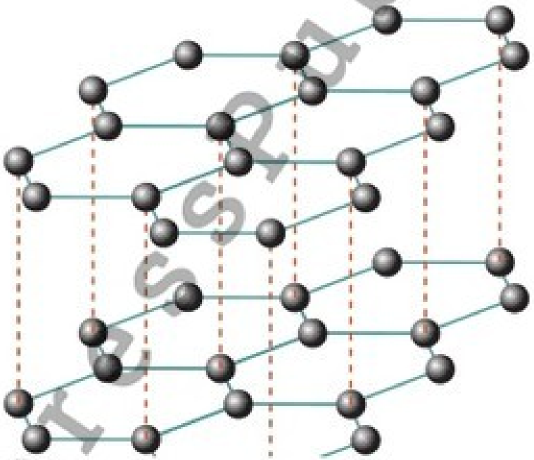


Figure 4.63
The structure of graphite

Metallic Bonding

Metals form Giant Metallic Lattice structures that are composed of positive metal ions surrounded by what is commonly termed a 'sea of delocalised electrons'.

In a metal like sodium, which has the electronic structure $1s^22s^22p^63s^1$,the electron in the 3s atomic orbital of one sodium atom shares space with the corresponding electron on a neighbouring atom to form a molecular orbital. Each sodium atom touches eight other sodium atoms and the sharing occurs between the central atom and the 3s orbitals on each of the eight other atoms.

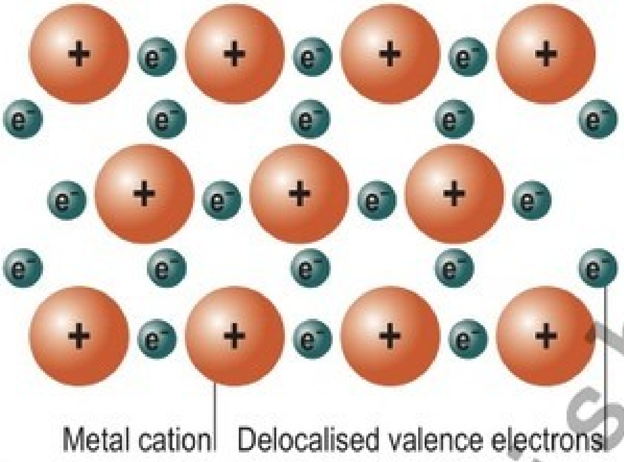


Figure 4.64
Metallic bonding

- In **metallic crystals**, the outer electrons are free to move throughout the crystal. The movement of the electrons away from their original position leaves behind positive ions. These ions are not pushed apart by mutual repulsion because each one is attracted to the delocalised electron cloud that surrounds them. This arrangement gives great strength to many metals, as all of the particles are held together tightly. For this reason also, most metals have high boiling and melting points. The arrangement allows the structure to change shape without fracturing, so metals are malleable and ductile.

Metals are good conductors of heat and electricity. Heat is readily conducted because the increase in kinetic energy is transmitted through the system of delocalised electrons to the rest of the metal. Because the outer electrons are not held rigidly in one place, but can move freely, electricity is conducted when a voltage is applied across a metal wire.

Metal crystals do not dissolve in polar or non-polar solvents. However, they are soluble in mercury, which is the only liquid metal at room temperature.

QUESTIONS

55 Explain the terms (a) crystal, (b) lattice points, (c) binding forces.

56 Name the species occupying the lattice points, and explain the binding forces in each of (a) ionic crystals, (b) molecular crystals, (c) metallic crystals, (d) covalent macromolecular crystals.

57 Why do most ionic crystals have high melting points?

58 Explain how crystals of sodium chloride dissolve in water.

59 Explain why ionic compounds conduct electricity in the molten state or in solution, but not in the solid state.

60 Why does ice have a much higher melting point than other molecular crystals?

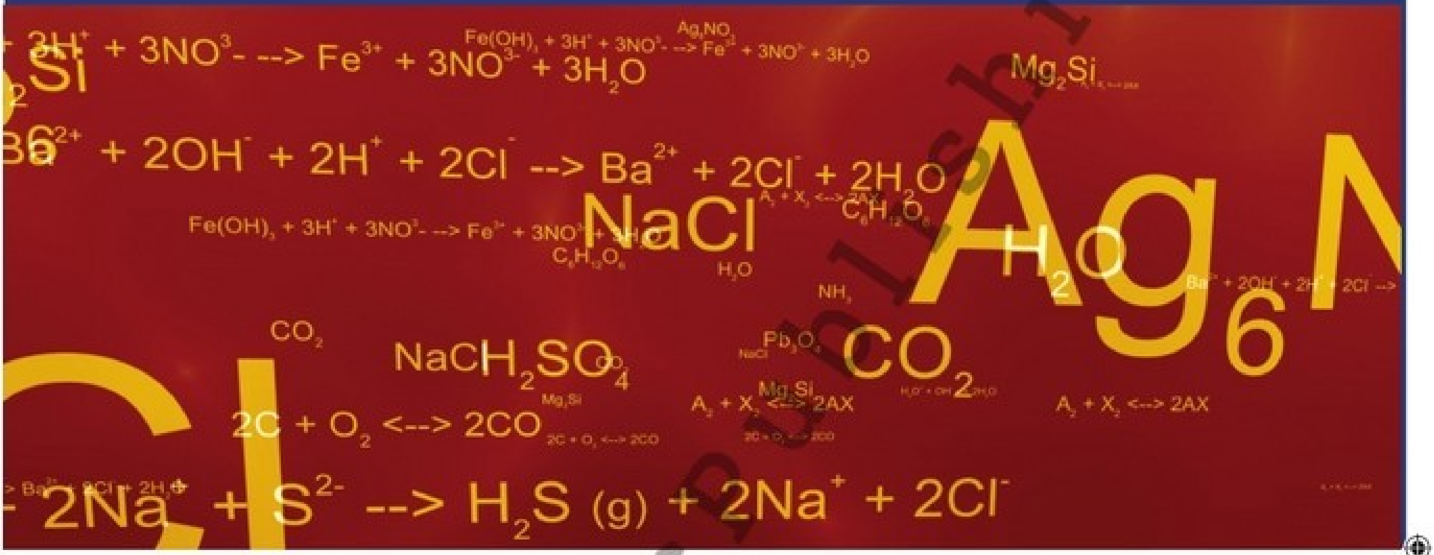
61 Explain the nature of the metallic bond.

62 Explain the difference in physical properties between diamond and graphite.

63 Name the three allotropes of carbon.

Chemical Reactions

MODULE 5



Learning objectives

- To recognise the principles of classification of chemical reactions and their expression in equations of reactants and products 10.2.1.7
- To identify the oxidation number of elements in a compound 10.2.3.1
- To write equations for redox reactions using the electron balance method 10.2.3.2
- To explain processes that occur when an electric current passes through aqueous solution or a melt 10.2.3.3
- To predict products which form when electrolysis occurs 10.2.3.4
- To complete electrolysis equations 10.2.3.5
- To calculate mass and gas volume of products when electrolysis occurs 10.2.3.6
- To identify qualitative composition of acid, hydroxide and salt solutions, using pH 10.3.4.1
- To predict the pH of salt solutions 10.3.4.2
- To differentiate exothermic and endothermic reactions 10.3.1.1
- To explain the significance of reaction heat 10.3.1.2
- To make calculations relating to heat of reaction 10.3.1.3

5.1 Classification of Chemical Reactions

Chemical reactions can generally be classified into one or more different basic types: oxidation–reduction reactions, acid–base reactions, exchange reactions, combination reactions and displacement reactions. As we will see in this Module, however, many of these reactions can be given more than one type classification.

Acid-base reactions and oxidation-reduction reactions are dealt with in detailed sections below, so in this section we will focus on the different types of and the contrasts between exchange, combination and decomposition reactions.

Exchange Reactions

Exchange reactions can be divided into two broad types: single replacement and double replacement reactions.

Single replacement reactions are of the general type:

$$AB + C \rightarrow AC + B.$$

In a metal replacement reaction a more reactive metal replaces a less reactive metal in a compound. An example of this would be magnesium replacing copper in an aqueous solution of copper (II) nitrate.

$$Mg_{(s)} + Cu(NO_3)_{2(aq)} \rightarrow Mg(NO_3)_{2(aq)} + Cu_{(s)}$$

Most metals also react with acids such as hydrochloric acid producing hydrogen gas as one of the products of the reaction as in this example:

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$

In such reactions, known as hydrogen replacement reactions, the active metal replaces the hydrogen in the acid. Some metals, such as Group 1 metals are so reactive that they can replace hydrogen in water forming a metal hydroxide and hydrogen gas:

$$2Li_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + H_{2(g)}$$

Another type of single replacement reaction is the halogen replacement reaction. In the halogen group [Group 17] the reactivity of each element decreases moving down the group.

This means that an element such as chlorine, which is above bromine, will replace it in reactions such as.

$$Cl_{2(g)} + 2NaBr_{(aq)} \rightarrow 2NaCl_{(aq)} + Br_{2(l)}$$

where chlorine reacts with an aqueous solution of sodium bromide producing aqueous sodium chloride and bromine.

Double Replacement Reactions

Double replacement reactions are of the general type:

$$AB + CD \rightarrow AD + BC$$

where the positive and negative ions of two ionic compounds exchange places and in the process form two new compounds. Such reactions can result in the formation of:

- a precipitate as in the reaction:

$$BaCl_{2(aq)} + Na_2SO_{4(aq)} \rightarrow BaSO4_{(s)} + 2\ NaCl_{(aq)}$$

- a gas as in the reaction

$Na_2S_{(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2S_{(g)}$

- a molecular compound such as water as in the reaction:

$HF_{(aq)} + NaOH_{(aq)} \rightarrow H_2O + NaF_{(aq)}$

The reaction in (c) is also termed a neutralisation reaction where an acid + base produces water + a salt.

Combination reactions

As the name suggests combination reactions are of the general type:

$A + B \rightarrow AB$

and the term covers a wide variety of different types of reaction. One type of combination reaction is where two elements combine to form a compound as in the following reaction:

$H_{2(s)} + Cl_{2(g)} \rightarrow 2HCl_{(g)}$

The term also covers the reaction of metals and non-metals with oxygen as in the reaction of igniting magnesium in air:

$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

Combination reactions can also occur between an element and a compound resulting in formation of a compound made up of larger number of atoms as in the reaction:

$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$

Two compounds can also combine – commonly seen in the combination of an oxide with water where the product is an aqueous hydroxide solution:

$K_2O + H_2O \rightarrow 2KOH$

Decomposition reactions

Decomposition reactions are of the general type:

$AB \rightarrow A + B$

where a compound breaks down into two(or more) simpler substances.

There are three types of decomposition reaction: thermal, electrolytic and photo.

An example of thermal decomposition, caused by heating a compound is the reaction:

$CaCO_{3(s)} + heat \rightarrow CaO_{(s)} + CO_{2(g)}$

Electrolytic decomposition reactions occur where an electric current is passed through an aqueous or molten solution as in the reaction:

$2NaCl_{(l)} \rightarrow 2Na_{(l)} + Cl_{2(g)}$

and photo decomposition describes the situation in which a reaction occurs in the presence of light [photons] as in the reaction:

$2AgCl + sunlight \rightarrow 2Ag + Cl_2$

QUESTIONS

1 Can you predict the products of each of these reactions will be and say what type of reaction will occur.

(a) Zinc metal is placed in sulphuric acid H_2SO_4 (aq).

(b) Heat is added to a test tube of calcium carbonate.

(c) Aluminium powder is added to a test tube of chlorine gas.

(d) Zinc sulphide reacts with oxygen in the air.

(e) Magnesium hydroxide is mixed with hydrochloric acid.

(f) Barium oxide is added to water

(g) A container of silver bromide is exposed to sunlight

(h) Copper is placed in a solution of silver nitrate.

5.2 Chemical Equations

A chemical equation tells us what substances react in a chemical reaction and what the products are. In order to describe a reaction accurately:

- **The correct formula for each of the reactants and products must be used.**
- **The equation must be balanced**, that is, the total number of atoms of each element in the reactants must equal the total number of atoms of that element in the products.

In balancing an equation, formulas cannot be altered in any way, but can only be multiplied by an appropriate number.

EXAMPLE 5.1

Carbon reacts with oxygen forming carbon monoxide. Find the balanced equation for the reaction, given that the unbalanced equation is

$$C + O_2 \rightarrow CO$$

Answer The unbalanced equation is

$$C + O_2 \rightarrow CO$$

(a) Carbon: There is one carbon atom on the left-hand side, and one on the right-hand side, so C and CO are left as they are.

(b) Oxygen: There are two oxygen atoms on the left-hand side, and one on the right-hand side. CO must therefore be multiplied by 2:

$$C + O_2 \rightarrow 2CO$$

After considering each element in turn, the equation should always be checked to see if there are equal numbers of atoms of each element on the two sides of the equation.

There are now two carbon atoms on the right-hand side, and one on the left-hand side. C must therefore be multiplied by 2:

$$2C + O_2 \rightarrow 2CO$$

The equation should now be checked again to ensure that there are now equal numbers of atoms of each element on the two sides of the equation.

In this case, there are two carbon atoms and two oxygen atoms on each side.

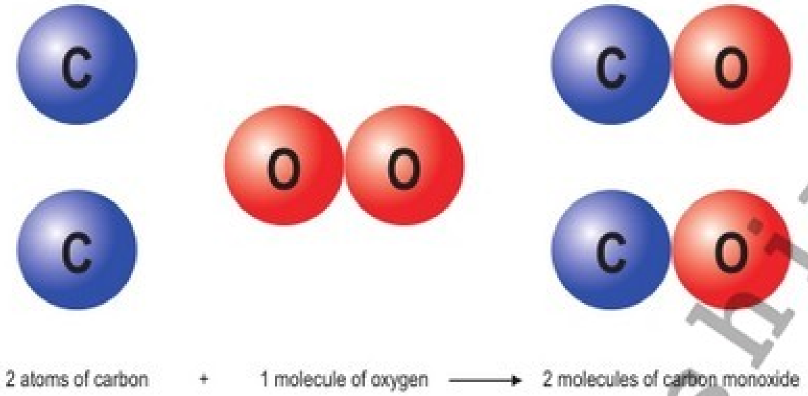


Figure 5.1
The reaction between carbon and oxygen forming carbon monoxide

EXAMPLE 5.2

Methane reacts with oxygen, forming carbon dioxide and water vapour only. Write a balanced chemical equation for the reaction.

Answer The unbalanced equation is

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

To balance the equation, each element is checked in turn to see whether or not there are equal numbers of atoms of that element on the two sides of the equation.

(a) Carbon: There is one carbon atom on each side of the equation, so CH_4 and CO_2 are left as they are.

(b) Hydrogen: There are four hydrogen atoms on the left-hand side, and only two on the right-hand side. H_2O must therefore be multiplied by two:

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$$

(c) Oxygen: There are now two oxygen atoms on the left-hand side, and four on the right-hand side. O_2 must therefore be multiplied by two:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

The equation should be checked to ensure that there are equal numbers of atoms of each element on the two sides of the equation.

In this case, there are one carbon atom, four hydrogen atoms and four oxygen atoms on each side.

QUESTIONS

2 Balance each of the following chemical equations:

(a) $MgCl_2 + AgNO_3 \rightarrow Mg(NO_3)_2 + AgCl$

(b) $N_2 + H_2 \rightarrow NH_3$

(c) $Fe + HCl \rightarrow FeCl_2 + H_2$

(d) $Al + O_2 \rightarrow Al_2O_3$

(e) $H_2SO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$

(f) $C_4H_{10} + O_2 \rightarrow CO_2 + H_2O$

(g) $Al + Cl_2 \rightarrow AlCl_3$

(h) $H_2 + Cl_2 \rightarrow HCl$

(i) $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

(j) $ZnS + O_2 \rightarrow ZnO + SO_2$

(k) $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + H_2O + N_2$

5.3 Redox reactions

Figure 5.2 Magnesium burning

Figure 5.3 Iron nails rusting

Magnesium burning and iron rusting are chemical reactions involving the transfer of electrons. Reactions involving transfer of electrons are known as **oxidation–reduction** (or redox) reactions. In the following redox reaction

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

electrons are lost by the zinc atom and gained by the copper ion. Everyday examples of redox reactions include browning of apples, respiration and photosynthesis.

Not all reactions involve electron transfer. In the reaction that occurs in the test for chloride ions, positive silver ions are attracted to negative chloride ions, and solid silver chloride forms.

$$Ag^{+}_{(aq)} + Cl^{-}_{(aq)} \rightarrow AgCl_{(s)}$$

There is no transfer of electrons; the positive silver ions are simply attracted to the negative chloride ions, and solid silver chloride forms.

QUESTIONS

3 What happens in a redox reaction?

4 Give two everyday examples of redox reactions.

5.4 Oxidation and Reduction

Oxidation is the loss of electrons.

A chemical species is said to be oxidised if it loses electrons, for example, Zn in the reaction

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

However, a species is reduced if it gains electrons, for example, Cu^{2+} in the above reaction.

Reduction is the gain of electrons.

In redox reactions, both **oxidation**, or loss of electrons, and **reduction**, or gain of electrons, occur.

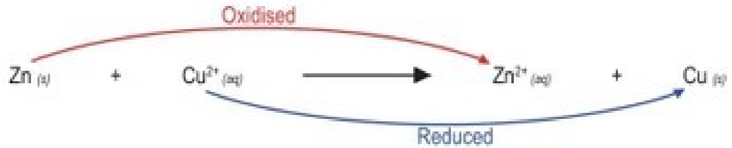


Figure 5.4

It is relatively easy to work out what has been oxidised and what has been reduced in reactions such as

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

where the charges on ions are clearly shown.

In reactions such as

$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$

the fact that metals when forming compounds are usually oxidised, since they form positive ions and therefore lose electrons, can be used. Non-metals, on bonding with metals, usually form negative ions by gaining electrons, and therefore are reduced. In the above example, the metal sodium loses electrons and is therefore oxidised. The non-metal chlorine gains electrons and is therefore reduced.

$2Na^0 - 2e^- \rightarrow 2Na^+$ oxidation
$Cl_2 + 2e^- \rightarrow 2Cl^-$ reduction
$2Na + Cl_2 \rightarrow 2Na^+ + 2Cl^-$

Rusting of iron

In the rusting of iron, iron reacts with oxygen and water, forming first Fe^{2+} ions and eventually Fe^{3+} ions. In this reaction the iron atoms lose electrons and are oxidised. Oxygen atoms gain electrons and are reduced.

Iron is oxidised when rusting occurs

EXAMPLE 5.3

What is oxidised and what is reduced in the following reaction?

$$2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$$

Answer Magnesium on reacting with oxygen forms positive ions by losing electrons, and is therefore oxidised. Oxygen gains electrons from magnesium, and is therefore reduced.

In a reaction such as

$$2NaCl_{(s)} \rightarrow 2Na_{(s)} + Cl_{2(g)}$$

sodium ions in sodium chloride gain electrons to form sodium atoms, and are therefore reduced. Chloride ions lose electrons to form chlorine molecules, and are oxidised.

EXAMPLE 5.4

What is the oxidation number of the phosphorus atom in the H_3PO_4 molecule?

$$CuSO_{4(aq)} + Mg_{(s)} \rightarrow Cu_{(s)} + MgSO_{4(aq)}$$

Answer Magnesium, on reacting, forms positive ions by losing electrons,and is therefore oxidised. Copper gains electrons from magnesium, and is therefore reduced. (The sulfate ion is neither oxidised nor reduced.)

QUESTIONS

5 In the following reactions, identify (a) what is oxidised (b) what is reduced.

(i) $2K_{(s)} + F_{2(g)} \rightarrow 2KF_{(s)}$

(ii) $FeSO_{4(aq)} + Zn_{(s)} \rightarrow Fe_{(s)} + ZnSO_{4(aq)}$

(iii) $CuSO_{4(aq)} + Pb_{(s)} \rightarrow Cu(s) + PbSO_{4(s)}$

(iv) $Fe_{(s)} + Cu(NO_3)_{2(aq)} \rightarrow Fe(NO_3)_{2(aq)} + Cu_{(s)}$

(v) $2KCl_{(l)} \rightarrow 2K_{(s)} + Cl_{2(g)}$

(vi) $FeSO_{4(aq)} + Mg_{(s)} \rightarrow Fe_{(s)} + MgSO_{4(aq)}$

5.5 Oxidation Numbers

It is usually easy to work out what is oxidised and what is reduced in redox reactions involving metal ions, because the gain and loss of electrons is readily seen. Redox reactions involving covalent compounds are more difficult to keep track of in this way. Consider the reaction between hydrogen and oxygen, forming water:

At the beginning of the reaction, the hydrogen atoms share a pair of electrons equally; the oxygen atoms also share electrons equally. After the reaction, each hydrogen atom shares a pair of electrons with an oxygen atom. Since hydrogen is less electronegative than oxygen, the sharing is unequal – there is a partial transfer of electrons from the hydrogen to the oxygen. To keep track of electron shifts like this, and of oxidation–reduction in general, oxidation numbers are very useful.

The oxidation number of an atom is the charge that the atom appears to have when the electrons are distributed according to certain rules.

According to these rules, electrons shared between unlike atoms are counted with the more electronegative atom, while electrons shared between like atoms are divided equally between them.

The main rules are as follows:

- **In free elements, each atom has an oxidation number of 0.** For example, in a nitrogen molecule (N_2) each nitrogen atom has an oxidation number of 0.
- **The sum of the oxidation numbers of all the atoms in a molecule is 0.** For example, in the water molecule (H_2O), where hydrogen has an oxidation number of +1 and oxygen has an oxidation number of –2, the oxidation numbers add up to 0:

  H_2O
  $2(+1) - 2 = 0$
- The oxidation number of a simple ion containing one atom is equal to the charge on the ion. For example, in a chloride ion (Cl^-) the oxidation number of chlorine is –1.
- The sum of the oxidation numbers of all the atoms in a complex ion is equal to the charge on the ion. For example, in a nitrate ion (NO^{3-}) where nitrogen has an oxidation number of +5 and oxygen has an oxidation number of –2, the oxidation numbers add up to –1:

  NO^{3-}
  $2(+1) - 2 = 0$
  $+5 + 3(-2) = -1$
- **Hydrogen has an oxidation number of +1 in its compounds, except in metallic hydrides where it is –1.**
- **Oxygen has an oxidation number of –2 in its compounds, except in hydrogen peroxide where it is –1, and when bonded to fluorine it is +2.**
- **The oxidation number of Group 1 elements in their compounds is always +1, and the oxidation number of Group 2 elements in their compounds is always +2.**
- **The oxidation number of a halogen when bonded to a less electronegative atom is –1.** Fluorine is the most electronegative element, and always has an oxidation number of –1 in its compounds.

Chlorine has an oxidation number of –1 in compounds where it is not bonded to oxygen or fluorine.

5.6 Calculation of Oxidation Numbers

The rules for oxidation numbers are very useful in calculating oxidation numbers of atoms whose oxidation numbers are not given directly by the rules.

EXAMPLE 5.5

What is the oxidation number of the phosphorus atom in the H_3PO_4 molecule?

Answer

Let the oxidation number of P = x
The oxidation number of H = +1 (from rule 5)
The oxidation number of O = –2 (from rule 6)
Therefore $3(+1) + x + 4(-2) = 0$ (from rule 2)
Therefore $x = -3 + 8 = +5$

EXAMPLE 5.6

What is the oxidation number of Mn in $KMnO_4$?

Answer

Let the oxidation number of Mn = x
The oxidation number of K = +1 (from rule 7)
The oxidation number of O = −2 (from rule 6)
Therefore +1 + x + 4(−2) = 0 (from rule 2)
Therefore x = −1 + 8 = +7

EXAMPLE 5.7

What is the oxidation number of C in $C_6H_{12}O_6$?

Answer

Let the oxidation number of C = x
The oxidation number of H = +1 (from rule 5)
The oxidation number of O = −2 (from rule 6)
Therefore 6(x) + 12(+1) + 6(−2) = 0 (from rule 2)
Therefore x = −12 + 12 = 0

EXAMPLE 5.8

What is the oxidation number of S in $Na_2S_4O_6$?

Answer

Let the oxidation number of S = x
The oxidation number of Na = +1 (from rule 7)
The oxidation number of O = −2 (from rule 6)
Therefore 2(+1) + 4(x) + 6(−2) = 0 (from rule 2)
Therefore 4x = −2 + 12 = +10
Therefore x = 2.5

QUESTIONS

6 Use the oxidation number rules to find the oxidation number of

(a) Cl in $KClO_4$
(b) S in Na_2SO_4
(c) C in CO_2
(d) H in CaH_2
(e) Zn in $ZnCl_2$
(f) Cr in $K_2Cr_2O_7$
(g) C in $C_{12}H_{22}O_{11}$
(h) P in H_3PO_3
(i) S in H_2SO_4
(j) Cu in CuO

7 Assign oxidation numbers to each atom in the following:

(a) Al_2O_3
(b) NaH
(c) HNO_3
(d) K_2CrO_4
(e) Co_2O
(f) FeO
(g) NH_3
(h) S_8
(i) $Mg(NO_3)_2$
(j) PO_4^{3-}
(k) Fe^{3+}
(l) OF_2
(m) H_2O_2
(n) $Na_2B_4O_7$
(o) $C_2O_4^{2-}$
(p) $C_2H_4O_2$
(q) $KHSO_4$
(r) $Cr_2(SO_4)_3$
(s) Fe_3O_4
(t) CoF_6^{3-}.

EXAMPLE 5.9

What is the systematic name of $FeCl_3$?

Answer

Let the oxidation number of Fe = x
The oxidation number of Cl = −1 (from rule 8)
Therefore $x + 3(-1) = 0$ (from rule 2)
Therefore $x = 3$
The name of the compound is therefore iron(III) chloride.

EXAMPLE 5.10

What is the formula of iron(III) sulfate-9-water?

Answer

The iron(III) ion has a charge of +3.
The sulfate ion has a charge of −2.
The formula is $Fe_2(SO_4)_3 \times 9H_2O$

QUESTIONS

8 What is the systematic name of

- (a) $CuCl_2$
- (b) CuCl
- (c) Cr_2O_3
- (d) $TiCl_4$
- (e) $TiCl_2$
- (f) V_2O_5
- (g) $NiNO_3 \times 6H_2O$
- (h) $NiSO_4$
- (i) $KMnO_4$
- (j) K_2CrO_4?

9 What is the formula of

- (a) chromium(III) chloride
- (b) manganese(IV) oxide
- (c) iron(II) chloride
- (d) nickel(II) sulfide
- (e) cobalt(II) chloride
- (f) iron(II) sulfate-7-water
- (g) copper(II) nitrate-3-water
- (h) sodium dichromate(VI)
- (i) silver(I) nitrate
- (j) copper(I) sulfate?

5.7 Oxidation and Reduction in terms of Oxidation Numbers

Oxidation is an increase in oxidation number.

Oxidation numbers may be used to find out what is oxidised and what is reduced in a redox reaction. **Oxidation**, in terms of oxidation numbers, is **an increase in oxidation number**, while **reduction is a decrease in oxidation number**.

In working out what is oxidised and what is reduced in a reaction, it is important to remember that oxidation number is not an actual charge. To avoid confusion, and errors in calculations, the oxidation number should be written below the atom to which it applies, as shown in the following examples:

$$\underset{+1\ -2}{H_2O} \qquad \underset{+6\ -2}{Cr_2O_7^{2-}} \qquad \underset{-2\ +1}{OH^-}$$

(Note that when doing this the oxidation number for only a single atom of each element should be written.)

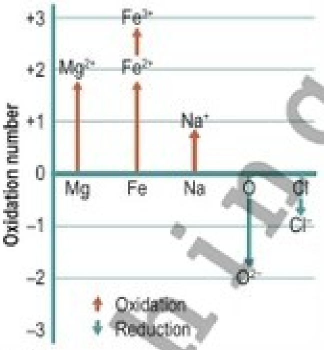


Figure 5.5
Oxidation is an increase in oxidation number: reduction is a decrease

Reduction is a decrease in oxidation number.

Example 5.11

What is (a) oxidised (b) reduced in the following redox reaction?

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Answer

Rules 1 and 6 respectively can be used to find the oxidation numbers of oxygen, while rule 2 can then be used to calculate the oxidation numbers of sulfur.

$$\underset{+4\ -2}{2SO_2} + \underset{0}{O_2} \rightarrow \underset{+6\ -2}{2SO_3}$$

Note that in all questions of this kind the number of moles given in the balanced equation for each substance should be ignored.

(a) The oxidation number of sulfur increases from +4 to +6. Therefore, sulfur is oxidised.

(b) The oxidation number of oxygen in O_2 decreases from 0 to −2. Therefore, the oxygen in O_2 is reduced.

Therefore x = −3 + 8 = +5

Example 5.12

What is (a) oxidised (b) reduced (c) the oxidising agent (d) the reducing agent in the following redox reaction?

$$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

Answer

Assign oxidation numbers to all of the atoms in the equation, using the rules:

$$\underset{+7\ -2}{2MnO_4^-} + \underset{+1}{16H^+} + \underset{+3\ -2}{5C_2O_4^{2-}} \rightarrow \underset{+2}{2Mn^{2+}} + \underset{+4\ -2}{10CO_2} + \underset{+1\ -2}{8H_2O}$$

(a) The oxidation number of carbon increases from +3 to +4. Therefore, carbon is oxidised.

(b) The oxidation number of manganese decreases from +7 to +2. Therefore, manganese is reduced.

(c) Manganese is the oxidising agent, because it is reduced itself.

(d) Carbon is the reducing agent, because it is oxidised itself.

QUESTIONS

10 What is (a) oxidised and (b) reduced in each of the following redox reactions?

(i) $C + O_2 \rightarrow CO_2$
(ii) $2Na + F_2 \rightarrow 2NaF$
(iii) $2H+ + Zn \rightarrow Zn^{2+} + H_2$
(iv) $PCl_3 + Cl_2 \rightarrow PCl_5$
(v) $ZnS + 2O_2 \rightarrow ZnSO_4$
(vi) $2C_2H_2 + 5O_2 \rightarrow 4CO_2 + 2H_2O$
(vii) $CuO + H_2 \rightarrow Cu + H_2O$

11 Using oxidation numbers, determine which of the following are redox reactions. For each redox reaction, state what is (a) oxidised (b) reduced (c) the oxidising agent (d) the reducing agent.

(i) $Sn + 4HNO_3 \rightarrow SnO_2 + 4NO_2 + 2H_2O$
(ii) $N_2O_4 \rightarrow 2NO_2$
(iii) $2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$
(iv) $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^- + H_2O$
(v) $NaOH + HCl \rightarrow NaCl + H_2O$
(vi) $MgCl_2 + 2AgBr \rightarrow MgBr_2 + 2AgCl$
(vii) $As_2O_3 + 2I_2 + 2H_2O \rightarrow As_2O_5 + 4I^- + 4H^+$

5.8 Balancing Redox Equations Using Oxidation Numbers

It is often not possible to correctly balance redox equations by inspection. A redox equation such as

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

may be balanced by a method using oxidation numbers. The method is as follows:

- Assign oxidation numbers to all the atoms in the equation. In the example above:

$$\begin{array}{llllll} Cr_2O_7^{2-} & + Fe^{2+} & + H^+ & \rightarrow Cr^{3+} & + Fe^{3+} & + H_2O \\ +6\ -2 & \ \ +2 & \ \ +1 & \ \ \ +3 & \ \ +3 & \ \ +1\ -2 \end{array}$$

- Identify atoms that are oxidised or reduced, and in each case write down the number of electrons lost or gained per atom:

$$\begin{array}{lll} Cr + 3e^- \rightarrow & Cr & \text{Reduced} \\ +6 & +3 & \\ Fe - e^- \rightarrow & Fe & \text{Oxidised} \\ +2 & +3 & \end{array}$$

- Attach subscripts (if any) as in the original equation to the oxidised and reduced atoms, and balance the resulting half equations:

$$\begin{array}{lll} Cr_2 + 6e^- \rightarrow & 2Cr & (1) \\ +6 & +3 & \\ Fe - e^- \rightarrow & Fe & (2) \\ +2 & +3 & \end{array}$$

- Balance electron loss and gain by multiplying one or both of the half equations, and then add the resulting half equations:

Leave half equation (1) as it is, and multiply half equation (2) by 6

$$\begin{array}{l} Cr_2 + 6e^- \rightarrow 2Cr \\ 6Fe - 6e^- \rightarrow 6Fe \\ \hline Cr_2 + 6Fe \rightarrow 2Cr + 6Fe \end{array}$$

- Attach species and/or charges that were attached to the oxidised or reduced atoms in the original equation:

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

- Include the remaining species from the original equation:

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

  and complete the balancing by inspection:

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

EXAMPLE 5.13

Balance the following redox equation

$$MnO_4^- + CH_3OH + H^+ \rightarrow Mn^{2+} + HCHO + H_2O$$

Answer

(a) $$\begin{array}{lllllllllll} MnO_4^- & + & CH_3OH & + & H^+ & \rightarrow & Mn^{2+} & + & HCHO & + & H_2O \\ +7\ -2 & & -2\ +1\ -2\ +1 & & +1 & & +2 & & +1\ 0\ +1\ -2 & & +1\ -2 \end{array}$$

(b) $$\begin{array}{llllll} Mn & + & 5e^- & \rightarrow & Mn & \text{Reduced} \\ +7 & & +2 & & & \\ C & - & 2e^- & \rightarrow & C & \text{Oxidised} \\ -2 & & 0 & & & \end{array}$$

(c) $$\begin{array}{llllll} Mn & + & 5e^- & \rightarrow & Mn & (1) \\ +7 & & +2 & & & \\ C & - & 2e^- & \rightarrow & C & (2) \\ -2 & & 0 & & & \end{array}$$

(d) Multiply half equation (1) by 2, and multiply half equation (2) by 5

$$\begin{array}{lllll} 2Mn & + & 10e^- & \rightarrow & 2Mn \\ 5C & - & 10e^- & \rightarrow & 5C \\ \hline 2Mn & + & 5C & \rightarrow & 2Mn + 5C \end{array}$$

(e) $2MnO_4^- + 5CH_3OH \rightarrow 2Mn^{2+} + 5HCHO$

(f) $2MnO_4^- + 5CH_3OH + H^+ \rightarrow 2Mn^{2+} + 5HCHO + H_2O$

Balancing by inspection:

$2MnO_4^- + 5CH_3OH + 6H^+ \rightarrow 2Mn^{2+} + 5HCHO + 8H_2O$

EXAMPLE 5.14

Balance the following redox equation

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

Answer

Assign oxidation numbers to all the atoms in the equation.

$$\underset{+6\ -2}{Cr_2O_7^{2-}} + \underset{+2}{Fe^{2+}} + \underset{+1}{H^+} \rightarrow \underset{+3}{Cr^{3+}} + \underset{+3}{Fe^{3+}} + \underset{+1\ -2}{H_2O}$$

Identify atoms that are oxidised or reduced, include any subscripts attached to them, and indicate the extent of the change in oxidation numbers:

Cr_2: 2(+6 → +3) i.e. decrease of $2 \times 3 = 6$ reduction
Fe: +2 → +3 i.e. increase of 1 oxidation

Since the total increase in oxidation number must equal the total decrease, the ratio of chromium to iron must be Cr_2: Fe = 1 : 6.

Rewrite original equation and apply the ratio Cr_2: Fe = 1 : 6

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

Balance the rest by inspection:

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

QUESTIONS

12 Using oxidation numbers, balance each of the following equations:

(i) $MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$

(ii) $Cr_2O_7^{2-} + CH_3OH + H+ \rightarrow Cr^{3+} + HCHO + H_2O$

(iii) $ClO_3^- + C_6H_{12}O_6 \rightarrow Cl^- + CO_2 + H_2O$

(iv) $NO_3^- + C \rightarrow NO_2 + CO_2 + O^{2-}$

(v) $Cr2O_7^{2-} + S + H^+ \rightarrow Cr_2O_3 + SO_2 + OH^-$

(vi) $MnO_4^- + C_2H_5OH + H^+ \rightarrow Mn^{2+} + CH_3COOH + H_2O$

13 Balance each of the following equations, and name the substances acting as oxidising agent and as reducing agent in each case:

(i) $Cr_2O_7^{2-} + C_2H_5OH + H^+ \rightarrow Cr^{3+} + CH_3COOH + H_2O$

(ii) $MnO_4^- + H_2O_2 + H^+ \rightarrow Mn^{2+} + O_2 + H_2O$

5.9 Oxidising Agents

An oxidising agent is a substance that allows oxidation to happen by gaining electrons itself.

In a redox reaction, the oxidising agent is itself reduced. For example, in the reaction

$$Cu^{2+}_{(aq)} + Mg_{(s)} \rightarrow Cu_{(s)} + Mg^{2+}_{(aq)}$$

the copper ion, which is itself reduced, is the oxidising agent.

In a number of everyday processes, such as rusting of iron, combustion of fuels and respiration in living organisms, oxygen acts as an oxidising agent. Hydrogen peroxide is a powerful oxidising agent; it is released by some detergents in water, and is quite effective at removing stains, by oxidising the substances causing the stains. Dilute solutions of hydrogen peroxide are used to bleach hair.

Oxidising agent	Use
Oxygen	Combustion, respiration
Potassium manganate(VII)	Titrations, organic preparations
Sodium dichromate(VI)	Organic preparations
Hydrogen peroxide	Stain removal, bleaching of hair

Table 5.1
Common oxidising agents

5.10 Reducing Agents

A reducing agent is a substance that allows reduction to happen by losing electrons itself.

In a redox reaction, the reducing agent is itself oxidised in the reaction. For example, in the reaction

$$Cu^{2+}_{(aq)} + Mg_{(s)} \rightarrow Cu_{(s)} + Mg^{2+}_{(aq)}$$

magnesium, which is itself oxidised, is the reducing agent.

Figure 5.6

Sulfur dioxide, which is used in industry to bleach, for example, wool and paper, acts as a reducing agent when it bleaches materials. Other reducing agents are used in the production of metals from ores (for example, carbon, in the form of coke, and carbon monoxide).

Reducing agent	Use
Sulfur dioxide	Bleaching agent
Carbon	Production of metals from ore
Carbon monoxide	Production of metals from ore
Hydrogen	Reduction of organic compounds

Table 5.2
Common reducing agents

EXAMPLE 5.15

What is (a) the oxidising agent and (b) the reducing agent in the following reaction?

$$Zn^{2+}_{(aq)} + Mg_{(s)} \rightarrow Zn_{(s)} + Mg^{2+}_{(aq)}$$

Answer

(a) Since zinc gains electrons in the reaction, it is reduced, and therefore is the oxidising agent.

(b) Since magnesium loses electrons in the reaction, it is oxidised, and therefore is the reducing agent.

QUESTIONS

14 What is meant by an oxidising agent?

15 Name two oxidising agents.

16 What is meant by a reducing agent?

17 Name two reducing agents.

18 In the following reactions, identify (a) the oxidising agent (b) the reducing agent.

(i) $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$

(ii) $2CaO_{(s)} \rightarrow 2Ca_{(s)} + O_{2(g)}$

(iii) $MgS_{(l)} \rightarrow Mg_{(s)} + S_{(s)}$

(iv) $2Fe^{2+}_{(aq)} + Cl_{2(g)} \rightarrow 2Fe^{3+}_{(aq)} + 2Cl^{-}_{(aq)}$

(v) $MgBr_{2(l)} \rightarrow Mg_{(s)} + Br_{2(l)}$

(vi) $Br_{2(l)} + 2NaI_{(aq)} \rightarrow I_{2(s)} + 2NaBr_{(aq)}$

5.11 Electrolysis

An electrolyte is a substance that conducts electricity when dissolved in water or when molten.

Acids, like hydrochloric acid, bases, like sodium hydroxide, and salts, like sodium chloride, are all electrolytes. Electrolytes are chemically changed when an electric current is passed through them. This process is called **electrolysis**.

In electrolysis, electrodes, which are conductors connected to the positive or negative

Electrolysis is the breaking up of a substance due to the passage of an electric current through it in aqueous solution or when molten.

terminals of a d.c. power supply, are dipped into an electrolyte in aqueous solution or in the molten state. Positive ions (**cations**) are attracted to the negative electrode (**cathode**), where they receive electrons and are reduced. Negative ions (**anions**) are attracted to the positive electrode (**anode**), where they lose electrons and are oxidised.

Oxidation occurs at the anode, and reduction occurs at the cathode.

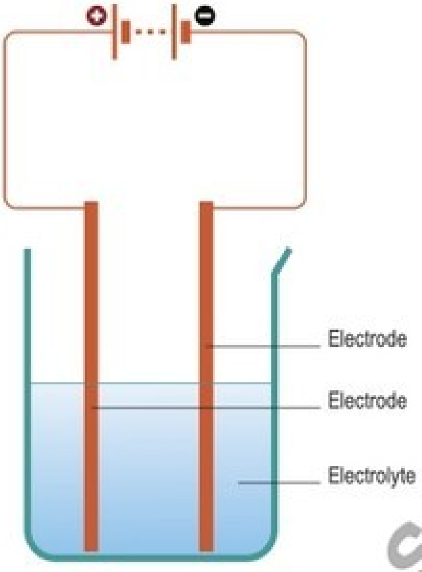


Figure 5.7
Electrolysis

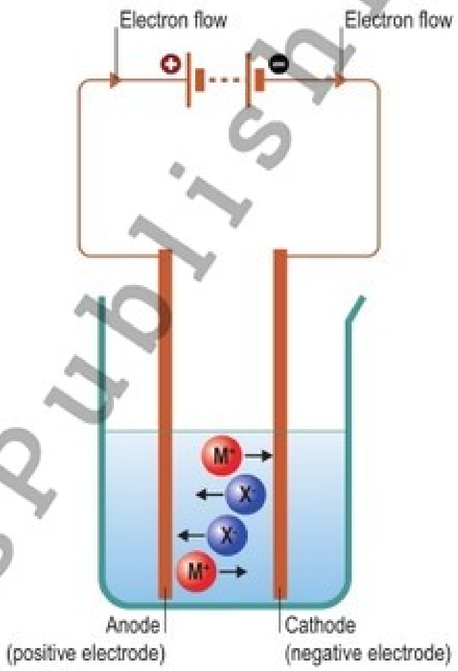


Figure 5.8
What happens during electrolysis

DEMONSTRATION

This demonstration should be observed using an animation or video clip.

Demonstration of ionic movement

During electrolysis of a solution, positive ions (cations) are attracted to the negative electrode (cathode) and negative ions (anions) are attracted to the positive electrode (anode). If these ions are coloured, their movement may be observed visually.
The coloured ions in this demonstration are:

copper(II) [$Cu^{2+}_{(aq)}$] – blue
chromate(VI) [$CrO_4^{2-}{}_{(aq)}$] – yellow

Chemicals needed
Urea
2 M hydrochloric acid
Copper(II) chromate

Equipment needed
20 V d.c. supply
Carbon electrodes
Wires and crocodile clips
Switch
Dropping (or Pasteur) pipette
U–tube
Gloves

Procedure

NB: Wear your safety glasses.

1. Dissolve 1 g of copper(II) chromate in 10 cm^3 of 2 M hydrochloric acid, and dissolve urea (approximately 10 g) in the solution to increase its density.
2. Add the resulting solution to a U–tube until it is about half full.
3. Add 2 M hydrochloric acid to each arm of the U–tube, using a dropping or Pasteur pipette, taking care to avoid mixing the layers.
4. Complete setting up the apparatus as shown in the diagram. The electrodes should just break the surface of the dilute hydrochloric acid.
5. Switch on the power supply, and observe and record what happens.

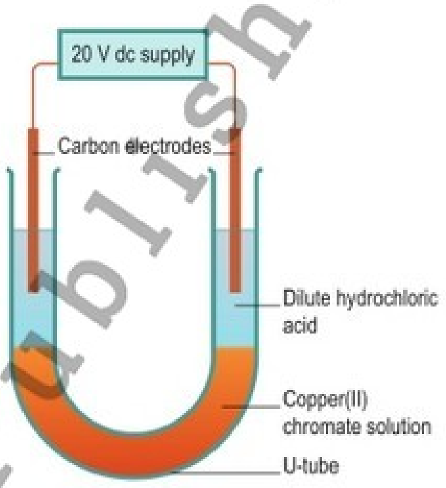


Figure 5.9

QUESTIONS

19 What is an electrolyte?

20 What is meant by electrolysis?

21 In the ionic movement demonstration, why are different colours observed at the anode and cathode?

5.12 Electrolysis of Aqueous Solutions

Electrolysis of an aqueous solution is complex, because there is usually a number of species present that could be oxidised, and also a number that could be reduced. In an aqueous solution, water itself, as well as any anions present, is capable of being oxidised. Water may also be reduced, as well as any cations in the solution. A number of factors determine what is actually oxidised and reduced. These include

- the type of electrode used
- the ease of oxidation or reduction of the different species present.

Type of electrode used

In the electrolysis of aqueous copper(II) sulfate using inert electrodes, oxygen is released at the anode, but if copper electrodes are used, the copper anode dissolves gradually as the copper is oxidised.

Electrolysis of aqueous copper(II) electrodes

Copper(II) sulfate solution contains Cu^{2+} ions, SO_4^{2-} ions and water molecules.
At the anode, copper is oxidised:

$$Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$$

In effect, the anode starts to dissolve as the atoms change into soluble ions.
At the cathode, copper is reduced:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

In effect, the cathode increases in size as dissolved copper ions change into copper atoms that are deposited onto the cathode.

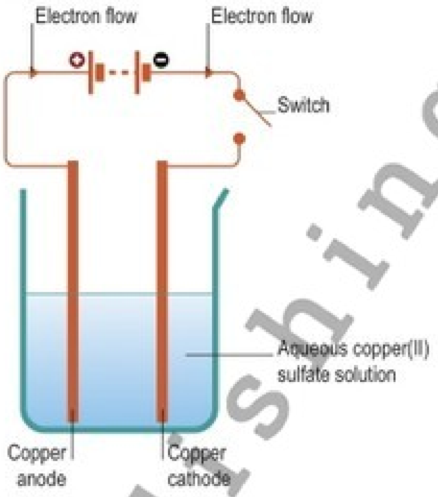


Figure 5.10
Electrolysis of aqueous copper(II) sulfate solution using copper electrodes

Ease of oxidation or reduction of the different species present

In the electrolysis of acidified water,
there are two species, H_2O and SO_4^{2-}, which co
oxidised than
SO_4^{2-}, and therefore it is water that is oxidised, releasing oxygen gas.

