G. C. E. (Advanced Level)

CHEMISTRY

Grade 12

Resource Book

Unit 1: Atomic Structure
Unit 2: Structure and Bonding
Unit 3: Chemical Calculations
Unit 6: Chemistry of *s*, *p* and *d* Block Elements

Department of Science
Faculty of Science and Technology
National Institute of Education
Maharagama
www.nie.lk

Chemistry
Resource Book
Grade 12

First Print - 2021
Second Print

ISBN : 978-955-654-913-3

Department of Science
Faculty of Science and Technology
National Institute of Education
Sri Lanka

Published By : Department of Printing and Publications
National Institute of Education
Maharagama
Sri Lanka

Message from the Director General

The National Institute of Education takes opportune steps from time to time for the development of quality in education. Preparation of supplementary resource books for respective subjects is one such initiative.

Supplementary resource books have been composed by a team of curriculum developers of the National Institute of Education, subject experts from the national universities and experienced teachers from the school system. Because these resource books have been written so that they are in line with the G. C. E. (A/L) new syllabus implemented in 2017, students can broaden their understanding of the subject matter by referring these books while teachers can refer them in order to plan more effective learning teaching activities.

I wish to express my sincere gratitude to the staff members of the National Institute of Education and external subject experts who made their academic contribution to make this material available to you.

Dr. (Mrs.) T. A. R. J. Gunasekara
Director General
National Institute of Education
Maharagama.

Message from the Director

Since 2017, a rationalized curriculum, which is an updated version of the previous curriculum is in effect for the G.C.E (A/L) in the general education system of Sri Lanka. In this new curriculum cycle, revisions were made in the subject content, mode of delivery and curricular materials of the G.C.E. (A/L) Physics, Chemistry and Biology. Several alterations in the learning teaching sequence were also made. A new Teachers' Guide was introduced in place of the previous Teacher's Instruction Manual. In concurrence to that, certain changes in the learning teaching methodology, evaluation and assessment are expected. The newly introduced Teachers' Guide provides learning outcomes, a guideline for teachers to mould the learning events, assessment and evaluation.

When implementing the previous curricula, the use of internationally recognized standard textbooks published in English was imperative for the Advanced Level science subjects. Due to the contradictions of facts related to the subject matter between different textbooks and inclusion of the content beyond the limits of the local curriculum, the usage of those books was not convenient for both teachers and students. This book comes to you as an attempt to overcome that issue.

As this book is available in Sinhala, Tamil, and English, the book offers students an opportunity to refer the relevant subject content in their mother tongue as well as in English within the limits of the local curriculum. It also provides both students and teachers a source of reliable information expected by the curriculum instead of various information gathered from the other sources.

This book authored by subject experts from the universities and experienced subject teachers is presented to you followed by the approval of the Academic Affairs Board and the Council of the National Institute of Education. Thus, it can be recommended as a material of high standard.

Dr. A. D. A. De Silva
Director
Department of Science

Guidance
Dr. (Mrs.) T. A. R. J. Gunasekara
Director General
National Institute of Education

Supervision
Dr. A. D. A. De Silva
Director, Department of Science
National Institute of Education

Mr. R. S. J. P. Uduporuwa
Former Director, Department of Science
National Institute of Education

Subject Leader
Mrs. M. S. Wickramasinghe
Assistant Lecturer, Department of Science
National Institute of Education

Internal Editorial Panel
Mr. L. K. Waduge
Senior Lecturer, Department of Science

Mrs. G. G. P. S. Perera
Assistant Lecturer, Department of Science

Mr. V. Rajudevan
Assistant Lecturer, Department of Science

Writing Panel
Dr. Russel C. L. de Silva - Senior Lecturer, Department of Chemistry, University of Kelaniya (Unit 1)
Dr. M.A.B. Prasantha - Senior Lecturer, Department of Chemistry, University of Sri Jayewardenepura (Unit 2)
Dr. M.N. Kaumal - Senior Lecturer, Department of Chemistry, University of Colombo (Unit 3 and 6)

External Editorial Panel
Prof. S. P. Deraniyagala - Senior Professor, Department of Chemistry, University of Sri Jayewardenepura
Prof. M. D. P. De Costa - Senior Professor, Department of Chemistry, University of Colombo
Prof. H. M. D. N. Priyantha - Senior Professor, Department of Chemistry, University of Peradeniya
Prof. Sudantha Liyanage - Dean, Faculty of Applied Sciences, University of Sri Jayewardenepura
Mr. K. D. Bandula Kumara - Deputy Commissioner, Education Publication Department, Ministry of Education

Mrs. Deepika Nethsinghe - SLTS-1 (Rtd), Ladies College, Colombo 07
Mrs. Muditha Athukorala - SLTS-1, Prajapathi Balika Vidyalaya, Horana
Miss. C. A. N. Perera - SLTS-1, Princess of Wales', Moratuwa
Mrs. V. K. W. D. Salika Madavi - SLTS-1, Muslim Ladies College, Colombo 04
Mrs. H.M.D.D. D. Manike - SLTS-1, Viharamhadevi Balika Vidyalaya, Kiribathgoda
Mr. S. Thillainathan - SLTS-1 (Rtd), Hindu Ladies College, Colombo 06
Miss. S. Veluppillai - SLTS-1 (Rtd), Hindu Ladies College, Colombo 06
Mrs. M. Thirunavukarasu - SLTS-1 (Rtd), Hindu Ladies College, Colombo 06
Mrs. S. Rajadurai - SLTS-1 (Rtd), St. Peters' College, Colombo 04

Language Editing

Dr. Chandra Amarasekara
Consultant, National Institute of Education

Mr. M. A. P. Munasinghe
Chief Project Officer (Rtd.), National Institute of Education

Cover Page

Mrs. R. R. K. Pathirana
Technical Assitant, National Institute of Education

Supporting Staff

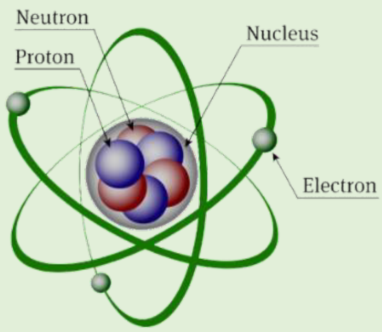
Mrs.Padma Weerawardana
Mr. Mangala Welipitiya
Mr. Ranjith Dayawansa

Content

***s* Block Elements**

***p* Block Elements**

***d* Block Elements**



1. Atomic Structure

Content

1.1 The atomic theory of matter
1.1.1 Properties of cathode rays (Experimental observations)
1.1.2 The nucleus of the atom
1.1.3 Properties of positive rays (Experimental observations)
1.1.4 Rutherford's gold foil experiment
1.1.5 Atomic number, isotopes and mass number
1.1.6 The atomic mass scale
1.1.7 Average atomic mass and relative atomic mass of an element
1.1.8 Ions

1.2 Electromagnetic radiation and wave-like properties of matter
- Electromagnetic radiation · Properties [speed (c), wavelength (λ), frequency (v), energy (E)]

1.2.1 Quantization of energy
- Electromagnetic spectrum
- $c = \nu\lambda$
- $E = h\nu$, $\lambda = \frac{h}{mV}$
- Wave- particle dual nature of matter

1.3 Electronic energy levels of atoms
- Variation of successive ionization energies of elements

1.3.1 The hydrogen spectrum
- Existence of electrons in energy levels

1.3.2 Shapes of orbitals
1.3.3 Orbitals and quantum numbers
- The principal quantum number (n)
- The angular momentum quantum number (l)
- The magnetic quantum number (m_l)
- The spin quantum number (m_s)

1.4 Electron configuration
1.4.1 The Aufbau principle
1.4.2 The Pauli exclusion principle
1.4.3 Hund's rule
1.4.4 Condensed electron configurations

1.5 Building of periodic table
- The long form of the periodic table

1.6 Periodic trends shown by *s* and *p* block elements
1.6.1 Sizes of atoms and ions
    - van der Waals radius
    - Covalent radius
    - Metallic radius
- Periodic trends in atomic radii
- Electron configurations of ions
- Periodic trends in ionic radii

1.6.2 Ionization energy
- Periodic trends in first ionization energies

1.6.3 Electron gain energy
1.6.4 Electronegativity

Introduction

Chemistry is the study of the properties and behaviour of matter. **Matter** is the physical material of the universe; it is anything that has mass and occupies space.

Although the materials in our world vary greatly in their properties, everything is formed from only about 100 elements and, therefore, from only about 100 chemically different kinds of atoms. (118 elements have been discovered so far but the heavier atoms are short lived and not found naturally.)

1.1 The atomic theory of matter

Philosophers from the earliest times speculated about the nature of the fundamental components from which the world is made. **Empedocles** (~ 440 BC) believed that the four elements-earth, fire, air and water made up all things. The Hindus believed that the four elements stated above makeup the world and space. However, **Democritus** (460–370 BC) and other early Greek philosophers described the material world as being made up of tiny, invisible, indivisible particles that they called 'atomos', meaning "indivisible" or "uncuttable."

Later, however, **Plato** and **Aristotle** formulated the notion that there can be no ultimately indivisible particles, and the "atomic" view of matter faded for many centuries during which Aristotelean philosophy dominated the Western culture.

It was in 1808 that an English scientist and school teacher, **John Dalton** (1766-1844), formulated a precise definition of the indivisible building blocks of matter that we call atoms. Dalton's atomic theory was based on four postulates.

1. Elements are made out of extremely small, indivisible particles called atoms.
2. All atoms of a given element are identical in mass and size, but the atoms of one element are different from the atoms of all other elements.
3. Atoms of one element cannot be changed into atoms of a different element by chemical reactions; atoms are neither created nor destroyed in chemical reactions.
4. Compounds are formed by union of two or more atoms of different elements in a simple numerical ratio.

Dalton's atomic model is called the "Golf ball model".


(a) (b)

Figure1.1 (a) John Dalton and (b) the golf ball model

Johnstone G. Stoney (1826-1911) named the fundamental unit carrying electricity as "electrons" in 1891 but did not have any experimental evidence of its existence. During the mid-1800s, scientists began to study electrical discharge through a glass tube pumped almost empty of air. This device was an invention of the British chemist and physicist **Sir William Crookes** (1832-1919) and is called **Crookes tube** or **cathode ray tube**.

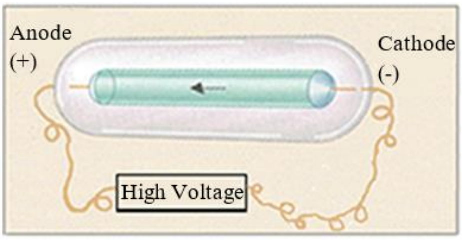


Figure 1.2 A cathode ray tube

The experiment of Crookes and the others showed that when two electrodes are connected to a high-voltage source, the heated negatively charged plate, called the cathode, produced a stream of invisible radiation. Although the rays could not be seen, their presence was detected because they cause gases at low pressure to glow and which made other substances to fluoresce, or to give off light. The radiation emitted from the cathode was given the name '**cathode rays**'.

Later it was known that these rays could be deflected by a magnetic field and they carried a negative electrical charge. Some scientists felt that these rays were waves and others were inclined to think they were particles.

The British scientist **J. J. Thomson** (1856–1940) observed that cathode rays are the same regardless of the identity of the cathode material or the gas in the tube. In 1897 he described cathode rays as streams of negatively charged particles. He used a cathode tube with an anode that had a hole at the centre. Using experimental measurements obtained from that cathode tube he then calculated a value of 1.76×10^8 coulombs per gram ($C\ g^{-1}$) for the ratio of the electron's electrical charge to its mass.

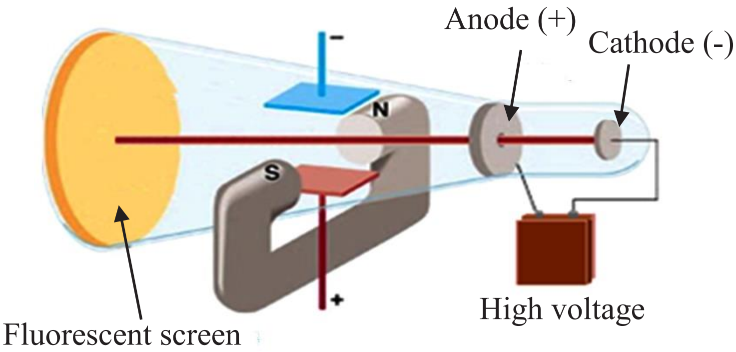


Figure 1.3 Thomson's cathode ray tube

1.1.1 Properties of cathode rays (Experimental observations)

- Cathode rays travel in straight lines. When an opaque object like a metal cross is placed in the path of cathode rays in a discharge tube, a shadow with sharp edges of the metal cross is formed at the end opposite to the cathode. The placement of the shadow proves that cathode rays emit from the cathode and they travel in a straight line.

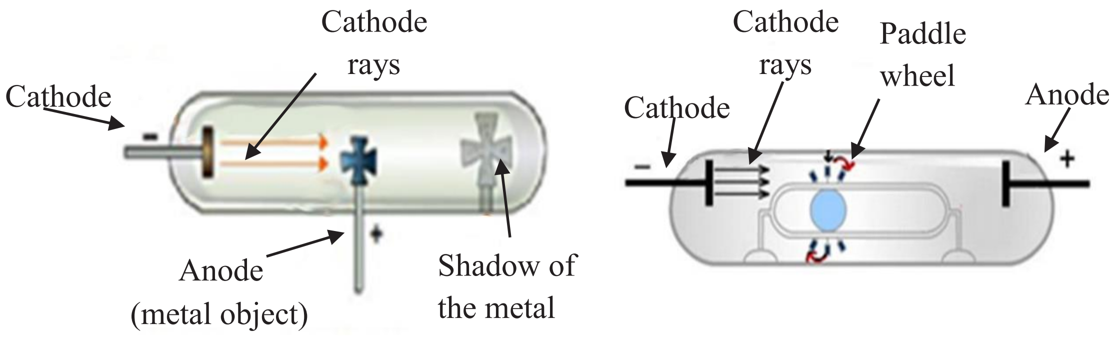


Figure 1.4 Cathode ray properties

- Cathode rays are a beam of particles having mass and possess kinetic energy. On placing a light paddle wheel in the path of cathode rays in a discharge tube, the blades of the paddle wheel rotate. This was considered evidence that electrons (cathode rays) have momentum.
  (However, there is doubt on this conclusion as heating of the tube can also make the paddles move.)
- When an electric field is applied in the path of cathode rays, they are deflected towards the positively charged plate. Hence the cathode rays are composed of negatively charged particles. They are affected by magnetic fields showing a deflection perpendicular to the magnetic field. The direction of deflection is similar to the deflection of any other negatively charged particles. Therefore, electron can be concluded as a negatively charged particle too.

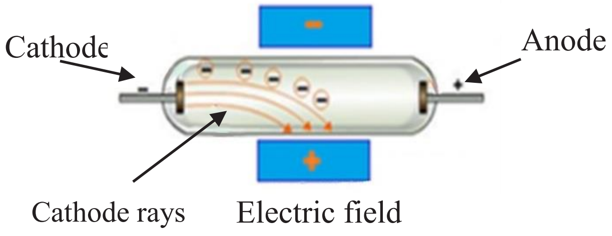


Figure 1.5 Interaction of cathode rays with external electrical fields

- The nature of the cathode rays does not depend on the nature of the gas taken in the discharge tube or the material of the cathode.
- The ratio of the charge to mass (e/m ratio) of cathode ray particles obtained from different gases was found to be exactly the same.

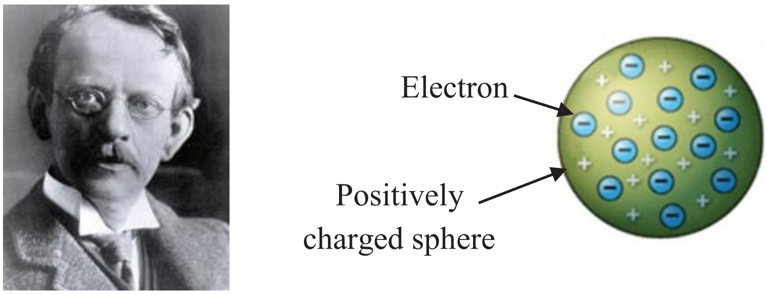
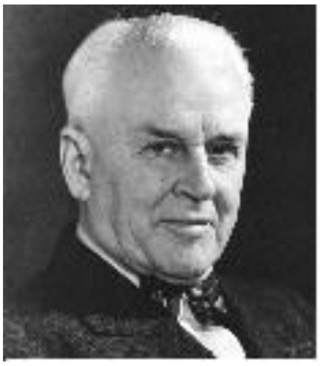


Figure 1.6 J. J. Thomson and his model

Using his findings in 1899 **J.J. Thomson** postulated the "plum-pudding" model of atomic structure. In 1909, **Robert Millikan** (1868–1953) succeeded in measuring the **charge of an electron as 1.602 × 10^{-19} C** by performing the oil drop experiment. The mass of the electron could be calculated by using the experimental values for the charge of electron and Thomson's charge-to-mass ratio.



$$\text{Electron mass} = \frac{1.602 \times 10^{-19}\ \text{C}}{1.76 \times 10^{8}\ \text{C g}^{-1}} = 9.10 \times 10^{-28}\ \text{g}$$

Figure 1.7 Robert Millikan and mass of an electron

This mass is about 1/1837 of a hydrogen atom which is the lightest atom. The **relative charge of an electron is -1**.

1.1.2 The nucleus of the atom

The German physicist, Eugen Goldstein experimentally proved the existence of positive charges in matter. In his experiments, a perforated cathode was used in a discharge tube along with air at very low pressure. When a high voltage of about 10,000 volts was applied across the electrodes, a faint red glow was observed behind the perforated cathode. When the high voltage is applied, its electric field accelerates the small number of ions present in the gas. These collide with atoms of the gas, knocking electrons off of them and creating more positive ions. These ions and electrons in turn strike more atoms, creating more positive ions. The positive ions are all attracted to the cathode, and some pass through the holes in the cathode. Goldstein called these positive rays "canal rays", because they were produced by the holes or channels in the cathode. Although the rays are not exactly formed at the positive electrode or anode, since they are formed away from the cathode close to the anode, they were also known as anode rays or positive rays.

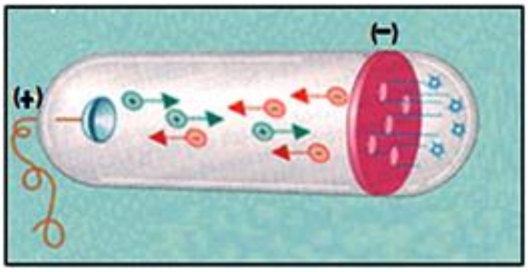


Figure 1.8 A cathode ray tube with a perforated cathode

1.1.3 Properties of positive rays (Experimental observations)

- They travel in straight lines and cast a shadow of the objects placed in their way.
- They can move a paddle wheel placed in their path.
- These rays are positively charged and when an electric field is applied in the path of the rays, they are deflected towards the negative plate of an electric field.
- The nature of the positive rays depends upon the gas taken in the discharge tube. Different gases give different types of positive rays, which contain particles having different masses and different charges. Therefore, the e/m ratio is not constant for positive ray particles obtained from different gases.

In 1907 a study of how this "ray" was deflected in a magnetic field, revealed that the particle making up the ray were not all the same mass. The lightest ones, formed when there was some hydrogen gas in the tube, were calculated to be about 1840 times heavier than an electron. The mass of any other positive particle is a multiplication of the mass of the lightest positive particle. Therefore, it should be a subatomic particle. They were named as protons. The relative mass of a proton is 1, hence, the **mass of a proton is 1.6×10^{-24} g** or **1.007276 u (atomic mass units) or Da (Daltons)**. (The unit was earlier given the name amu.)

The proton has a charge equal and opposite to that of an electron. Hence the absolute charge of a proton is 1.6×10^{-19} coulomb and its charge is positive. Proton is the smallest positive charge carrying particle in an atom and the **relative charge of proton is +1.**

Following the discovery of radioactivity in 1896 by the French scientist **Henri Becquerel (1852–1908),** the British physicist **Lord Ernest Rutherford (1871-1937)** showed that radioactive materials produce three types of emissions alpha (α), beta (β) and gamma (γ). The paths of α and β radiation are bent by an electric field.

Alpha (α) rays consist of positively charged particles, called **α particles,** and therefore are deflected away from the positively charged plate. **Beta (β) rays** or **β particles** have the identity of electrons and are deflected away from the negatively charged plate. The third type of radioactive radiation consists of high–energy rays called **gamma (γ) rays**. Like X rays, γ rays have no charge and are not affected by an external electric or magnetic field.

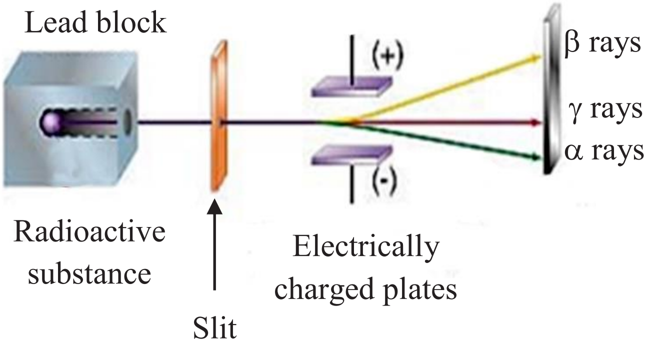


Figure 1.9 Behaviour of alpha (α), beta (β) and gamma (γ) rays in an electric field

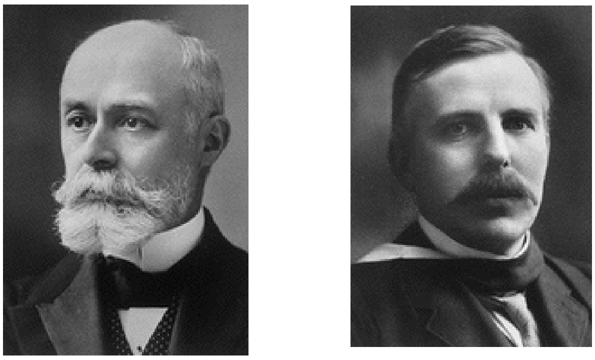

(a) (b)

Figure 1.10 (a) Henri Becquerel and (b) Lord Ernest Rutherford

1.1.4 Rutherford's gold foil experiment

In **1908-09,** Rutherford together with his associate **Johannes Hans Wilhelm Geiger (1882-1945)** a German physicist and an undergraduate named **Ernest Marsden**, carried out a series of experiments using very thin foils of gold and other metals as targets for α particles from a radioactive source.

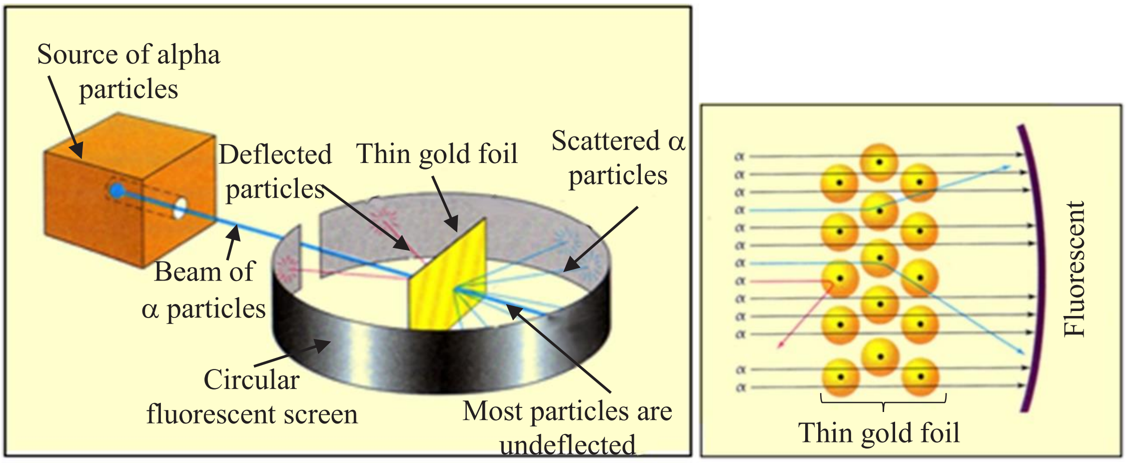


Figure 1.11 Rutherford's gold foil experiment

They observed that the majority of particles penetrated the foil either undeflected or only with a slight deflection. They also noticed that a few α particles were scattered (or deflected) at a large angle. Very few α particles bounced back in the direction from which it came.

To explain the results of the experiment, Rutherford devised a new model of atomic structure, suggesting that most of the atom must be empty. This structure would allow most of the α particles to pass through the gold foil with little or no deflection. The atom's positive charges, Rutherford proposed, are all concentrated in the **nucleus,** a dense central core within the atom. Whenever an α particle came close to a nucleus in the scattering experiment, it experienced a large repulsive force and therefore a large deflection. Moreover, an α particle traveling directly toward a nucleus would experience an enormous repulsion that could completely reverse the direction of the moving particle.

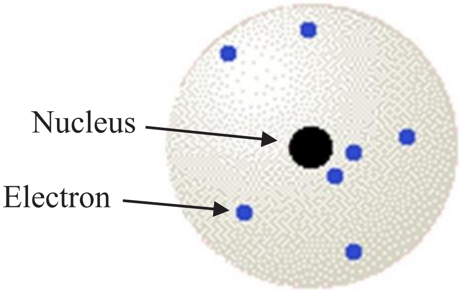


Figure 1.12 Rutherford's model (1911)

Subsequent studies, mainly based on mass spectroscopy revealed that the masses of atoms were much greater than the masses of protons and electrons present. Therefore, another subatomic particle should be present to contribute towards the mass of the atom. In1932 **Sir James Chadwick (1891-1972)** a British scientist discovered the ‘neutron’. The charge of a neutron is 0 (zero) and its mass is 1.6749×10^{-24}g or 1.008665 amu.

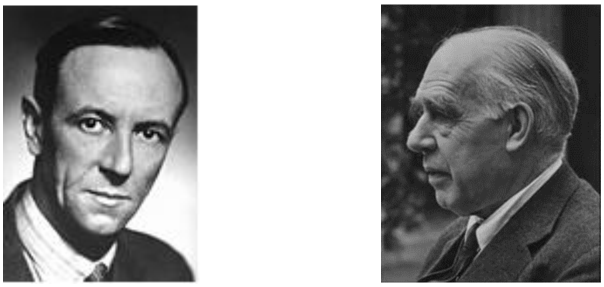

(a) (b)

Figure 1.13 (a) James Chadwick and (b) Niels Bohr

Since Rutherford’s time, physicists have learned more and more about atomic nuclei. In 1913 **Niels Henrik David Bohr** (1885-1962) a Danish physicist, combined the ideas at that time and suggested that the atomic nucleus was surrounded by electrons moving in orbit, like planets around the sun. He postulated that the electrons in order to remain in orbit, the electrostatic attraction between the nucleus and electron must be equal to the centrifugal force. In other words, the electrons have to travel in a constant speed around the nucleus keeping the distance from the nucleus constant. The model he introduced is known as the **Rutherford–Bohr model** or the **Bohr model.** Particles found in the nucleus are called **nucleons**, including the protons and neutrons in to the atom. A **nuclide** is the nucleus of an atom that has specific numbers of protons and neutrons (all **nucleons**). Therefore, nuclides are **composite particles of nucleons**.

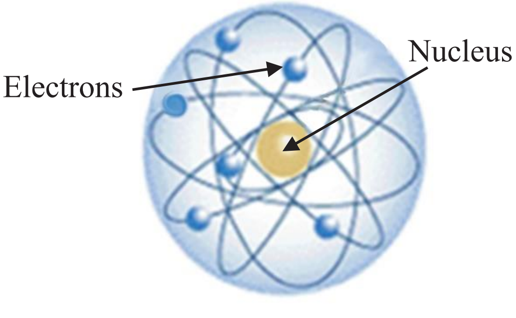


Figure 1.14 The Bohr model

1.1.5 Atomic number, isotopes and mass number

Henry Gwynn Jeffrey Moseley (1887-1915), an English physicist and a co-worker of Rutherford, found that the number of positive charges on the nucleus increases in atoms by single electron units. The atoms of each element have a characteristic number of protons. The number of protons in an atom of any particular element is called that element's **atomic number.**

Atomic number (Z) = Number of protons in the nucleus = Number of electrons in an atom

Since an atom has no net electrical charge, the number of electrons it contains is equal to the number of protons found in its nucleus. All atoms of carbon, for example, have six protons and six electrons, whereas all atoms of oxygen have eight protons and eight electrons. Thus, carbon has atomic number 6 and oxygen has atomic number 8.

British scientists **J. J. Thomson** and **Francis William Aston (1877-1945)** perfected the ‘mass spectrometer' which they used in 1912-13 to discover the first isotopes (of neon).

Atoms of a given element can differ in the number of neutrons they contain and therefore their mass can also vary. The number of protons plus neutrons (nuclide) in an atom is called its **mass number.**

Mass number (A) = Number of protons (Z) + Number of neutrons

In the atomic symbol used to represent a particular atom the mass number is given at the top left of the element symbol and the atomic number may be given at the bottom left. However, since the symbol also gives the same information, the atomic number usually may not be shown in the symbol.

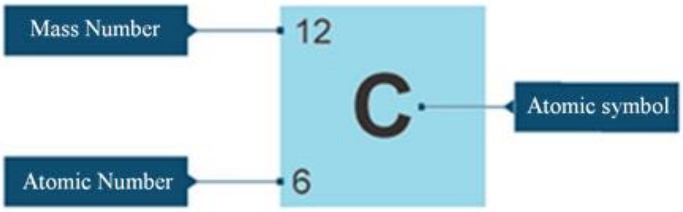


Figure 1.15 Atomic symbol of carbon

Example 1.1

How many protons, neutrons and electron are there in an atom of ^{197}Au?

Answer:

The superscript 197 is the mass number (protons + neutrons). According to the periodic table gold has atomic number 79. Hence, an atom of 197 Au has 79 protons, 79 electrons and 197-79 = 118 neutrons.

Atoms with identical atomic numbers but different mass numbers (that is, same number of protons but different numbers of neutrons) are called **isotopes** of one another.

For example, while most atoms of carbon have six neutrons, some have more. The carbon atoms containing six protons and six neutrons have a mass number 12 and are depicted as ^{12}C, while atoms that contain six protons and seven neutrons have mass number 13 and are depicted as ^{13}C. The atoms with six protons and eight neutrons have mass number 14 and are depicted as ^{14}C. Isotopes of an element that are stable in nature are called stable isotopes and those that are not stable called radioisotopes.

1.1.6 The atomic mass scale

Atoms are very small pieces of matter; however, they have a mass. However, it is convenient to use the **unified atomic mass unit (u)** when dealing with these extremely small masses, where;

1 u or **1Da** (earlier **amu**) $= \frac{12\text{ g}}{6.02214 \times 10^{23}} \times \frac{1}{12} = 1.66054 \times 10^{-24}\text{g}$

$\mathbf{1\ u = 1.66054 \times 10^{-24}\ g}$ **and** $\mathbf{1\ g = 6.02214 \times 10^{23}}$ **u** or **Da**

The unified atomic mass unit is defined as a mass of exactly 1/12 of a chemically unbound atom of the ^{12}C isotope of carbon. In these units, a ^{1}H atom has a mass of 1.0078 u or Da and a ^{16}O atom has a mass of 15.9949 u or Da.

1.1.7 Average atomic mass and relative atomic mass of an element

Most elements occur in nature as mixtures of isotopes. The mass of an atom can be given as **relative atomic mass or atomic mass**. It can be obtained by summing over the masses of its isotopes multiplied by their relative abundances:

Average atomic mass = Σ [(isotope mass) × (fractional isotope abundance)]

Example 1.2

Naturally occurring carbon is composed of 98.93% ^{12}C, 1.07% ^{13}C and a negligible amount of ^{14}C. The relative masses of two initial isotopes are 12 u (exactly) and 13.00335 u, respectively. Calculate the average atomic mass of carbon.

Answer:

$(0.9893 \times 12.00 \text{ u}) + (0.0107 \times 13.00335 \text{ u}) = 12.01 \text{ u}$

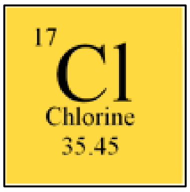
Relative atomic mass = 12.01

When the atomic mass is given as mass per mole of atoms (in units of **g mol^{-1}**), it is known as the **molar mass** of the element or atom.

Since 1 g = 6.02214×10^{23} u and 1 mole of atoms = 6.02214×10^{23} atoms, the molar mass of carbon will be 12.01 g mol^{-1}.

Relative atomic mass (A_r) is a dimensionless physical quantity. It is the ratio of the average mass of atoms of an element to ⅟₁₂ the mass of an atom of carbon-12 (known as the unified atomic mass unit). Hence the relative atomic mass of carbon will be 12.01.

In periodic tables the relative atomic mass of the element is usually given below the symbol of the element.



1.1.8 Ions

The nucleus of an atom is unchanged by chemical processes, but some atoms can readily gain or lose electrons. If electrons are removed from or added to an atom, a charged particle called an **ion** is formed. An ion with a positive charge is a **cation** and a negatively charged ion is an **anion**.

e.g.: The sodium atom, which has11 protons and 11 electrons can easily lose one electron. The resulting cation has 11 protons and 10 electrons, which means it has a net charge of +1.

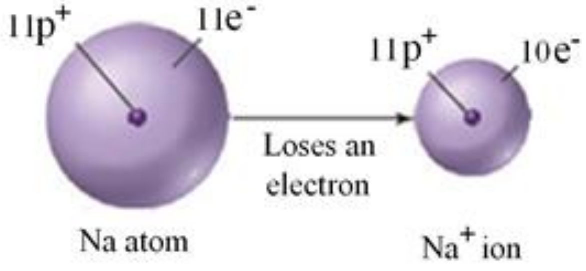


Figure 1.16 Ionization of sodium atom

e.g.: Chlorine, with 17 protons and 17 electrons, can gain an electron in chemical reactions, producing the Cl^- ion.

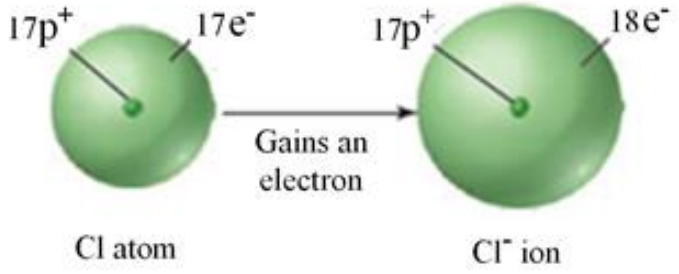


Figure 1.17 Formation of chloride ion

The net charge on an ion is represented by a superscript right to the atomic symbol. Hence the symbol for the ferric ion (an iron atom that has lost 3 electrons) will be:

$$ {}^{58}_{26}\mathrm{Fe}^{3+} $$

In addition to simple ions such as Na^+ and Cl^-, there are **polyatomic ions**, given as NH_4^+ (ammonium ion) and SO_4^{2-}(sulfate ion), which consist of joined atoms to form molecules carrying a net positive or negative charge.

1.2 Electromagnetic radiation and wave-like properties of matter

Much of our present understanding of the electronic structure of atoms has come from analysis of the light either emitted or absorbed by substances. Electromagnetic radiation (EMR) consists of **electromagnetic waves**, which are synchronized oscillations of electric and magnetic fields that propagate at the speed of light through a vacuum. The oscillations of the two fields are perpendicular to each other and perpendicular to the direction of wave propagation.

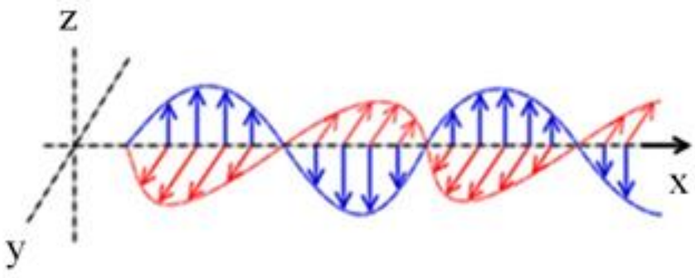


Figure 1.18 Electro-magnetic radiation

The light we see with our eyes, visible light, is one type of electromagnetic radiation. All types of electromagnetic radiation move through a vacuum at a speed of 2.998×10^8 m s^{-1}, the speed of light **(c)** and have wave-like characteristics.

Waves are periodic, which means that the pattern of peaks and troughs repeats itself at regular intervals. The distance between two adjacent peaks or between two adjacent troughs (distance between a cycle) is called the **wavelength (λ)**. The number of complete wavelengths, or cycles, that pass a given point each second is the **frequency (ν)** of the wave. Frequency is expressed in cycles per second using a unit called **hertz** (Hz). Since it is understood that cycles are involved, it may also be simply called "per second," which is denoted by s^{-1}. Hence,

$$\boxed{c = \lambda\nu}$$

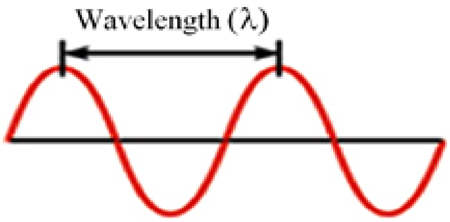


Figure 1.19 An electromagnetic wave

Example 1.3

The yellow light given off by a sodium vapour lamp used for public lighting has a wavelength of 589 nm. Calculate the frequency of this radiation.

Answer:

$$\nu = \frac{c}{\lambda} = \left(\frac{3.00 \times 10^{8}\ \mathrm{m\ s^{-1}}}{589\ \mathrm{nm}}\right)\left(\frac{1\ \mathrm{nm}}{10^{-9}\ \mathrm{m}}\right) = 5.09 \times 10^{14}\ \mathrm{s^{-1}}$$

Different types of electromagnetic radiations have different properties due to their different wavelengths. The display of electromagnetic radiation arranged in order of increasing wavelength is called the **electromagnetic spectrum**.

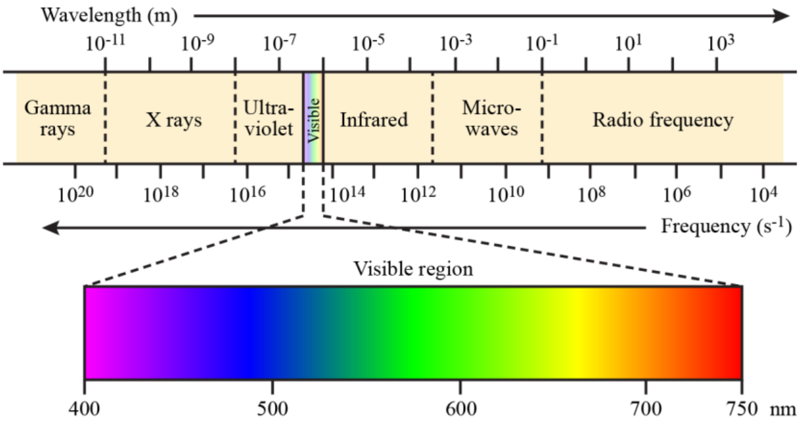


Figure 1.20 The electromagnetic spectrum

1.2.1 Quantization of energy

In 1900 a German physicist named **Max Planck (1858–1947)** proposed that energy is quantized; that is the energy can be either released or absorbed by atoms only in discrete quantities of some minimum size. Planck gave the name **quantum** (meaning “fixed amount”) to the smallest quantity of energy that can be emitted or absorbed as electromagnetic radiation. He proposed that the energy ***E*****,** of a single quantum equals a constant time the frequency of the radiation:

$$\boxed{E = h\nu}$$

The constant ***h*** is called **Planck constant** and has a value of 6.626 × 10^{-34} J s.

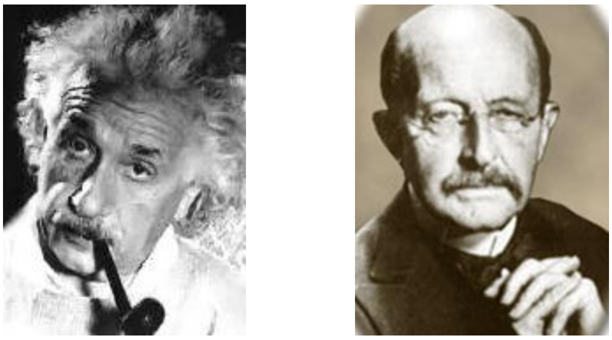

(a) (b)

Figure 1.21 (a) Albert Einstein and (b) Max Planck

In 1905, **Albert Einstein (1879–1955)** extending Planck's quantum theory, deduced that the radiant from a metal surface behaves like a stream of tiny energy packets. Each packet, which is like a "particle" of energy, is called a **photon** and each photon must have an energy equal to Planck constant times the frequency of the light:

Energy of a photon $= E = h\nu$

Example 1.4

Calculate the energy of one photon of yellow light that has a wavelength of 589 nm.

Answer:

$\nu = \frac{c}{\lambda} = 5.09 \times 10^{14}\ \text{s}^{-1}$

$\text{E} = h\nu = (6.626 \times 10^{-34}\ \text{J s} \times 5.09 \times 10^{14}\ \text{s}^{-1})$

$\quad = 3.37 \times 10^{-19}\ \text{J}$

If one photon of radiant energy supplies 3.37×10^{-19} J,

Energy of one mole of photons = $(6.02 \times 10^{23}\ \text{mol}^{-1})\ (3.37 \times 10^{-19}\ \text{J})$

$= 2.03 \times 10^{5}\ \text{J mol}^{-1}$ of energy.