Electrolysis of acidified water

Water acidified with sulfuric acid contains H^+ ions, water molecules and SO_4^{2-} ions.
At the anode, water is oxidised:

$$H_2O_{(l)} \rightarrow 2H^+_{(aq)} + ½O_{2(g)} + 2e^-$$

At the cathode, H^+ ions are reduced:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$$

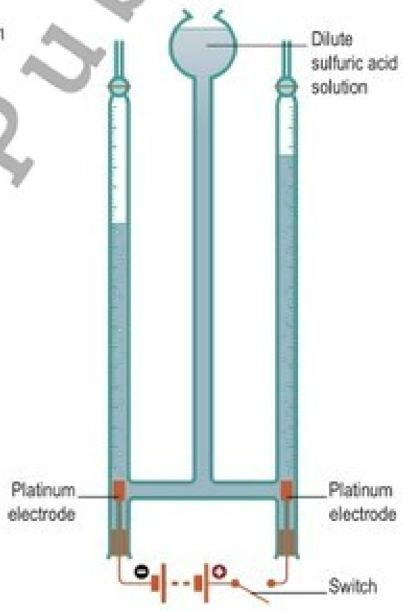


Figure 5.11
Electrolysis of acidified water

EXPERIMENT 5.1

Electrolysis of aqueous sodium sulfate solution using universal indicator

In the electrolysis of aqueous sodium sulfate, the main species present are: Na^+ and SO_4^{2-} from the sodium sulfate, and molecules of water, H_2O. At the cathode, the Na^+ ions are too stable to be discharged. Molecules of water are reduced according to the equation:

$$2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$$

At the anode, the SO_4^{2-} ions are too stable to be discharged. Molecules of water are oxidised according to the equation:

$$H_2O_{(l)} \rightarrow 2H^+_{(aq)} + \tfrac{1}{2}O_{2(g)} + 2e^-$$

Chemicals needed

0.5 M potassium iodide solution
Phenolphthalein indicator solution

Equipment needed

Hoffman or other suitable voltameter
Platinum or graphite electrodes
Voltage generator
Wires and crocodile clips
Ammeter

Procedure

NB: Wear your safety glasses.

1 Draw a table similar to the following:

	Results
Gas collected at anode	
Colour change at anode	
Gas collected at cathode	
Colour change at cathode	

2 Rinse the voltameter thoroughly with water. Add a little universal indicator to check that nothing acidic or alkaline is present.

3 Add about 2 cm³ of universal indicator solution to 250 cm³ sodium sulfate solution. Stir well, and fill the voltameter with this solution.

4 Switch on the power supply, and increase the voltage to 10 V.

5 Describe and explain what happens at each electrode.

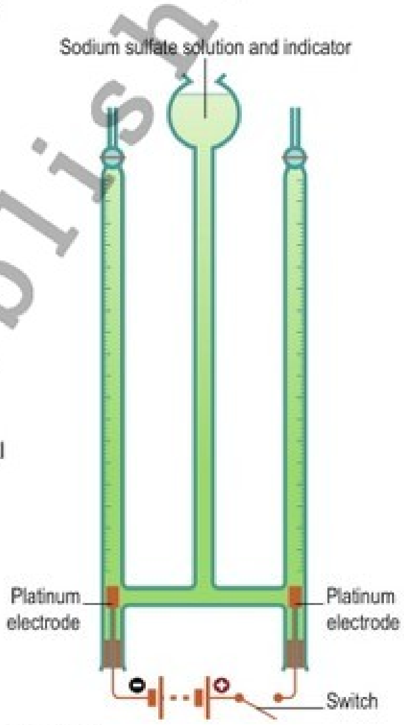


Figure 5.12

5.13 Electrolysis calculations

Half-equations indicate what happens at one of the electrodes during electrolysis. In half-equations, electrons are shown as e⁻. In order to balance a half-equation, it is necessary to add or subtract a number of electrons equal to the total number of ions in the equation.

EXAMPLE 5.16

To balance this unbalanced equation for hydrogen ions forming hydrogen gas:

$$H^+ + e^- \rightarrow H_2$$

Answer

adjust the number of ions:

$$2H^+ + e^- \rightarrow H_2$$

and then make sure that each side of the equation has the same number of charges:

$$2H^+ + 2e^- \rightarrow H_2$$

QUESTIONS

22 Balance the following unbalanced equations:

(a) $O^{2-} \rightarrow O_2 + e^-$ (b) $Mg^{2+} \rightarrow Mg$ (c) $Br^- \rightarrow Br_2 + e^-$ (d) $Al^{3+} + e^- \rightarrow Al$

Mass and volume calculations

Knowing the amount of a substance produced at one electrode, makes it possible to calculate theoretically the amount of a substance formed at the other electrode. To do this, we first need to calculate the ratio of the electrons involved in the two electrode reactions.

We know that:

in g

$$\boxed{\text{moles} = \frac{\text{mass}}{M_r}}$$

in cm³

$$\boxed{\text{moles of gas} = \frac{\text{vol}}{24{,}000}}$$

EXAMPLE 5.17

Calculate the mass and volume of oxygen formed in the electrolysis of a copper sulfate solution, where 381 g of copper is deposited on the negative electrode?

Answer

Half-equation (at the cathode)

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Half-equation (at the anode)

$$4OH^- - 4e^- \longrightarrow 2H_2O + O_2$$

2 moles of electrons form 1 mole of solid copper from 1 mole of copper(II) ions, Cu^{2+}

4 moles of electrons form 1 mole of oxygen from 4 moles of hydroxide, OH^- ions.

mole ratio of Cu : O_2 from the electrolysis is 2 : 1

We know that 381 g of copper were formed

Mr = 63.5

381/63.5 = 6 moles

Thus, moles oxygen formed

= 3 moles

$Mr(O_2) = 16$

Mass of oxygen formed = 3 x 16

= 48g

volume of oxygen = 3 x 24

= 72 dm³

To extend to the calculation to predict actual yields that we might expect in any given electrolysis reaction we have to take into account two other factors: current flow and time.
Current = the rate of flow of charge
Time = duration of the electrolysis in seconds
The amount of product produced at each electrode will be proportional to current flow and time.

In these calculations:

- Q = quantity of current transferred in Coulomb.
- I = current flow (amperes, A)
- t = time (seconds, s)
- Q = I x t
- Faraday's Constant:
  Charge to produce 1 mole of an element from its ions = 96500 $Cmol^{-1}$

EXAMPLE 5.18

Calculate the amount of copper deposited at the cathode if a current of 0.4 Amps is passed for 45 minutes through a copper(II) sulfate solution?

Half-equation: $Cu^{2+} + 2^{e-} \rightarrow Cu$

Answer Q = I x t
= 0.4 x 45 x 60 = 1080 C
1080 / 95600 = 0.0112

Knowing that two moles of electrons are needed to form 1 mole of copper
0.0112 / 2 = 0.0056
mass of copper = 0.0056 x 64
= 0.3584 g

QUESTIONS

23 In the electrolysis of molten lead bromide, a current of 8 amps is allowed to flow through molten lead bromide for 4 hours. Calculate the amount of lead deposited at the cathode.

24 Calculate the moles of Mg produced when a current of 80 amps is passed through a magnesium chloride solution for 30 minutes.

25 In the electrolysis of molten sodium chloride 23g of sodium are deposited at the cathode. Calculate the mass and volume of chlorine obtained.

5.14 Acids and Bases

Acids are substances that turn blue litmus red, neutralise bases, and usually react with active metals such as zinc, releasing hydrogen. Hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and nitric acid (HNO_3) are examples of acids. There are many examples of **household acids**. These include vinegar, which contains the weak acid ethanoic acid (CH_3COOH), lemon juice, containing the weak acid citric acid, and dilute sulfuric acid (a strong acid) in car batteries.

All acids contain hydrogen. Acids can be classified as monobasic, dibasic or tribasic, depending on the number of hydrogen atoms per molecule that are removable by reaction with a base.

For example, hydrochloric acid (HCl) is a **monobasic** acid, while sulfuric acid (H_2SO_4) is **dibasic**.

Figure 5.13
Foodstuffs containing acids

5.15 Bases

Bases are substances that turn red litmus blue, and neutralise acids. Sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3) and ammonia (NH_3) are examples of bases.

Figure 5.14
Common acids

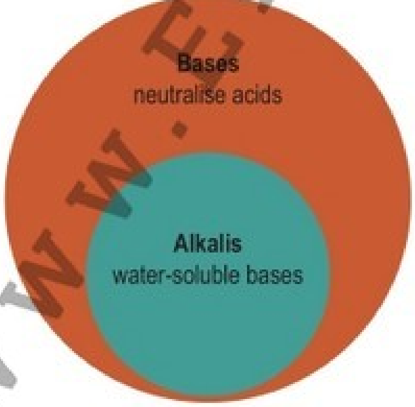


Figure 5.15

Milk of magnesia can be used as an antacid

A base that dissolves in water is called an **alkali**. Sodium hydroxide is an alkali; a solution of sodium hydroxide is said to be alkaline.

Household bases include ammonia (used for cleaning), sodium hydroxide (used in oven cleaners), and magnesium hydroxide (used as a laxative and antacid in milk of magnesia).

5.16 Neutralisation

When an acid reacts with a base, a salt is formed. For example, when hydrochloric acid reacts with sodium hydroxide,

$$HCl + NaOH \rightarrow NaCl + H_2O$$

the salt sodium chloride is formed. Hydrochloric acid when neutralised by a base forms salts called chlorides.

Figure 5.16
Preparation of the salt sodium chloride.

When sulfuric acid reacts with ammonia,

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$$

the salt ammonium sulfate is formed. Sulfuric acid when neutralised by a base forms salts called sulfates. **Neutralisation** of an acid by a base has many **everyday applications**. Indigestion is caused by too much acid in the stomach. The discomfort can be cured by taking stomach powders such as magnesium hydroxide or sodium hydrogencarbonate, which are bases. The excess hydrochloric acid is neutralised:

$$2HCl + Mg(OH)_2 \rightarrow MgCl_2 + 2H_2O$$

$$HCl + NaHCO_3 \rightarrow NaCl + H_2O + CO_2$$

Sodium hydrogencarbonate can also be used to treat bee stings, which are acidic.

Lime (calcium hydroxide) is a base used in agriculture to neutralise acidic soil.

Stomach powders are bases

Lime neutralises acid soil

QUESTIONS

26 State one property of an acid.
27 State one property of a base.
28 What is an alkali? Give an example.
29 What is a monobasic acid? Give an example.
30 What is a dibasic acid? Give an example.
31 What is a salt? Give an example.
32 Give two examples of household acids, stating what each is used for.
33 Give two examples of household bases, stating what each is used for.
34 What is meant by neutralisation?
35 Give two everyday examples of neutralisation.

5.17 The pH scale

The pH scale goes from 0 to 14. A value of 0 represents very high [H_3O^+], such as would be present in a fairly concentrated (1 M) solution of a strong acid; a value of 14 represents very high [OH^-]. The [H_3O^+] decreases as the pH value increases, and the [OH^-] increases. A neutral solution will have a pH of 7.

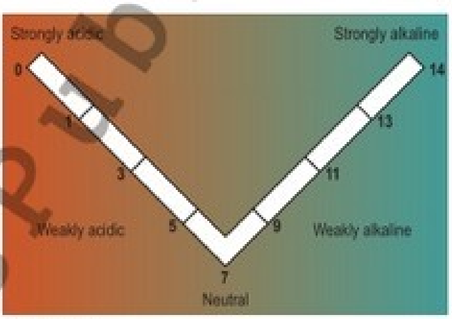
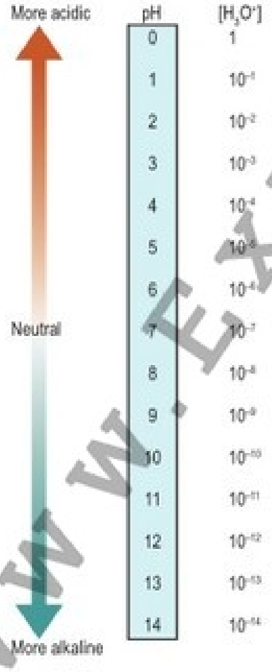


Figure 5.17
The pH scale



pH	[H_3O^+]
0	1
1	10^{-1}
2	10^{-2}
3	10^{-3}
4	10^{-4}
5	10^{-5}
6	10^{-6}
7	10^{-7}
8	10^{-8}
9	10^{-9}
10	10^{-10}
11	10^{-11}
12	10^{-12}
13	10^{-13}
14	10^{-14}

Figure 5.18
The relationship between pH and hydrogen ion concentration

Limitations of the pH scale

- The pH scale is not useful outside the 0 to 14 range.
- This is because in more concentrated solutions of strong acids and bases, the acid or base does not dissociate fully in solution, making a pH calculation difficult.
- The pH scale is limited to aqueous solutions.

5.18 Measuring pH

Universal indicator solution, or universal indicator paper, can be used to find the pH of a solution. Universal indicator is a mixture of indicators that changes colour as the pH is changed. The pH of a solution is measured after adding universal indicator by comparing the colour of the solution with a colour chart.

The pH of a solution can also be measured using a **pH meter**. This instrument gives a numerical reading for the pH directly (Figure 5.19). A pH sensor, connected to a data logger, can also be used to get a numerical reading for the pH of a solution directly. In this case the pH value is displayed on a calculator or computer.

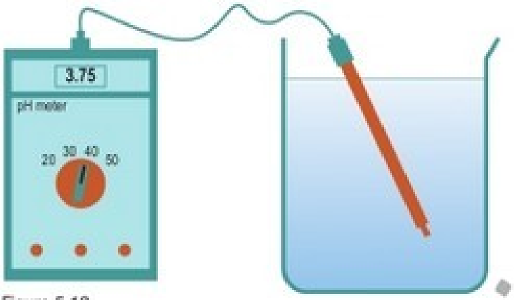


Figure 5.19

5.19 Calculation of the pH of Solutions of Strong Acids

Figure 5.20

The pH of a strong acid may be readily calculated, since a strong acid dissociates fully into its ions in dilute aqueous solution. For example, a 0.2 M HCl solution contains 0.2 mol l^{-1} of H_3O^+ ions and 0.2 mol l^{-1} of Cl^- ions.

EXAMPLE 5.19

Find the pH of a 0.2 M solution of hydrochloric acid.

Answer

$$\begin{aligned} pH &= -\log_{10} [H_3O^+] \\ &= -\log_{10} (0.2) \\ &= 0.699 \end{aligned}$$

EXAMPLE 5.20

Find the pH of a solution containing 6.3 g of nitric acid in 250 cm^3 of solution.

Answer The nitric acid solution contains 6.3 g of nitric acid in 250 cm^3

$$= \frac{6.3 \times 1000}{250} \text{ g l}^{-1}$$

$= 25.2$ g l^{-1}

The molar mass of HNO_3 is 63 g mol^{-1}

Therefore $[HNO_3] = 25.2 / 63$ mol l^{-1}

$= 0.4$ mol l^{-1}

Since HNO_3 is a strong acid, $[H_3O^+] = [HNO_3] = 0.4$ mol l^{-1}

$pH = -\log_{10} [H_3O^+]$

$= -\log_{10} (0.4)$

$= 0.3979$

QUESTIONS

36 Find the pH of each of the following solutions:
(a) 0.001 M HCl (b) 0.02 M HNO3 (c) 0.00004 M HCl (d) 1 M HCl.

37 What is the pH of a solution containing 3.65 g of HCl in 1 litre of solution?

38 What is the pH of a solution containing 3.15 g of HNO_3 in 500 cm^3 of solution?

5.20 Calculation of the pH of Solutions of Strong Bases

Strong bases also dissociate fully in dilute aqueous solution. For example, a 0.1 M NaOH solution contains 0.1 mol l^{-1} of Na^+ ions and 0.1 mol l^{-1} of OH^- ions.

pOH

In calculating the pH of a strong base, the idea of pOH is used. pOH is defined as $-\log_{10} [OH^-]$.

Since $[H_3O^+] [OH^-] = 10^{-14}$
$\log_{10} [H_3O^+] + \log_{10} [OH^-] = -14$.
Therefore, $-\log_{10} [H_3O^+] - \log_{10} [OH^-] = +14$
Therefore, $pH + pOH = 14$,
or $pH = 14 - pOH$.

In the examples that follow, the pOH value is calculated first, and then the pH value is obtained by subtracting the pOH from 14.

Figure 5.21

EXAMPLE 5.21

Find the pH of 0.1 M NaOH solution.

Answer [NaOH] = 0.1 mol l^{-1}

$[OH^-] = [NaOH]$

$pOH = -\log_{10}[OH^-]$

$= -\log_{10}(0.1)$

$= 1.$

$pH = 14 - pOH$

$= 14 - 1$

$= 13.$

EXAMPLE 5.22

Find the pH of a solution containing 4 g of NaOH in 500 cm^3 of solution.

Answer The NaOH solution contains 4 g of NaOH in 500 cm^3

$$= \frac{4 \times 1000}{500} \text{ g } l^{-1}$$

$= 8$ g l^{-1}

The molar mass of NaOH is 40 g mol^{-1}

Therefore [NaOH] = 8 / 40 mol l^{-1}

$= 0.2$ mol l^{-1}

Since NaOH is a strong base, $[OH^-] = [NaOH] = 0.2$ mol l^{-1}

$pOH = -\log_{10}[OH^-]$

$= -\log_{10}(0.2)$

$= 0.6990$

$pH = 14 - pOH$

$= 13.3010$

QUESTIONS

39 Find the pH of each of the following solutions:

(a) 0.001 M NaOH (b) 0.05 M KOH (c) 0.06 M KOH (d) 0.003 M NaOH

40 What is the pH of a solution containing 0.8 g of NaOH per litre?

41 Find the pH of a solution containing 1.6 g of NaOH in 250 cm^3 of solution.

5.21 Solutions of Weak Acids

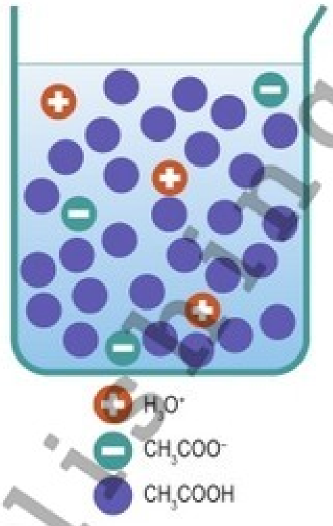


Figure 5.22
A weak acid dissociates in water to a relatively small extent

Weak acids, when dissolved in water, do not transfer all unlike strong acids, for which total proton transfer occurs. A weak acid such as ethanoic acid, CH_3COOH, will react as follows:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

The CH_3COO^-, when formed, will react with H_3O^+, forming CH_3COOH and H_2O. Eventually a state of equilibrium is reached at which as much CH_3COOH is being formed by the reaction of CH_3COO^- with H_3O^+, as is breaking down to form CH_3COO^- and H_3O^+.

At equilibrium, $K_c = [CH_3COO^-]\,[H_3O^+]$ / $[CH_3COOH]\,[H_2O]$. The concentration of H_2O is effectively constant, since it is present in a large excess (approximately 55 mol l^{-1}), and is omitted, giving a new constant K_a, where $K_a = [CH_3COO^-]\,[H_3O^+]$ / $[CH_3COOH]$.

K_a is called the **dissociation constant** of the acid. (The term **ionisation constant** is also used for K_a.) The K_a values for a number of weak acids are given in Table 19.3. (The units of K_a are mol l^{-1}.)

Acid	Formula	K_a value
Ethanoic acid	CH_3COOH	1.8×10^{-5}
Methanoic acid	$HCOOH$	1.6×10^{-4}
Hydrofluoric acid	HF	5.6×10^{-4}
Propanoic acid	CH_3CH_2COOH	1.3×10^{-5}
Butanoic acid	$CH_3CH_2CH_2COOH$	1.5×10^{-5}
Hydrogen sulfide	H_2S	8.9×10^{-8}
Nitrous acid	HNO_2	4.7×10^{-4}

Table 5.3
Common reducing agents

These values may be contrasted with much larger values for strong acids such as HCl, HNO_3 and H_2SO_4; for example, nitric acid has a K_a value of 40. The stronger the acid, the greater the value of K_a. Hydrofluoric acid is the strongest of the acids in the table, while hydrogen sulfide is the weakest.

EXAMPLE 5.23

Write an expression for the dissociation constant, K_a, for each of the following weak acids:

(a) HF (b) HCOOH

Answer (a) HF dissociates in water as follows:

$$HF + H_2O \rightleftharpoons F^- + H_3O^+$$

$$K_a = \frac{[F^-]\,[H_3O^+]}{[HF]}$$

(b) HCOOH dissociates in water as follows:

$$HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$$

$$K_a = \frac{[HCOO^-]\,[H_3O^+]}{[HCOOH]}$$

EXAMPLE 5.24

A weak acid, HX, is 2.1% dissociated in a 0.1 M aqueous solution.

Find the value of the acid dissociation constant, K_a.

Answer The solution can be made up by adding 0.1 moles of the pure acid to water, and making up the solution to 1 litre with water. The reaction is

$$HX + H_2O \rightleftharpoons X^- + H_3O^+$$

Ignoring the concentration of water, which is present in excess, the initial concentrations of each of the other species are

[HX]	[X⁻]	[H₃O⁺]
0.1	0	0

At equilibrium, 2.1% of the acid has dissociated, and so the equilibrium concentrations are

[HX]	[X⁻]	[H₃O⁺]
0.1 – 0.0021	0.0021	0.0021
= 0.0979	0.0021	0.0021

Substituting these values into the equilibrium constant expression,

$$K_a = [X^-]\,[H_3O^+] / [HX] = (0.0021)^2 / 0.0979 = 4.5 \times 10^{-5}$$

QUESTIONS

42 Write an expression for the dissociation constant, K_a, for each of the following weak acids: HCN, HNO_2, H_2S, CH_3CH_2COOH.

43 A weak acid, HX, is 3.5% dissociated in a 0.1 M aqueous solution.
Find the value of the acid dissociation constant, K_a.

44 A weak acid, HX, is 2.5% dissociated in a 0.2 M aqueous solution.
Find the value of the acid dissociation constant, K_a.

5.22 Calculation of the pH of Solutions of Weak Acids

The K_a value for a weak acid can be used to work out the pH of a solution of the acid, provided that the concentration of the solution is known. In calculations of this kind, a simplifying assumption is made that the concentration of the acid does not change. This approximation is justified because the extent of dissociation of a weak acid is small.

EXAMPLE 5.25

Find the pH of a 0.1 M solution of CH_3COOH, given that the K_a value for this acid is 1.8×10^{-5}.

Answer A 0.1 M solution of CH_3COOH can be made up by adding 0.1 moles of the pure acid to water, and making up the solution to 1 litre with water.

The reaction is

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

Ignoring the concentration of water, which is present in excess, the initial concentrations of each of the other species are

$[CH_3COOH]$	$[CH_3COO^-]$	$[H_3O^+]$
0.1	0	0

At equilibrium, a certain amount (say x moles) of the acid has dissociated, and so the equilibrium concentrations are

$[CH_3COOH]$	$[CH_3COO^-]$	$[H_3O^+]$
$0.1 - x$	x	x

Substituting these values into the dissociation constant expression,

$$K_a = [CH_3COO^-]\,[H_3O^+]\,/\,[CH_3COOH] = 1.8 \times 10^{-5}$$
$$= (x^2)\,/\,(0.1 - x)$$

Since x is very small compared to 0.1, $(0.1 - x)$ can be taken to be equal to 0.1, and so

$$K_a = [CH_3COO^-]\,[H_3O^+]\,/\,[CH_3COOH] = 1.8 \times 10^{-5}$$
$$= (x^2)\,/\,(0.1)$$

Therefore, $x^2 = 0.1 \times 1.8 \times 10^{-5} = 0.0000018$

Therefore, $x = \sqrt{(0.0000018)} = 0.001342$

$[H_3O^+] = x = 0.001342$

$pH = -\log_{10} [H_3O^+]$

$= -\log_{10} (0.001342)$

$= 2.8723$

EXAMPLE 5.26

Find the pH of a solution containing 6 g of ethanoic acid in 100 cm^3 of solution given that the K_a value for this acid is 1.8×10^{-5}.

Answer The ethanoic acid solution contains 6 g of ethanoic acid in 100 cm^3

$= \frac{6 \times 1000}{100}\ g\ l^{-1}$

$= 60\ g\ l^{-1}$

The molar mass of CH_3COOH is 60 g mol^{-1}

Therefore $[CH_3COOH] = 60 / 60\ mol\ l^{-1}$

$= 1\ mol\ l^{-1}$

The reaction is

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

Ignoring the concentration of water, which is present in excess, the initial concentrations of each of the other species are

$[CH_3COOH]$	$[CH_3COO^-]$	$[H_3O^+]$
1	0	0

At equilibrium, a certain amount (say x moles) of the acid has dissociated, and so the equilibrium concentrations are

$[CH_3COOH]$	$[CH_3COO^-]$	$[H_3O^+]$
1 – x	x	x

Substituting these values into the dissociation constant expression,

$K_a = [CH_3COO^-]\ [H_3O^+] / [CH_3COOH] = 1.8 \times 10^{-5}$

$= (x^2) / (1 - x)$

Since x is very small compared to 1, (1 – x) can be taken to be equal to 1.

$K_a = [CH_3COO^-]\ [H_3O^+] / [CH_3COOH] = 1.8 \times 10^{-5}$

$= (x^2) / (1)$

Therefore, $x^2 = 1.8 \times 10^{-5} = 0.000018$

Therefore, $x = \sqrt{(0.000018)} = 0.004243$

$[H_3O^+] = x = 0.004243$

$pH = -\log_{10} [H_3O^+]$

$= -\log_{10} (0.004243)$

$= 2.3723$

5.23 Solutions of Weak Bases

Weak bases, like weak acids, only dissociate to a slight extent in water. Ammonia, when placed in water, reacts as follows:

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

The reverse reaction occurs to a significant extent, and eventually a state of equilibrium is reached at which the rate of breakdown of NH_4^+ equals its rate of formation. At equilibrium,
$K_c = [NH_4^+] [OH^-] / [NH_3] [H_2O]$
The concentration of H_2O is effectively constant, and is omitted, giving a new constant K_b, where
$K_b = [NH_4^+] [OH^-] / [NH_3]$.
K_b is called the **dissociation constant** of the base. (The term **ionisation constant** is also used for K_b.)

The K_b values for a number of weak bases are given in Table 19.4. (The units of K_b are mol l^{-1}.)

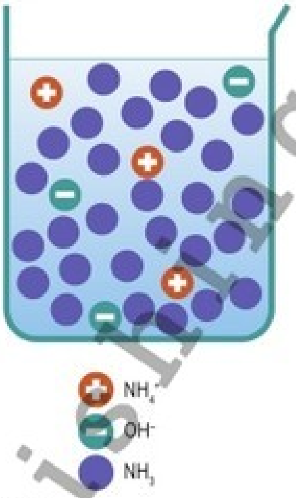


Figure 5.23
A weak base dissociates in water to a relatively small extent

Base	Formula	K_b value
Ammonia	NH_3	1.8×10^{-5}
Methylamine	CH_3NH_2	4.4×10^{-4}
Ethylamine	$C_2H_5NH_2$	5.6×10^{-4}
Phenylamine	$C_6H_5NH_2$	3.8×10^{-10}
Beryllium hydroxide	$Be(OH)_2$	5.0×10^{-11}

Table 5.4

The stronger the base, the greater the value of K_b. The strongest of the bases listed in the table is ethylamine, while beryllium hydroxide is the weakest.

EXAMPLE 5.27

Write an expression for the dissociation constant, K_b, for the following weak bases:

(a) CH_3NH_2 (b) $Be(OH)_2$

Answer (a) CH_3NH_2 reacts with water as follows:

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

$$K_b = \frac{[CH_3NH_3^+] [OH^-]}{[CH_3NH_2]}$$

(b) $Be(OH)_2$ dissociates in water as follows:

$$Be(OH)_2 \rightleftharpoons Be(OH)^+ + OH^-$$

$$K_b = \frac{[Be(OH)^+] [OH^-]}{[Be(OH)_2]}$$

QUESTIONS

45 Write an expression for the dissociation constant, K_b, for each of the following weak bases: $C_2H_5NH_2$, $C_6H_5NH_2$

46 A weak base, XOH, is 2.1% dissociated in a 0.1 M aqueous solution. Find the value of the dissociation constant, K_b.

5.24 Calculation of the pH of Solutions of Weak Bases

The K_b value for a weak base can be used to work out the pH of a solution of the base, provided that the concentration of the solution is known. As in the calculation of pH of strong bases, the pOH is calculated first.

In calculations of this kind, a simplifying assumption is made that the concentration of the base does not change. This approximation is justified because the extent of dissociation of a weak base is small.

EXAMPLE 5.28

Find the pH of a 0.01 M solution of ammonia, given that the K_b value for this base is 1.8×10^{-5}.

Answer The solution is made by making up 0.01 moles of ammonia to 1 litre with water. The reaction of ammonia with water is as follows:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Ignoring the concentration of water, which is present in excess, the initial concentrations of each of the other species are

$[NH_3]$	$[NH_4^+]$	$[OH^-]$
0.01	0	0

At equilibrium, a certain amount (say x moles) of the base has dissociated, and so the equilibrium concentrations are

$[NH_3]$	$[NH_4^+]$	$[OH^-]$
$0.01 - x$	x	x

Substituting these values into the dissociation constant expression,

$$K_b = [NH_4^+]\,[OH^-] / [NH_3] = 1.8 \times 10^{-5}$$
$$= (x^2) / (0.01 - x)$$

Since x is very small compared to 0.01, $(0.01 - x)$ can be taken to be equal to 0.01. Therefore,

$$K_b = [NH_4^+]\,[OH^-] / [NH_3] = 1.8 \times 10^{-5}$$
$$= (x^2) / (0.01)$$

Therefore, $x^2 = 0.01 \times 1.8 \times 10^{-5} = 0.00000018$

Therefore, $x = \sqrt{(0.00000018)} = 0.0004243$

$[OH^-] = x = 0.0004243$

$pOH = -\log_{10}[OH^-]$
$= -\log_{10}(0.0004243)$
$= 3.3723$

$pH = 14 - pOH$
$= 14 - 3.3723$
$= 10.6277$

EXAMPLE 5.29

Find the pH of a solution containing 1.7 g of ammonia in 500 cm^3 of solution, given that the K_b value for this base is 1.8×10^{-5}.

Answer The ammonia solution contains 1.7 g of ammonia in 500 cm^3.

$$= \frac{1.7 \times 1000}{500}\ g\ l^{-1}$$

$$= 3.4\ g\ l^{-1}$$

The molar mass of NH_3 is 17 g mol^{-1}
Therefore $[NH_3] = 3.4 / 17\ mol\ l^{-1}$
$= 0.2\ mol\ l^{-1}$

The reaction is

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Ignoring the concentration of water, which is present in excess, the initial concentrations of each of the other species are

$[NH_3]$	$[NH_4^+]$	$[OH^-]$
0.2	0	0

At equilibrium, a certain amount (say x moles) of the base has dissociated, and so the equilibrium concentrations are

$[NH_3]$	$[NH_4^+]$	$[OH^-]$
0.2 – x	x	x

Substituting these values into the dissociation constant expression,

$$K_b = [NH_4^+][OH^-] / [NH_3] = 1.8 \times 10^{-5}$$
$$= (x^2) / (0.2 - x)$$

Since x is very small compared to 0.2, (0.2 – x) can be taken to be equal to 0.2. Therefore,

$$K_b = [NH_4^+][OH^-] / [NH_3] = 1.8 \times 10^{-5}$$
$$= (x^2) / (0.2)$$

Therefore, $x^2 = 0.2 \times 1.8 \times 10^{-5} = 0.0000036$

Therefore, $x = \sqrt{(0.0000036)} = 0.001897$

$[OH^-] = x = 0.001897$

$$pOH = -\log_{10}[OH^-]$$
$$= -\log_{10}(0.001897)$$
$$= 2.7219$$

$$pH = 14 - pOH$$
$$= 14 - 2.7219$$
$$= 11.2781$$

5.25 Hydrolysis reactions

Salts placed in water often react with the water to produce either H_3O^+ or OH^-. This type of reaction is called a hydrolysis reaction. The pH of the aqueous salt solution will depend on the particular acid and base that are reacted. Various types of result are possible based on the relative strengths of the acid and base in the salt.

We will consider four types of combinations.

Salts from strong acids and strong bases do not hydrolyse. The cations and anions in table 5 do not react in water.

Cations	**Anions**
Li^+ lithium ion	Cl^- chloride ion
Na^+ sodium ion	Br^- bromide ion
K^+ potassium ion	I^- iodide ion
Rb^+ rubidium ion	NO_3^- nitrate ion
Sr^{2+} strontium ion	ClO_4^- perchlorate ion
Ba^{2+} barium ion	SO_4^{2-} sulfate ion

Table 5.5

QUESTIONS

47 Can you predict whether each of the following salt solutions will be acidic, basic or neutral?

(a) sodium chloride

(b) ammonium chloride

(c) sodium acetate

(d) ammonium acetate

48 Can you predict what the pH of each solution might be?

These ions are termed spectator ions, meaning that a soluble compound of two of these e.g. sodium chloride (NaCl) will have no effect on the pH of water.

Salts from strong bases and weak acids hydrolyse, giving the solution a pH > 7.00. In the reaction with water, the anion from the weak acid accepts the proton from the water. The cation from the strong base is a spectator ion in the reaction. The production of the OH^- ion makes the solution basic.

Salts from weak bases and strong acids hydrolyse, giving the solution a pH < 7.00. Here the anion becomes the spectator ion and the weak base donate a proton to the water. The production of the hydronium ion H_3O^+ makes the solution acidic.

Salts from a weak base and a weak acid hydrolyse but the resulting pH of the solution will depend on relative strengths of the acid and base and which ion more readily reacts with water.

EXPERIMENT 5.2

Solute	Predicted pH
A. sodium chloride	0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
B. ammonium chloride	0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
C. sodium acetate	0 1 2 3 4 5 6 7 8 9 10 11 12 13 14
D. ammonium acetate	0 1 2 3 4 5 6 7 8 9 10 11 12 13 14

Determining the pH of four salt solutions

Chemicals needed ☒

100 mL of sodium chloride
100 mL of ammonium chloride
100 mL of sodium acetate
100 mL of ammonium acetate

Equipment needed

4 test tubes
1 test tube rack
litmus paper or pH indicator

Procedure

1. Pour about 100 mL of 0.1 M of each solution into a test tube.
2. Use either a clean strip of litmus paper or a pH – rinse thoroughly between each measurement – to find the pH of each solution.
3. Record your measurements in a table and compare the results to your predictions.

Solute	Recorded pH
A. sodium chloride	
B. ammonium chloride	
C. sodium acetate	
D. ammonium acetate	

QUESTIONS

49 (a) Explain why solutions of ammonium chloride are acidic.

(b) Complete the table

SALT	PARENT ACID	PARENT BASE	TYPE OF SOLUTION acidic, basic, neutral
NH_4Cl	HCl	NH_4OH	Acidic
MgF_2			
$ZnCl_2$			
KCl			
$NaNO_3$			
Na_2SO_4			

5.26 Exothermic and Endothermic Reactions

In the course of a chemical reaction, bonds between atoms are broken and new bonds are made as the atoms rearrange themselves to form new substances. Energy is needed to break bonds, and is given out when new bonds form. This means that the reaction is usually accompanied by a change in energy, mainly in the form of heat.

If the amount of heat produced in forming bonds is greater than the amount needed to break bonds, heat is given out and the temperature of the reaction mixture increases. Such a reaction is said to be **exothermic**, and most chemical reactions are of this type. For example, the reaction between magnesium and hydrochloric acid is exothermic.

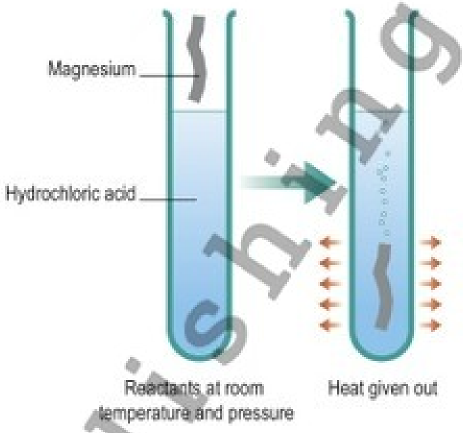


Figure 5.24
The reaction between magnesium and hydrochloric acid is exothermic

A reaction in which heat is given out is exothermic.

If the amount of heat produced in forming bonds is less than the amount needed to break bonds, heat is taken in from the surroundings and the temperature of the reaction mixture decreases. Such a reaction is said to be **endothermic**. A smaller number of chemical reactions are of this type, one of which is the reaction of sodium hydrogencarbonate with citric acid.

A reaction in which heat is taken in is endothermic.

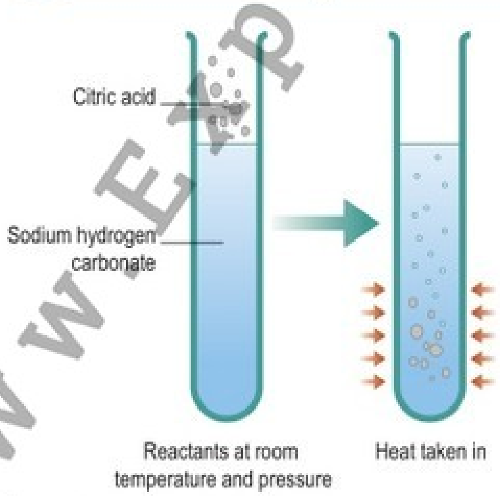


Figure 5.25
The reaction between sodium hydrogencarbonate and citric acid is endothermic

One of the most important properties of hydrocarbons in general, and the alkanes in particular, is that they burn in air or oxygen. When sufficient oxygen is present, complete combustion occurs and carbon dioxide and water vapour are produced. Heat is produced in combustion reactions, and so they are classified as exothermic reactions. The large amount of heat produced when alkanes burn makes them particularly suitable as fuels. Methane, the first member of the alkanes, is the principal component of natural gas. Propane and butane are used as bottled gas. Petrol is made up of a large number of different compounds, mostly alkanes.

DEMONSTRATION

Demonstration of (a) an exothermic reaction and (b) an endothermic reaction

Chemicals needed
Magnesium (small pieces)
3 M hydrochloric acid
Ammonium nitrate crystals
Water

Equipment needed
Thermometer
Heat-resistant test tubes
Test tube holder
Stirring rod

Procedure

NB: Wear your safety glasses.

(a) Exothermic reaction

1. Place about 5 cm^3 of hydrochloric acid in a test tube and record its temperature.
2. Drop in a few pieces of magnesium.
3. When the reaction has stopped take the temperature again.

Note that the temperature of the mixture has risen because the reaction of magnesium metal with hydrochloric acid is an exothermic reaction.

(b) Endothermic reaction

1. Place about 5 cm^3 of water in a test tube and record its temperature.
2. Add a few crystals of ammonium nitrate.
3. Stir gently until the crystals have dissolved.
4. Take the temperature again.

Note that the temperature of the mixture has fallen because dissolving ammonium nitrate in water is an endothermic process. This reaction is made use of in cold packs for treating minor injuries. The pack consists of a thin plastic bag containing water, inside a stronger bag containing ammonium nitrate. When the pack is shaken strongly, the inner bag breaks allowing the water and ammonium nitrate to mix. The resulting endothermic reaction causes the temperature to fall sharply.

QUESTIONS

50 Explain what is meant by the term exothermic reaction.

51 Explain what is meant by the term endothermic reaction.

52 Name the combustion products when hydrocarbons are completely burned in air or oxygen.

5.27 Changes of State

Melting

In solids, particles are in fixed positions, free only to vibrate. When the solid melts, energy must be supplied to enable the particles to break free and move around randomly. Melting is thus an endothermic process:

$$X_{(s)} + \text{energy} \rightarrow X_{(l)}$$

Evaporation

If energy is supplied to a liquid, the particles move more quickly and begin to escape from the main body of liquid, becoming a gas. In other words evaporation occurs. This is also an endothermic process.

$X_{(l)}$ + energy → $X_{(g)}$

Condensation

When a gas is cooled, the particles lose energy and slow down. If this continues, the attractive forces between the particles become more effective and the gas condenses into a liquid. Since the system is losing energy the process is exothermic.

$X_{(g)}$ – energy → $X_{(l)}$

Freezing

When a liquid cools it freezes to form a solid. This is also an exothermic process as the system is losing energy.

$X_{(l)}$ – energy → $X_{(s)}$

5.28 Heat of Reaction

The heat of reaction, ΔH, of a chemical reaction is the heat in kilojoules released or absorbed when the number of moles of reactants indicated in the balanced equation describing the reaction react completely.

The heat change in a particular reaction depends on what amounts of reactants are involved, and this is indicated by the balanced equation. If one mole of hydrogen gas burns in oxygen to form water,

$H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(g)}$

242 kilojoules of heat are produced. As this is an exothermic reaction, the heat of reaction is negative because heat energy has been lost from the chemical reactants to the surroundings, i.e. ΔH = –242 kJ mol^{-1}.

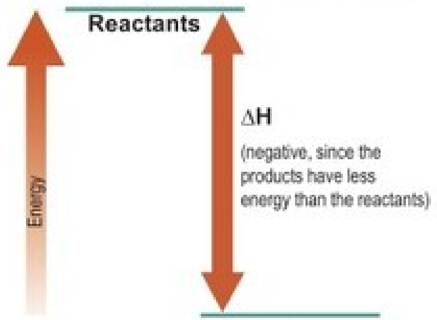


Figure 5.26
An exothermic reaction

If two moles of hydrogen gas burn in oxygen to form water,

$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$

484 kilojoules of heat are produced.
Since there is twice as much hydrogen being burned, twice as much heat is produced. This time ΔH = –484 kJ mol^{-1}. The heat change is doubled because the quantities as indicated by the balanced equation are doubled.

In an endothermic reaction, the surroundings are cooled because the reactants gain energy from the surroundings. Because of this, the heat of reaction is positive for endothermic reactions. For example, to break down one mole of water in the liquid state into hydrogen and oxygen gas,

$$H_2O_{(l)} \rightarrow H_{2(g)} + \tfrac{1}{2}O_{2(g)}$$

286 kilojoules are required i.e.
$\Delta H = +286\ kJ\ mol^{-1}$.

The measurement of the heat change of a reaction is carried out with known amounts of reactants in a suitable insulated container, called a calorimeter, for example an expanded polystyrene cup. The temperature change due to the reaction is measured and the value obtained used to calculate the heat of reaction.

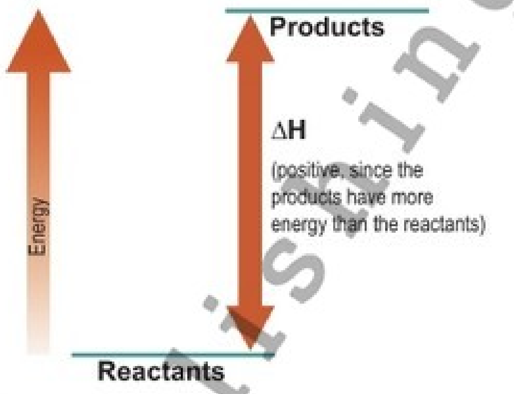


Figure 5.27
An endothermic reaction

EXAMPLE 5.30

When 100 cm³ of 1 M nitric acid solution, HNO_3, react with 100 cm³ of 1 M potassium hydroxide solution, KOH, the temperature rises by 6.7 kelvins. Calculate the heat of reaction described by the equation

$$HNO_{3(aq)} + KOH_{(aq)} \rightarrow KNO_{3(aq)} + H_2O_{(l)}$$

Answer The amount of heat produced in the reaction can be calculated from the formula Heat change = $mc\,\Delta T$

where m is the mass in kg of liquid heated by the reaction, c is the specific heat capacity of the liquid, and ΔT is the rise in temperature. As the reactants and products are very dilute solutions, it is assumed that their densities and specific heat capacities are the same as those of water. Thus 100 cm³ of each reacting solution can be taken to have a mass of 0.1 kilograms. The specific heat capacity of water is $4.2\ kJ\ kg^{-1}\ K^{-1}$.

Heat change = $mc\,\Delta T$
$= 0.2 \times 4.2 \times 6.7$
$= 5.628$ kJ.

The number of moles of HNO_3 in 100 cm³ of 1 M nitric acid solution is calculated as follows:

No. of moles = volume in litres × molarity
$= 0.1 \times 1$
$= 0.1$ moles.

Since 0.1 moles of HNO_3 produce 5.628 kJ of heat when reacted with KOH, one mole, the quantity indicated by the balanced equation, produces $56.28\ kJ\ mol^{-1}$. In other words the heat of reaction $\Delta H = -56.28\ kJ\ mol^{-1}$, the minus sign indicating that the reaction is exothermic, with heat being produced.

EXPERIMENT 5.3

Determination of the heat of reaction of hydrochloric acid with sodium hydroxide

In this experiment a definite volume of a standard hydrochloric acid solution is mixed with an equal volume of sodium hydroxide solution of the same concentration in an insulated container. The rise in temperature of the mixture is then measured and from this the heat of reaction is calculated. The equation for the reaction is

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

Chemicals needed	Equipment needed
1 M hydrochloric acid	Accurate thermometers
1 M sodium hydroxide	Polystyrene cups with lids
	Graduated cylinders

Procedure

NB: Wear your safety glasses.

1 Place 50 cm^3 of the 1 M hydrochloric acid solution into one of the polystyrene cups.

2 Place 50 cm^3 of the 1 M sodium hydroxide solution into the second polystyrene cup.

3 Measure the temperature of each solution. The average of the two temperatures is taken as the initial temperature.

4 Quickly add the base to the acid, stirring with a thermometer. The lid is used to reduce heat loss.

5 Record the maximum temperature reached.

6 The results may be summarised as follows:

Initial temperature of HCl solution = °C
Initial temperature of NaOH solution = °C
Average initial temperature = °C
Highest temperature reached = °C
Rise in temperature = °C
= K
Number of moles of HCl used =

7 Calculate the heat of reaction, i.e. the heat liberated when one mole of acid reacts fully.

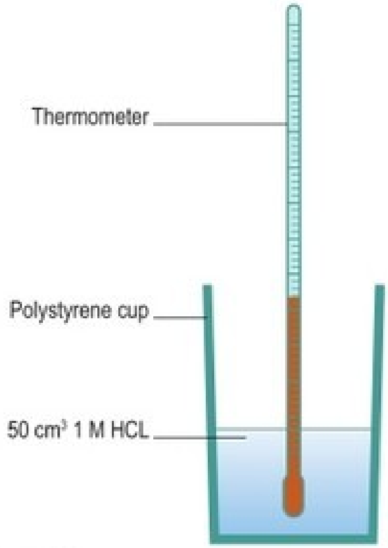


Figure 5.28

QUESTIONS

53 Define heat of reaction.

54 What is the sign of ΔH for an endothermic reaction?

55 An experiment was carried out to measure the heat of reaction of hydrochloric acid and sodium hydroxide, according to the equation $HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$.

Using a polystyrene cup as a calorimeter, 200 cm^3 of each of the reactant 1 M solutions were mixed and the rise in temperature was found to be 7.1 kelvins.

(a) Why was a polystyrene cup used as a calorimeter?

(b) Calculate the heat of reaction.

Rates of Reaction

MODULE 6

Learning objectives

- To observe through experiment the impact of temperature, concentration and pressure on the rate of chemical reactions 10.3.2.1
- To explain how different factors effect the rate of a chemical reaction 10.3.2.2
- To make calculations relating to the effect of concentration and temperature on the rate of chemical reactions 10.3.2.3
- To explain how catalysts and inhibitors work 10.3.2.4
- To differentiate between homogenous and heterogeneous catalysis 10.3.2.5
- To identify areas of the development of catalytic chemistry in Kazakhstan 10.3.2.6

6.1 Rates of Reaction

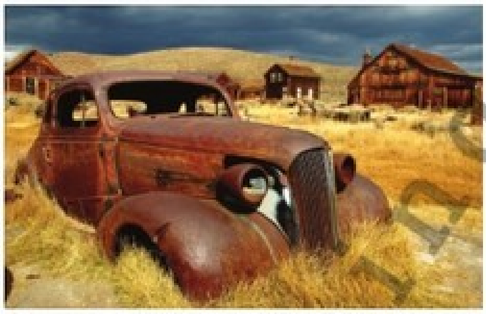


Figure 6.1
Rusting is a slow reaction

Different chemical reactions occur at different rates. The rusting of iron is a slow reaction, whereas the burning of a piece of magnesium in oxygen is a fast reaction. The rate of a chemical reaction is a measure of how quickly the reaction proceeds. It may be defined as the change in concentration in unit time of any one reactant or product, i.e.

$$\text{Rate} = \frac{\text{Change in concentration of reactant or product}}{\text{Time taken}}$$

For example, in the decomposition of hydrogen peroxide into water and oxygen,

$$H_2O_{2(aq)} \rightarrow H_2O_{(l)} + \tfrac{1}{2}O_{2(g)}$$

the reaction rate can be calculated by measuring the change in concentration of hydrogen peroxide. If its initial concentration is 1.0 mol l^{-1}, and 10 seconds later this has decreased to 0.4 mol l^{-1}, then the reaction rate is

$$(1.0 - 0.4)/10 = 0.6/10 = 0.06 \text{ mol } l^{-1} s^{-1}.$$

However, this is merely an average rate. Reaction rate depends on the concentration of the reactants, and since reactant concentration drops as the reaction proceeds, the reaction rate itself also drops as the reaction proceeds.

The rate of reaction is the change in concentration in unit time of any one reactant or product.

Reaction rate graphs

- Both axes should be labelled.
- Time is on the horizontal axis (x-axis), which is labelled: Time (minutes). (Seconds may be more appropriate units than minutes in some situations.)
- Volume of gas produced is on the vertical axis (y-axis), which is labelled: Volume (cm^3).
- Suitable graduations should be marked out in regular steps on each axis.
- The points should be marked accurately with a cross or a dot.
- The point (0, 0) is the first on every rates graph of this type, since the volume of gas collected at zero time is 0 cm^3.
- A smooth curve, or a line of best fit, is drawn through the points, beginning at (0, 0).
- If the graph is a curve, it is steepest at the start, when concentrations of reactants are at their greatest, and the rate of reaction is fastest.
- The rate decreases as the reactants are used up, so the slope is less steep.
- The reaction is finished when there are several identical readings, and the curve becomes horizontal.

EXAMPLE 6.1

In an experiment to study reaction rates, some manganese(IV) oxide was added to 25 cm^3 of hydrogen peroxide solution. The oxygen gas produced was collected in a gas syringe. The reaction and a stop-clock were started at the same time, and the total volume of oxygen collected was noted at half-minute intervals. The results are given in the following table.

Time/minutes	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Volume/cm^3	0	24.0	36.0	42.2	46.0	47.6	48.0	48.0	48.0

(a) Plot a graph of volume against time.

(b) Is the rate of reaction faster after 1.0 minute or after 3.0 minutes? Justify your answer from the shape of the graph.

(c) What volume of oxygen had been collected after 1.75 minutes?

(d) How long did it take to collect exactly 30.0 cm^3?

(e) After how many minutes was the reaction finished? Explain your answer.

Answer (a) See graph below

Figure 6.2

(b) The rate of reaction is faster after 1.0 minute. The slope of the graph is a measure of the rate at any point in time. The slope of the graph is much steeper at 1.0 minute than it is at 3.0 minutes so it can be deduced that the rate is faster at 1.0 minute.

(c) 44.5 cm^3.

(d) 0.72 minutes = 43.2 seconds.

(e) The reaction was finished after 3.0 minutes because no further oxygen was produced after this time.

6.2 Average and Instantaneous Rates

In Example 6.1, 48 cm^3 of oxygen gas were produced in 3 minutes. The **average rate** of production of oxygen is volume/time = 48 cm^3/3 minutes = 16 cm^3 min^{-1}. However the rate is not constant throughout the reaction; for example, the average rate for the first minute is volume/time = 36 cm^3/1 minute = 36 cm^3 min^{-1}. In fact the rate of reaction changes throughout the reaction.

The instantaneous rate of reaction is the rate at a particular point in time during the reaction.

The instantaneous rate can be found by drawing a tangent to the curve at the appropriate point on the curve. The slope of the curve, which is calculated as shown in Example 6.2, is a measure of the reaction rate.

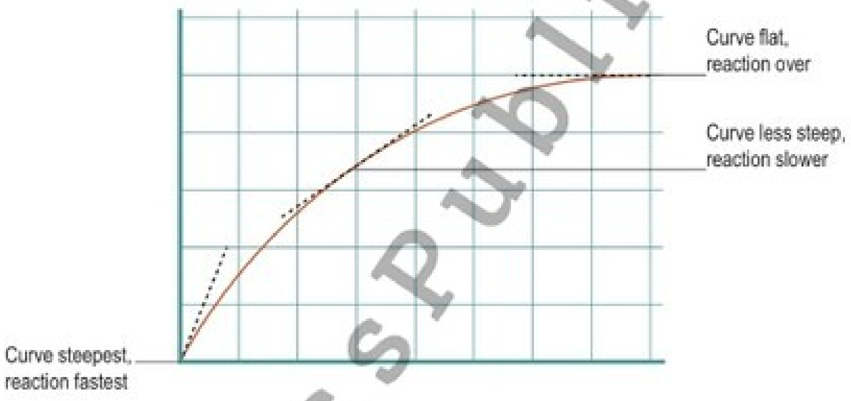


Figure 6.3

EXAMPLE 6.2

In the experiment described in Example 6.1, calculate the instantaneous rate of reaction after 1 minute.

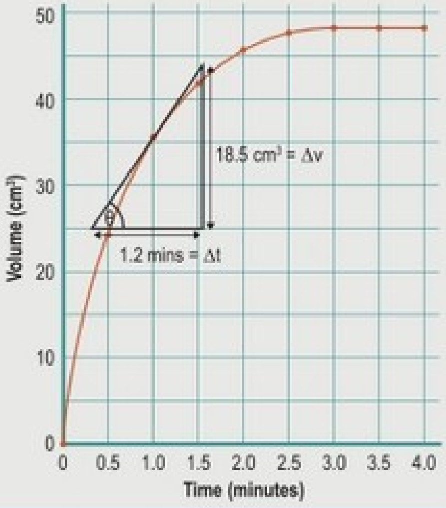
Answer

(1) A tangent to the curve is drawn at the point where time t = 1 minute.

(2) A right-angled triangle is drawn with the tangent as hypotenuse, and the other two sides, of lengths Δt and Δv respectively, parallel to the horizontal and vertical axes of the graph.

(3) The angle equals the angle made by the tangent with the horizontal axis.

(4) Slope = tan Θ = Δv/Δt = 18.5/1.2 = 15.4 cm^3 min^{-1}.



QUESTIONS

1 Define the rate of a chemical reaction.

2 Explain why the average rate of a chemical reaction is different from the instantaneous rate.

3 Manganese dioxide was added to hydrogen peroxide in a flask, and the oxygen produced was collected in a gas syringe. The equation for the reaction is

$$H_2O_{2(aq)} \rightarrow H_2O_{(l)} + \frac{1}{2} O_{2(g)}.$$

The total volume of oxygen collected was recorded every 30 seconds, and the data is shown in the table:

Time (sec)	0	30	60	90	120	150	180	210	240
Volume of oxygen (cm^3)	0	20	35	46	53	57	60	60	60

(a) Draw a graph of volume (y-axis) against time (x-axis).

(b) How long did it take for 55 cm3 of oxygen to be produced?

(c) What volume of oxygen had been collected after 135 seconds?

(d) Why is manganese dioxide added?

(e) After how many seconds was the reaction complete?

(f) Suggest two ways in which the reaction rate could have been increased.

(g) At what stage of the reaction was the rate greatest? Describe the slope of the graph at this stage.

(h) Calculate the instantaneous rate of reaction after 90 seconds.

6.3 Factors Affecting Reaction Rates

There are a number of factors which can influence the rate of a chemical reaction:

- Concentration of reactants
- Temperature of the reaction
- Particle size of solid reactants
- Nature of reactants, i.e. whether ionic or covalent
- Presence of a catalyst.

6.4 Concentration of Reactants

An increase in the concentration of the reactants usually increases the rate of the reaction. In a gas-phase reaction, for example the steam reforming of natural gas to form hydrogen and carbon monoxide

$$CH_{4(g)} + H_2O_{(g)} \rightarrow 3H_{2(g)} + CO_{(g)}$$

an increase in concentration of methane and/or water vapour causes an increase in the reaction rate.

In reactions involving solutions, changing the concentrations has a similar effect. In the decomposition of hydrogen peroxide using manganese(IV) oxide as a catalyst

$$H_2O_{2(aq)} \rightarrow H_2O_{(l)} + ½\,O_{2(g)}$$

the more concentrated the peroxide solution, the more rapidly the oxygen gas is produced. The peroxide concentration decreases as the reaction proceeds, so the reaction rate decreases. The continuous decrease in the slope of the graphs in Figure 6.4 indicates a continuously decreasing rate in each case.

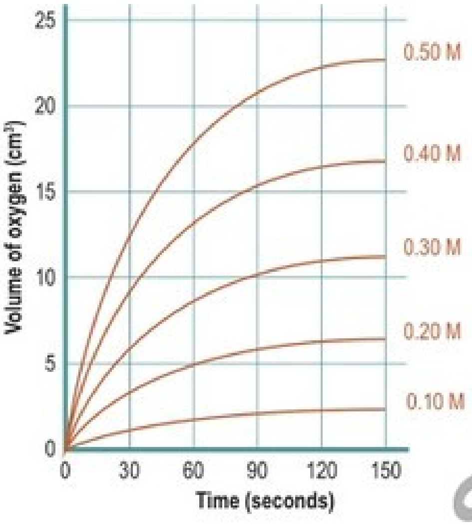


Figure 6.4
The decomposition of hydrogen peroxide solutions of different concentrations, using the same amount of catalyst each time. There are two effects of increasing the concentration: greater initial rate of reaction, and greater amount of product.

6.5 Temperature

An increase in temperature usually brings about an increase in reaction rate, though the extent of this varies from one reaction to another. In some cases, a temperature increase of about 10K causes the reaction rate to double. Exothermic reactions can be explosive if the heat produced cannot escape quickly enough. In such cases the rising temperature increases the reaction rate, causing even more heat to be produced

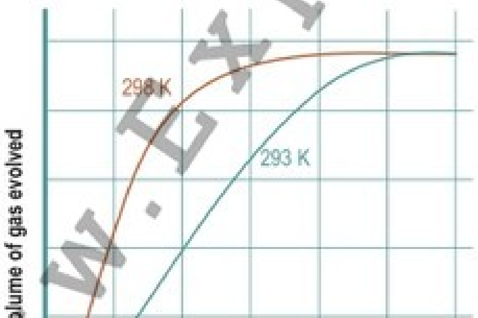


Figure 6.5
The decomposition of hydrogen peroxide solutions at two different temperatures. The only effect of raising the temperature is to increase the rate of reaction, with a consequent shortening of reaction time.

EXPERIMENT 6.1

Studying the effects on the reaction rate of (a) concentration and (b) temperature, using sodium thiosulfate solution and hydrochloric acid.

Sodium thiosulfate solution reacts with hydrochloric acid solution according to the following equation:

$$2HCl_{(aq)} + Na_2S_2O_{3(aq)} \rightarrow 2NaCl_{(aq)} + SO_{2(aq)} + S_{(s)}\downarrow + H_2O_{(l)}$$

The pale yellow precipitate of sulfur formed gradually obscures a cross marked on paper placed beneath the reaction flask. The time taken to obscure the cross, which is inversely proportional to the rate of reaction, depends on variables such as temperature and concentration. By varying one of these and keeping other variables constant, the effect on rate can be studied.

The **inverse of the time taken** to obscure the cross is the **measure of reaction rate** used in this experiment. Reaction time and reaction rate are inversely related.

(a) Effect of concentration

The concentration and volume of the hydrochloric acid solution used in this experiment are kept constant in order that only one variable (i.e. the concentration of the sodium thiosulfate solution) is changed.

Chemicals needed
0.1 M sodium thiosulfate solution
Dilute hydrochloric acid (3 M) ☒

Equipment needed
Conical flasks
Graduated cylinders
Stop-clock

Procedure

NB: Wear your safety glasses.

1. Place 100 cm³ of the sodium thiosulfate solution into a conical flask.
2. Add 10 cm³ of 3 M hydrochloric acid to the flask and swirl, while starting the stop-clock at the same time.
3. Place the flask on a piece of white paper marked with a cross.
4. Stop the clock when the cross disappears completely and record the time taken.
5. Repeat the experiment using 80 cm³ of sodium thiosulfate solution mixed with water to make the volume up to 100 cm³.
6. Repeat using 60, 40 and 20 cm³ of sodium thiosulfate solution respectively in turn.
7. If the initial sodium thiosulfate concentration is 0.1 M, subsequent concentrations will be 0.08 M, 0.06 M, 0.04 M and 0.02 M respectively.

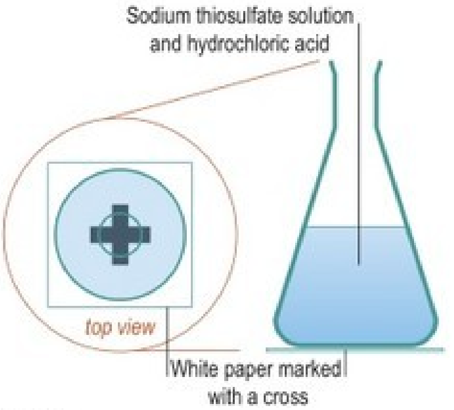


Figure 6.6

8 Record the results in a table similar to the following:

Concentration of thiosulfate	Reaction time (sec)	Rate of reaction (sec^{-1})
0.1 M		
0.08 M		
0.06 M		
0.04 M		
0.02 M		

9 Draw a graph of reaction rate i.e. 1/time (vertical axis) against concentration of thiosulfate solution (horizontal axis).

QUESTIONS

4 Name five factors that can affect the rate of a chemical reaction.

5 A graph of volume of hydrogen gas produced in the reaction of magnesium with hydrochloric acid is shown in the diagram.

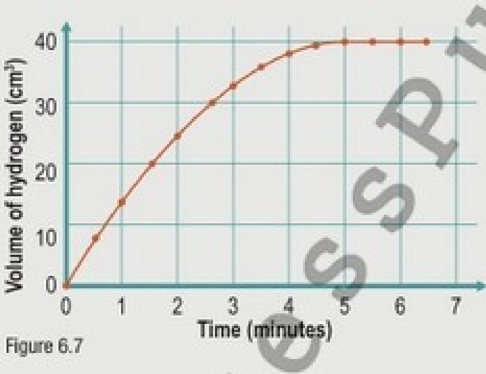


Figure 6.7

Draw a rough sketch of the graph in your copy. Mark on the graph

(a) the region that represents the greatest rate of reaction,

(b) where the reaction has ended.

What difference would you expect in the shape of the graph if the concentration of one of the reactants had been increased?

6 In terms of rates of reaction, explain why food is kept in a refrigerator.

7 Each of two beakers contains 25 cm^3 of 30-volume hydrogen peroxide solution. At the same instant, 1 gram of manganese dioxide is dropped into each beaker and beakers are swirled. In beaker A the manganese dioxide is in the form of a single lump and in beaker B it is in powder form.

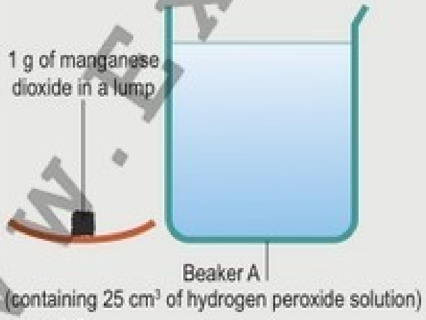


Figure 6.8

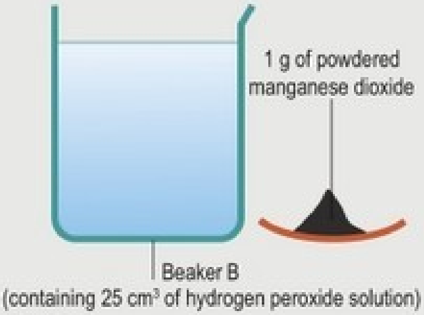


Figure 6.9

In which beaker will the bubbles: (a) be produced more vigorously, (b) cease being produced first? Explain your answers.

8 Explain why reactions between ionic compounds in solution are generally faster than reactions between covalent compounds.

6.6 Catalysts

A catalyst is a substance that alters the rate of a chemical reaction but is chemically unchanged at the end of the reaction.

Catalysts are often transition metals or their compounds, which speed up reactions in solution or in the gas phase. Catalysts are extremely important in chemical manufacturing. They work by lowering the energy needed to start a reaction – the activation energy – so the operating temperature can be lowered and costs reduced as a result. Catalysts are also important in laboratory reactions and in living organisms.
Manganese(IV) oxide catalyses the decomposition of hydrogen peroxide into oxygen and water. In this reaction, the catalyst is in a different phase from the reactant. This type of catalysis is **heterogeneous**. Normally heterogeneous catalysis involves a solid catalyst and liquid or gaseous reactants.

Further examples of heterogeneous catalysis include the dehydration of ethanol to form ethene with aluminium oxide, Al_2O_3, as catalyst

$$C_2H_5OH_{(l)} \xrightarrow{Al_2O_{3(s)}} C_2H_{4(g)} + H_2O_{(g)}$$

and the use of iron as catalyst in the manufacture of ammonia from its elements

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe_{(s)}} 2NH_{3(g)}$$

In **homogeneous catalysis** the catalyst is in the same phase as the reactants. For example, aqueous potassium iodide solution catalyses the decomposition of hydrogen peroxide to water and oxygen:

$$H_2O_{2(aq)} \xrightarrow{KI_{(aq)}} H_2O_{(l)} + ½O_{2(g)}$$

The reactant and the catalyst are both in aqueous solution.

Enzymes act as catalysts in living systems. Part of the enzyme, often containing a transition metal ion, is the active site where the reaction takes place.

Catalase is an enzyme found in the livers of mammals and is responsible for decomposing harmful peroxides. It decomposes hydrogen peroxide, lowering the activation energy from 75 kJ mol^{-1} for the uncatalysed reaction, to 23 kJ mol^{-1}.

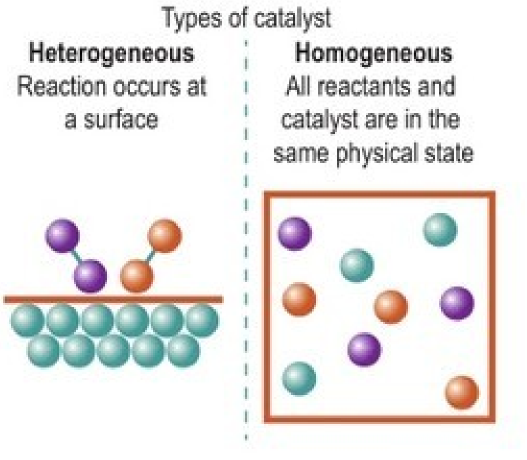


Figure 6.10

Zymase is the collective name of a series of enzymes found in microscopic fungi called yeasts. Zymase helps control the fermentation of sugar to alcohol in the production of alcoholic drinks.

Autocatalysis occurs when a product of a reaction increases the rate of the reaction. For example, in the reduction of manganate(VII) ions as in:

$$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \rightarrow Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + 4H_2O_{(l)}$$

the $Mn^{2+}{}_{(aq)}$ ions produced catalyse the reaction. The first few drops of the purple $MnO_4^-{}_{(aq)}$ solution added to the $Fe^{2+}{}_{(aq)}$ solution are decolourised slowly, while subsequent drops are decolourised rapidly. The $Mn^{2+}{}_{(aq)}$ formed by the initial slow reaction catalyses the subsequent reaction, the rate of which is increased.

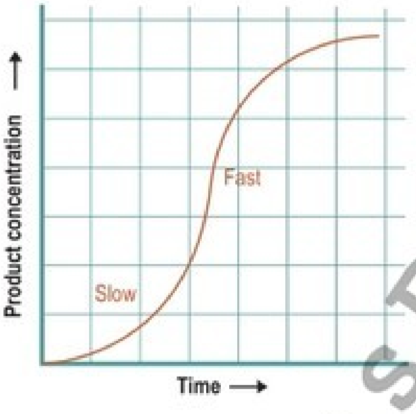


Figure 6.11
In a reaction with autocatalysis, the initial rate of reaction is slow, but increases once the catalyst is formed in the reaction

DEMONSTRATION

The effect on reaction rate of a catalyst

Hydrogen peroxide decomposes into water and oxygen gas. The reaction proceeds extremely slowly in the absence of a catalyst. However, if a few grains of manganese dioxide are added, bubbles of gas are immediately formed.

$$2H_2O_{2(aq)} \rightarrow O_{2(g)} + 2H_2O_{(l)}$$

Chemicals needed
20 volume hydrogen peroxide
Manganese dioxide powder ✖ n

Equipment needed
250 cm^3 beaker
Spatula

Procedure

NB: Wear your safety glasses.

1. Place about 25 cm^3 of hydrogen peroxide solution in the beaker. Note that there is no significant formation of bubbles.
2. Using the spatula, sprinkle a few grains of manganese dioxide on the surface of the hydrogen peroxide. Note that a vigorous reaction takes place, with the production of bubbles of gas.

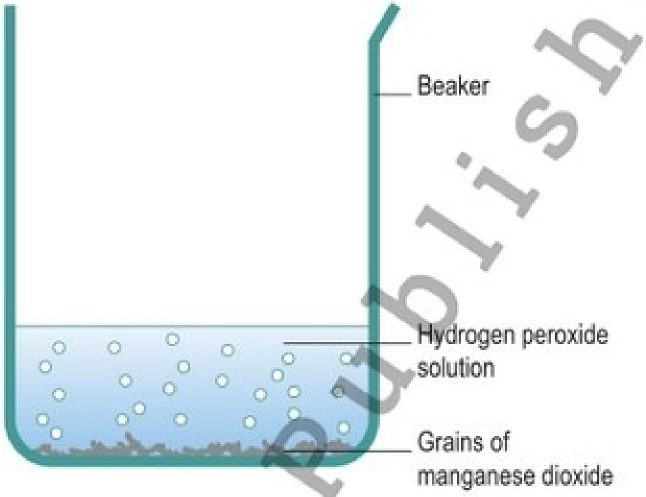


Figure 6.12

6.7 Everyday and industrial uses of catalytic chemistry in Kazakhstan.

Even the most efficient of modern car engines produce pollutants, which are found in their exhaust emissions. Amongst the pollutants are carbon monoxide, nitrogen monoxide, and unburned hydrocarbons.

- Carbon monoxide is formed by the incomplete combustion of petrol vapour:

$$C_8H_{18(g)} + 8\tfrac{1}{2}O_{2(g)} \rightarrow 8CO_{(g)} + 9H_2O_{(g)}$$

- This is the reason why running a car engine in an enclosed space may be lethal. Carbon monoxide prevents the haemoglobin in the blood from transporting oxygen, with potentially fatal results.
- Nitrogen monoxide is formed when the spark from the spark plug causes the petrol/air mixture to explode. The very high temperature of up to 2500 °C causes nitrogen and oxygen from the air in the mixture to react. Nitrogen monoxide is formed:

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

- Nitrogen monoxide reacts readily with oxygen to form nitrogen dioxide, which in turn reacts with water to form nitric acid:

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$
$$4NO_{2(g)} + 2H_2O_{(l)} + O_{2(g)} \rightarrow 4HNO_{3(aq)}$$

- These reactions occurring in the atmosphere cause acid rain. In sunlight, nitrogen dioxide also reacts with hydrocarbons and other volatile organic compounds to form an irritating photochemical smog.
- Incomplete combustion of petrol vapour, as well as producing carbon monoxide, can result in unburned hydrocarbons being emitted. These can act as greenhouse gases and form smog, while some of them are toxic.

Catalytic Converters

The introduction of tax regimes and the adoption of international emissions standards has led to a sharp increase in the number of vehicles fitted with catalytic converters in their exhaust systems. The catalytic converters help to reduce the emission of gases such as nitrogen monoxide, carbon monoxide and hydrocarbons. The catalyst in the converter speeds up reactions that have the effect of reducing atmospheric pollution, and the catalyst remains unchanged at the end of the reactions.

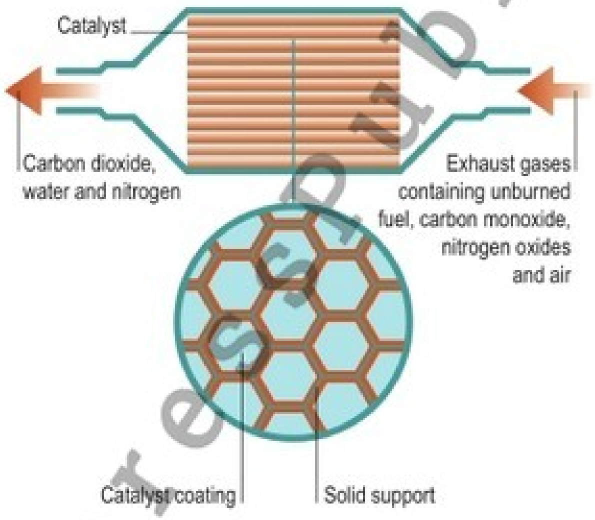


Figure 6.13
A catalytic converter

Nature of catalysts

The catalyst is a mixture of transition metals – platinum, rhodium and palladium, in the form of a very fine powder. The catalyst is spread in a very thin layer over a ceramic support material full of tiny holes that provide a large surface area.

As the catalyst is solid and the reactants are gaseous, this is an example of heterogeneous catalysis.

Reactions catalysed

- Carbon monoxide is converted into carbon dioxide by reaction with oxygen:

$$CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$

- Carbon monoxide is also converted into carbon dioxide in a reaction with nitrogen monoxide:

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

- This reaction has the advantage of reducing the pollutant nitrogen monoxide to nitrogen gas. By catalysing both of these reactions, the converter removes two pollutants quite effectively from exhaust gases.
- Unburned hydrocarbons are also oxidised to carbon dioxide and water, e.g. octane:

$$C_8H_{18(g)} + 12\tfrac{1}{2}O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(g)}$$

Environmental benefits

- Prior to the introduction of catalytic converters, road vehicles were responsible for about 90% of all emissions of the toxic gas, carbon monoxide. Since their introduction in many countries, emissions of carbon monoxide have approximately halved despite an increase in the number of vehicles on the road.
- The amount of nitrogen oxides emitted has also been reduced greatly. This has removed one cause of acid rain.
- The emission of other toxic gases such as unburned hydrocarbons has also been reduced, bringing about a further improvement in air quality.

Catalysts and industry in Kazakhstan

Catalysts are crucial to many different types of reaction used in industrial processes but particularly important in the modern petroleum industry in Kazakhstan. Catalysts are often used to accelerate reaction rates and remove hazardous sulfur and arsenic from crude oil and also in processes known as **fluid catalytic cracking** (FCC).

Fluid catalytic cracking (FCC) is one of the most important conversion processes used in petroleum refineries. The cracking of petroleum hydrocarbons was originally done by thermal cracking, which has been almost completely replaced by catalytic cracking because it produces more gasoline with a much higher octane rating. The process also produces by-product gases that have more carbon-carbon double bonds and can, therefore, be turned into more useful products than the gases produced by thermal cracking.

In the FCC process crude oil with an initial boiling point of 340 °C or higher at atmospheric pressure, known as heavy gas oil or vacuum gas oil (HVGO), is fed in and this feedstock is heated to a high temperature and moderate pressure, and brought into contact with a hot, powdered catalyst. The catalysts used break down the long-chain molecules of high-boiling hydrocarbon liquids into much shorter molecules.

Other important uses of catalysts in industry are the use of the catalyst vanadium pentoxide to reduce sulfur emissions in power plants; the use of phosphoric acid in the production of ethanol and the use of iron and potassium hydroxide in the Haber process for the production of ammonia.

QUESTIONS

9 Explain what is meant by a heterogeneous catalyst, and give an example.

10 Why are catalysts of economic importance in industry? Give an example of an industrial catalyst.

11 Explain what is meant by a homogeneous catalyst, and give an example.

12 Give two examples of enzymes as catalysts.

13 Explain what is meant by the term autocatalysis.

14 Name two elements commonly used in catalytic converters.

15 Name two substances produced by car engines that can be changed to less harmful substances by catalytic converters.

16 What feature of catalytic converters ensures a large surface area of catalyst?

Chemical Equilibrium

MODULE 7

Learning objectives

- To observe through experiment the impact of different factors on equilibrium shift 10.3.3.1
- To predict the impact of change in temperature, concentration and pressure on chemical equilibrium 10.3.3.2
- To make calculations related to the equilibrium constant 10.3.3.3

7.1 Reversible Reactions and Dynamic Equilibrium

Ammonia (NH_3) is an important industrial chemical that is used, for example, in the manufacture of fertilisers. It is manufactured by reacting nitrogen with hydrogen:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The $\rightleftharpoons$ symbol indicates that the reaction is **reversible**; it can go in either direction.

If ammonia gas is placed in a closed container at 700 K, it decomposes, forming the gaseous products, nitrogen and hydrogen:

$$2NH_3 \rightarrow N_2 + 3H_2 \qquad (1)$$

The breakdown of ammonia is never complete.

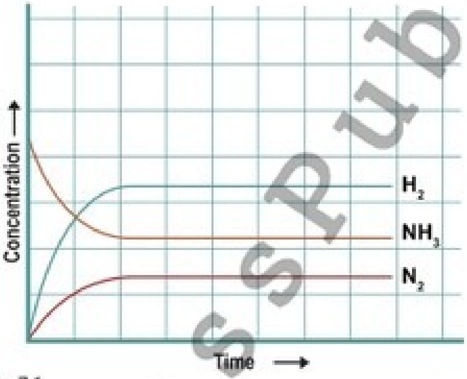


Figure 7.1
When ammonia breaks down, the reaction does not go to completion

If a mixture of nitrogen gas and hydrogen gas is placed in a closed container at 700 K, nitrogen molecules and hydrogen molecules only are present initially.

As they react forming ammonia molecules:

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (2)$$

the concentrations of both nitrogen and hydrogen decrease, while the concentration of ammonia increases. The conversion of reactants to products is never complete no matter how long the reaction is allowed to continue.

Eventually, however, they level off and become constant.
Reaction (2) is clearly the reverse of reaction (1); since (1) and (2) both occur to an appreciable extent, they are reversible and may be written:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Reactions (1) and (2) do not go to completion. In each case, the reverse reaction will always also occur to an appreciable extent.

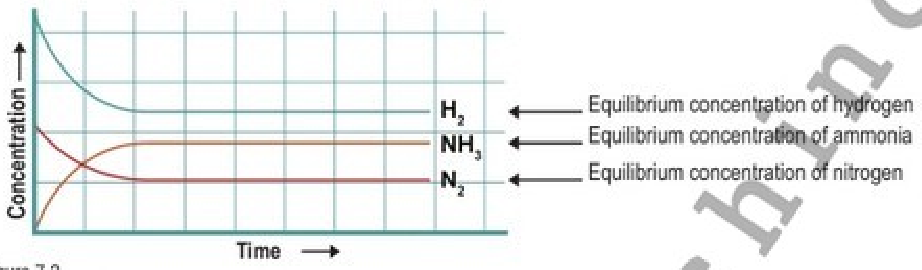


Figure 7.2
Concentrations of nitrogen, hydrogen and ammonia level off to equilibrium values

When the concentrations of reactants (N_2 and H_2) and product (NH_3) have become constant, a state of **chemical equilibrium** is said to have been reached. This is a **dynamic** equilibrium; even though no reactions appear to be occurring, there are in fact two reactions continuing to happen.

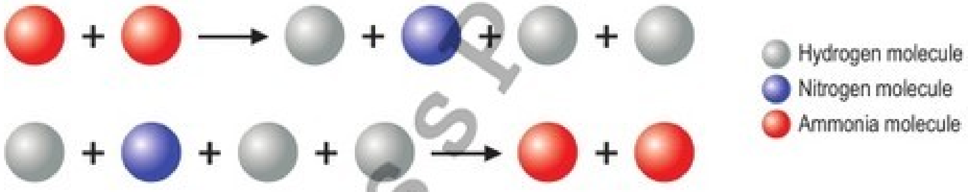


Figure 7.3
Dynamic equilibrium: at equilibrium, reactions continue to take place

To see why chemical equilibrium is dynamic, consider what happens from the time that nitrogen and hydrogen are introduced into a container (which is then sealed) at 700 K. The rate of the forward reaction

$$N_2 + 3H_2 \rightarrow 2NH_3$$

decreases as the concentrations of reactants, N_2 and H_2, decrease. The rate of the reverse reaction

$$2NH_3 \rightarrow N_2 + 3H_2$$

increases as the concentration of NH_3 increases. **At equilibrium, the rate of the forward reaction equals the rate of the reverse reaction**. This is why the concentrations at equilibrium remain constant.

Chemical equilibrium is the state in which the rate of the forward reaction equals the rate of the reverse reaction.

At equilibrium, the amounts reacting per second of nitrogen and hydrogen respectively at any given time equal the amounts being formed per second of nitrogen and hydrogen. At equilibrium also, the amount of ammonia decomposing per second is equal to the amount being formed per second from nitrogen and hydrogen.

Chemical equilibrium is said to be dynamic because, at equilibrium, there are reactions continuously occurring.

7.2 Equilibrium Constants

In the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

as much hydrogen iodide is decomposing at equilibrium as is being formed, and so the concentrations of all three substances remain constant. The equilibrium concentrations at a constant temperature of 764 K of the three species, for a number of sets of different starting concentrations, are given in Table 7.1. The square brackets denote concentrations in mol l^{-1}.

QUESTIONS

1 What is meant by a reversible reaction? Give an example of a reversible reaction.

2 What is meant by a state of dynamic equilibrium?

3 At equilibrium in the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

how does the rate of the forward reaction compare to the rate of the reverse reaction?

4 In the reaction

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

why is the conversion of reactants to products never complete?

5 When equilibrium is reached in the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

why is the equilibrium described as dynamic equilibrium?

$[H_2]\times10^3$	$[I_2]\times10^3$	$[HI]\times10^3$	$\frac{[HI]^2}{[H_2]\times[I_2]}$
1.894	1.896	12.83	45.9
2.265	2.840	17.15	45.7
1.699	4.057	17.79	45.7
2.484	2.514	16.95	46.0
1.971	1.981	13.42	46.1

Table 7.1

Although these equilibrium concentrations are all different, there is a constant relationship within the limits of experimental error that holds here, namely

$$\frac{[HI]^2}{[H_2]\times[I_2]} = \text{constant}$$

where the square brackets denote concentrations in mol l^{-1}.

A similar type of relationship holds for other reversible reactions at a specified temperature. For example, in the reaction of nitrogen and hydrogen forming ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\frac{[NH_3]^2}{[N_2]\times[H_2]^3} = \text{constant}$$

In general, if m moles of A react with n moles of B forming p moles of C and q moles of D:

$$mA + nB \rightleftharpoons pC + qD$$

$$\frac{[C]^p \times [D]^q}{[A]^m \times [B]^n} = K_c$$ at equilibrium

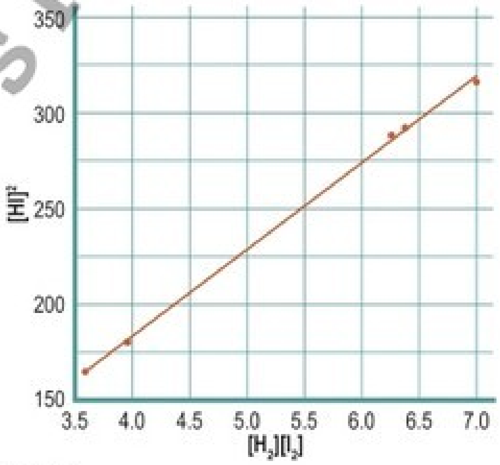


Figure 7.4
The straight line graph indicates that $\frac{[HI]^2}{[H_2]\times[I_2]}$ = constant

where K_c is a constant, called the **equilibrium constant** in terms of molar concentration. Note that the multiplication sign is usually omitted:

$$\frac{[C]^p\,[D]^q}{[A]^m\,[B]^n} = K_c$$

This relationship is known as the **Equilibrium law**.

The magnitude of the equilibrium constant gives an indication of the **position** of equilibrium. A large value of K_c indicates that at equilibrium the concentration of products is large compared to the concentration of reactants. For example, the value of K_c for the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

at 764 K is 45.9. This indicates that HI predominates at equilibrium at this temperature.

A small value of K_c indicates that at equilibrium the concentration of products is small compared to the concentration of reactants. For example, the value of K_c for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at 800 K is 0.03. This indicates that there is relatively little NH_3 present at equilibrium at this temperature.

The value of the equilibrium constant K depends on the temperature, as indicated in Table 7.2. If the forward reaction is exothermic, the equilibrium constant decreases as the temperature rises. If the forward reaction is endothermic, the equilibrium constant increases as the temperature rises.

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ Forward reaction exothermic		$N_2O_4 \rightleftharpoons 2NO_2$ Forward reaction endothermic	
Temperature	K_c	Temperature	K_c
400 K	43,900	200 K	0.0000000551
600 K	4.03	400 K	1.46
800 K	0.03	600 K	362

Table 7.2
Effect of temperature changes on Kc values at atmospheric pressure

EXAMPLE 7.1

Write an expression for the equilibrium constant, K_c, for the following reversible reactions:

(a) $N_2O_4 \rightleftharpoons 2NO_2$

(b) $2NH_3 \rightleftharpoons N_2 + 3H_2$

Answer a) $K_c = \dfrac{[NO_2]^2}{[N_2O_4]}$ b) $K_c = \dfrac{[N_2]\,[H_2]^3}{[NH_3]^2}$

Important points about equilibrium constants

- **The value of K_c only applies at equilibrium.**
- **K_c is constant only if the temperature remains constant.**
- **The value of K_c is not affected by changes in concentrations of reactants or products.**
- **The units of K_c depend on the relative numbers of moles on each side of the equation for the reaction. In a reaction in which there are equal numbers of moles on each side of the equation, such as**

  $H_2 + I_2 \rightleftharpoons 2HI$

  K_c has no units, as all units cancel in the K_c expression. Otherwise, K_c has units. For example, the unit of K_c for the reaction

  $2NO + O_2 \rightleftharpoons 2NO_2$ is $(1/\text{mol l}^{-1}) = \text{mol}^{-1}\,\text{l}$.

QUESTIONS

6 What does a large value of K_c indicate about relative concentrations of species at equilibrium?

7 If the value of K_c increases as the temperature increases, what does this indicate?

8 Write equilibrium constant expressions for each of the following:

a) $2NO + O_2 \rightleftharpoons 2NO_2$

b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

c) $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

d) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

e) $CO_2 + H_2 \rightleftharpoons CO + H_2O$

f) $2SO_3 \rightleftharpoons 2SO_2 + O_2$

g) $CoCl_4^{2-} + 6H_2O \rightleftharpoons Co(H_2O)_6^{2+} + 4Cl^-$

h) $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2CrO_4^{2-} + 2H^+$

i) $Fe^{3+} + CNS^- \rightleftharpoons Fe(CNS)^{2+}$

j) $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O$

7.3 Calculations of Equilibrium Constant Values

If the equilibrium concentrations of all species in a given reaction are known, as in Example 7.2, the equilibrium constant value may readily be calculated.

EXAMPLE 7.2

In a reaction at a particular temperature between sulfur dioxide and oxygen forming sulfur trioxide

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

it was found that at equilibrium the concentrations of SO_2, O_2 and SO_3 were 0.07 mol l^{-1}, 0.035 mol l^{-1} and 0.03 mol l^{-1} respectively. Calculate the value of the equilibrium constant (K_c) for this reaction at this temperature.

Answer

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{(0.03)^2}{(0.07)^2(0.035)} = 5.25\ \text{mol}^{-1}\,\text{l}$$

To find the value of the equilibrium constant for a reaction, it is usually necessary to calculate the equilibrium concentrations of all the species first.

EXAMPLE 7.3

1120 cm^3 of hydrogen (measured at s.t.p.) were placed in a 2-litre flask with 12.7 g of iodine. The flask was sealed, heated to 700 K, and allowed to come to equilibrium. The mass of hydrogen iodide formed was found to be 10.24 g. Calculate the equilibrium constant (K_c) for this reaction at 700 K.

Answer

The equation for the reaction is: $H_2 + I_2 \rightleftharpoons 2HI$

Amounts present at the start of the experiment:

H_2	I_2	HI
1120 / 22400 moles = 0.05 moles	12.7 / 254 moles = 0.05 moles	0 moles

Moles of hydrogen iodide present at equilibrium = 10.24 / 128 moles = 0.08 moles

From the equation, two moles of HI are formed when one mole of H_2 reacts with one mole of I_2. Therefore, 0.08 moles of HI are formed when 0.04 moles of H_2 reacts with 0.04 moles of I_2.

Amounts present at equilibrium:

H_2	I_2	HI
0.05 – 0.04 moles = 0.01 moles	0.05 – 0.04 moles = 0.01 moles	0.08 moles

Concentrations in mol l^{-1} present at equilibrium:

$[H_2]$	$[I_2]$	[HI]
0.01 / 2 = 0.005	0.01 / 2 = 0.005	0.08 / 2 = 0.04

The following table summarises the steps taken so far in the calculation:

	H_2	I_2	HI
Initial amount	0.05 moles	0.05 moles	0 moles
Change	– 0.04 moles	– 0.04 moles	+ 0.08 moles
Equilibrium amount	0.01 moles	0.01 moles	0.08 moles
Equilibrium concentration	0.01/2 = 0.005 mol l^{-1}	0.01/2 = 0.005 mol l^{-1}	0.08/2 = 0.04 mol l^{-1}

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(0.04)^2}{0.005 \times 0.005} = 64$$

In reversible reactions where neither the forward nor the reverse reactions causes a change in the number of molecules present, it is possible to calculate the equilibrium constant **even if the volume of the equilibrium mixture is unknown**, using the method shown in Example 7.4.

EXAMPLE 7.4

Ethanol reacts with ethanoic acid as follows:

CH_3COOH	+	C_2H_5OH	$\rightleftharpoons$	$CH_3COOC_2H_5$	+	H_2O
Ethanoic acid		Ethanol		Ethyl ethanoate		Water

In an experiment at 373 K where the initial amounts present were

Ethanoic acid	Ethanol	Ethyl ethanoate	Water
180 g	138 g	0 g	0 g

it was found that 46 g of ethanol remained at equilibrium.

Calculate the equilibrium constant (K_c) for this reaction at 373 K.

Answer

The equation for the reaction is:

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

Amounts present at the start of the experiment:

CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
180 / 60 moles = 3 moles	138 / 46 moles = 3 moles	0 moles	0 moles

At equilibrium, there is 46 g of ethanol = one mole of ethanol.
This means that two moles of ethanol were consumed. From the balanced equation for the reaction, this means that two moles of ethanoic acid were also consumed, and that two moles of ethyl ethanoate and two moles of water were formed.

Amounts present at equilibrium:

CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
1 mole	1 mole	2 moles	2 moles

Let V litres be the total volume of the mixture at equilibrium.

Concentrations in mol l^{-1} present at equilibrium:

$[CH_3COOH]$	$[C_2H_5OH]$	$[CH_3COOC_2H_5]$	$[H_2O]$
1 / V	1 / V	2 / V	2 / V

The following table summarises the steps taken so far in the calculation:

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial amount	3 moles	3 moles	0 moles	0 moles
Change	– 2 moles	– 2 moles	+ 2 moles	+ 2 moles
Equilibrium amount	1 mole	1 mole	2 moles	2 moles
Equilibrium concentration	1 / V mol l^{-1}	1 / V mol l^{-1}	2 / V mol l^{-1}	2 / V mol l^{-1}

Since the V values cancel,

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} = \frac{(2 / V)(2 / V)}{(1 / V)(1 / V)} = 4$$

QUESTIONS

9 In a reaction at a particular temperature between nitrogen and hydrogen forming ammonia

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

it was found that at equilibrium the concentrations of N_2, H_2 and NH_3 were 0.06 mol l^{-1}, 0.07 mol l^{-1} and 0.02 mol l^{-1} respectively.
Calculate the value of the equilibrium constant (K_c) for this reaction at this temperature.

10 Four moles of $COCl_2$ are placed in a 4-litre flask at 668 K. The following reaction occurs:

$$COCl_2 \rightleftharpoons CO + Cl_2$$

and, at equilibrium, 1.6 moles of $COCl_2$ remain. Calculate K_c for the reaction.

11 In the reaction

$$C_4H_9COOH + C_2H_5OH \rightleftharpoons C_4H_9COOC_2H_5 + H_2O$$

at 473 K, it is found that if an initial mixture containing 2 moles of C_4H_9COOH and 2 moles of C_2H_5OH is allowed to come to equilibrium, 1 mole of C_4H_9COOH remains. Calculate the equilibrium constant for the reaction at 473 K.

12 Calculate K_c for the reaction

$$CH_3COOCH_3 + H_2O \rightleftharpoons CH_3COOH + CH_3OH$$

if an initial mixture of 7.4 g of CH_3COOCH_3 and 2.0 g of water yields 4.0 g of CH_3COOH at equilibrium.

7.4 Calculations of Equilibrium Concentrations

Once the value of the equilibrium constant for a reaction at a particular temperature is known, it can be used to calculate the equilibrium concentrations of all the species in the reaction, provided only that their initial concentrations are known.

In examples of this type, a quadratic equation in terms of x will usually be arrived at during the calculation. For a quadratic equation $ax^2 + bx + c = 0$, the value of x is found using the formula

$$x = \frac{-b \pm \sqrt{(b^2-4ac)}}{2a}$$

Two different values of x will usually be obtained, one of which (often either a negative value or a value which is too large to be possible) will have to be rejected.

EXAMPLE 7.5

Phosphorus(V) chloride decomposes into phosphorus(III) chloride and chlorine at 523 K according to the equation:

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

The equilibrium constant in terms of molar concentration (K_c) for the reaction at this temperature is 0.04 mol l^{-1}. If 1 mole of phosphorus(V) chloride is heated in a closed 10-litre vessel at 523 K, calculate the concentration at equilibrium of phosphorus(V) chloride, phosphorus(III) chloride and chlorine respectively.

EXAMPLE 7.5 (CONTINUED)

Answer The balanced equation for the reaction is

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

Amounts present at the start of the experiment:

PCl_5	PCl_3	Cl_2
1 mole	0 moles	0 moles

Assume that x moles respectively of PCl_3 and Cl_2 are formed at equilibrium. From the balanced equation, this means that x moles of PCl_5 are used up when equilibrium is reached.

Amounts present at equilibrium:

PCl_5	PCl_3	Cl_2
1−x moles	x moles	x moles

The volume of the reaction vessel is 10 litres.