In the years following the development of Bohr's model for the hydrogen atom, scientists established that depending on the experimental circumstances, radiation appears to have a wave-like and a particle-like (photon) character.

Louis de Broglie (1892–1987), extended the idea that if radiant energy could, under appropriate conditions, behave as though it were a stream of particles (photons), matter under appropriate conditions, possibly would show the properties of a wave.

De Broglie suggested that an electron moving about the nucleus of an atom behaves like a wave and therefore has a wavelength. He proposed that the wavelength of the electron, or of any other particle, depends on its mass, *m*, and on its velocity, v:

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

where h is the Planck constant. The quantity *m*v for any object is called its **momentum (*p*)**.

Because de Broglie's hypothesis is applicable to all matter, any object of mass (*m)* and velocity(v) would give rise to a characteristic matter wave. However, the wavelength associated with an object of ordinary size, such as a golf ball, is so tiny as to be completely unobservable. This is not so for an electron because its mass is so small.

1.3 Electronic energy levels of atoms

The **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion. The magnitude of the ionization energy tells us how much energy is required to remove an electron; the greater the ionization energy, the more difficult it is to remove an electron.

The ionization energies for a given element increase as successive electrons are removed. This trend is because with each successive removal, an electron is being pulled from an increasingly more positive ion, requiring increasingly more energy.

The sharp increase in ionization energy that occurs when an inner-shell electron is removed is a clear evidence for the fact that electrons are in discrete energy levels.

Table 1.1 Successive values of ionization energies I, for the elements from sodium to argon (kJ mol^{-1})

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4562					
Mg	738	1451	7733		(Inner-shell electrons)		
Al	578	1817	2745	11577			
Si	786	1577	3232	4356	16091		
P	1012	1907	2914	4964	6274	21267	
S	1000	2252	3357	4556	7004	8496	27107
Cl	1251	2298	3822	5159	6542	9362	11018
Ar	1521	2666	3931	5771	7238	8781	11995

1.3.1 The hydrogen spectrum

Most common radiation sources, including light bulbs and stars, produce radiation containing many different wavelengths. A **spectrum** is produced when radiation from such sources is separated into its component wavelengths. This range of colours, containing light of all wavelengths, is called a **continuous spectrum**. Not all radiation sources produce a continuous spectrum. When a high voltage is applied to tubes that contain different gases under reduced pressure, the gases emit different colours of light. For example, the light emitted by neon gas is the familiar red-orange glow of many "neon" lights. When light emitted from such tubes is passed through a prism, only a few wavelengths are present in the resultant spectrum. A spectrum containing radiation of only specific wavelengths is called a **line spectrum.**

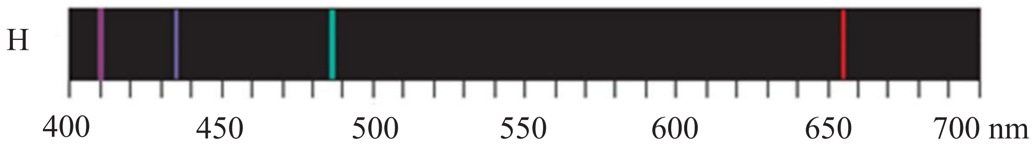


Figure 1.22 Line spectrum of hydrogen

Scientists studied the line spectrum of hydrogen thoroughly in the mid-1800s. At that time, only four lines at wavelengths of 410 nm (violet), 434 nm (blue) 486 nm (blue-green) and 656 nm (red) were observed in the spectrum.

Bohr's atomic model together with Planck's idea that energies are quantized was capable of explaining the line spectrum of hydrogen.

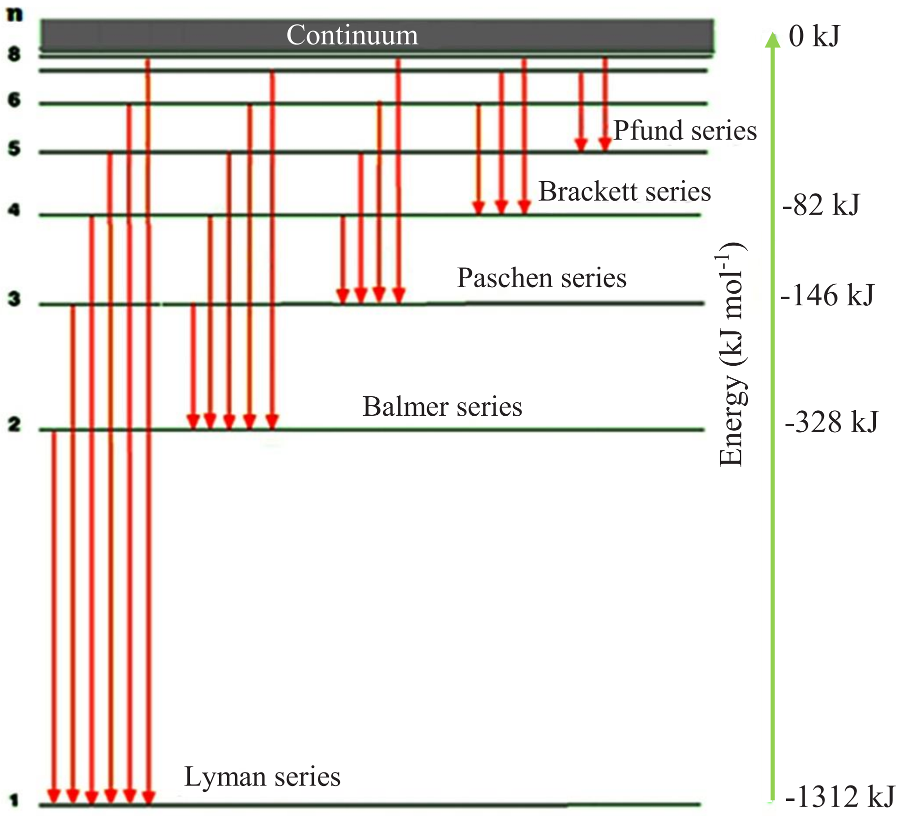


Figure 1.23 Possible electron emissions in hydrogen

Each allowed orbit around the atom corresponds to a different value of n (n is a whole number). The radius of the orbit gets larger as n increases. Thus, the first allowed orbit (the one closest to the nucleus) has $n = 1$, the next allowed orbit (the one second closest to the nucleus) has $n = 2$, and so forth.

The line spectra are the result of emission when electrons fall from an initial energy level (n_i) to a final energy level (n_f), so $\boldsymbol{E_{photon} = h\nu = hc/\lambda = -\Delta E = -(E_f - E_i)}$ for these transitions. ΔE is negative for emission as n_f is less than n_i; the electron is falling in energy to a lower-energy orbit. The possible emissions results in the line spectra seen in hydrogen.

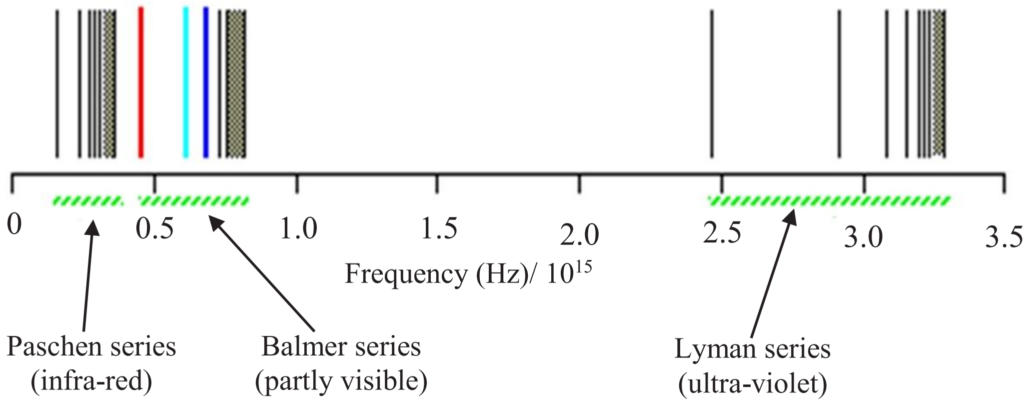


Figure 1.24 (a) The line spectrum of hydrogen

Figure 1.24(a) shows the spectrum as it varies with frequency. However, the variation of wavelength has shown in Figure 1.24(b).

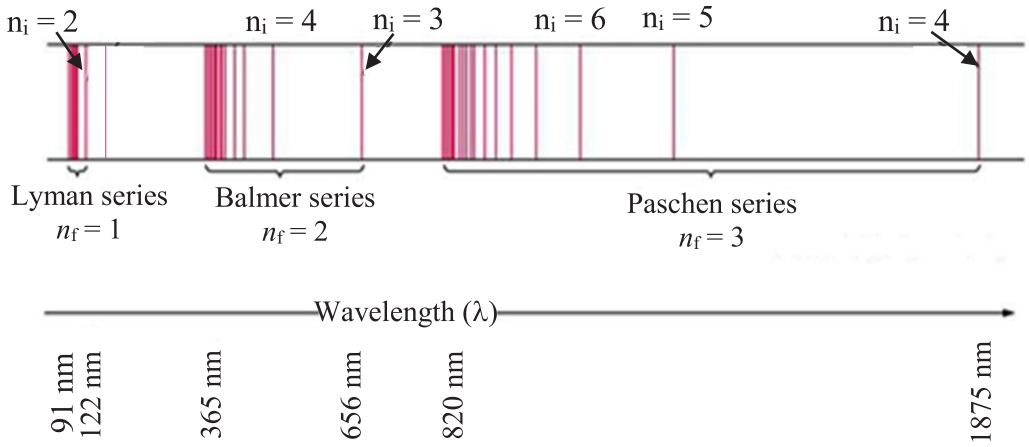


Figure 1.24 (b) The line spectrum of hydrogen

1.3.2 Shapes of orbitals

An electron's probable location in space around an atom (shapes of orbitals) shows us how the electron density is distributed around the nucleus.

The electron density for an *s* orbital is spherically symmetric and centered on the nucleus or in other words the *s* orbitals are spherical in shape.

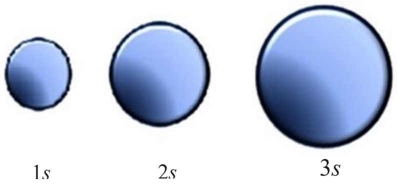


Figure 1.25 Shapes of the *s* orbitals

Each *p* subshell has three orbitals, corresponding to the three allowed values of m_l: -1, 0 and +1. The electron density is not distributed spherically as in an *s* orbital. Instead, the density is concentrated in two regions on either side of the nucleus, separated by a node at the nucleus. This dumbbell-shaped orbital has two lobes.

For each value of *n,* the three *p* orbitals have the same size and shape but differ from one another in spatial orientation. It is convenient to label these as p_x, p_y, and p_z orbitals where the letter subscript indicates the Cartesian axis along which the orbital is oriented.

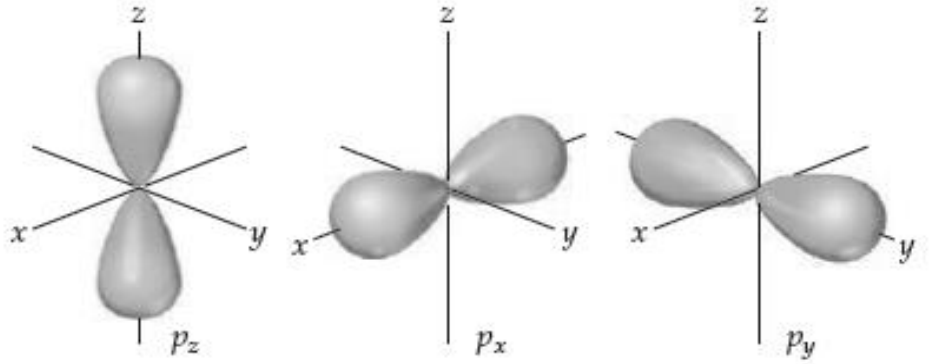


Figure 1.26 Shapes of the *p* orbitals

The different *d* orbitals in a given shell have different shapes and orientations in space. The shapes of the *f* orbitals are even more complicated than those of the *d* orbitals.

1.3.3 Orbitals and quantum numbers

The Bohr model introduced a single quantum number, *n*, to describe an orbit. The quantum mechanical model uses three quantum numbers, *n*, *l* and m_l, which result naturally from the mathematics used to describe an orbital that electrons occupy in an atom and m_s that describes the spin of the electron.

1. **The principal quantum number *n*,** can have positive integral values 1, 2, 3, ... This quantum number defines the main energy level (electron shell) that the electron occupies in the atom. As *n* increases, the orbital becomes larger, and the electron spends more time further from the nucleus.

2. **The angular momentum (or azimuthal) quantum number *l*,** can have integral values from 0 to (*n* - 1) for each value of *n*. This quantum number defines the shape of the orbital. The value of ***l*** for a particular orbital is generally designated by the letters *s*, *p*, *d* and *f* corresponding to *l* values of 0, 1, 2 and 3 respectively.

   The set of orbitals that have the same *n* and *l* values is called a **subshell**. Each subshell is designated by a number (the value of *n*) and a letter (*s*, *p*, *d* or *f* corresponding to the value of *l*). For example, the orbitals that have $n = 3$ and $l = 2$ are called 3*d* orbitals and are in the 3*d* subshell.

3. **The magnetic quantum number m_l,** can have integral values between $-l$ and l, including zero. This quantum number describes the orientation of the orbital in space and the number of possible values for l denotes the number of orbitals in the subshell. For example, for $l = 2$ the values possible will be 2, 1, 0, -1 and -2 denoting that a *d* subshell has five orbitals.

4. **The spin quantum number m_s.** Two possible values are allowed for m_s, + ½ or -1/2, which indicate the two opposite directions in which the electron can spin. A spinning charge produces a magnetic field. The two opposite directions of spin therefore produce oppositely directed magnetic fields.

Table 1.2 Relationship between values n, l, and m_l

n	Possible values of l	Subshell designation	Possible values of m_l	Number of orbitals in subshell	Total number of orbitals in shell
1	0	1*s*	0	1	1
2	0	2*s*	0	1	4
	1	2*p*	-1, 0, 1	3	
3	0	3*s*	0	1	9
	1	3*p*	-1, 0, 1	3	
	2	3*d*	-2, -1, 0, 1, 2	5	
4	0	4*s*	0	1	16
	1	4*p*	-1, 0, 1	3	
	2	4*d*	-2, -1, 0, 1, 2	5	
	3	4*f*	-3, -2, -1, 0, 1, 2, 3	7	

The restrictions on possible values for quantum numbers give rise to the following very important observations:

1. The shell with principal quantum number n consists of exactly n subshells. Each subshell corresponds to a different allowed value of l from 0 to $(n - 1)$. Thus, the first shell ($n = 1$) consists of only one subshell, the 1*s* ($l = 0$); the second shell ($n = 2$) consists of two subshells, the 2*s* ($l = 0$) and 2*p* ($l = 1$); the third shell consists of three subshells, 3*s*, 3*p*, and 3*d*, and so forth.
2. Each subshell consists of a specific number of orbitals. Each orbital corresponds to a different allowed value of m_l. For a given value of l, there are $(2l + 1)$ allowed values of m_l, ranging from $-l$ to $+l$. Thus, each *s* ($l = 0$) subshell consists of one orbital; each *p* ($l = 1$) subshell consists of three orbitals; each *d* ($l = 2$) subshell consists of five orbitals, and so forth.

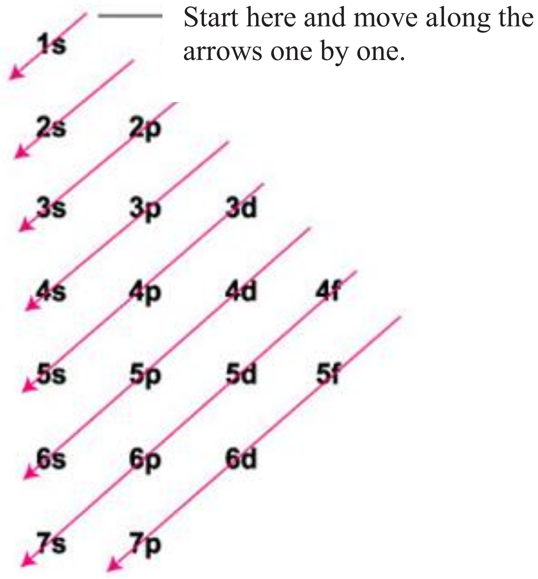
3. The total number of orbitals in a shell is n^2, where n is the principal quantum number of the shell. The resulting number of orbitals for the shells 1, 4, 9 and 16 is related to a pattern seen in the periodic table: We see that the number of elements in the rows of the periodic table 2, 8, 18 and 32 equals twice these numbers.

1.4 Electron configuration

When considering the electronic structures of atoms: In a many-electron atom, for a given value of n, the energy of an orbital increases with increasing value of l. For example, $n = 3$ orbitals increase in energy in the order $3s < 3p < 3d$ and all orbitals of a given subshell (such as the five $3d$ orbitals) have the same energy, just as they do in the hydrogen atom. Orbitals with the same energy are said to be **degenerate**.

1.4.1 The Aufbau principle

The filling of electrons in an atom begins with the subshell lowest energy and continues upwards according to the “Aufbau principle” (The German word 'Aufbau' means 'building up').



Start here and move along the arrows one by one.

Figure 1.27 Sequence of filling of electrons

Thus, the general order of energies of energy levels and sub energy levels are shown in Figure 1.28.

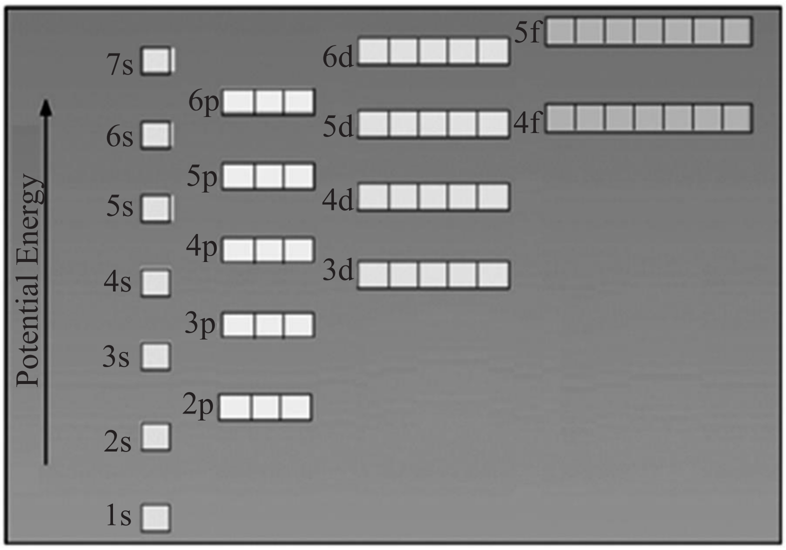


Figure 1.28 Order of the energy levels in an atom

1.4.2 The Pauli exclusion principle

The **Pauli Exclusion Principle,** which was postulated by **Wolfgang Pauli** in 1925, states that *no* two electrons in an atom can have the same set of four quantum numbers n, l, m_l, and m_s.

For a given orbital, the values of n, l, and m_l are fixed. Thus, if we want to put more than one electron in an orbital and satisfy the Pauli Exclusion Principle, our only choice is to assign different m_s values to the electrons. This indicates that an orbital can hold a maximum of two electrons and they must have opposite spins. This restriction allows us to index the electrons in an atom by giving their quantum numbers.

Thus, each *s* subshell which consists of one orbital can hold a maximum of two electrons; each *p* subshell that consists of three orbitals can hold a maximum of six electrons; each *d* subshell which consists of five orbitals can hold a maximum of ten electrons, and so forth.

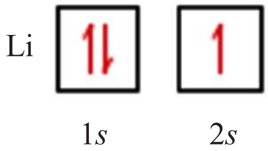
Electrons are distributed among the various orbitals of an atom based on the relative energies of orbitals and the Pauli Exclusion Principle and this distribution is called the **electron configuration** of the atom. The most stable electron configuration, known as the ground state, is that in which the electrons are in the lowest possible energy states.

According to the Pauli Exclusion Principle however, there can be only two electrons in any single orbital. Thus, the orbitals are filled in the order of increasing energy, with no more than two electrons per orbital.

For example, in the lithium atom, which has three electrons, the 1*s* orbital can accommodate two electrons. The third one goes into the next lowest-energy orbital, the 2*s*.

Any electron configuration can be represented by writing the symbol for the occupied subshell and adding a superscript to indicate the number of electrons in that subshell. For example, for lithium we write $1s^22s^1$ and for sodium $1s^22s^22p^63s^1$.

In another representation, called an **orbital diagram**, each orbital is denoted by a box or circle and each electron by a half arrow/ full arrow. A half/ full arrow pointing up represents an electron with a positive spin magnetic quantum number ($m_s = +1/2$) and a half/ full arrow pointing down represents an electron with a negative spin magnetic quantum number ($m_s = -1/2$).



Electrons having opposite spins are said to be paired when they are in the same orbital. An unpaired electron is one not accompanied by a partner of opposite spin.

In the lithium atom the two electrons in the 1*s* orbital are paired and the electron in the 2*s* orbital is unpaired.

1.4.3 Hund's rule

The Hund's rule states that for degenerate orbitals, the lowest energy is attained when the number of electrons having the same spin is maximized.

This means that electrons occupy orbitals singly to the maximum extent possible and that these single electrons in a given subshell all have the same spin magnetic quantum number. Electrons arranged in this way are said to have parallel spins.

e.g. Carbon atom; the two 2*p* electrons singly occupy two of the three 2*p* orbitals and they will be parallel to each other so that they can have the same spin.

Table 1.3 Electron distribution of some elements in second and third period

Element	Total electrons	Orbital diagram				Electron configuration
		$1s$	$2s$	$2p$	$3s$	
Li	3	⇅	↑	☐☐☐	☐	$1s^2\ 2s^1$
Be	4	⇅	⇅	☐☐☐	☐	$1s^2\ 2s^2$
B	5	⇅	⇅	↑☐☐	☐	$1s^2\ 2s^2\ 2p^1$
C	6	⇅	⇅	↑↑☐	☐	$1s^2\ 2s^2\ 2p^2$
N	7	⇅	⇅	↑↑↑	☐	$1s^2\ 2s^2\ 2p^3$
Ne	10	⇅	⇅	⇅⇅⇅	☐	$1s^2\ 2s^2\ 2p^6$
Na	11	⇅	⇅	⇅⇅⇅	↑	$1s^2\ 2s^2\ 2p^6\ 3s^1$

1.4.4 Condensed electron configurations

The electron configuration (also known as the electron distribution) of sodium, atomic number 11, is written as $1s^22s^22p^63s^1$. However, the filling of the $2p$ subshell is complete at neon, which has a stable configuration with eight electrons (an *octet*) in the outermost occupied shell. The next element, sodium, marks the beginning of a new row of the periodic table. Sodium has a single $3s$ electron beyond the stable configuration of neon. The configuration of sodium can therefore be abbreviated as $[\mathrm{Ne}]3s^1$.

The part represented by the bracketed symbol is the noble-gas core of the atom. More usually, these inner-shell electrons are referred to as the **core electrons**.

The electrons given after the noble-gas core are called the **outer-shell electrons** or valence shell electrons. The outer-shell electrons include the electrons involved in chemical bonding, as they are called the **valence electrons**.

Similarly, phosphorous, which has 15 electrons can be represented as $1s^22s^22p^63s^23p^3$ or $[\mathrm{Ne}]3s^23p^3$.

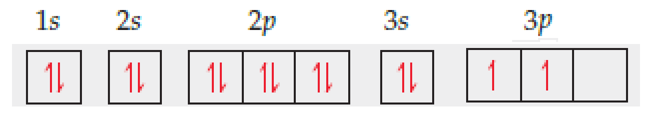
Example 1.5

(a) Write the electron configuration for silicon, element 14, in its ground state.
(b) How many unpaired electrons does a ground-state silicon atom possess?

Answer:

(a) $1s^2 2s^2 2p^6 3s^2 3p^2$ or $[Ne]3s^2 3p^2$

(b)



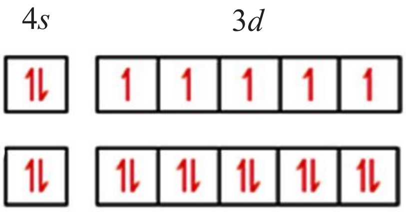
two unpaired electrons.

After the noble-gas element argon ($1s^2 2s^2 2p^6 3s^2 3p^6$), according to Aufbau principle, it is not the 3*d* but 4*s* orbital that the next electron goes to. Hence, the element that follows Argon, which is potassium (K) has the electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or $[Ar]4s^1$. Calcium, with 20 electrons hence is written as $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ or $[Ar]4s^2$.

Following the complete filling of the 4*s* orbital (this occurs in the calcium atom), the next set of orbitals to be filled is the 3*d*.

Mn: $[Ar]\ 3d^5\ 4s^2$ or [Ar]

Zn: $[Ar]\ 3d^{10}\ 4s^2$ or [Ar]



Once all the 3*d* orbitals have been filled with two electrons each, the 4*p* orbitals begin to be occupied until the completed octet of outer electrons ($4s^2 4p^6$) is reached with krypton (Kr), atomic number 36, another of the noble gases.

Elements with completely filled or precisely half-filled sub energy levels appear to be relatively more stable than elements with other electron configurations. Thus elements with configurations ending with s^2, p^6 and d^{10} will be more stable.

e.g.: Zn: $[Ar]3d^{10}4s^2$, Mg: $[Ne]3s^2$, Ar: $[Ne]3s^2 3p^6$, N: $[He]2s^2 2p^3$ and Mn: $[Ar]3d^5 4s^2$ will be relatively stable atoms.

The electron configurations of certain elements appear to deviate from the rules of configuration discussed. For an example, the electron configuration of chromium (element 24) is $[Ar]3d^5 4s^1$ rather than $[Ar]3d^4 4s^2$ which we might expect. Similarly, the configuration of copper (element 29) is [Ar]$3d^{10}4s^1$ instead of [Ar]$3d^94s^2$.This anomalous behaviour is largely a consequence of the closeness of the 3*d* and 4*s* orbital energies. It frequently occurs when there are enough electrons to form precisely half-filled sub energy levels (as in chromium) or a completely filled sub energy levels (as in copper), that would result in relatively stable configurations. (Note that the filling of the 3*d* orbitals occurs after filling of 4*s*. However, the electronic configuration is commonly written as 3*d* first and then 4*s*).

1.5 Building of the periodic table

The discovery of chemical elements has been ongoing since ancient times. Certain elements, such as gold (Au), appear in nature in elemental form and were thus discovered thousands of years ago. In contrast, some elements, such as technetium (Tc), are radioactive and intrinsically unstable and were discovered after the development of technology during the twentieth century.

As the number of known elements increased, scientists began classifying them. In 1869, **Dmitri Ivanovich Mendeleev** in Russia and **Lothar Meyer** in Germany published nearly identical classification schemes. Both noted that similar chemical and physical properties occur periodically when the elements are arranged in order of increasing atomic mass. Scientists at that time had no knowledge of atomic numbers. However with the introduction of the concept of atomic number the modern periodic table was constructed.

:

(a) (b)

Figure 1.29 (a) Dmitri Mendeleev and (b) Lothar Meyer

-

Key:

atomic number
Symbol
name
conventional atomic weight
standard atomic weight

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 **H** hydrogen 1.008 [1.0078, 1.0082]																	2 **He** helium 4.0026
3 **Li** lithium 6.94 [6.938, 6.997]	4 **Be** beryllium 9.0122											5 **B** boron 10.81 [10.806, 10.821]	6 **C** carbon 12.011 [12.009, 12.012]	7 **N** nitrogen 14.007 [14.006, 14.008]	8 **O** oxygen 15.999 [15.999, 16.000]	9 **F** fluorine 18.998	10 **Ne** neon 20.180
11 **Na** sodium 22.990	12 **Mg** magnesium 24.305 [24.304, 24.307]											13 **Al** aluminium 26.982	14 **Si** silicon 28.085 [28.084, 28.086]	15 **P** phosphorus 30.974	16 **S** sulfur 32.06 [32.059, 32.076]	17 **Cl** chlorine 35.45 [35.446, 35.457]	18 **Ar** argon 39.948
19 **K** potassium 39.098	20 **Ca** calcium 40.078 (4)	21 **Sc** scandium 44.956	22 **Ti** titanium 47.867	23 **V** vanadium 50.942	24 **Cr** chromium 51.996	25 **Mn** manganese 54.938	26 **Fe** iron 55.845 (2)	27 **Co** cobalt 58.933	28 **Ni** nickel 58.693	29 **Cu** copper 63.546 (3)	30 **Zn** zinc 65.38 (2)	31 **Ga** gallium 69.723	32 **Ge** germanium 72.630 (8)	33 **As** arsenic 74.922	34 **Se** selenium 78.971 (8)	35 **Br** bromine 79.904 [79.901, 79.907]	36 **Kr** krypton 83.798 (2)
37 **Rb** rubidium 85.468	38 **Sr** strontium 87.62	39 **Y** yttrium 88.906	40 **Zr** zirconium 91.224 (2)	41 **Nb** niobium 92.906	42 **Mo** molybdenum 95.95	43 **Tc** technetium	44 **Ru** ruthenium 101.07 (2)	45 **Rh** rhodium 102.91	46 **Pd** palladium 106.42	47 **Ag** silver 107.87	48 **Cd** cadmium 112.41	49 **In** indium 114.82	50 **Sn** tin 118.71	51 **Sb** antimony 121.76	52 **Te** tellurium 127.60 (3)	53 **I** iodine 126.90	54 **Xe** xenon 131.29
55 **Cs** caesium 132.91	56 **Ba** barium 137.33	57 **La** lanthanum 138.91	72 **Hf** hafnium 178.49 (2)	73 **Ta** tantalum 180.95	74 **W** tungsten 183.84	75 **Re** rhenium 186.21	76 **Os** osmium 190.23 (3)	77 **Ir** iridium 192.22	78 **Pt** platinum 195.08	79 **Au** gold 196.97	80 **Hg** mercury 200.59	81 **Tl** thallium 204.38 [204.38, 204.39]	82 **Pb** lead 207.2	83 **Bi** bismuth 208.98	84 **Po** polonium	85 **At** astatine	86 **Rn** radon
87 **Fr** francium	88 **Ra** radium	89 **Ac** actinium	104 **Rf** rutherfordium	105 **Db** dubnium	106 **Sg** seaborgium	107 **Bh** bohrium	108 **Hs** hassium	109 **Mt** meitnerium	110 **Ds** darmstadtium	111 **Rg** roentgenium	112 **Cn** copernicium	113 **Nh** nihonium	114 **Fl** flerovium	115 **Mc** moscovium	116 **Lv** livermorium	117 **Ts** tennessine	118 **Og** oganesson
				58 **Ce** cerium 140.12	59 **Pr** praseodymium 140.91	60 **Nd** neodymium 144.24	61 **Pm** promethium	62 **Sm** samarium 150.36 (2)	63 **Eu** europium 151.96	64 **Gd** gadolinium 157.25 (3)	65 **Tb** terbium 158.93	66 **Dy** dysprosium 162.50	67 **Ho** holmium 164.93	68 **Er** erbium 167.26	69 **Tm** thulium 168.93	70 **Yb** ytterbium 173.05	71 **Lu** lutetium 174.97
				90 **Th** thorium 232.04	91 **Pa** protactinium 231.04	92 **U** uranium 238.03	93 **Np** neptunium	94 **Pu** plutonium	95 **Am** americium	96 **Cm** curium	97 **Bk** berkelium	98 **Cf** californium	99 **Es** einsteinium	100 **Fm** fermium	101 **Md** mendelevium	102 **No** nobelium	103 **Lr** lawrencium

Figure 1.30 The periodic table of elements

The way in which the columns (groups) are labeled is somewhat arbitrary. The labeling scheme widely used in the past had Arabic numerals and A and B designations. Thus the numbers ran from 1A-8A and 1B-8B. The group headed by fluorine (F) hence was group 7A.

In a similar convention, the columns are numbered using Roman numerals rather than Arabic numerals together with the letters A and B.

In an effort to eliminate this confusion, the International Union of Pure and Applied Chemistry (IUPAC) has proposed a convention that numbers the groups from 1 to18 with no A or B designations, as shown in the Figure 1.30.

The electron configurations of the elements correspond to their locations in the periodic table. The rows of the table are called periods and elements of the same row show trends in some of their properties.

Elements in the same column of the table, which are called groups, have related outer-shell (valence) electron configurations. For example, all group 2 elements have an ns^2 outer configuration, and all group 3 elements have an ns^2np^1 outer configuration, with the value of ‘n’ increasing as we move down each column.

Table 1.4 Electron configurations of Group 2 and 13 elements

Group 2		**Group 13**	
Be	[He]$2s^2$	B	[He]$2s^2\ 2p^1$
Mg	[Ne]$3s^2$	Al	[Ne]$3s^2 3p^1$
Ca	[Ar]$4s^2$	Ga	[Ar]$4s^2 4p^1$
Sr	[Kr]$5s^2$	In	[Kr]$5s^2 5p^1$
Ba	[Xe]$6s^2$	Tl	[Xe]$6s^2 6p^1$
Ra	[Rn]$7s^2$		

Elements in a group in the periodic table, often exhibit similarities in physical and chemical properties.

Table 1.5 Names of some groups in the periodic table

Group	Name	Elements
1	Alkali metals	Li, Na, K, Rb, Cs, Fr
2	Alkaline earth metals	Be, Mg, Ca, Sr, Ba, Ra
16	Chalcogens	O, S, Se, Te, Po
17	Halogens	F, Cl, Br, I, At
18	Noble gases (rare gases)	Ne, Ar, Kr, Xe, Rn

Since the total number of orbitals in each shell equals n^2: 1, 4, 9 and 16 respectively and because two electrons can be placed in each orbital, each shell accommodates up to $2n^2$ electrons: 2, 8, 18, or 32. The overall structure of the periodic table too reflects these electron numbers: Each row of the table has 2, 8, 18 or 32 elements in it.

The periodic table can be further divided into four blocks based on the filling order of orbitals.

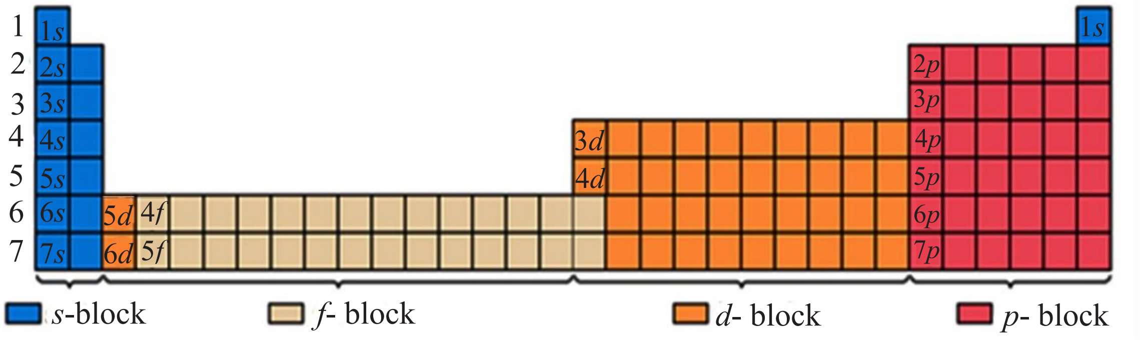


Figure 1.31 Regions of the periodic table

The two columns of elements on the left known as the alkali metals (group 1) and alkaline earth metals (group 2), are those in which the valence *s* orbitals are being filled. These two columns make up the ***s* block** of the periodic table.

The block on the far right with *six* columns (group 13 to group 18) comprises the ***p* block**, where the valence *p* orbitals are being filled. The *s* block and the *p* block elements together are the **representative elements**, sometimes called the **main-group elements**.

The block before the *p*-block in the Figure 1.31 has *ten* columns containing the **transition metals**. However, the elements in 10th column are not considered as transition metals. These are the elements in which the valence *d* orbitals are being filled and make up the ***d* block.**

The elements in the two rows between and *s* block and *d* block, containing 14 columns are the ones in which the valence *f* orbitals are being filled and make up the ***f* block**. (However, filling of electrons and hence their electron configurations are complicated). These elements are often referred to as the ***f* block metals** or **inner transition elements**.

The number of columns in each block corresponds to the maximum number of electrons that can occupy each kind of subshell. Since that 2, 6, 10, and 14 are the numbers of electrons that can fill the *s*, *p*, *d* and *f* subshells, respectively, the *s* block has 2 columns, the *p* block has 6, the *d* block has 10 and the *f* block has 14.

1.6 Periodic trends shown by *s* and *p* block elements

Many properties of atoms depend on their electron configuration and on how strongly the outer electrons in the atoms are attracted to the nucleus. Coulomb's law tells us that the strength of the interaction between two electrical charges depends on the magnitudes of the charges and on the distance between them. Therefore, the attractive force between an electron and the nucleus depends on the magnitude of the nuclear charge and on the average distance between the nucleus and the electron. The force increases as the nuclear charge increases and decreases as the electron moves further from the nucleus.

In an atom that containing a large number of electrons, in addition to the attraction of each electron to the nucleus, each electron experiences a repulsion due to the proximity of other electrons. These electron–electron repulsions cancel some of the attraction of the electron to the nucleus so that the electron experiences less attraction than it would if the other electrons were not there. Each electron in an atom is said to be screened or shielded from the nucleus by the other electrons and the phenomenon is hence termed the **screening effect** or **shielding effect** of electrons. Therefore, all atoms show shielding effect except hydrogen.

An electron, therefore, experiences a net attraction by the nucleus that is less than it would be in the absence of other electrons. This partially screened nuclear charge is termed the **effective nuclear charge**, $\boldsymbol{Z_{\text{eff}}}$. The effective nuclear charge is always less than the actual nuclear charge ($Z_{\text{eff}} < Z$).

For a valence electron, most of the shielding is due to the core electrons, which are much closer to the nucleus. As a result, the greater the number of core electrons and the higher the number of core shells, the greater will be the screening effect.

The effective nuclear charge increases from left to right across any period of the periodic table. Although the number of core electrons stays the same across the period, the number of protons increases. The valence electrons added to counterbalance the increasing nuclear charge thus it screens ineffectively. Thus, Z_{eff} increases steadily across the period.

1.6.1 Sizes of atoms and ions

Atoms are not hard, spherical objects as many of us think. According to the quantum mechanical model, atoms do not have sharply defined boundaries. We can define atomic size in several ways, based on the distances between atoms in various situations.

van der Waals radius

The van der Waals radius (nonbonding atomic radius) refers to one half the distance between two equivalent non-bonded atoms in their most stable arrangement, that is, where attractive forces are maximum.

Covalent radius

A chemical bond is the attractive interaction between any two adjacent atoms in a molecule. The two bonded atoms are closer together than they would be in a nonbonding collision. The bonding atomic radius for any atom in a molecule is equal to half of the bond distance (the distance between two bonded atoms). The bonding atomic radius (also known as the covalent radius) is smaller than the nonbonding atomic radius.

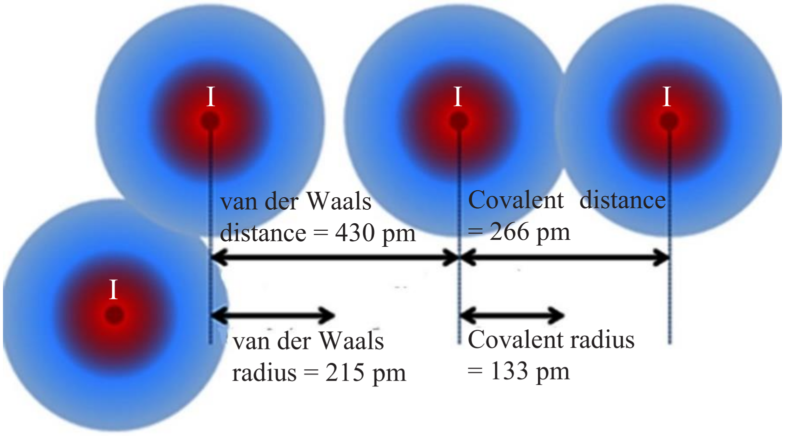


Figure 1.32 Covalent and van der Waals radius for Iodine (I_2)

Metallic radius

Metal atoms in a metallic structure are bonded to each other by metallic bonds. Half of the bond distance between the nuclei of two adjacent metal atoms in a metallic structure is called the **metallic radius**.

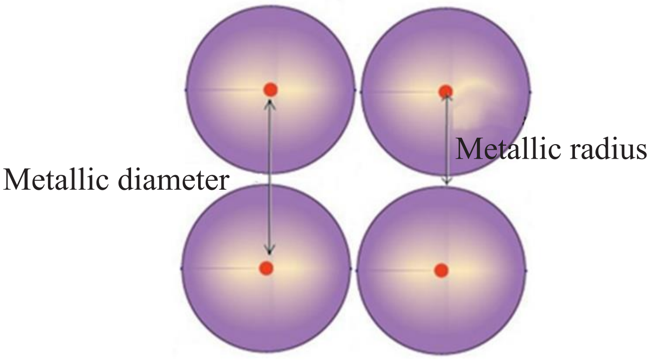


Figure 1.33 The metallic radius

Periodic trends in atomic radii

The atomic sizes within the periodic table show two interesting trends:

Within each group, the atomic radius tends to increase from top to bottom. This trend results primarily from the increase in the principal quantum number (*n*) of the outer electrons. As we go down a column, the outer electrons have a greater probability of being further away from the nucleus, causing the atomic radius to increase.