Concentrations at equilibrium:

$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
(1−x) / 10 moles l^{-1}	x / 10 moles l^{-1}	x / 10 moles l^{-1}

The following table summarises the steps taken so far in the calculation:

	PCl_5	PCl_3	Cl_2
Initial amount	1 mole	0 moles	0 moles
Change	− x moles	+ x moles	+ x moles
Equilibrium amount	1−x moles	x moles	x moles
Equilibrium concentration	(1−x) / 10 moles l^{-1}	x / 10 moles l^{-1}	x / 10 moles l^{-1}

$$K_c = 0.04 \text{ mol } l^{-1} = \frac{[PCl_3] \times [Cl_2]}{[PCl_5]}$$

Substituting values for the equilibrium concentrations:

$$0.04 \text{ mol } l^{-1} = \frac{[PCl_3] \times [Cl_2]}{[PCl_5]} \text{ mol } l^{-1} = \frac{(0.1x) \times (0.1x)}{0.1(1-x)} \text{ mol } l^{-1}$$

$0.01x^2 = 0.004(1-x) = 0.004 - 0.004x$
$0.01x^2 + 0.004x - 0.004 = 0$

Using the formula $x = (-b \pm \sqrt{[b^2 - 4ac]}) / 2a$, we obtain:
$x = (-0.004 \pm \sqrt{[0.000016 + 0.00016]}) / 0.02$
$= (-0.004 \pm \sqrt{[0.000176]}) / 0.02$
$= (-0.004 \pm 0.013) / 0.02$
$= 0.009 / 0.02$ or $-0.017/0.02$
$= 0.45$ or -0.85

The negative value of x, −0.85, can be disregarded.
Concentrations at equilibrium:

$[PCl_5]$	$[PCl_3]$	$[Cl_2]$
(1−x) / 10 moles l^{-1}	x / 10 moles l^{-1}	x / 10 moles l^{-1}
= 0.055 moles l^{-1}	= 0.045 moles l^{-1}	= 0.045 moles l^{-1}

In reversible reactions where neither the forward nor the reverse reactions causes a change in the number of moles present, it is possible to calculate the **equilibrium amounts** of all species, **even if the volume is unknown**, using the method shown in Example 7.6.

EXAMPLE 7.6

The value of K_c for the reaction

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

is 4 at 373 K. If 10 moles each of ethanoic acid and ethanol are allowed to react at 373 K in a sealed tube, how many moles of ethyl ethanoate and water respectively are formed at equilibrium? How many moles of ethanoic acid and ethanol respectively remain at equilibrium?

Answer Let V litres be the total volume of the mixture at equilibrium. Assume that x moles of ethyl ethanoate and water respectively are formed at equilibrium.

	CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
Initial amount	10 moles	10 moles	0 moles	0 moles
Change	– x moles	– x moles	+ x moles	+ x moles
Equilibrium amount	10–x moles	10–x moles	x moles	x moles
Equilibrium concentration	(10–x) / V	(10–x) / V	x / V	x / V

$$K_c = \frac{[CH_3COOC_2H_5]\,[H_2O]}{[CH_3COOH]\,[C_2H_5OH]} = \frac{(x / V)(x / V)}{((10-x) / V)((10-x) / V)} = 4$$

Since the V values cancel,

$$K_c = 4 = \frac{(x)\,(x)}{(10-x)\,(10-x)}$$

From this the following quadratic equation is obtained:

$3x^2 - 80x + 400 = 0$

$x = 6.67$ or 20

Since x is the number of moles of ethyl ethanoate or water formed, x = 20 is impossible, since the initial amounts (10 moles each) of ethanoic acid and ethanol are not capable of producing 20 moles of ethyl ethanoate and water respectively.

Amounts at equilibrium:

CH_3COOH	C_2H_5OH	$CH_3COOC_2H_5$	H_2O
10 – x = 3.33 moles	3.33 moles	x = 6.67 moles	6.67 moles

QUESTIONS

13 At 760 K, the value of K_c for the reaction

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

is 33. Calculate the equilibrium concentrations of all species if 10 moles of PCl_5 are placed in a 1-litre flask at 760 K and allowed to reach equilibrium.

14 For the reaction

$$H_2 + CO_2 \rightleftharpoons H_2O + CO$$

at 1200 K, the value of K_c for the reaction is 1.40.

Calculate the concentrations of all species at equilibrium after 1 mole of H_2O and 1 mole of CO react together in a 4-litre flask.

15 Ethanoic acid reacts with propan-1-ol at 373 K according to the equation

$$CH_3COOH + C_3H_7OH \rightleftharpoons CH_3COOC_3H_7 + H_2O$$

If the equilibrium constant for the reaction at this temperature is 6.25, calculate the equilibrium amounts in moles of all species when 210 g of CH_3COOH and 210 g of C_3H_7OH are placed in a flask at 373 K.

16 Benzoic acid reacts with ethanol at 473 K according to the equation

$$C_6H_5COOH + C_2H_5OH \rightleftharpoons C_6H_5COOC_2H_5 + H_2O$$

If the equilibrium constant for the reaction at this temperature is 2.73, calculate the equilibrium amounts in moles of all species when 1 mole of C_6H_5COOH and 3 moles of C_2H_5OH are placed in a flask at 473 K.

7.5 Le Chatelier's Principle

What happens when a chemical system at equilibrium is disturbed, for example by changes in temperature or pressure or in the concentration of one of the chemical species present? This situation is governed by Le Chatelier's Principle:

Le Chatelier's Principle
When a system at equilibrium is subjected to a stress, the equilibrium shifts in such a way as to minimise the effect of the stress.

Applying this principle enables us to predict correctly the effect of changes in individual variables (temperature, concentration, catalyst, etc.) on the equilibrium.

Henri Le Chatelier was a French chemist whose principle guided chemists in producing industrial products with a minimum of waste.

(a) Changes in concentration of one species

In the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

at 763 K, the equilibrium constant

$$K_c = \frac{[HI]^2}{[H_2]\,[I_2]} = 45.9$$

If the concentration of H_2 is increased, when the mixture is at equilibrium, the equilibrium shifts in such a way as to minimise this change by using up the hydrogen, forming more hydrogen iodide (Figure 7.5). The reaction therefore tends to go preferentially from left to right, with the concentrations of hydrogen and iodine decreasing and the concentration of hydrogen iodide increasing until the equilibrium value of 45.9 for K_c is again reached.

Figure 7.5

If the concentration of I_2 is increased, when the mixture is at equilibrium, the reaction also tends to go preferentially to the right, using up excess iodine and forming more hydrogen iodide (Figure 7.6). Again the equilibrium value of 45.9 for K_c is reached.

Figure 7.6

If the concentration of HI is increased, when the mixture is at equilibrium, the change is minimised by the breaking down of HI, forming more hydrogen and iodine (Figure 7.7). The reaction continues to go preferentially from right to left until the equilibrium value of 45.9 for K_c is reached.

Figure 7.7

A decrease in the concentration of HI, when the mixture is at equilibrium, has the opposite effect; hydrogen and iodine react forming more HI (Figure 7.8).

Figure 7.8

A decrease in the concentration of H_2, when the mixture is at equilibrium, shifts the equilibrium to the left; hydrogen iodide decomposes, forming more hydrogen (and iodine) (Figure 7.9).

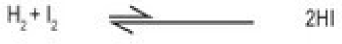


Figure 7.9

A decrease in the concentration of I_2, when the mixture is at equilibrium, also shifts the equilibrium to the left (Figure 7.10); more iodine (and hydrogen) is formed, as hydrogen iodide decomposes.

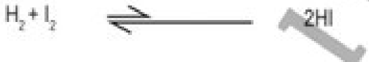


Figure 7.10

(b) Changes in temperature

The reaction

$$H_2 + I_2 \rightarrow 2HI \qquad \Delta H = -12.6 \text{ kJ mol}^{-1}$$

is exothermic, while the reverse reaction

$$2HI \rightarrow H_2 + I_2 \qquad \Delta H = +12.6 \text{ kJ mol}^{-1}$$

is endothermic. **If the temperature is raised** when the system is at equilibrium, the extra heat is absorbed by allowing the **endothermic reaction**, forming hydrogen and iodine, to take place preferentially (Figure 7.11). A consequence of this is that the value of K_c changes – in this case, it decreases.

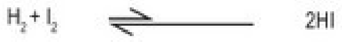


Figure 7.11

Lowering the temperature of the equilibrium mixture has the opposite effect. The **exothermic reaction**, forming hydrogen iodide, is favoured (Figure 7.12), as this releases heat, counteracting the effect of lowering the temperature. Again the value of K_c changes – in this case, it increases.

Figure 7.12

(c) Addition of a catalyst

A catalyst increases the rate of a reaction by lowering the activation energy for the reaction. The activation energy for the reverse reaction is lowered to the same extent, and so the rate of the reverse reaction is increased to an equal extent. Equilibrium, at which the rate of the forward reaction equals the rate of the reverse reaction, is therefore reached more quickly if a catalyst is added at the beginning of the reaction.

If a catalyst is added once equilibrium has been reached, however, it has no effect on the equilibrium. The rate of the forward reaction will be increased to the same extent as the rate of the reverse reaction, and therefore the concentrations of all species will remain constant.

(d) Changes in pressure

Pressure changes at equilibrium only affect gases. If the pressure of an equilibrium mixture of gases is increased, Le Chatelier's Principle predicts that, if possible, the number of molecules in the container will be reduced, thus reducing the pressure. In the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

there are four molecules on the left and only two on the right. If a mixture of nitrogen, hydrogen and ammonia at equilibrium is subjected to **increased pressure**, the equilibrium shifts to the right, forming more ammonia. This counteracts the effect of the increase in pressure, as the number of molecules present is reduced (Figure 7.13).

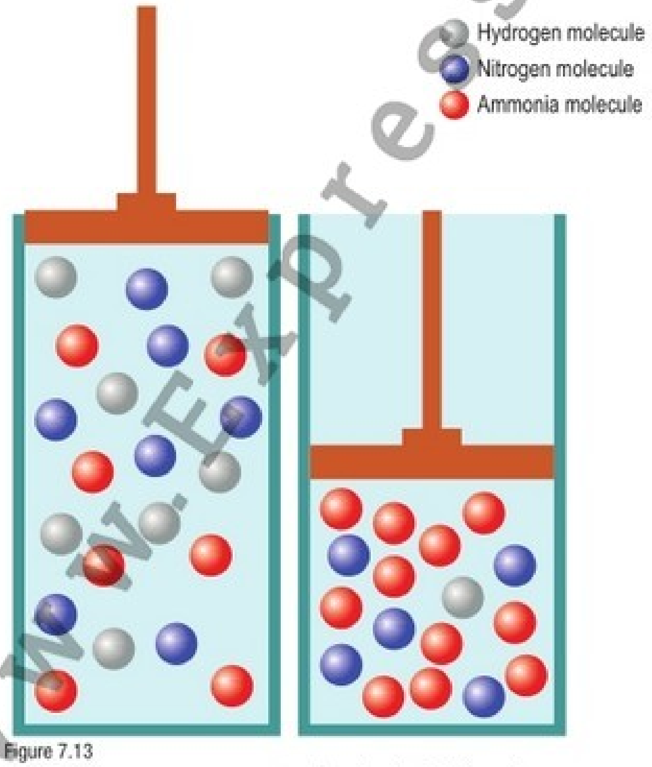


Figure 7.13
Increased pressure causes more ammonia molecules to be formed.
The number of hydrogen molecules and nitrogen molecules decreases accordingly.

If the pressure of an equilibrium mixture of gases is decreased, Le Chatelier's Principle predicts that the disturbance will be minimised, if possible, by reactions occurring which increase the number of molecules in the container, thus increasing the pressure. If a mixture of nitrogen, hydrogen and ammonia at equilibrium is subjected to **decreased pressure**, the equilibrium shifts to the left, forming more nitrogen and more hydrogen. This counteracts the effect of the decrease in pressure, as the number of molecules present is increased (Figure 7.14).

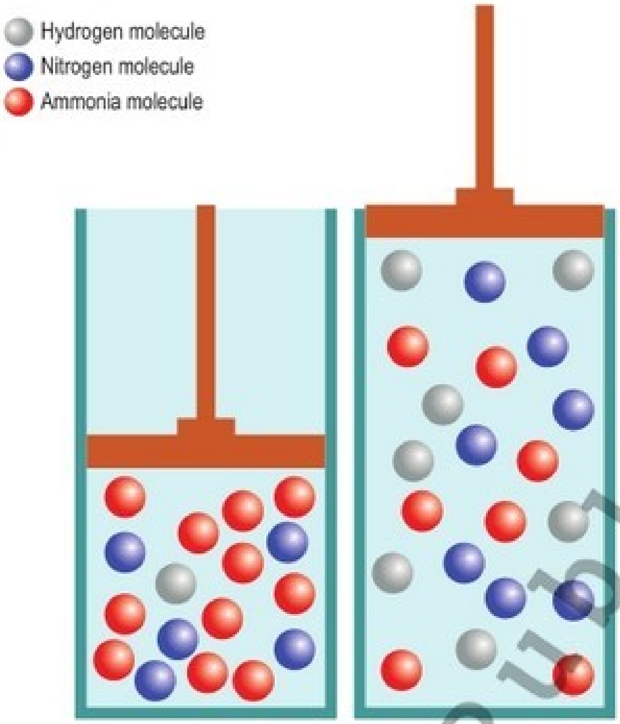


Figure 7.14
Decreased pressure causes more hydrogen molecules and nitrogen molecules to be formed. The number of ammonia molecules decreases correspondingly.

Increasing or decreasing the pressure on a mixture of gases at equilibrium does not always have an effect, however.

In the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

there is the same number of molecules on the left as on the right. If two molecules of hydrogen iodide break down, two molecules – one of hydrogen and one of iodine – are formed. Increasing or decreasing the pressure on an equilibrium mixture of hydrogen, iodine and hydrogen iodide has therefore no effect.

(e) Changes in the volume of the container

Increasing the volume of the container for a mixture of gases at equilibrium causes a decrease in pressure. In the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

the equilibrium shifts to the left, forming more nitrogen and hydrogen.
In the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

there is no effect on the equilibrium.

Decreasing the volume of the container for a mixture of gases at equilibrium causes an increase in pressure. In the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

the equilibrium shifts to the right, forming more ammonia.
In the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

there is again no effect on the equilibrium.

Table 7.3 summarises the changes at equilibrium predicted by Le Chatelier's Principle (X refers to one of the components of the equilibrium mixture).

Type of stress	Resultant change
Increase in concentration of X	Reaction that removes X is favoured
Decrease in concentration of X	Reaction that forms X is favoured
Increase in temperature	Endothermic reaction is favoured
Decrease in temperature	Exothermic reaction is favoured
Increase in pressure	Reaction that produces fewer molecules is favoured
Decrease in pressure	Reaction that produces more molecules is favoured
Adding a catalyst	No change

Table 7.3

QUESTIONS

17 In the reversible reaction

$COCl_2 \rightleftharpoons CO + Cl_2$

ΔH is negative for the forward reaction. At equilibrium, what is the effect of:

a) raising the temperature
b) increasing the pressure
c) removing some $COCl_2$
d) increasing the volume of the container
e) adding a catalyst
f) adding some Cl_2?

18 What is the effect at equilibrium of

a) decreasing the volume of the container
b) decreasing the pressure
c) lowering the temperature
d) adding HCl
e) raising the temperature
f) removing O_2
g) increasing the pressure?

in the reaction

$4HCl + O_2 \rightleftharpoons 2Cl_2 + 2H_2O \qquad \Delta H = -110\ kJ\ mol^{-1}$,

19 In the reversible reaction

$H_2 + Cl_2 \rightleftharpoons 2HCl$

in which the forward reaction is exothermic, what is the effect at equilibrium of

a) lowering the temperature
b) lowering the pressure
c) making the reaction container smaller
d) decreasing the amount of catalyst
e) decreasing the amount of HCl
f) decreasing the amount of H_2
g) decreasing the amount of Cl_2?

20 In the reaction

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

concentrated sulfuric acid is used as a catalyst and as a dehydrating agent. What effect will the addition of sulfuric acid have on the system at equilibrium?

EXPERIMENT 7.1

Simple experiments to illustrate Le Chatelier's Principle
The effects of (i) concentration changes, and (ii) temperature changes, on the equilibrium between Fe^{3+} and $Fe(CNS)^{2+}$

(i) A solution of iron(III) chloride reacts with a solution of thiocyanate ions as follows:

$$Fe^{3+}_{(aq)} + CNS^{-}_{(aq)} \rightleftharpoons Fe(CNS)^{2+}_{(aq)}$$

yellow red

Adding hydrochloric acid reduces the concentration of Fe3+ by forming a complex ion containing iron and chlorine. This causes a shift of equilibrium to the left. The equilibrium can be shifted to the right-hand side by adding some potassium thiocyanate solution. This experiment is used to demonstrate the effects of concentration changes on an equilibrium mixture.

Chemicals needed	**Equipment needed**
Concentrated hydrochloric acid	Boiling tubes and racks
Iron(III) chloride solution (0.01 M)	Dropping pipettes
Potassium thiocyanate solution (0.01 M)	Safety glasses

Procedure:

NB: Wear your safety glasses.

1. Mix together about 5 cm^3 respectively of solutions of iron(III) chloride and potassium thiocyanate in a beaker. Note the formation of the red complex. What does the fact that the red colour predominates tell us about the equilibrium?
2. Divide the mixture into three portions in separate boiling tubes. Keep one of these as a control.
3. Using a fume cupboard, add some concentrated hydrochloric acid to the second tube until the red colour disappears. Explain why this happens.
4. Add an equivalent amount of water to the third tube, and compare. This comparison should indicate that the extent of lightening of the colour is not due to a diluting effect.
5. To the second tube, add some potassium thiocyanate solution. Describe and explain what happens.

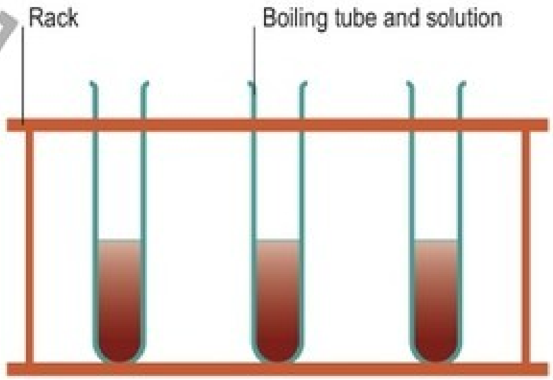


Figure 7.15

(ii) In the equilibrium

$$Fe^{3+}_{(aq)} + CNS^{-}_{(aq)} \rightleftharpoons Fe(CNS)^{2+}_{(aq)}$$

yellow red

the forward reaction is exothermic. If the temperature is lowered the equilibrium moves in the exothermic direction, increasing the amount of $Fe(CNS)^{2+}$ present and the red colour darkens. If the temperature is raised the equilibrium moves in the endothermic direction, increasing the amount of Fe^{3+} present and the red colour lightens before turning yellow.

Chemicals needed	**Equipment needed**
Concentrated hydrochloric acid	Boiling tubes and racks
Iron(III) chloride solution (0.01 M)	Dropping pipettes
Potassium thiocyanate solution (0.01 M)	Safety glasses
Ice-water	250 cm^3 beaker
	Hot plate

Procedure:

NB: Wear your safety glasses.

1. Mix together about 5 cm^3 respectively of solutions of iron(III) chloride and potassium thiocyanate in a beaker. Note the formation of the red complex. What does the fact that the red colour predominates tell us about the equilibrium?
2. Divide the mixture into three portions in separate boiling tubes. Keep one of these as a control.
3. Stand one test tube into a beaker of water that is kept at or near boiling point on a hotplate. The red colour lightens and then turns yellow. Explain why this happens.
4. Stand a second test tube into a beaker of ice-water. The red colour becomes more intense. Explain why this happens.

Metals and Non-metals

MODULE 8

Learning objectives

- Describe the atomic structure of metals and non-metals: atomic radius, ionization energy, electronegativity and crystal types 10.2.1.11
- Predict periodic trends in properties of metals and non-metals and their compounds 10.2.1.12
- Describe general properties of metals and non-metals 10.2.1.13
- Understand the structure of the reactivity series of metals 10.2.1.14
- Complete chemical equations for reactions involving metals and non-metals 10.2.1.15
- Investigate the chemical reactivity of metals, non-metals and metalloids 10.2.1.16
- Describe occurrence of metals and non-metals and their compounds in nature 10.2.1.17
- Consider the ecological impact of certain metals and non-metals on the environment 10.4.1.1

In Modules 1 and 4 we considered features of the atomic structure of elements and trends in groups and across periods of elements in the periodic table. In this module we consider further these kinds of distinctions in terms of the basic differences between metals and non-metals.

8.1 Physical properties of metals and non-metals

The properties of metals are very different from those of non-metals. For example, metals are **malleable**, which means they may be bent or pressed into different shapes. Metals are also **ductile**, and can be stretched to form thin wires.

The crystal lattice structure of metals represented in Figure 8.1 shows that metallic crystals are arranged in close-packed, regular patterns of positive ions bound together by delocalised electrons. This makes them both good thermal and electrical conductors and results in metals having typically high melting points.

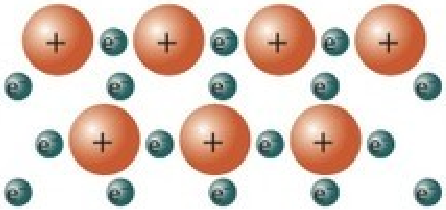


Figure 8.1
Metallic bonding

Figure 8.2
Metallic elements. The piece of jewellery is made of silver (Ag), the balls are nickel (Ni), the rod is iron (Fe), the strip is copper (Cu), the black lump is manganese (Mn) and the grey lump is cobalt (Co)

The non-metals in the periodic table are shown in Figure 8.3 below. There are twenty-one non-metals altogether.

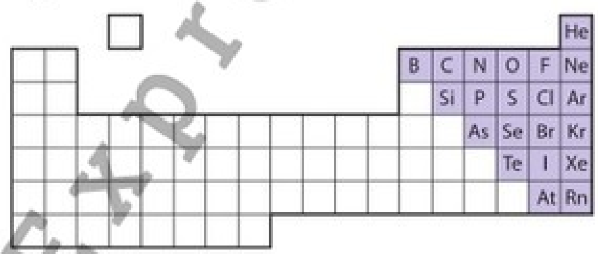


Figure 8.3
Periodic table for the non-metals

Many of the non-metals are liquids or gases at STP but the molecular crystal lattice structure of a non-metal solid like iodine shows clear differences with metals.

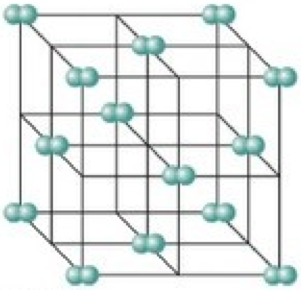


Figure 8.4
The iodine crystal with the lattice points occupied by molecules of iodine

The bonds in such crystals are relatively weak, making them brittle in a solid state and poor conductors of electricity with relatively low melting points. The weaker bonds of non-metals generally result in low melting and boiling points.

Non-metal	Melting point °C	Boiling point °C
Sulfur	113	445
Oxygen	−218	−183
Chlorine	−101	−35
Helium	−272	−269
Neon	−249	−248

Table 8.1
The melting and boiling points of some non-metals

Figure 8.5
Non-metallic elements. Clockwise from top left: sulfur (S), bromine (Br), phosphorus (P), iodine (I) and carbon (C)

Carbon in its different covalent macromolecular crystal forms represents an exception to these typical properties of non-metals. In its graphite form, it is a good conductor of electricity and in its diamond form it is extremely strong with a very high melting point.

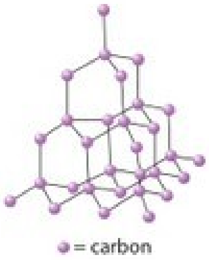


Figure 8.6
Diamond

The table below summarises the main differences in physical properties between metals and non-metals.

Physical properties of metals	Physical properties of non-metals
Most metals are hard	Some solid non-metals are hard but brittle, and have relatively low melting points
Most metals have lustre	Non-metals do not have lustre
Metals are malleable and ductile	Non-metals are neither malleable nor ductile
Metals are good conductors of heat and electricity	Non-metals are good insulators

Table 8.2

8.2 Chemical properties of metals and non-metals and periodic trends

Trends in the periodic table apply both to moving down groups and across the table from left to right or vice-versa. In terms of characterising trends between metals, transition metals and non-metals, it is mainly the trends going across the table that we will focus on.

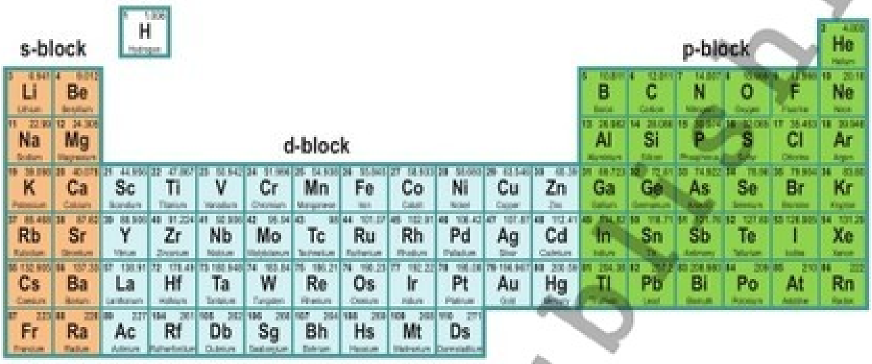
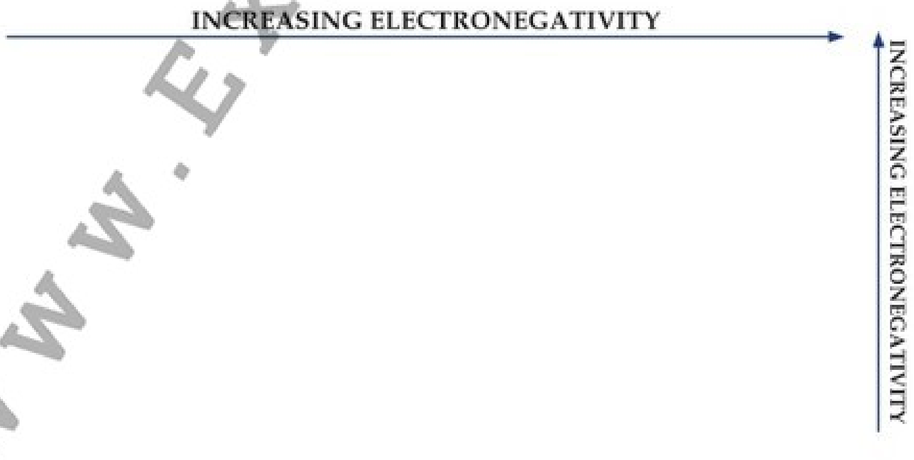


Figure 8.7

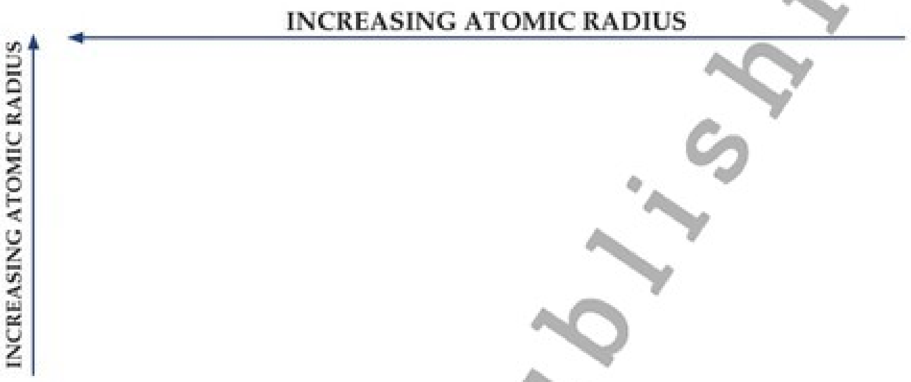
Electronegativity

Excluding the noble gases, which have complete valence shells, the trend in electronegativity values across the periodic table is relatively clear. The metals on the left-hand side of the table, generally lose electrons when forming bonds since their outer valence shells are less than half-full. The converse is true of the non-metals on the right-hand side of the table which tend to gain electrons in reactions. Electronegativity thus increases from left-right across the table and, as we saw, in Module 4, decreases going down groups as the atomic radii of elements increase, with the addition of extra energy levels, and consequent extra screening, meaning less attraction between the nucleus and the outermost electrons. Trends in electronegativity can thus be represented ad follows:



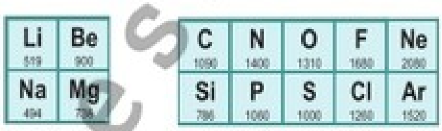
Atomic radius

We have seen that atomic radii increase going down groups, but they decrease moving across the table from left to right [from metals to non-metals]. The screening effect of the inner levels remains the same as there are the same number of levels within the period but the atomic radius decreases on going from left to right, because of the increasing nuclear charge, which exerts a greater attractive force on the outer electrons. The trend can be represented thus:



Ionisation energies

The first ionisation energy values shown below, which represent the minimum energy in kilojoules required to remove the most loosely bound electron from each isolated atom, reflect the general increase in ionisation energies from left to right across the table – highlighting the higher ionisation energies of non-metals.



Li 519	Be 900	C 1090	N 1400	O 1310	F 1680	Ne 2080
Na 494	Mg 738	Si 786	P 1060	S 1000	Cl 1260	Ar 1520

Figure 8.8

This is due to the increase in nuclear charge across the period caused by the addition of protons in each successive element and the decrease in the size of atomic radii.

QUESTIONS

1 Explain the nature of the metallic bond.
2 How is the crystal structure of carbon different to that of other non-metals?
3 Identify three contrasting physical properties of metals and non-metals.
4 Explain the general trends moving from left to right across a period in:
   a) atomic radius b) electronegativity c) ionisation energies

8.3 Reactions of metals and non-metals

Trends in electronegativity are often good indicators of the type of bonding and the physical states of non-metal compounds. As we have seen, non-metals generally have higher electronegativities than metals, and thus compounds formed between non-metals and metals are generally ionic in nature due to the large differences in electronegativity between them. The metals form cations and the non-metals form anions, generally giving compounds which are solids.

Compounds formed of reactions between two non- metals, which generally show only small differences in electronegativity between the atoms, tend to result in covalent bonding, where electrons are shared. Such substances tend to be molecular in nature and can be gases, liquids, or volatile solids at STP.

In terms of redox reactions, non-metals generally oxidise metals and more electronegative non-metals oxidise less electronegative non-metals or their anions. This latter behaviour is clearly seen in the halogens.

The Group VII elements can all act as oxidising agents, oxidising, for example, solutions containing sulfite ions or iron(II) ions. Fluorine is the most powerful of all oxidising agents, and oxidises chloride, bromide and iodide to the free halogens. Within the halogen group, chlorine is the next strongest oxidising agent, and is capable of releasing bromine and iodine respectively from solutions of their salts:

$Cl_{2(aq)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$
Reduction: $Cl_{2(aq)} + 2e^- \rightarrow 2Cl^-_{(aq)}$
Oxidation: $2Br^-_{(aq)} - 2e^- \rightarrow Br_{2(aq)}$
$Cl_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + I_{2(aq)}$
Reduction: $Cl_{2(aq)} + 2e^- \rightarrow 2Cl^-_{(aq)}$
Oxidation: $2I^-_{(aq)} - 2e^- \rightarrow I_{2(aq)}$

Bromine can release iodine from a solution of its salts
$Br_{2(aq)} + 2I^-_{(aq)} \rightarrow 2Br^-_{(aq)} + I_{2(aq)}$
Reduction: $Br_{2(aq)} + 2e^- \rightarrow 2Br^-$
Oxidation: $2I^-_{(aq)} - 2e^- \rightarrow I_2$

Solutions of chlorine, bromine and iodine are all able to oxidise iron(II) ions to iron(III) ions, and to oxidise sulfite ions to sulfate ions in aqueous solution. For example, chlorine reacts with iron(II) ions as follows:
$Cl_{2(aq)} + 2Fe^{2+}_{(aq)} \rightarrow 2Cl^-_{(aq)} + 2Fe^{3+}_{(aq)}$
Reduction: $Cl_{2(aq)} + 2e^- \rightarrow 2Cl^-_{(aq)}$
Oxidation: $2Fe^{2+}_{(aq)} - 2e^- \rightarrow 2Fe^{3+}_{(aq)}$

Chlorine reacts with sulfite ions as shown:
$Cl_{2(aq)} + SO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow 2Cl^-_{(aq)} + SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)}$
Reduction: $Cl_{2(aq)} + 2e^- \rightarrow 2Cl^-_{(aq)}$
Oxidation: $SO_3^{2-}{}_{(aq)} + H_2O_{(l)} - 2e^- \rightarrow SO_4^{2-}{}_{(aq)} + 2H^+_{(aq)}$

Bromine reacts with iron(II) ions as follows:
$Br_{2(aq)} + 2Fe^{2+}_{(aq)} \rightarrow 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)}$
Reduction: $Br_{2(aq)} + 2e^- \rightarrow 2Br^-_{(aq)}$
Oxidation: $2Fe^{2+}_{(aq)} - 2e^- \rightarrow 2Fe^{3+}_{(aq)}$

Bromine reacts with sulfite ions as shown:

$Br_{2(aq)} + SO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow 2Br^-{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$

Reduction: $Br_{2(aq)} + 2e^- \rightarrow 2Br^-{}_{(aq)}$

Oxidation: $SO_3^{2-}{}_{(aq)} + H_2O_{(l)} - 2e^- \rightarrow SO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$

Iodine reacts with iron(II) ions as follows:

$I_{2(aq)} + 2Fe^{2+}{}_{(aq)} \rightarrow 2I^-{}_{(aq)} + 2Fe^{3+}{}_{(aq)}$

Reduction: $I_{2(aq)} + 2e^- \rightarrow 2I^-{}_{(aq)}$

Oxidation: $2Fe^{2+}{}_{(aq)} - 2e^- \rightarrow 2Fe^{3+}{}_{(aq)}$

Iodine reacts with sulfite ions as shown:

$I_{2(aq)} + SO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow 2I^-{}_{(aq)} + SO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$

Reduction: $I_{2(aq)} + 2e^- \rightarrow 2I^-{}_{(aq)}$

Oxidation: $SO_3^{2-}{}_{(aq)} + H_2O_{(l)} - 2e^- \rightarrow SO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)}$

The trend in oxidising power of the halogens on going down the group is due to:

- the increase in atomic radius, which makes it more difficult for the atom to gain electrons
- the extra screening caused by the addition of extra energy levels, which has the same effect.

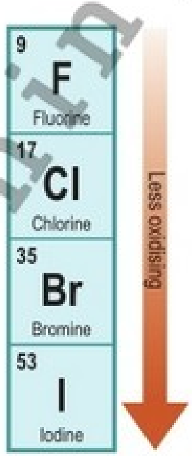


Figure 8.9
Trend in oxidising ability of the halogens

EXPERIMENT 8.1

Redox reactions of the halogens

The halogens chlorine, bromine and iodine are very reactive elements. They often react by taking an electron from another element or ion. This means that they act as oxidising agents. The smaller the halogen atom, the stronger the oxidising agent it is. In terms of oxidising power

Cl > Br > I

(a) Reactions with halides

Chemicals needed
Chlorine solution ☠ ✕
Bromine solution ☠ ⚠
Iodine solution
Sodium chloride solution
Sodium bromide solution
Potassium iodide solution

Equipment needed
Safety glasses
PVC gloves
Fume cupboard or well-ventilated room
Pasteur pipettes
Test tubes
Test tube rack
Test tube brush

Procedure

NB: Wear your safety glasses

1 Draw a table with the following headings:

Solutions added to the test tube	Observation	Conclusion
(a) Chlorine and bromide ions		
(b) Chlorine and iodide ions		
(c) Bromine and iodide ions		

2 Add 2 cm^3 of the chlorine solution and the sodium bromide solution respectively to separate test tubes and mix. Record your observations and conclusions in the table.

3 Add 2 cm^3 of the chlorine solution and the potassium iodide solution respectively to separate test tubes and mix. Record your observations and conclusions in the table.

4 Add 2 cm^3 of the bromine solution and the potassium iodide solution respectively to separate test tubes and mix. Record your observations and conclusions in the table.

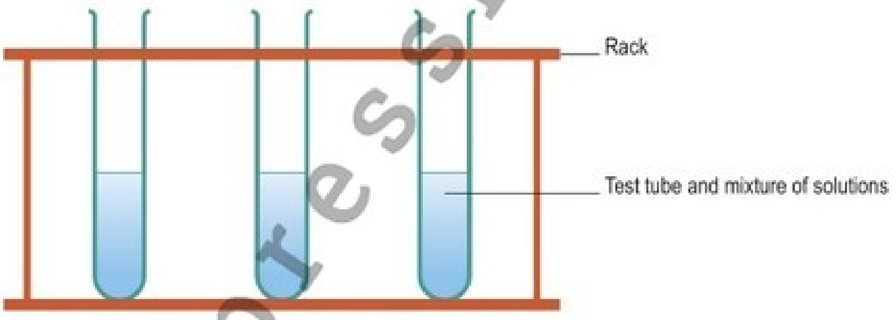


Figure 8.10

(b) Reactions with iron(II) salts and with sulfites

Chemicals needed
Chlorine solution
Iron(II) sulfate solution
Iron(III) chloride solution
Sodium sulfite solution
Sodium hydroxide solution
Silver nitrate solution
Barium chloride solution
Dilute hydrochloric acid
Dilute ammonia solution

Equipment needed
Safety glasses
PVC gloves
Fume cupboard or well-ventilated room
Pasteur pipettes
Test tubes
Test tube rack
Test tube brush

Procedure

NB: Wear your safety glasses

1 Draw a table with the following headings:

Solutions added to the test tube	Observation	Conclusion
(d) Chlorine and iron(II) sulfate solutions followed by 10 drops of sodium hydroxide solution		
(e) Chlorine and sodium sulfite solutions followed by the test for the presence of sulfate ions		

2 Add 2 cm^3 of the chlorine solution and the iron(II) sulfate solution respectively to separate test tubes and mix. Then add 10 drops of the sodium hydroxide solution to the mixture. If an orange-brown precipitate is formed, then iron(III) ions are present. Record your observations and conclusions in the table.

3 Add 2 cm^3 of the chlorine solution and the sodium sulfite solution respectively to separate test tubes and mix. Using a dropping pipette add a few drops of barium chloride solution. A white precipitate forms. Now add 2 cm^3 of dilute hydrochloric acid. If the white precipitate does not dissolve, then sulfate ions are present. Record your observations and conclusions in the table.

QUESTIONS

5 Name four solutions that can be oxidised by chlorine solution.

6 Which of these solutions can be oxidised by bromine water?

7 Which of these solutions can be oxidised by iodine solution?

8 Would you expect boiling points to increase or decrease for halogen elements moving down the group? Explain your answer.

9 Which of the halogens has the highest electronegativity of all elements?

8.4 The Electrochemical Series

When metals react chemically, their atoms tend to be oxidised, forming positive ions. Some metal atoms, such as the atoms of alkali metals, have a greater tendency to lose electrons than others, such as transition metal atoms. Therefore, alkali metal atoms are more reactive. In the **electrochemical series** the metals are arranged in order of tendency to be oxidised.

Displacement of metals

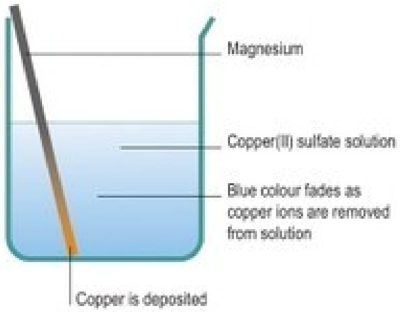


Figure 8.11
Displacement of copper by magnesium

Figure 8.12
The electrochemical series

If magnesium ribbon is dipped in copper sulfate solution, it becomes coated with copper, and the blue colour of the solution becomes paler, as the following reaction occurs:

$$Mg_{(s)} + CuSO_{4(aq)} \rightarrow MgSO_{4(aq)} + Cu_{(s)}$$

The magnesium loses electrons and is oxidised. The copper gains electrons and is reduced.

In general, a metal will displace a less reactive metal, that is, one which is below it in the electrochemical series, from a solution of its salts. The more reactive metal is oxidised, and the less reactive metal is reduced. The further apart metals are in the electrochemical series, the more readily will this type of displacement reaction occur.

Applications of Displacement Reactions

An application of this type of reaction is the use of a less valuable metal, such as scrap iron, to displace a more valuable and less reactive metal, such as copper, from a solution of its salts:

$$Fe_{(s)} + CuSO_{4(aq)} \rightarrow FeSO_{4(aq)} + Cu_{(s)}$$

EXPERIMENT 8.2

Displacement reactions of metals

A metal will displace a less reactive metal, that is, one which is below it in the electrochemical series, from a solution of its salts. The more reactive metal is oxidised, and forms a water-soluble positive ion. The less reactive metal is reduced, and the solid metal is formed.

In this experiment, zinc and magnesium respectively are reacted with a solution of copper(II) sulfate.

Equations

$Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$
$Mg_{(s)} + CuSO_{4(aq)} \rightarrow MgSO_{4(aq)} + Cu_{(s)}$

This experiment works best under acidic conditions; under these conditions, the following reactions take place simultaneously:

$Zn_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$
$Mg_{(s)} + H_2SO_{4(aq)} \rightarrow MgSO_{4(aq)} + H_{2(g)}$

Chemicals needed

Acidified copper(II) sulfate solution
Zinc powder
Magnesium ribbon

Equipment needed

Safety glasses
Test tubes
Test tube rack
Test tube brush
Pasteur pipettes

Procedure

NB: Wear your safety glasses.

1 Copy the following table:

Metal added to the test tube containing copper(II) sulfate solution	Observations	Conclusion
Magnesium		
Zinc		

2 Half fill two test tubes with the acidified copper(II) sulfate solution.

3 Add the magnesium ribbon to the solution in one test tube. Record your observations and conclusions.

4 Add the zinc powder to the solution in the other test tube. Record your observations and conclusions.

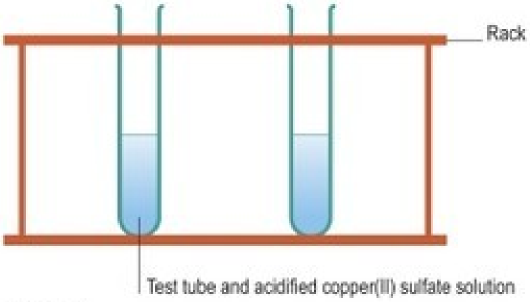


Figure 8.13

QUESTIONS

10 Zinc is above iron in the electrochemical series. What information does this statement give about the relative ability of these metals to lose electrons?

11 What happens when (a) zinc is added to silver nitrate solution (b) magnesium is added to copper sulfate solution (c) copper is added to silver nitrate solution (d) zinc is added to magnesium chloride solution? Write an equation in each case where a reaction occurs.

12 Describe an everyday application of displacement reactions of metals.

8.5 Extraction of metals

A metal's place in the electrochemical series has practical implications for how it is extracted for commercial and industrial use. Metals are found in nature in the form of metal ores: rocks containing the metal or metal compound. Extraction is the generic term used to describe one of a number of processes used to remove the metal from the other substances that it is mixed with when found in its metal ore state.

The position of a metal in the reactivity series above or below carbon, dictates whether a metal is extracted using electrolysis or reduction with carbon. Reactive metals such as aluminium, for example, are extracted by electrolysis, whereas a metal such as iron which is less reactive, is extracted through a reduction process involving carbon or carbon monoxide. This process is cheaper than electrolysis because of the ready availability of materials such as coke. Copper which is even less reactive is extracted through processes involving reactions with hydrogen.

Metals – most to least reactive	Method of extraction used
• potassium • sodium • magnesium • aluminium	Extracted by **electrolysis**
• iron • tin • lead	Extracted by reaction with **carbon** or **carbon monoxide**
• copper • gold	extracted by chemical reactions with hydrogen

Table 8.3
Reactivity and extraction method

Metals that are higher than carbon in the reactivity series have to be extracted using electrolysis. When an electric current is passed through a molten sample of a metal compound, the compound will split up and release the metal.

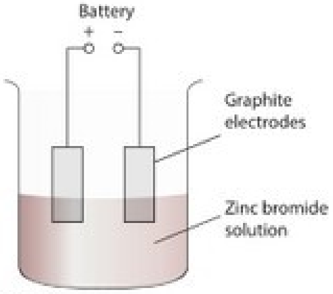


Figure 8.14

Electrolysis of aluminium

Aluminium oxide has a high melting point and to reduce costs it is dissolved in molten cryolite, an aluminium compound with a lower melting point. Even so, a high temperature is used and for safety the whole system is encased in steel.

There are several electrodes. These are conductors used to make electrical contact with some part of the circuit – the negative electrode is called a cathode, and the positive electrode is called the anode. They are made of graphite (a form of carbon) and are used to pass current through the molten aluminium oxide and cryolite.

Aluminium is separated out of the compound and falls to the bottom of the vessel from where it can be removed.

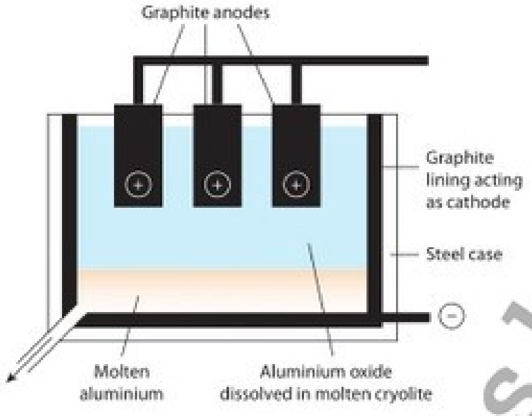


Figure 8.15
Electrolysis of aluminium

Reduction with carbon

A more reactive metal can displace a less reactive metal from its compound. This is what happens when carbon is reacted with the compounds formed by the metals below it in the reactivity series.

Figure 8.16
Extracting iron from ore

- Coke is mainly composed of carbon, and the ore is reduced by reaction with carbon:

  $Fe_2O_{3(s)} + 3C_{(s)} \rightarrow 2Fe_{(s)} + 3CO_{(g)}$
- The carbon monoxide causes further reduction in the upper, cooler regions of the furnace:

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

QUESTIONS

13 When alumina is electrolysed, what is oxidised? At which electrode does oxidation occur?

14 During the electrolysis of alumina, the following reactions occur:
Cathode: $2Al^{3+}$ (i) $+ 6e^-$
Anode: $3O^{2-}$ (ii) $- 6e^- \rightarrow 1\frac{1}{2}O_{2(g)}$
Write the balanced molecular equation for this process.

15 In the blast furnace process for the extraction of iron from iron ore, what reducing agents are used?

8.6 Occurrence of metals and non-metals in nature

Figure 8.17
Gold found as a free element in nature

A few unreactive metals, such as gold, platinum and silver are found as the metal itself rather than as a compound. Most metals, however, which typically react with oxygen, moisture, carbon dioxide or other reagents, are found in the form of compounds which are extracted from rocks (ores) using a chemical reaction. A metal ore is an ionic compound which is comprised of the metal and a non-metal. Iron, for example, occurs in ores such as haematite (impure Fe_2O_3), magnetite (impure Fe_3O_4) and iron pyrites (impure FeS). Aluminium is found in nature in aluminium oxide form (alumina) which is extracted from the ore bauxite.

The table below shows the top six metals according to approximate percentage of the Earth's crust.

Aluminium	8.1%
Iron	5%
Calcium	3.6%
Sodium	3.8%
Potassium	2.6%
Magnesium	2.1%

Table 8.4

QUESTIONS

16 Identify the ores [compounds] in which these metals are mainly found in nature and find those for which Kazakhstan is amongst the world's top ten producers.

17 Identify a company, plant or region typically associated with the mining or production of metals from these ores in Kazakhstan.

Environmental problems associated with metals result either from the extraction and production of metals and alloys or the dumping of products containing metals which can act as toxins.

If iron is being extracted from a sulfide ore, some sulfur dioxide will be formed in the blast furnace. When coke is being produced from coal, for use in the blast furnace, smoke and sulfur dioxide are formed. Emissions of these must be kept to a minimum. Fumes from a blast furnace must also be cleared of dust particles before being released into the atmosphere.

Metals with high relative atomic masses such as mercury, cadmium and lead are known as heavy metals. Quantities of these elements are sometimes dumped e.g. car batteries containing lead or dry batteries containing cadmium.

Dipositive ions of these metals, i.e. Hg^{2+}, Cd^{2+} and Pb^{2+}, sometimes get into waterways from industrial effluent, and consequently into drinking water. These elements are cumulative poisons in that frequent exposure causes a build-up in the body, with consequent serious health damage.

Before the effluent is run into a waterway, the metal ions can be removed by means of precipitation. For example, lead(II) hydroxide, $Pb(OH)_2$, is insoluble in water, so that if effluent containing Pb^{2+} ions is treated with calcium hydroxide solution, the lead will precipitate as $Pb(OH)_2$:

$$Pb^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Pb(OH)_{2(s)}.$$

Hydroxide precipitation is ineffective for mercury removal, but alternatives such as carbonate or sulfide precipitation are available. Flocculating agents are often used to increase the size of the solid particles before their removal by filtration.

Non-metals can be thought of as ever-present in nature in the elements that comprise water [hydrogen and oxygen], make up the atmosphere [mainly oxygen and nitrogen], are present in all organic compounds [carbon, hydrogen, oxygen] and comprise the majority of the Earth's crust [oxygen 46%, silicon 28%, phosphorus 1% , hydrogen 1% and fluorine 0.6%] and, given that oxygen and silicon are the most abundant elements in the Earth's crust, it is not surprising that the most common minerals are the silicates.

The carbon and the nitrogen cycles through which animals and plants use and recycle carbon dioxide and nitrogen in various ways are essential to life on Earth. The environmental health of the Earth is directly affected by the actions of the human population which impact these cycles whether it is through the release of greenhouse gases such as carbon dioxide, methane, and chlorofluorocarbons, which all contribute to global warming, or the release of gases such as sulfur dioxide from industrial emissions that contribute to acid rain.

8.7 Metals and Non-metals in biological organisms

The percentage composition of the human body is given in the table below:

ELEMENT	%	OF TOTAL BODY WEIGHT
Oxygen	65.0	
Carbon	18.5	
Hydrogen	9.5	
Nitrogen	3.2	
Calcium	1.5	
Phosphorus	1.0	
Potassium	0.4	
Sodium	0.22	
Chlorine	0.2	
Magnesium	0.1	
Sulfur	0.04	

Table 8.5

The six most common elements found in food are: carbon (C), hydrogen (H), oxygen (O), nitrogen (N), phosphorus (P) and sulfur (S) but other elements are vital in the diet for the effective functioning of organisms such as chlorine, calcium and potassium which are found in the form of dissolved salts. Each element has specific biological roles such as calcium in the strengthening of teeth and bones and chlorine in the production of hydrochloric acid in the stomach. The human organism receives these essential elements from different dietary sources and deficiency of these elements can lead to serious diseases.

QUESTIONS

18 Deficiency of which essential elements can lead to the following diseases in humans: (a) anemia (b) rickets (c) hypokalemia (d) osteomalacia?

19 Name three metals that are considered heavy metals and are considered serious toxins.

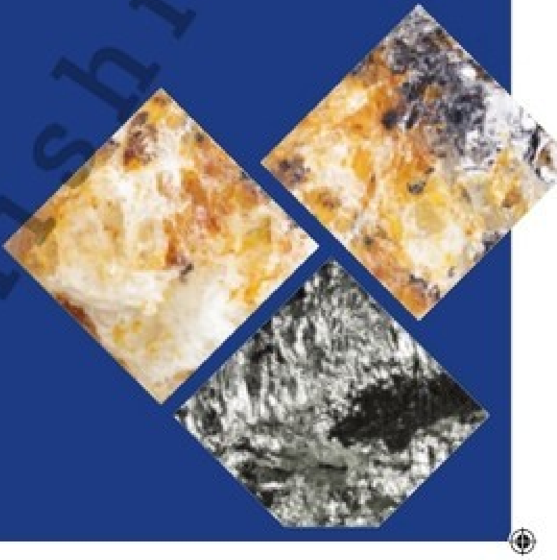
20 What is the difference between a mineral compound and an ore?

s-block Elements and their compounds

MODULE 9

s-block

Group I	Group II
3 **Li** Lithium	4 **Be** Beryllium
11 **Na** Sodium	12 **Mg** Magnesium
19 **K** Potassium	20 **Ca** Calcium
37 **Rb** Rubidium	38 **Sr** Strontium
55 **Cs** Caesium	56 **Ba** Barium
87 **Fr** Francium	88 **Ra** Radium



Learning objectives

- Explain the general properties of the s-block elements using their atomic structure 10.2.1.18
- Compare the metallic properties and reducing ability of the s-block elements and write chemical equations 10.2.1.19
- Describe ways of producing sodium, potassium and their compounds 10.2.1.19
- Explain the difference between the chemical activity of sodium, potassium and calcium in reactions with water 10.2.1.20
- Explain the biological role of compounds of sodium and potassium 10.4.1.3
- Write chemical equations, which describe the general chemical properties of calcium, magnesium and their compounds 10.2.1.22
- Investigate flame tests for sodium, potassium and calcium ions 10.2.1.23
- Explain the biological role of compounds of calcium and magnesium 10.4.1.4
- Explain what makes water hard and describe ways to "soften" hard water 10.4.1.5
- Identify natural compounds of alkali and alkaline earth metals in Kazakhstan 10.4.1.6
- Calculate mass, the numbers of moles of reactants or products, using chemical equations, which describe the genetic correlation between metals and their compounds 10.2.2.1

9.1 s-block Elements

The s-block elements of the Periodic Table cover the groups of elements where the last electron enters the outermost s-orbital. This means that the s-block covers Groups I and II as the s-orbital can accommodate only two electrons. Group I elements: lithium, sodium, potassium, rubidium, caesium and francium are known as the alkali metals because they form strongly alkaline hydroxides when they react with water. Group II elements: beryllium, magnesium, calcium, strontium, barium and radium are commonly referred to as the alkaline earth metals because they have alkaline oxides which are found in the Earth's crust.

9.2 Alkali Metals

The alkali metals are elements that have the following physical and chemical properties:

- shiny, silvery appearance
- soft, they can easily be cut with a knife
- quick to tarnish when exposed to the air due to oxidation
- stored under oil to prevent reaction with air
- highly reactive at STP
- react vigorously with water – heavier ones reacting more vigorously than the less dense ones which float on water
- readily lose their outermost electron to form cations with a charge of +1

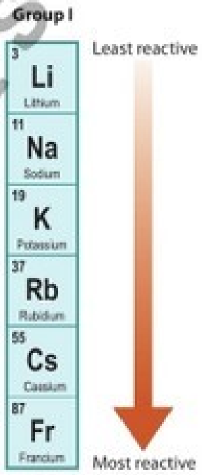


Figure 9.1
Reactivity trend in Group

9.3 Reactions of Alkali Metals

In reactions with water, the halogens and acids the alkali metals react vigorously giving off large amounts of heat and light. All the elements in Group I react with oxygen to form oxides which are characterised by their lower reactivity and duller appearance than the elements in their pure form. The oxides readily react with water to form hydroxides, which completely dissociate in water to form very strong bases with many industrial and everyday uses. Sodium hydroxide, for example, is used in oven and drain cleaners and potassium hydroxide is used as the electrolyte in alkaline batteries.

QUESTIONS

1 What reasons can you suggest for why Group I metals become more reactive moving down the group?

2 Why are Group I metals kept under oil?

3 Balance the following chemical equations involving Group I elements and compounds:

(a) $H_2SO_4 + NaOH \rightarrow Na_2SO_4 + H_2O$

(b) $KOH + H_3PO_4 \rightarrow K_3PO_4 + H_2O$

(c) $KNO_3 + H_2CO_3 \rightarrow K_2CO_3 + HNO_3$

(d) $Li + O_2 \rightarrow 2Li_2O$

9.4 Alkaline Earth Metals

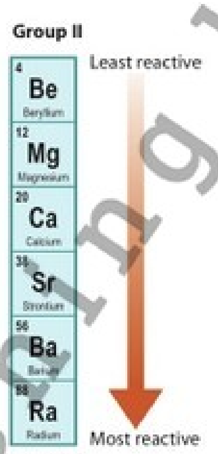


Figure 9.2
Reactivity trend in Group II

The Group II elements are called the alkaline earth elements. They are all reactive elements, with reactivity increasing down the group.

Physical properties

- They are metals which are harder than the alkali metals.
- They are shiny and silvery-white in appearance.
- They have low densities, low melting and low boiling points.

Chemical properties

- They are less reactive than the corresponding alkali metals. For example, magnesium reacts very slowly with water. Calcium reacts more quickly, but less vigorously than the corresponding alkali metal:

  Calcium + water → calcium hydroxide + hydrogen
- The alkaline earth metals have two electrons in their valence shell, so they lose two electrons to form cations with a 2+ charge.
- The alkaline metals have the second-lowest first ionization energies in their respective periods of the periodic table because of their ability to attain a full outer shell configuration by losing just two electrons. The second ionization energy of all of the alkaline metals is also relatively low.
- All isotopes of radium are radioactive.

Moving down the group the following four trends are observed

- Atomic radius increases
- First ionisation energy decreases
- Chemical reactivity increases
- Electronegativity decreases

Complete the electronic configuration column of table 9.1.

Element	Symbol	Atomic number	Electronic Configuration
Beryllium	Be	4	
Magnesium	Mg	12	
Calcium	Ca	20	
Strontium	Sr	38	
Barium	Ba	56	
Radium	Ra	88	

Table 9.1

Reactions of Alkaline Earth Metals

The alkaline earth metals react with the halogens to form ionic alkaline earth metal halides. All the alkaline earth metals except beryllium also react with water to form strongly alkaline hydroxides which must be handled carefully.

The chlorides and fluorides of all the alkaline earth metals except beryllium are ionic in nature and hence good conductors of electricity in solid as well as dissolved states. Beryllium reacts with neither water or steam and its halides are covalent.

Oxides

The oxides of alkaline earth metals can be obtained by heating the metal in oxygen or by heating their carbonates to high temperatures as in the reactions below.

$$Ca + O_2 \rightarrow CaO$$

$$CaCO_3 \rightarrow CaO + CO_2$$

Their oxides are highly stable white crystalline solids with strong crystal lattice structures.

QUESTIONS

4 What is the electronic configuration structure for magnesium and strontium?

5 Give two ways in which beryllium differs from the other alkaline earth metals.

6 For which alkaline earth metal are all isotopes radioactive?

7 Explain why the oxides of alkaline earth metals form strong crystal lattice structures.

8 Choose one alkaline earth metal and a corresponding Group I metal and prepare a short presentation for the group, on their comparative physical and chemical properties.

As a result of their low ionization energies, all Group I and Group II elements tend to lose their valence electrons and act as strong reducing agents. Group I elements are stronger reducing agents than Group II elements and the relative strengths as the most powerful reducing agents are reflected in a table such as the one below [Standard Electron Potentials].

9.5 Standard Electron Potentials of Group I and II elements

Standard Electron Potentials are a way of comparing the relative potential of elements to lose electrons to form ions in solution.
The measurement represents:

- the potential set up when an electrode is in contact with one molar solution of its own ions at 298 K
- a potential measured against the standard electrode potential of hydrogen which is taken as zero.

Negative values on this scale indicate how readily the element loses electrons and forms ions; positive values represent that the element does not readily give up its electrons to form ions in solution.

Element	Reduction Half-Equation	Standard Electron Potential
Lithium	$Li^{+}_{(aq)} + e^{-} \rightarrow Li_{(s)}$	-3.04
Potassium	$K^{+}_{(aq)} + e^{-} \rightarrow K_{(s)}$	-2.92
Barium	$Ba^{2+}_{(aq)} + 2e^{-} \rightarrow Ba_{(s)}$	-2.90
Calcium	$Ca^{2+}_{(aq)} + 2e^{-} \rightarrow Ca_{(s)}$	-2.84
Sodium	$Na^{+}(aq) + e^{-} \rightarrow Na_{(s)}$	-2.71
Magnesium	$Mg^{2+}_{(aq)} + 2e^{-} \rightarrow Mg_{(s)}$	-2.37
Aluminium	$Al^{3+}_{(aq)} + 3e^{-} \rightarrow Al_{(s)}$	-1.68
Zinc	$Zn^{2+}_{(aq)} + 2e^{-} \rightarrow Zn_{(s)}$	-0.76
Iron	$Fe^{2+}_{(aq)} + 2e^{-} \rightarrow Fe_{(s)}$	-0.44
Nickel	$Ni^{2+}_{(aq)} + 2e^{-} \rightarrow Ni_{(s)}$	-0.26
Tin	$Sn^{2+}_{(aq)} + 2e^{-} \rightarrow Sn_{(s)}$	-0.14
Lead	$Pb^{2+}_{(aq)} + 2e^{-} \rightarrow Pb_{(s)}$	-0.13
Hydrogen	$2H^{+}_{(aq)} + 2e^{-} \rightarrow H_{2(g)}$	+0.00
Copper	$Cu^{+}_{(aq)} + e^{-} \rightarrow Cu_{(s)}$	+0.52
Iodine	$I_{2(aq)} + 2e^{-} \rightarrow 2I^{-}_{(aq)}$	+0.54
Mercury	$Hg_2^{2}+ + 2e^{-} \rightarrow 2Hg_{(l)}$	+0.79
Silver	$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$	+0.80
Bromine	$Br_{2(aq)} + 2e^{-} \rightarrow 2Br^{-}_{(aq)}$	+1.07

Table 9.2
Standard Electron Potentials

QUESTIONS

9 What are standard reduction potentials measured relative to?
10 What does a negative value on this scale indicate?

9.6 Extraction of Sodium – the Downs Cell

In Module 8, we saw that how metals are extracted from their ores depends on their position in the reactivity series.

The extraction of metals such as sodium and potassium, which are near the top of the electrochemical series, is carried out by **electrolysis**. This is because these metals have particularly stable ores.

In such processes, salts such as potassium chloride are heated to a molten form in which they will conduct electricity and then electrolysis is used to separate the elements in the ionic compound. Below we consider this process in more detail using the example of sodium chloride.

Sodium is extracted from its ores by the electrolysis of molten sodium chloride using the Downs cell (Figure 9.3).

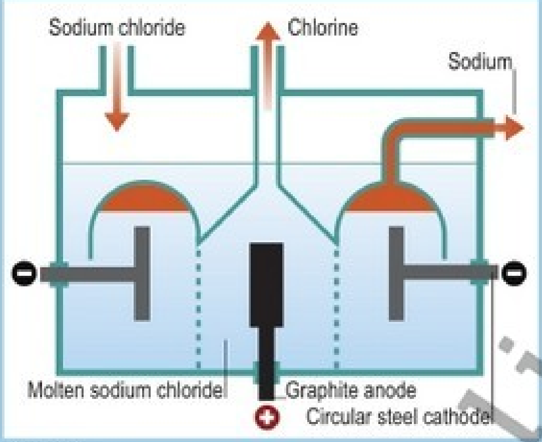


Figure 9.3
The Downs cell

- The electrolyte is a molten mixture of sodium chloride and calcium chloride. The calcium chloride is added to reduce the melting point of the mixture – this reduces the amount of electricity needed.
- Steel cathodes are used.
- The anodes are made of inert carbon, so that the chlorine gas formed at the anode during the electrolysis will not react with them.
- The steel gauze, which separates the two electrode compartments, prevents the sodium formed at the cathode from reaction with this chlorine.

At the cathode, the reaction is

$$Na^{+}_{(l)} + e^{-} \rightarrow Na_{(l)}$$

The molten sodium formed floats on the electrolyte, and is removed using the collecting pipe. The sodium is 99.5 % pure, the main impurity being calcium.

The anode reaction is

$$Cl^{-}_{(l)} - e^{-} \rightarrow ½Cl_{2(g)}$$

i.e. producing the important by-product, chlorine gas, which is removed through the hood.

The overall reaction in the Downs cell is

$$NaCl_{(l)} \rightarrow Na_{(l)} + ½Cl_{2(g)}$$

Uses of sodium

Sodium is the most widely used of the alkali metals. Sodium vapour is used in street lighting. Sodium, alloyed with potassium, is used as a coolant in some nuclear reactors.

QUESTIONS

11 In the extraction of sodium in the Downs cell

(a) Why is calcium chloride added?

(b) What is reduced?

(c) At what electrode does reduction occur?

(d) What type of anode is used?

12 (a) In the Downs cell, how are the sodium and chlorine formed prevented from recombining?

(b) Why does the molten sodium formed in the Downs cell float on the electrolyte?

13 In what forms does sodium occur naturally? What is the element used for?

14 Complete the balanced chemical equation for each reaction:

(a) $2NaCl \rightarrow$ ____________________

(b) $2KCl \rightarrow$ ____________________

9.7 Flame Tests

In Module 4, we saw how Group I elements reacted violently with water. Here we consider how the salts of Group I and Group II can be identified by the colour they emit in a flame.

Emission and Absorption of Group I and Group II Elements by Light

When atoms of an element are supplied with energy under certain conditions, they emit light. The energy may be supplied by a flame, as in Experiment 9.1. Many elements and their salts, when vaporised in a flame, emit light. As indicated in Table 9.3, the light emitted has a colour characteristic of the particular element.

Element	Flame colour
Barium	Yellow-green
Lithium	Deep red
Potassium	Lilac
Sodium	Yellow
Strontium	Red

Table 9.3

EXPERIMENT 9.1

Flame tests (Li, Na, K, Ba, Sr)

When salts of the metals lithium, barium, potassium, copper, strontium and sodium are heated in the flame of a Bunsen burner, colours characteristic of the particular element are given off. Platinum or nichrome wire, or wooden splints (e.g. lollipop sticks) soaked overnight in water, can be used in this experiment.

Method 1 – using a platinum wire

Chemicals needed

Lithium chloride
Sodium chloride
Potassium chloride
Barium chloride
Strontium chloride
Concentrated hydrochloric acid

Equipment needed

Platinum (or nichrome) wire held in glass rod
Bunsen burner
Five small beakers
Test tubes
Pestle and mortar

Procedure

NB: Wear your safety glasses

1. Clean the platinum wire using concentrated hydrochloric acid in a test tube. This should be done in the fume cupboard.
2. Crush the salt to be tested with a pestle and mortar.
3. Dip the platinum wire in concentrated hydrochloric acid and then in the salt to be tested.
4. Place the platinum wire in the flame of the Bunsen burner (Figure 9.4) and note the colour given off.
5. Repeat the experiment for each of the other salts. Again, note the colour in each case.

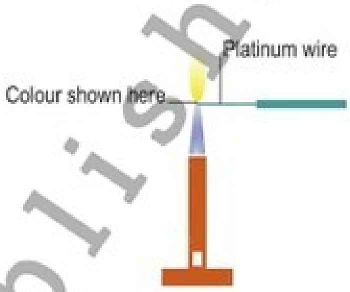


Figure 9.4

Method 2 – using a soaked wooden splint

You will need a wooden splint for each sample to avoid cross-contamination.

Chemicals needed

Lithium chloride
Sodium chloride
Potassium chloride
Barium chloride
Strontium chloride

Equipment needed

Bunsen burner
Five small beakers
Test tubes
Pestle and mortar
Wooden splints soaked overnight

Procedure

NB: Wear your safety glasses

1. Crush the salt to be tested with a pestle and mortar.
2. Dip the soaked splint in the salt to be tested.
3. Place the splint in the flame of the Bunsen burner and note the colour given off.
4. Repeat the experiment for each of the other salts. Again, note the colour in each case.

The colours that particular elements, such as strontium and barium, emit in a flame are often seen in firework displays. For example, strontium nitrate is used to give a red colour in fireworks, while barium nitrate gives a green colour.

A discharge tube is a long glass tube fitted with a metal electrode at each end, with a gas inside at a very low pressure. If an element is

Figure 9.5
Fireworks display

a gas, like neon, or is easily vaporised, like mercury or sodium, it will emit light of a characteristic colour when placed in a discharge tube at low pressure and subjected to a high voltage.

For example, a sodium discharge tube emits yellow light when subjected to a high voltage. Yellow street lights are a type of discharge tube containing sodium vapour.

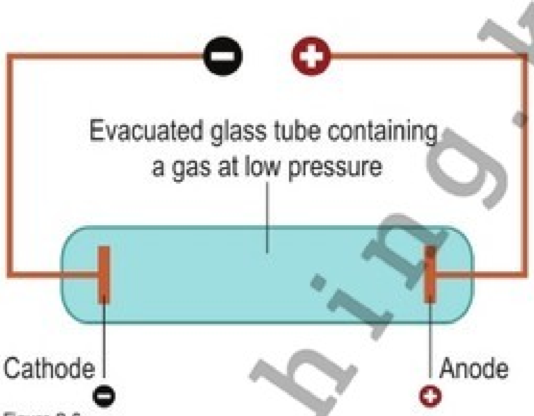


Figure 9.6
Discharge tube

QUESTIONS

15 Describe two methods by which the light emitted by an element can be observed.

16 Name a metal that gives off a lilac colour in a flame test.

17 What element is used in yellow street lights?

18 Work in groups. Identify a Group II compound commonly used in:

- (a) aluminium alloys
- (b) the making of cement
- (c) icy weather on the roads
- (d) medical uses with x-rays
- (e) removing oxide impurities in the steel industry
- (f) reducing the acidity of soil
- (g) electrical insulation

9.8 Biological roles of Group I and Group II elements

Magnesium, calcium, sodium and potassium are essential minerals and have various roles in living organisms.

Magnesium is an essential element of some enzymes and is important in the functioning of neuromuscular systems. Calcium is needed to build strong bones and teeth. It is also an important chemical in physiological processes such as blood clotting, muscle contraction, and nerve-cell communication. A dietary intake of calcium which is considerably below recommended levels may impact on the development of bones and lead to diseases such as osteoporosis. Bones increase in size and mass during childhood and adolescence, which means that a healthy intake of calcium and vitamin D are particularly important.

Sodium is vital in the regulation of blood volume and blood pressure in humans and sodium ions and potassium ions are involved in the functioning of neurons and osmoregulation between cells and extracellular fluid through a mechanism known as the Na^+/K^+ pump.

A stimulus triggers both electrical and chemical changes in the neuron. There are different ions on either side of the cell membrane. The exterior side has sodium ions that are positively charged and are more in number. The interior side of the cell is negatively charged with more potassium ions.

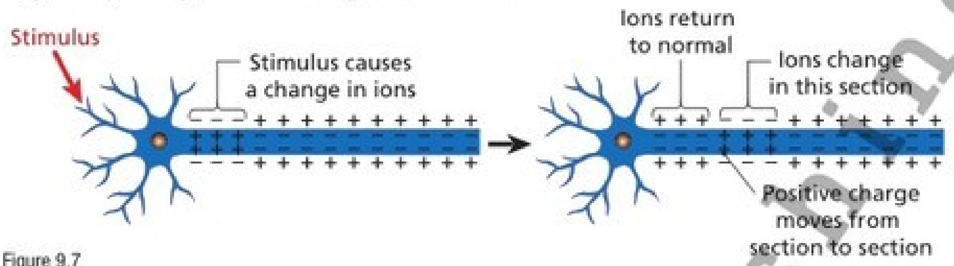


Figure 9.7
Transmission of nerve impulses

Due to this difference in the charges, there is an electrochemical difference. The generation of a nerve impulse causes a change in the permeability of the cell membrane. The sodium ions flow inside and potassium ions flow outside, causing a reversal of charges. The cell is now depolarised. This depolarisation results in an action potential which causes the nerve impulse to move along the length of the axon as shown in Figure 9.7.

Potassium also has important roles in cell enzyme function and protein synthesis and strontium is important in aquatic life as part of the exoskeletons of corals.

Figure 9.8

Beyond these physiological roles in organisms, the salts of Group I and Group II elements are involved in the phenomenon known as the hardness of water.

9.9 Hardness in water

Hard water is water that will not easily form a lather with soap.

Water is said to be hard when it is difficult for it to form a lather with soap. Hardness is caused by dissolved calcium and magnesium salts, e.g. calcium sulfate, $CaSO_4$, magnesium sulfate, $MgSO_4$, calcium chloride, $CaCl_2$, magnesium chloride, $MgCl_2$, calcium hydrogencarbonate, $Ca(HCO_3)_2$, and magnesium hydrogencarbonate,

$Mg(HCO_3)_2$. In effect, hardness in water is caused by calcium and magnesium ions, $Ca^{++}_{(aq)}$ and $Mg^{++}_{(aq)}$.

Soap molecules are the sodium or potassium salts of long chain carboxylic acids such as stearic acid, e.g. sodium stearate, $C_{17}H_{35}COONa$. When soap dissolves in water, the sodium ion Na^+ immediately dissociates from the stearate ion $C_{17}H_{35}COO^-$:

$$C_{17}H_{35}COONa_{(s)} + \text{water} \rightarrow C_{17}H_{35}COO^-_{(aq)} + Na^+_{(aq)}$$

This process releases the stearate ion, which is the active part of soap. If the water is hard, i.e. containing calcium or magnesium ions, these ions will immediately precipitate with the dissolved stearate ions forming insoluble calcium stearate or magnesium stearate. For example, with calcium ions

$$Ca^{++}_{(aq)} + 2C_{17}H_{35}COO^-_{(aq)} \rightarrow (C_{17}H_{35}COO)_2Ca_{(s)}$$

These precipitates appear as an unsightly scum in the water. Furthermore, the effect is to remove the stearate ions from the solution so that they are no longer available to produce lather and act as soap.

If soap is continuously added to the water, all of the calcium and magnesium ions will eventually be precipitated with stearate ions, and then soap molecules will at last be available to form a lather. However, the presence of scum may be unacceptable, and a great deal of soap will have been wasted in reaching this stage.

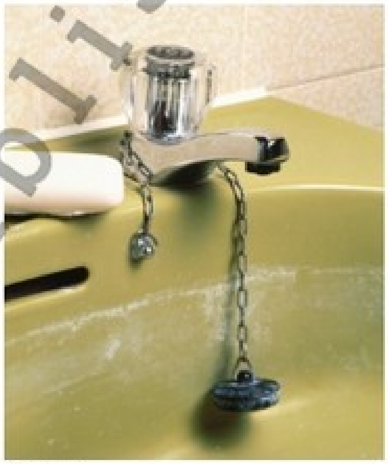


Figure 9.9
Soap scum formed around a sink

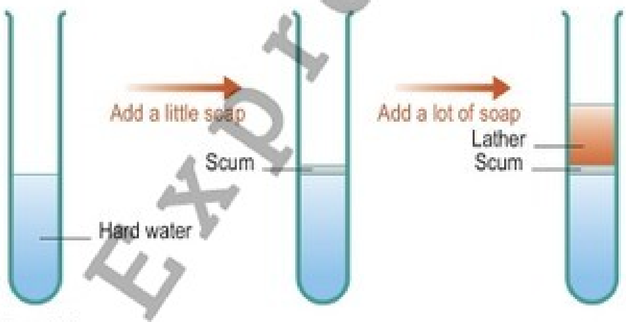


Figure 9.10
The effect of adding soap to hard water

To avoid these problems, methods of removing hardness, i.e. softening the water, may be used, such as ion exchange and distillation. All methods involve removing the calcium and magnesium ions from the water, so as to prevent them from precipitating with the soap anions.

Hardness caused by dissolved calcium hydrogencarbonate, $Ca(HCO_3)_2$, and magnesium hydrogencarbonate, $Mg(HCO_3)_2$, is different to that caused by other salts. It can be removed by **boiling** the water. Such hardness is said to be **temporary**. Hardness caused by salts other than calcium hydrogencarbonate or magnesium hydrogencarbonate cannot be removed by boiling, and is said to be **permanent**.

Temporary hardness is hardness in water that can be removed by boiling.

Causes of temporary hardness

Temporary hardness is found in parts of the country where limestone, i.e. calcium carbonate, $CaCO_3$, is found in the earth. As calcium carbonate is insoluble in water, its calcium ions are not immediately available to cause hardness. However, reactions occur involving atmospheric carbon dioxide and rainwater that release calcium ions from calcium carbonate into the water, resulting in hardness.

As rain falls, the water comes in contact with carbon dioxide in the atmosphere. Carbon dioxide is fairly soluble in water.

$$CO_{2(g)} + \text{excess } H_2O_{(l)} \rightarrow CO_{2(aq)}$$

Some of this solution reacts with the water forming the weak acid, carbonic acid, H_2CO_3.

$$CO_{2(aq)} + H_2O_{(l)} \rightarrow H_2CO_{3(aq)}$$

The result is that a dilute solution of carbonic acid falls on the ground and seeps into the earth. In limestone regions, the calcium carbonate on or in the earth reacts with the carbonic acid forming soluble calcium hydrogencarbonate.

$$H_2CO_{3(aq)} + CaCO_{3(s)} \rightarrow Ca(HCO_3)_{2(aq)}$$

Unlike calcium carbonate, calcium hydrogencarbonate is soluble in water and so the presence of dissolved calcium ions now means that the water is hard. Whether from surface or underground streams and rivers, the water may end up in domestic or industrial supplies, causing problems that include waste of soap and scum formation.

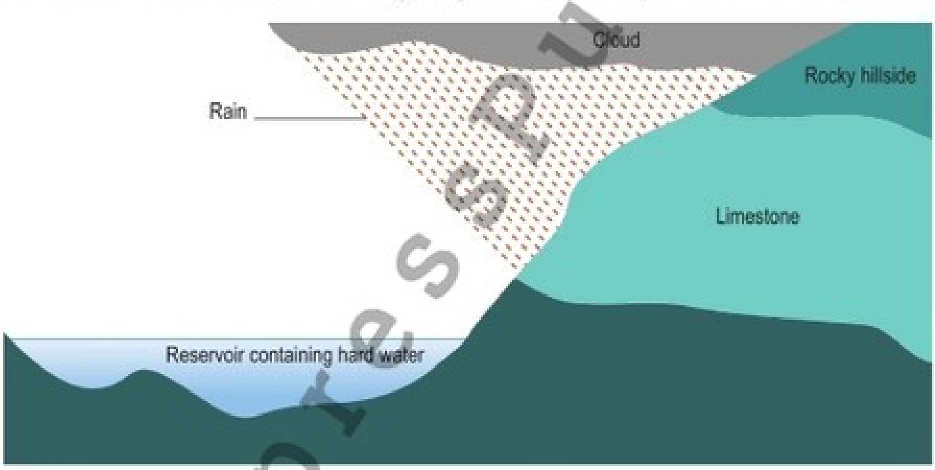


Figure 9.11
Rainwater reacts with limestone to form a soluble product which makes the water in the reservoir hard

Removing temporary hardness

Temporary hardness may be removed by ion exchange and by distillation. Unlike permanent hardness, it may also be removed by boiling. If a hydrogencarbonate is heated, it decomposes and becomes a carbonate, with carbon dioxide and water eliminated.

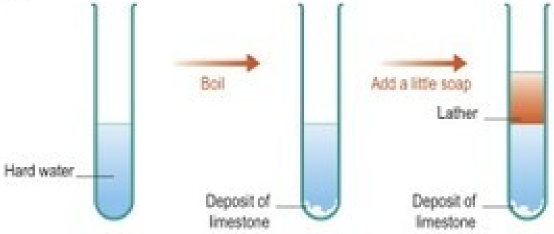


Figure 9.12
Boiling water that contains temporary hardness softens the water

If water containing temporary hardness, i.e. containing dissolved calcium hydrogencarbonate, is heated or boiled, the following reaction occurs:

$$Ca(HCO_3)_{2(aq)} + heat \rightarrow CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)}$$

This means that a precipitate of calcium carbonate is formed, and since the calcium ions are now combined in an insoluble substance they are no longer available to react with soap anions. Consequently the hardness is removed. An undesirable side effect of this is that the calcium carbonate precipitate can adhere to the inside surfaces of the vessel involved, perhaps a kettle or central heating pipes or boiler. The build-up of this substance, called limescale, can cause problems such as wasting heat, or even explosions, due to pipes becoming completely clogged.

Figure 9.13
Boiling hard water in a kettle causes a build-up of limescale on the inside of the kettle

DEMONSTRATION 9.2

Tests on scale deposits in a kettle

Chemicals needed
Dilute hydrochloric acid solution
Methanoic acid solution (40%) or commercial kettle descaler
Vinegar or ethanoic acid solution (5%)
Water
Limescale
Limewater

Equipment needed
Test tubes
PVC tubing
Single-holed rubber stopper
Safety glasses

Procedure

NB: Wear your safety glasses

1. Place a small quantity of limescale in a test tube.
2. Add 5 cm^3 of dilute hydrochloric acid.
3. Quickly connect the test tube to a test tube containing 2 cm^3 of limewater, to test any gas evolved.
4. Repeat the experiment using methanoic acid, vinegar and water in turn, instead of hydrochloric acid.
5. Record your observations in a table and write a conclusion.

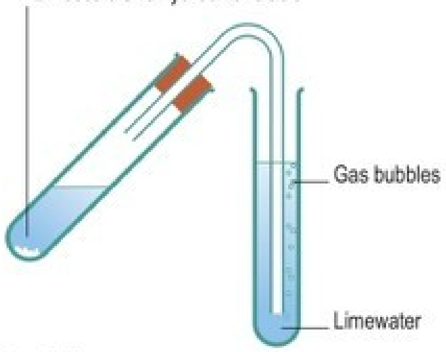


Figure 9.14

Reagent	Effect on limewater	Gas evolved

Causes of permanent hardness

Permanent hardness is caused by any source of calcium ions other than calcium hydrogencarbonate, and by sources of magnesium ions other than magnesium hydrogencarbonate. Normally the chlorides and sulfates of calcium and magnesium cause permanent hardness. For example, water acquires permanent hardness by flowing through rocks such as gypsum, which is mainly calcium sulfate.

Permanent hardness is hardness in water that can only be removed by methods other than boiling (such as ion exchange and distillation).

QUESTIONS

19 Which two types of ion create the opposite charge characteristic of a neuron's membrane?

20 Which element is important in the exoskeleton of hard coral?

21 A lack of which element can lead to osteoporosis?

22 What are the disadvantages of hard water?

23 How does water acquire temporary hardness?

24 What causes permanent hardness in water?

25 Explain why limescale forms on the inside of a kettle in which water containing temporary hardness is boiled.

26 Describe a test that can be carried out on limescale.

27 (i) Which of the following salts causes hardness in water: (a) sodium hydrogencarbonate (b) calcium hydrogencarbonate (c) magnesium sulfate (d) potassium sulfate (e) calcium chloride (f) magnesium hydrogencarbonate (g) sodium chloride (h) calcium sulfate?

(ii) Which of these salts causes temporary hardness?

9.10 Mineral deposits, mining and metallurgical industries in Kazakhstan

The mining of mineral deposits and related metallurgical industries in the areas of ferrous, non-ferrous and precious metals form a major part of the economy of Kazakhstan. Long-standing and new areas of mineral exploitation relating to the metallurgical sector include the mining of magnesite from which magnesium is obtained and in the fertiliser industry include the mining of sylvinite and polyhalite – sedimentary rocks from which the minerals sylvite (KCl, or potassium chloride), halite

(NaCl, or sodium chloride) and sulfates of potassium and calcium can be obtained. All of these minerals are used in the production of the fertilizer potash. Kazakhstan has large reserves of such minerals.

Major sites of magnesite deposits in Kazakhstan are in areas around the Aral and Caspian seas and major deposits of sylvinite and polyhalite for the production of potash are the Zhilyanskoe deposit in the Aktobe region in the northeast of the country and the Chelkarskaya deposit in the west of the country 100 km to the south of Uralsk.

Figure 9.15
Open-pit mine

Most of Kazakhstan's mines are open-pit ones, and developing and future projects are likely to exploit deeper underground mining as well.

9.11 Stoichiometric calculations

Empirical formulas from combination data

The empirical formula of a compound such as magnesium oxide that is formed by the direct combination of the two elements may be found as shown in Example 9.1.

EXAMPLE 9.1

When 0.72 g of magnesium is heated in excess oxygen, 1.20 g of magnesium oxide is formed. What is the empirical formula of magnesium oxide?

Answer

Mass of magnesium consumed = 0.72 g
Mass of oxygen consumed = (1.20 – 0.72) g = 0.48 g
Moles of magnesium atoms consumed = 0.72 / 24 = 0.03
Moles of oxygen atoms consumed = 0.48 / 16 = 0.03
Ratio of magnesium atoms to oxygen atoms = 0.03 : 0.03 = 1 : 1
Empirical formula of magnesium oxide = MgO

Percentage Mass by composition

If the empirical formula of a compound is known, the percentage by mass of each element present can be calculated.

EXAMPLE 9.2

Calculate the percentage by mass of each element in sodium hydroxide (NaOH).

Answer

Moles of sodium per mole of sodium hydroxide = 1
Mass of sodium per mole of sodium hydroxide = 23 g
Molar mass of sodium hydroxide = 40 g mol^{-1}
Percentage of sodium in sodium hydroxide = 23 X 100 / 40%
= 57.5%

Moles of oxygen per mole of sodium hydroxide = 1
Mass of oxygen per mole of sodium hydroxide = 16 g
Molar mass of sodium hydroxide = 40 g mol^{-1}
Percentage of oxygen in sodium hydroxide = 16 X 100 / 40%
= 40%

Moles of hydrogen per mole of sodium hydroxide = 1
Mass of hydrogen per mole of sodium hydroxide = 1 g
Molar mass of sodium hydroxide = 40 g mol^{-1}
Percentage of hydrogen in sodium hydroxide = 1 X 100 / 40%
= 2.5%

QUESTIONS

28 Calculate the percentage by mass of each element in
  (a) sodium chloride (NaCl)
  (b) anhydrous sodium carbonate (Na_2CO_3)
  (c) potassium manganate(VII) ($KMnO_4$)
  (d) sodium hydrogencarbonate ($NaHCO_3$)
  (e) calcium hydroxide ($Ca(OH)_2$)
  (f) potassium nitrate (KNO_3)

29 The safe level of sodium intake set by a national health authority for adults is 2.4g a day. How many grams of sodium chloride can you consume and still be within these guidelines?

Calculations Based on Balanced Chemical Equations

A balanced equation for a chemical reaction gives the relative amounts of each reactant and each product involved in the reaction. Therefore, if the amount consumed of one of the reactants is known, it is possible to calculate how much of each product of the reaction is formed, and also how much of each reactant is consumed.

If the amount formed of one of the products is known, it is possible to calculate how much of each product of the reaction is formed, and also how much of each reactant is consumed. For example, in the reaction

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$$

if the amount of sodium sulfate formed is known, the amounts of sodium hydroxide and sulfuric acid respectively can be calculated. The amount of water formed can also be found.

EXAMPLE 9.3

In the reaction

$$2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$$

if 5 moles of sodium sulfate are formed, calculate:

(a) the number of moles of water formed

(b) the number of moles of sulfuric acid consumed and

(c) the number of moles of sodium hydroxide consumed.

Answer From the equation

$$\begin{array}{lcccccc}
 & 2NaOH_{(aq)} & + H_2SO_{4(aq)} & \rightarrow & Na_2SO_{4(aq)} & + & 2H_2O_{(l)} \\
 & \text{2 moles} & \text{1 mole} & & \text{1 mole} & & \text{2 moles} \\
\text{Therefore: } 5 \times & \text{(2 moles} & \text{1 mole} & & \text{1 mole} & & \text{2 moles)} \\
= & \text{10 moles} & \text{5 moles} & & \text{5 moles} & & \text{10 moles}
\end{array}$$

(a) 10 moles of water (b) 5 moles of sulfuric acid (c) 10 moles of sodium hydroxide

Calculation of masses of reactants or products from balanced chemical equations

The first step in problems of this type is to change the given quantity (mass, or volume of gas at s.t.p.) into moles. Dividing the given mass by the molar mass, or the given volume by the molar volume, does this.

EXAMPLE 9.4

Calcium reacts with water to form calcium hydroxide and hydrogen, according to the equation

$$Ca_{(s)} + 2H_2O_{(l)} \rightarrow Ca(OH)_{2(aq)} + H_{2(g)}$$

If 100 g of calcium is reacted with excess water, calculate the mass of calcium hydroxide produced.

Answer 100 g Ca = 100 / 40 moles Ca = 2.5 moles Ca

From the equation

$$\begin{array}{lccccccc}
 & Ca_{(s)} & + & 2H_2O_{(l)} & \rightarrow & Ca(OH)_{2(aq)} & + & H_{2(g)} \\
 & \text{1 mole} & & \text{2 moles} & & \text{1 mole} & & \text{1 mole} \\
\text{Therefore:} & \text{2.5 moles} & & \text{5 moles} & & \text{2.5 moles} & & \text{2.5 moles}
\end{array}$$

1 mole $Ca(OH)_2$ = 74 g $Ca(OH)_2$

2.5 moles $Ca(OH)_2$ = 2.5 × 74 g = 185 g

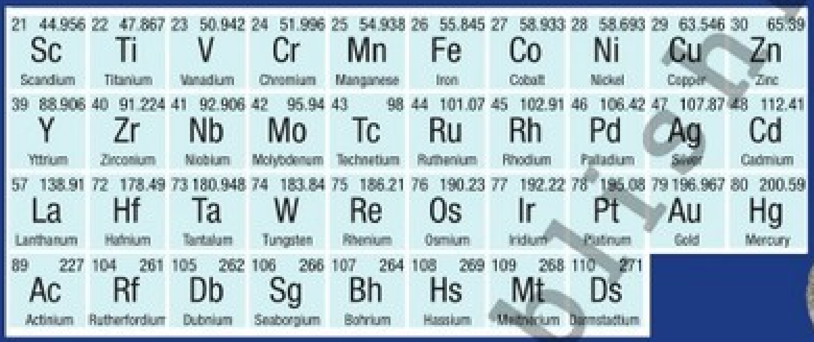
QUESTIONS

30 A solution containing 7.4 g of calcium hydroxide reacts fully with carbon dioxide according to the equation
$Ca(OH)_{2(aq)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(l)}$
What mass of calcium carbonate is formed?

31 A solution of sodium hydroxide is reacted with enough sulfuric acid solution to exactly neutralise it. The equation for the reaction is
$2NaOH_{(aq)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2H_2O_{(l)}$
On evaporation of the water, 284 g of sodium sulfate are obtained. Calculate
(a) the number of moles of sulfuric acid consumed in the reaction
(b) the number of water molecules formed
(c) the mass of sodium hydroxide used to make up the solution.

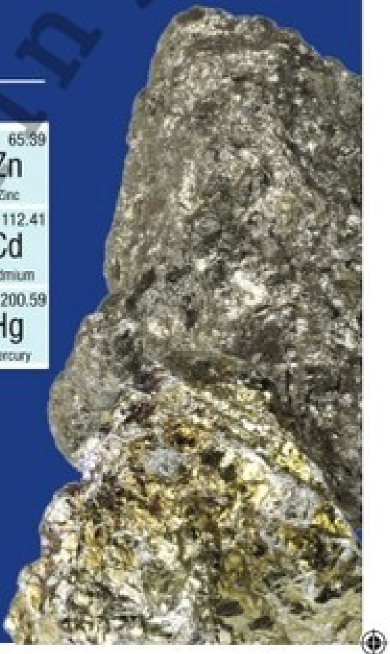
d-block Elements

MODULE 10



d-block

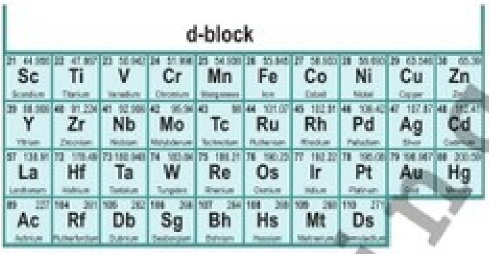
21 44.956 Sc Scandium	22 47.867 Ti Titanium	23 50.942 V Vanadium	24 51.996 Cr Chromium	25 54.938 Mn Manganese	26 55.845 Fe Iron	27 58.933 Co Cobalt	28 58.693 Ni Nickel	29 63.546 Cu Copper	30 65.39 Zn Zinc
39 88.906 Y Yttrium	40 91.224 Zr Zirconium	41 92.906 Nb Niobium	42 95.94 Mo Molybdenum	43 98 Tc Technetium	44 101.07 Ru Ruthenium	45 102.91 Rh Rhodium	46 106.42 Pd Palladium	47 107.87 Ag Silver	48 112.41 Cd Cadmium
57 138.91 La Lanthanum	72 178.49 Hf Hafnium	73 180.948 Ta Tantalum	74 183.84 W Tungsten	75 186.21 Re Rhenium	76 190.23 Os Osmium	77 192.22 Ir Iridium	78 195.08 Pt Platinum	79 196.967 Au Gold	80 200.59 Hg Mercury
89 227 Ac Actinium	104 261 Rf Rutherfordium	105 262 Db Dubnium	106 266 Sg Seaborgium	107 264 Bh Bohrium	108 269 Hs Hassium	109 268 Mt Meitnerium	110 271 Ds Darmstadtium		



Learning objectives

- Describe the location of the d-block elements in the Periodic Table using their atomic structure 10.2.1.24
- Identify the main deposits of copper, zinc, iron, chromium and their compounds in Kazakhstan 10.4.1.7
- Explain properties and uses of copper and zinc and their compounds 10.1.2.25
- Recognize test reactions for Cu^2+, Zn^{2+} 10.2.1.26
- Describe properties and uses of chromium and its compounds 10.2.1.25
- Describe physical and chemical properties of iron and its compounds and processes involved in their manufacture 10.2.1.28
- Recognise test reactions for Fe^{2+}, Fe^{3+} 10.2.1.29
- Carry out an experiment in order to obtain the hydroxides of iron (II) and (III), copper (II), zinc, chromium (III) and investigate their interaction with acids and alkalis 10.2.1.30
- Identify types of corrosion and why it occurs and explain disadvantages of corrosion 10.2.3.7
- Write balanced chemical equations for reactions involving metals and perform calculations if reactants have admixtures to calculate percentage yields 10.2.2.2

10.1 d-block elements



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds		

Figure 10.1

d-block elements with similar outer electronic configurations, but with inner orbitals incomplete that are filled, will be fairly similar chemically. This is because the inner electrons have a lesser effect on chemical properties than outer electrons have.

10.2 Transition Metals

Transition metals have variable valencies, form coloured compounds and they and their compounds have catalytic properties


Figure 10.2
Potassium manganate (VII) is a coloured compound of the transition element manganese


Figure 10.3
Manganese dioxide has catalytic activity

Iron and copper are **transition elements**:

- They form **coloured compounds**, such as iron(II) sulfate-7-water, which is green, and copper(II) sulfate-5-water, which is blue.
- They have a number of **different oxidation states (variable valencies)** – iron in its compounds usually has an oxidation state of +2 or +3, while copper in its compounds usually has an oxidation state of +2 or +1.
- They have **catalytic activity** – for example, an iron catalyst is used in the Haber process for the synthesis of ammonia, while finely divided copper is used in the industrial synthesis of methanal.