Within each period, the atomic radius generally tends to decrease from left to right. The major factor influencing this trend is the increase in effective nuclear charge across a period. The increasing effective nuclear charge steadily draws the valence electrons closer to the nucleus, causing the atomic radius to decrease.

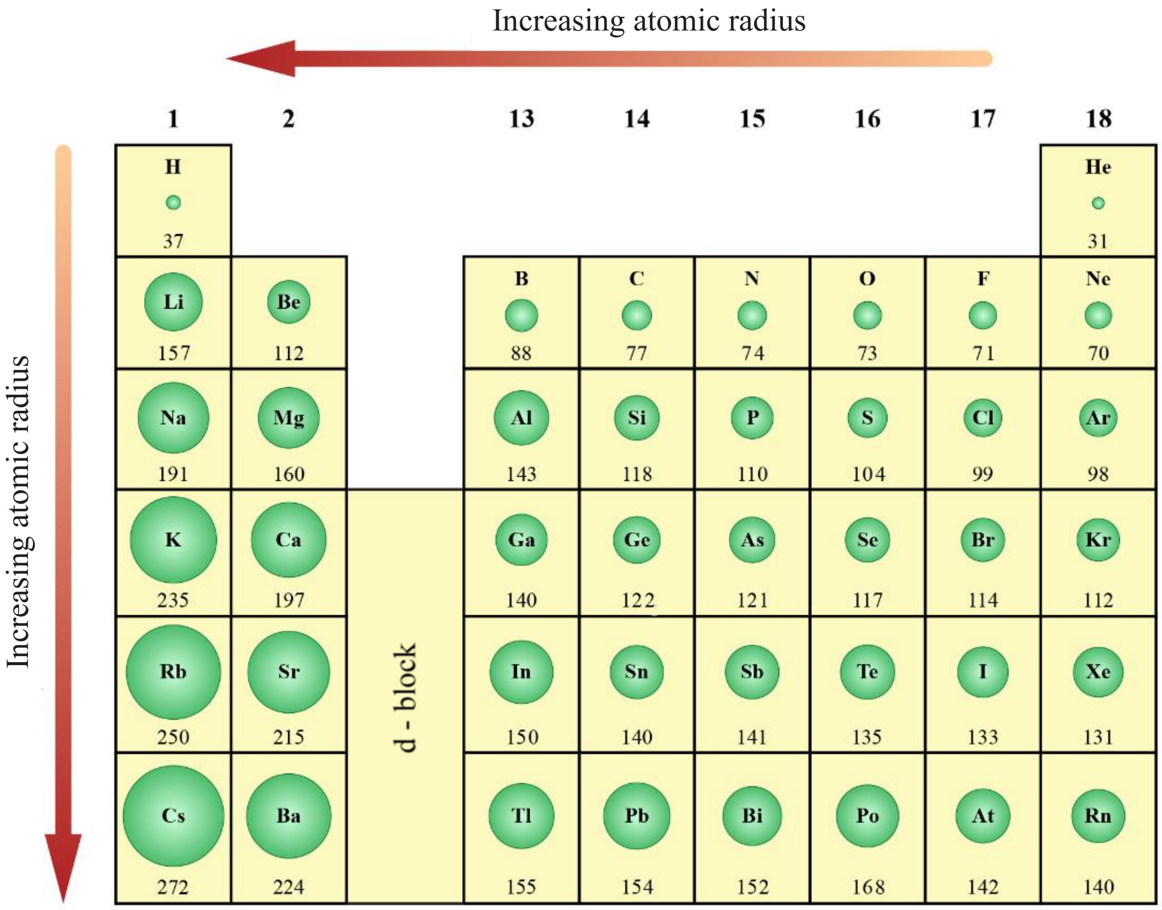


Figure 1.34 (a) Trends in atomic radii in the periodic table in pm

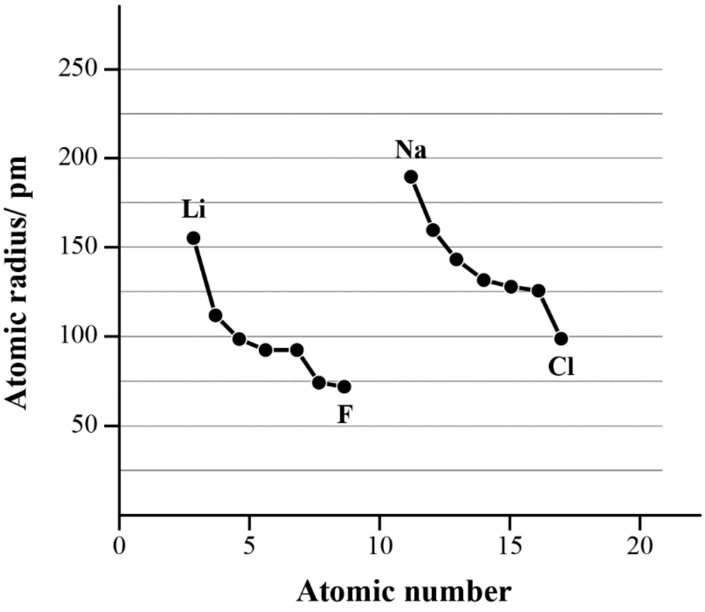


Figure 1.34 (b) Trends in atomic radii in the periodic table

Electron configurations of ions

When electrons are removed from an atom to form a cation, they are always removed first from the occupied orbitals having the highest principal quantum number, *n*.

For example, when one electron is removed from a sodium atom ($1s^2 2s^2 2p^6 3s^1$), it is the $3s^1$ electron that is removed.

$$\mathrm{Na}(1s^2 2s^2 2p^6 3s^1 \text{ or } [\mathrm{Ne}]3s^1) \longrightarrow \mathrm{Na}^+(1s^2 2s^2 2p^6 \text{ or } [\mathrm{Ne}]) + \mathrm{e}$$

If there is more than one occupied subshell for a given value of *n*, the electrons are first removed from the orbital with the highest value of *l*. For example, a boron atom loses its $2p$ electron before it loses its $2s$ electrons.

$$\mathrm{B}(1s^2 2s^2 2p^1) \longrightarrow \mathrm{B}^+(1s^2 2s^2) + \mathrm{e}$$

$$\mathrm{B}^+(1s^2 2s^2) \longrightarrow \mathrm{B}^{3+}(1s^2) + 2\mathrm{e}$$

When two electrons are removed from Fe ($[\mathrm{Ar}]3d^6 4s^2$), the $4s^2$ electrons are the ones that are removed even though in filling the $4s$ fills before the $3d$.

$$\mathrm{Fe}([\mathrm{Ar}]3d^6 4s^2) \longrightarrow \mathrm{Fe}^{2+}([\mathrm{Ar}]3d^6) + 2\mathrm{e}$$

If an additional electron is removed, forming Fe^{3+}, it comes from a $3d$ orbital because all the orbitals with $n = 4$ are empty.

$$\mathrm{Fe}^{2+}([\mathrm{Ar}]3d^6) \longrightarrow \mathrm{Fe}^{3+}([\mathrm{Ar}]3d^5) + \mathrm{e}$$

Electrons added to an atom to form an anion are added to the empty or partially filled orbital having the highest value of *n,* which is the valence shell. For example, an electron added to a fluorine atom to form the F^- ion goes into the one remaining vacancy in the $2p$ subshell.

$$F(1s^22s^22p^5) \;+\; e \longrightarrow F^-(1s^22s^22p^6)$$

Periodic trends in ionic radii

Like the size of an atom, the size of an ion depends on its nuclear charge, the number of electrons it possesses, and the orbitals in which the valence electrons reside. When a cation is formed from a neutral atom, electrons are removed from the occupied atomic orbitals that are the most spatially extended from the nucleus. Also, when a cation is formed the number of electron–electron repulsions is reduced. Therefore, cations are smaller than their parent atoms.

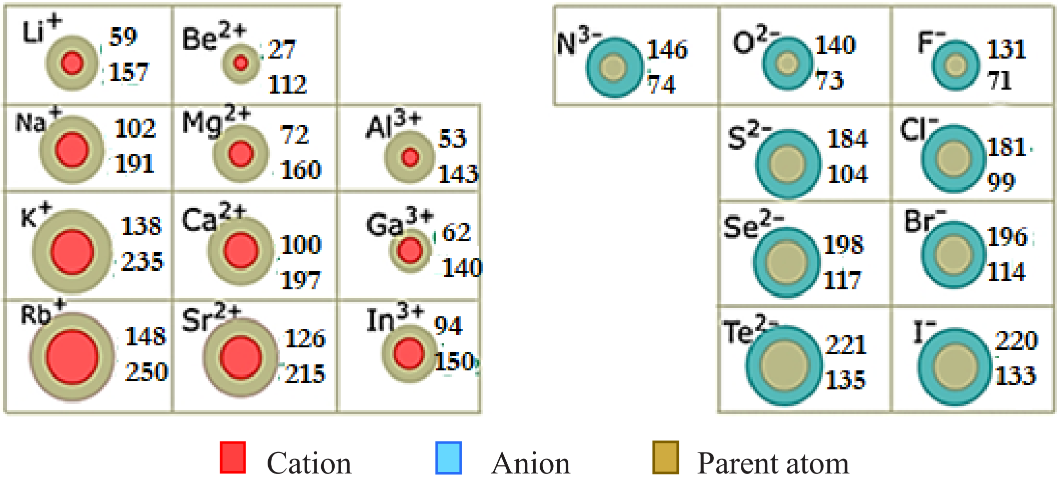


Figure 1.35 Radii of cations and anions compared to parent atoms in pm

The opposite is true of anions. When electrons are added to an atom to form an anion, the increased electron–electron repulsions cause the electrons to spread out more in space. Thus, anions are larger than their parent atoms.

For ions carrying the same charge (both positively or negatively charged ions), ionic radius increases as we move down a column in the periodic table. In other words, as the principal quantum number of the outermost occupied orbital of an ion increases, the radius of the ion increases.

An **isoelectronic series** is a group of ions/ atoms containing the same number of electrons. For example, each ion/ atom in the isoelectronic series O^{2-}, F^-, Ne, Na^+ and Mg^{2+} has a total number of 10 electrons. In any isoelectronic series the nuclear charge increases with increasing atomic number in the series. Because the number of electrons remains constant, ionic radius decreases with increasing nuclear charge as the electrons are more strongly attracted to the nucleus.

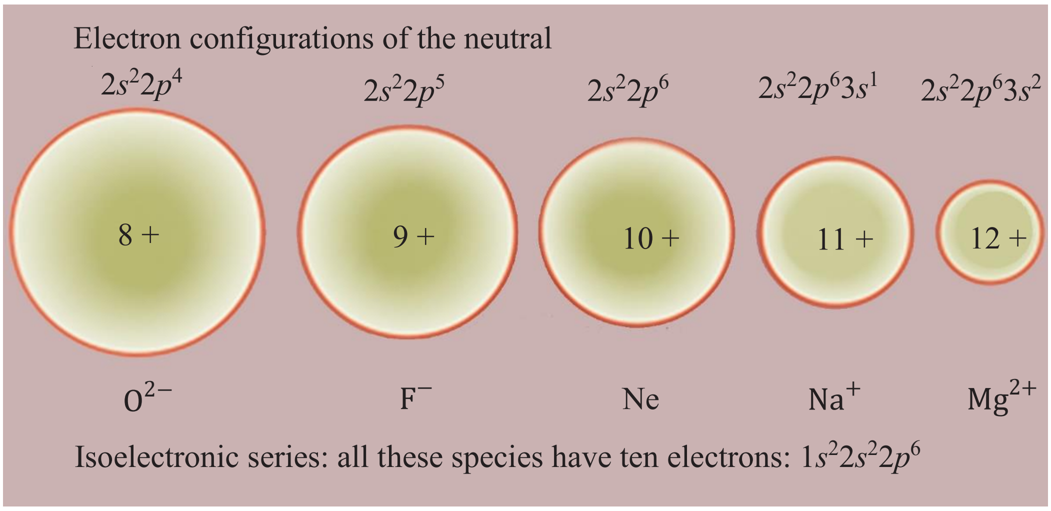


Figure 1.36 Radii in an isoelectronic series

1.6.2 Ionization energy

As explained at the beginning of section 1.3, the **ionization energy** of an atom or ion is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion.

In general, the first ionization energy (I_1) is the energy needed to remove the most loosely bound electron from a neutral gaseous atom. For example, the first ionization energy for the lithium atom is the energy required for the process; $Li(g) \longrightarrow Li^+(g) + e$

The second ionization energy (I_2) is the energy needed to remove the second loosely bound electron of an atom from a gaseous monovalent cation to form a gaseous divalent cation, and so forth, for successive removals of additional electrons. Thus, second ionization energy for the lithium atom is the energy associated with the process; $Li^+(g) \longrightarrow Li^{2+}(g) + e$

The ionization energies for a given element increase as successive electrons are removed; $I_1 < I_2 < I_3$, and so forth. This trend is because with each successive removal, an electron is being pulled away from an increasingly more positive ion, requiring increasingly more energy. Furthermore, a sharp increase in ionization energy occurs when an inner-shell electron is removed compared to the removal of outer shell electrons. This is because the electrons of the inner shell are closer to the nucleus and hence are attracted to it more strongly.

Frequently ionization energy is expressed in kJ mol^{-1} by considering one mole of atom/ion.

Periodic trends in the first ionization energies

The first ionization energy generally increases as we move across a period. The alkali metals show the lowest ionization energy in each period, and the noble gases show the highest.

Generally, the first ionization energy decreases as we move down any column in the periodic table. For example, the ionization energies of the group 1 elements (alkali metals) follow the following order

Li >Na > K > Rb > Cs > Fr.

The *s* and *p* block elements show a larger range of I_1 values than do the transition metal elements. Generally, the ionization energies of the transition metals increase slightly from left to right in a period.

The same factors that influence atomic size also influence ionization energies. The energy needed to remove an electron from the outermost occupied shell depends on both the effective nuclear charge and the average distance of the electron from the nucleus. Either increasing the effective nuclear charge or decreasing the distance from the nucleus increases the attraction between the electron and the nucleus. As this attraction increases, it becomes more difficult to remove the electron, and thus the ionization energy increases.

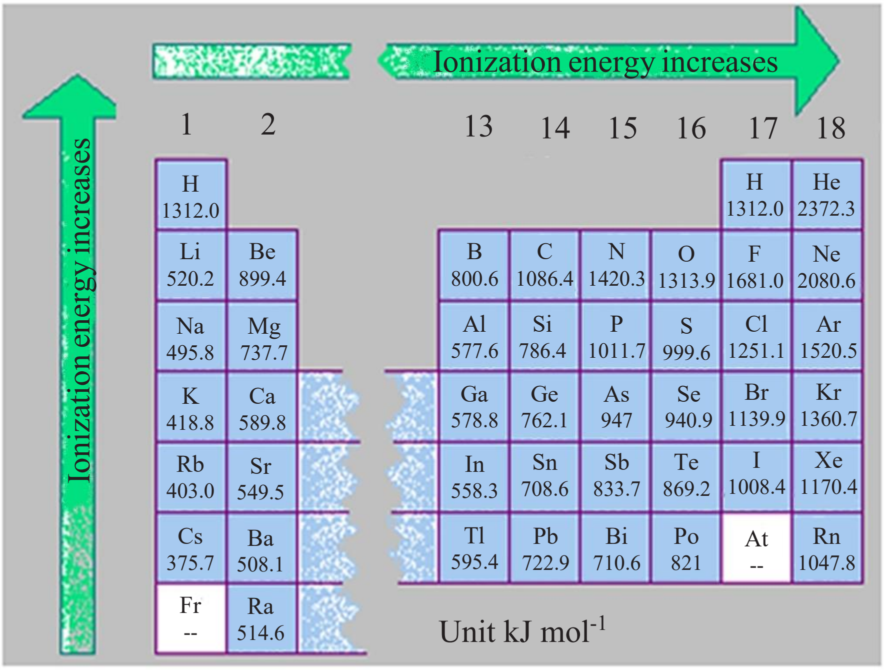


Figure 1.37 Trends in the first ionization energies in the periodic table

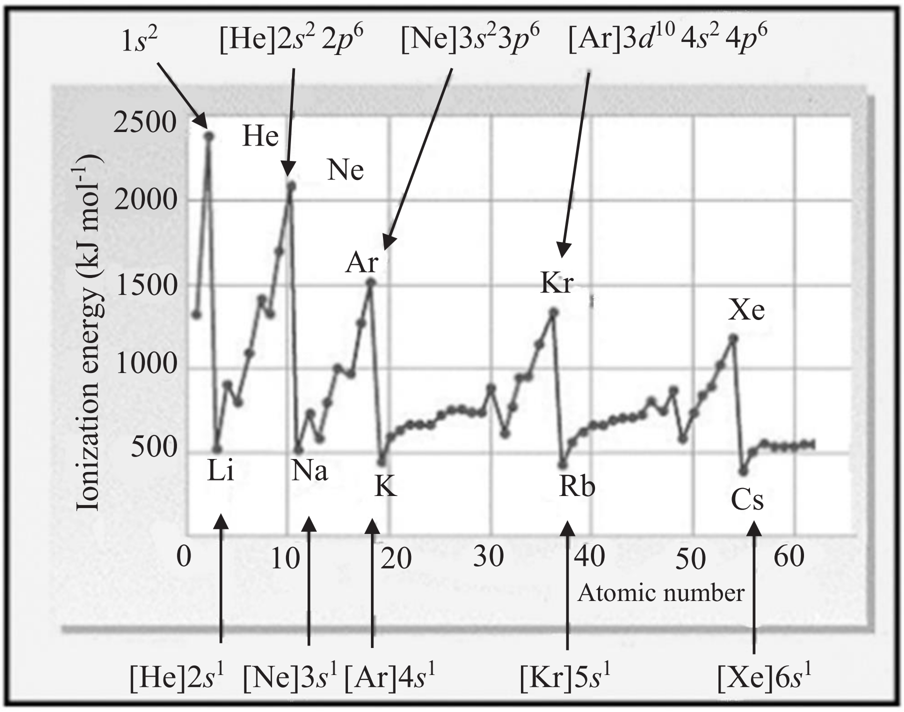


Figure 1.38 Variation of the first ionization energies with atomic number of elements

The irregularities in the trend of the first ionization energy in a given period are small but still readily explained. Removal of electrons from a completely filled subshell (e.g. group 2, group 12 and group 18) or a half filled subshell (e.g. group 7 and group 15), which are generally stable, will require more energy and thus the ionization energy will be higher than is expected from the common trend.

For example, in the second period neon with a completely filled shell has the highest first ionization energy. Beryllium with a complete *s* subshell shows the first ionization energy greater than expected and it even exceeds the I_1 of boron. Similarly, nitrogen with an exactly half filled *p* subshell shows an I_1 higher than what the common trend predicts.

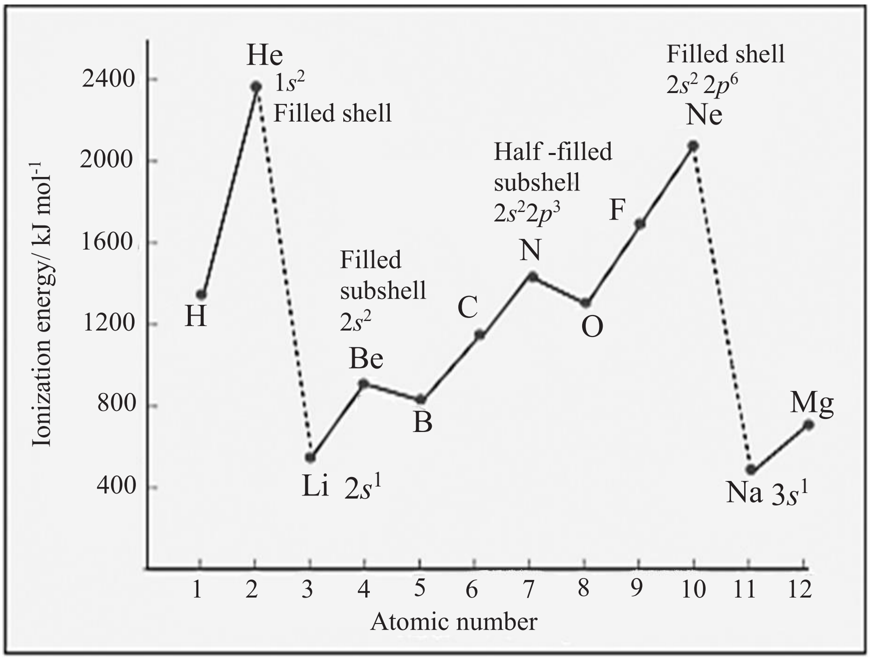


Figure 1.39 Variation of the first ionization energies along the first and second periods

1.6.3 Electron gain energy

The energy change that occurs when an electron is added to a gaseous atom is called the **electron gain energy.** For most atoms, energy is released when an electron is added.

For example, electron gain energy for the chlorine atom shown in the process below is -349 kJ mol^{-1}. The negative sign indicates that energy is released during the process.

$$Cl(g) + e \longrightarrow Cl^{-}(g) \qquad \Delta E_{EG} = -349 \text{ kJ mol}^{-1}$$

(ΔE_{EG} = Electron gain energy)

However, there are few atoms with positive electron gain energy. E.g.: Be, N. This is because they possess relatively stable configuration Be (s^2) and N (p^3) and as a result adding of an electron would be somewhat difficult with electron – electron repulsion is the dominating factor.

$$N(g) + e \longrightarrow N^{-}(g) \qquad \Delta E_{EG} = +134 \text{ kJ mol}^{-1}$$

$$Be(g) + e \longrightarrow Be^{-}(g) \qquad \Delta E_{EG} = +231 \text{ kJ mol}^{-1}$$

The electron gain energy become less positive across a period and more positive down a group.

As accepted internationally, ΔE_{EG} is used as a quantitative physical quantity to measure the attraction of an electron by an atom and related to electron affinity as follows.

$$\text{Electron gain energy } (\Delta E_{EG}) = - \text{ Electron affinity } (E_A)$$

Thus the electron affinity of an atom can be closely related to ΔE_{EG} and defined as the change in energy when the anion of the element loses an electron in the gaseous phase ($A^-(g) \longrightarrow A(g) + e$; $\Delta E = E_A$ which is equal in magnitude and opposite in sign to ΔE_{EG}) become more positive across a period and less positive down a group.

1.6.4 Electronegativity

It is defined as the ability of an atom in a molecule to attract electrons to itself. The greater an atom's electronegativity, the greater its ability to attract electrons.

The American chemist Linus Pauling (1901–1994) developed the first and most widely used electronegativity scale, which is known as the Pauling scale. Generally there is an increase in electronegativity from left to right across a period in the periodic table. With some exceptions (especially in the transition metals), electronegativity decreases with increasing atomic number in a group. Noble gases too have very small but non zero electronegativity according to the Pauling scale. In molecules, the difference between electronegativities of two atoms forming a bond will determine the ionic or covalent nature of the bond.

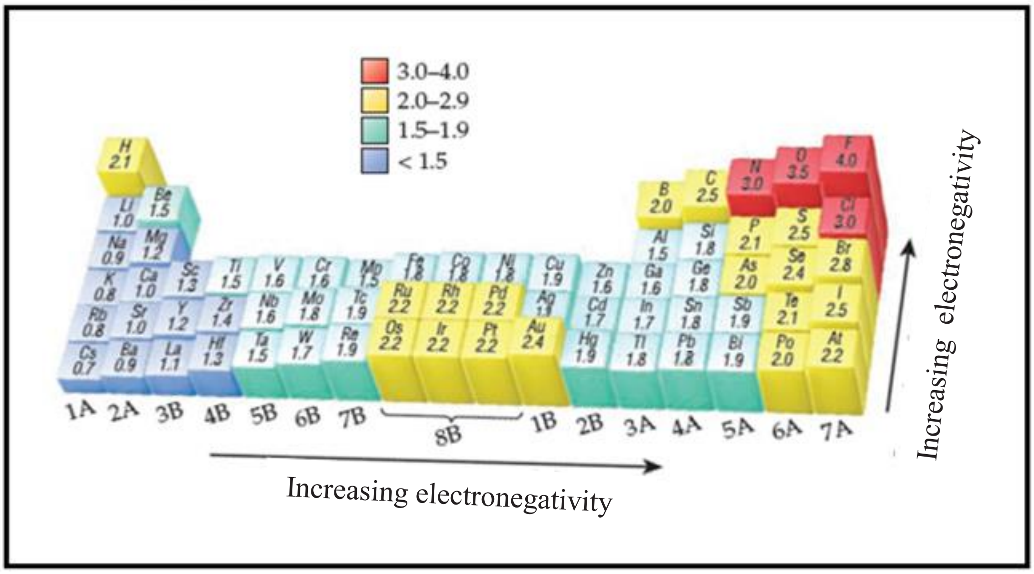
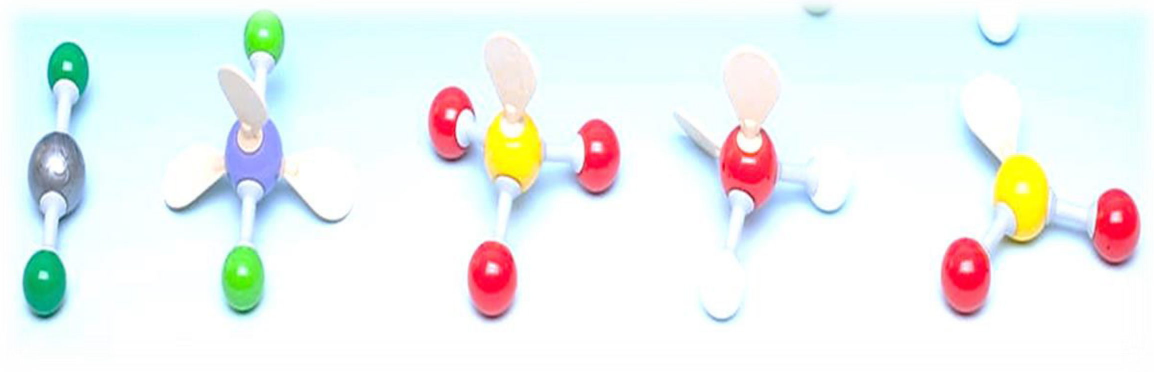


Figure 1.40 Pauling electronegativity values and the trends in the periodic table

Table 1.6 A summary of equations

Equation
Atomic number (Z) = Number of protons = Number of electrons in a atom
Mass number (A) = Number of protons (Z) + Number of neutrons
1 u or Da = 1.66054×10^{-24} g and 1 g = 6.02214×10^{23} u or Da
Atomic mass = Σ [(isotope mass) x (fractional isotope abundance)]
Speed of light = $c = \lambda\nu = 3.00 \times 10^{8}$ m s^{-1}
Energy of a photon = $E = h\nu$ constant h is called Planck constant and has a value of 6.626×10^{-34} J s



2. Structure and Bonding

Content

Introduction

Chemical bonds and structure of molecules are conceptual models based on the modern atomic model, in order to explain the physical and chemical properties of matter.

Many atoms do not have stable outermost valance shell configurations, therefore chemical bonds occur between atoms in order to achieve stability. The following table (Figure 2.1) explains how valence electrons participate in different types of chemical bonding using several acceptable models.

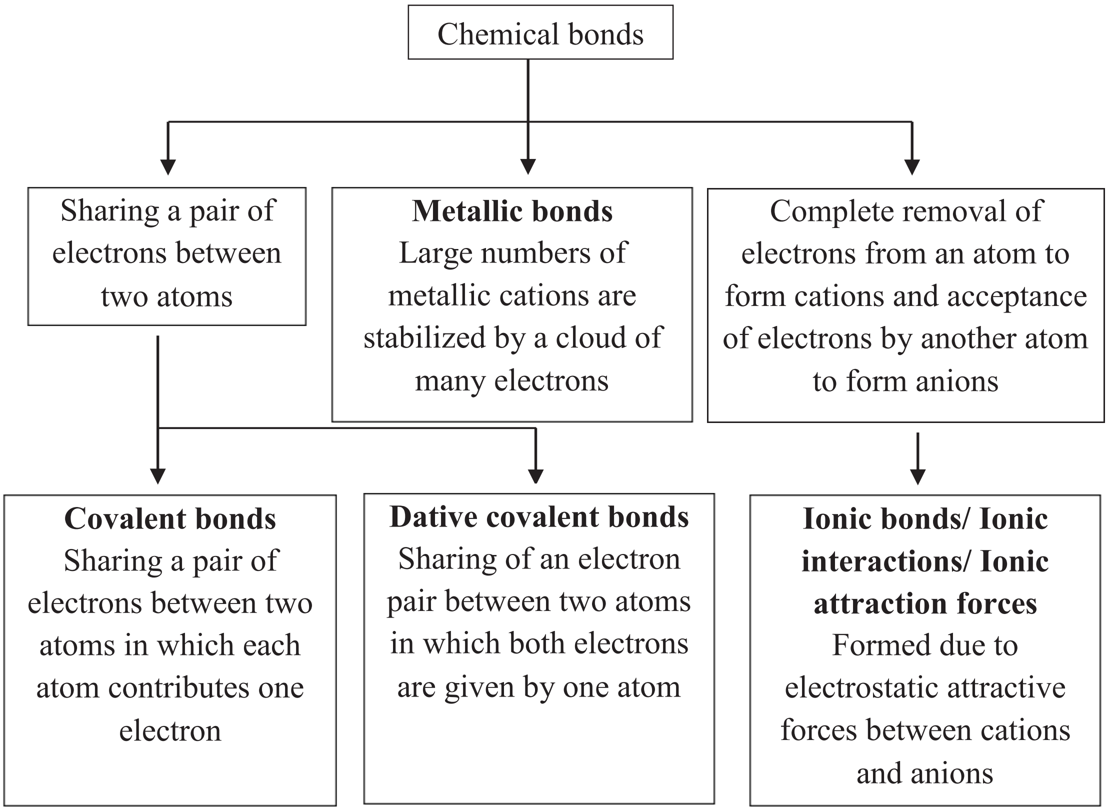


Figure 2.1 Types of chemical bonds

2.1 Covalent bonds

Covalent bonds are formed when a pair of electrons is shared between two atoms of the same element or different elements. The sharing pair of electrons contribute one electron from each atom to form the electron pair. Consequently, stable electron configurations are often achieved by both atoms in respect to the total number of electrons in the valence shells.

Kossel, Langmuir and Lewis stated that the filling of electrons into a valance shell up to the maximum value of 8 results a stable electron configuration, hence called 'octet' rule.

According to the current knowledge of electron configurations, the maximum number of valance electrons in 2*s* and 2*p* orbitals of elements in the second period (n=2) is 8.

Therefore, elements in the second period complete the octet when forming chemical bonds thereby achieving a greater stability. This is more likely for elements such as C, N, O and F which form chemical bonds to complete the octet.

The valance shell of elements in the third period (n=3) and subsequent periods consist of *d* sub energy level in addition to *s* and *p* sub energy levels. Therefore, when forming chemical bonds, there could be instances where the number of electrons in the valance shell may exceed eight. Examples of such molecules are SO_2 and SO_3. In such molecules the number of electrons in the valance shell of sulphur is greater than eight. The presence of *d* orbitals in the valence shell of the sulphur atom permits 18 electrons. Since, the *d* orbitals in the valance shell also participate in bonding, the number of valance electrons in the sulphur atom can exceed the octet. However, for such atoms, it is not always necessary for the *d* orbitals to participate in bonding. For example, in the H_2S molecule, the sulphur atom complete the octet without involving *d* orbitals.

There are other situations where atoms of some elements do not necessarily complete the octet. Elements like Be, B and Al form some electron deficient compounds such as $BeCl_2$, BH_3, BCl_3 and $AlCl_3$ are examples of such compounds with an incomplete valance shell. In the case of hydrogen atom where only 1*s* orbital is present, the stable electron configuration is achieved when the valance shell consists of two electrons. In all instances described above, the number of electrons in the valance shell after forming chemical bonds is an even number. However, this is not always true, as there are compounds such as NO and NO_2 each having an odd number of electrons even without completing the octet.

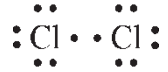
In order to understand the arrangement of bond pairs and lone pairs in molecules and ions, a “model” was introduced by Gilbert Lewis known as “Lewis dot structure”.

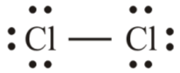
2.1.1 Lewis dot diagrams and Lewis dot-dash structures

The Lewis dot diagram is used to illustrate the atomic skeleton, nature of the bonding present (single, double and triple bond) and the distribution of the valance shell electrons around each atom of the given chemical formula. In Lewis dot-dash structure, a bonding electron pair is denoted by a short line drawn between the two atoms.

Chemical formula → Lewis dot diagram →Lewis dot-dash structure

Cl_2





The following factors need to be considered when drawing Lewis dot diagrams:

- Elements H and F are generally not considered as the central atom since these can form only single bonds. Atoms which are capable of forming multiple bonds are placed as the central atom.
- The element with the lower electronegativity is generally the central atom.

It is important to consider the following facts for molecules and ions with one central atom.

(i) Identification of the central atom and surrounding atoms.

(ii) Calculating the total number of electrons for a given chemical formula considering all electrons in the valence shell of each atom.
e.g.: In H_2O, oxygen atom contributes 6 electrons and one electron from each hydrogen atom (two electrons from two hydrogen atoms), which sum up to 8 when considering the total electron count (6 + 2 = 8) of the valence shells.

If it is a negatively charged ion, then negative charges should be counted as well.
e.g.: In the OH^- ion, contribution of electrons from oxygen atom is six and hydrogen atom one together with one electron due to negative charge of the ion adding up to eight as the total number of electrons (6 + 1 + 1 = 8).

If the ion is positively charged, then an equivalent number is deducted from the total valance electron count.
e.g.: In NH_4^+ ion, N atom contributes 5 valance electrons and four hydrogen atoms contribute 4 electrons. However, since it is a cation, then one electron (equivalent to number of positive charges) is deducted resulting 8 electrons in the valance shell of nitrogen atom (5 + 4 – 1 = 8).

(iii) A bond is denoted by a pair of dots between the central atom and a surrounding atom. Each surrounding atom is connected to the central atom with at least one bond.

(iv) Bonding electron pairs are denoted first as a pair of dots (Lewis dot diagram) or a short line (Lewis dot-dash diagram) drawn between central atom and each of surrounding atoms. Next, the remaining electrons are distributed, starting from the most electronegative atom, to complete the octet. Each electron pair is marked by pair of dots (lone pair electrons). If the electronegative atoms are surrounding atom, then lone pairs are marked on these surrounding atoms in order to complete the octet of each atom. CCl_4 is an example for this.

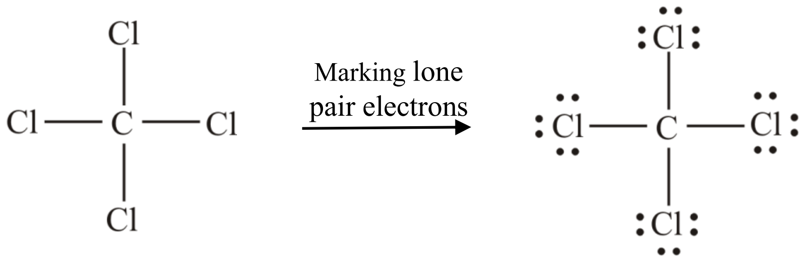


Figure 2.2 Lewis dot-dash structure of CCl_4

In the case of ammonia, surrounding atoms are hydrogen, remaining pair of electrons is marked on the nitrogen atom.

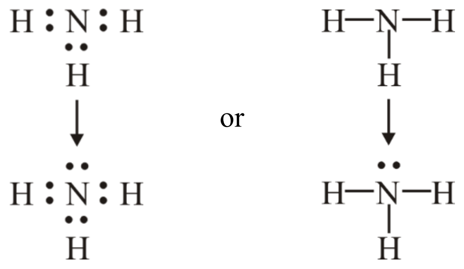


Figure 2.3 Lewis dot-dash structure of NH_3

In the Lewis dot diagrams bond electrons between two atoms can be represented as follows.

Single bond	⟶	M••L or M : L
Double bond	⟶	M :: L
Triple bond	⟶	M ⁝⁝ L
Dative bond from L to M	⟶	L : M

(v) If electron pairs are remaining after distributing electron pairs on the surrounding atoms (satisfying the octet rule), then left over pairs of electrons are marked on the central atom.

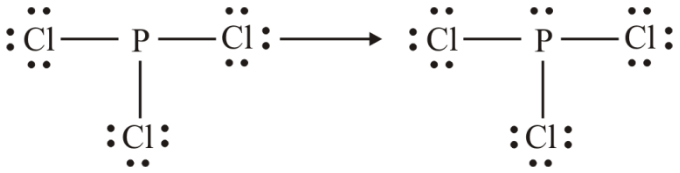
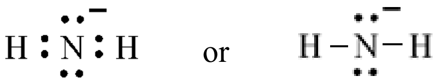


Figure 2.4 Lewis dot-dash structure of PCl_3

(vi) After distributing all the electron pairs, the number of electrons on each atom should be compared with the number of electrons in the non-bonded state of the atom (free atom) to assign the formal charge and then check completion of the octet. In the case of a bond, one electron is counted for each atom and if lone pairs are present, both electrons are counted to the particular atom. Priority is given for completion of the octet.

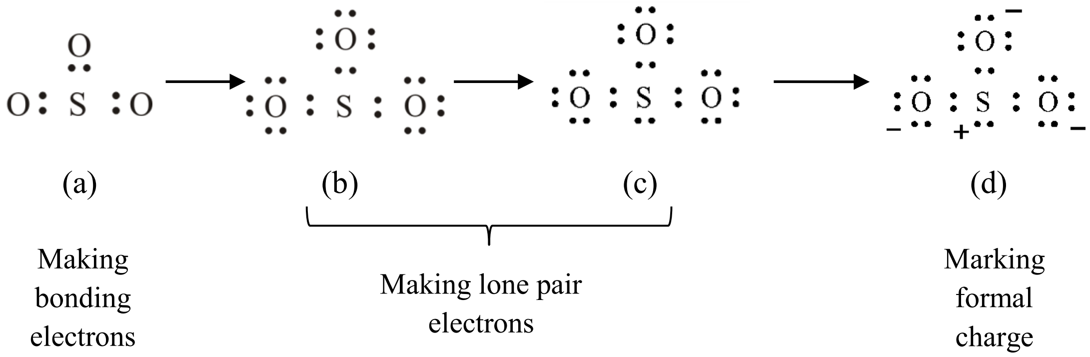
As an example, NH_2^- ion:



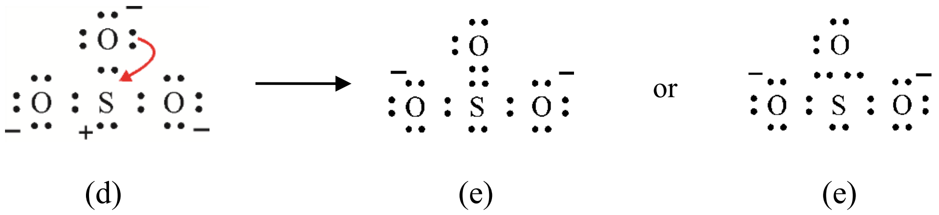
Here the total electron count on the nitrogen atom is 8. Though the nitrogen atom has contributed only 5 electrons, from the Lewis dot diagram, it appears as if the nitrogen has contributed 6 electrons. Since it has one extra electron, (-1) the charge is marked on the nitrogen atom as the formal charge.

(vii) Electron distribution shall be rearranged in order to minimize the formal charge on atoms and completion of octet by converting lone pair of electrons to bonding pairs of electrons.

If SO_3^{2-} ion is taken as an example, sulphur atom will contribute 6 electrons and each oxygen will contribute 6 electrons. Hence 18 electrons come from three oxygen atoms. Addition of two more electrons due to (-2) charge add up to 26 electrons (6 + 3(6) + 2 = 26) for the Lewis dot structure.



All atoms of Lewis dot structure (d) have satisfied the octet, but it is not stable, since it has maximum formal charge distribution. Hence the lone pair electrons are rearranged in order to obtain the stable Lewis structure having minimum formal charge distribution. The following sketch shows the way of rearrangement.



Finally, the Lewis dot dash structure for SO_3^{2-} is given as below.

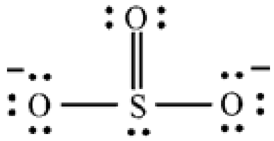
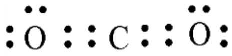
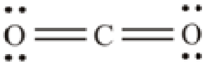
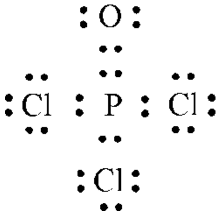
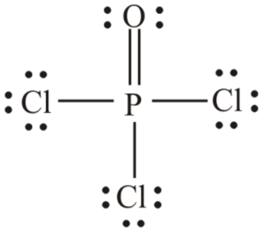
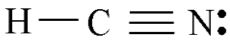
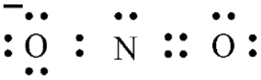
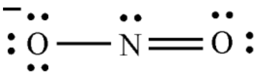
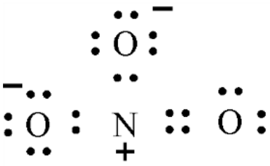
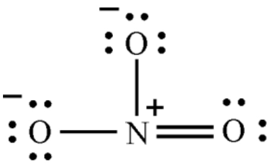
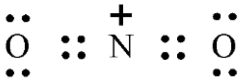
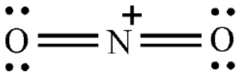


Figure 2.5 Lewis dot dash structure of SO_3^{2-}

Here, all oxygen atoms have completed octets. There are total of 10 electrons in the valance shell of sulphur atom which exceeds the octet. However, this is allowed due to the presence of empty *d* orbitals in addition to the *p* orbitals in the valance shell of the sulphur atom.

It is important to know the skeleton of atoms of a given chemical formula when multiple central atoms (e.g.: C_3H_6O) are present. Table 2.1 shows Lewis dot diagrams and Lewis dot-dash structures of selected molecules and ions.

Table 2.1 Lewis dot diagrams and Lewis dot dash structures of some selected molecules and ions

Formula	Number of valance shell electrons	Lewis dot diagram	Lewis dot dash structure
CO_2	16		
$POCl_3$	32		
HCN	10		
NO_2^-	18		
NO_3^-	24		
NO_2^+	16		

Example 2.1

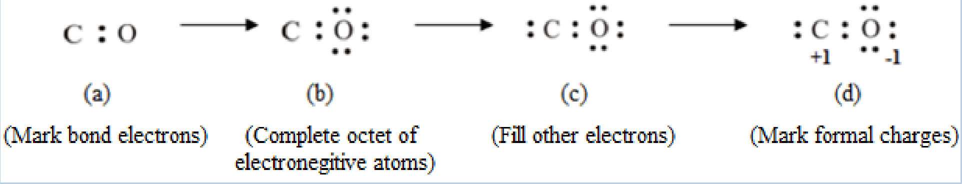
Draw the Lewis dot diagram and the Lewis structure of carbon monoxide (CO)

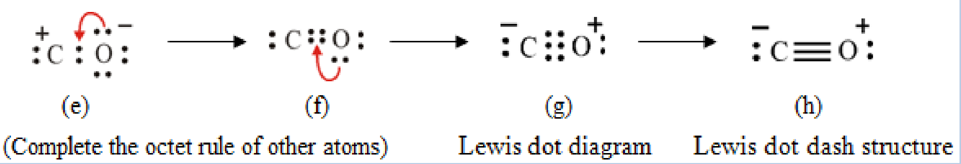
Answer

Valance electrons from C atom = 4*e*
Valance electrons from O atom = 6*e*
Total number of valance electrons = 4*e* + 6*e* = 10*e*

After marking the bonding electron pair, the number of remaining electrons is eight. After distributing the electron pairs around the more electronegative oxygen atom completing octet, another pair is left. This lone pair of electrons is marked on the carbon atom.

The initial electron distribution is illustrated below. However, the octet is not completed for the carbon atom. Therefore, rearrangement of a lone pair of electrons on the oxygen atom as shown by curved arrows in (e) and (f) is done in order to complete the octet on the C atom whilst attempting to minimize the formal charge result in structure (g). Therefore, the structure (g) is considered to be the Lewis dot diagram and (h) illustrates the Lewis structure of CO. Notice that there is a positive charge marked on the more electronegative oxygen atom. Although positive charge is on the more electronegative oxygen atom, it is very unlikely and in this case it is accepted since higher priority is given to completion of octet where possible. This is the fundamental principal of the octet rule. This example shows that octet rule is more powerful than the charge criteria.



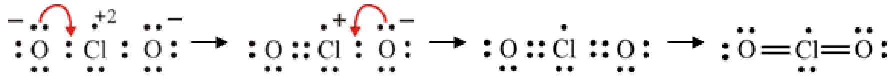


Example 2.2

Draw the Lewis dot diagram and the Lewis dot dash structure for ClO_2.

Answer

This is an example for a species with an odd number of electrons. The total number of the valance electrons is 19 in ClO_2 ($7e + 2(6e) = 19e$). The following illustrates the initial distribution of the electrons and the final Lewis dot diagram and Lewis dot-dash structure of ClO_2.



(a) Maximum charge distribution (unstable)

(b)

(c) Lewis dot diagram

(d) Lewis dot-dash diagram

2.2 Dative covalent bonds

In a molecule or ion, dative bonds are formed when atoms with empty orbitals interact with atoms with a lone pair of electrons. In certain cases when the free atom of the element has less than four valance electrons (as in Be, B), the number of covalent bonds that the particular atom can form is less than four. This results in incomplete octet with lower stability. Therefore, such electron deficient central atoms preferably react with the atom having lone pairs which can donate an electron pair to the central atom to complete the octet. The reaction of BH_3 with CO to produce borane carbonyl and the reaction with CN^- to produce cyanoborohydride are example with such dative bonds. Furthermore, reaction of NH_3 with BF_3 to form a dative covalent bond between B and N is another example. The dative bond is formed when the empty orbitals in B overlaps with the orbital having the lone pair in the nitrogen atom. In this case a central atom cannot be chosen precisely. Since the lone pair on the nitrogen atom is donating the electron pair to B, the bond can be denoted by an arrow. The arrow head is pointed to the electron deficient atom. This can be illustrated using formal charges as well as shown below.

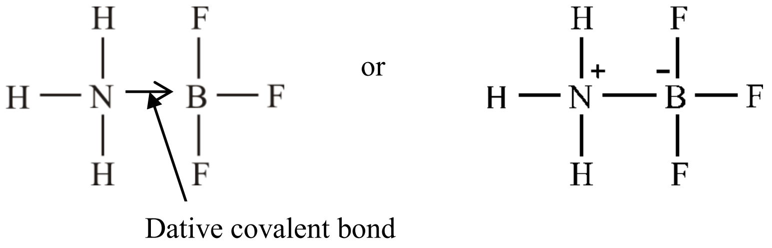


Figure 2.6 Dative covalent bond (H_3N-BF_3)

Dative covalent bonds are also formed when metal ions or some metal atoms react with molecules or ions having lone pairs (H_2O, NH_3, CO molecules and CN^- ions) in order to form complexes. The following illustrates the formation of a complex ion when Cu^{2+} is reacted with four NH_3 molecules to form dative covalent bonds.

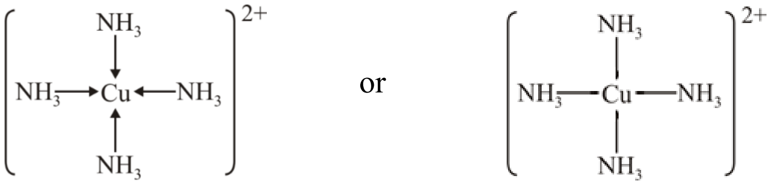


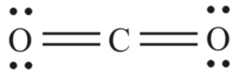
Figure 2.7 Dative covalent bond in $[Cu(NH_3)_4]^{2+}$ complex

2.3 Valance Shell Electron Pair Repulsion theory (VSEPR theory)

Ronald Gillespie and **Ronald Sydney Nyholm** suggested that electron pairs surrounding the central atoms of a given molecule or ion are arranged in a way to keep maximum spatial distance apart from each other. Gillespie has explained the shapes of molecules when the central atom is a main group element while Nyholm discussed the shapes of molecules with transition elements as the central atom. By 1963, Gillespie introduced VSEPR theory for finding shape of molecules or ions.

There are mainly two kinds of electron pairs surrounding the central atom. The first type is the bonding electron pair which is held between two nuclei, by attractive forces. The second type is electron pairs not participating in the bonding known as lone pairs. Since lone pair of electrons are under the influence of a single nucleus, the electron cloud occupies a relatively larger spatial volume. Both bonding and lone pairs of electrons of an atom act as repulsive unit to keep further away from each other. If multiple bonds (double or triple bonds) are present between atoms, each multiple bond is considered as a single repulsive unit.

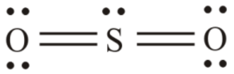
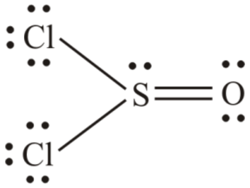
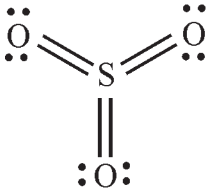
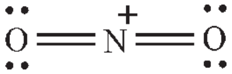
There are three different types of bonding when the number of covalent bonds formed between the central atom and a surrounding atom is considered. These are single bonds, double bonds and triple bonds where double and triple bonds represent multiple bonds. For example, in the CO_2 molecule, double bonds are present between the central carbon atom and the surrounding oxygen atoms. In the HCN molecule a triple bond is present between the central C atom and N atom as shown below. Each single, double, triple bond or lone pair is considered as one repulsive unit or a VSEPR unit.



The three pairs of electrons in the triple bond of HCN molecule is considered as a single repulsive unit. This is because the three electron pairs are located between C and N atoms preventing independent movement of three electron pairs from each other, thus the triple bond can be considered as a single repulsive unit or single VSEPR unit.

The number of repulsive units surrounding the central atom can be clearly identified using the Lewis structure. Table 2.2 gives few examples on how to identify the number of electron pairs surrounding the central atom and the VSEPR units around the central atom.

Table 2.2 Lewis dot dash structure, electron pairs and VSEPR units around the central atom of selected molecules and ions

Lewis dot dash structure	Electron pairs around the central atom	Repulsion (VSEPR) units around the central atom
	5	3
	5	4
	6	3
 $H-C\equiv N:$	4	2
	4	2

According to the VSEPR theory, molecules/ ions achieve stability by maintaining a maximum distance between repulsion units, to get the minimum repulsion force between them.

A lone pair of electrons occupies greater spatial distribution (spatial volume) compared to a bonding electron pair. Hence, it is considered that the repulsion between two lone pairs of electrons (lone pair ↔ lone pair) is higher than the repulsion between two pairs of bonding electrons (bonding pair ↔ bonding pair). This results in intermediate repulsive force for interaction between lone pair and bonding pair (lone pair ↔ bonding pair) of electrons.

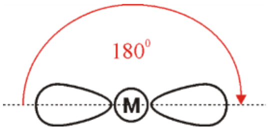
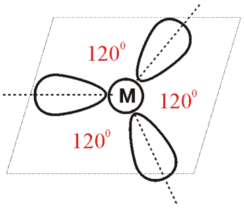
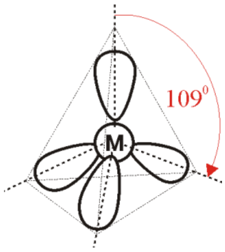
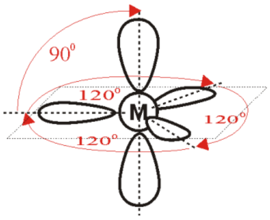
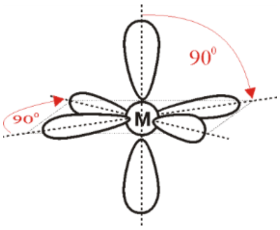
Repulsion between two bonding electron pairs 〈 Repulsion between bonding electron pair and lone pair of electrons 〈 Repulsion between two lone pairs of electrons

Figure 2.8 Comparison of repulsive forces between bonding and lone pairs of electrons

The distribution of repulsive units (bonding or lone pairs) in space around the central atom is called "electron pair geometry". When stating the geometry of a particular molecule or ion it is necessary to report bonding angles. Table 2.3 summarizes the different electron pair geometries depending on how the repulsive units are distributed in 3D space. When reporting the shape of a molecule/ ion, it is not mandatory to report the bond angles. However, when stating the geometry of a molecule/ ion it is necessary to mention the bond angles. Therefore, electron pair geometry, shape and geometry of a molecule/ ion are considered as three independent parameters. Geometry of a molecule carries the shape and the angle.

Geometry of molecule associated with the bond angle in Lewis structure representing the shape. Shape of the molecule represents the Lewis structure in order to illustrate the shape without the bond angles. Electron pair geometry represents geometry of repulsive units.

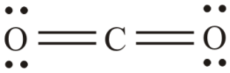
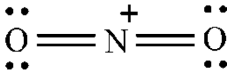
Table 2.3 Electron pair geometry of repulsion units

Repulsion units	Electron pair geometry	
2		Linear
3		Trigonal planar
4		Tetrahedral
5		Trigonal bipyramidal Three repulsive units are on the same plane with 120° angle. The other two repulsive units lie perpendicular to this plane.
6		Octahedral Four repulsive units are in one plane with 90° angle between them. The other two repulsive units lie perpendicular to this plane.

Linear electron pair geometry

Here two VSEPR units are present around the central atom. Consider the situation where the central atom is bonded to two other atoms. The shape of such a species is linear. Table 2.4 provides more examples for linear molecules.

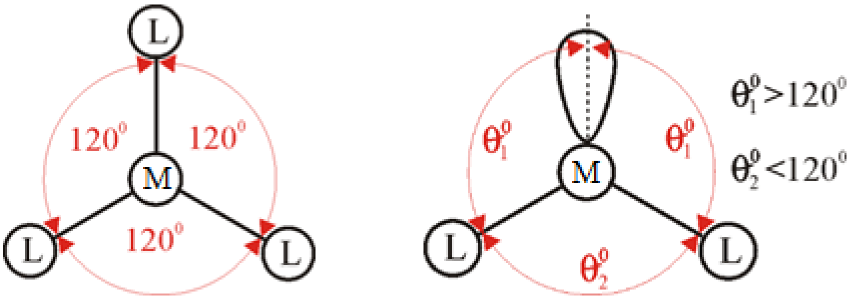
Table 2.4 Molecules/ ions with two repulsion units

Chemical Formula	Lewis dot dash structure	Shape
CO_2	 $\ddot{\underset{..}{O}}=C=\ddot{\underset{..}{O}}$	Linear
HCN	$H-C\equiv N:$	Linear
NO_2^+	 $\ddot{\underset{..}{O}}=\overset{+}{N}=\ddot{\underset{..}{O}}$	Linear

Trigonal planar electron pair geometry

Two types of electron pair geometries can be identified when electron pairs are divided as bonding and lone pairs.

- All three repulsive (VSEPR) units are bonding
- Two repulsive (VSEPR) units are bonding and the other is a lone pair



(a)

All three repulsive
units are bonding

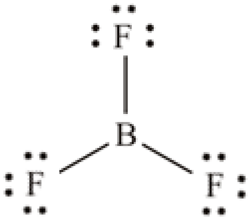
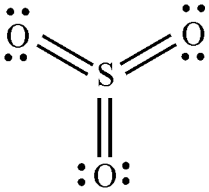
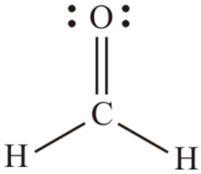
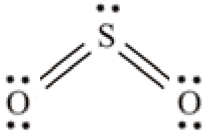
(b)

Two repulsive units are bonding
while the other is a lone pair

Figure 2.9 Trigonal planar electron pair geometry

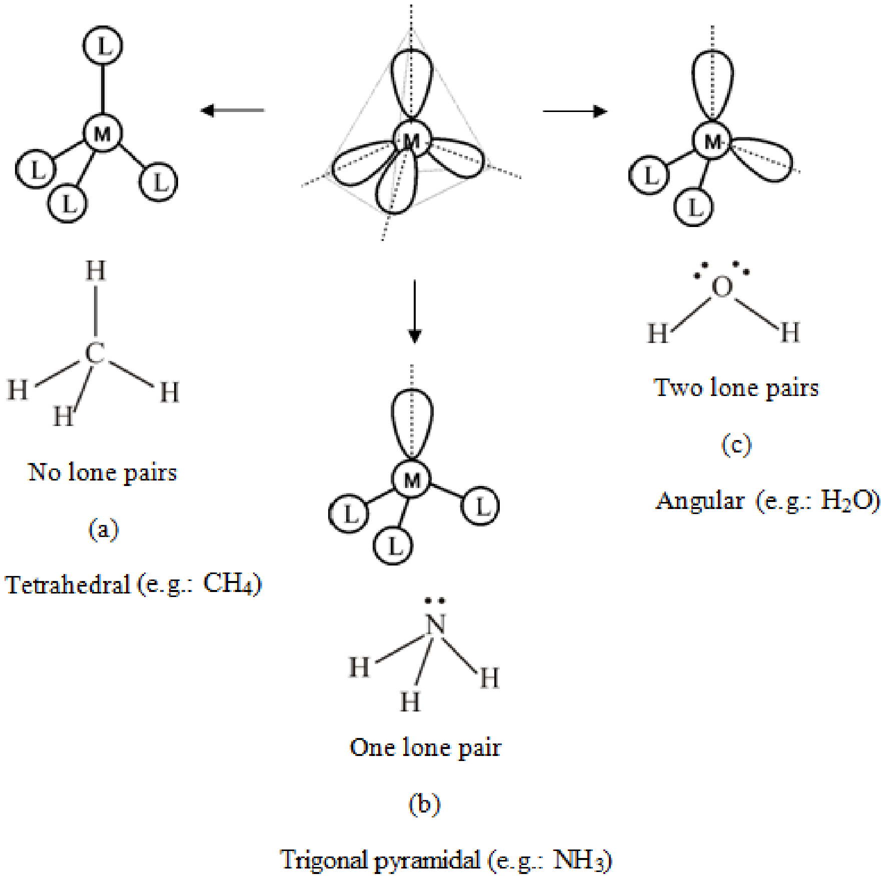
In Table 2.5 the central atoms in BF_3, SO_3 and HCHO do not contain lone pairs of electrons resulting in trigonal planar shape. However, in SO_2 the presence of a lone pair of electron on ‘S’ atom results in an angular shape.

Table 2.5 Molecules/ ions with three repulsive units

Chemical formula	**Lewis dot dash structure showing the shape**	**Shape**
BF_3		Trigonal planar
SO_3		Trigonal planar
HCHO		Trigonal planar
SO_2		Angular

Tetrahedral electron pair geometry

There are three possibilities when four repulsive units (VSEPR pairs) are considered separately as bonding and lone pairs of electrons. Figure 2.10 illustrates these briefly.



No lone pairs

(a)

Tetrahedral (e.g.: CH_4)

One lone pair

(b)

Trigonal pyramidal (e.g.: NH_3)

Two lone pairs

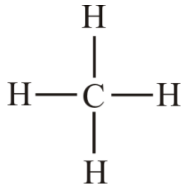
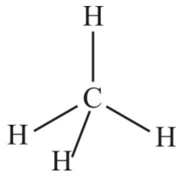
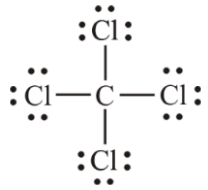
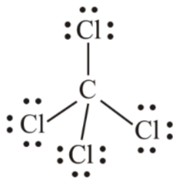
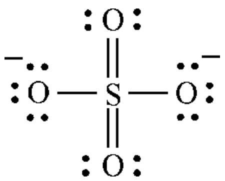
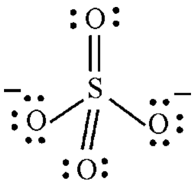
(c)

Angular (e.g.: H_2O)

Figure 2.10 Tetrahedral electron pair geometry

Table 2.6 provides more examples for molecules with tetrahedral geometry.

Table 2.6 Examples for tetrahedral molecules/ ions

Molecule	Lewis dot dash structure	Shape
CH_4		
CCl_4		
SO_4^{2-}		

Trigonal bipyramidal electron pair geometry

Here there are five VSEPR units/ repulsive units around the central atom. These are arranged in four different types when bonding and lone pairs are considered.

- All five repulsive units around the central atom are bonding electron pairs. e.g.: PCl_5. The shape of PCl_5 is given below.

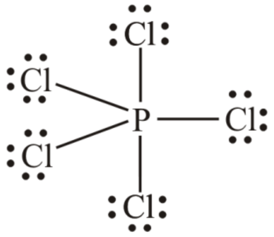
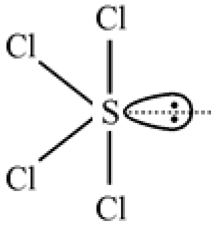
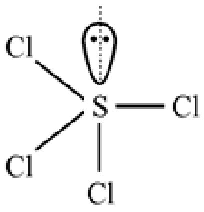


Figure 2.11 Electron pair geometry of PCl_5

- Four repulsive units are bonding while the remaining electron pair is a lone pair of electrons. e.g.: SCl_4. There are two possible positions for the lone pair at the S atom of the SCl_4 molecule as shown below.



(a)



(b)

The structure (a) has less repulsion than structure (b). Therefore structure (a) is more stable than structure (b) as per the VESPER model.

The theoretical shapes of molecules with four bonding pairs and a lone pair of electrons is called '*see-saw*'(distorted see-saw/ irregular see-saw) shape. The imaginary axis for lone pair of electrons and the two S-Cl bonds are in one plane while the remaining two S – Cl bonds are placed perpendicular to this plane.

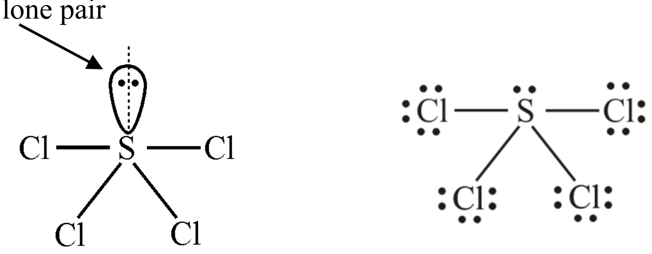

Imaginary axis for lone pair

Figure 2.12 Electron pair geometry of SCl_4

However, the repulsion of the lone pair on S-Cl bonding electrons slightly distorts the regular see-saw shape. Hence the shape of SCl_4 is called distorted tetrahedral/ distorted see-saw/ irregular see-saw.

- Three repulsive units are bonding while the other two repulsive units are lone pair of electrons. e.g.: ICl_3

  In the case of ICl_3, the most stable shape with minimum repulsive forces between VSEPR units is given below. The sketch of ICl_3 results in 'T' shape (distorted T' shape/ irregular T' shape) when the surrounding Cl atoms are considered. Therefore, it is called a 'T' shape molecule. Here, two lone pairs and one I–Cl bond are in one plane while the remaining two I – Cl bonds lie perpendicular to this plane.

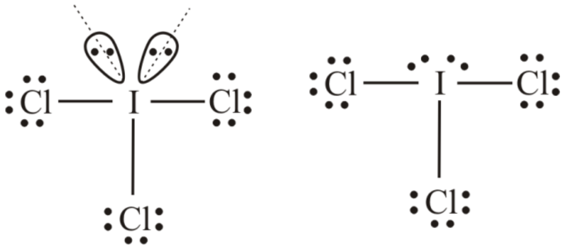


Figure 2.13 Electron pair geometry of ICl_3

- Two repulsive units are bonding while the remaining three units are lone pairs of electrons. e.g.: XeF_2

  In this type, all atoms are in line thus the molecule has 'linear' shape. The following Lewis structure illustrates the linear shape of the XeF_2 molecule. Note that all three lone pairs are in one plane which is perpendicular to the F-Xe-F axis.

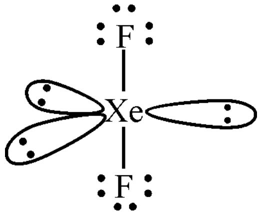
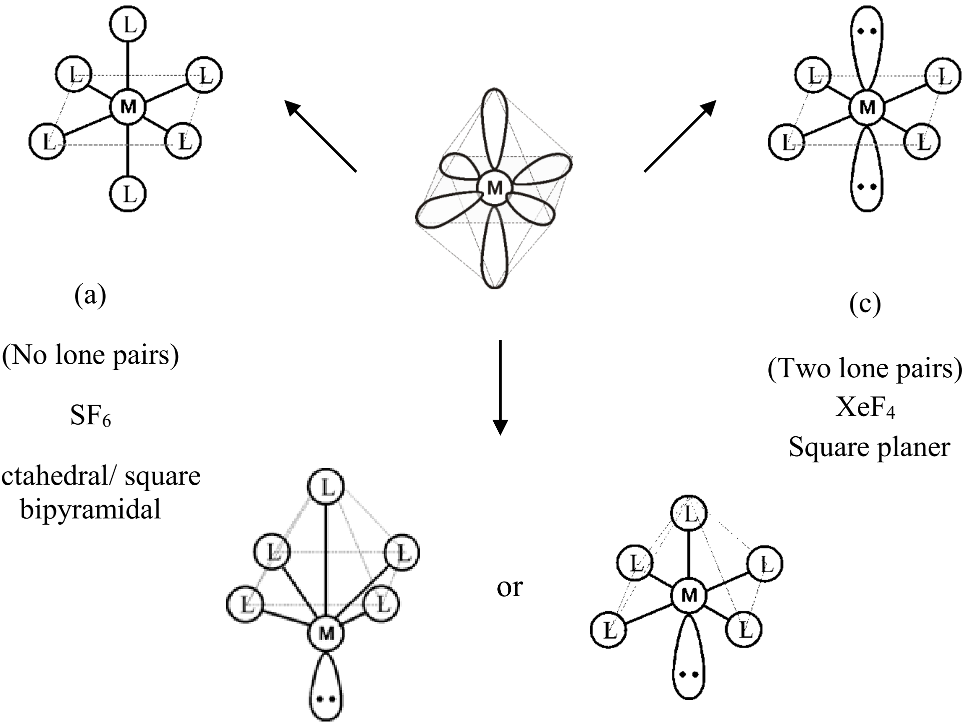


Figure 2.14 Electron pair geometry of XeF_2

Octahedral electron pair geometry

In this geometry, the angle between each two adjacent repulsion units is 90°. The following Figure 2.15 illustrates the octahedral electron pair geometry of such molecules having three possible shapes. Four repulsive units are in one plane while remaining two units lie perpendicular to this plane.



(a)

(No lone pairs)

SF_6

Octahedral/ square bipyramidal

(c)

(Two lone pairs)
XeF_4
Square planer

or

(b)

(One lone pair)

$XeOF_4$

Square pyramidal/ distorted square pyramidal

Figure 2.15 Octahedral electron pair geometry

First consider the situation where all the repulsive units are bonding (e.g.: SF_6). When the substituted atoms surrounding the center are connected with imaginary dotted lines, an octahedron with eight planes is created. Therefore, shape of such molecules are called ‘octahedral’.

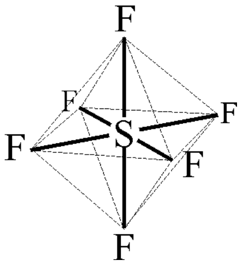


Figure 2.16 Electron pair geometry of SF_6

Next, consider the molecules with five repulsive units in the form of bonding pairs and one repulsive unit in the form of lone pair of electrons ($XeOF_4$). The electron pair geometry of $XeOF_4$ is octahedral. When the surrounding atoms of $XeOF_4$ are connected with imaginary lines pyramid, with a square shaped base is created. Therefore the theoretical shape is 'square pyramidal'. The repulsion between the lone pair on the Xe atom and Xe - F bond has changed the regular shape of the molecule. Therefore the shape of $XeOF_4$ is called distorted square pyramidal.

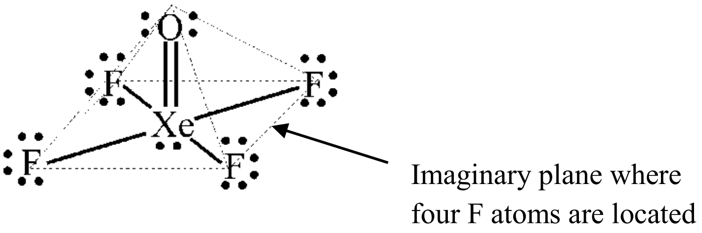


Figure 2.17 Electron pair geometry of $XeOF_4$

When a molecule consists of four repulsive units in the form of bonding electron pairs and two repulsive units in the form of lone pairs, then the shape is called 'square planar' as illustrated by the XeF_4 molecule.

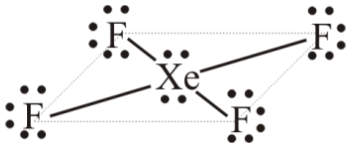


Figure 2.18 Electron pair geometry of XeF_4

For XeF_4 molecule,
Electron pair geometry = octahedral
Shape = square planar
Geometry = square planar
In general use, when the word geometry is used, it is not necessary to state the angle(s).

Example 2.3

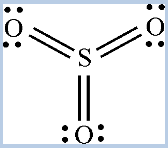
Draw the Lewis dot-dash structures of the following molecules and predict their shapes

(i) SO_3 (ii) CH_2Cl_2

Answer

(i) SO_3

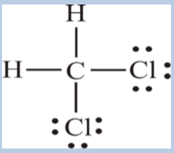
Electrons from S atom = 6
Electrons from 3 O atoms = 3(6e) =18
Total electrons =24



Lewis dot-dash structure

Distribute 24 electrons in order to represent the Lewis dot-dash structure
Repulsive units around the central atom = 3
Lone pairs on "S" atom = 0
Shape = trigonal planar

(ii) CH_2Cl_2
Electrons from C atom = 4
Electrons from 2H atoms = 2(1e) = 2
Electrons from 2 Cl atoms = 2(7e) =14


Lewis dot-dash structure

Distribute 14 electrons in order to represent the Lewis dot-dash structure
Total electrons =20
Repulsive units around the central atom = 4
Lone pairs on "C" atom = 0
Shape = tetrahedral

2.3.1 Hybridization of atomic orbitals

The conceptual model of hybridization can be explained qualitatively using a carbon atom. The valance shell of carbon atom in the ground state consists of one electron pair and two unpaired electrons ($2s^2\ 2p^2$). However, in order to form four covalent bonds, the presence of four orbitals with an unpaired electron in each is necessary. Therefore, electrons in the ground state rearrange to form an excited state with four unpaired electrons.

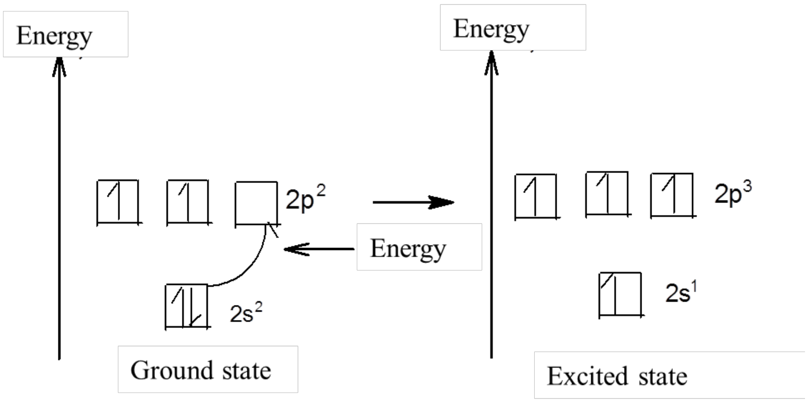


Figure 2.19 Energy level diagram of carbon atom in ground and excited states

Here, one of the 2*s* electrons in the valance shell of carbon atom absorbs energy and gets promoted to an empty 2*p* orbital as shown in Figure 2.19. This transition is feasible as the energy gap between 2*s* and 2*p* orbitals is relatively low. Now the atom is in the excited state with unpaired electrons in 2*s* and 2*p* energy levels as illustrated above. Though there are four unpaired electrons available for bonding, these electrons are in two different energy levels and in two different shapes of atomic orbitals (spherical *s* orbital and dumbbell shaped *p* orbitals). At this state, if C atom forms 4 bonds with 4 H atoms to form CH_4, the type of bonding consists of one C-H bond formed between 2s orbital of carbon with the *s* orbital of the hydrogen and three C-H bonds formed with overlap of 2*p* orbitals from carbon and *s* orbitals from hydrogen. Then the CH_4 molecule is expected to have two different types of bonds with different bond angles.

However, all four C-H bonds and bond angle in CH_4 are identical. Therefore, a valid assumption is mixing of these 2*s and* 2*p* orbitals to form four atomic orbitals with same energy and same shape when forming the C-H bonds. This concept is called '**hybridization**'. It is not possible to depict a valid structure for the CH_4 molecule without the concept of hybridization, for the formation of identical four C-H bonds by 2*s* and 2*p* orbitals of the C atom, if considered separately. It is also not possible to explain the bond angle of HCH as 109.5°.

The following facts are important for understanding the model of hybridization of atomic orbitals.

(i) The concept of hybridization cannot be used for an atom alone, but it is used to describe the bonding formed by a particular atom in a molecule.

(ii) There should be a minimum of two atomic orbitals with different shapes and energy mixed to form hybrid orbitals.

e.g.: A *s* orbital can hybridize with one or more of *p* orbitals (up to 3) of the same atom. These hybrid orbitals do not have clear identity; hence, has a shape different from original orbitals.

(iii) The number of hybrid orbitals formed is equal to the number of atomic orbitals that participate in the hybridization. Though atomic orbitals at different energy levels are mixed, the resulting hybrid orbitals will be at the same energy level. These hybrid orbitals differ only in the orientation in 3D space but are identical in shape and energy when the atomic orbitals are *s* and *p*.

(iv) A hybrid orbital in a particular atom can overlap (linear overlap) with a hybrid orbital or un-hybridized atomic orbital of another atom to form bonds.

Note that hybridization is not a true physical process and is an imaginary process presented as a concept. According to this imaginary process, there are three different kinds of hybridizations possible with a carbon atom in the excited state. A summary is given below.

(i) Mixing of the *s* orbital with three *p* orbitals to form four ***sp***^{3} **hybridized** orbitals. (**tetrahedral** geometry)

(ii) Mixing of the *s* orbital with two *p* orbitals to form three ***sp***^{2} **hybridized** orbitals. (**trigonal planar** geometry)

(iii) Mixing of the *s* orbital with one *p* orbital to form two ***sp*** **hybridized** orbitals. (**linear** geometry)

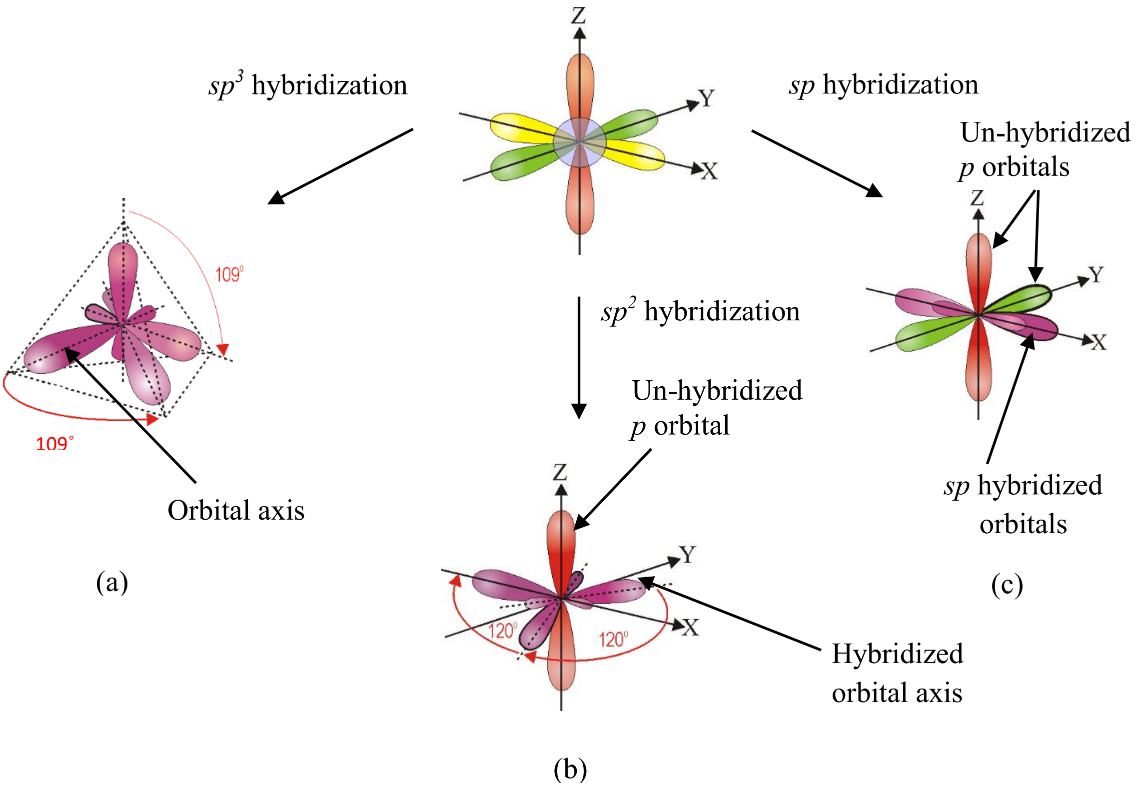
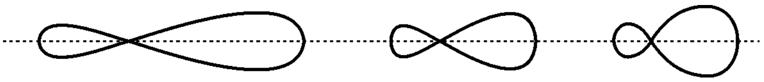


Figure 2.20 sp^3, sp^2 and sp hybridization

The following diagrams compare the sp^3, sp^2 and sp hybridized orbitals in terms of shape and percentage of s and p character.



	sp^3 hybridized orbital	**sp^2 hybridized orbital**	**sp hybridized orbital**
s character	25%	33.3%	50%
p character	75%	66.3%	50%

Figure 2.21 Comparison of sp^3, sp^2 and sp hybridized orbitals comparison

(a) **Orientation of sp^3 hybrid orbitals**: The orbitals are located inside a tetrahedron with 109°28′ angle among orbitals.

(b) **Orientation of sp^2 hybrid orbitals**: The axis of all three hybrid orbitals is in one plane with 120° angle among hybrid orbitals. One of the p orbitals does not participate in hybridization and lies perpendicular to this plane.

(c) **Orientation of sp hybrid orbitals**: There is a180° angle between axes of hybrid orbitals, so both axes are in a straight line. The axes of two p orbitals which do not participate in hybridization lie perpendicular to each other as well perpendicular to the axis of sp hybrid orbital.

2.3.2 Formation of double and triple bonds

If there are two bonds between two atoms, one bond is called a ‘σ bond’ while the other bond is called a‘π bond’. Consider the formation of a double bond between two carbon atoms in the ethene molecule (CH_2CH_2). Linear overlap of two hybridized orbitals form a σ bond and the π bond is formed with lateral overlap of the unhybridized *p* orbitals in each carbon atom.

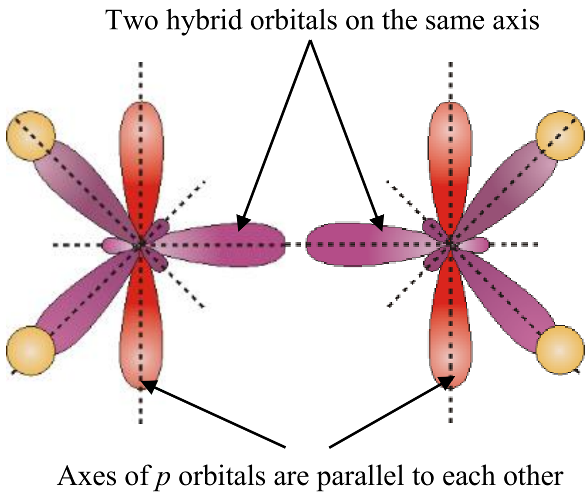


Figure 2.22 sp^2 hybridized orbitals and *p* orbital orientation in C_2H_4

Since the axes of two *p* orbitals are parallel to each other, *lateral overlap* is observed between these dumbbell shaped *p* orbitals. If the axes of *p* orbitals are not parallel to each other, there is less chance for these orbitals to overlap. In the above diagram, the axes of two hybrid orbitals are aligned on a straight line, thus the overlap between these orbitals is considered a *linear overlap*.

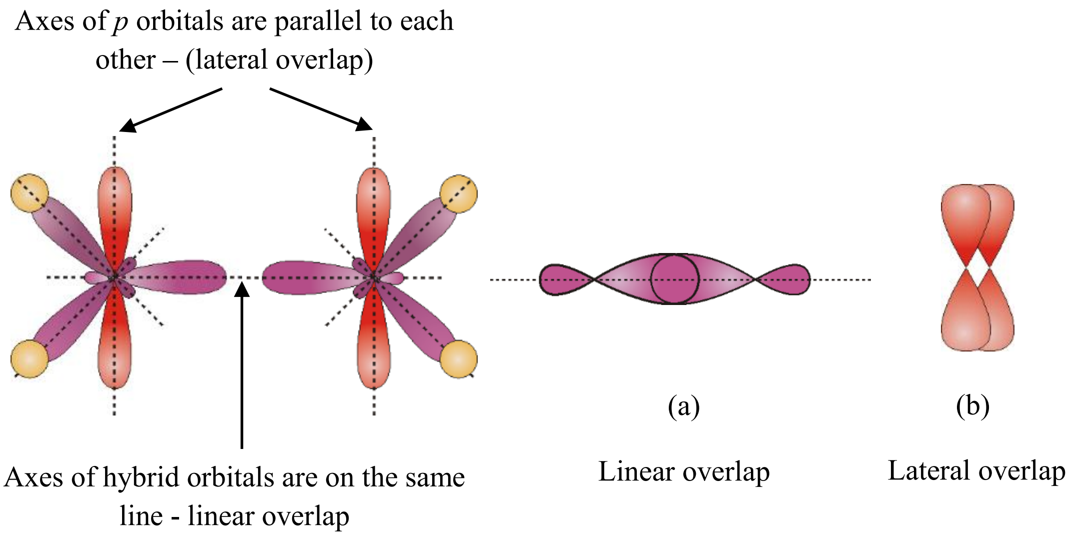


Figure 2.23 Linear and lateral overlap of orbitals in C_2H_4

The Figure 2.24 shows the general idea of the proposed model for the arrangement of bonding orbitals in double bond.