Two of the d-block elements have electronic configurations which are exceptions to the rules looked at in Module 4.

Element	'Expected' configuration	Actual electronic configuration
Copper	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^9$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
Chromium	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$

Table 10.1

These unexpected configurations are due to the extra stability in the case of chromium of a structure with half-filled 3d and 4s sublevels, and in the case of copper of a structure with a full 3d and a half-filled 4s sublevel.

10.3 Naming of Transition Metal Compounds

Oxidation numbers are used when naming compounds of transition metals systematically. In the case of a compound containing two elements only, the ending '-ide' is used as usual, and the oxidation number of the metal is indicated by a roman number in brackets after the name of that metal (for example, copper(II) oxide). If the compound contains a complex ion, for example $CuNO_3$, then the name ends with the name of the complex ion – copper(I) nitrate in this case. If the compound contains water of crystallisation, then the number of molecules of water of crystallisation is indicated at the end of the name as shown for $CuSO_4$ x $5H_2O$. The systematic name of this compound is copper(II) sulfate-5-water.

Figure 10.4
Crystals of copper(II) sulfate-5-water

Example 10.1

What is the formula of iron(III) sulfate-9-water?

Answer The iron(III) ion has a charge of +3.

The sulfate ion has a charge of –2.

The formula is $Fe_2(SO_4)_3$ x $9H_2O$

QUESTIONS

1 What is the systematic name of

(a) $CuCl_2$
(b) $CuCl$
(c) Cr_2O_3
(d) $TiCl_4$
(e) $TiCl_3$
(f) V_2O_5
(g) $NiNO_3$ x $6H_2O$
(h) $NiSO_4$
(i) $KMNO_4$
(j) K_2CrO_4?

2 What is the formula of

(a) chromium(III) chloride
(b) manganese(IV) oxide
(c) iron(II) chloride
(d) nickel(II) sulfide
(e) cobalt(II) chloride
(f) iron(II) sulfate-7-water
(g) copper(II) nitrate-3-water
(h) sodium dichromate(VI)
(i) silver(I) nitrate
(j) copper(I) sulfate

Tests for transition metals

Transition metals form coloured compounds with other elements. Most of these compounds are soluble in water and form coloured solutions. Mixing these solutions with a sodium hydroxide solution gives a transition metal hydroxide. As these hydroxides are insoluble, they form different coloured precipitates in these reactions and this provides the basis for determining which ions are present.

The table below shows the colour of the precipitates in such tests.

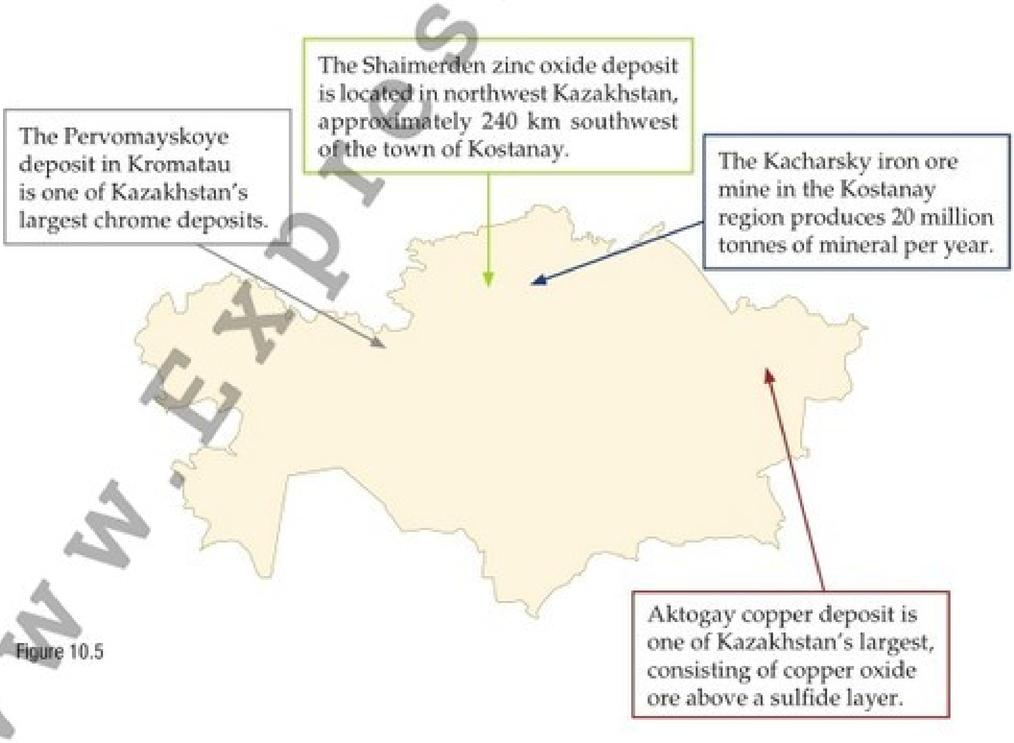
Metal ion	Test colour
Copper(II), Cu^{2+}	Blue
Iron(II), Fe^{2+}	Green, turning to orange brown
Iron(III), Fe^{3+}	Orange-brown
Zinc Zn^{2+}	White
Chromium(III) ion: Cr^{3+}	Grey-green

Table 10.2

Production of transition metals in Kazakhstan

Kazakhstan is the third largest producer of chromium in the world with 16% of world output. It the fourth largest producer of titanium, cadmium, and magnesium metal accounting for 11%, 8%, and 3% of total world output, respectively. Kazakhstan also has very large reserves of copper and it ranks the top ten producing countries.

It is estimated that Kazakhstan holds one-third of the world's total manganese and chromium deposits and about 4% of the world's gold deposits.



The Shaimerden zinc oxide deposit is located in northwest Kazakhstan, approximately 240 km southwest of the town of Kostanay.

The Pervomayskoye deposit in Kromatau is one of Kazakhstan's largest chrome deposits.

The Kacharsky iron ore mine in the Kostanay region produces 20 million tonnes of mineral per year.

Aktogay copper deposit is one of Kazakhstan's largest, consisting of copper oxide ore above a sulfide layer.

Figure 10.5

Copper

Only silver has better electrical conductivity than copper, which means that copper is the most widely used metal in electrical cables and wiring. This property, together with the fact that it can easily be wound into a coil, means that it also is extensively used in electromagnetic devices such as motors, dynamos and transformers.

Figure 10.6

Copper also has very good thermal conductivity which means that it has a range of applications where heat transfer is important such as saucepans, heating pipes, heat exchangers in water tanks and heat sinks in devices such as TVs and computers.

As copper is low in the reactivity series, it does not easily corrode, which also makes it the metal of choice for many of these applications.

Copper alloys easily and is thus an element in many well-known alloys such as bronze, nickel silver and gunmetal which is an alloy of copper, tin and zinc. Copper is also anti-microbial which means that it quickly kills bacteria and viruses that come into contact with its surface. This is the reason that many surfaces in hospitals are made from copper or one of its alloys.

Zinc

Zinc has strong anti-corrosive properties which means that much of the zinc produced is used to galvanise steel or iron, a process which involves adding a thin layer of zinc to these materials. It alloys easily and so is found in many types of metal alloy used to make car parts, electrical components and domestic appliances.

Its most important compound is zinc oxide, which can be produced in a pure form by burning zinc vapour in air. It has high thermal conductivity which results in it being added to certain types of rubber to add heat dissipating qualities. It is also used in a wide range of paints, cosmetics and inks and in different types of photocopying processes because its electrical conductivity is greatly impacted by the effect of light.

QUESTIONS

3 Name two properties of copper that explain why it is widely used in heating pipes.
4 Why are copper and alloys of copper used to cover hospital surfaces?
5 In what type of ores are copper and zinc found in Kazakhstan?
6 Why is zinc important in the manufacture of steel and iron?

Chromium

Chromium is a hard, brittle metal with a lustrous quality and it can be highly polished. It is corrosion resistant and does not tarnish in air so chromium plating is used to give metals a shiny, silvery mirror finish. It is used in the manufacture of paints and dyes and chromium salts are added to glass to give it a green colour. It is also widely used as a catalyst in leather tanning processes.

High exposure to chronium (VI) is associated with human health problems such as respiratory problems, skin rashes and lung cancer. Such levels of exposure are only potentially found in industrial settings relating to its main applications: steel plating, textile dying and leather tanning.

Iron

Iron along with nickel and cobalt is one of the three naturally occurring magnetic elements. The main qualities that result in its wide range of uses in manufacturing and construction are:

- Its tensile strength
- Its workability
- Its ability to alloy in different types of steel

What has to be compensated for in manufacturing and construction is its reactivity with moist air to form iron oxide Fe_2O_3 (known as rust).

Iron and steel products are found in most domains of human activity from car to rail transport, from shipbuilding to construction, from industrial machinery to home appliances. We shall look in detail at the process involved in steel production in Module 12. It is, however, the wide variety of elements beyond the basic elements in steel [iron and carbon] such as silicon, chromium, vanadium, titanium and molybdenum to name just a few of its alloys that variously give it qualities of strength, flexibility and wear-resistance.

10.4 Corrosion

Corrosion of a metal is the surface chemical reaction on the metal by the action of air, water or other chemicals.

Corrosion of metals is caused by the action of air, water, and other chemicals, such as acids, on the metal surface. The very reactive alkali metals – lithium, sodium and potassium – have to be stored under paraffin to prevent corrosion occurring. The paraffin excludes the corroding agents.

Some metals form oxide coatings when exposed to air. The oxide coatings formed by aluminium, nickel, chromium and magnesium do not flake off easily, and so these metals are protected from further corrosion.

Corrosion of iron or steel

The corrosion of iron or steel results in the formation of hydrated iron(III) oxide (rust), which does not protect the metal from further corrosion.

If a drop of water is placed on a piece of clean steel, an electrochemical cell is formed with a cathode and an anode. The cathode and anode regions differ in composition. The anode gets eaten away as the iron is oxidised:

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$$

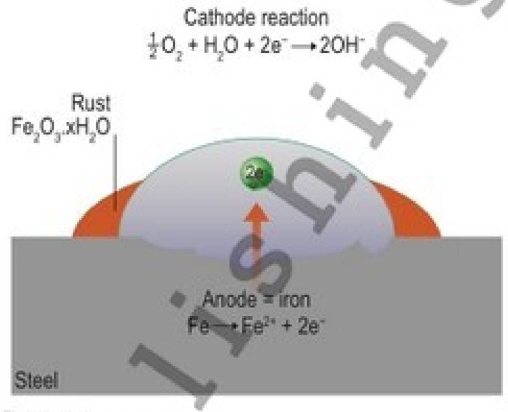


Figure 10.7
Rusting of steel

At the cathode, the dissolved oxygen in the water reacts as follows:

$$H_2O_{(l)} + ½O_{2(aq)} + 2e^- \rightarrow 2OH^-_{(aq)}$$

The Fe^{2+} and OH^- ions diffuse away from the electrodes, and form a precipitate of iron(II) hydroxide:

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$$

This is then oxidised by dissolved oxygen to form rust, Fe_2O_3. x H_2O, where x is variable.

Acceleration of corrosion

The presence of salt in water, which is likely near the sea, or in winter when de-icing salts are used on roads, accelerates corrosion of iron and steel. This is because it increases the conductivity of the electrochemical cell solution. If iron is in contact with a metal such as lead, which is below it in the electrochemical series, as for example, when lead piping is joined to an iron storage tank, the rate of corrosion is accelerated greatly.

10.5 Prevention of Corrosion

Corrosion of iron and steel may be prevented or retarded in a number of ways. The metal may be painted to exclude air, or coated with tin, plastic, grease or oil. The protection against rust afforded by these methods lasts only until the coating is scratched.

Galvanising, which involves coating the metal with zinc, affords protection even after scratching. Since zinc is above iron in the electrochemical series, it, rather than the iron, reacts forming ions which go into solution:

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

The zinc corrodes and the iron is protected. This is a type of cathodic protection, where the cathode is protected and the anode is eaten away.

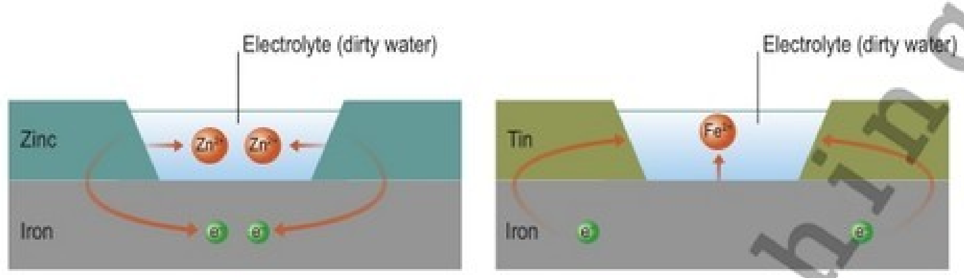


Figure 10.8
Zinc protects iron from rusting even after scratching, whereas tin does not

If a **sacrificial anode** made from a more reactive metal such as magnesium or zinc is connected to steel, the steel is protected. This method is widely used to protect the steel of ships and underground or submerged oil pipelines and water pipes. The anode is eaten away, and the steel, which is the cathode, is protected.

QUESTIONS

7 What must be present for corrosion of iron and steel to occur?

8 Name two substances that accelerate the corrosion of iron and steel. Give a reason in each case.

9 List two methods of preventing corrosion of iron and steel.

10 What is the chemical composition of rust?

11 Why does zinc not corrode?

12 How does tin prevent iron from rusting?

13 Why does zinc prevent iron from rusting more effectively than tin?

14 Give an example of the use of a sacrificial anode, and explain how it works.

EXPERIMENT 10.1

Transition metal ions in solution

Chemicals needed
0.1M Copper Sulfate
0.1M Ammonium Ferrous Sulfate
0.1M Iron (III) Chloride
0.1M Chromium (III) Chloride
0.1 M Zinc Chloride
2M Sodium Hydroxide
1M Sodium Carbonate
Concentrated hydrochloric acid

Equipment needed
Pasteur pipettes
Test tubes
Test tube racks
Deionised water

Procedure

NB: Wear your safety glasses.

In test tubes containing approximately 3 cm^3 Cu^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Zn^{2+} of solution, carry out the following tests and record your observations in the table below.

1. Determine the pH of each solution and note its colour.
2. Using a pipette add drops of 2M NaOH to excess. Note the colour of any precipitates that form and which precipitates dissolve indicating that they are amphoteric hydroxides. Allow precipitates to stand for several minutes and observe if atmospheric oxidation occurs.
3. Add concentrated hydrochloric acid to excess and note changes in colour. The water molecules will be repaced as ligands by Cl$^-$ ions.
4. Add 1M Sodium carbonate to excess. Again record the colour of any precipitate formed and compare to the colour in step 2. Note if any gas is produced.
5. Complete the table and ionic equations for any reactions occurring in the table as well.

	Fe^{2+}	Fe^{3+}	Cu^{2+}	Cr^{3+}	Zn^{2+}
In aqueous solution Formula pH colour					
adding hydroxide ions					
adding concentrated HCl					
adding carbonate ions					

10.6 Percentage Yields

Calculations using reacting masses based on balanced equations give the maximum amount of product(s) possible from the reactants involved – the **theoretical yield**. When a chemical reaction occurs, the amounts of products isolated are often less than those calculated. This can be due, for example, to the reaction being reversible, or to some of the products reacting further to form other products, or to losses when purifying the products. In reactions where theoretical yields of products are not obtained, the idea of **percentage yield** is useful.

$$\text{Percentage yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100\%$$

When performing calculations involving impurities in ore, before calculating the reacting masses, do a simple calculation which takes into account the impurity of the ore. Thus, if you are told that a magnetite iron ore contains 80% iron oxide and 20% waste silicate materials, simply base product calculations on an 80% ratio of the initial ore quantities used.

Example 1.1

A magnetite iron ore is found to contain 76% of the iron oxide compound Fe_3O_4. How much iron can be extracted from 1000 kg of magnetite ore by carbon reduction?

Atomic masses:
Fe = 56
C = 12
O = 16

The reduction equation is $Fe_3O_4 + 2C \rightarrow 3Fe + 2CO_2$

Answer $1Fe_3O_4 \rightarrow 3Fe$

reacting masses

$(3 \times 56) + (4 \times 16) \rightarrow 3 \times 56$

$232\ Fe_3O_4 \rightarrow 168\ Fe$

solving the ratio, $x = 0.76 \times 168/232 = 0.55$

= Fe (550 kg) from the magnetite ore

QUESTIONS

15 How much iron (Formula Fe_2O_3) can be obtained theoretically from 1000 tonnes of pure haematite in a blast furnace? What is the percentage yield if only 630 tonnes are obtained?

16 Nitrogen monoxide is prepared using the reaction

$3Cu_{(s)} + 8HNO_{3(aq)} \rightarrow 3Cu(NO_3)_{2(aq)} + 2NO_{(g)} + 4H_2O_{(l)}$

If 12.7 g of copper are used to produce 1.12 l NO (measured at s.t.p.), calculate the percentage yield of NO.

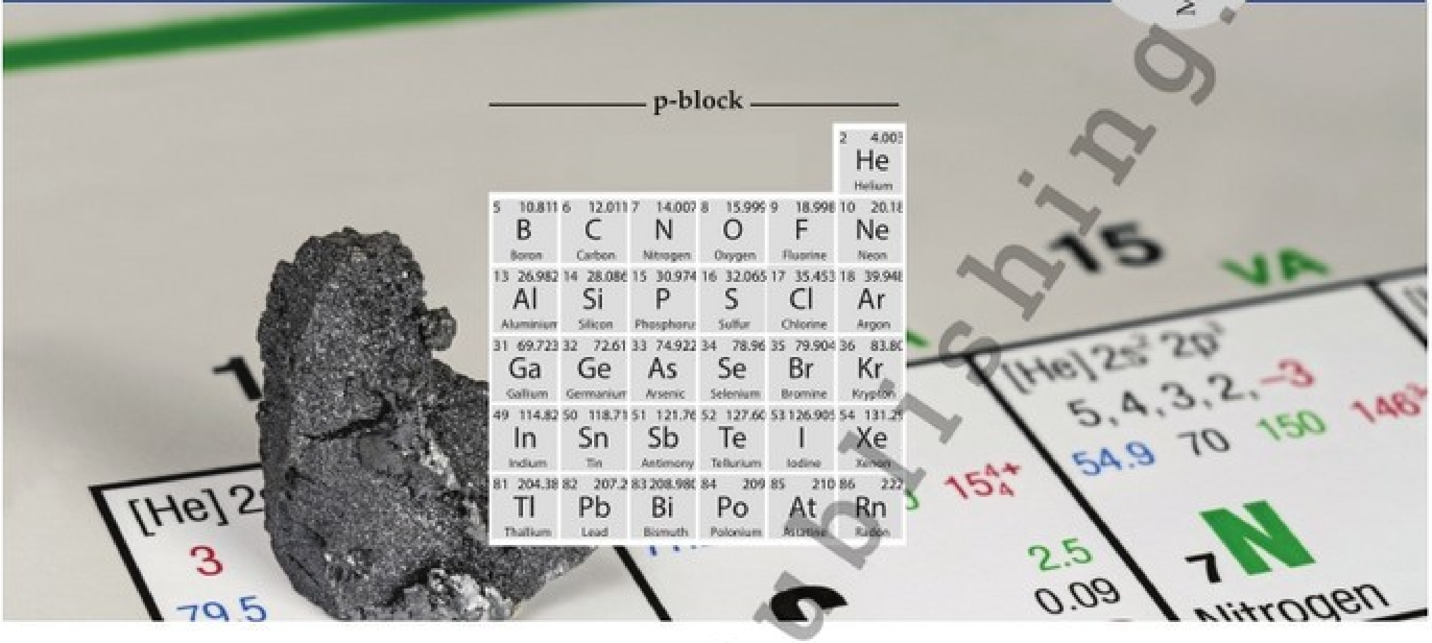
17 Copper(II) oxide can be reduced by heating carbon in the reaction

$2CuO_{(s)} + C_{(s)} \rightarrow 2Cu_{(s)} + CO_{2(g)}$

In the copper smelter what is the theoretical yield of copper if 1.5 tonnes of carbon are used? If 14 tonnes of copper are actually produced what is the percentage yield?

p-block elements

MODULE 11



Learning objectives

- Explain Periodic Trends in the properties of the p-block elements and their compounds according to their atomic structure 10.2.1.31
- Investigate the amphoteric properties of aluminium oxide and hydroxide 10.2.1.32
- Describe the uses of aluminium and its alloys 10.2.1.33
- Describe the physical and chemical properties of carbon and silicon and their compounds 10.2.1.34
- Explain the mechanism of carbon monoxide poisoning and first aid for carbon monoxide poisoning 10.2.1.35
- Explain the unreactivity of the nitrogen molecule according to its atomic structure 10.2.1.36
- Complete chemical equations which describe the manufacture and chemical activity of ammonia gas and ammonia solution 10.2.1.37
- Analyze the impact of nitrogen oxides on the atmosphere and nitrates on soil and water resources 10.4.1.8
- Suggest ways to reduce nitrogen and phosphorous compounds effect on the environment 10.4.1.9
- Describe the formation of sulfur dioxide in the combustion of sulfur-containing fuel 10.2.1.39
- Explain the impact of sulfur dioxide on the environment and describe how acid rain forms 10.4.1.10
- Compare properties of dilute and concentrated sulfuric acid 10.2.1.40
- Explain areas of the application of sulfur dioxide in the food industry 10.4.1.11
- Explain the regularities of changes in the physical and chemical properties of the halogens group 10.2.1.41
- Study chemical properties of hydrochloric acid and to know areas of its application 10.2.1.42
- Describe the biological role of iodine for the human organism and explain ways of preventing iodine deficiency disorders 10.4.1.12
- Recognise tests for identifying chloride-, bromide-, iodide-, sulfate-, carbonate-, phosphate-, nitrate-, silicate- ions 10.2.1.43
- Create a plan for testing some anions and carry out the experiment 10.2.1.44

11.1 p-block elements

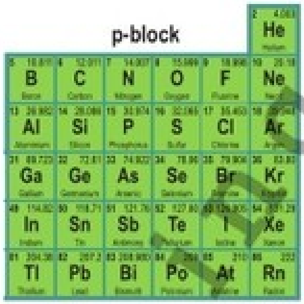


Figure 11.1

The elements in Groups III, IV, V, VI, VII and 0 are called the **p-block elements**. These are mainly non-metals, but the lower members of some of these groups, for example tin and lead in Group IV, are metals. As we saw in Module 1, all p-block elements have the outermost electrons in their atoms occupying a p sublevel.

11.2 Aluminium

Alumina (aluminium oxide) is first extracted from the ore bauxite by chemical means. Aluminium is then extracted from alumina by electrolysis.

Figure 11.2
Plant for extraction of alumina from bauxite

Alumina from bauxite

- Crushed bauxite is added, with mixing, to a hot solution of sodium hydroxide.
- The slurry formed is then pumped to pressure vessels operated at high temperatures. The following reaction occurs, in which soluble sodium aluminate is formed:

  $2NaOH_{(aq)} + Al_2O_3 \times 3H_2O_{(s)} \rightarrow 2NaAlO_{2(aq)} + 4H_2O_{(l)}$
- The impurities in the ore, which are mainly oxides of iron, silicon and titanium, do not dissolve, and are allowed to settle before being removed by filtration.

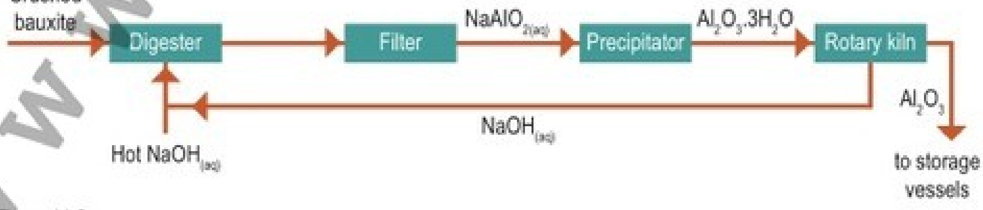


Figure 11.3
The extraction of alumina from bauxite

- The clear sodium aluminate solution is next pumped to precipitator tanks. Here the solution is seeded with very pure small crystals of aluminium oxide-3-water. On cooling, the following reaction occurs:

  $2NaAlO_{2(aq)} + 4H_2O_{(l)} \rightarrow 2NaOH_{(aq)} + Al_2O_3 \text{ x } 3H_2O_{(s)}$

- The precipitate of hydrated aluminium oxide is removed by vacuum filtration, while the sodium hydroxide solution is recycled to the start of the process.
- The hydrated aluminium oxide is then heated at about 1373 K to remove the water of crystallisation:

  $Al_2O_3 \text{ x } 3H_2O_{(s)} \rightarrow Al_2O_3(s) + 3H_2O_{(l)}$

  The alumina formed is a white powder.

Aluminium from alumina

The electrolysis of alumina is carried out in large steel boxes lined with carbon.

- Carbon anodes and a carbon cathode are used.
- Alumina has a very high melting point (2288 K), so an electrolyte is used consisting of a mixture of molten cryolite (Na_3AlF_6) and aluminium fluoride (AlF_3). The aluminium oxide dissolves in the electrolyte. Cryolite is used as a solvent in the electrolysis to save energy because it has a much lower melting point than alumina itself.
- A low voltage is used in the electrolysis to avoid decomposing the electrolyte.
- During the electrolysis, the following reactions occur:

  Cathode: $2Al^{3+}_{(l)} + 6e^- \rightarrow 2Al_{(l)}$

  Anode: $3O^{2-}_{(l)} - 6e^- \rightarrow 1_{1/2}O_{2(g)}$

- The molten aluminium formed settles at the bottom of the tank, and is siphoned from there.
- The electrolysis is carried out at a high temperature, at which the large carbon anodes are steadily burned away by the oxygen liberated there and have to be replaced at regular intervals.
- The electrolysis of alumina consumes enormous amounts of electricity and is therefore normally carried out where electricity is relatively cheap.

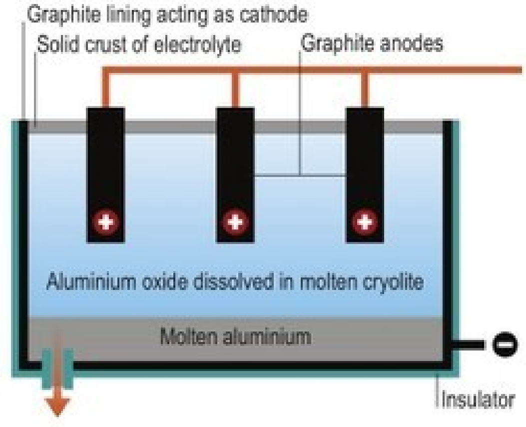


Figure 11.4
The electrolysis of alumina

Uses of aluminium and its alloys

Aluminium is used to make strong, light, corrosion-resistant alloys, which are used in the construction of aeroplanes and ships. Aluminium silicon, for example, is an alloy that has highly corrosion-resistant and wear-resistant properties and is used to produce functional parts of engines such as pistons, cylinder liners and coatings for pipelines. Aluminium is a good conductor of heat and so is used to make saucepans and as a cooking foil. It is also an excellent electrical conductor and so is used in electricity wires.

The non-corrosive properties of aluminium are due to an effect known as anodising. Aluminium forms a protective layer of aluminium oxide Al_2O_3, which prevents it from oxidising further. Anodised coatings with aluminium are used on all sorts of surfaces from building exteriors to mobile phones.

Recycling of aluminium

The **recycling** of aluminium is an economically viable process. It is also desirable from an environmental point of view, saving energy and conserving natural resources. When aluminium is being recycled the aluminium waste is melted. The impurities are either burned off or separated from the aluminium.

QUESTIONS

1 What is the main compound present in bauxite, and what are the major impurities?
2 What is alumina, and how is it formed from bauxite?
3 In the electrolysis of alumina, why do the anodes have to be replaced regularly?
4 When alumina is electrolysed, what is oxidised? At which electrode does oxidation occur? What type of cathode is used?
5 In what form does aluminium occur naturally? What is the element used for?

Aluminum and its compounds are amphoteric, meaning that they react with both acids and bases. Aluminium hydroxide, for example, reacts:

- with OH^- solutions to produce $Al(OH)^{4-}$
- with H_3O^+ solutions to produce $[Al(H_2O)_6]^{3+}$

DEMONSTRATION 11.1

You are going to observe the reactions of dropping a ball of aluminium foil into a beaker of

(a) a dilute solution of hydrochloric acid
(b) a dilute solution of sodium hydroxide

QUESTIONS

6 What is an amphoteric substance?
7 Complete the equations with the products for each reaction

(a) $2Al + 6HCl \rightarrow$ ____________________________

(b) $2Al + 2NaOH + 6H_2O \rightarrow 2Na[Al(OH)_4] +$ ____________________________

11.3 Oxides and silicon

Silicon and its compounds silicon dioxide and silicon carbide form **covalent macromolecular crystals**. In such crystals the atoms form lattice points and covalent bonding holds the atoms together.

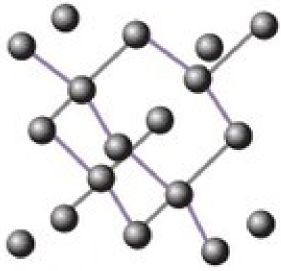


Figure 11.5
Silicon

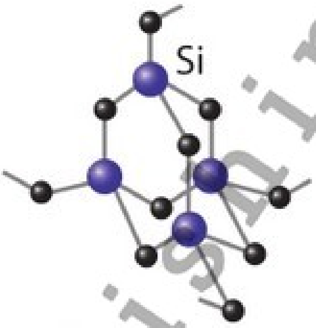


Figure 11.6
Silicon carbide

These structures are similar to the carbon allotropes: diamond and graphite and have a regular three-dimensional structure.

Materials such as diamond, quartz and silicon carbide are extremely hard and have very high melting points because of the energy required to break the covalent bonds. As electrons cannot easily move from one atom to another, they are also poor conductors of electricity and do not dissolve in polar or non-polar solvents.

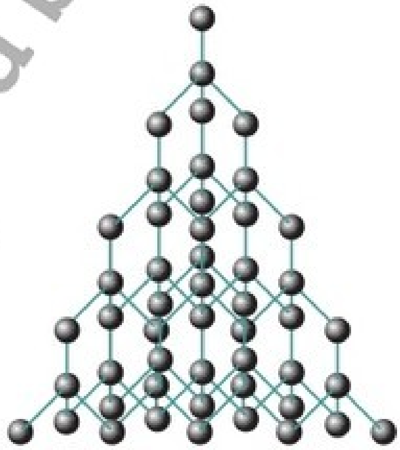


Figure 11.7
Diamond

Silicon dioxide is commonly found in the form of quartz. It can also be obtained by either burning silicon in air or through the slow decomposition of silicon in a red-hot state when exposed to steam. It is used in processes such as sandblasting and hydraulic fracturing in the oil and gas industry.
Silicon carbide, which is produced at extremely high temperatures using a mixture of pure silica (sand)and finely ground coke (carbon), is one of the hardest substances known. It is an extremely wear-resistant material used in heating elements and tools used for cutting and grinding hard materials.

QUESTIONS

8 Why do crystal structures such as diamond and silicon carbide have such high melting points?
9 In what form is silicon dioxide naturally found?
10 By what process can pure silicon dioxide be made?
11 Name one industrial use of (a) silicon dioxide and (b) silicon carbide

11.4 Oxides of Carbon

Figure 11.8
Cigarette smoke contains some carbon monoxide

When carbon is burned in a limited supply of oxygen, incomplete combustion occurs and carbon monoxide is formed:

$$C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$$

Carbon monoxide is a neutral gas that is also formed when the incomplete combustion of hydrocarbons occurs. It is a deadly poison, which prevents the uptake of oxygen by the haemoglobin of the blood.

Carbon monoxide has no smell or colour and does not irritate the lungs or the eyes, so it can easily be breathed in without being noticed.

Carbon monoxide poisoning is usually caused by burning fuels in unventilated spaces or by poorly maintained household appliances such as cookers or central heating boilers.

People exposed to carbon monoxide will feel sick and experience dizziness, tiredness and confusion, stomach pain and shortness of breath. They should immediately seek medical advice at a local hospital where their carboxyhaemoglobin levels will be checked and they can be treated with pure oxygen to bring levels down to below 10% which is normal.

Carbon monoxide is emitted through vehicle exhausts, particularly in the absence of catalytic converters, and is also found in cigarette smoke which are reasons why some carboxyhaemoglobin is generally present in blood. It can be difficult to assess the extent of exposure to a carbon monoxide leak in heavy smokers.

Figure 11.9
Fizzy drinks contain carbon dioxide

When carbon is burned in excess oxygen, complete combustion occurs and carbon dioxide is formed:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$$

Carbon dioxide is also formed when complete combustion of hydrocarbons occurs. In brewing, carbon dioxide is a co-product in the production of ethanol by fermentation:

$$C_6H_{12}O_{6(aq)} \rightarrow 2C_2H_5OH_{(aq)} + 2CO_{2(g)}$$

Carbon dioxide is an acidic gas, which is used to make fizzy drinks. It is dissolved in water under pressure, with the result that bubbles of gas are produced when the container is opened.

DEMONSTRATION 11.2

The effect of carbon dioxide on universal indicator solution

In this demonstration, the carbon dioxide gas formed in the reaction is bubbled through water to remove HCl, and then into universal indicator solution.

Universal indicator is a mixture of indicators that shows a wide range of colours, depending on the pH of the substance being tested. As carbon dioxide gas is bubbled into a sample of the indicator, the pH is gradually lowered as the amount of dissolved CO_2 increases. A series of colour changes is seen as the pH drops.

Chemicals needed
Universal indicator
Marble chips
3 M hydrochloric acid

Equipment needed
100 cm^3 beaker
Magnetic stirrer and pellet
Teat pipette
Test tubes and stoppers with two holes
Delivery tube
Retort stand and clamp

Procedure

NB: Wear your safety glasses

1. Place about 25 cm^3 of universal indicator into a 100 cm^3 beaker and dilute with an equal volume of water. Place the beaker on a magnetic stirrer, add a pellet, and start the stirrer at a slow speed.
2. Place a few marble chips in a test tube and set up the apparatus as in the diagram. The end of the delivery tube should be well below the surface of the universal indicator.
3. Add dilute HCl from the teat pipette, a few drops at a time.
4. As the carbon dioxide bubbles through the indicator, a series of colour changes can be observed.

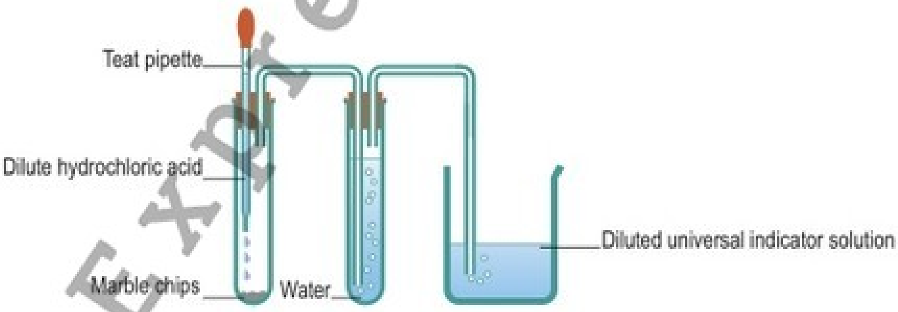


Figure 11.10

QUESTIONS

12 Under what conditions is carbon monoxide produced by combustion?

13 Explain how carbon monoxide acts as a poison.

14 What effect does (a) carbon monoxide (b) carbon dioxide have on litmus?

11.5 Carbon Dioxide in Water

Carbon dioxide is an **acidic oxide**.

An acidic oxide is an oxide that increases the hydrogen ion concentration in water.

Carbon dioxide is fairly soluble in water:

$$CO_{2(g)} + \text{excess } H_2O_{(l)} \rightleftharpoons CO_{2(aq)}$$

A small proportion of dissolved carbon dioxide reacts with the water to form carbonic acid, H_2CO_3:

$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons \underset{\text{Carbonic acid}}{H_2CO_{3(aq)}}$$

As this is a weak acid, it dissociates to a small extent in aqueous solution:

$$\underset{\text{Carbonic acid}}{H_2CO_{3(aq)}} \rightleftharpoons H^+_{(aq)} + \underset{\text{Hydrogencarbonate ion}}{HCO_3^-{}_{(aq)}}$$

The hydrogencarbonate ion, HCO_3^-, is itself a weak acid so further dissociation can occur, but to a lesser extent:

$$\underset{\text{Hydrogencarbonate ion}}{HCO_3^-{}_{(aq)}} \rightleftharpoons H^+_{(aq)} + \underset{\text{Carbonate ion}}{CO_3^{2-}{}_{(aq)}}$$

This is more likely to occur under alkaline conditions.

The interaction of water with carbon dioxide is of value in reducing the amount of carbon dioxide in the atmosphere. At the surface of the oceans, air is constantly coming into contact with water. Some of the carbon dioxide that dissolves in water is changed into hydrogencarbonates and carbonates, as described above. Some of it is used up in photosynthesis by marine plants, while some is dispersed to deeper regions by ocean currents where the low temperatures ensure that it remains dissolved. These interactions of atmospheric carbon dioxide with the oceans are a significant factor in limiting the greenhouse effect.

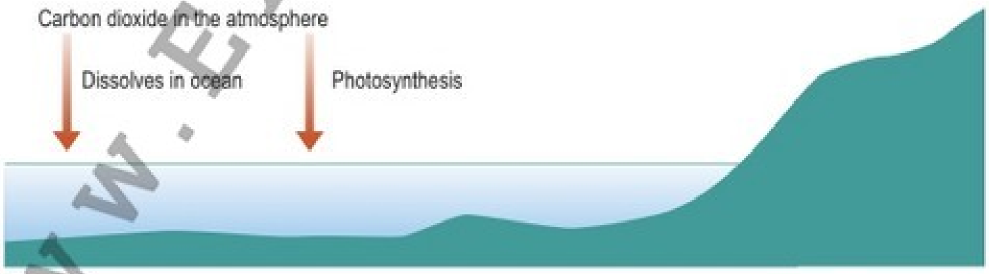


Figure 11.11
Dissolving carbon dioxide in the ocean helps to reduce levels of the gas in the atmosphere

11.6 The Carbon Cycle

The carbon cycle indicates why the level of carbon dioxide in the atmosphere does not change greatly over short periods of time. Some carbon dioxide is removed from the atmosphere by dissolving in rain or in ocean water.

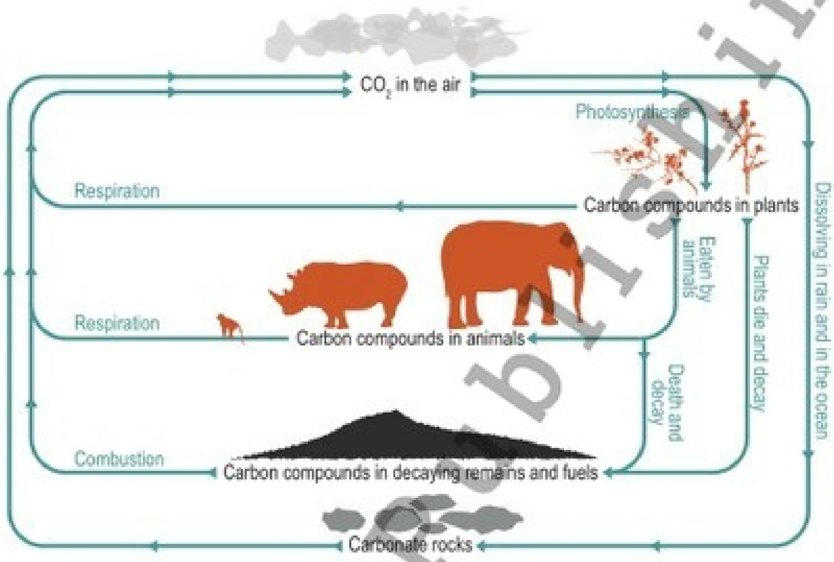


Figure 11.12
The carbon cycle

The major process by which atmospheric carbon dioxide levels are reduced is photosynthesis. Atmospheric carbon dioxide is used by green plants in photosynthesis to make more complex carbon compounds. These may be eaten by animals, which digest them and use them for energy in respiration. Alternatively, they may be used by the plants themselves in respiration. In both cases carbon dioxide is formed, and returned to the atmosphere. Another way that carbon dioxide is returned to the atmosphere is when fossil fuels are burned.

QUESTIONS

15 Write an equation for the formation of carbonic acid from carbon dioxide.
16 Name the three forms in which carbon dioxide is found in the oceans.
17 How is the interaction of carbon dioxide with the oceans of benefit to the environment?
18 Explain the importance of the carbon cycle.

11.7 Nitrogen

N_2, in nature is found as a diatomic gas with the two nitrogen atoms joined by a non-polar covalent triple bond.

The bond energy of the N≡N bond is very large, which means that a lot of energy is needed to break the bond. Consequently, nitrogen is very stable and chemically unreactive. Nitrogen has an extremely low boiling point and liquid nitrogen is used as a coolant and refrigerant. It has several uses in medicine in its liquid form. It is used, for example, in the long-term storage of viable human cells such as sperm and it is used in certain skin treatments to kill damaged cells and thus allowing new cells to grow in their place.

Oxides of Nitrogen

Nitrogen monoxide is released from car exhausts and power plants where the high temperatures bring about the oxidation of atmospheric nitrogen:

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

It is also formed in some biological processes and by lightning discharges. Nitrogen monoxide, NO, is quickly oxidised in air to nitrogen dioxide, NO_2:

$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)}$$

Nitrogen dioxide dissolves in water and reacts to form a mixture of nitrous acid, HNO_2, and nitric acid, HNO_3:

$$2NO_{2(g)} + H_2O_{(l)} \rightarrow HNO_{2(aq)} + HNO_{3(aq)}$$

Thus the release of nitrogen monoxide into the atmosphere is likely to result in rain containing nitric acid and nitrous acid.

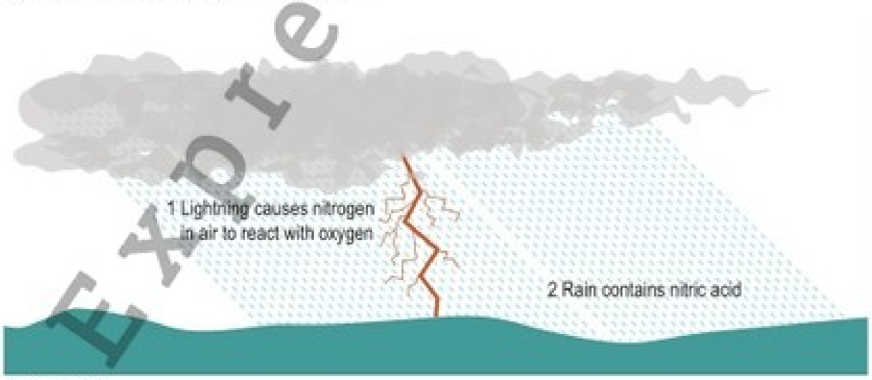


Figure 11.13
Formation of nitric acid in the atmosphere

Nitrates in soil and water

Nitrogen is essential for the growth of most living things, and is a vital ingredient of proteins. In order for plants and animals to make use of nitrogen, the unreactive nitrogen gas in the atmosphere must be converted into more reactive nitrogen compounds, which can then find their way into the soil. This process is called **nitrogen fixation**.

One mechanism for this occurs during thunderstorms, when lightning flashes provide the high energies necessary to split the N_2 bond and allow it to react with oxygen to form nitrogen oxides, such as NO and NO_2. These can then dissolve in the water in clouds to form nitric acid (HNO_3) and nitrous acid (HNO_2). These compounds are changed into nitrates in the soil that are then absorbed into the root systems of plants.

The roots of legumes (plants such as clover, peas, and beans) are colonised by nitrogen-fixing bacteria that have the ability to directly convert N_2 into useful nitrogen compounds via the use of a special enzyme called nitrogenase. The virtue of this system is that these plants provide their own fertiliser.


Figure 11.14
Pea plants

Sewage treatment

For many years, domestic sewage running untreated into rivers, lakes and the sea has been one of the most serious causes of pollution around the world. The absence of sewage treatment plants in some areas meant that waterways have been, and in some cases still are, treated like sewers. In most cases, a small quantity of the particular pollutant would not pose a problem for the waterway, as it would be degraded quickly, posing no threat to the environment. However, large quantities of sewage cannot be broken down in a reasonable period of time and so constitute serious pollution.

While the exact processes may vary from one plant to the next, there are three recognised stages known as primary, secondary and tertiary treatment respectively.

(a) Primary treatment

Primary treatment involves **screening** and **settlement**, and is a physical process. The sewage entering the plant is forced through metal screens that remove large solids and physically break up the sewage. On the way to the primary settling tanks, the effluent passes slowly through long grit channels. As it does so, more dense matter settles and is removed periodically.

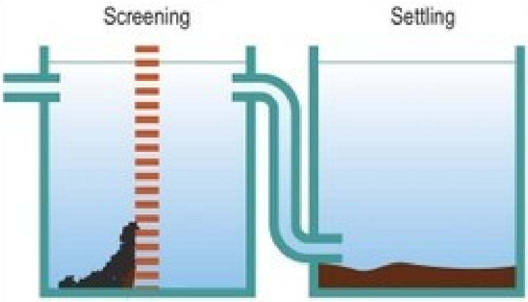


Figure 11.15
Primary sewage treatment

With some of the solid matter now removed, the effluent flows into a primary settling tank. It enters through the bottom of the tank, and rises slowly allowing the sludge to settle. The tank has a mechanism at the top that skims floating particles. It has a scraper at the bottom of the tank to remove sludge periodically. The clearing effluent at the top of the tank flows away to secondary treatment.

Primary treatment involves screening and settlement, and is a physical process.

(b) Secondary treatment

Secondary treatment is a biological process involving the **oxidation by micro-organisms** of the nutrients present in the effluent. The waste is oxidised by micro-organisms in a **trickling filter** or in an **activated sludge unit**. In a trickling filter, the effluent flows through a bed of stones where micro-organisms digest the nutrients in the presence of air, i.e. aerobically. An activated sludge unit also operates aerobically. The effluent is fed continuously into an aerated tank that is kept oxygenated by mechanical agitators. Once again, micro-organisms decompose most of the organic matter.

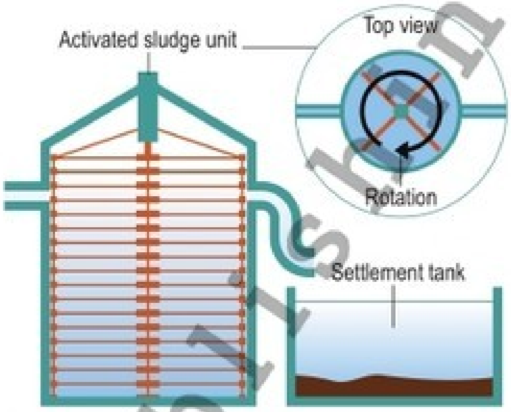


Figure 11.16
Secondary sewage treatment

Secondary treatment is a biological process involving the oxidation by micro-organisms of the nutrients present in the effluent.