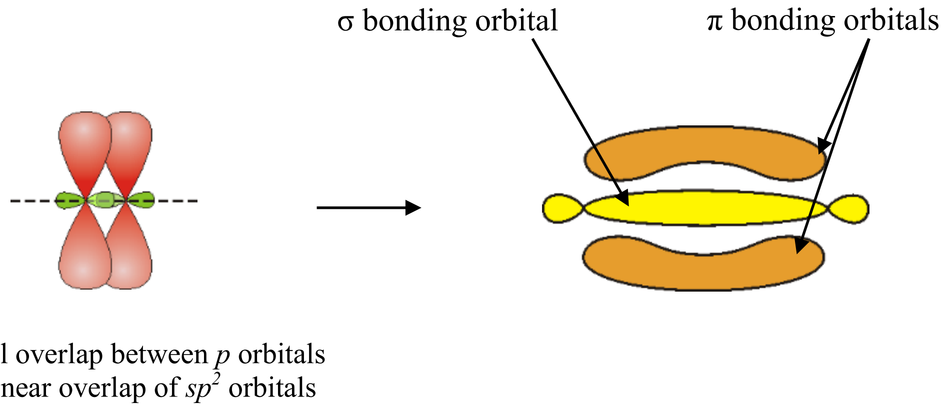
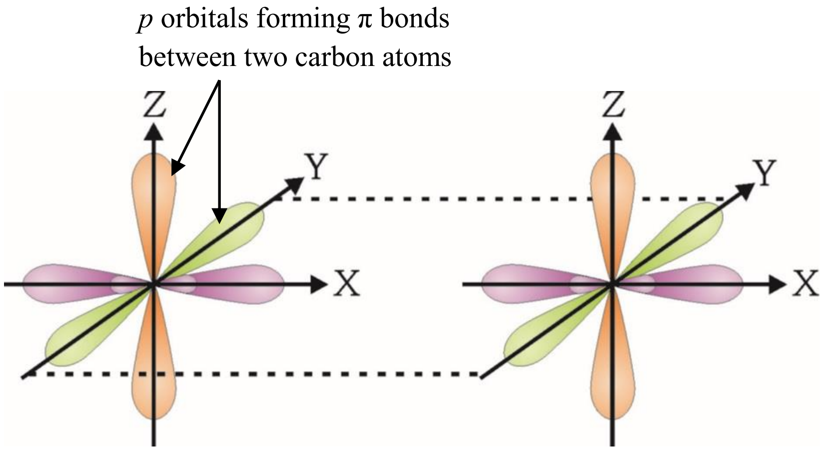


Figure 2.24 σ bond and π bond

The triple bond between two carbon atoms in ethyne (C_2H_2) can be used to study how triple bonds are formed. This triple bond consists of one σ bond and two π bonds between two carbon atoms. The Lewis structure of ethyne is shown below.

$$H - C \equiv C - H$$

Each carbon atom in ethyne forms two σ bonds (C-H and C-C). Therefore, these carbon atoms have *sp* hybridization and the axes of the remaining two *p* orbitals of two carbon atoms lie parallel to each other. It is clearly illustrated in the Figure 2.25.



- Axes of p_y orbitals are parallel to each other
- Axes of p_z orbitals are parallel to each other
- Two *sp* hybridized orbitals facing each other in the x axis from a σ bond between the two carbon atoms

Figure 2.25 *sp* hybridized orbitals and *p* orbitals interaction between the two carbon atoms in ethyne

The axes of *p* orbitals forming a particular π bond are parallel to each other. However the axes of the remaining *p* orbitals forming the other π bond are perpendicular to the orbitals forming the first π bond. In a triple bond, imaginary axes of π electron distribution are perpendicular to each other.

2.3.3 Resonance structures

It is possible to draw a number of Lewis structures for a certain molecule or ion. These Lewis structures with the same skeleton or atom positions are called '**Resonance structures**'. The reason is when there are multiple bondings present (double or triple bonds), the position of the π bond and lone pair of electrons could be changed without changing the atomic arrangement (skeleton of the molecule). The following Figure 2.26 are the two resonance structures for NO_2^- ion, in which the position of π bond has been changed without changing the atomic arrangement.

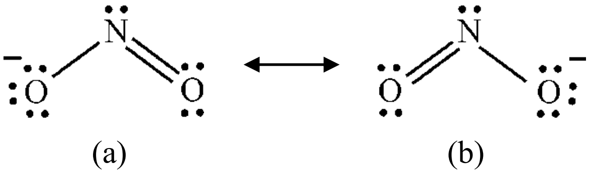


Figure 2.26 Resonance structures of the NO_2^- ion

In NO_2^- ion, two resonance structures can be drawn changing the position of the negative charge and the π bond. In this case, both structures (a) and (b) are identical and cannot be distinguished from each other. Figure 2.27 clearly explains how one resonance structure can be converted to the other using curved arrows. In general, to mark the movement of a lone pair of electrons or π bonding electrons, a curved arrow is used. The arrow head is pointed to the place where electrons have moved. The diagram given below shows the formation of resonance structure in NO_2^- ion.

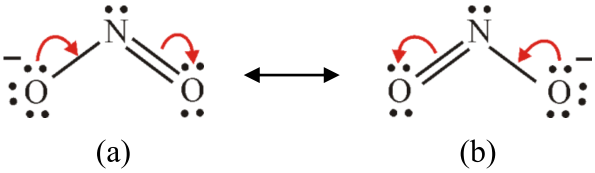


Figure 2.27 Conversion of the resonance structures of the NO_2^- ion into one another

Characteristics of resonance

(i) Resonance structures (contributing structures) do not have real existence. They are imaginary structures drawn for convenience of understanding the nature of molecules or ions. It is assumed that the concept/ model of resonance hybrid represents real existence of molecule or ion.

(ii) Resonance for equal resonance structures, the bond lengths in the resonating unit becomes equal (e.g.: NO_2^-, where both N – O bond lengths are equal).

(iii) The resonance hybrid has comparatively lower energy and thus a greater stability than any of the contributing structures.

(iv) Equivalent resonance structures make equal contribution to the resonance hybrid.

(v) Non–equivalent resonance structures make unequal contribution to the resonance hybrid, whereas most stable resonance structures make major contribution.

Formal Charges

Formal charge is the hypothetical charge on an atom in a molecule or polyatomic ion. This concept is used to identify the energetically most stable Lewis structure. In general, it is considered that the formal charge on each of the atom is zero or close to zero, when the Lewis structure is stable.

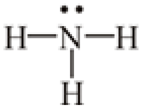
The following steps help to evaluate the formal charge (FC).

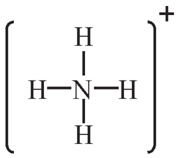
(i) $$\text{FC} = \begin{bmatrix}\text{Number of valence}\\ \text{electrons in the atom}\end{bmatrix} - \left[(\text{Number of bonds}) + \begin{bmatrix}\text{Number of electrons}\\ \text{in lone pairs}\end{bmatrix}\right]$$

(ii) In a Lewis formula, an atom that has the same number of bonds as its number of valence electrons in the atom, its formal charge is zero.

(iii) Add formal charges of all the atoms to find the total value.
   (a) In a molecule, the sum of the formal charges is zero.
   (b) In a polyatomic ion, the sum of the formal charges is equal to the net charge of the ion.

e.g.:





In NH_3 the N atom has three bonds and two unshared electrons (which are not involved in bond formation).

For N atom of NH_3

$$\text{FC} = \begin{bmatrix}\text{Number of valence}\\ \text{electrons in the atom}\end{bmatrix} - \left[(\text{Number of bonds}) + \begin{bmatrix}\text{Number of electrons}\\ \text{in lone pairs}\end{bmatrix}\right]$$

$$= 5 - (3+2) = 0$$

Formal charge of N atom in ammonia is zero.

For H atom of NH_3

$$FC = \begin{bmatrix}\text{Number of valence}\\\text{electrons in the atom}\end{bmatrix} - \left[(\text{Number of bonds}) + \begin{bmatrix}\text{Number of electrons}\\\text{in lone pairs}\end{bmatrix}\right]$$

$$= 1 - (1+0) = 0$$

Formal charge of H atom of ammonia is zero.

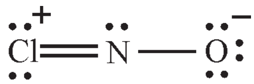
The formal charges of N and H are both zero in NH_3, so the sum of the formal charges of the molecules is zero.

In NH_4^+ the N atom has 4 bonds and no unshared electrons is on the N atom. Hence, formal charge on the N atom of NH_4^+ ion is +1 and formal charge on each H atom is zero. Total of formal charges of NH_4^+ ion is equal to +1 and it is the charge of ammonium ion.

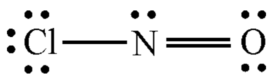
(i) The most likely Lewis structure for a molecule or ion is the one in which the formal charge on each atom is zero or closer to zero as possible.
(ii) Negative formal charges are more likely to occur on more electronegative elements.
(iii) Lewis structure in which adjacent atoms have formal charges of the same sign are not stable, hence not an accurate representations.

Following examples assign formal charges to the atoms in nitrosyl chloride, NOCl. The Cl atom and the O atom are both bonded to the N atom. Two Lewis formulae that satisfy the octet rule whereas formal charges are not same.

(a)



(b)



(a)	(b)
For Cl, FC = 7 – (2 + 4) = +1	For Cl, FC = 7 – (1 + 6) = 0
For N, FC = 5 – (3 + 2) = 0	For N, FC = 5 – (3 + 2) = 0
For O, FC = 6 – (1 + 6) = -1	For O, FC = 6 – (2 + 4) = 0

These two structures have satisfied the octet rule. But the Lewis structure (b) is energetically more stable since the formal charge on each atom is zero.

Although the structure (a) is drawn with a double bond between N and Cl atoms to explain the concept of charge distribution. Keep in mind that drawing multiple covalent bonds should be limited to only between C, N, O, S and P and halogens (Cl, Br, I) and oxygen (O), when drawing Lewis dot-dash structures/ resonance structures.

Rules to estimate relative stability of resonance structures

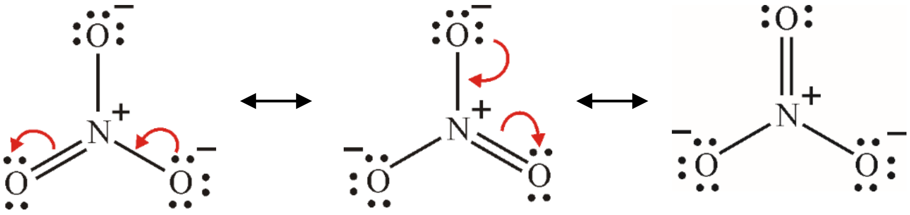
(i) The most stable resonance structure has the least formal charge separation. Thus it contains the greater number of covalent bonds and it contributes mostly to the resonance hybrid. Both maximizing the number of bonds and satisfying the octet rule should be achieved.

(ii) Structures in which adjacent atoms have formal charges of the same sign tend to be unstable.

(iii) When opposite formal charges are placed on adjacent atoms, positive charge should fall on electropositive atom and negative charge on electronegative atom.

(iv) When positive formal charges placed on highly electronegative atoms such as F and O, the structures are unstable.

Formation of resonance structures of nitrate ion (NO_3^-) is given in Figure 2.28.

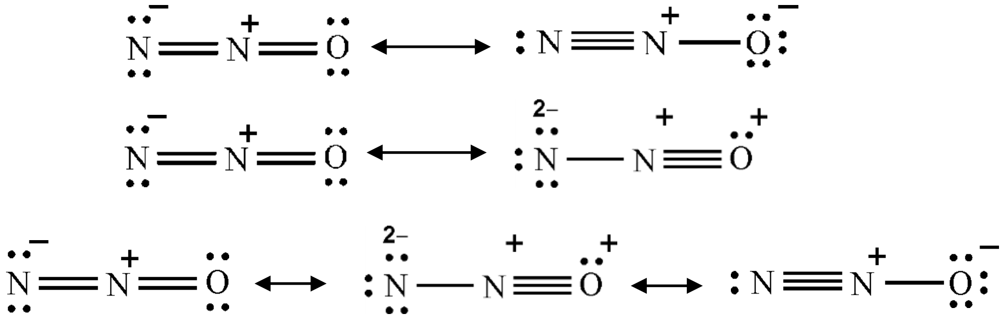


(a) (b) (c)

Figure 2.28 Conversion of resonance structures of NO_3^- ion to one another

All the resonance structures are equivalent. Hence their stabilities are equal. Hence, they contribute equally for the resonance hybrid.

The resonance structures of N_2O are as follows. These resonance structures have satisfied the octet rule.



(a) (b) (c)

Figure 2.29 Resonance structures of N_2O

However based on the formal charge concept, the stability of these resonance structures are not equivalent. According to the rule (iii) given, structure (b) makes the least contribution to the resonance hybrid. (a) and (c) are the stable structures compared to (b) and hence (a) and (b) are the main contributors for the resonance hybrid.

Formation of resonance structures of the carbonate ion (CO_3^{2-}) is given in Figure 2.30 below.

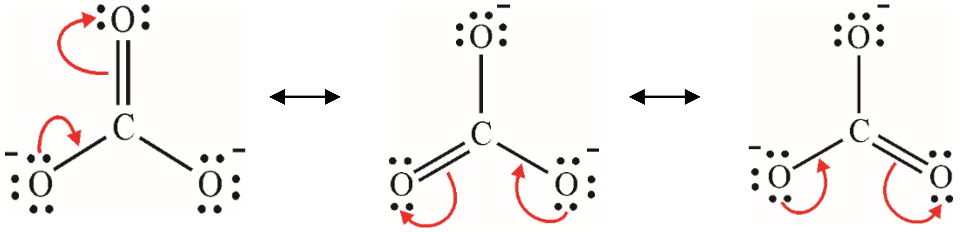


Figure 2.30 Formulation of resonance structures of CO_3^{2-} ion into one another

The corresponding resonance structures of carbonate ion are as follows.

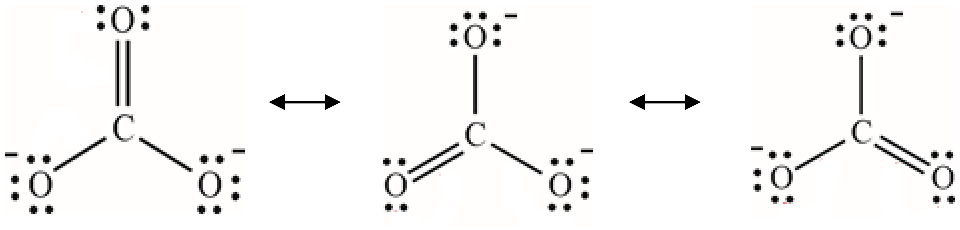


Figure 2.31 Resonance structures of the CO_3^{2-} ion

Resonance structures of the carbonate ion can be used to describe the structure of the resonance hybrid. When resonance structures of the carbonate ion are considered, there are at least two lone pairs of electrons present on each oxygen atom. However the third lone pair may or may not be present on oxygen atoms as position of π bond is changed when forming the resonance structures. Since the position of the π electron cloud is changed, then the electron cloud is delocalized among all three C-O bonds. The resonance hybrid can be represented by Figure 2.32. Note that delocalized electron cloud on C-O bonds is denoted by dotted lines. Bond lengths of CO_3^{2-} are the same since actual structure is the combination of all features of the three resonance structures (resonance hybrid).

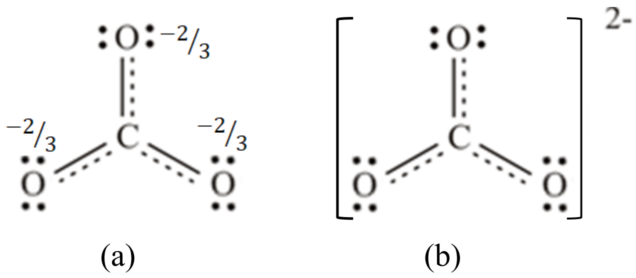


Figure 2.32 (a) Resonance hybrid of the CO_3^{2-} ion with charges (b) resonance hybrid of the CO_3^{2-} ion without charges on terminal atoms

The hybrid shown above with the charges on individual atoms is valid only when equivalent resonance structures are used to draw the hybrid (e.g.: O_3, NO_3^-, CO_3^{2-}, NO_2^-). However, this is not valid for unsymmetrical molecules/ ions (e.g.: N_2O, $S_2O_3^{2-}$).
The ozone molecule can be represented by two resonance structures as shown below.

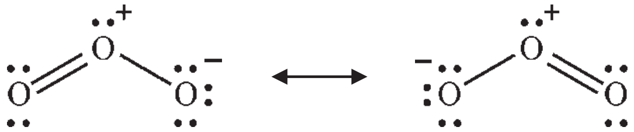


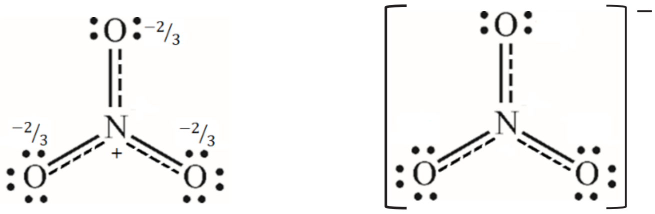
Figure 2.33 Resonance structures of O_3

The bond lengths of the two bonds formed by central atom of O_3 molecule with the other two oxygen atoms in O_3 molecule are same and hence the real structure of O_3 is considered a combination of these two. The combination of the two resonance structures (resonance hybrid) of O_3 is illustrated as follows.

(a) (b)

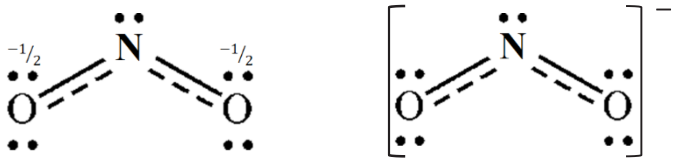
Figure 2.34 (a) Resonance hybrid of the O_3 with charges (b) Resonance hybrid of the O_3 without charges on terminal/ central atom(s)

Similarly the resonance hybrid structure of NO_3^- and NO_2^- is given in Figure 2.35 and Figure 2.36 respectively.



(a) (b)

Figure 2.35 (a) Resonance hybrid of the NO_3^- with charge (b) Resonance hybrid of the NO_3^- without charges on terminal/ central atom(s)



(a) (b)

Figure 2.36 (a) Resonance hybrid of the NO_2^- with charge (b) Resonance hybrid of the NO_2^- without charges on terminal atoms

2.3.4 Effect of electronegativity and geometry on the polarity of molecules

If the electronegativity difference between the atoms forming a chemical bond is large, then electron cloud can be considered to be polarized. The electrons in this polarized covalent bond have higher probability of being found closer to the more electronegative atom. Electronegativity difference plays a vital role in determining the polarity of a bond. Therefore, the higher the electronegativity difference, the higher is the polarity. However, when considering polarity of the entire molecule, then the geometry of the molecule is also important; for example, though C=O bond is polar, CO_2 molecule is non-polar. The reason is the total symmetric linear geometry of the CO_2 molecule. Similarly, C-Cl bond is polar but, CCl_4 molecule is non-polar due to the total symmetric tetrahedral shape of the molecule. Diatomic molecules of same element (e.g.: Cl_2, O_2, N_2 etc.) are examples for nonpolar simple molecules. Bonds of those molecules are examples for the totally nonpolar covalent bonds.

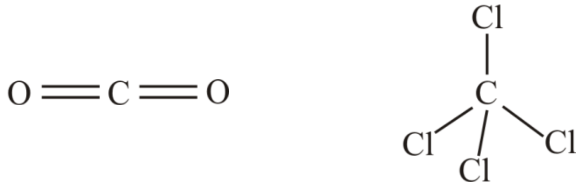


Figure 2.37 CO_2 and CCl_4 molecules

2.3.5 Dipole moment

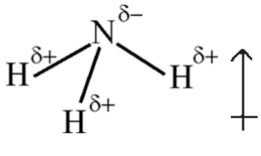
This concept can be clearly understood by taking a molecule with one single bond such as HCl. In a polar molecule, negative pole is created on one end of the molecule, and the positive pole is created on the opposite end of the molecule. Accordingly, in HCl molecule, negative pole is on the Cl atom and the positive pole is created on the H atom. Following is the way of representing such polar bonds.

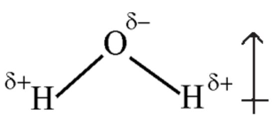
$$^{\delta+}H - Cl^{\delta-}$$

Dipole is notated as ' $+\!\!\!\longrightarrow$ ' and the arrow head is pointed towards the negative pole of the molecule.

$$\underset{+\!\!\!\longrightarrow}{^{\delta+}H - Cl^{\delta-}}$$

e.g.:





If there is a permanent dipole present in a molecule, then the magnitude of polarization on each pole of dipole is equal, resulting in an electrically neutral molecule. Dipole moment is calculated by multiplying the magnitude of a polarity by the distance between the two atoms. When considering HCl molecule, due to asymmetric distribution of the electron cloud, one of the poles is located on the H atom and the other pole is on the Cl atom. The dipole moment of the HCl molecule can be calculated as follows:

Magnitude of dipole moment (μ) = charge of the pole (δ) × bond length (r)

In the above equation units of δ is Coulombs (C) and r is meters (m). Therefore the unit of dipole moment is C m.

Dipole moments (vector quantity- it has a magnitude and direction) of molecules are usually expressed in Debye (D), a unit equal to 3.34×10^{-30} C m.
Since the electronegativity of an atom describes the ability to pull electrons towards itself, models are available to estimate the percentage of ionic nature in a chemical bond using the electronegativity difference. Information on dipole moment and bond length can also be used to calculate percentage ionic character. However, it should be supported by experimental details. Hence the bond between atoms of two different elements is not purely covalent. It has certain percentage of ionic characteristics.

2.3.6 Factors affecting the magnitude of electronegativity

The electronegativity of an element varies slightly depending on the environment of the element, although it is invariably assumed to be a constant. Given below are four important factors that influence the electronegativity.

- **Hybridization**
  Higher the *s* character, greater the electronegativity.
  Electronegativity of C: C(sp^3) < C(sp^2) < C(sp)
  Hence, the electronegativity of carbon atoms in CH_4, C_2H_4 and C_2H_2 increases in the given order $CH_4 < C_2H_4 < C_2H_2$.
- **Charge**
  e.g.: electronegativity of N: $NH_2^- < NH_3 < NH_4^+$
  All nitrogen atoms are sp^3 hybridized, electronegativity $N^- < N < N^+$; Higher the positive charge on the atom, greater the electronegativity when compared to the neutral atom which in turn has a higher electronegativity than an atom with a negative charge.
- **Oxidation number**
  The hybridization of sulphur atom in H_2S, SO_3^{2-} and SO_4^{2-} species is sp^3 and the charge on sulphur atom is zero. The hybridization and the charge of the given three molecules are same. Therefore electronegativity of sulphur in the given species are determined by oxidation number of the sulphur atom in each species. The oxidation numbers on the sulphur atom of H_2S, SO_3^{2-} and SO_4^{2-} are -2, +4 and +6 respectively. The higher the positive charge, greater the electronegativity when compared to the neutral atom. Therefore the electronegativity of sulphur in $H_2S < SO_3^{2-} < SO_4^{2-}$

- **Nature of the other atoms to which the atom of interest is attached in the molecule**
  e.g.: Electronegativity of C in CF_4 is greater than that of CCl_4. Higher electronegativity of fluorine makes the carbon atom is attached to four fluorine atoms highly positive compared to the carbon atom attached to four chlorine atoms. This makes the carbon attached to fluorine to have a higher electronegativity.

In applying the above rules, when an atom of same element in different molecules, priority is always given for hybridization over the charge of the atom. If the hybridization is same, then the priority is given based on the charge of the atom. For an example, hybridization of nitrogen in NH_3 and NH_4^+ are the same. Hence, electronegativity of nitrogen atoms in these two forms is determined by the charge. Nitrogen atom of NH_3 is neutral and nitrogen atom of NH_4^+ is positive and hence nitrogen atom of NH_4^+ is more electronegative.

Likewise, if the hybridization and the charge are same, then the oxidation number can be considered. For an example, hybridization and charge in CH_3F and CH_4 are the same. The oxidation number of carbon in CH_3F is -2 and in CH_4 is -4. Therefore, the electronegativity can be determined based on the oxidation number of carbon atoms. The electronegativity of carbon in CH_3F which has higher oxidation number is higher than that of CH_4.

The effect of the other atoms to be considered when the hybridization, charge and oxidation number are same. For an example, electronegativity of carbon atom in $CHCl_3$ and CHF_3 can be compared with respect to the electronegativity of the atoms attached to the carbon atom. Hence, carbon atom of CHF_3, is more negative than that of $CHCl_3$.

2.4 Ionic bonds/ ionic interactions

Ionic bonds are created due to electrostatic attractive forces between positive and negative ions. These positive and negative ions are packed in a certain pattern called **'lattice structure'** in solid (crystalline) state. Here, each positive ion is surrounded by negatively charged ions and vice versa. In NaCl lattice, each Na^+ ion is surrounded by six Cl^- ions and each Cl^- ion is surrounded by six Na^+ ions.

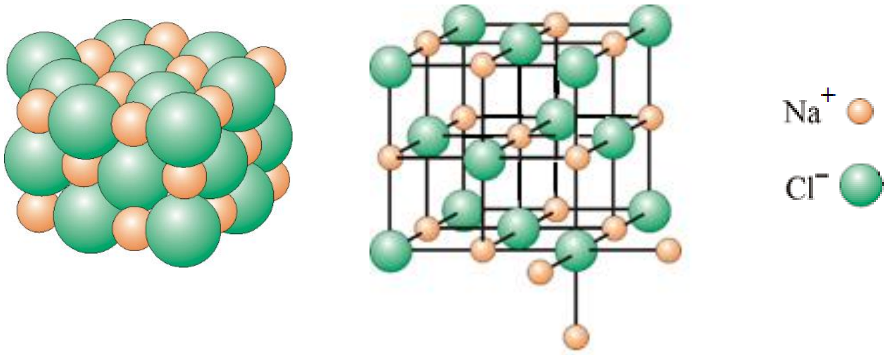
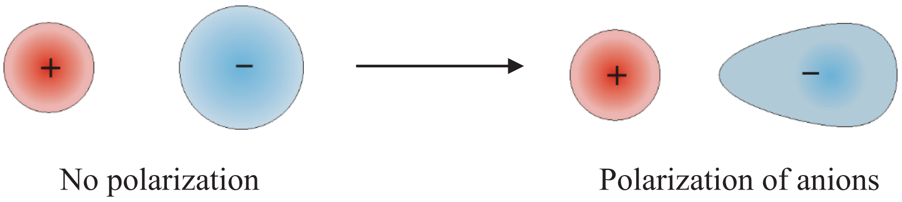
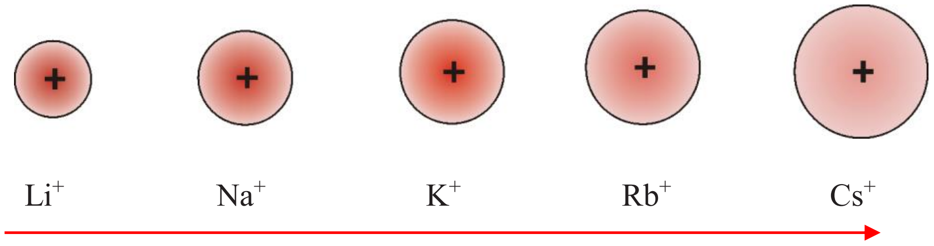


Figure 2.38 Lattice structure of NaCl

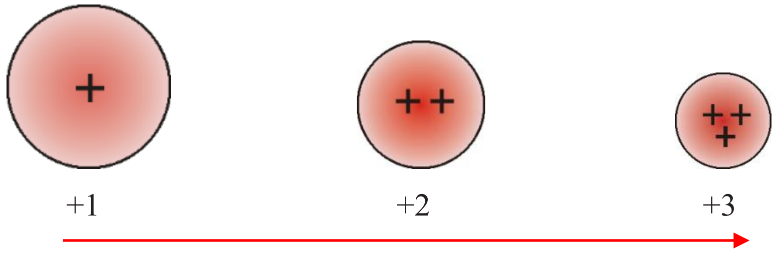
The cation is the smaller ion in an ionic lattice and its electron cloud is strongly bound to the nucleus. The anion is the large ion in an ionic lattice and hence has more loosely held outermost electrons compared to the cation. The shape of the electron cloud of an anion can easily be changed as a result of an external electric field. Large anions are more susceptible to a change in the shape of the electron cloud under the influence of an electrostatic attraction of cation. The field strength of a cation can pull the electron cloud of an anion. The ability of a cation to pull the electron cloud of an anion is called **polarizing power**. When a cation moves towards an anion, the tendency of the electron cloud of an anion to change its spherical shape, as a result of the positive field strength of the cation, is called **polarizability**.



Cation has a strong polarizing power, if it is small and highly charged.

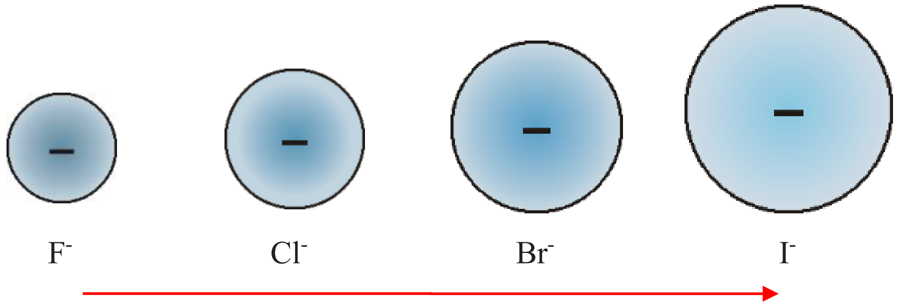


Size of the cation increases.
Polarizing power decreases.

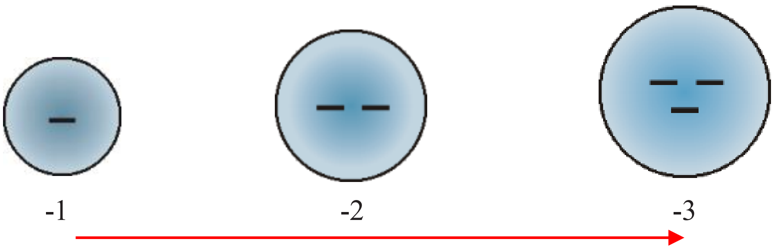


In isoelectronic species:

- Charge of the cation increases.
- Size of the cation decreases.
- Charge density increases.
- Polarizing power increases.



Size of the anion increases.
Polarizability increases.



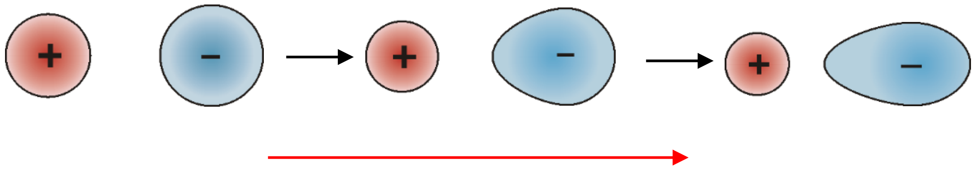
In isoelectronic species:

- Charge of the anion increases.
- Size of the anion increases.
- Polorizability increases.

The degree of ionic character and covalent character of a bond depend on the polarization (polarizing power of the cation and polarizability of the anion).

Polarization is increased by:

- High charge and small size of the cation
- High charge and large size of the anion



Ionic characters decreases as polarization increases.
Covalent character increases.

2.5 Metallic bonds

In general, small molecules with simple covalent bonding exhibit relatively low melting points compared to ionic compounds. Ionic solids do not conduct electricity in the solid state but are capable of conducting electricity in the liquid (molten) state due to the mobility of ions. The melting point of different metals can be observed in a wide range and metals are excellent conductors of electricity and heat regardless of liquid or solid state. For example, melting point of mercury (Hg) is as low as -39 °C while tungsten (W) melts at 3410 °C. Also, in nuclear reactions, liquid sodium is used as a coolant due to its heat transfer capacity. These differences in metals compared to ionic and covalent compounds cannot be explained using models of covalent or ionic bonding.

The model for metallic bonding was proposed by Paul Karl Ludwig Drude and Hendrik Lorentz based on the kinetic model on the behaviour of gases. According to this model, metal atoms are converted to positive ions donating electrons in the valance shell to form the metallic bond. Therefore, a massive electron cloud is created by valance electrons released by large number of atoms. This electron cloud is capable of overcoming repulsive forces among positively charged metal ions keeping them in a lattice. The entire arrangement of lattice structure in massive electron cloud including the electrostatic force between the electron cloud and positively charged metal ions (cations) is considered as metallic bond. In order to stabilize this lattice of positively charged metal ions and electrons are constantly moving in the lattice structure. The strength of a metallic bond is primarily dependent on three main factors.

- **Number of electrons donated by atoms to create the metallic bond**
  For example, sodium atom can donate one electron as it has one electron in the valance shell while, magnesium atom donates two electrons to the metallic bond. When the number of electrons donated by an atoms increases, the strength of the metallic bond is enhanced as well.

- **Ionic radius**
  When the radii of the cations increase, the density of the electron clouds decrease resulting in poor metallic bonds.
- **Ionic nature**
  This means the extent to which valance shell electrons are contributing towards the metallic bond. For example, sodium completely releases the electron on the valance shell to form the metallic bond. However, with increasing ionization energy, there is a less probability to release these electrons to form the metallic bond. This factor has almost no influence on alkaline metals and alkaline earth metals, but it is important when transition metal elements are considered.

2.6 Secondary interactions

All types of intermolecular interactions exist among molecules are known as secondary interactions. They are commonly referred as van der Waals interactions. Those interactions can be categorized into five types.

- Ion - dipole interactions
- Dipole - dipole interactions and hydrogen bonding
- Ion - induced dipole interactions
- Dipole - induced dipole interactions
- Dispersion interactions (London forces)

Van der Waals forces are the attractive or repulsive forces between molecular entities or between groups within the same molecular entity. It includes dipole – dipole interaction, dipole – induced dipole interactions and London forces.

Ion – dipole interactions

Ionic salts such as NaCl are soluble in water due to secondary interactions between positive ions and negative ions with water molecules. The cation in an ionic compound (e.g.: Na^+ in NaCl) interacts with a negatively polarized atom (δ-) in a molecule (O in water) and vice versa to establish ion-dipole interactions. Therefore, in an aqueous solution of NaCl, cations (Na^+) and anions (Cl^-) are surrounded by water molecules to achieve stability in an aqueous medium through these ion-dipole interactions.

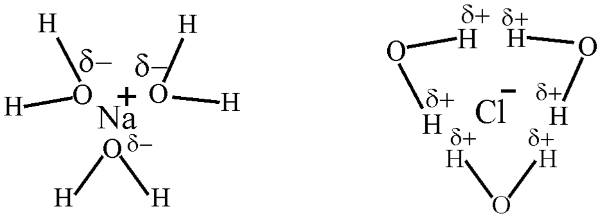


Figure 2.39 Ion dipole interactions formed between H_2O and ions of NaCl

Dipole – dipole interactions

Interactions among molecules with a permanent dipole moment are called **dipole – dipole interactions**. It is clearly illustrated as a model by Figure 2.40. The strength of these attractive forces are generally ranged between 0.5 – 15 kJ mol^{-1}.

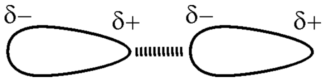


Figure 2.40 Dipole – dipole interactions

Attractive forces between two opposite poles (δ^+ and δ^-) of polar molecule can be more specifically called dipole–dipole interactions. Interactions between two formaldehyde molecules can be taken as an example for dipole – dipole interactions.

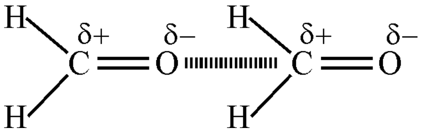


Figure 2.41 Dipole – dipole interactions in formaldehyde

Hydrogen bonding

This is a type of dipole-dipole interactions, some of hydrogen bonds are stronger than the other kinds of dipole–dipole interactions (0.5 – 15 kJ mol^{-1}). In general, the strength of hydrogen bonds range between 4 - 40 kJ mol^{-1}.

When a hydrogen atom is bonded to a N, O or F atom, the partial positive charge on hydrogen atom (δ+) is much higher compared to the bonding with other atoms. The reason is the relatively higher electronegativity difference between hydrogen and these electronegative atoms (N, O, F). Since hydrogen is a smaller atom, a strong electrostatic field is available. When it has an electrostatic interaction between a hydrogen atom with a partial positive charge (δ+) and an electronegative atom (N, O, F) with a partial negative charge (δ-) is called a **hydrogen bond**. It is not necessary that the electronegative atom with (δ-) is bonded to a hydrogen atom (H-O, H-N, H-F), but could be any other atom. (e.g.: Hydrogen bonding between H atom of $CHCl_3$ and O atom of acetone).

In the Figure 2.42, one water molecule is bonded to another water molecule forming hydrogen bonds. Examples for hydrogen bonds formed between same molecules are H_2O and NH_3.

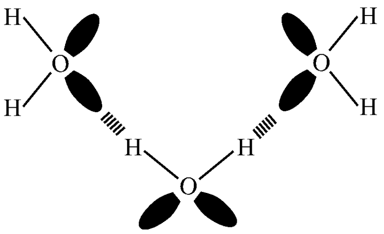


Figure 2.42 Hydrogen bonds in water

The model of polarity could be matched with the behaviour and the properties of molecular substance, e.g.: water. Ice floats on water since it is about 9% less dense than liquid water. As the thermal energy of water is removed by cooling, kinetic energy of molecules decreases freezing water to ice at 0 ^{0}C. Lowering of kinetic energy of water molecules leads to increase the number of hydrogen bonds around each water molecule. Water molecules become compact in a regular order since each of the water molecule forms maximum number of hydrogen bonds with the nearby water molecules when the kinetic energy is lowered by cooling it to 0 ^{0}C.

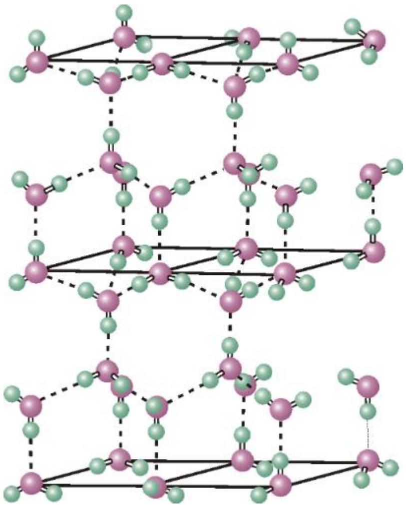


Figure 2.43 Arrangement of H_2O molecules in ice

Each water molecule can form two hydrogen bonds using the two hydrogen atoms and it can form another two hydrogen bonds by attracting two hydrogen atoms of adjacent water molecules using two lone pairs of electrons on the oxygen atom. These four hydrogen bonds at 0 ^{0}C lead to a compact tetrahedral arrangement around each water molecule. The arrangement of water molecules in a regular ordered state of ice occupies 9% more space than the free space of liquid water. There are number of crystal structures of ice and the nature of the crystal structures depends on the condition of cooling.

However, hydrogen bonds can also be formed as intermolecular interactions among different molecules. Hydrogen bonding present in a mixture of acetone and water clearly illustrates this.

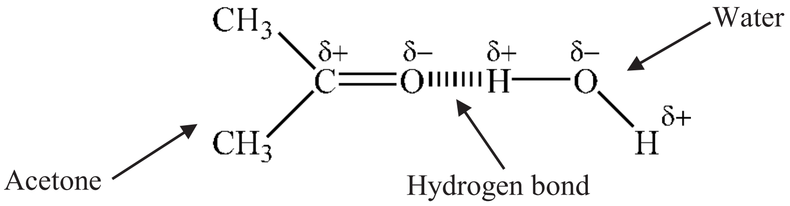


Figure 2.44 Hydrogen bonds in acetone/ water mixture

Hydrogen bonding in acetic acid is possible between the hydrogen atom in the carboxylic group and the oxygen atom in the carbonyl group (C=O) of the carboxylic acid group as indicated below. The electronegative atom with (*δ*-) charge is not necessarily bonded to hydrogen. It shows that the presence of required degree of polarity at H atom and the other electronegative atoms (O, N, F) is important, in order to form hydrogen bonding.

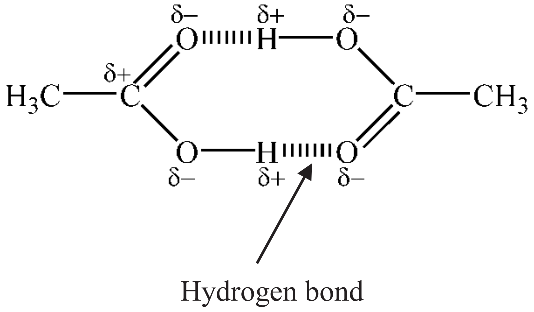
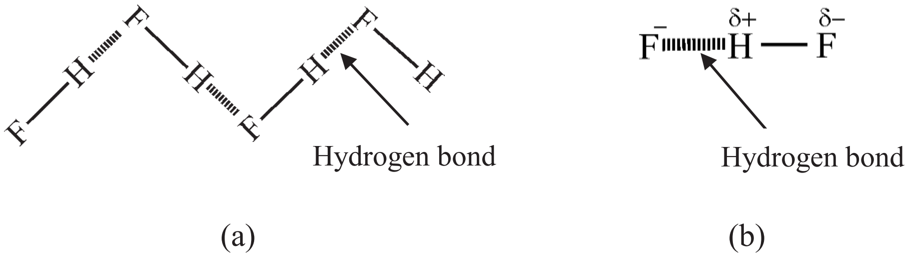


Figure 2.45 Hydrogen bonds in acetic acid

Hydrogen bonds, are present in pure HF. The Figure 2.46 (a) below shows the arrangement of HF molecules in pure HF. In the case of a solution of a mixture of HF and F$^-$, hydrogen bonds can form between F$^-$ ions and *δ*+ charged hydrogen atoms in HF molecules (b).