After the biological stage, the effluent is subjected to further **settlement** in tanks. Even though it is now safe enough to be discharged into waterways, where dilution renders it even less harmful to the environment, the effluent is still rich in nutrients such as phosphates and nitrates. Ideally it requires tertiary treatment.

(c) Tertiary treatment

Tertiary treatment involves the removal of **phosphates and nitrates** from the effluent resulting from secondary treatment. It is much less common in many countries than primary or secondary treatment, largely because of its high cost.

Figure 11.17
Secondary sewage treatment

Phosphates are removed by precipitation. They are reacted with a compound such as aluminium sulfate, $Al_2(SO_4)_3$, producing an insoluble salt – in this case aluminium phosphate, $AlPO_4$, which can be removed by filtration.

Several methods of removing nitrates are available, the most common being biological denitrification, which is sometimes incorporated into secondary treatment plants. The effluent containing the nitrates is placed in a tank that has no free oxygen. Bacteria in the tank require oxygen and they take it from the only available source – oxygen bonded to nitrogen in nitrate ions, i.e. $NO_3^- \rightarrow N_2$. In other words, the bacteria reduce nitrates to nitrogen gas.

Tertiary treatment involves the removal of phosphates and nitrates from the effluent.

Stage	Type	Action taken	Result
Primary	Physical	Screening and settlement	Solids are removed
Secondary	Biological	Exposure to micro-organisms	Nutrients are oxidised
Tertiary	Chemical and biological	Phosphates precipitated; nitrates denitrified	Phosphates and nitrates are removed

Table 11.1
Stages in sewage treatment

QUESTIONS

19 What does primary sewage treatment remove from wastewater?
20 What is the purpose of secondary sewage treatment, and how is it carried out?
21 What is the purpose of tertiary sewage treatment?

11.8 Eutrophication

Eutrophication is the presence of excessive nutrient content in a water body to an extent that causes over-abundant plant growth.


Figure 11.18
Algal bloom

Eutrophication is caused by the over-enrichment of water by nutrients such as phosphates and nitrates, caused by untreated or partially treated sewage, or by run-off from farmland of slurry or fertilisers. In effect, the nutrients behave as fertilisers that increase the growth of plants such as algae in lakes and rivers. This problem may be noticed by the appearance of algal bloom on the water.

The algae are short-lived. As they decay, micro-organisms use up much of the dissolved oxygen in the water, leading to the death of many forms of animal life. The occurrence of eutrophication is a strong argument in favour of tertiary treatment of sewage, which contains nitrates and phosphates in significant quantities.

Another of the causes of eutrophication of waterways is the run off of excess fertiliser from farmland. The fertiliser spread on the land may be artificial, or it may be natural, i.e. animal slurry. Either way, if the quantity used is not carefully controlled, excess nitrate may be washed into rivers or lakes by rainwater. Once again eutrophication may result. Increased regulation of the use of fertilisers in many countries has brought about a reduction in the amount of pollution of waterways.

QUESTIONS

22 What is meant by eutrophication?

23 Why does uncontrolled use of fertilisers cause eutrophication?

24 What is likely to happen to the water in a lake if a large quantity of untreated sewage is discharged into the lake, and why?

25 Why is tertiary treatment of sewage important in the prevention of eutrophication?

Ammonia

Ammonia is a colourless gas with a pungent smell. NH_3 fumes are toxic and exposure to and inhalation of ammonia can seriously affect your eyes, nose and throat. Ammonia readily dissolves in water in an exothermic reaction. It forms ammonium hydroxide (NH_4OH) which is a weak base solution.

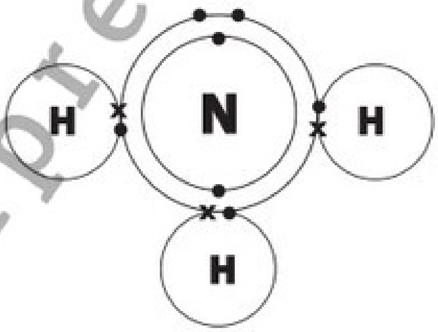


Figure 11.19

Demonstration 11.3

We have looked at how ammonia is manufactured in industrial processes in Module 7 and will consider this process in more detail in Module 12. Here we will conduct an experiment that will allow us to produce ammonia gas in the lab and consider some of its properties. Because of the dangers of the inhalation of ammonia, this experiment should be carried out in a fume cupboard.

Chemicals needed
Ammonium chloride
Calcium hydroxide
Calcium oxide
Concentrated hydrochloric acid

Equipment needed
1 x small beaker
1 x large beaker
Spatula
Retort stand clamp
Boiling tube with stopper
Delivery tube
2 x test tubes [one with stopper]
Test tube rack
Retort stand
Clamp
Bunsen burner
Heat resistant mat
Universal indicator paper

Procedure

NB: Wear your safety glasses

1. Have ready a large beaker two-thirds filled with water. Also have ready a test tube with a few drops of hydrochloric acid with a stopper in it. You will need these later in the experiment.
2. Mix 2 spatulas of ammonium chloride with an equal amount of calcium hydroxide in beaker. You should observe an immediate reaction as they begin to mix.
3. Place a piece of universal indicator paper over the beaker and record the change in colour.
4. Transfer the contents of the beaker into a boiling tube and add a small amount of calcium oxide [to absorb any water produced in the reaction].
5. Place the boiling tube containing the ammonium chloride and calcium hydroxide mixture in a clamp and insert a delivery tube and stopper.
6. Heat the mixture gently.
7. Take the test tube containing the hydrochloric acid prepared earlier. Remove the stopper and place near the mouth of the delivery tube. Record your observations and then replace the stopper and return to the rack.
8. Continue heating and then hold another boiling tube inverted over the delivery tube.
9. Remove the boiling tube holding it upside down and quickly place mouth down in the beaker of water prepared earlier. Record your observations.

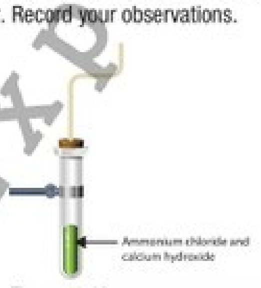


Figure 11.20

Figure 11.21

QUESTIONS

26 Complete the equation for the reactions:

(a) $NH_{3(g)} + HCl_{(g)} \rightarrow$ ______________________________

(b) $2NH_4Cl_{(s)} + Ca(OH)_{2(s)} \rightarrow$ ______________________________

Sulfur and its oxides

Oxides of sulfur are mainly formed by the combustion of fossil fuels, particularly coal. They can also be released by volcanoes and by the decay of organic matter.

Sulfur in fossil fuels forms sulfur dioxide, SO_2, which is a dangerous pollutant. Sulfur dioxide dissolves in water to form sulfurous acid, H_2SO_3.

$$SO_{2(g)} + H_2O_{(l)} \rightarrow H2SO_{3(aq)}$$

In the atmosphere, sulfur dioxide is oxidised to sulfur trioxide, SO_3. Sulfur trioxide dissolves in rainwater to form sulfuric acid, H_2SO_4.

$$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(aq)}$$

Thus the release of SO_2 into the atmosphere is likely to result in rain containing H_2SO_3 and H_2SO_4.

Iron occurs in ores such as haematite (impure Fe_2O_3), magnetite (impure Fe_3O_4) and iron pyrites (impure FeS). The extraction of iron from its ores is carried out in a **blast furnace**, in which the iron ore is reduced to molten iron, using coke at a high temperature. Unlike more reactive metals, this extraction is a **chemical reduction process** rather than an electrochemical process.

Figure 11.22
Acid rain caused by sulfur dioxide emissions

DEMONSTRATION 11.4

The effect of sulfur dioxide on universal indicator solution.

As sulfur dioxide gas is bubbled into a sample of universal indicator, the pH is gradually lowered as the amount of dissolved SO_2 increases. A series of colour changes is seen as the pH drops.

Chemicals needed

Universal indicator

Sodium sulfite

3 M Hydrochloric acid solution

Equipment needed

100 cm^3 beaker

Magnetic stirrer and pellet

Teat pipette

Test tube and stopper with two holes

Delivery tube

Retort stand and clamp

Procedure

NB: Wear your safety glasses

1. Place about 25 cm^3 of universal indicator into a 100 cm^3 beaker and add an equal volume of water. Place the beaker on a magnetic stirrer, add a pellet, and start the stirrer at a slow speed.
2. Place a spatula full of sodium sulfite in a test tube and set up the apparatus as in the diagram. The end of the delivery tube should be well below the surface of the universal indicator.
3. Add dilute HCl from the teat pipette, a few drops at a time.
4. As the sulfur dioxide bubbles through the indicator, a series of colour changes can be observed.

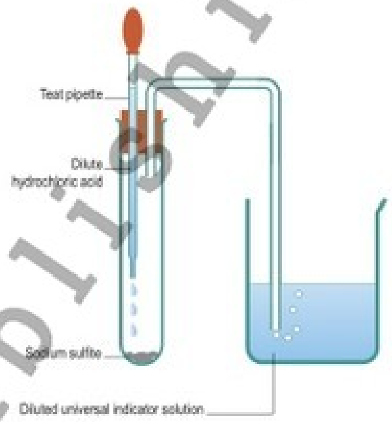


Figure 11.23

11.9 Scrubbing Waste Gases

Limestone is used to reduce sulfur dioxide emissions from coal-fired power stations. Coal is mixed with finely ground limestone. The high temperatures in the furnace cause the limestone to decompose:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$$

The calcium oxide reacts with much of the sulfur dioxide forming calcium sulfite:

$$CaO_{(s)} + SO_{2(g)} \rightarrow CaSO_{3(s)}$$

This prevents the release of sulfur dioxide into the atmosphere. The process is called **scrubbing**.

$$CaO + SiO_2 \rightarrow CaSiO_3$$

$$CaO + Al_2O_3 \rightarrow CaAl_2O_4$$

QUESTIONS

27 What is the approximate pH of unpolluted rainwater?

28 What is meant by the term acid rain?

29 What are the main causes of acid rain?

30 Explain how oxides of nitrogen get into the atmosphere.

31 Name two acids that are formed in the atmosphere from oxides of nitrogen.

32 Explain how oxides of sulfur get into the atmosphere.

33 Name two acids that are formed in the atmosphere from oxides of sulfur.

34 How are sulfur dioxide emissions from coal-fired power stations reduced?

Sulfuric acid has a wide range of industrial uses and applications in industry such as the treating of ores and metals and the making of fertilisers such as phosphate fertilisers and ammonium sulfate. Sulfuric acid has a strong affinity for water and is thus used in dehydration processes such as the dehydration of ethanol and to dehydrate hydrated crystals.

Sulfur dioxide is also used widely in the food and drinks industry as a preservative and antioxidant. It is used mainly to help preserve dried fruits, vegetables, soft drinks and alcoholic drinks. Its use is usually governed by food safety directives as it can aggravate asthma in those with a predisposition to the condition. Young children with asthma are usually advised to avoid soft drinks which have been treated with sulfur dioxide.

11.10 The Halogens

The halogens are the only group of elements which exist in three out of the four main states of matter at room temperature and pressure (solid, liquid, gas) at STP.
The four most common halogen elements are:

- fluorine (F)
- chlorine (Cl)
- bromine (Br)
- iodine (I)

The word halogen in Greek means 'salt forming', which points to their common property to react with other elements to form salts. Common table salt [sodium chloride] is the most obvious example.

Properties of Halogens

Halogens are reactive non-metals with seven valence electrons. As pure elements, they form diatomic molecules with atoms joined by non-polar covalent bonds. Fluorine and chlorine (F_2 and Cl_2) are gases at STP; bromine(Br_2) is a liquid and iodine (I_2) is a solid. Halogens have very high electronegativities and are highly reactive with alkali metals and alkaline earth metals and form stable ionic crystals.

QUESTIONS

35 Would you expect boiling points to increase or decrease for halogen elements moving down the group? Explain your answer.

36 Which of the halogens has the highest electronegativity of all elements?

Common uses of halogens:

- fluorine, in fluoride form, is used in various products and in some countries added to water to help prevent tooth decay.
- halogen lamps which typically use iodine or bromine
- pesticides and refrigerants
- disinfectants and detergents
- brominated flame retardants

11.11 Chlorination and Fluoridation of water

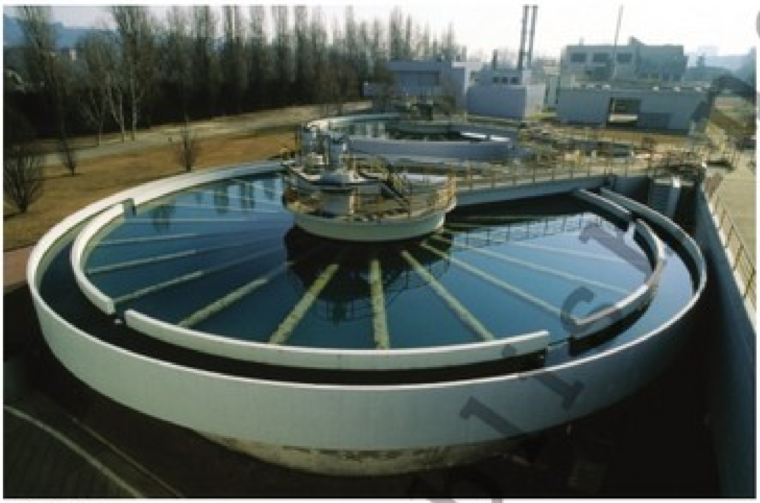


Figure 11.24
Flocculation and settling stage for purifying drinking water at a water works

When water emerges from a filtration process it is completely clear, but still requires some further treatment.

Chlorination

As water is likely to contain disease-causing bacteria, it is important to get the bacteria down to safe levels. This is done by chlorination – the addition of chlorine or chlorine compounds, which kill micro-organisms by oxidation.

The element chlorine may be used directly, but this is an unpleasant and dangerous process. Consequently, the use of elemental chlorine has been discontinued in some plants. The addition of sodium hypochlorite, NaOCl, is a common alternative. Both chlorine and sodium hypochlorite react with water to form chloric(I) acid, HOCl, which is the active disinfecting agent.

Care must be taken to add a suitable quantity of chlorine. The water may have to travel a considerable distance through distribution pipes, or it may be stored for some time before use. Thus sufficient chlorine must be added to give continued protection until use, but not so much as to subject the consumer to too large a dose.

Fluoridation

In some countries, fluoridation of drinking water is carried out to prevent tooth decay. The fluoride ion F^- is added, usually using sodium fluorosilicate, Na_2SiF_6, as its source.

Swimming-pool water treatment

Water in swimming pools is kept in good condition by the addition of oxidising agents that kill micro-organisms by oxidising them. Chlorine or compounds of chlorine such as sodium hypochlorite are used. When either of these substances is added to water, the oxidising agent HOCl is formed.

When this acts as an oxidising agent, it is reduced to the chloride ion (Cl^-).

Figure 11.25
Chlorine in a swimming pool kills micro-organisms by oxidising them

Hazards

As well as having many beneficial uses, the halogens are associated with various forms of hazard: fire and explosion, health and environmental hazards.

It is not surprising that elements which have such similar chemical properties can have similar physiological effects. The most common of these is that fluorine and chlorine (gases) and iodine and bromine vapours can harm the respiratory system. These gases and vapours even in small quantities can cause coughing and severe constriction of the chest. Breathing in such chemicals can cause a condition known as pulmonary oedema – a serious and potentially fatal illness - where damaged lung tissue results in excess fluid in the lungs.

Hydrochloric acid

There are different ways in which the gas hydrogen chloride can be formed. When hydrogen gas and chlorine gas are exposed to sunlight or temperatures above 250° C, they react violently to produce hydrogen chloride. The gas is also commonly produced through the reaction of sodium chloride and sulfuric acid.

Hydrogen chloride dissolves in water to produce hydrochloric acid. The acid is fully ionised in solution so it is a strong acid and care must be taken when handling it. Hydrochloric acid has a wide range of uses which include:

- dissolving concrete in retreating or cleaning old surfaces
- manufacture of glue, batteries and fireworks
- purifying common salt
- bleaching textiles

The acid also has a biological role as part of the gastric juices in the stomach which help to break down food.

QUESTIONS

37 Complete the equations:

(a) $H_2 + Cl_{2(g)} \rightarrow$ ______________ (b) $NaCl + H_2SO_4 \rightarrow$ ______________ $+ HCl$

38 What would you predict the pH of hydrochloric acid solution to be? Explain your reasons.

39 What sort of remedy would you take for acid reflux – where stomach acid passes back up your oesophagus?

Thyroxine

Iodine has an important biological role as a component of the thyroid hormone thyroxine.

Thyroxine is made when an amino acid (tyrosine) combines with iodine. Thyroxine controls the rate of all the body's reactions, i.e. it controls metabolism.

Underproduction of thyroxine in young children results in low metabolic rates and retarded mental and physical development. This condition is called cretinism.

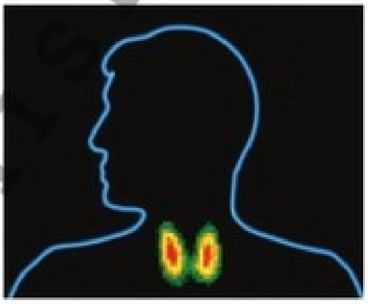


Figure 11.26
Scan of a normal thyroid gland

Deficiency of thyroxine in an adult results in a reduced metabolic rate. This is seen as tiredness, lack of energy, slow mental and physical activity and weight gain caused by the build-up of fluid under the skin. These symptoms are collectively called myxoedema.

Newborn babies are tested for low thyroxine levels as part of what is called the 'heel test'. If necessary, thyroxine can be administered to prevent the occurrence of cretinism. In adults, thyroxine tablets or iodine can be taken to prevent myxoedema.

Overproduction of thyroid hormone results in an increased metabolic rate (often 60% higher than normal). This causes symptoms such as bulging eyes, hunger, loss of weight, heat production, nervousness, irritability and anxiety. The metabolic condition is called Graves' disease.

Graves' disease can be cured by surgically removing part of the thyroid or by killing part of the gland using radioactive iodine.

The main way of avoiding the effects of iodine deficiency such as mental retardation and conditions such as goitre, cretinism and dwarfism is by introducing iodised salt into the household diet. Each tonne of salt only needs to contain around 57 grams of potassium iodate to counter the risk of such conditions in the general population.

In 1999 it was estimated that only 29% of households in Kazakhstan were using iodised salt and a campaign began to introduce its use to 100% of the population. Health experts involved in the campaign had to overcome considerable suspicion amongst sections of the population about iodization, but with the help of a massive government-sponsored marketing campaign and the cooperation of national producers of edible salt, in 2006 Kazakhstan was certified as a country that had achieved Universal Salt Iodization.

11.12 Tests for Anions

Positively charged ions, cations, in ionic substances may be identified by carrying out flame tests. Negatively charged ions, anions, may be identified by tests carried out on their aqueous solutions as in Experiment 11.1. Easily identifiable results, which may include the production of characteristically coloured precipitates, are obtained when the aqueous solutions react with certain reagents.

EXPERIMENT 11.1

Tests for anions in aqueous solutions: chloride, Cl^-, carbonate, CO_3^{2-}, nitrate, NO_3^-, sulfate, SO_4^{2-}, phosphate, PO_4^{3-}, sulfite, SO_3^{2-}, hydrogencarbonate, HCO_3^-.

Chemicals needed
Deionised water
Dilute hydrochloric acid
Limewater ☒
Solution of magnesium sulfate
Solution of barium chloride ☒
Solution of silver nitrate
Dilute ammonia solution
Cold saturated solution of iron(II) sulfate
Concentrated sulfuric acid
Solution of disodium hydrogen phosphate
Ammonium molybdate reagent ☒
Dilute solutions of the salts being tested

Equipment needed
Test tubes
Test tube rack
Test tube holder
Stoppers for test tubes fitted with plastic delivery tubing
Labels
Bunsen burner
Droppers
Beakers
Wash bottle
Thermometer

(a) To test for the carbonate (CO_3^{2-}) and hydrogencarbonate (HCO_3^-) anions

Carbonate and hydrogencarbonate ions both react with dilute hydrochloric acid producing carbon dioxide gas.

(i) $NaHCO_{3(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$
(ii) $Na_2CO_{3(aq)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

To distinguish between carbonate and hydrogencarbonate ions, a solution of magnesium sulfate is added. Since magnesium carbonate is insoluble in water, a white precipitate indicates that the salt is a carbonate.

$$Na_2CO_{3(aq)} + MgSO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + MgCO_{3(s)}$$

The absence of a precipitate indicates a hydrogencarbonate because magnesium hydrogencarbonate is soluble in water:

$$2NaHCO_{3(aq)} + MgSO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + Mg(HCO_3)_{2(aq)}$$

However, on heating this solution a white precipitate is formed because hydrogencarbonates decompose into carbonates on heating:

$$Mg(HCO_3)_{2(aq)} \rightarrow MgCO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$$

Procedure

NB: Wear your safety glasses

1 Add 2 cm^3 of a carbonate solution to a test tube.

2 Add some dilute hydrochloric acid using a dropper.

3 Carbon dioxide gas is produced, which can be shown to turn lime water milky.

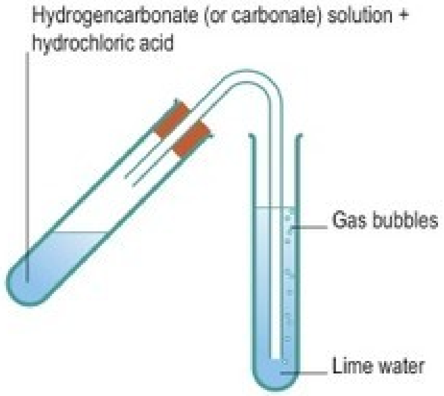


Figure 11.27

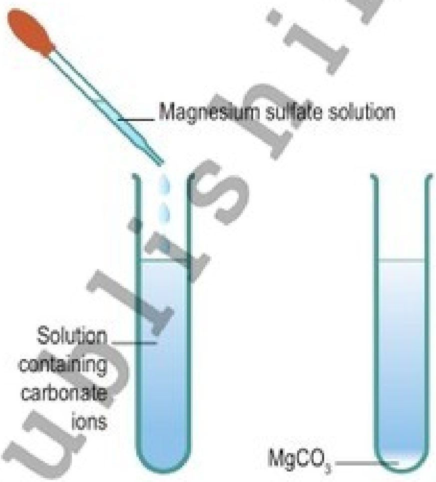


Figure 11.28

5 To some fresh solution in a clean test tube, add a few cm^3 of magnesium sulfate solution.

6 A white precipitate indicates that the salt being tested is a carbonate.

7 Repeat steps 1 to 4, using a hydrogencarbonate solution instead of a carbonate solution.

8 No precipitate should be formed on addition of magnesium sulfate solution. Heat the test tube gently. If a white precipitate is now formed, this confirms that the salt being tested is a hydrogencarbonate.

(b) To test for the sulfite (SO_3^{2-}) and sulfate (SO_4^{2-}) anions

Both sulfite and sulfate ions react with barium chloride solution, producing white precipitates of barium sulfite and barium sulfate respectively.

$$\text{(i)}\ Na_2SO_{3(aq)} + BaCl_{2(aq)} \rightarrow 2NaCl_{(aq)} + BaSO_{3(s)}$$
$$\text{(ii)}\ Na_2SO_{4(aq)} + BaCl_{2(aq)} \rightarrow 2NaCl_{(aq)} + BaSO_{4(s)}$$

Barium sulfite reacts with and dissolves in hydrochloric acid, but barium sulfate does not.

$$BaSO_{3(s)} + 2HCl_{(aq)} \rightarrow BaCl_{2(aq)} + H_2O_{(l)} + SO_{2(g)}$$

This reaction is used to distinguish between sulfite and sulfate ions.

Procedure

NB: Wear your safety glasses

1 Add 2 cm^3 of a sulfite solution to a clean test tube and add some barium chloride solution using a dropper.

2 A white precipitate indicates the presence of sulfate or sulfite ions (Figure 11.27).

3 Add a few cm^3 of hydrochloric acid and mix gently.

4 The precipitate should dissolve, confirming that the salt being tested is a sulfite.

5 Repeat steps 1 to 3, using a sulfate solution instead of a sulfite solution.

6 The precipitate should not dissolve on addition of hydrochloric acid, confirming that the salt being tested is a sulfate.

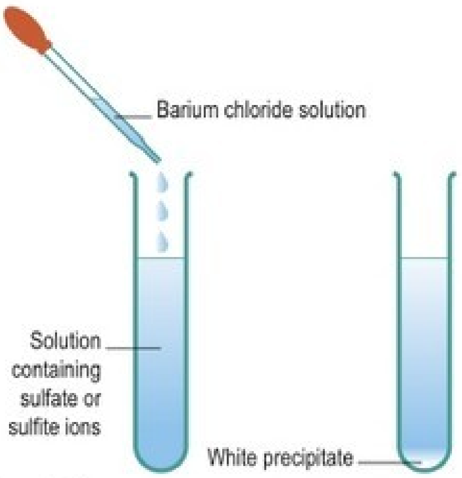


Figure 11.29

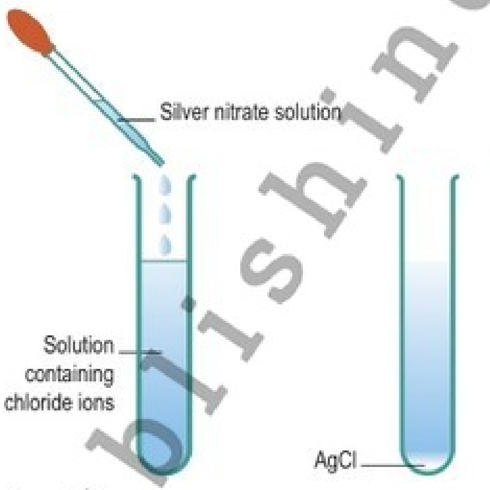


Figure 11.30

(c) To test for the chloride (Cl^-) anion

Solutions containing chloride ions react with silver nitrate solution, producing a white precipitate of silver chloride.

$$NaCl_{(aq)} + AgNO_{3(aq)} \rightarrow NaNO_{3(aq)} + AgCl_{(s)}$$

This precipitate dissolves on addition of dilute ammonia solution.

Procedure

NB: Wear your safety glasses

1 Add 2 cm^3 of chloride solution to a clean test tube. Add a few drops of silver nitrate solution using a dropper.

2 A white precipitate indicates the presence of chloride ions (Figure 11.28).

3 This is confirmed by adding a few cm^3 of dilute ammonia solution. The precipitate should dissolve.

(d) To test for the nitrate (NO_3^-) anion

Solutions containing nitrate ions react with a mixture of iron(II) sulfate solution and concentrated sulfuric acid. When concentrated sulfuric acid is added to a mixture of nitrate and iron(II) sulfate solutions, a brown ring develops slowly at the interface of the sulfuric acid layer and the layer containing the mixture. This test is therefore known as the 'brown ring test'.

Procedure

NB: Wear your safety glasses

1 Add 2 cm^3 of potassium nitrate solution to a clean test tube. Add 3 cm^3 of cold **freshly-prepared** saturated iron(II) sulfate solution using a dropper.

2 Carefully add 2 cm^3 of concentrated sulfuric acid slowly down the wall of the test tube using a dropper. Do not mix the contents of the test tube.

3 After a few minutes, a brown ring will form at the interface of the two layers, indicating that the salt being tested is a nitrate.

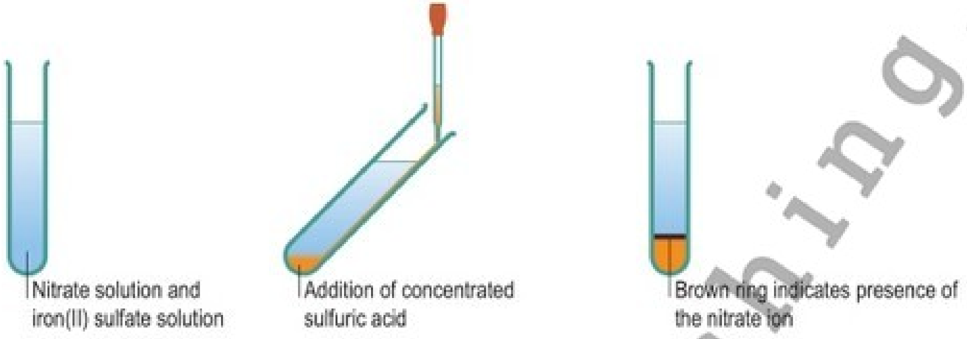


Figure 11.31

(e) To test for the phosphate (PO_4^{3-}) anion

Solutions containing phosphate ions react on heating with an ammonium molybdate reagent, forming a yellow precipitate. This precipitate dissolves on addition of ammonia solution.

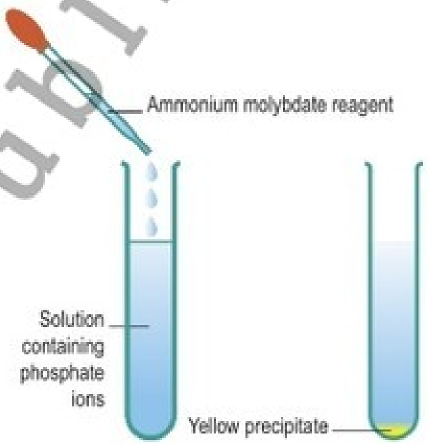


Figure 11.32

Procedure

NB: Wear your safety glasses.

1 Add 2 cm^3 of disodium hydrogenphosphate(V) solution to a clean test tube.

2 Add about 6 cm^3 of the clear ammonium molybdate reagent to the test tube using a dropper.

3 Add a few drops of concentrated nitric acid.

4 Warm gently by placing in a beaker of water at a temperature not exceeding 40°C. A yellow precipitate suggests the presence of phosphate ions in the salt being tested.

5 Add an equal volume of ammonia solution to the contents of the test tube at the end of step 4. The precipitate dissolves, indicating that the original salt is a phosphate.

QUESTIONS

40 What is observed when hydrochloric acid is added to a solution of carbonate ions? What gas is given off?

41 What is observed if a solution of magnesium sulfate is added to a solution of hydrogencarbonate ions? What effect would heating have on the resulting mixture?

42 What is observed when barium chloride solution is added to a solution of sulfate or sulfite ions? How would you distinguish between sulfate and sulfite ions?

43 Describe how to carry out the test for nitrate ions.

44 What is the test for nitrate ions called?

45 Describe how to carry out the test for phosphate ions.

QUESTIONS

46 What is observed if a solution of silver nitrate is added to a solution of chloride ions? What is the confirmatory test for chloride ions?

47 Complete the following table:

Test for	Reagents needed	Positive result
Chloride	Silver nitrate solution Ammonia solution	
		Brown ring
Sulfate	Barium chloride solution Hydrochloric acid	
Phosphate		
Carbonate	Hydrochloric acid Magnesium sulfate solution	
Hydrogencabonate		

48 The clock glasses shown in the diagram contained pure samples of the following salts: KCl, KNO_3, $Na_2HPO_4.12H_2O$, $Na_2SO_3.7H_2O$, $NaHCO_3$ and $Na_2SO_4.10H_2O$. Each clock glass (A – F) contained a different salt. A student was provided with standard laboratory apparatus and reagents, and was asked to identify the six salts.

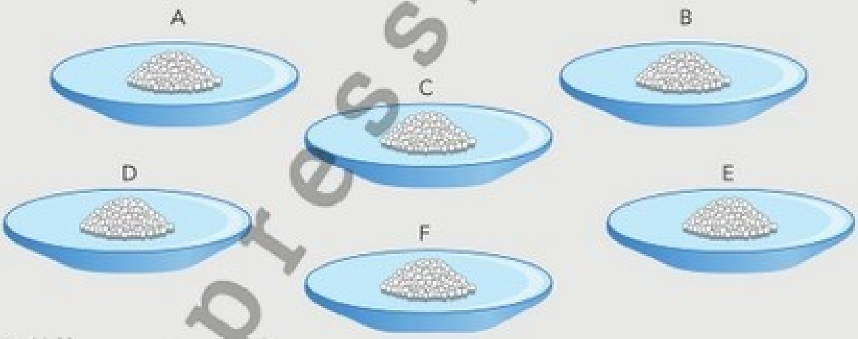


Figure 11.33

(a) Which of the substances listed above was identified by the addition of silver nitrate, $AgNO_3$, solution to a solution of each sample in turn? What observation indicated a positive test result?

(b) One of the samples gave a brown ring when a little concentrated sulfuric acid was carefully poured down the inside of a slanting test tube which contained a solution of the salt, together with another reagent. What was the other reagent? Which salt was identifiable by the appearance of a brown ring?

(c) Describe how you would test the samples for the presence of the phosphate anion.

Industrial Chemistry

MODULE 12

Learning objectives

- Understand processes of manufacture in chemical and metallurgical industries 10.2.3.8
- Recognise the composition of the main alloys: steel, cast iron, brass, bronze, cupronickel, duralumin 10.2.3.9
- Describe the main methods of production of iron and steel 10.2.3.10
- Explain some of the environmental problems associated with the chemical industry in kazakhstan 10.4.1.13
- Describe the stages of the Contact process in the manufacture of sulfuric acid and describe the role of sulfuric acid for industry 10.2.1.45
- Describe the manufacture of ammonia and nitric acid, and their applications 10.2.1.46
- Describe the manufacture of glass and cement and their uses 10.2.3.11
- Assess the impact of chemical and metallurgical waste on the environment 10.4.1.14

12.1 The Contributions of Chemistry to Society

Useful materials are being continually produced by the chemical industry:

- In the area of health, medicines and the chemicals needed to make water safe to drink.
- In agriculture, fertilisers, herbicides and pesticides, used to improve crop yields.
- A wide variety of metals, plastics, synthetic fibres, fuels, detergents, enzymes, dyes, paints, semiconductors, liquid crystals and chemicals used in food processing.

Figure 12.1
Fertilisers are an important product of the chemical industry

12.2 Industrial Chemical Processes

- Batch processes

A batch process is an industrial process in which an amount of the product is made in a reaction vessel during a definite time interval, and is then removed from the vessel.

In a **batch process**, an amount of the product is made in a reaction vessel during a particular time interval. The product is removed from the vessel, which is then cleaned and prepared for further use. The process is then repeated. Batch processes are widely used in the manufacture of pharmaceuticals.

- **Continuous processes**

A continuous process is an industrial process in which the reactants are continuously fed into the reaction vessel, and the products are continuously removed.

In a **continuous process**, the reactants are continuously fed into the reaction vessel, and the products are continuously removed. The Haber process used in the production of ammonia, which we shall look at later in this module, is an example of a continuous process – with the raw materials being fed in continuously and the ammonia being continuously produced.

- **Semi-continuous processes**

A semi-continuous process is an industrial process in which part of the process is a continuous process, and part is a batch process.

In a **semi-continuous process**, part of the process is a continuous process, and part is a batch process. For example, the brewing of beer is a batch process, but the processes of adding carbon dioxide and of bottling the beer are continuous.

Figure 12.2
An ammonia plant

12.3 Characteristics of Industrial Chemical Processes

(a) Feedstock

The reactants in an industrial process are called the **feedstock**. In the industrial synthesis of ammonia, the reactants are nitrogen gas and hydrogen gas. Feedstock is produced from the **raw materials**.

The feedstock is the reactants in an industrial process.

The raw material from which nitrogen is isolated is air. Natural gas (or oil) is the raw material from which hydrogen is made.

(b) Reaction rate

The temperature, pressure and catalyst for an industrial chemical reaction all affect the reaction rate, and the conditions have to be selected for the process to occur at a satisfactory rate.

(c) Product yield

The reaction conditions chosen for a chemical reaction in industry must be such as to result in a satisfactory yield. However, as in the industrial synthesis of ammonia, there may need to be a compromise found between the conditions for a good yield and the conditions for a satisfactory rate.

(d) Co-products

Co-products are the other products formed along with the main product being manufactured.

Co-products have to be separated from the main products, and either disposed of, or, if they are useful, sold or used on site. In the industrial synthesis of ammonia, the co-product is carbon dioxide, formed as part of the process of producing hydrogen. It is isolated by dissolving it in an alkaline solution. It can be sold to soft drinks manufacturers and breweries.

(e) Waste disposal and effluent treatment

Satisfactory methods of controlling air emissions, of disposing of waste and of waste water treatment have to be used.

(f) Quality control

Instrumentation is invaluable in monitoring the quality of materials at various stages of an industrial process. In the industrial synthesis of ammonia, analyses of the gas mixtures at all stages of ammonia production can be carried out using gas chromatography and infrared spectroscopy. The performance of the catalyst can be monitored using these methods.

(g) Safety

Safety considerations include monitoring of hazards, on-site training of the staff in first aid and in fire fighting, and safety features incorporated in the plant. The location of the site is also important. The site should be designed so as to allow access by fire engines to central parts of the plant.

(h) Costs

Fixed costs in an industrial process are those costs that have to be paid regardless of the rate of production.

These include labour costs, plant depreciation, land rental and repayments on loans.

Variable costs in an industrial process are those costs that depend directly on the level of plant output.

These include the cost of heat, electricity, raw materials and the costs of waste disposal.

Methods that are used to reduce costs include the following: use of heat exchangers, use of catalysts, recycling of feedstock and the sale of useful co-products.

(i) Site location

Site location should take into account the source of raw materials, the proximity of a market for the product, the availability of water and of transport for raw materials and products, and the availability of a suitable workforce.

(j) Construction materials

Plant construction materials must not react with the feedstocks, solvents, catalysts or products involved in the process. The construction materials therefore need to be unreactive and resistant to corrosion by the chemicals with which they come in contact.

QUESTIONS

1 Explain the difference between a continuous process and a batch process in the chemical industry.

2 Distinguish between the terms **feedstock** and **raw materials** as used in industrial chemistry.

Alloys

An alloy is a mixture of two or more elements, at least one of which is a metal.

An alloy can have very different properties from the elements from which it is formed. The elements are usually mixed by melting them, mixing the molten elements, and then allowing the mixture to solidify

Steel, for example, contains mainly iron with, typically, about 0.3% of carbon. Small, carefully measured amounts of transition metals such as chromium, nickel, tungsten, titanium, vanadium or manganese may also be added. These elements are chosen to give the steel particular properties to suit its use, such as hardness, rigidity, flexibility, and resistance to corrosion. Steel is much harder than iron and can be used in making cutting tools, girders for bridges and steel-framed buildings and reinforcements for building foundations, amongst many other uses.

QUESTIONS

3 Complete the table below with either the name of the alloy or the missing constituent elements.

Alloy	Constituent elements
Brass	Copper and zinc
Bronze	Copper and ______________
______________	Iron, chromium, nickel and carbon
Cast iron	Iron and ______________ [possibly with silicon]
______________	Copper, nickel, [iron or manganese]
Duralumin	aluminium and ______________

4 Which of the alloys in the table above is used for:

(a) bridge construction
(b) pipes laid in the sea
(c) musical instruments
(d) aircraft construction
(e) car exhaust systems, zips, cladding buildings
(f) cast statues?

12.4 Manufacture of Iron and Steel

Iron occurs in ores such as haematite (impure Fe_2O_3), magnetite (impure Fe_3O_4) and iron pyrites (impure FeS). The extraction of iron from its ores is carried out in a **blast furnace**, in which the iron ore is reduced to molten iron, using coke at a high temperature. Unlike more reactive metals, this extraction is a **chemical reduction process** rather than an electrochemical process.

Manufacture of iron

The raw materials for the blast furnace process for the extraction of iron from ores such as haematite are: coke, limestone and the ore itself. In the blast furnace process, the ore, coke and limestone are fed regularly into the furnace from the top. Hot air is added from the bottom.

- Coke is mainly composed of carbon, and the ore is reduced by reaction with carbon:

  $Fe_2O_{3(s)} + 3C_{(s)} \rightarrow 2Fe_{(s)} + 3CO_{(g)}$

- The carbon monoxide causes further reduction in the upper, cooler regions of the furnace:

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

  Most of the reduction of the iron ore is caused by carbon monoxide. The gases formed (CO, CO_2) are drawn off through ducts.

- The limestone decomposes into calcium oxide and carbon dioxide. The calcium oxide reacts with impurities in the iron ore, forming slag:

  $CaO + SiO_2 \rightarrow CaSiO_3$

  $CaO + Al_2O_3 \rightarrow CaAl_2O_4$

  The molten iron and slag trickle down into the hearth, where the less dense slag floats on the iron. The slag and iron are separately tapped off into large tanks.

- At this stage the iron is not very pure and, if allowed to solidify, forms pig iron. Pig iron is brittle, with a high carbon content, and is much less useful than steel.

  The slag is used in roadmaking

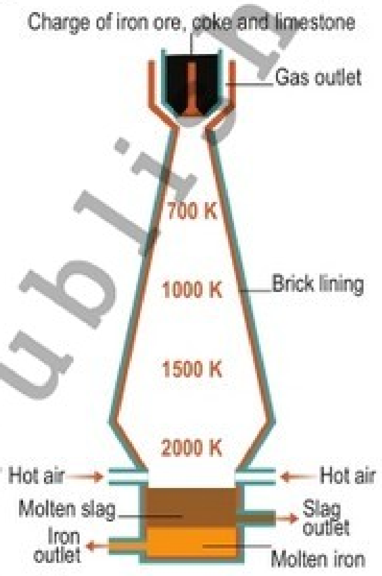


Figure 12.3
The blast furnace

Manufacture of steel

To make steel from iron, the iron must first be purified.

- Oxygen is blown onto the surface of the liquid iron at the base of the furnace. This oxidises silicon, manganese and some iron, and the products are removed as slag. Carbon is also oxidised and the gaseous products escape to the atmosphere.
- The molten iron, which is now sufficiently pure, is poured into a ladle and carefully measured amounts of carbon and other elements are added. This process is called the **basic oxygen process**.

Properties of different steels

Alloying carbon with iron to make steel increases the hardness and strength of the metal. Other metals may be added in controlled amounts as well. By a correct choice of metal, and by adding a suitable proportion of this metal to iron, steels can be made which are very hard, or very resistant to corrosion, or of great strength. Metals such as tungsten are used to harden steel. Corrosion-resistant steels are made using chromium and nickel. Manganese is used to make very tough steel.

Uses of iron and steel

Steel is used in the manufacture of car bodies, and in the construction of bridges and buildings. The uses of iron are more limited. It is used, for example, in manhole covers, chains and gates.

QUESTIONS

5 Why is iron converted to steel?
6 In the blast furnace process for the extraction of iron from iron ore, what reducing agents are used?
7 How is iron from a blast furnace further purified?
8 How is steel made (a) harder (b) more corrosion-resistant (c) tougher?
9 Why are the reactions that take place in a blast furnace regarded as redox reactions?

12.4 Electric Arc Process for Steel Manufacture

Steel can be made from recycled steel, which is melted in an **electric arc furnace** before it is refined and cast and rolled into steel products.

There are five main stages in making steel using the electric arc furnace.

(a) Charging

An overhead crane is used to add the scrap to the furnace. Lime (calcium oxide) is added to absorb the acidic impurities during the melting and refining stages and to form slag.

(b) Melting

An electric arc is struck between carbon electrodes and the scrap. This generates very high temperatures, melting the steel quickly.

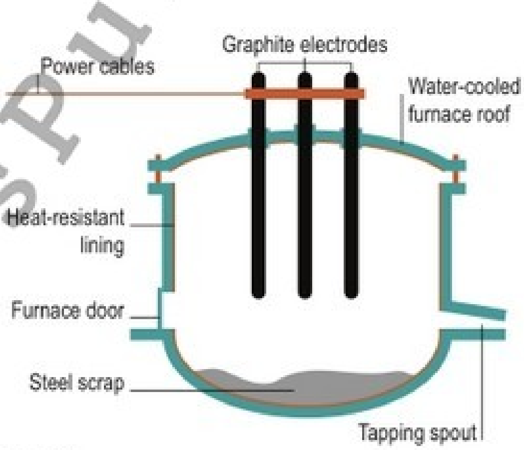


Figure 12.4
The electric arc furnace

(c) Refining

Oxygen is blown onto the molten steel to oxidise non-acidic impurities to their oxides. Excess carbon burns to form carbon monoxide and carbon dioxide:

$$2C_{(s)} + O_{2(g)} \rightarrow 2CO_{(g)}$$
$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$

Non-metals present, such as silicon, will form oxides, which then react with lime to form calcium silicate, a component of slag:

$$Si + O_2 \rightarrow SiO_2$$
$$CaO + SiO_2 \rightarrow CaSiO_3$$

Phosphorus and aluminium oxides are removed in a similar manner.
Slag is less dense than liquid steel and floats on top, which means that it can be easily removed. Tilting the furnace pours off the liquid slag.

(d) Tapping

The liquid steel is next released from the furnace into an insulated ladle. The composition of the steel is adjusted by adding the required amounts of alloying elements, such as carbon, silicon, manganese, and chromium.

(e) Casting

The molten steel is then poured into a casting machine where a slab of solid steel is formed.

QUESTIONS

10 What are the main stages in the electric arc furnace process?
11 Why is lime used in the electric arc furnace process?
12 What happens during the refining stage of the electric arc furnace process?
13 Name one compound present in slag.
14 What is slag used for?

12.5 The Haber Process

The synthesis of ammonia from its elements:

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \ \Delta H = -92 \text{ kJ mol}^{-1}$$

is an important process in the fertiliser industry. The process used to make ammonia is called the Haber process.

Since the reaction is reversible, Le Chatelier's Principle is applicable. In the industrial synthesis of ammonia, the objective is to produce the maximum possible amount of ammonia at the lowest cost and in the shortest possible time. A balance has to be struck between factors that favour a reasonable rate of reaction and those that favour a reasonable yield.

(i) Temperature

$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)} \qquad \Delta H = -92 \text{ kJ mol}^{-1}$$

Since the forward reaction is exothermic, it is favoured by a lowering of the reaction temperature at equilibrium. The extent to which this can be done is limited by the fact that the temperature must be high enough to allow the reaction to proceed at a reasonable rate. If the temperature is too low, not enough nitrogen and hydrogen molecules will have the activation energy for the reaction, and the reaction rate will be too slow. This would cause production costs (such as fuel and labour) to rise to an uneconomic level. In practice, temperatures of about 673 K are used. This results in a low yield, but unreacted nitrogen and hydrogen can be collected and sent back into the reaction vessel again and again.