(a) (b)

Figure 2.46 (a) Hydrogen bonds in HF, (b) H bonds in NaF and HF mixture

When hydrogen bonding is present between two molecules then it is called **inter-molecular hydrogen bond** while hydrogen bonding is present between a hydrogen atom and an electronegative atom of the same molecule it is called **intra-molecular hydrogen bond.** The hydrogen bonding present in *ortho*-nitrophenol and *para*-nitrophenol are given below in Figure 2.47 to illustrate the difference between inter-molecular and intra-molecular hydrogen bonding.

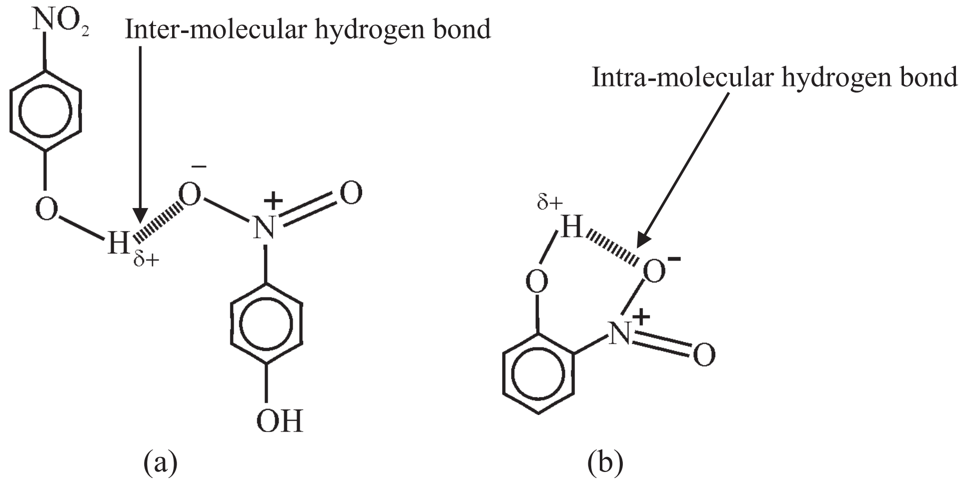


Figure 2.47 Hydrogen bonds in (a) *ortho*-nitrophenol and (b) *para*-nitrophenol

In certain cases, possibility of having hydrogen bond is defined (the strength of a hydrogen bond is less) when the electronegative atom is Cl. Therefore there is another rule including Cl as well. It is called FONCl rule. In general, stronger hydrogen bonds are observed between a polarized hydrogen atom (δ+) and polarized F, O or N atom (δ-).

Ion – induced dipole interactions

Iodine (I_2) is a non-polar molecule which is slightly soluble in water. However, iodine in solid state can be dissolved in an aqueous KI solution. This observation can only be explained with ion –induced dipole interactions. In this case, interaction of an iodide ion (I^-) can induce a dipole on an iodine molecule. The positive pole of induced dipole interacts with I^- ion to combine I_2 molecule in order to form the I_3^- ion. Hence, I_2 dissolves in KI solution.

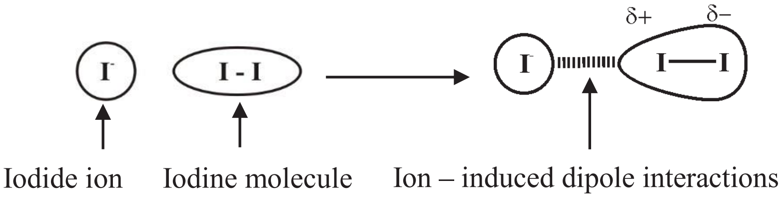


Figure 2.48 Ion –induced dipole interactions

Therefore, ion – induced dipole interactions can make iodine soluble in an aqueous KI solution.

Dipole – induced dipole interaction

This is a weak attractive force that results when a polar molecule induces a dipole in an atom or a nonpolar molecule. The polarization of outer electron cloud of atom or nonpolar molecule takes place as a result of the impact of electrostatic force of the dipole of the polar molecule.

This interaction energy is proportional to $1/r^6$ where "r" is the distance between two molecules. The magnitude of dipole moment of induced dipole depends upon polarizability of nonpolar molecule or atom and the magnitude of the dipole moment of the polar molecule. The interaction between HCl molecule and Ar atom is one example.

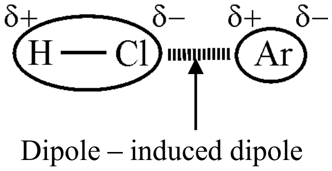


Figure 2.49 Dipole – induced dipole interactions

London interactions (forces) (Instantaneous induced dipole – induced dipole interaction)

Non polar molecules are held together by weak interactions. These interactions are also present in gas, liquid and solid states of inert elements and these weak interactions are called **London forces**. Though the molecule is non-polar, due to continuous movement of electrons, regions of relatively high and low electron densities are created instantaneously. However, location of these two poles can instantaneously change in the next moment. Interaction between a momentarily polarized dipole of a molecule with an oppositely charged such a dipole of another molecule (δ^+--- δ^-) is a London interactions. They are also called dispersion forces. Molecule has a high probability for forming London interaction when the surface area of the molecule is large. The net strength of interaction between two molecules is significant as they have relatively large surface areas.

London forces exist among all the atoms and molecules irrespective of whether they are polar or non-polar. In determining physical properties of molecules having larger molecular weights, dispersion forces are likely to be more important than dipole – dipole forces exist between them. London forces are the dominant interactions in order to compact the iodine molecules in solid state.

Compacting of iodine molecules in solid state

Iodine is a nonpolar molecule and solid state of iodine is considered to be a molecular crystal. Iodine molecule is a heavy molecule having a large size. Thermal energy at room temperature is not sufficient for molecular movement of iodine molecules in the solid state. London forces hold these molecules in an orderly arrangement in the solid state.

Large surface area of the I_2 molecule creates London forces with neighbouring molecules giving rise to a molecular lattice structure. Since I_2 molecules are nonpolar, solubility of iodine is greater in non-polar solvents than in polar solvents.

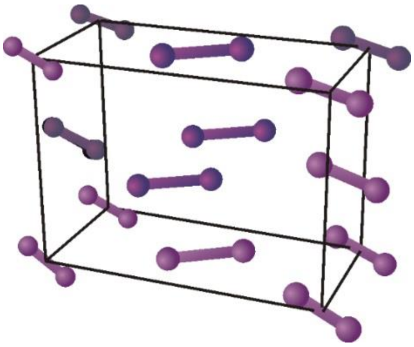


Figure 2.50 Lattice structure of iodine

The following chart shows the variation of boiling points of some simple molecules. The variation of boiling points can be explained using the dipole moment and intermolecular forces.

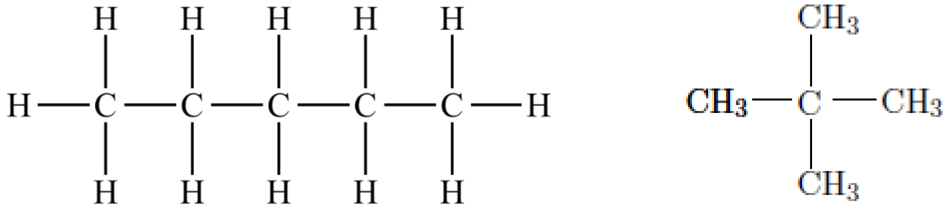
Table 2.7 Variation of boiling points of some simple molecules with dipole moment

Molecule	Molar mass/ g mol^{-1}	Dipole moment/ D	Boiling point/ ^{0}C	Type of dominant interaction
O_2	32	0	-183	London
NO	30	0.153	-152	Dipole-dipole
Kr	83.8	0	-152	London
HBr	81	0.82	-62	Dipole-dipole
Br_2	160	0	59	London
ICl	162.5	1.6	97	Dipole- dipole

Molar masses of NO and O_2 are comparable but boiling point of NO is greater than O_2. Hence, the relative strength of inter molecular interaction forces among NO molecules should be greater than the intermolecular interaction strength among O_2 molecules. The model of dipole moment and polarity of molecule can be used to explain this observation. NO is a molecule with atoms of different electronegativity and hence, it is a polar molecule having a dipole moment (0.153 D). Oxygen molecule is a nonpolar molecule with zero dipole moment. Polar NO has dipole–dipole attractions among the molecules. Nonpolar oxygen molecules have relatively weak London interactions. Hence, liquid NO needs more energy than liquid oxygen in order to break the intermolecular interactions in the liquid state.

Molecules of bromine (Br_2) and iodine monochloride (ICl) are isoelectronic. Bromine molecules are non-polar and liquid Br_2 boils at 59 ^{0}C. ICl consists of polar molecules and boils at 97 ^{0}C almost 40 ^{0}C higher. The boiling point indicates that intermolecular forces among ICl molecules are stronger than those of Br_2. Any substance with strong dipole-dipole forces has to absorb substantially more energy to melt and boil.

The net strength of intermolecular attraction also depends on the molecular shape. Electrons in elongated molecules are easily polarized or distorted. For example, *n*-pentane boils at 36 ^{0}C, whereas *neo*-pentane boils at 9 ^{0}C. Boiling points increase with increasing attraction among molecules. Hence the London forces in *n*- pentane are stronger than those in *neo*-pentane. This is because the spherical shape of *neo*-pentane molecule and the valence electrons in C-C bonds are well shielded from the CH_3 groups whereas *n*-pentane is chain shaped so that valence electrons in C-C bonds are more exposed in order to form London interaction.



(a) (b)

Figure 2.51 Structure of (a) *n*-pentane and (b) *neo*-pentane

3. Chemical Calculations

Content

Introduction

Basic mathematical calculations used in chemistry and the knowledge required in respect of understanding chemistry principles are acquired in this unit.

3.1 Oxidation number

Oxidation number is used to determine the number of electrons transfer between atoms/ions in compounds and molecules. The oxidation number describes the loss or gain of electrons from an atom in a chemical compound. The oxidation number describes the charge that an atom would have if all bonds are considered to be ionic with no covalent component. The oxidation number of an atom in a covalent compound is found by assigning the electrons shared by atoms to the particular atom as follows:

(a) For **covalent bonds formed between similar atoms** – When there is no electronegativity difference between the two bonded atoms, the electrons are split equally between the atoms. For such bonds the oxidation number of atoms is zero.

(b) For **covalent bonds formed between different atoms** – When the covalent molecule is made up of different atoms the bonded electrons are not shared equally between the atoms. In these bonds, the bonded electrons are assigned to the atom that has the highest electronegativity. Accordingly, plus and minus oxidation numbers are introduced to explain the oxidation number.

The examples for different types of oxidation number exhibited by atoms/ ions are given in Table 3.1.

Table 3.1 The examples for various oxidation numbers exhibited by atoms/ ions

Type	Oxidation number	Example
Atoms in elemental state	Zero	Na(s), He(g), Hg(l), N_2(g)
Monoatomic ions	Equal to the charge	Na^+, O^{2-},Ca^{2+}
Fluorine	-1	NaF, OF_2
Oxygen	-2 +2 -1 -1 and zero	H_2O, P_2O_5 OF_2 only peroxides/ O_2^{2-} superoxides/ O_2^-
Hydrogen	+1 -1	H_2O, CH_4 Metal hydrides only (NaH)

3.1.1 Basic rules that applied in the determination of the oxidation number of an atom in a molecule/ polyatomic ion or in a compound

Two basic rules used to allocate oxidation numbers for atoms and ions in simple molecules, molecular ions and compounds are given below.

(a) The sum of the oxidation numbers of all the atoms in an compound is equal to zero.

(b) The sum of the oxidation numbers of all the atoms in an ion is equal to its charge.

Examples of the use of the above two rules are shown below.

The determination of oxidation number of an atom in molecules

Example 1: Phosphine (PH_3)

The oxidation number of P in PH_3

Total charge of PH_3 is zero,

3 [oxidation number of H] + [oxidation number of P] = 0

3 [+1] + [oxidation number of P] = 0

Oxidation number of P = -3

Example 2: Phosphoric acid (H_3PO_4)

The oxidation number of P in H_3PO_4

Total charge of H_3PO_4 is zero,

3 [oxidation number of H]+[oxidation number of P]+4[oxidation number of O] = 0

3 [+1] + [oxidation number of P] + 4[-2] = 0

Oxidation number of P = +5

The determination of oxidation number of an atom in polyatomic ions

Example 1: Sulphate ion (SO_4^{2-})

The oxidation number of S in SO_4^{2-}

Total charge of SO_4^{2-} is -2,

4 [oxidation number of O] + [oxidation number of S] = -2

4 [-2] + [oxidation number of S] = -2

Oxidation number of S = +6

The determination of oxidation number of an atom in compounds

Example 1: Calcium oxide (CaO)

The oxidation number of Ca in CaO

Total charge of CaO is zero,

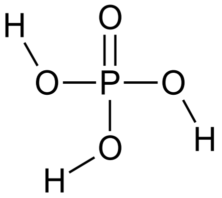
[oxidation number of Ca] + [oxidation number of O] = 0

[oxidation number of Ca] + [-2] = 0

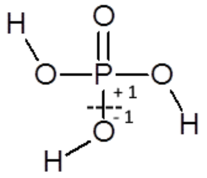
Oxidation number of Ca = +2

The structural formula of a molecule shows a graphic representation of its molecular structure and how the atoms are arranged. It also can be used to assign the oxidation number to each atom in the molecule using the electronegativity difference between the component atoms. This approach is mainly used to determine the oxidation number of atoms in covalent bonds. In this method, each pair of electrons in a covalent bond must be assigned to the most electronegative atom accordingly. The most electronegative atom gains the electron and it is marked with a (-1) charge. The atom that has less electronegativity loses an electron and it is marked with a (+1) charge. After assigning the electrons the final charge on the central atom is called as the oxidation number of the central atom. This is illustrated in the examples given below.

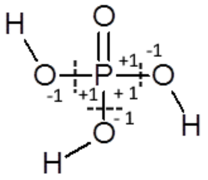
Example 1: Phosphoric acid (H_3PO_4)



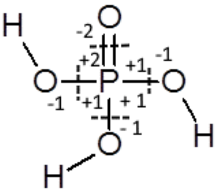
Step 1
Draw the bond structure of the compound.



Step 2
Based on the electronegativity difference assign +1 or -1 to atoms bonded together.



Step 3
Continue step 2 with all the bonds around the target element.

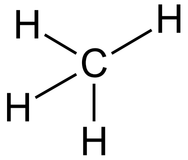


Step 4
Add all the assigned values around the target element.
Phosphorus = (+2)+(+1)+(+1)+(+1) = +5
Oxidation number of the central atom of phosphorus is +5.

Figure 3.1 Steps in determining oxidation number of P atom in H_3PO_4

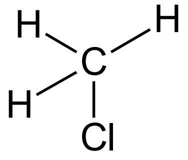
Oxidation number of carbon in compounds in which carbon at the center.

Example 1: Methane (CH_4)



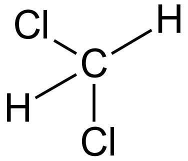
Oxidation number of C = -4

Example 2: Chloromethane (CH_3Cl)



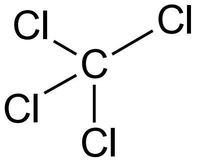
Oxidation number of C = -2

Eample 3: Dichloromethane (CH_2Cl_2)



Oxidation number of C = 0

Example 4: Tetrachloromethane (CCl_4)



Oxidation number of C = +4

3.1.2 Use of oxidation numbers to understand electron transfer between atoms in redox reactions

New products are formed by transfer of electrons from one atom to another when chemicals react. Consider the reaction between solid sodium and chlorine gas;

$$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$$

In this reaction, elemental sodium and chlorine become a positively charged sodium ion and negatively charged chloride ion respectively. (Na^+ and Cl^-).

In such reactions, one or more electrons are transferred from one atom to another atom. Reactions showing such electron transfers are called **oxidation-reduction reactions** or **redox reactions**.

- The loss of an electron/s from an atom/ ion is called **oxidation**.
- Conversely the gain of an electron/s by an atom/ ion is called **reduction**.

Oxidation (Loss of electrons) $\underset{0}{Na(g)} \longrightarrow \underset{+1}{Na^+(g)} + e$

In oxidation, oxidation number of an atom/ion increases. Therefore sodium is oxidized to sodium ion.

Reduction (Gain of electrons) $\underset{0}{Cl_2(g)} + 2e \longrightarrow \underset{-1}{2Cl^-(g)}$

In reduction, oxidation number of an atom/ion decreases. Therefore chlorine is reduced to chloride ions.

In the above example, chlorine is identified as the oxidizing agent and sodium is the reducing agent.

Further examples are given below to help to understand the electron transfer that occurs in redox reactions.

Example 1: Combustion of methane (CH_4)

This can be shown using the following balanced equation. In this reaction, oxidation numbers of C and O is changed when CO_2 and H_2O are formed as products.

Reaction	$CH_4(g)$	+	$2O_2(g)$	$\longrightarrow$	$CO_2(g)$	+	$2H_2O(l)$
Oxidation number	C = -4		O = 0		C = +4		H = +1
	H = +1				O = -2		O = -2

The oxidation number of hydrogen remains unchanged.

The oxidation number of carbon changes from -4 to +4. Therefore, carbon is oxidized.

The oxidation number of oxygen changes from 0 to -2. Therefore, oxygen is reduced.

Oxidation reaction: Carbon in CH_4 is oxidized to produce CO_2.
Each carbon atom loses 8 electrons.
Reduction reaction: Oxygen is reduced to produce H_2O and CO_2.
Each oxygen atom gains 2 electrons.

Example 2: Combustion of propane (C_3H_8)
This is shown using the following balanced equation. In this reaction, oxidation numbers of C and O will change when CO_2 and H_2O are formed as products.

Reaction	${}^{x}CH_3{}^{y}CH_2{}^{z}CH_3(g)$	+	$5O_2(g)$	$\longrightarrow$	$3CO_2(g)$	+	$4H_2O(l)$
Oxidation number	${}^{x}C = -3$, ${}^{y}C = -2$, ${}^{z}C = -3$		$O = 0$		$C = +4$		$O = -2$
Cumulative oxidation number of carbon	$(-3)+(-2)+(-3) = -8$				$(+4) \times 3 = +12$		

The cumulative oxidation number of the three carbons changes from -8 to +12. Therefore, there is a total of 20 electrons **loss** when forming the product CO_2. Hence carbon is oxidized.

The oxidation number of oxygen changes from 0 to -2 in the product. Therefore, there is a total of 4 electrons **gain** when forming the product of two O^{2-}. Hence oxygen is reduced.

Oxidation reaction: Carbon in $CH_3CH_2CH_3(g)$ is oxidized to produce CO_2.
Reduction reaction: Oxygen is reduced to produce H_2O and CO_2.

Example 3: Formation of propane (C_3H_8) from propene (C_3H_6)
This is shown using the following balanced equation. In this reaction, oxidation numbers of C in C_3H_8 will change when C_3H_6 is produced and this can be shown as follows.

Reaction	${}^{x}CH_3{}^{y}CH{}^{z}CH_2(g)$	+	$H_2(g)$	$\longrightarrow$	${}^{x}CH_3{}^{y}CH_2{}^{z}CH_3(g)$
Oxidation number	${}^{x}C= -3$, ${}^{y}C =-1$, ${}^{z}C= -2$		$H=0$		${}^{x}C= -3$, ${}^{y}C= -2$, ${}^{z}C= -3$
Cumulative oxidation number of carbon	$(-3)+(-1)+(-2) = -6$		$H=0$		$(-3) + (-2) + (-3) = -8$

The cumulative oxidation number of the three carbons changes from -6 to -8. Therefore, there is a total of 2 electrons **gain** when forming the product. Hence carbon is reduced.

The oxidation number of hydrogen changes from 0 to +1in the product. Therefore, there is a 2 electrons **loss** in respect of hydrogen when forming the two H^+ in the product C_3H_8. Hence hydrogen is oxidized.

Reduction reaction: Carbon in $CH_3CHCH_2(g)$ is reduced to produce $CH_3CH_2CH_3(g)$
Oxidation reaction: Hydrogen is oxidized to produce $CH_3CH_2CH_3(g)$.

3.2 Nomenclature of inorganic compounds

IUPAC recommendations for nomenclature are used in the systematic way of naming compounds. IUPAC stands for *International Union of Pure and Applied Chemistry*. This section deals only with the inorganic nomenclature. With the aid of nomenclature chemical compounds can be specified with a unique name.

Trivial names (name used before the IUPAC nomenclature was introduced) are often still commonly used for some compounds in addition to the IUPAC names.

3.2.1 Names of ionic compounds derived from monoatomic ions

The way of writing the unmodified name for the monoatomic cation and then writing the modified name for the monoatomic anion with the suffix ***-ide*** at the end is shown in the Table 3.2.

Table 3.2 Names of common monoatomic ions

Cation	Name	Anion	Name
H^+	hydrogen	H^-	hydride
Na^+	sodium	Cl^-	chloride
K^+	potassium	Br^-	bromide
Ca^{2+}	calcium	O^{2-}	oxide
Al^{3+}	aluminium	S^{2-}	sulfide
Zn^{2+}	zinc	N^{3-}	nitride

Rules for writing the name of ionic compounds with an element that can only form one type of cation:

1. Name of the cation must always come first.
2. Name of the cation is the name of its element.
3. Name of the anion is the part of its element name and the suffix *–ide*.
4. Leave a space between the name of the cation and the anion.

Applications are shown in the examples below.

e.g.: NaCl - sodium chloride
MgO - magnesium oxide
CsBr - caesium bromide

3.2.2 Names of ionic compounds derived from elements that form more than one type of cations

The metal ions with variable oxidation numbers form more than one type of cations. In the trivial names, suffix *–ic* for the cation of higher charge (higher oxidation number) and *–ous* for the cation of lower charge (lower oxidation number) are used.

This can be seen in naming Fe^{2+} as ferrous and Fe^{3+} as ferric. Trivial and systematic names for common cations are given below in Table 3.3. However, in systematic names, the charge of the metal ion is shown using Roman numerals in parentheses after the name of the metal according to the oxidation number of the metal ions. It is also shown in Table 3.3 below.

Table 3.3 Names of cations that can form more than one positively charged ions

Cation	Trivial name	Systematic (IUPAC) name
Fe^{2+}	ferrous	iron(II)
Fe^{3+}	ferric	iron(III)
Cu^{+}	cuprous	copper(I)
Cu^{2+}	cupric	copper(II)
Co^{2+}	cobaltous	cobalt(II)
Co^{3+}	cobaltic	cobalt(III)
Sn^{2+}	stannous	tin(II)
Sn^{4+}	stannic	tin(IV)
Pb^{2+}	plumbous	lead(II)
Pb^{4+}	plumbic	lead(IV)
Hg_2^{2+}	mercurous	mercury(I)
Hg^{2+}	mercuric	mercury(II)

Rules for writing the name of ionic compounds composed of the elements showing variable oxidation numbers:

1. Name of the cation must always come first.
2. Name of the element is used as the name of the cation and the oxidation number (charge) is shown by capital Roman numerals in parentheses at the end of the cationic name.
3. Name of the anion is the part of its element's name which is written with the suffix *–ide* at the end of the anionic name.
4. Leave a space between the name of the cation and the anion.

e.g.: FeS - iron(II) sulfide**
Fe_2S_3 - iron(III) sulfide
$CuCl$ - copper(I) chloride
$CuCl_2$ - copper(II) chloride

**Both sulfide and sulphide are correct and accepted, however for nomenclature only sulfide is accepted.

Trivial names for few of the above compounds are given below.

FeS - ferrous sulfide
Fe_2S_3 - ferric sulfide
$CuCl$ - cuprous chloride
$CuCl_2$ - cupric chloride

3.2.3 Names of simple covalent compounds

Many elements form covalent compounds. When naming this type of compounds, the element with the positive oxidation number must be written first followed by the element with the negative oxidation number.

Rules for writing the name of simple covalent compounds:

1. First part of the name is written representing the less electronegative element and the second part of the name is written indicating the more electronegative element in the compound.
2. Write the name of the compound leaving a space between the first part and the second part.
3. Name the most electronegative atom by modifying its name with the suffix *–ide.*
4. Prefixes are used to represent the number of similar atoms in the compound. Based on the number of similar atoms prefixes are given as follows.
   1 = *mono*, 2 = *di*, 3 = *tri*, 4 = *tetra*, 5 = *penta*, 6 = *hexa*, 7 = *hepta*, 8 = *octa*
   However, the prefix *mono* is never used when naming the first element.
5. When the prefix ends in "*a"* or "*o"* and the second element name begins with "*a"* or "*o"*, the final vowel of the prefix is dropped for ease of pronunciation.
   e.g.: mono + oxide = monoxide
   tetra + oxide = teroxide

e.g.: CO - carbon monoxide
H_2S - dihydrogen monosulfide
SO_3 - sulfur trioxide
N_2O_3 - dinitrogen trioxide
N_2O_4 - dinitrogen tetroxide
P_4O_6 - tetraphosphorus hexoxide
H_2O - dihydrogen monoxide
OF_2 - oxygen difluoride

3.2.4 Polyatomic ions

Some nonmetal atoms can bind covalently to form polyatomic ions. Polyatomic anions are more common than polyatomic cations.

Rules for writing the name of polyatomic ions.
The names of these ions are written using the following suffixes.

1. Names of polyatomic cations end with -*ium*.
2. Names of polyatomic anions end with suffixes *–ide*, -*ite* and -*ate*.

Names for common polyatomic ions are given in Table 3.4.

Table 3.4 Formulae and the name of the polyatomic ions

Ion	Name	Ion	Name
NH_4^+	ammonium	NO_3^-	nitrate
OH^-	hydroxide	ClO_3^-	chlorate
CN^-	cyanide	MnO_4^{2-}	manganate
HS^-	hydrogen sulfide	MnO_4^-	permanganate
O_2^{2-}	peroxide	CrO_4^{2-}	chromate
O_2^-	superoxide	$Cr_2O_7^{2-}$	dichromate
SO_3^{2-}	sulfite	$C_2O_4^{2-}$	oxalate
NO_2^-	nitrite	CO_3^{2-}	carbonate
ClO_2^-	chlorite	HCO_3^-	hydrogen carbonate
HSO_3^-	hydrogen sulfite	$S_2O_3^{2-}$	thiosulfate
SO_4^{2-}	sulfate	$S_4O_6^{2-}$	tetrathionate
HSO_4^-	hydrogen sulfate	PO_4^{3-}	phosphate
AlO_2^-	aluminate	HPO_4^{2-}	hydrogen phosphate
ZnO_2^{2-}	zincate	$H_2PO_4^-$	dihydrogen phosphate

Naming compounds with polyatomic ions

Several compounds are named below by referring to the rules discussed above.

$K_2Cr_2O_7$ has a simple cation and a polyatomic anion.
Name of the cationic part = potassium
Name of the anionic part = dichromate
Name of the compound = potassium dichromate

$(NH_4)_2Cr_2O_7$ has a polyatomic cation and a polyatomic anion.
Name of the cationic part = ammonium
Name of the anionic part = dichromate
Name of the compound = ammonium dichromate
Names of some common compounds with a polyatomic anion
KH_2PO_4 = potassium dihydrogen phosphate
FeC_2O_4 = iron(II) oxalate
$NaHCO_3$ = sodium hydrogen carbonate

3.2.5 Inorganic acids

Compounds with one or more ionizable protons in aqueous solutions and **an anion without oxygen** are named using the prefix *hydro-* followed by the name of the other nonmetal or group of non-metals modified with an *-ic* ending. The full name is composed of the term acid at the end.

HCl (hydrogen chloride) = hydrochloric acid
HBr (hydrogen bromide) = hydrobromic acid
HCN (hydrogen cyanide) = hydrocyanic acid
H_2S (dihydrogen sulfide) = hydrosulfuric acid

Compounds with one or more ionizable protons in aqueous solutions and **an anion with oxygen** are called oxoacids. The name of the anion is written with suffix and it is used as the name of the acid.

When the anion name ends in –ate, the suffix –ic is used.
H_2SO_4 (anion is SO_4^{2-} - sulfate) = sulfuric acid
When the anion name ends in –ite, the suffix –ous is used.
H_2SO_3 (anion is SO_3^{2-} - sulfite) = sulfurous acid

Naming different oxoanions (oxyanions) formed from the same central atom

An oxyanion or oxoanion is an ion with the generic formula $A_xO_y^{z-}$ where A represents a chemical element and O represents an oxygen atom. Some elements are able to form more than one oxoanion each containing different number of oxygen atoms. Series of oxoanions containing different numbers of oxygen atoms are generally named as follows.

The prefix *per–* is used for the anion with a higher number of oxygen atoms, and the prefix *hypo–* is used for the anion with a lower number of oxygen atoms.

According to the increasing order of oxidation number of the central atom of the oxoanion, their names can be derived as follows:

hypo____ite	*___ite*	*___ate*	*per___ate*
ClO^- = hypochlorite	ClO_2^- = chlorite	ClO_3^- = chlorate	ClO_4^- = perchlorate
(+1)	(+3)	(+5)	(+7)

These oxoanions are available in the form of oxoacids or salts. Chloro oxoacids and their sodium salts are given in Table 3.4.

Table 3.5 Formulae and names of chloro oxoacids and their sodium salts

Oxidation number of Cl	Formula of oxoacid	Name of oxoacid	Formula of salt	Name of salt
+1	$HClO$	hypochlorous acid	$NaClO$	sodium hypochlorite
+3	$HClO_2$	chlorous acid	$NaClO_2$	sodium chlorite
+5	$HClO_3$	chloric acid	$NaClO_3$	sodium chlorate
+7	$HClO_4$	perchloric acid	$NaClO_4$	sodium perchlorate

**Nomenclature considered in G. C. E. (A/L) Chemistry syllabus is referred to 2005 IUPAC red book*

3.3 Atomic mass, mole and Avogadro constant

3.3.1 The connection among atomic mass unit, mole and Avogadro constant

Since atoms are so small, the normal units of mass such as grams and kilograms are inconvenient to express their mass. Hence a smaller unit of mass called atomic mass unit (u) was introduced. Atomic mass is the mass of an atom of a chemical element expressed in atomic mass units. Different types of isotopes are found in elements. For an example, carbon has three isotopes namely ^{12}C, ^{13}C and ^{14}C. Therefore commonly average atomic mass of elements are used as the atomic mass.

3.3.2 Calculation of average atomic mass of elements

The average atomic mass of any atom can be calculated in the following way, illustrated for carbon and chlorine as typical elements.

Example 1:

The calculation of average atomic mass of natural carbon.

The mass percentage of the isotopes in a sample of carbon is 98.89% of ^{12}C, 1.11% of ^{13}C and the amount of ^{14}C is negligibly small.

Mass of a sample of 100 natural carbon atoms $= [(98.89 \times 12\ u) + (1.11 \times 13\ u)]$

The average atomic mass of natural carbon atom $= [(98.89 \times 12\ u) + (1.11 \times 13\ u)]/\ 100$

$= 12.01\ u$

Example 2:

The calculation of average atomic mass of chlorine.

The mass percentage of the isotopes in a sample of chlorine is 75.77% of ^{35}Cl and 24.23% of ^{37}Cl.

.

Mass of a sample of 100 natural chlorine atoms $= [(75.77 \times 35\ u) + (24.23 \times 37\ u)]$

The average atomic mass of natural chlorine atom $= [(75.77\times34.97\ u)+(24.23\times36.97\ u)]/\ 100$

$= 35.45\ u$

3.3.3 Mole

The amount of substance containing the same number of units/ entities equal to the number of atoms in exactly 12 g of ^{12}C or Avogadro's number is referred to as one mole.

Given below are examples for the number of entities contained in one mole of elements, molecules or ions.

1 mol of ^{12}C contains 6.022×10^{23} of ^{12}C atoms.

1 mol of $C_6H_{12}O_6$ contains 6.022×10^{23} of $C_6H_{12}O_6$ molecules.

1 mol of $CaCl_2$ contains 6.022×10^{23} of Ca^{2+} ions.

This concept can be used to understand further the relationship between the use of u and gram to count the number of atoms. Since 6.022×10^{23} atoms of ^{12}C have a mass of exactly 12 g, and each ^{12}C atom has a mass of 12 u, then,

$1\ u = 1.66 \times 10^{-24}\ g$

$6.022 \times 10^{23}\ u = 1\ g$

$(6.022 \times 10^{23}\ \text{atoms}) \times (12\ u/1\ \text{atom}) = 12.00\ g$

3.3.4 Molar mass

The molar mass is the mass of one mole of the substance. This is calculated as the mass of the given substance (chemical element or chemical compound) divided by the amount (moles) of that substance. The SI unit of molar mass is kg mol^{-1}. However usually molar mass is expressed in g mol^{-1}.

$$\text{molar mass of O} = 16.00\ \text{g mol}^{-1}$$
$$\text{molar mass of } H_2 = 2 \times 1.008\ \text{g mol}^{-1} = 2.016\ \text{g mol}^{-1}$$
$$\text{molar mass of } H_2O = (2 \times 1.008\ \text{g mol}^{-1}) + 16.00\ \text{g mol}^{-1}$$
$$= 18.016\ \text{g mol}^{-1}$$

A mass of 18.016 g of water contains, Avogadro constant (one mol) of water molecules.

Example 3.1
Calculate the molar mass of NaCl.

Answer:

Molar mass of Na^+ = 22.99 g mol^{-1}
Molar mass of Cl^- = 35.45 g mol^{-1}
Molar mass of NaCl = 22.99 g mol^{-1} + 35.45 g mol^{-1}
= 58.44 g mol^{-1}

A mass of 58.44 g NaCl contains one mole of Na^+ ions and one mol of Cl^- ions. It also contains one mole of NaCl.

3.4 Types of chemical formulae

The chemical formula is used to represent the type of atoms and the number of atoms with the element symbols of each atom showing their exact numbers. More than one type of chemical formulae can be used to represent information of a compound. Two types of chemical formulae are discussed in this section which are used for chemical calculations.

(a) Empirical formula

This is the simplest type of formula derived from the composition of the atomic masses of the elements in a compound. The relative number of atoms of each element in a compound is shown using the empirical formula.

e.g.: For hydrogen peroxide (H_2O_2), the empirical formula is HO.
For ethane (C_2H_6), the empirical formula is CH_3.
For benzene (C_6H_6), the empirical formula is CH.
For ethyne (C_2H_2), the empirical formula is CH.

(b) Molecular formula

The molecular formula is the formula that shows the actual number of atoms of each element in a molecule of a compound.

e.g.: The molecular formula of hydrogen peroxide is H_2O_2.
The molecular formula of ethane is C_2H_6.
The molecular formula of benzene is C_6H_6.
The molecular formula of ethyne is C_2H_2.

3.4.1 Chemical calculations using chemical formulae

Mass percentage of an element in the chemical formula

The mass percentage of a given element in a compound can be determined using the following equations.

$$\boxed{\text{Mass \% of element A} = \frac{\text{moles of A in formula} \times \text{atomic mass of A (g mol}^{-1})}{\text{molar mass of the compound (g mol}^{-1})} \times 100}$$

Always cumulative individual mass percentages of all elements in a compound adds up to 100%. As an example the calculation of mass percentage of carbon and hydrogen of ethane is given below.

Example 3.2

Calculate the mass percentage of carbon and hydrogen of ethane

Answer:

Molecular formula of ethane is C_2H_6.

Two moles of carbon and six moles of hydrogen are present in one mole of ethane.

$$\text{Mass percentage of carbon} = \frac{2\text{ mol} \times 12\text{ g mol}^{-1}}{(2\text{ mol} \times 12\text{ g mol}^{-1}) + (6\text{ mol} \times 1\text{ g mol}^{-1})} \times 100$$

$$= 80\%$$

$$\text{Mass percentage of hydrogen} = \frac{6\text{ mol} \times 1\text{ g mol}^{-1}}{(2\text{ mol} \times 12\text{ g mol}^{-1}) + (6\text{ mol} \times 1\text{ g mol}^{-1})} \times 100$$

$$= 20\%$$

3.4.2 Determination of the empirical and molecular formula of a compound

Basic steps to determine the empirical formula

1. Obtain the mass of each element present in the compound concerned in grams.
2. Divide each mass by the molar mass of the corresponding element to determine the number of moles of each type of element present.
3. Divide the number of moles of each element by the smallest number of moles obtained in step 2, to convert the smallest number to 1. If all numbers produced are integers or very close to integers, then these numbers represent the subscript values of each element in the empirical formula. However, if one or more numbers are not integers, then follow the step 4.

4. Multiply the numbers produced at the end of step 3 by the smallest possible integer that will convert all of them to whole numbers.
   (When the decimal value is less than 2 or more than 8, round off the number to the closest integer).
   These numbers represent the subscript values of each element in the empirical formula.

3.4.3 Determination of molecular formula using the empirical formula mass and molecular mass

1. Calculate the empirical formula mass from the empirical formula.
2. Divide the molecular mass by the empirical formula mass.
3. The division produces a whole number.
4. Multiply the subscripts in the empirical formula by this number to determine the molecular formula.

An example to understand the above process is given below.

Example 3.3

Determine the molecular formula of a compound with the elemental percentages of Cl = 71.65%, C =24.27% and H = 4.07% and the molar mass of the compound is 98 g mol^{-1}

Answer:

Step 01: Mass percentages: Cl = 71.65%, C = 24.27%, H = 4.07%

Step 02: In 100 g of the compound; Cl= 71.65 g, C=24.27 g and H=4.07 g
Atomic masses of Cl = 35.5, C = 12 and H = 1.
In 100 g of the compound, number of moles present;
Moles of Cl = 71.65 g/35.5 g mol^{-1} = 2.043 mol
Moles of C = 24.27 g/ 12 g mol^{-1} = 2.022 mol
Moles of H = 4.07 g/ 1 g mol^{-1} = 4.07 mol

Step 03: Cl = 2.043 ÷ 2.022 = 1.01 C = 2.022 ÷ 2.022 = 1 H = 4.07 ÷ 2.022 = 2.01

Step 04: Empirical formula = CH_2Cl
Empirical formula mass = 49 g mol^{-1}

If molar mass of the compound is known, then the chemical formula of the compound can be determined.

Step 05: $$\frac{\text{Molecular formula mass}}{\text{Empirical formula mass}} = 98 \text{ g mol}^{-1} \div 49 \text{ g mol}^{-1} = 2$$

Molecular formula = (empirical formula) × 2
= $(CH_2Cl)_2 \times 2$ = $C_2H_4Cl_2$

3.5 Composition of a substance in a mixture

3.5.1 Composition given in fractions

Three common methods are used to express the composition of a substance in a mixture based on fraction values.

Equation		
Mass fraction of A (w/w)	=	$\frac{\text{mass of A}}{\text{total mass of each substance in the mixture}}$
Volume fraction of A (v/v)	=	$\frac{\text{volume of A}}{\text{total volume of the mixture}}$
Mole fraction of A (x_A)	=	$\frac{\text{amount of moles of A}}{\text{total number of moles in the mixture}}$

Explanation of fractions using mole fraction

The mole fraction (x), is the ratio between the amount of moles of a component and the total amount of moles of all the components present in the mixture.

e.g.: The mole fraction of solute (A) dissolved in a solution is the number of moles of that component (n_A) divided by the total number of moles of all the components in the mixture ($n_A + n_B + n_C + \ldots\ldots$).

$$\boxed{\text{Mole fraction on of A } (x_A) \; = \; \frac{n_A}{n_A + n_B + n_C + \ldots}}$$

3.5.2 Percentage composition in a solution (homogeneous mixture)

Equation		
Mass percent (w/w)	=	$\frac{\text{mass of the solute}}{\text{mass of the solution}} \times 100$
Volume percent (v/v)	=	$\frac{\text{volume of the solute}}{\text{volume of the solution}} \times 100$
Mole percentage	=	$\frac{\text{moles of the solute}}{\text{total number of moles of solute and solvent}} \times 100$

Since numerator and denominator are expressed with the same units, final expression do not have units.

The composition of a solution can be specified using the amount of solute present in a given quantity of the solution. One such common way to describe the composition of a solution in terms of the mass percentage is given below.

e.g.: using mass percentage

$$\text{Mass percent} = \frac{\text{mass of the solute}}{\text{mass of the solution}} \times 100\%$$

$$\text{Mass percent} = \frac{\text{mass of the solute}}{\text{mass of the solute} + \text{mass of the solvent}} \times 100\%$$

When the mass of the solute is very small compared to the mass of the solution (homogeneous mixture), the composition of the solute can be expressed as follows.

Equation			Alternative expression of composition
parts per thousand (ppt)	=	$\frac{\text{mass of the solute}}{\text{mass of the solution}} \times 10^3$	g kg^{-1} mg g^{-1}
parts per million (ppm)	=	$\frac{\text{mass of the solute}}{\text{mass of the solution}} \times 10^6$	mg kg^{-1} µg g^{-1}
parts per billion (ppb)	=	$\frac{\text{mass of the solute}}{\text{mass of the solution}} \times 10^9$	µg kg^{-1}

When volume of the solute is very small compared to the volume of the solution (homogeneous mixture), the composition of the solute can be expressed as follows.