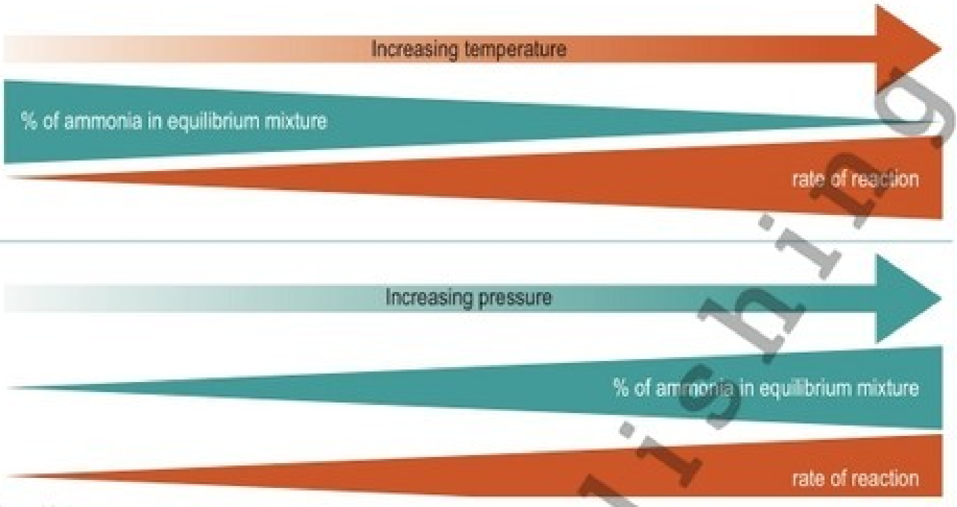


Figure 12.5
A high yield of ammonia is favoured by (a) lower temperatures and (b) higher pressures

(ii) Pressure

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
4 moles 2 moles

An increase in pressure at equilibrium favours the formation of ammonia. For this reason the reaction is carried out under pressure. The Haber process uses high pressures (about 200 atmospheres) to increase the yield of ammonia. Higher pressures have been used, but are more costly.

(iii) Catalyst

In the absence of a catalyst, the reaction has a high activation energy. A catalyst is used both because it brings the system to equilibrium faster, and because, by lowering the activation energy, it keeps fuel costs down by allowing the reaction to be carried out at a lower temperature.

12.6 The Contact Process

In the industrial manufacture of sulfuric acid, the slowest step is the following reaction

$$SO_{2(g)} + ½O_{2(g)} \rightleftharpoons SO_{3(g)}$$

$$\Delta H = -98 \text{ kJ mol}^{-1}$$

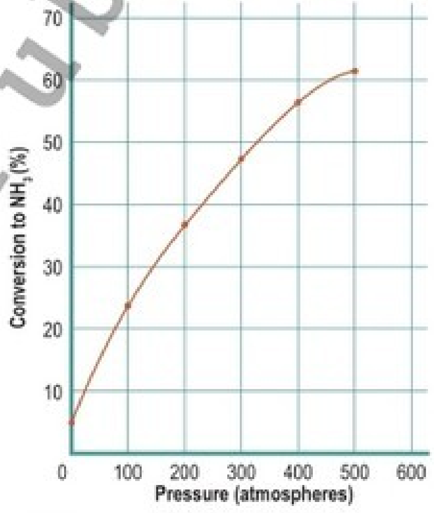


Figure 12.6
The effect of pressure on the yield of ammonia at 673 K

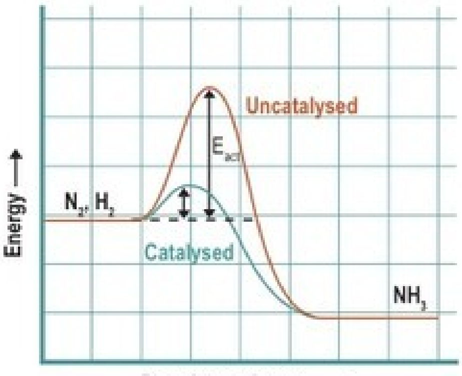


Figure 12.7
The effect of pressure on the yield of ammonia at 673 K

The process used to make sulfur trioxide is called the Contact process.
The sulfur trioxide is the desired product, as it reacts readily with water forming sulfuric acid:

$$SO_{3(g)} + H_2O_{(l)} \rightarrow H_2SO_{4(l)}$$

As the reaction between sulfur dioxide and oxygen forming sulfur trioxide is reversible, Le Chatelier's Principle may also be applied to it.

(i) Temperature

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow SO_{3(g)} \qquad \Delta H = -98 \text{ kJ mol}^{-1}$$

Since the forward reaction is exothermic, this reaction is favoured at equilibrium by a lowering of the reaction temperature. In practice, a temperature of about 713 K is chosen, as this is the lowest temperature that can be used without reducing the rate to too low a level.

(ii) Pressure

$$SO_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow SO_{3(g)}$$

1½ moles   1 mole

The forward reaction brings about a reduction in the number of molecules present, and so is favoured by high pressures. In practice, a high yield is obtained using atmospheric pressure or a pressure slightly higher than that, and so higher pressures are not economically justified.

(iii) Concentration

The forward reaction is favoured if the sulfur trioxide is removed as it is formed. Sulfuric acid synthesis plants therefore incorporate a method for removal of the sulfur trioxide formed, allowing unreacted oxygen and sulfur dioxide to react further.

(iv) Catalyst

A catalyst is used as it brings the reactants to equilibrium faster by lowering the activation energy.

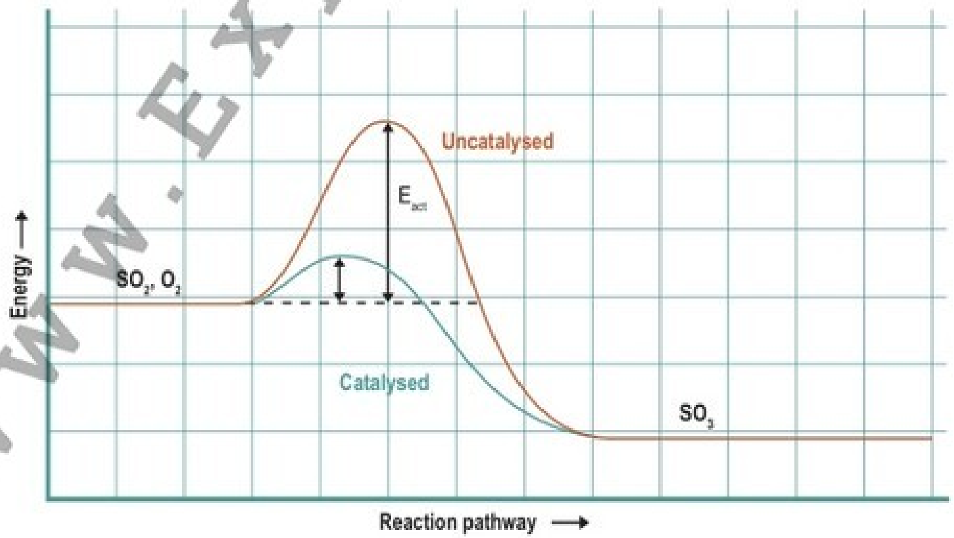


Figure 12.8

Uses of sulfuric acid

Sulfuric acid is a transparent, oily liquid with no discernible smell. It has a wide range of industrial uses and applications in industry such as the treating of ores and metals and the making of fertilisers such as phosphate fertilisers and ammonium sulfate. Sulfuric acid has a strong affinity for water and is thus used in dehydration processes such as the dehydration of ethanol and to dehydrate hydrated crystals. A catalyst is used as it brings the reactants to equilibrium faster by lowering the activation energy.

12.7 The production of nitric acid – the Oswald process

The nitric acid molecule contains a hydrogen atom, a nitrogen atom with a positive charge and three oxygen atoms – one of which carries a negative charge. The nitrogen atom is bonded to all three oxygen atoms.

Pure nitric acid is liquid at room temperature but becomes a white solid below –41°C and it boils at 83°C. Nitric acid is miscible in water forming hydrates at a low temperature.

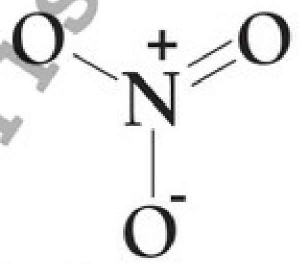


Figure 12.9

The industrial production of nitric acid uses a process known as the Oswald process. This involves four stages to produce a concentrated form of nitric acid.

Stage 1:

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

In this reaction anhydrous ammonia is oxidised to nitric oxide at high temperatures using a platinum catalyst.

Stage 2:

$2NO + O_2 \leftrightarrow 2NO_2$

Nitric oxide from Stage 1 is cooled and oxidises to form nitrogen dioxide.

Stage 3:

$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$

The nitrogen dioxide obtained in Stage 2 is reacted with water in a special chamber. As the nitrogen dioxide is absorbed into the water nitric acid is obtained.

Stage 4:

To increase the concentration of the nitric acid obtained in Stage 3 HNO_3, vapours are passed over concentrated H_2SO_4.

Nitric acid has a wide range of uses including the production of fertilizers such as ammonium nitrate and the production of explosives such as nitroglycerin and trinitrotoluene (TNT). It is also used in the manufacture of dyes, and in processes such as photo-engraving.

QUESTIONS

15 Complete these equations and name the industrial process each one is part of:

(a) $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons$ ______________

(b) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons$ ______________

(c) $3NO_{2(g)} + H_2O_{(l)} \rightarrow$ ______________

(d) $SO_{3(g)} + H_2O_{(l)} \rightarrow$ ______________

16 Why are high pressures used in the Haber process?

17 What happens to the unreacted nitrogen and hydrogen in the Haber process?

18 In the Contact process why is the sulfur trioxide removed at frequent intervals?

19 What are the products of the first stage of the Oswald process ?

20 Why is sulfuric acid used in the final stage of the Oswald process?

12.8 Environmental problems of the chemical and metallurgical industries in Kazakhstan

The generic environmental issues of the chemical and metallurgical industries broadly relate to three areas:

- the mining and extraction of ores
- processes in the production of metals and chemicals
- dealing with chemical waste

(a) Mining and Extraction

Large scale mining and extraction has a range of negative impacts on the environment. Foremost amongst these is the removal of rock from quarries which causes scarring of the landscape. The majority of mines from which ores are extracted in Kazakhstan are open-pit mines which makes this a general concern for the industry in the country.

Figure 12.10
Open-pit quarrying

A more specific concern relates to the method widely used for uranium extraction in Kazakhstan. The in situ recovery process of extracting uranium is one in which rather than removing ore from a deposit, a solution of sulfuric acid is injected into the deposit which dissolves the uranium. This solution is then pumped back to the surface and the uranium is recovered. While this process gets around many typical mining dangers, it also has risks of leakage from injection well pipes which can then contaminate local ground water. Mining companies in the industry need to be vigilant in monitoring groundwater quality and restoring ground water quality as a result of any leaks.

(b) Processes in the production of metals and chemicals

In the production of steel by blast furnace, where iron is being extracted from a sulfide ore, some sulfur dioxide will be formed in the blast furnace. When coke is being produced from coal, for use in the blast furnace, smoke and sulfur dioxide are formed. Emissions of these must be kept to a minimum. Fumes from a blast furnace must also be cleared of dust particles before being released into the atmosphere. Problems with high emission levels in the form of hydrogen sulfide have been recorded in Termitau near Karanganda the centre of the country's steel and iron industry.

In the electric arc process, all emissions from the steel-making plant have to be carefully monitored. Fumes are filtered to remove dust particles, and water used for cooling purposes is recycled. The use of natural gas for heating eliminates emissions of sulfur dioxide, which can be a problem if oil or coal is used instead.

(c) Dealing with chemical waste

The metallurgical industries in particular produce high levels of industrial waste. The extraction of aluminium oxide from bauxite, for example, results in the formation of very large amounts of red mud, which is unsightly. The most promising initiatives in dealing with such waste around the country are those that involve recycling. In Pavlodar, for example, the Pavlodar Ash-Sludge Waste Processing Plant, takes materials such as bauxite slime from the aluminium production process and ash from the combustion of coal and uses them in the manufacture of bricks and additives to cement.

Non-hazardous waste can with initiative and planning be recycled into materials that can be used, for example, in road construction but hazardous waste materials need more specialist treatment plants if they are to be recycled. An example of one such plant is Vodokanalstroy Company in Termitau which uses blast furnace slag as additives in the production of construction materials. Such initiatives, however, will need to continue to grow and be supported to deal with Kazakhstan's estimated 22 billion ton accumulation of solid waste, which largely due to the importance of the extraction and processing industries in the country is estimated to increase at about a billion tons a year.

QUESTIONS

21 Describe the in situ recovery method for the extraction of uranium.

22 The emission of which type of gases needs to be monitored and controlled carefully in the iron and steel industries?

23 What is one of the main environmental problems in the process of extracting aluminium from bauxite?

24 What is needed if more hazardous waste is to be productively recycled?

Glossary

A

abrasive A very hard, brittle, heat-resistant substance that is used to grind the edges or rough surfaces of an object.

acid-base indicator A weak acid which is of a different colour from its conjugate base. In solution, it varies in colour as the concentration of hydrogen ions changes.

acid-base reaction This is a reaction involving proton transfer.

acid An acid is a proton donor. It is a substance which turns blue litmus red and has a pH less than 7.

acid rain Rainwater with a pH of less than 5.5.

acid–base pair A pair of two species that transform into each other by gain or loss of a proton.

activation energy The minimum energy required to start a reaction by the breaking of bonds.

actual yield The amount of product obtained from a reaction.

adhesive Any substance that is capable of holding materials together in a functional manner by surface attachment that resists separation.

adsorption The process that occurs when a gas or liquid or solute is held to the surface of a solid.

aldehyde Any of a class of organic compounds containing the group –CHO, which yields acids when oxidised and alcohols when reduced.

algae Photosynthetic organisms of aquatic or moist habitats, ranging in size from single-celled diatoms to large seaweeds such as kelp, and characterised by a lack of complex organs and tissues.

aliphatic hydrocarbon Hydrocarbons are compounds made solely of carbon and hydrogen atoms in which each carbon forms four covalent bonds. The aliphatic hydrocarbons are the alkanes, alkenes and alkynes.

alkali A substance which reacts with an acid to form a salt and water. Alkalis are bases that dissolve in water.

alkali metals The elements of Group 1 of the periodic table, e.g. sodium.

alkaline earth metals The elements of Group II of the periodic table, e.g. calcium.

alkanes The hydrocarbon homologous series with single carbon-to-carbon bonds and the general formula: C_nH_{2n+2}.

alkenes The hydrocarbon homologous series with one double carbon-to-carbon bond and the general formula: C_nH_{2n}.

alkyl group A side chain formed by removing a hydrogen atom removed from an alkane chain, an alkyl group can be represented as R.

alkynes The hydrocarbon homologous series with one triple carbon-to-carbon bond and the general formula: C_nH_{2n-2}.

alloy A metal made by combining two or more metallic elements.

alpha particle A positively charged particle consisting of two protons and two neutrons, emitted in radioactive decay or nuclear fission; the nucleus of a helium atom.

amount of substance The quantity whose unit of the mole is used as a means of counting any species such as atoms, ions and molecules.

amphoteric A substance capable of acting as either an acid or a base.

angular quantum number The angular momentum quantum number, ℓ, is the quantum number associated with the angular momentum of an atomic electron. It determines the shape of the electron's orbital.

anhydrous Containing no water molecules.

anion A negatively charged ion with more electrons than protons.

anode The charged positive electrode in a polarised electrical device through which current flows in from an outside circuit.

anodising (anodise vb) An electrolytic process for producing thick oxide coatings, usually on aluminium and its alloys.

aromatic hydrocarbons These are stable, unsaturated cyclic compounds composed mainly of hydrogen and carbon atoms. The electrons that create the double bonds are delocalised and can move between parent atoms. Examples include benzene, toluene, purines and pyrimidines.

atomic number (Z) This is equal to the number of protons in the nucleus of the atom. It is also equal to the number of electrons in the neutral atom.

atomic orbital A region around the nucleus that can hold up to two electrons, with opposite spins.

atomic radius Half the distance between the nuclei of atoms of that element when bonded together by a single covalent bond.

atom The smallest part of an element that still has the properties of that element.

Aufbau principle Electrons occupy the lowest available energy level.

Avogadro constant This is the number of atoms in exactly 12g of carbon-12 (6.02×10^{23} mol^{-1})

B

balanced chemical equation This occurs when the number of the different atoms of elements in the reactants side is equal to that of the products side.

base A base is a proton acceptor.

beta particle (symbol β) A high-energy, high-speed electron or positron emitted by the radioactive decay of an atomic nucleus during the process of beta decay.

binary compound A compound containing two elements only.

biodegradable A substance which can be chemically decomposed (broken down to simpler components) by natural biological processes such as soil bacteria, weather, plants and animals.

boiling point The temperature at which a liquid boils.

bond angle The angle between two bonds of an atom.

bonded pair A pair of electrons shared between two atoms to make a covalent bond.

bond energy The energy required to break bonds of a molecule into individual atoms.

Brønsted-Lowry acid A species that is a proton, H + , donor.

Brønsted-Lowry base A species that is a proton, H^+ , acceptor.

buffer solution A solution which is resistant to changes in pH on addition of small quantities of acid or alkali, or upon dilution with water.

C

calorific value The quantity of heat produced by the complete combustion of a given mass of a fuel, usually expressed in joules per kilogram.

carbon footprint The total amount of carbon dioxide and other greenhouse gases produced by an individual, organisation, product or event; usually expressed in equivalent tons of carbon dioxide (CO_2).

carbon reservoir A place on Earth where there is a build-up of carbon dioxide.

carbon sink Part of the Earth that can absorb carbon dioxide from the atmosphere.

carboxylic acid An organic acid, for example, acetic acid, containing one or more carboxyl groups.

catalyst A substance that increases the rate of a chemical reaction without being used up in the process.

catalytic cracking The breaking down of long-chain hydrocarbon molecules into short-chain molecules for which there is a greater demand, using heat and catalysts.

cathode The metallic electrode through which current flows out in a polarised electrical device.

cation A positively charged ion with fewer electrons than protons.

chain reaction A reaction in which the propagation steps release new radicals that continue the reaction.

chemical bond Any of several forces, especially the ionic bond, covalent bond, and metallic bond, by which atoms or ions are bound in a molecule or crystal.

chemical change A change (reaction) in which a new substance is formed.

chemical energy Energy stored inside materials in the chemical bonds holding them together.

chemical equilibrium The point at which the concentrations of reactants and products do not change with time. It appears as though the reaction has stopped but in fact the rates of the forward and reverse reactions are equal ,so reactants and products are being created at the same rate.

chlorination The addition of chlorine to water to kill bacteria.

chromatography A technique for the separation of a mixture by passing it in solution or suspension through a medium in which the components move at different rates.

closed system A system isolated from its surroundings.

collide In a chemical reaction, the reactant particles can only react with each other when they bump into one another. When molecules collide, bonds between their atoms can break and new bonds can form to create new molecules.

collision theory This is based on the assumption that for a reaction to occur it is necessary for the atoms or molecules to come together or collide. When molecules collide, bonds between their atoms can break, and then new bonds can form to make new molecules.

composites Materials which are made up of at least two different materials.

compounds Made up of two or more different types of atom chemically combined.

concentrated solution A solution which contains a large amount of solute in a small amount of solvent.

condensation Where cooling a gas causes it to change into a liquid.

conjugate acid A species that releases a proton to form a conjugate base.

conjugate base A species that accepts a proton to form a conjugate acid.

conservation of mass When matter is changed from one form into another but there is no change in the overall mass.

corrosion An undesirable process whereby a metal changes to its oxide or some other compound by combining with oxygen from air.

covalent bond A bond that consists of a pair of electrons shared between two non-metal atoms.

cross-contamination The process by which bacteria or other microorganisms are unintentionally transferred from one substance or object to another, with harmful effect.

crystal lattice A crystal is a solid material that contains atoms or groups of atoms arranged in a highly ordered, three-dimensional structure.

crystallisation The formation of crystals by cooling a saturated solution or by evaporating off solvent.

D

decompose A decomposition reaction is a type of chemical reaction in which a single compound breaks down into two or more elements or new compounds. These reactions often involve an energy source such as heat, light, or electricity that breaks apart the bonds of compounds.

dehydration An elimination reaction in which water is removed from a saturated molecule to make an unsaturated molecule.

dehydrocyclisation The use of catalysts to convert straight-chained alkanes into cyclic compounds.

denaturing agent Denaturation – the alteration of a protein shape – can occur when proteins and nucleic acids are subjected to elevated temperature or to extremes of pH, or to non-physiological concentrations of salt, organic solvents, urea, or other chemical agents.

deposit A sediment precipitated out of solution by chemical action.

diatomic molecules Composed of only two atoms, of the same or different chemical elements. Common examples are: hydrogen, oxygen and nitrogen.

diffusion The name used to describe the way particles in gases and liquids spread throughout the space in which they are placed.

dilute solution A solution containing a small amount of solute in a large amount of solvent.

diode A passive electronic component that allows current to flow in only one direction.

dipole-dipole force This occurs when a permanently polarised molecule attracts another permanently polarised molecule. The positive end of a polarised molecule attracts the negative end of another polarised molecule.

displacement reaction A reaction in which a more reactive element displaces a less reactive element from an aqueous solution of its ions.

dissociation A general process in which molecules (or ionic compounds such as salts, or complexes) separate or split into smaller particles such as atoms, ions or radicals, usually in a reversible manner.

distillation A process used to separate two miscible liquids with different boiling points, e.g. alcohol and water.

doping The addition of impurities to a semiconductor to control the electrical resistivity.

dynamic equilibrium The equilibrium that exists in a closed system when the rate of the forward reaction is equal to the rate of the reverse reaction and concentrations do not change.

E

electrochemical series A list of metals arranged in order of decreasing reactivity or in order of decreasing ease of oxidation. The elements in the electrochemical series are arranged in order of their standard electrode potentials.

electrolysis An electric current is passed through a molten sample of a metal compound causing it to split up and release the metal.

electrolyte A chemical compound that conducts electricity by changing into ions when melted or dissolved into a solution.

electrolytic The addition of a solvent or of energy in the form of heat causes molecules or crystals of the substance to break up into ions (electrically charged particles).

electromagnetic radiation A form of energy that is produced by oscillating electric and magnetic disturbance, or by the movement of electrically charged particles travelling through a vacuum or matter.

electron affinity Reflects the ability of an atom to accept an electron. It is the energy change that occurs when an electron is added to a neutral atom or molecule in the gaseous state to form a negative ion.

electron A negatively charged particle in an atom.

electron configuration A shorthand representation that shows how electrons occupy sub-shells in an atom.

electronegativity The relative power of an atom in a molecule to attract electrons to itself.

electron pair repulsion The principle that electron pairs around a central atom tend to orient themselves as far apart as possible. Electron pair repulsion is used to predict the geometry of a molecule or a polyatomic ion.

electron spin number The spin quantum number describes the shape and energy of electron orbitals.

elimination reaction A chemical reaction in which a molecule decomposes to two different molecules.

empirical formula The formula that gives the simplest whole-number ratio of atoms of each element present in a compound.

endothermic A reaction where energy is absorbed by the chemicals from its surroundings in order for the reaction to take place.

energy profile diagram Shows the energy transfer in a chemical reaction.

equilibrium constant Kc is a measure of the position of equilibrium. It indicates whether there are more reactants or more products in an equilibrium system.

esters Any of a class of organic compounds that react with water to produce alcohols and organic or inorganic acids.

eutrophication The undesirable overgrowth of vegetation in an ecosystem caused by chemical nutrients, often compounds containing nitrogen, phosphorus, or both. Eutrophication is almost always caused by the discharge of nitrate or phosphate-containing detergents, fertilizers, or sewage into an aquatic system.

exothermic reaction A reaction where energy is transferred from the chemicals to the surroundings.

F

fermentation The process in which a substance breaks down into a simpler substance. Microorganisms like yeast and bacteria usually play a role in the fermentation process, creating beer, wine, bread, kimchi, yogurt and other foods.

fibrous proteins These provide structural support for cells and tissues. Fibrous protein molecules are long, spiral chains that are folded to form strong structures such as hair, fingernails and muscle tissue.

filtration A method used to separate insoluble solids from liquids.

fluoridation Addition of fluorides (often as sodium monoflurophosphate) to drinking-water, aimed at reducing the rate of tooth decay in the general population.

fossil The remains of an animal or plant that have been turned into rock and preserved. They are only found in sedimentary rocks (since the changes that produce metamorphic and igneous rocks would destroy any fossils)

fossil fuel A natural fuel, coal, oil, peat and gas, that was formed over millions of years from the remains of dead plants and animals.

foundry A factory where castings are produced by melting metal, pouring liquid metal into a mould, then allowing it to solidify.

fractional distillation The separation of a mixture into its component parts, or fractions. Chemical compounds are separated by heating them to a temperature at which one or more fractions of the mixture will vaporise.

free radical substitution These are reactions in which one atom in a molecule is replaced by another atom or group of atoms. It involves breaking a carbon-hydrogen bond in alkanes such as methane.

freezing Where a liquid is cooled and changes into a solid.

fuel A substance that burns in oxygen and produces heat.

functional group An atom or group of atoms joined in a specific manner, which gives the chemical properties of the organic compound and are the centres for chemical reactivity.

G

galvanic cells Electrochemical cells in which spontaneous oxidation-reduction reactions produce electrical energy.

gamma rays Electromagnetic radiation with no charge and high penetrating power. The nucleus remains unchanged.

general formula The simplest algebraic formula of a member of a homologous series, eg. the general formula of the alkanes: C_nH2_{n+2}.

global warming An increase in the temperature in the Earth's atmosphere due to the greenhouse effect.

globular proteins Unlike fibrous proteins, globular proteins have the spiral chains folded into spherical shapes and are responsible for substances in the human body such as haemoglobin, enzymes and certain hormones like insulin.

greenhouse effect When the heat energy of the Sun is trapped within the Earth's atmosphere.

group A vertical column in the periodic table. Elements in a group have similar chemical properties and their atoms have the same number of outer shell electrons.

H

Haber process An industrial process for producing ammonia from nitrogen and hydrogen, using an iron catalyst at high temperature and pressure.

half-life The time taken for the concentration of a reactant to decrease by half.

halogens The elements of Group VII of the periodic table, e.g. chlorine.

heat A form of energy that is transferred from warmer bodies to colder ones.

heat of combustion The heat change which occurs when one mole of a substance is burnt in an excess of oxygen.

heat of formation The heat change which occurs when one mole of a compound is formed from its elements in their standard states.

Hess's law The heat change for a given reaction depends only on the initial and the final states of the system, and is independent of the path followed.

heterogeneous catalysis A reaction where the catalyst has a different physical state from the reactants, e.g. reactants are gases, whereas the catalyst is a solid.

homogeneous catalysis A reaction in which the catalyst and reactants are in the same physical state, usually gaseous or aqueous state.

homogeneous equilibrium An equilibrium in which all the species making up the reactants and products have the same physical state.

homologous series A group of organic chemical compounds, usually listed in order of increasing size, that have a similar structure (and hence also similar properties) and whose structures differ only by the number of CH_2 units in the main carbon chain.

hydrated A crystalline compound containing water molecules.

hydration A chemical reaction in which a substance combines with water. One of the commonest hydration reactions is the hydration of alkenes to produce alcohols. For example, industrial ethanol is manufactured by the hydration of ethene.

hydrocarbon A compound of hydrogen and carbon only.

hydrogenation The process of hydrogenation involves the use of hydrogen molecules to saturate organic compounds, in the presence of a catalyst.

hydrogen bond The electrostatic force of attraction between a proton that has been denuded of electrons, by direct attachment to a highly electronegative atom such as N, O or F, and the lone pair on another highly electronegative atom.

hydrolysis A reaction with water that breaks a chemical compound into two compounds, the H and OH in a water molecule becomes incorporated into the two compounds.

hydroxyl group A functional group consisting of a hydrogen atom covalently bonded to an oxygen atom.

I

incineration Involves the combustion of organic substances contained in waste materials. Waste destruction takes place in a furnace by controlled burning at high temperatures.

indicators Chemicals that show by changing colour whether a substance is acidic, alkaline or neutral.

initial rate of reaction The change in concentration of a reactant or product per unit time at the start of the reaction: t = 0.

insoluble Solids that do not dissolve in a liquid.

instantaneous rate of reaction The instantaneous rate of a reaction is equal to the tangent line at a specific point at a particular time.

intermediate A species formed during a reaction that reacts further and is not present in the final products.

intermolecular force The forces which mediate interaction between molecules, including forces of attraction or repulsion.

intermolecular hydrogen bonds Hydrogen bonds formed between neighbouring molecules.

ion A positively or negatively charged atom or a (covalently bonded) group of atoms.

ionic bond An ionic bond is the electrostatic force of attraction between oppositely charged ions, formed as a result of complete electron transfer.

isomerisation The heat change for a given reaction depends only on the initial and the final states of the system, and is independent of the path followed.

isomers These are molecules that have the same molecular formula but different structural or spatial arrangements of the atoms within the molecule.

isotopes Atoms that have the same number of protons but different numbers of neutrons.

IUPAC system A systematic method of naming organic chemical compounds as recommended by the International Union of Pure and Applied Chemistry (IUPAC).

L

Le Chatelier's principle If the equilibrium of a system is disturbed by a change in one or more of the determining factors (as temperature, pressure, or concentration) the system tends to adjust itself to a new equilibrium by counteracting as far as possible the effect of the change.

limewater A chemical that turns from clear to cloudy (or milky) if carbon dioxide is present.

limiting reagent The reactant that is not in excess, which will be used up first and stop the reaction.

lone pair An outer shell pair of electrons that is not involved in chemical bonding.

lubricant A substance, usually organic, introduced to reduce friction between surfaces in mutual contact, which ultimately reduces the heat generated when the surfaces move.

M

macromolecular structure Covalent structures that have many atoms joined together by covalent bonds. Diamond and graphite are examples of macromolecular structures.

magnetic quantum number An integer that expresses the component of the quantised angular momentum of an electron, atom, or molecule in the direction of an externally applied magnetic field.

malleable Malleability is one of the unique properties of metals which allow them to change shape by hammering or pressing to form sheets.

mass number Equal to the total number of protons plus neutrons in the nucleus of the atom.

mass spectrometer An apparatus for measuring the masses of isotopes, molecules, and molecular fragments by ionising them and determining their trajectories in electric and magnetic fields.

mass The amount of matter in an object. This amount never changes.

matter Anything that occupies space and has mass.

melting point The temperature at which solid materials turn to a liquid.

metabolic reactions The chemical processes that occur in all living organisms, which help them complete their life cycles, such as digestion and respiration.

metabolism The whole range of biochemical processes that occur within a living organism consisting of anabolism (the build-up of substances) and catabolism (the breakdown of substances).

metallic bond The electrostatic attraction between positive metal ions and delocalised electrons.

minerals The chemical substances from which rocks are made.

miscible liquids Liquids that mix, e.g. alcohol and water.

mixture Contains two or more different substances mixed together but not chemically combined.

molar gas volume The volume per mole of gas molecules at a stated temperature and pressure.

molar mass The mass per mole of a substance, in units of g mol^{-1}.

mole 1 mole is the amount of substance which contains the same number of particles as there are atoms in exactly 12g of carbon- 12.

molecular formula This shows the number of each kind of atom in a molecule. For example, CH_4 has one carbon atom and four hydrogen atoms.

molecule The smallest part of a covalent compound that can exist while retaining its chemical identity, consisting of two or more atoms covalently bonded together.

mole fraction The number of moles of a particular component of a mixture divided by the total number of moles present.

molten An object that is reduced to liquid form by heating.

monomer A small molecule that combines with many other monomers to form a polymer.

N

neutralisation A chemical reaction in which an acid and a base react together to produce a salt.

neutron An uncharged subatomic particle found in the nucleus of an atom.

noble gases The elements of Group VIII of the periodic table, e.g. helium.

nomenclature A system of naming compounds.

non-polar With no charge separation across a bond or in a molecule.

non-renewable Sources of energy that cannot be replaced once they are used.

nuclear energy Energy from making and breaking nuclear bonds.

nucleus The central part of an atom that is made up of protons and neutrons.

nuclide A distinct kind of atom or nucleus characterised by a specific number of protons and neutrons.

nutrients Chemical compounds in food that are used by the body to function properly and maintain health, including proteins, fats, carbohydrates, vitamins, and minerals.

O

octane number The percentage of iso-octane in an iso-octane/heptane mixture that gives the same engine performance of the fuel.

organic chemistry A branch of chemistry that is concerned with carbon and especially carbon compounds which are found in living things.

oxidation Loss of electrons or an increase in oxidation number.

oxidation number A measure of the number of electrons that an atom uses to bond with atoms of another element. Oxidation numbers are derived form a set of rules.

oxidation state The oxidation number.

oxidising agent An oxidising agent (oxidant) is an electron acceptor.

ozone depletion The reduction of the amount of ozone in the stratosphere. A serious environmental problem, as it increases the amount of ultraviolet (UV) radiation that reaches the Earth's surface.

P

p-block elements The p-block elements are found on the right side of the periodic table. They include the boron, carbon, nitrogen, oxygen and flourine families, in addition to the noble gases. The noble gases have full p-orbital's and are non-reactive.

partial dissociation The splitting of some of a species in solution into ions.

Pauli exclusion principle No more than two electrons can occupy an orbital, and this they can only do if they have opposite spin.

percentage yield Actual amount, in mol, of product theoretical amount, in mol, of product × 100.

period A horizontal row of elements in the periodic table. Elements show trend in properties across a period.

periodicity The tendency of chemical elements to have similar properties when arranged according to their atomic number. The position of an element in the periodic table.

periodic table A table that is an arrangement of elements in order of increasing atomic number arranged in rows called periods and columns called groups.

periodic trend A repeating trend in properties of the elements across each period of the periodic table.

pH scale The pH of a solution is the negative logarithm to base ten of the molar hydrogen ion concentration.

physical change A change in which no new substance is formed.

planar A planar molecule is one in which the atoms are all on the same plane: the molecule is flat.

plastics Man-made materials made from crude oil.

polar covalent A polar bond is a covalent bond between two atoms where the electrons forming the bond are unequally distributed. This causes the molecule to have a slight electrical dipole moment where one end is slightly positive and the other is slightly negative.

pollution The addition of harmful or unwanted materials to an environment.

polyatomic alcohols Alcohols that have multiple hydroxyl groups OH, such as glycerol.

polyatomic ion An ion containing more than one atom.

polymer A large molecule formed from many thousands of repeat units of smaller molecules known as monomers.

polymerisation A chemical process that combines several monomers to form a polymer or polymeric compound.

polysaccharides A long-chain carbohydrate made up of smaller carbohydrates called monosaccharides, typically used by our bodies for energy or to help with cellular structure.

polythene A light, versatile synthetic resin made from the polymerisation of ethylene. Polythene is resistant to chemicals and moisture, has good insulating properties, and can be used especially in packaging and insulation.

position of equilibrium The relative quantities of reactants and products, indicating the extent of a reversible reaction at equilibrium.

precipitates Often formed when two aqueous solutions are mixed together.

precipitation reaction The formation of a solid from a solution during a chemical reaction.

precipitation The emergence of the insoluble solid from solution is called precipitation.

primary alcohol An alcohol in which the OH group is attached to a carbon atom that is attached to two or three hydrogen atoms.

principal quantum number n A number that indicates the main energy level, or shell number, of an electron in an atom.

proton A positively charged subatomic particle found in the nucleus of an atom.

proton number The number of protons in the nucleus of an atom; also known as atomic number.

π-bond A bond formed by the sideways overlap of two p-orbitals, with the electron density above the plane of the bonding atoms.

Q

quantum numbers A set of values that describes the state of an electron including its distance from the nucleus, the orientation and type of orbital where it is likely to be found, and its spin.

R

rate of reaction The change in concentration of a reactant or a product in a given time.

reaction mechanism The sequence of bond-breaking and bond-forming steps that shows the path taken by electrons during a reaction.

reactivity series A list of metals placed in order of how reactive they are.

redox reaction A reaction involving electron transfer.

reducing agent A reducing agent -reductant- is an electron donor.

reduction Gain of electrons or a decrease in oxidation number.

relative atomic mass The average mass per atom of the natural isotopic composition of the element, relative to the mass of an atom of carbon-12, which is assigned a value of exactly 12.

relative charge Protons and electrons have an electrical charge. This electrical charge is the same size for both, but protons are positive and electrons are negative.

relative molecular mass The average mass per molecule in the naturally occurring substance, relative to the mass of an atom of carbon-12 which is assigned a value of exactly 12 units. Its value is equal to the sum of all the relative atomic masses which make up the molecular formula.

reversible reaction A reaction that takes place in both forward and reverse.

rigidity The property of a structure that it does not bend or flex under an applied force. The opposite of rigidity is flexibility.

S

s-block elements The elements found in Group 1 and Group 2 on the periodic table. Group 1 are the alkali metals which have one valence electron. They have low ionisation energies which makes them very reactive. Group 2 is the alkali earth metals which have two valence electrons, filling their s sublevel.

salt The product of a reaction in which the H–ions from the acid are replaced by metal or ammonium ions.

saturated hydrocarbon A hydrocarbon with single bonds only.

saturated solution A solution that contains as much dissolved solute as possible at that temperature.

sealant A substance used to block the passage of fluids through the surface or joints or openings in materials.

secondary alcohol An alcohol in which the –OH group is attached to a carbon atom that is attached to two carbon chains and one hydrogen atom.

semi-viscous Property of a liquid with moderate resistance to flow.

shell A group of atomic orbitals with the same principal quantum number, n.

soluble Solids that dissolve in a liquid.

solute A substance that dissolves.

solution A mixture of a solute and a solvent.

solvent A liquid in which a solute dissolves.

species If one atom is identical to another, we can say they are the same chemical species.

spectator ions Ions that are present but take no part in a chemical reaction.

standard conditions Pressure =100 kPa temperature = 298 K concentration (reactions with aqueous solutions) = 1 mol dm^{-3}

stratosphere The layer of the Earth's atmosphere above the troposphere, extending to about 50 km above the Earth's surface.

strong acid An acid that dissociates completely in solution.

structural formula A formula showing the minimal detail for the arrangement of atoms in a molecule.

structural isomers Molecules with the same molecular formula but with different structural formulae.

substitution reaction A reaction in which an atom or group of atoms is replaced with a different atom or group of atoms.

surface area The measure of how much surface of reactants is exposed.

synthetic materials Made from man-made materials rather than natural materials.

σ-bond A bond formed by the overlap of one orbital from each bonding atom, consisting of two electrons and with the electron density centred around a line directly between the nuclei of the two atoms.

T

temperature A measure of how hot or cold an object is.

tetrahedral A term used to describe molecules and polyatomic ions that have one atom in the centre and four atoms at the corners of a tetrahedron.

theoretical yield The yield resulting from complete conversion of reactants into products.

thermal decomposition The breaking up of a chemical substance with heat into at least two chemical substances.

Time It is measured by a basic unit called the second (symbol s).

trace elements A chemical element whose concentration (or other measure of amount) is very low (a 'trace amount').

transistor A device that regulates current or voltage flow and acts as a switch or gate for electronic signals.

transition metals A metal which forms one or more stable ions which have incompletely filled d orbitals.

U

unsaturated When referring to chemical solutions, an unsaturated solution is able to dissolve more solute; when referring to organic compounds, unsaturated means a molecule contains double or triple carbon-carbon bonds.

V

valency of an element The number of electrons an atom of that element wants to gain, lose or share, in order to be chemically stable and have a full outer shell.

van der Waals' forces Temporary dipoles caused by the random movement of electrons, i.e. the 'sloshing around' of electrons within a molecule.

volatility The ease with which a liquid turns into a gas. Volatility increases as boiling point decreases.

W

water of crystallisation Water molecules that are bonded into a crystalline structure of a compound.

weak acid An acid that dissociates only partially in solution.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** 1.00794																	2 **He** 4.0026
2	3 **Li** 6.941	4 **Be** 9.01218											5 **B** 10.811	6 **C** 12.0107	7 **N** 14.0067	8 **O** 15.9994	9 **F** 18.9984	10 **Ne** 20.1797
3	11 **Na** 22.9898	12 **Mg** 24.305											13 **Al** 26.9815	14 **Si** 28.0855	15 **P** 30.9738	16 **S** 32.065	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.0983	20 **Ca** 40.078	21 **Sc** 44.9559	22 **Ti** 47.867	23 **V** 50.9415	24 **Cr** 51.9961	25 **Mn** 54.938	26 **Fe** 55.845	27 **Co** 58.9332	28 **Ni** 58.6934	29 **Cu** 63.546	30 **Zn** 65.38	31 **Ga** 69.723	32 **Ge** 72.63	33 **As** 74.9216	34 **Se** 78.96	35 **Br** 79.904	36 **Kr** 83.798
5	37 **Rb** 85.4678	38 **Sr** 87.62	39 **Y** 88.9059	40 **Zr** 91.224	41 **Nb** 92.9064	42 **Mo** 95.96	43 **Tc** [98]	44 **Ru** 101.07	45 **Rh** 102.906	46 **Pd** 106.42	47 **Ag** 107.868	48 **Cd** 112.411	49 **In** 114.818	50 **Sn** 118.71	51 **Sb** 121.76	52 **Te** 127.6	53 **I** 126.904	54 **Xe** 131.293
6	55 **Cs** 132.905	56 **Ba** 137.327	57–71	72 **Hf** 178.49	73 **Ta** 180.948	74 **W** 183.84	75 **Re** 186.207	76 **Os** 190.23	77 **Ir** 192.217	78 **Pt** 195.084	79 **Au** 196.967	80 **Hg** 200.59	81 **Tl** 204.383	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** [210]	85 **At** [210]	86 **Rn** [222]
7	87 **Fr** [223]	88 **Ra** [226]	89–103	104 **Rf** [267]	105 **Db** [268]	106 **Sg** [269]	107 **Bh** [270]	108 **Hs** [269]	109 **Mt** [278]	110 **Ds** [281]	111 **Rg** [281]	112 **Cn** [285]	113 **Uut** [286]	114 **Fl** [289]	115 **Uup** [288]	116 **Lv** [293]	117 **Uus** [294]	118 **Uuo** [294]
			57 **La** 138.905	58 **Ce** 140.116	59 **Pr** 140.908	60 **Nd** 144.242	61 **Pm** [145]	62 **Sm** 150.36	63 **Eu** 151.964	64 **Gd** 157.25	65 **Tb** 158.925	66 **Dy** 162.5	67 **Ho** 164.93	68 **Er** 167.259	69 **Tm** 168.934	70 **Yb** 173.054	71 **Lu** 174.967	
			89 **Ac** [227]	90 **Th** 232.038	91 **Pa** 231.036	92 **U** 238.029	93 **Np** [237]	94 **Pu** [244]	95 **Am** [243]	96 **Cm** [247]	97 **Bk** [247]	98 **Cf** [251]	99 **Es** [252]	100 **Fm** [257]	101 **Md** [258]	102 **No** [259]	103 **Lr** [262]	

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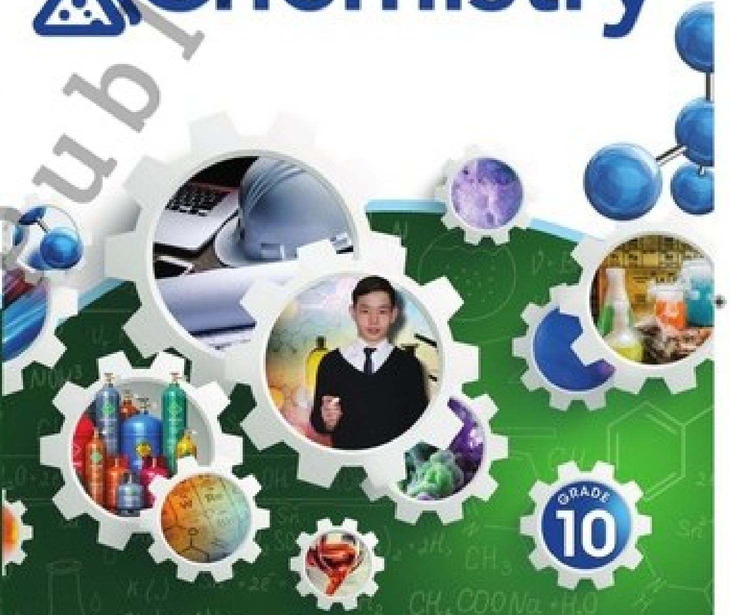

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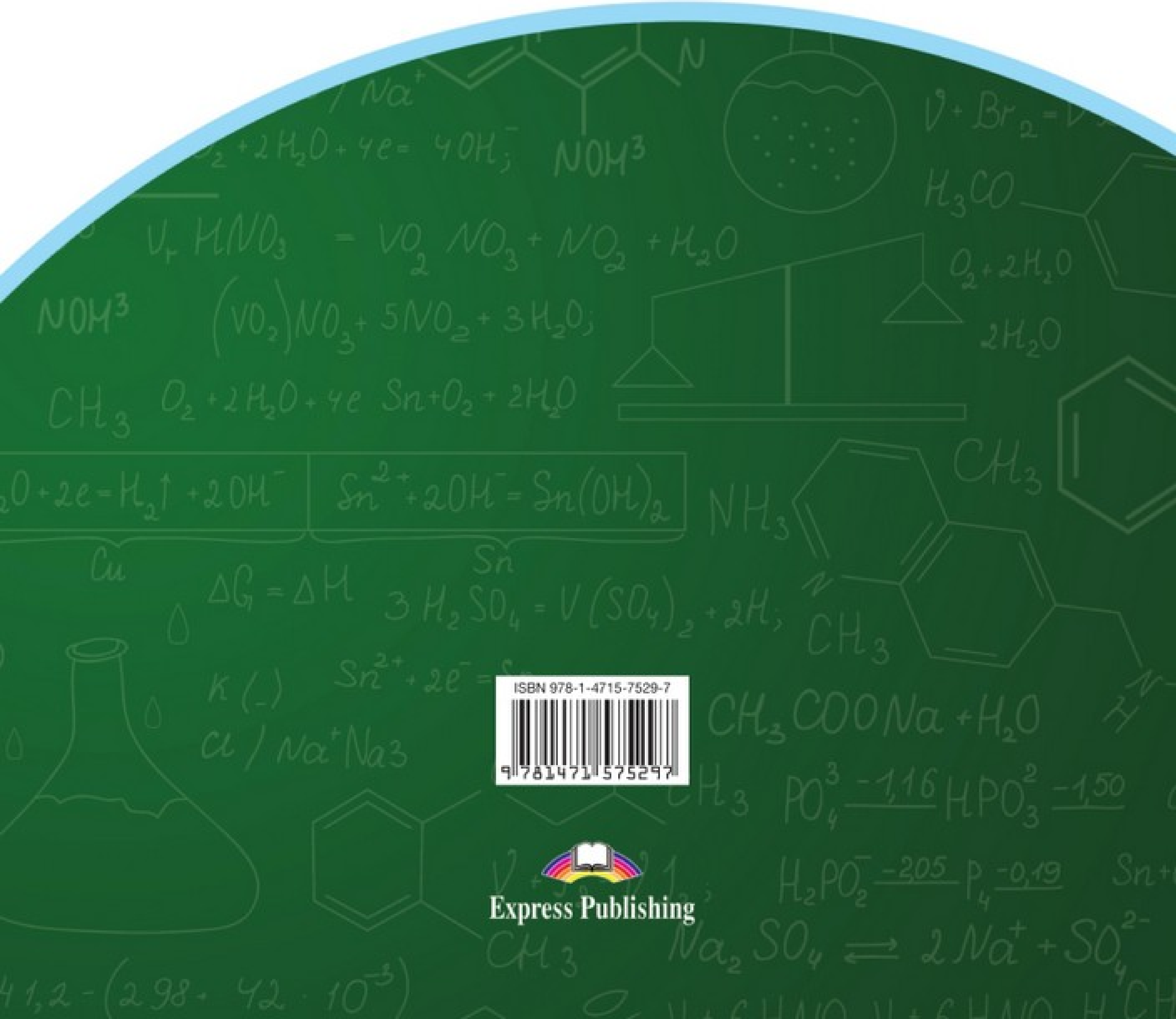

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