Equation			Alternative expression of composition
parts per thousand (ppt)	=	$\frac{\text{volume of the solute}}{\text{volume of the mixture}} \times 10^3$	mL L^{-1}
parts per million (ppm)	=	$\frac{\text{volume of the solute}}{\text{volume of the mixture}} \times 10^6$	µL L^{-1}
parts per billion (ppb)	=	$\frac{\text{volume of the solute}}{\text{volume of the mixture}} \times 10^9$	nL L^{-1}

For dilute solutions composition can be expressed using weight/volume. It can be expressed in ppm and ppb. These can be given in alternative units of mg dm^{-3} and µg dm^{-3} respectively.

Metric prefixes are used to distinguish between units of different size and it is useful to describe quantities in a more scientific manner (see Table 3.6).

Table 3.6 Metric prefixes

Metric Prefix	Metric Symbol	Multiple	Metric Prefix	Metric Symbol	Multiple
tera-	T	10^{12}	deci-	d	10^{-1}
giga-	G	10^{9}	centi-	c	10^{-2}
mega-	M	10^{6}	milli-	m	10^{-3}
kilo-	k	10^{3}	micro-	µ	10^{-6}
hecto-	h	10^{2}	nano-	n	10^{-9}
deca-	da	10^{1}	pico-	p	10^{-12}

Example 3.4
Calculate the mole fraction and the mole percentage of a 20.0% hydrogen peroxide solution by mass.

Answer:

Mole fraction of H_2O_2 ($X_{H_2O_2}$) $= n_{H_2O_2}/n_{\text{total}} = \dfrac{(\text{moles of } H_2O_2)}{[(\text{moles of } H_2O_2 + (\text{moles of } H_2O)]}$

In the hydrogen peroxide solution, mass of H_2O_2 = 200.0 g, mass of H_2O
= 800.0 g

moles of H_2O_2 = 200.0 g/ 34 g mol^{-1} = 5.88 mol
moles of H_2O = 800.0 g/ 18 g mol^{-1} = 44.44 mol
Mole fraction of H_2O_2 = 5.88 mol/ (5.88 + 44.44) mol = 0.116
Mole percentage of H_2O_2 = mole fraction ($X_{H_2O_2}$) × 100 = 11.6%

3.5.3 Molality *

The molality (m) of a solution is the amount of moles of the solute per kilogram of the solvent.

Equation			Unit
Molality	=	$\dfrac{\text{moles of the solute}}{\text{mass of the solvent}} = \dfrac{\text{mol}}{\text{kg}}$	mol kg^{-1}
Molality	=	$\dfrac{\text{milimoles of the solute}}{\text{mass of the solvent}} = \dfrac{\text{mmol}}{\text{kg}}$	mmol kg^{-1}

e.g.: Sucrose solution contains 1.25 mol of sucrose (solute) in every kilogram of water (solvent). Therefore the molality of the sucrose solution is 1.25 mol kg^{-1}.

**Not relevant to current G. C. E. (A/L) syllabus*

3.5.4 Molarity (Commonly used to express concentration)

The volume of a solution can be measured more conveniently than its mass. The concentration of a solution is defined as the number of moles of solute in a litre or one cubic decimetre volume of a solution. The SI unit of molarity (M) is mol m^{-3}. However more commonly used unit is mol dm^{-3} or mol L^{-1}.

e.g.: A 1.25 mol dm^{-3} or 1.25 M sucrose solution contains 1.25 moles of sucrose (solute) in 1 dm^3 of solution.

Equation			Unit
Molarity	=	$\frac{\text{moles of the solute}}{\text{volume of the solution}} = \frac{\text{mol}}{\text{dm}^3}$	mol dm^{-3}
Molarity	=	$\frac{\text{milimoles of the solute}}{\text{volume of the solution}} = \frac{\text{mmol}}{\text{dm}^3}$	mmol dm^{-3}

The amounts of water used to prepare 1.25 mol dm^{-3} and 1.25 mol kg^{-1}, sucrose solutions are not the same due to the density criteria. This means, for a given solution, the molarity and the molality are not the same, however the difference can be negligible for dilute solutions.

Examples 3.5

A solution of NaCl is prepared by mixing 10 mg of NaCl and 500 g of water. Calculate the molality and the composition (in ppm) of the solution.

Answer:

To calculate the molality of the solution,
Molality (m) = moles of the solute/ mass of the solvent
Amount of moles of NaCl = 0.01 g/ 58.5 g mol^{-1} = 1.71×10^{-4} mol
Molality (m) = moles of the solute/ mass of the solvent = 1.71×10^{-4} mol/ 0.5 kg
= 3.42×10^{-4} mol kg^{-1}

Composition of NaCl (ppm)
Composition = (mass of NaCl (in grams)/ mass of the solution (in grams)) × 10^6
= (0.01 g/(500 + 0.01)g)× 10^6 = 19.9 ppm

3.6 Balancing chemical reactions

The chemicals initially involved in a reaction are called reactants. Substances formed from a chemical reaction are called products. Chemical changes can yield one or more products. A chemical change such as carbon combining with oxygen to produce carbon dioxide is an example of a chemical reaction. This chemical reaction can be represented using the chemical equation given below.

$$\underset{\text{Reactants}}{C(s) + O_2(g)} \longrightarrow \underset{\text{Products}}{CO_2(g)}$$

During a chemical reaction, atoms are neither created nor destroyed. Hence, there is a mass balance between reactants and products. In other words the total number of atoms in the reaction molecules is equal to the total number of atoms in the product molecules. A chemical reaction which depicts the aforesaid material balance is known as a **balance chemical reaction**.

Any balanced chemical reaction must obey these rules.

Rules for balancing a chemical equation

(a) Number of atoms of the reactant side must be equal to the respective numbers of atoms of the product side.
(b) Formulae of reactants and products must never be changed to balance a given chemical equation.
(c) All parts of any balanced chemical equation can be divided or multiplied by any number to produce a new balanced equation.
(d) The best balanced (accepted) equation is the one that has the smallest whole number ratio between reactants and products. These integers are called **"coefficients"** of the balanced equation. These coefficient numbers are expressed as **stoichiometric numbers** in a balanced equation.

There are two methods of balancing chemical equations.

(a) Inspection method
(b) Redox method

3.6.1 Balancing a chemical reaction by inspection method

Step 1: Identify the reactants, products and their physical states. Write the appropriate formulae and the unbalanced chemical equation.
Step 2: Balance the equation by inspection, starting with the element/s which appears at the least number of places. Continue element by element to determine the coefficients to balance the atoms on both the reactants and products.
Step 3: Use coefficients to balance the atoms/ ions on both sides of the arrow. Also, check whether the coefficients used are the smallest integers that can be used to balance the equation.

Simple chemical equations can be balanced using the inspection method. Consider the examples given below.

Example 1:Reaction between sulfuric acid and sodium hydroxide to produce sodium sulphate and water.

Step 1: Reactants = sulfuric acid and sodium hydroxide
Products = sodium sulfate and water
Unbalanced chemical equation:

$H_2SO_4 + NaOH \longrightarrow Na_2SO_4 + H_2O$

Step 2: Balancing the chemical equation using sodium atoms on the product side. The total number of sodium atoms on the product side is two. Therefore the coefficient of the reaction with respect to sodium is 2.

Then the chemical equation is,

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

Step 3: Balance the rest of the atoms/ ions on both sides of the arrow.

The balanced chemical equation:

$H_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O$

The balanced chemical equation with the physical states is given below.

$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$

Example 2: Reaction between nitrogen and hydrogen to produce ammonia.

Step 1: Reactants = nitrogen and hydrogen

Products = ammonia

Unbalanced chemical equation:

$N_2 + H_2 \longrightarrow NH_3$

Step 2: Balancing the chemical equation using nitrogen atoms on the reactant side. The total number of nitrogen atoms on the reactant side is two. Therefore the coefficient of the reaction with respect to nitrogen is 2.

Then the chemical equation is,

$N_2 + H_2 \longrightarrow 2NH_3$

Step 3: Using the coefficients balance the atoms/ions on both sides of the arrow.

The balanced chemical equation:

$N_2 + 3H_2 \longrightarrow 2NH_3$

The balanced chemical equation with the physical states is given below.

$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$

3.6.2 Balancing a chemical reaction by the redox method

Redox reactions are a type of chemical interactions that involve the change of oxidation number of atoms. The redox reactions are balanced using the following methods.

Method 01 - Oxidation number change method

This considers the change in oxidation number and uses them as coefficients of reactants.

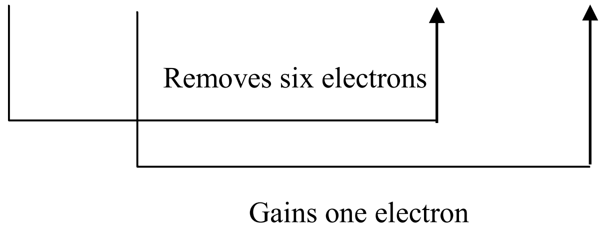
As an example, the reaction between S and HNO_3 is shown below. The following steps are applied to balance the equation.

Step 1: Correctly write the formulae for the reactants and the products of the chemical reaction.

$S(s) + HNO_3(aq) \longrightarrow H_2SO_4(aq) + NO_2(aq) + H_2O(l)$

Step 2: Determine correctly the atoms that undergo oxidation and reduction and calculate the oxidation number change as shown below in the cited example.

$$\underset{0}{S(s)} + \underset{+5}{HNO_3(aq)} \longrightarrow \underset{+6}{H_2SO_4(aq)} + \underset{+4}{NO_2(aq)} + H_2O(l)$$



Step 3: If the oxidation number change is not equal then multiply it to such a number, so that these numbers become equal as shown below. (The number of electrons exchange should be equal.)

$$S(s) + 6HNO_3(aq) \longrightarrow H_2SO_4(aq) + 6NO_2(aq) + H_2O(l)$$

Step 4: Balance the remaining atoms.

$$S(s) + 6HNO_3(aq) \longrightarrow H_2SO_4(aq) + 6NO_2(aq) + 2H_2O(l)$$

Method 02 - Half reaction method

In every oxidation-reduction reaction, one reactant is reduced and another reactant is oxidized. In some cases the same atom in the reactant is oxidized and reduced and such reactions are called disproportionation reactions. These two reactions (oxidation and reduction) are referred to as half reactions. The relevant steps to identify and balance the redox reaction using half reactions is given below.

Steps to balance redox reactions

Step A: Split the reaction into two half ionic reactions.

Step B: Balance both half ionic equations separately.

Step C: Combine the two half reactions to give a simplified balance equation and the final balanced chemical reaction.

example: Reaction of $K_2Cr_2O_7$ with SO_2 in the presence of $H_2SO_4(aq)$ giving Cr^{3+} ions and SO_4^{2-} ions as main products.

Step A: Split the reaction into two half reactions.

$$Cr_2O_7^{2-} + SO_2 \longrightarrow Cr^{3+} + SO_4^{2-}$$

Two half reactions are:

$$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$$
$$SO_2 \longrightarrow SO_4^{2-}$$

Step B: Balance both half equations separately.

Methodology for step B.

Step 1: Assign oxidation numbers to each element on both sides of the reaction.
Step 2: Balance the atoms of each element being oxidized or reduced.
Step 3: Multiply the oxidation number by the number of atoms to obtain the “total” oxidation number on both sides.
Step 4: Balance the difference of oxidation number of half reaction by adding electrons to the other side.
Step 5: Balance the charge by adding H^+ ions in acidic solutions and OH^- ions in basic solutions.
Step 6: Balance the hydrogen/oxygen by adding H_2O molecules.
Step 7: Check the atoms on both sides.

Balance each half reaction using the methodology given in Step B as follows.
Reduction of $Cr_2O_7^{2-}$ to Cr^{3+} ions in acidic medium

Step 1: Assign oxidation number of chromium.

$$\begin{array}{ccc} Cr_2O_7^{2-}(aq) & \longrightarrow & Cr^{3+}(aq) \\ (+6) & & (+3) \end{array}$$

Step 2: Balance the chromium atoms of both sides.

$$Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq)$$

Step 3: Multiply the oxidation number by the number of atoms to get the total oxidation number on both sides.

$$\begin{array}{ccc} Cr_2O_7^{2-}(aq) & \longrightarrow & 2Cr^{3+}(aq) \\ (+6) \times 2 & & (+3) \times 2 \end{array}$$

The difference of oxidation number is six.
(+12 to +6)

Step 4: Add electrons to balance the difference of oxidation number.

$$6e + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq)$$

Calculate the total charge of both sides.

$$\underbrace{6e + Cr_2O_7^{2-}(aq)}_{\text{total charge is minus eight}} \longrightarrow \underbrace{2Cr^{3+}(aq)}_{\text{total charge is plus six}}$$

Step 5: Then add H^+ ions to balance the charge.

$$14H^+(aq) + 6e + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq)$$

Step 6: Balance the hydrogen by adding H_2O molecules.

$$14H^+(aq) + 6e + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Step 7: Check the atoms on both sides for balance.

$$14H^+(aq) + 6e + Cr_2O_7^{2-}(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$

Oxidation of SO_2 to SO_4^{2-} ions in acidic medium

Steps 1, 2 and 3:

$$\underbrace{\underset{(+4)}{SO_2(g)} \longrightarrow \underset{(+6)}{SO_4^{2-}(aq)}}_{\text{The difference of oxidation number is two.}}$$

Step 4: Add electrons to balance the difference of oxidation number

$$SO_2(g) \longrightarrow SO_4^{2-}(aq) + 2e$$

Step 5: Calculate the total charge of both sides.

$$\underbrace{SO_2(g)}_{\substack{\text{total charge}\\ \text{is zero}}} \longrightarrow \underbrace{SO_4^{2-}(aq)}_{\substack{\text{total charge is}\\ \text{minus four}}} + 2e$$

Then add H^+ ions to balance the charge.

$$SO_2(g) \longrightarrow SO_4^{2-}(aq) + 2e + 4H^+(aq)$$

Steps 6 and 7: Add H_2O molecules to balance hydrogen.

$$2H_2O(l) + SO_2(g) \longrightarrow SO_4^{2-}(aq) + 2e + 4H^+(aq)$$

Step C: Combine the two half reactions to give a simplified balanced equation and the final balanced chemical reaction.

Multiply the oxidation half equation by 3 to equalise the electrons on both sides.
The combined equation is,

$$14H^+(aq) + Cr_2O_7^{2-}(aq) + 3SO_2(g) + 6H_2O(l) + 6e \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + 12H^+(aq) + 7H_2O(l) + 6e$$

Simplified equation (balanced ionic equation) is,

$$2H^+(aq) + Cr_2O_7^{2-}(aq) + 3SO_2(g) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$$

and the balanced chemical equation is,

$$H_2SO_4(aq) + K_2Cr_2O_7(aq) + 3SO_2(g) \longrightarrow Cr_2(SO_4)_3(aq) + K_2SO_4(aq) + H_2O(l)$$

The information that can be obtained from balanced reactions

- The number of moles that react with each other in a reaction.
- The number of moles of products that are formed.
- The number of electrons that are involved in the redox reaction.

Thus in the reaction of $K_2Cr_2O_7$ with SO_2 in the presence of H_2SO_4(aq) discussed above,

1. $K_2Cr_2O_7$ is an ionic compound. One ion of $Cr_2O_7^{2-}$ reacts with three molecules of SO_2.
2. One mole of $K_2Cr_2O_7$ reacts with three moles of SO_2 to produce one mole of $Cr_2(SO_4)_3$, one mole of K_2SO_4 and one mole of H_2O.

Two other examples to illustrate the applications of balancing equations using the half reaction method are given below.

Example 3.6

Balance the redox ionic equation for the reaction between Fe^{2+}(aq) and NO_3^- (aq) in basic medium.

$Fe^{2+}(aq) + NO_3^-(aq) \longrightarrow Fe^{3+}(aq) + NO(g)$

Answer:

Balance half reactions:

Oxidation half reaction: $Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e$ ------ (1)

Reduction half reaction: $NO_3^-(aq) + 2H_2O(l) + 3e \longrightarrow NO(g) + 4OH^-(aq)$ ----- (2)

Multiply the oxidation half equation (1) by 3.

$3[Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e]$

$3Fe^{2+}(aq) \longrightarrow 3Fe^{3+}(aq) + 3e$ ----- (3)

Combine half equations (3) and (2).

$3Fe^{2+}(aq) + NO_3^-(aq) + 2H_2O(l)\ ) +3e \longrightarrow 3Fe^{3+}(aq) + NO(g) + 4OH^-(aq) + 3e$

Eliminate electrons.

$3Fe^{2+}(aq) + NO_3^-(aq) + 2H_2O(l) \longrightarrow 3Fe^{3+}(aq) + NO(g) + 4OH^-(aq)$

Example 3.7

Balance the redox ionic equation for the reaction between MnO_4^- and Fe under basic medium.

$MnO_4^- + Fe \longrightarrow MnO_2 + Fe^{2+}$

Answer:

Balance half reactions:

Oxidation half reaction: $Fe \longrightarrow Fe^{2+} + 2e$ ------ (1)

Reduction half reaction: $2H_2O + 3e + MnO_4^- \longrightarrow MnO_2 + 4OH^-$ ----- (2)

Multiply the oxidation half equation (1) by 3 and reduction half equation (2) by 2 and eliminate electrons while combining the two half equations.

$3Fe + 2MnO_4^- + 4H_2O \longrightarrow 3Fe^{2+} + 2MnO_2 + 8OH^-$

Limiting reagent/ reactant

In a reaction mixture, the reactant that is completely consumed is called the limiting reactant. Other reactants are called excess reactants. The following example shows the use of limiting reagent concept to calculate the amount of product produced by a given reaction.

Example: How many moles of NH_3 can be produced from 3 mol of N_2 and 6 mol of H_2?

Balanced chemical equation;

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

The number of moles of H_2 required to complete consumption of 3 moles of N_2
= number of moles of N_2 × 3 = 9 mol
The required amount of moles is greater than the available amount of moles of H_2.
Therefore the limiting reagent is H_2.

The amount of N_2 moles required for complete consumption of 6 moles of H_2.
= amount of H_2 moles × 1/3 = 2 mol
The required number of moles of N_2 is less than the available number of moles of N_2.
Therefore the excess reagent is N_2.
Based on the amount of limiting reagent (H_2), the amount of product (NH_3) formed
= amount of H_2 moles × 2/3 = 6 mol × 2/3 = 4 moles of NH_3

3.6.3 Balancing simple nuclear reactions

Radioactive nuclide can undergo radioactive decay by ejecting nuclear particles/electrons or producing energy in the form of gamma (γ) radiation. General characteristics of such emissions are given in Table 3.7.

Table 3.7 Characteristics of α, β and γ emissions

Name	Symbol	Charge	Mass
Alpha	${}^{4}_{2}He^{2+}, {}^{4}_{2}\alpha$	+2	Equal to the mass of a helium atom
Beta	${}^{0}_{-1}e,\ {}^{0}_{-1}\beta$	-1	Equal to the mass of an electron
Gamma	${}^{0}_{0}\gamma$, γ	0	No mass

The spontaneous change of a radioactive isotope of one element into an isotope of a different or same element is known as **radioactivity**. Such changes are called nuclear reactions or transmutations.

For example, radioactive decay of ${}^{226}_{88}Ra$ to ${}^{222}_{86}Rn$ can be written as follows.

$$\underset{\text{Parent nucleus}}{{}^{226}_{88}Ra} \longrightarrow \underset{\text{Daughter nucleus}}{{}^{222}_{86}Rn} + {}^{4}_{2}He$$

Rules for balancing nuclear reactions

Rule 01 The sum of the mass numbers of reacting nuclei must be equal to the sum of the mass numbers of the nuclei produced.

Rule 02 The sum of the atomic numbers of reacting nuclei must be equal to the sum of the atomic numbers of the nuclei produced.

Application of these rules are illustrated in the two examples given below.

Example 1:

	${}^{226}_{88}\mathrm{Ra}$	$\longrightarrow$	${}^{4}_{2}\mathrm{He}$	+	${}^{222}_{86}\mathrm{Rn}$
	Parent nucleus (Radium 226)		Alpha particle		Daughter nucleus (Radon 222)
Mass number :	226	$\longrightarrow$	4	+	222
Atomic number:	88	$\longrightarrow$	2	+	86

Example 2:

	${}^{7}_{4}\mathrm{Be}$	+	${}^{0}_{-1}\mathrm{e}$	$\longrightarrow$	${}^{7}_{3}\mathrm{Li}$
	Parent nucleus (Beryllium 7)		Beta particle		Daughter nucleus (Lithium 7)
Mass number :	7	+	0	$\longrightarrow$	7
Atomic number:	4	+	-1	$\longrightarrow$	3

In some nuclear reactions protons (${}^{1}_{1}\mathrm{p}$) and neutrons (${}^{1}_{0}\mathrm{n}$) are also involved.

3.7 Preparation of solutions

When a solute is dissolved in a solvent to form a homogeneous mixture it is known as a solution.

The solutions prepared with exactly known concentrations are called **standard solutions**. These standard solutions are standardized against primary standards. If a standard solution is prepared by using extremely pure, stable, not hydrated and highly water soluble compounds with higher molecular weights are considered as primary standards. Few examples for such compounds are anhydrous Na_2CO_3, $K_2Cr_2O_7$, and KIO_3.

A secondary standard is a chemical that has been standardized against a primary standard for use in specific analysis.

Solutions with known concentration can be prepared using the following methods and the exemplary procedures are given below.

Methods:

1. Dissolving an accurately measured mass or volume of a pure compound in a suitable solvent
2. Diluting a stock (concentrated) solution

Different ways of preparing solutions using the two methods indicated above are given below.

1. Preparation of 500.00 cm^3 of 1.0 mol dm^{-3} Na_2CO_3 solution

a. Calculate the required number of moles and then the required mass of Na_2CO_3.
b. Accurately weigh the required amount of Na_2CO_3 using a balance.
c. Place the Na_2CO_3 weighed in a 500.00 cm^3 volumetric flask and dissolve well with distilled water (The solute should be dissolved completely by using a minimum amount of water).
d. Dilute the solution up to 500.00 cm^3 mark, using distilled water and mix well to make a homogeneous solution.

2. Preparation of 250.00 cm^3 of 1.0 mol dm^{-3} HCl solution from conc. HCl solution (36% (w/w) with a density of 1.17 g ml^{-1} (1.17 g cm^{-3})

a. First calculate the concentration of the conc. HCl as follows.

Mass of HCl in 1 dm^3 of conc. HCl acid $= 1.17 \text{ g cm}^{-3} \times 1000 \text{ cm}^3 \times 36\%$
$= 421.2 \text{ g}$
Number of HCl moles in 1 dm^3 of conc. HCl $= 421.2 \text{ g} \div 36.5 \text{ g mol}^{-1}$
Concentration of the conc. HCl acid solution $= 11.5 \text{ mol dm}^{-3}$

b. Calculate the number of moles require to prepare the desired solution.

Amount of HCl moles in 250.00 cm^3 of 1.0 mol dm^{-3} HCl solution
$= (1.0 \text{ mol} \times 250 \text{ cm}^3) \div 1000 \text{ cm}^3$
$= 0.25 \text{ mol}$

The required volume of the concentrated HCl solution is v cm^3 (mL).

The calculation of volume v:
$0.25 \text{ mol} = (11.5 \text{ mol} \times v) \div 1000 \text{ cm}^3$
$v = 21.7 \text{ cm}^3$

c. Preparation of the solution

Accurately measured volume of 21.7 cm^3 of concentrated HCl is diluted up to the mark of the volumetric flask to prepare the solution of 250.00 cm^3 of 1.0 mol dm^{-3} HCl.

3. **Preparation of 100.00 cm^3 of 0.2 mol dm^{-3} Na_2CO_3 solution using 1.0 mol dm^{-3} Na_2CO_3 as the stock solution**
    a. Calculate the number of moles in 100.00 cm^3 of 0.2 mol dm^{-3} Na_2CO_3 solution.
    b. Calculate the volume of 1.0 mol dm^{-3} Na_2CO_3 needed to prepare 100.00 cm^3 of 0.2 mol dm^{-3} Na_2CO_3 solution.
    c. Accurately measure the calculated volume from 1.0 mol dm^{-3} Na_2CO_3 solution and place the solution in a 100.00 cm^3 volumetric flask.
    d. Dilute the solution up to 100.00 cm^3 mark using distilled water.

4. **Preparation of 250.00 cm^3 of 1 mol dm^{-3} HCl solution from 6 mol dm^{-3} stock solution of HCl.**

Assume the volume required from 6 mol dm^{-3} HCl solution is v cm^3.

The calculation for volume v is:
$0.25 \text{ mol} = 6 \text{ mol} \times v/1000 \text{ cm}^3$
$v = 41.6 \text{ cm}^3$

Then accurately measure the volume of 41.60 cm^3 of the 6 mol dm^{-3} HCl solution and add into a 250.00 cm^3 volumetric flask. Dialute up to the mark with distilled water to prepare the required solution.

5. **Preparation of 250.00 cm^3 of 1 mol dm^{-3} HCl solution by mixing of two stock solutions (example: 3 mol dm^{-3} and 0.5 mol dm^{-3} HCl solutions)**

Assume the volume required from the 3 mol dm^{-3} HCl be v cm^3.
Therefore the volume required from the 0.5 mol dm^{-3} HCl be (250.00 - v) cm^3.
Then the required number of moles of HCl in the solution to be prepared is 0.25 mol.

The calculation for volume v is:
$(v \times 3 \text{ mol dm}^{-3}/1000) + ((250.00 - v) \times 0.5 \text{ mol dm}^{-3}/1000) = 0.25 \text{ mol}$
$v = 50.00 \text{ cm}^3$
The volume required from 3 mol dm^{-3} HCl = 50.00 cm^3
The volume required from 0.5 mol dm^{-3} HCl = (250.00 - 50.00) cm^3

Mix 50.00 cm^3 of 3 mol dm^{-3} HCl and 200.00 cm^3 of 0.5 mol dm^{-3} HCl to prepare the solution of 250.00 cm^3 of 1 mol dm^{-3} HCl.

3.8 Calculations based on chemical reactions

Chemical reactions can be used to determine the concentration of an aqueous solution with an unknown amount of a substance using a solution with a known concentration. The solution with the known concentration (standard solution) reacts with the solution of an unknown concentration at a known stoichiometry. At the point in which the solution with an unknown amount of substance completely reacts with the standard, the concentration of the unknown solution can be calculated using concentration of the standard solution and the stoichiometry of the reaction.

example 1: Acid-base reaction

Calculate the concentration of $Ba(OH)_2$ solution which is reacted with a standard solution of 0.1 mol dm^{-3} HNO_3. A volume required from 0.1 mol dm^{-3} HNO_3 to react completely with 25.00 cm^3 of $Ba(OH)_2$ is 34.00 cm^3.

The balanced chemical equation for the reaction between nitric acid and barium hydroxide is,

$$2HNO_3(aq) + Ba(OH)_2(aq) \longrightarrow Ba(NO_3)_2(aq) + 2H_2O(l)$$

Based on the balanced equation, two moles of HNO_3 react with one mole of $Ba(OH)_2$. Hence, the stoichiometry between HNO_3: $Ba(OH)_2$ is 2:1.

The calculation of the number of moles of HNO_3 consumed :

Amount of HNO_3 consumed $= 0.1\text{ mol} \times \frac{34.00\text{ cm}^3}{1000\text{ cm}^3} = 0.0034\text{ mol}$

Amount of HNO_3 consumed = Amount of $Ba(OH)_2$ in 25.00 cm^3 × 2

0.0034 mol = Concentration of $(Ba(OH)_2 \times 0.025\text{ dm}^3 \times 2$

Concentration of $Ba(OH)_2$ = 0.068 mol dm^{-3}

example 2: Redox reaction

Calculate the volume of 0.6 mol dm^{-3} $KMnO_4$ required to react completely with 27.00 cm^3 of 0.25 mol dm^{-3} $Fe(NO_3)_2$.

The balanced chemical reaction between MnO_4^- and Fe^{2+} is,

$$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 4H_2O(l)$$

The stoichiometry between MnO_4^-: $Fe^{2+}$is 1:5.

Amount of Fe^{2+} consumed $= 0.25\text{ mol} \times 27.00\text{ cm}^3/1000\text{ cm}^3$

$= 6.75 \times 10^{-3}$ mol

The amount of MnO_4^- required $= 6.75 \times 10^{-3}\text{ mol} \div 5$

The volume of $KMnO_4$ solution required is v cm^3.

The calculation of volume v:

$$6.75 \times 10^{-3}\text{ mol} \div 5 = 0.6\text{ mol dm}^{-3} \times v$$

$$v = 0.00225\text{ dm}^3 = 2.25\text{ cm}^3$$

example 3: Gravimetry
Calculate the mass of $BaSO_4$ that gets precipitated when a solution of 0.1 mol dm^{-3} $Ba(OH)_2$ completely reacts with 30.00 cm^3 of 0.2 mol dm^{-3} H_2SO_4 acid

The balanced chemical equation is,
$H_2SO_4(aq) + Ba(OH)_2(aq) \longrightarrow BaSO_4(s) + 2H_2O(l)$

Based on the balanced equation,
Calculation of the mass of $BaSO_4(s)$ formed

Amount of H_2SO_4 consumed = $0.2 \text{ mol dm}^{-3} \times \frac{30.00 \text{ cm}^3}{1000 \text{ cm}^3} = 0.006 \text{ mol}$
Amount of $BaSO_4$ precipitated = 0.006 mol
Molar mass of $BaSO_4$ = 233 g mol^{-1}
Mass of $BaSO_4$ precipitated = $0.006 \text{ mol} \times 233 \text{ g mol}^{-1}$
= 1.4 g

Solved Problems

Question 1:

A soil sample contains hematite (iron(III) oxide) as the main compound.

(a) Calculate the mass percentages of iron and oxygen in iron(III) oxide?

(b) Calculate the number of grams of iron that can be extracted from one kilogram of Fe_2O_3?

(c) How many kilograms of hematite ore, whch contains 66.4% Fe_2O_3, should be processed to produce one kilogram of iron?

Answer:

(a) Mass % of Fe

$$\frac{\text{mass of two moles of Fe}}{\text{mass of one mole of Fe}_2\text{O}_3} \times 100 = \frac{112\ \text{g}}{160\ \text{g}} \times 100 = 70\%$$

Mass % of O

Mass % O = 100% - mass % Fe = 100% - 70 % = 30 %

(b) The mass of Fe extracted from one kilogram of Fe_2O_3

Mass of Fe_2O_3 $= 1.0 \times 10^3 g$

Percentage of Fe in Fe_2O_3 = 70%

Mass of Fe $= 1.0 \times 10^3 g \times \frac{70\ g}{100\ g}$

= 700 g

(c) Mass of hematite needed

Mass of Fe_2O_3 $= 1\ kg \times \frac{100\ g}{66.4\ g}$

Mass of hematite ore processed $= 1kg \times \frac{100\ g}{66.4\ g} \times \frac{100\ g}{70\ g}$

= 2.151 kg

Question 2

A student prepares a solution by mixing 4.0 mg of sodium ions (in the form of NaCl), 4.00 g of glucose ($C_6H_{12}O_6$), and 96 g of water.

(a) What is the molality of the glucose in solution?

(b) How many ppm of Na^+ does this solution contain?

Answer:

(a) molality $= \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$

moles of glucose $= \frac{4.0\ g}{180\ g\ mol^{-1}} = 0.022\ mol$

mass of solvent (water) in kg = 0.096 kg

$$\text{molality} = \frac{0.022\ \text{mol}}{0.096\ \text{kg}} = 0.23\ \text{mol kg}^{-1}$$

(b) Mass of the solution = 0.004 g + 4.00 g + 96 g = 100.004 g

$$\text{ppm of Na}^+ = \frac{\text{mass of Na}^+}{\text{mass of the solution}} \times 10^6$$

$$= \frac{0.004\ \text{g}}{100.004\ \text{g}} \times 10^6 = 39.99\ \text{ppm}$$

Question 3

A mixture of NaCl and KCl weighed 5.48 g. The sample was dissolved in water and treated with excess of silver nitrate ($AgNO_3$). The resulting AgCl weighed 12.70 g. Calculate the mass percentage of NaCl in the mixture?

$$AgNO_3(aq) + Cl^-(aq) \longrightarrow AgCl(s) + NO_3^-(aq)$$

Answer:

$$\text{Moles of AgCl} = \frac{12.70\ \text{g}}{143.32\ \text{g mol}^{-1}} = 0.088\ \text{mol}$$

Number of moles of NaCl + Number of moles of KCl = 0.088 mol

$$0.088\ \text{mol} = \frac{\text{mass of NaCl}}{58.48\ \text{g mol}^{-1}} + \frac{\text{mass of KCl}}{74.5\ \text{g mol}^{-1}}$$

Also, mass of NaCl + mass of KCl = 5.48 g

Assuming the mass of NaCl is x.

The mass of KCl = (5.48 g – x)

Calculation of x using the total number of moles of Cl^- ions:

$$0.088\ \text{mol} = \frac{x}{58.48\ \text{g mol}^{-1}} + \frac{(5.48\ \text{g} - x)}{74.5\ \text{g mol}^{-1}}$$

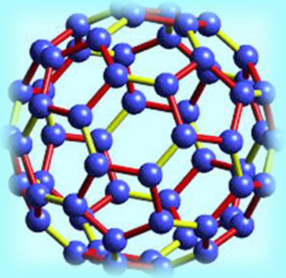
Mass of NaCl = x = 3.93 g

$$\text{Mass percentage of NaCl} = \frac{3.93\ \text{g}}{5.48\ \text{g}} \times 100 = 71.71\%$$

Table 3.8 A summary of equations

Equation	Units
$\textbf{Mass fraction of A (w/w)} = \dfrac{\text{mass of A}}{\text{mass of substance or mixture}}$	- -
$\textbf{Volume fraction of A (v/v)} = \dfrac{\text{volume of A}}{\text{volume of mixture}}$	-
$\textbf{Mole fraction of A } (x\text{A}) = \dfrac{\text{moles of A}}{\text{total moles of mixture}}$	-
$\text{Mass \% of element } x = \dfrac{\text{moles of } \boldsymbol{x} \text{ in formula} \times \text{molar mass of } \boldsymbol{x} \text{ (g mol}^{-1}\text{)}}{\text{molar mass of compound}} \times \mathbf{100}$	-
$\textbf{Mass Percent (w/w)} = \dfrac{\text{mass of the substance}}{\text{mass of the mixture}} \times \mathbf{100\%}$	-
$\textbf{Volume Percent (v/v)} = \dfrac{\text{volume of substance}}{\text{volume of mixture}} \times \mathbf{100\%}$	-
$\textbf{Parts per thousand (ppt)} = \dfrac{\text{mass of substance}}{\text{mass of mixture}} \times \mathbf{10^3}$	-
$\textbf{Parts per million (ppm)} = \dfrac{\text{mass of substance}}{\text{mass of mixture}} \times \mathbf{10^6}$	-
$\textbf{Parts per billion (ppb)} = \dfrac{\text{mass of substance}}{\text{mass of mixture}} \times \mathbf{10^9}$	-
$\textbf{Molality (m)} = \dfrac{\text{moles of solute}}{\text{mass of solvent}}$	mol kg^{-1}
$\textbf{Molarity (M)} = \dfrac{\text{moles of solute}}{\text{volume of solution}}$	mol dm^{-3}
$\textbf{Mole fraction of A } (x_A) = \dfrac{n_A}{n_A+n_B+n_C+\ldots}$	-

4. Chemistry of *s*, *p* and *d* Block Elements



Content

Introduction

This section describes the physical and chemical properties of elements in *s*, *p* and *d* blocks. This section will help to identify trends and patterns among elements in the periodic table.

s Block Elements

4.1 Group 1 elements

All Group 1 elements are metals except hydrogen which is a nonmetal. Unlike most other metals, they have low densities. All Group 1 elements have the valence shell electron configuration of ns^1 therefore they are highly reactive.

Sodium can be found naturally as various salts such as NaCl (rock salt) and $Na_2B_4O_7\cdot 10H_2O$ (borax). Some examples of naturally occurring potassium salts are KCl (sylvite) and $KCl.MgCl_2.6H_2O$ (carnallite).

4.1.1 Group trends

All alkali metals are lustrous. They are high electrical and thermal conductors. These metals are soft and become even softer when progress down the group. The melting point of Group 1 metals decreases down the group. The values given in Table 4.1 below can be used to understand the trends among these elements. Group 1 metals always show oxidation number of +1 when they form compounds. Most compounds are stable ionic solids.

Table 4.1 Properties of Group 1 elements

	Li	**Na**	**K**	**Rb**	**Cs**
Ground state electronic configuration	[He]2s^1	[Ne]3s^1	[Ar]4s^1	[Kr]5s^1	[Xe]6s^1
Metallic radius/ pm	152	186	231	244	262
Melting point/ °C	180	98	64	39	29
Radius of M^+/ pm	59	102	138	148	174
1st ionization energy/ kJ mol^{-1}	520	495	418	403	375
2nd ionization energy/ kJ mol^{-1}	7298	4562	3052	2633	2234

Increase in the atomic radius from Li to Cs makes the ionization energy of these elements to decrease down the group, and this can be used to explain the chemical properties of Group 1 elements. Reactivity of the Group 1 elements increases down the group.

** When writing equations for inorganic chemistry, it is not always essential to indicate the physical state of each reactants or products. However, always balance equations must be written to consider as a complete answer.

4.1.2 Reactions of Group 1 elements

With oxygen (O_2)	$4M + O_2 \longrightarrow 2M_2O$
With excess oxygen (O_2) Na form peroxides	$2Na + O_2 \longrightarrow Na_2O_2$
With excess oxygen (O_2) K, Rb and Cs form superoxides	$M + O_2 \longrightarrow MO_2$
With nitrogen (N_2) only Li forms stable nitride	$6Li + N_2 \longrightarrow 2Li_3N$
With hydrogen (H_2)	$2M + H_2 \longrightarrow 2MH$
With water (H_2O)	$2M + 2H_2O \longrightarrow 2MOH + H_2$
With acids (H^+)	$2M + 2H^+ \longrightarrow 2M^+ + H_2$

Reaction with water

Group 1 metals show an increase in reactivity with water down the group. The reactivity trend with water is as follows.

Li	**Na**	**K**	**Rb**	**Cs**
Relatively slow	Vigorously	Vigourously with ignition	Explosively	Explosively

Lithium reacts non-vigorously with water or with water vapour available in the air to produce lithium hydroxide and hydrogen gas. However, both sodium and potassium react vigorously with water to produce metal hydroxide and hydrogen gas. These reactions are highly exothermic except with Li.

Reactions with oxygen/ air

Lithium can react both with oxygen and nitrogen. When heated, lithium burns to produce lithium oxide (Li_2O), a white powder. With nitrogen gas, lithium gives lithium nitride (Li_3N). However, both sodium and potassium do not react with nitrogen gas. When sodium is burnt in air, sodium peroxide is mainly produced with some sodium oxide. In contrast, when potassium is burnt in air, potassium superoxide is formed as the main product with some potassium oxide and potassium peroxide. Oxidation numbers of oxygen in sodium or potassium peroxide are -1 and in potassium superoxide, oxidation numbers are -1 and 0.

Group 1 metal oxides react with water to produce metal hydroxides as shown below.

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

When heated, lithium forms lithium nitride with nitrogen. Only lithium forms a stable alkali-metal nitride. With water, lithium nitride produces ammonia and lithium hydroxide.

$$Li_3N(s) + 3H_2O(l) \longrightarrow 3LiOH(aq) + NH_3(g)$$

Group 1 hydroxides react with carbon dioxide to produce relevant carbonates. These carbonates can further react with carbon dioxide to produce metal hydrogen carbonates.

$$2NaOH(aq) + CO_2(g) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

$$Na_2CO_3(aq) + CO_2(g) + H_2O(l) \longrightarrow 2NaHCO_3(s)$$

Sodium hydrogen carbonate is less soluble than sodium carbonates in water.

Reactions with hydrogen gas

Group 1 elements react with hydrogen to produce solid, ionic metal hydrides. In these hydrides, hydrogen has the oxidation number of –1. These metal hydrides react vigorously with water to produce hydrogen gas.

$$2Na(s) + H_2(g) \longrightarrow 2NaH(s)$$

$$NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

Reactions with acids

Lithium, sodium and potassium react vigorously with dilute acids to produce hydrogen gas and relevant metal salts. These reactions are highly exothermic and explosive. A few selected reactions are shown below.

$$2Li(s) + \text{dil. } 2HNO_3(aq) \longrightarrow 2LiNO_3(aq) + H_2(g)$$

$$2Na(s) + \text{dil. } H_2SO_4(aq) \longrightarrow Na_2SO_4(aq) + H_2(g)$$

4.1.3 Thermal stability of salts

Decomposition of nitrates

Group 1 nitrates are used as fertilizers and explosives. These nitrates decompose upon heating. $LiNO_3$ decomposes to produce lithium oxide, nitrogen dioxide and oxygen. However, the other Group 1 nitrates on heating produce relevant metal nitrite and oxygen.

$$4LiNO_3(s) \xrightarrow{\triangle} 2Li_2O(s) + 4NO_2(g) + O_2(g)$$

$$2KNO_3(s) \xrightarrow{\triangle} 2KNO_2(s) + O_2(g)$$

Decomposition of carbonates

Carbonates are stable and they will melt before they decompose into oxides. However, Li_2CO_3 is less stable and decomposes readily.

$$Li_2CO_3(s) \xrightarrow{\Delta} Li_2O(s) + CO_2(g)$$

Decomposition of bicarbonates

Decomposition of bicarbonates of Group 1 is shown below.

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + H_2O(l) + CO_2(g)$$

Thermal stability increases down the group.

4.1.4 Solubility of Group 1 salts

All Group 1 salts are soluble in water except some lithium salts such as LiF, Li_2CO_3 and Li_3PO_4. All these salts are white solids unless the salt anion is a coloured ion.

Solubility of Group 1 halides increase down the group is shown in Table 4.2.

Table 4.2 The solubility of halides of sodium

Salt	Solubility/ mol L^{-1}
NaF	0.99
NaCl	6.2
NaBr	9.2
NaI	12.3

Variation in the solubility can be understood using the energy cycle for the solvation of ionic solids. The solubility can be explained using Gibbs free energy. For almost all ionic solids of Group 1, are soluble in water due to the negative Gibbs free energy in the solvation process.

Enthalpy and entropy cycles for the solvation process are shown below.

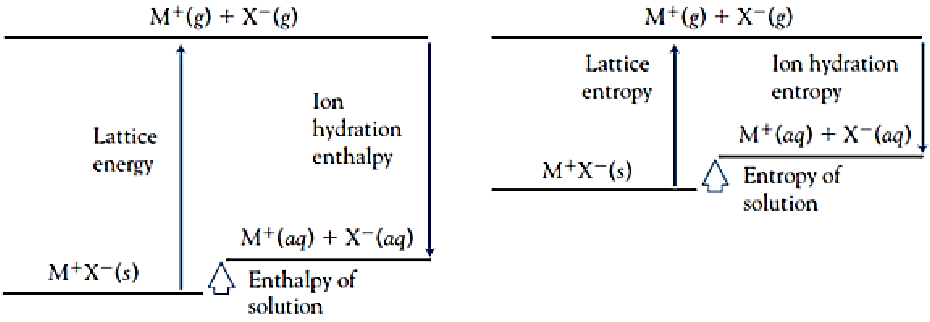


Figure 4.1 Enthalpy and entropy cycles for the solvation process

Using these two energy cycles, enthalpy and entropy change of solvation can be calculated and these calculated values are given in Table 4.3. Free energy is calculated using the equation,

$$\Delta G^{\Theta} = \Delta H^{\Theta} - T\,\Delta S^{\Theta}$$

Table 4.3 Free energy change of salts during solvation

Salt	Enthalpy change/ kJ mol^{-1}	Entropy change × T (K × kJ mol^{-1} K^{-1})	Free energy change/ kJ mol^{-1}
NaF	+ 1	-2	+3
NaCl	+ 4	+13	-9
NaBr	-1	+18	-19
NaI	-9	+23	-32

Calculated Gibbs free energies match with the solubility trend for the sodium halides. The free energy change gets more negative from sodium fluoride to sodium iodide.

4.1.5 Flame test

The flame test can be used to identify alkali metals and their compounds. Flame colours of Group 1 metals and compounds are given below.

Lithium – Red
Rubidium – Red-violet
Potassium – Lilac
Sodium – Yellow
Caesium – Blue - violet

4.2 Group 2 elements

Group 2 elements are known as alkaline earth metals. They are less reactive than Group 1 metals due to its valence shell ns^2 electron configuration.

Both calcium and magnesium can be found naturally in dolomite ($CaCO_3.MgCO_3$). Magnesite ($MgCO_3$), kieserite ($MgSO_4.H_2O$) and carnallite ($KMgCl_3.6H_2O$) are examples of minerals with magnesium. Fluoroapatite [$3(Ca_3(PO_4)_2).CaF_2$] and gypsum ($CaSO_4.2H_2O$) are commercially important calcium contacting minerals.

4.2.1 Group trends

Beryllium and magnesium are greyish metals and other Group 2 metals are soft and silvery in colour. Group 2 metal oxides produce basic oxides except for BeO which shows amphoteric properties. Beryllium behaves similar to Al and this can be understood using the diagonal relationship between Al and Be in the periodic table.

Elements of Group 2 have higher densities and stronger metallic bonds compared to the Group 1 metals. This is due to the availability of a greater number of electrons to form a stronger metallic bond and their smaller size in atomic radii.

The first ionization energies of Group 2 elements are higher than that of Group 1 elements due to their electron configuration of ns^2. Elements become more reactive and produce +2 oxidation state easily down the group. The properties of Group 2 elements are given in Table 4.4.

Table 4.4 Properties of Group 2 elements

	Be	**Mg**	**Ca**	**Sr**	**Ba**
Ground state electronic configuration	[He]2s^2	[Ne]3s^2	[Ar]4s^2	[Kr]5s^2	[Xe]6s^2
Metallic radius/ pm	112	150	197	215	217
Melting point/ °C	1280	650	850	768	714
Radius of M^{2+}/ pm	27	72	100	126	142
1st ionization energy/ kJ mol^{-1}	899	736	589	548	502
2nd ionization energy/ kJ mol^{-1}	1757	1451	1145	1064	965
3rd ionization energy/ kJ mol^{-1}	14850	7733	4912	4138	3619

4.2.2 Reactions of Group 2 elements (alkaline earth metals)

With oxygen (O_2)	$2M + O_2 \longrightarrow 2MO$
With excess oxygen (O_2) Ba forms its peroxide	$Ba + O_2 \longrightarrow BaO_2$
With nitrogen (N_2), at high temperatures	$3M + N_2 \longrightarrow M_3N_2$
With water ($H_2O(l)$), at room temperature (e.g.: Ca, Sr and Ba)	$M + 2H_2O \longrightarrow M(OH)_2 + H_2$
With hot water ($H_2O(l)$) (e.g.: Mg reacts slow)	$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$
With steam ($H_2O(g)$)	$Mg + H_2O \longrightarrow MgO + H_2$
With acids (H^+)	$M + 2H^+ \longrightarrow M^{2+} + H_2$
With hydrogen (H_2), at high temperatures with Ca, Sr, Ba at high pressure with Mg	$M + H_2 \longrightarrow MH_2$
With concentrated acids	$Mg + 2H_2SO_4 \longrightarrow MgSO_4 + SO_2 + 2H_2O$ $Mg + 4HNO_3 \longrightarrow Mg(NO_3)_2 + 2NO_2 + 2H_2O$

Reaction with water

Beryllium does not react with water, but it reacts with steam. The reaction of magnesium with water at room temperature is negligible. However, magnesium reacts slowly with hot water. Calcium, strontium and barium react readily with cold water. Reaction with water produces metal hydroxide and hydrogen gas.

$$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$$

Reactions with hydrogen

All Group 2 elements, except Be, react with hydrogen to produce metal hydrides which are ionic solids. In these hydrides, hydrogen has an oxidation number of – 1. These metal hydrides (not violent as Group 1) react vigorously with water to produce hydrogen gas.

$$Ca(s) + H_2(g) \longrightarrow CaH_2(s)$$

$$CaH_2(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + 2H_2(g)$$

Reaction with nitrogen

All Group 2 elements burns in nitrogen to form M_3N_2, nitrides. These nitrides react with water to produce ammonia in the same way as lithium does.

$$3Mg(s) + N_2(g) \longrightarrow Mg_3N_2(s)$$

$$Mg_3N_2(s) + 6H_2O(l) \longrightarrow 3Mg(OH)_2(aq) + 2NH_3(g)$$

4.2.3 Thermal stability of salts

Decomposition of nitrates

Upon heating, Group 2 nitrates behave much similar to lithium nitrate. Group 2 nitrates decompose to produce metal oxide, nitrogen dioxide and oxygen. All Group 2 nitrates are soluble in water.

$$2Mg(NO_3)_2(s) \xrightarrow{\triangle} 2MgO(s) + 4NO_2(g) + O_2(g)$$

Decomposition of carbonates

Thermal stability of these carbonates increases down the group. Thermal stability of these carbonates increases with the size of the cation. The polarizing power of the cation decreases down the group due to the decrease of charge density of the cation. Carbonate anion attached to Mg^{2+} cation is highly polarized than that of carbonate attached to Ba^{2+}. Highly polarized carbonate anion can undergo decomposition easily and this explains the lower decomposition temperature of $MgCO_3$ than that of $BaCO_3$.The general decomposition of metal carbonates is shown below.

$$MCO_3 \xrightarrow{\triangle} MO + CO_2$$

Decomposition temperature increases from 540 °C for $MgCO_3$ to 1360 °C for $BaCO_3$.

Decomposition of bicarbonates

Group 2 hydrogen carbonates are only stable in aqueous solutions and solid Group 2 hydrogen carbonates are not stable at room temperature.

$$Ca(HCO_3)_2(aq) \xrightarrow{\triangle} CaCO_3(s) + CO_2(g) + H_2O(l)$$

4.2.4 Solubility of Group 2 salts

Solubility of Group 2 salts changes depending on the compound. Some compounds such as nitrate, nitrite, halides, hydroxides, sulphides, bicarbonates all are soluble in water. The solubility varies down the group for certain compounds such as hydroxides, sulphate, sulphite, carbonate, phosphate and oxalate showing the patterns given in Table 4.5.

Salts of Group 2 metals with uninegative anions, such as chloride and nitrates are generally soluble. However, salts formed with anions containing more than one negative charge, such as carbonates and phosphates, are insoluble. All carbonates are insoluble except $BeCO_3$. Hydrogen carbonates are more soluble than carbonates. The solubility of Group 2 sulphates changes from soluble to insoluble when comparing solubility from $MgSO_4$ to $BaSO_4$. On the other hand, hydroxides change solubility from insoluble to soluble when moving down the group. For example, $Mg(OH)_2$ is sparingly soluble whereas $Ba(OH)_2$ is soluble and produces a strongly basic solution.

Table 4.5 Solubility of Group 1 and 2 compounds

	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
Cl^-	aq	aq	aq	aq	aq	aq
Br^-	aq	aq	aq	aq	aq	aq
I^-	aq	aq	aq	aq	aq	aq
OH^-	aq	aq	IS	SS	SS	aq
CO_3^{2-}	aq	aq	IS	IS	IS	IS
HCO_3^-	aq	aq	aq	aq	aq	aq
NO_2^-	aq	aq	aq	aq	aq	aq
NO_3^-	aq	aq	aq	aq	aq	aq
S^{2-}	aq	aq	aq	aq	aq	aq
SO_3^{2-}	aq	aq	SS	IS	IS	IS
SO_4^{2-}	aq	aq	aq	SS	IS	IS
PO_4^{3-}	aq	aq	IS	IS	IS	IS
CrO_4^{2-}	aq	aq	aq	aq	IS	IS
$C_2O_4^{2-}$	aq	aq	SS	IS	IS	SS

aq – soluble, IS – insoluble, SS – sparingly soluble

4.2.5 Flame test

Alkaline earth metals and compounds produce characteristic colours with the flame, and the flame test can be used to identify these elements using the flame colors shown below.

Calcium – Orange-red Strontium – Crimson red Barium – Yellowish-green

p Block Elements

4.3 Group 13 elements

4.3.1 Group trends

Boron is a metalloid, and most of the boron compounds are covalent. However, aluminium is a metal with amphoteric properties. Gallium, indium and thallium are metals. The first member, B, of Group 13 is different from the other members due to its smaller atomic radius. Boron shows a strong diagonal relationship with Si in Group 14. All elements in Group 13 produce +3 oxidation state. The properties of Group 13 elements are given in Table 4.6.

Table 4.6 Properties of Group 13 elements

	**B	Al	**Ga	**In	**Tl
Ground state electronic configuration	$[He]2s^22p^1$	$[Ne]3s^23p^1$	$[Ar]3d^{10}4s^24p^1$	$[Kr]4d^{10}5s^25p^1$	$[Xe]4f^{14}5d^{10}6s^26p^1$
Metallic radius/ pm	-	143	141	166	171
Covalent radius/ pm	80	125	125	150	155
Melting point/ °C	2300	660	30	157	304
Radius of M^{3+}/ pm	27	53	62	94	98
1st ionization energy/ $kJ\ mol^{-1}$	799	577	577	556	590
2nd ionization energy/ $kJ\ mol^{-1}$	2427	1817	1979	1821	1971
3rd ionization energy/ $kJ\ mol^{-1}$	3660	2745	2963	2704	2878

**Not a part of current G. C. E. (A/L) Chemistry syllabus

4.3.2 Aluminium

Aluminium is the third most abundant element in the earth crust. The exposed surface of aluminium produces a layer of Al_2O_3. This layer makes aluminium resistant to further reactions with oxygen. Due to this impermeable layer, Al can be considered as a non-reactive element with air.

Reactions of aluminium

Aluminium reacts readily with O_2 and halogens. Also, it reacts with N_2.

With oxygen (O_2) : $4Al + 3O_2 \longrightarrow 2Al_2O_3$

With halogen (X_2): $2Al + 3X_2 \longrightarrow 2AlX_3$

With nitrogen (N_2): $2Al + N_2 \longrightarrow 2AlN$

Aluminum is less reactive than Groups 1 and 2 elements. Similar to beryllium, aluminium reacts with both acids and bases. The equations for the reactions of Al with acids and bases are given below.

$$2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$$

$$2Al(s) + 2OH^-(aq) + 6H_2O(l) \longrightarrow 2[Al(OH)_4]^-(aq) + 3H_2(g)$$

Aluminium ion in aqueous solution is expected to be present as hexaaquaaluminium ion. However, hydrolysis of Al^{3+} produces $[Al(OH_2)_5(OH)]^{2+}$(pentaaquahydroxidoaluminium ion) and then produces $[Al(OH_2)_4(OH)_2]^+$ (tetraaquadihydroxidoaluminium ion) as shown below.

$$[Al(OH_2)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(OH_2)_5(OH)]^{2+}(aq) + H_3O^+(aq)$$

$$[Al(OH_2)_5(OH)]^{2+}(aq) + H_2O(l) \rightleftharpoons [Al(OH_2)_4(OH)_2]^+(aq) + H_3O^+(aq)$$

Addition of OH^- ions to aluminum ions first produces a gelatinous precipitate of aluminum hydroxide. With excess OH^- ions, the precipitated aluminum hydroxide is converted to tetrahydroxidoaluminate complex ion.

$$Al^{3+}(aq) + 3OH^-(aq) \longrightarrow Al(OH)_3(s) \text{ (white gelatinous ppt)}$$

$$Al(OH)_3(s) + OH^-(aq) \longrightarrow [Al(OH)_4]^-(aq) \text{ or } AlO_2^-(aq) + 2H_2O(l)$$

Group 13 elements can have six electrons in their valence shell by forming three covalent bonds due to their ns^2np^1 electron configuration. As a result, many of the Group 13 covalent compounds have an incomplete octet, so can act as Lewis acids to accept a pair of electrons from a donor. These compounds with incomplete octet are called **electron deficient compounds.** Both B and Al compounds with incomplete octet form dimers in the gaseous phase to satisfy the octet rule (Figure 4.2).

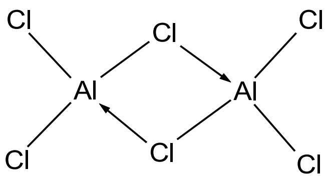


Figure 4.2 Structure of gaseous Al_2Cl_6

4.4 Group 14 elements

4.4.1 Group trends

Due to the formation of covalent bond network structure, first three elements of group 14 have high melting points. Carbon is a nonmetal,whereas silicon and germanium are metalloids. Last two elements in the group, tin and lead are metals.

Carbon can be found in the nature mainly in coal, crude oil, calcite ($CaCO_3$), CO_2 in air, magnesite ($MgCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$). Graphite, diamond and fullerenes are the allotropic forms of carbon. Fullerenes are recently found, and most well-known fullerene is C_{60}, buckminsterfullerene (or bucky-ball). Carbon is the basis of life and the most important element in organic chemistry. Silicon and germanium are mainly used in the semiconductor industries. In addition, silicon is heavily used in inorganic polymer industry.

The properties of Group 14 elements are given in Table 4.7.

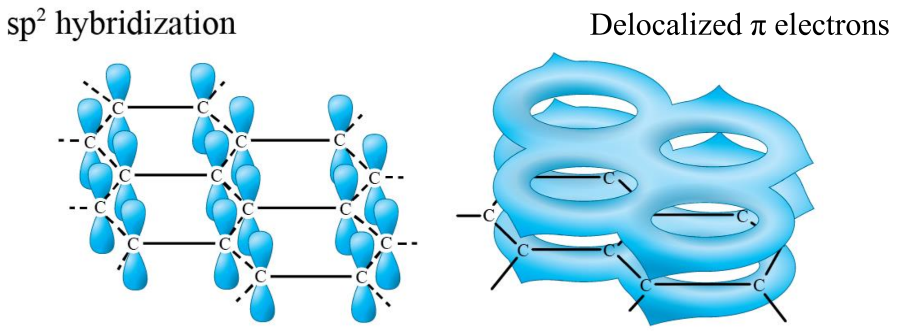
Table 4.7 Properties of Group 14 elements

	C	**Si	**Ge	**Sn	**Pb
Ground state electronic configuration	[He]$2s^22p^2$	[Ne]$3s^23p^2$	[Ar]$3d^{10}4s^24p^2$	[Kr]$3d^{10}5s^25p^2$	[Xe]$4f^{14}5d^{10}6s^26p^2$
Metallic radius/ pm	-	-	-	158	175
Atomic radius/ pm	77	117	122	140	154
Melting point/ °C	3730	1410	937	232	327
Radius of M^{4+}/ pm	-	-	53	69	78

***Not a part of current G. C. E. (A/L) Chemistry syllabus*

4.4.2 Diamond and graphite

Diamond and graphite are composed of homoatomic (same atoms) latice structures. Diamond (sp^3 hybridized carbon, tetrahedral) has a cubic crystalline structure. Graphite (sp^2 hybridized carbon, trigonal planar) has stacked two-dimensional carbon layers. Carbon-carbon bonds in graphite are shorter than that of diamond (diamond 154 pm and graphite 141 pm) due to the hybridization of carbon atoms. These two crystalline lattice structures are hard however diamond structure is the strongest lattice. Graphite is an electrical and a thermal conductor due to delocalizing π electrons (Figure 4.3). Interactions between layers of carbon in graphite are weak and this makes graphite a good lubricant.


sp^2 hybridization

Delocalized π electrons

Figure 4.3 Delocalizing π electrons of graphite

Fullerenes are another series of carbon allotropes. In fullerenes, carbon atoms are connected in a spherical manner. Structures of graphite, diamond and fullerene (C_{60}) are shown in Figure 4.4.

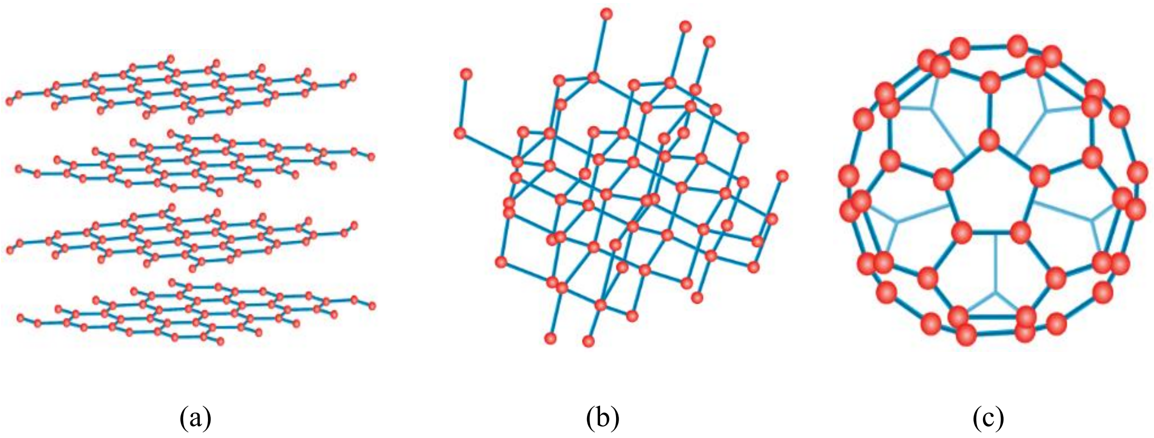
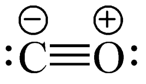

(a) (b) (c)

Figure 4.4 Structures of (a) graphite, (b) diamond and (c) fullerene (C_{60})

4.4.3 Carbon monoxide and carbon dioxide

Carbon monoxide is a colourless, odourless, highly poisonous gas. Bond enthalpy of carbon monoxide is more than that of the C=O double bond. In carbon monoxide CO bond length is shorter than that of a typical C=O double bond. This suggests that the bonding between C and O in carbon monoxide is not a typical C=O double bond. It has a triple bond nature between the two atoms of C and O. The Lewis structure of CO is shown in Figure 4.5.



$$:\overset{\ominus}{C}\equiv\overset{\oplus}{O}:$$

Figure 4.5 The Lewis structure of CO

Carbon monoxide is mostly used as a reducing agent in the production of iron. Also, CO plays an important role in many catalytic reactions as a ligand due to the lone pair of electrons on the C atom.

Carbon dioxide (Figure 4.6) solidifies due to London forces at low temperatures and/ or under high pressures. Solid CO_2 (dry ice) sublimes to produce gaseous carbon dioxide under normal atmosperic conditions. It is commonly used as a freezing agent in the food industry and to produce artificial rain.

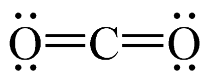


Figure 4.6 The Lewis structure of CO_2

4.4.4 Oxoacid of carbon

Oxoacid of carbon is referred to as carbonic acid (H_2CO_3) which is a weak acid. The bond structure of H_2CO_3 is given in Figure 4.7. Carbonic acid can be prepared by dissolving CO_2 in water under pressure.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

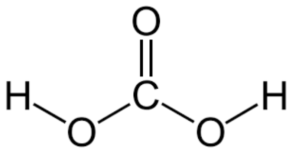


Figure 4.7 The bond structure of H_2CO_3

Hydrogen atom which is directly connected to oxygen atom can be released as a proton to the solution by exhibiting the acidic property of carbonic acid.

Carbon dioxide reacts with bases to produce carbonates showing its acidic property. In the presence of excess CO_2 thus formed carbonates of Group 1 and 2 produce hydrogen carbonates.

$$CO_2(g) + 2NaOH(aq) \longrightarrow Na_2CO_3(aq) + H_2O(l)$$

$$Na_2CO_3(aq) + \text{excess } CO_2(g) + H_2O(l) \longrightarrow 2NaHCO_3(aq)$$

4.5 Group 15 elements

4.5.1 Group trends

The first element, nitrogen of Group 15 shows different properties from the other elements in this group (Table 4.8). Metallic character of the Group 15 elements increases down the group. Nitrogen and phosphorous are nonmetals and show oxidation numbers -3 to +5. Nitrogen can achieve +5 oxidation state with oxygen and fluorine. Dinitrogen, N_2 is greatly stable (inert) under normal conditions due to strong triple bond (942 kJ mol^{-1}). Except nitrogen, all the other elements exist as solids. The higher electronegativity, the smaller atomic radius and the absence of *d* orbitals make nitrogen different from the other elements in the group.

Table 4.8 Properties of Group 15 elements

	N	****P**	****As**	****Sb**	****Bi**
Ground state electronic configuration	$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]3d^{10}4s^24p^3$	$[Kr]3d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$
Metallic radius/ pm	-	-	-	-	182
Atomic radius/ pm	74	110	121	141	170
Melting point/ °C	-210	44 (white) 590 (red)	613	630	271
Pauling electronegativity	3.0	2.1	2.0	1.9	1.9

***Not relevant to the current G. C. E. (A/L) Chemistry syllabus*

4.5.2 Chemistry of nitrogen

Nitrogen (boiling point is -195.8 °C) is slightly soluble in water under atmospheric pressure, but the solubility greatly increases with pressure. Nitrogen does not form allotropes. Dinitrogen shows only a few reactions and one of them is given below.

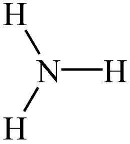
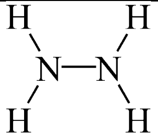
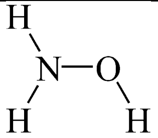
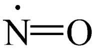
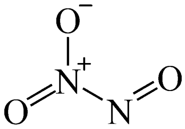
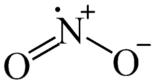
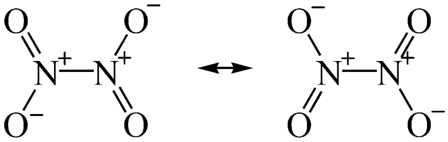
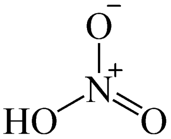
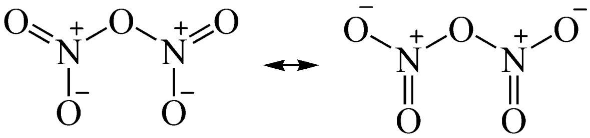
$$3Mg(s) + N_2(g) \xrightarrow{\triangle} Mg_3N_2(s)$$

Since nitrogen is an inert gas its chemical reactions occur under strong conditions. For an instance nitrogen gas reacts with oxygen in the presence of external energy from an elctrical spark. This reaction naturally occurs in lightening.

$$N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$$

Nitrogen shows oxidation states from –3 to +5. Compounds with these oxidation states are shown in Table 4.9.

Table 4.9 Oxidation states of nitrogen

Oxidation state	Compound	Formula	Bond structure
-3	Ammonia	NH_3	
-2	Hydrazine	N_2H_4	
-1	Hydroxylamine	NH_2OH	
0	Dinitrogen	N_2	$N\equiv N$
+1	Dinitrogen monoxide	N_2O	 $\overset{-}{N}=\overset{+}{N}=O \leftrightarrow N\equiv\overset{+}{N}-\overset{-}{O}$
+2	Nitrogen monoxide	NO	 $\dot{N}=O$
+3	Dinitrogen trioxide	N_2O_3	
+4	Nitrogen dioxide	NO_2	
+4	Dinitrogen tetroxide	N_2O_4	
+5	Nitric acid	HNO_3	
+5	Dinitrogen pentoxide	N_2O_5	

4.5.3 Oxoacids of nitrogen

Nitrous acid which is unstable under normal atmospheric conditions is a weak acid. The bond structure of nitrous acid is given in Figure 4.8.

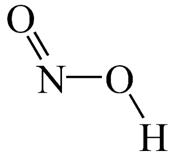


Figure 4.8 The bond structure of nitrous acid

Nitrous acid can undergo disproportionation to produce nitric acid and nitrogen monoxide which is a colourless gas.

$$3HNO_2(aq) \longrightarrow HNO_3(aq) + 2NO(g) + H_2O(l)$$

Futher reaction of nitrogen monoxide with oxygen forms nitrogen dioxide which is redish brown in colour.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Nitric acid (Figure 4.9) is an oily and hazardous liquid. This acid is a strong oxidizing agent and can undergo vigorous chemical reactions.

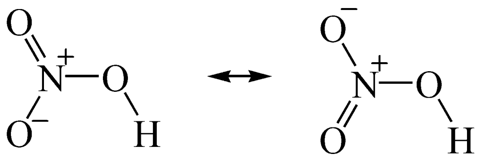


Figure 4.9 The bond structure of nitric acid

Due to the light-induced decomposition, nitric acid produces oxygen and nitrogen dioxide.

$$4HNO_3(aq) \xrightarrow{hv} 4NO_2(g) + O_2(g) + 2H_2O(l)$$

Due to this reason concentrated nitric acid is stored in brown colour glass bottles in laboratories.

Oxidizing reactions of nitric acid

Dilute nitric acid reacts with metals to produce metal nitrate and hydrogen gas. In these reactions nitric acid acts as an oxidizing agent with respect to hydrogen. When magnesium and copper reacts with concentrated nitric acid it acts as an oxidizing agent with respect to nitrogen.

$Mg(s) + \text{dil. } 2HNO_3(aq) \longrightarrow Mg(NO_3)_2(aq) + H_2(g)$

$Mg(s) + \text{conc. } 4HNO_3(l) \longrightarrow Mg(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

$3Cu(s) + \text{dil. } 8HNO_3(aq) \longrightarrow 3Cu(NO_3)_2(aq) + 2NO(g) + 4H_2O(l)$

$Cu(s) + \text{conc. } 4HNO_3(l) \longrightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O(l)$

The reactions of conc. HNO_3 acting as an oxidizing agent with non metals such as carbon and sulphur are given below.

$C(s) + \text{conc. } 4HNO_3(l) \longrightarrow CO_2(g) + 4NO_2(g) + 2H_2O(l)$

$S(s) + \text{conc. } 6HNO_3(l) \longrightarrow H_2SO_4(l) + 6NO_2(g) + 2H_2O(l)$

4.5.4 Ammonia and ammonium salts

Ammonia is a colourless gas with a strong characteristic smell. Ammonia is a basic gas which is readily soluble in water.

$NH_3(g) + H_2O(l) \rightleftharpoons NH_4OH(aq)$

Ammonium hydroxide is a weak base and partially dissociates to produce ammonium ions and hydroxide ions.

$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Like any other base it reacts with dilute acids to produce aqueous salts.

$2NH_4OH(aq) + \text{dil. } H_2SO_4(aq) \longrightarrow (NH_4)_2SO_4(aq) + 2H_2O(l)$

Hydrolysis of the ammonium ion in aqueous solution produces the conjugate base, ammonia.

$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(l)$

All amonium salts reacts with alkali to liberate ammonia.

$NH_4Cl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + NH_3(g) + H_2O(l)$

Reactions of ammonia

Ammonia acts as a reducing agent with chlorine, and the products vary with the amount of ammonia and chlorine used. In the presence of excess ammonia, chlorine produces nitrogen gas as one of the products. However, with excess chlorine, nitrogen trichloride is produced as one of the products, which is used for water disinfection.

excess ammonia, $8NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6NH_4Cl(aq)$

The formed HCl further reacts with unreacted ammonia to form NH_4Cl.

excess chlorine, $3Cl_2(g) + NH_3(g) \longrightarrow 3HCl(g) + NCl_3(l)$

Nitrogen trichloride is a covalent chloride. It reacts with water to produce ammonia and hypochlorous acid. Due to the ability to produce hypochlorous acid, nitrogen trichloride is used as a water disinfecting agent.

$$NCl_3(l) + 3H_2O(l) \longrightarrow NH_3(g) + 3HOCl(aq)$$

Gaseous ammonia reacts with hydrogen chloride to produce a white smoke of solid ammonium chloride. This can be used as a confirmation test for ammonia.

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$$

Ammonia acts as a weak reducing agent with CuO and Cl_2.

$$3CuO(s) + 2NH_3(g) \longrightarrow N_2(g) + 3Cu(s) + 3H_2O(g)$$

$$2NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6HCl(g)$$

Ammonia can act as an oxidizing agent as well as an acid with metals under dry condition.

$$2Na(s) + 2NH_3(l) \longrightarrow 2NaNH_2(l) + H_2(g)$$

$$3Mg(s) + 2NH_3(l) \longrightarrow Mg_3N_2(l) + 3H_2(g)$$

Thermal decomposition of ammonium salts

Some ammonium salts decompose upon heating to ammonium gas and to the acidic gas.

$$(NH_4)_2CO_3(s) \longrightarrow 2NH_3(g) + CO_2(g) + H_2O(g)$$

$$NH_4Cl(s) \longrightarrow NH_3(g) + HCl(g)$$

$$(NH_4)_2SO_4(s) \longrightarrow NH_3(g) + H_2SO_4(g)^*$$

*Prodcts of this reaction can vary with conditions.

However, anions in some ammonium salts can oxidize the ammonium ion to produce many products upon heating.

$$NH_4NO_2(s) \longrightarrow N_2(g) + 2H_2O(g)$$

$$NH_4NO_3(s) \longrightarrow N_2O(g) + 2H_2O(g)$$

$$(NH_4)_2Cr_2O_7(s) \longrightarrow N_2(g) + Cr_2O_3(s) + 4H_2O(g)$$

Identification of ammonium salts

All ammonium salts produce ammonium gas with NaOH on warming. This gas produces white fumes of ammonium chloride when a glass rod moistened with concentrated hydrochloric acid.

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

$$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s) \text{ white fumes}$$

Reactions of nitrate

Reaction of nitrate with iron(II)/ conc. sulphuric acid can be used to identify nitrate ion. This test is known as brown ring test. The brown coloured $[Fe(NO)]^{2+}$ ring formed in the test tube, confirms the presence of nitrate.

$$NO_3^-(aq) + 2H_2SO_4(l) + 3Fe^{2+}(aq) \longrightarrow 3Fe^{3+}(aq) + NO(g) + 2SO_4^{2-}(aq) + 2H_2O(l)$$

$$Fe^{2+}(aq) + NO(g) \longrightarrow [Fe(NO)]^{2+}(aq) \text{ brown colour}$$

Nitrate reacts with Al/ NaOH to produce ammonia.

$$3NO_3^-(aq) + 8Al(s) + 5OH^-(aq) + 18H_2O(l) \longrightarrow 3NH_3(g) + 8[Al(OH)_4]^-(aq)$$

4.6 Group 16 elements

4.6.1 Group trends

First element, oxygen of Group 16 shows different properties to the other elements in the group. Metallic nature increases going down the group. However, none of the Group 16 elements behaves as a true metal. Both oxygen and sulphur are non-metals and other elements in the group show metallic and nonmetallic properties. Only oxygen exists as a gas, and other elements in the group are solids. Except oxygen, other elements in the group can form even-numbered oxidation states from +6 to -2. Stability of +6 and -2 oxidation states decreases down the group whereas the stability of the +4 oxidation state increases.

Table 4.10 Properties of Group 16 elements

	O	S	**Se	**Te	**Po
Ground state electronic configuration	$\text{[He]}2s^22p^4$	$\text{[Ne]}3s^23p^4$	$\text{[Ar]}3d^{10}4s^24p^4$	$\text{[Kr]}4d^{10}5s^25p^4$	$\text{[Xe]}4f^{14}5d^{10}6s^26p^4$
Ionic radius X^{2-}/ pm	140	184	198	221	-
Covalent radius/ pm	74	104	117	137	140
Melting point/ °C	-218	113(α)	217	450	254
Pauling electronegativity	3.5	2.5	2.4	2.1	2.0
1st electron gain enthalpy/ kJ mol^{-1} $X(g) + e \longrightarrow X^-(g)$	-141	-200	-195	-190	-183
2nd electron gain enthalpy/ kJ mol^{-1} $X^-(g) + e \longrightarrow X^{2-}(g)$	844	532	-	-	-

*** Not a part of the current G. C. E. (A/L) Chemistry syllabus*

4.6.2 Hydrides of Group 16

Group 16 elements form simple hydrides with hydrogen. All of them are covalent hydrides. The variation of selected properties down the group of hydrides are shown in Table 4.11.

Table 4.11 Selected properties of Group 16 hydrides

	H_2O	H_2S	H_2Se	H_2Te
Melting point/ °C	0.0	-85.6	-65.7	-51
Boiling point/ °C	100.0	-60.3	-41.3	-4
Bond length/ pm	96	134	146	169
Bond angle/ °	104.5	92.1	91	90

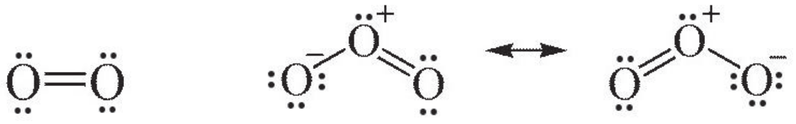
Due to the extensive hydrogen bonding, H_2O shows abnormally high boiling and melting points than the other hydrides of the group. Water is the only non-poisonous hydride among all the other hydrides of the group.

The observed varation in bond length of covalent hydrides is due to the increase of size of the central atom. Therefore, bond length increases down the group.

The covalent bond angle decreases as you come down in the group due to the less repulsion of the bonding electrons as a result of electronegativity of the central atom decreases down the group. In H_2S, H_2Se and H_2Te the bond angles become close to 90°. This may also suggest that almost pure *p* orbitals on selenium and tellurium especially are used for binding with hydrogen.

4.6.3 Oxygen

Oxygen has two allotropes, dioxygen (O_2) and trioxygen (ozone, O_3). Dioxygen is a colourless and an odourless gas which is slightly soluble in water. Ozone has a pungent odour. Ozone has a bond angle of 111.5°. Structure of these two allotropes are shown below.



(a) (b)

Figure 4.10 Structure of oxygen and ozone

Catalytic decomposition of potassium chlorate and hydrogen peroxide can be used to produce oxygen.

$$2KClO_3(s) \longrightarrow 2KCl(s) + 3O_2(g)\text{, heating in the presence of }MnO_2\text{ or Pt}$$

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)\text{, heating in the presence of }MnO_2$$

Metals react with dioxygen to produce metal oxides. Ozone is a powerful oxidizing agent stronger than dioxygen. Ozone is used to disinfect water in many developed countries to kill pathogens. Unlike chlorine, ozone does not produce any harmful byproducts in the disinfection process.

4.6.4 Sulphur

Sulphur can be classified as it is explained below.

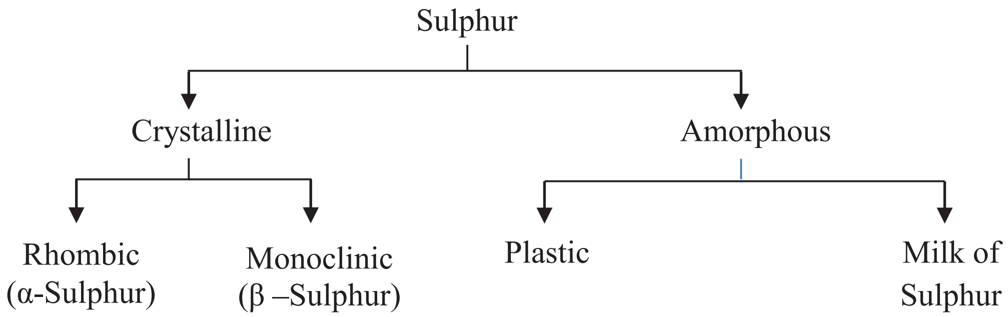
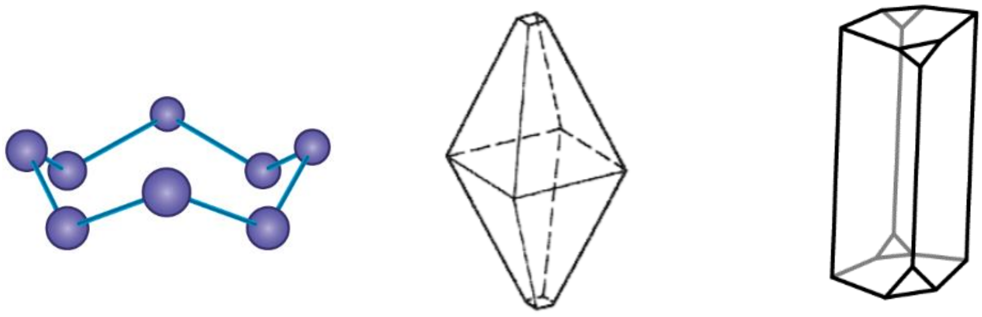


Figure 4.11 Classification of sulphur

Unlike oxygen, sulphur forms single bonds with itself rather than double bonds. The most commonly occurring allotrope is rhombic sulphur which is refered to as α-sulphur (α-S_8).

It has a crown shape with eight-membered ring that has a cyclic zigzag arrangement as shown below. When heated above 93 °C, α-S_8 changes its packing arrangement to the other commonly found form of monoclinic sulphur, β-sulphur (β-S_8). These two forms are allotropes of each other.



(a) (b) (c)

Figure 4.12 (a) crown form of S_8 (b) Rhombic sulphur (c) Monoclinic sulphur

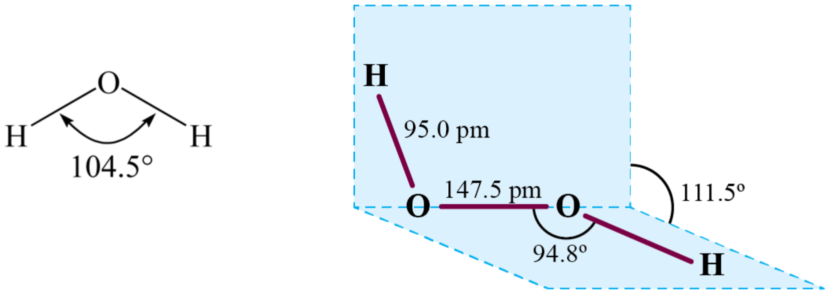
Crystalline form of rhombic and monoclinic sulphur consist of S_8 rings in the shape of crown. These can be packed together in two different ways to form rhombic crystals and to form needle shaped monoclinic crystals as shown above. Below 95 °C the rhombic form is the most stable allotropic form of sulphur.

Amorphous sulphur is an elastic form of sulphur which is obtained by pouring melted sulphur into water. Sudden cooling of molten sulphur converts liquid sulphur to amorphous sulphur with open chains. With time, amorphous sulphur converts to crystalline sulphur. The amorphous form of sulphur is malleable but it is unstable.

4.6.5 Oxygen containing compounds

Water and hydrogen peroxide

Structures of H_2O and gaseous H_2O_2 are shown in the figures below.



(a) (b)

Figure 4.13 Structures of (a) H_2O and (b) H_2O_2

Water is the most widely used solvent. Water ionizes as follows. This is reffered to as self-ionization of water.

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

An amphiprotic molecule can either donate or accept a proton. Therefore, it can act as an acid or a base. Water is an amphiprotic compound since it has the ability to accept and release a proton. The amphiprotic nature of water is shown below

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

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

4.6.6 Hydrogen peroxide

Hydrogen peroxide (H_2O_2) is a nonplanar molecule. The H_2O_2 molecule contains two OH groups which do not lie in the same plane and have a bent molecular shape with the bond angle in the gaseous phase for H-O-O as 94.8°. The structure shown in Figure 4.13 is the one that reduces with a minimum repulsion between the lone pairs found on the 'O' atoms. The two H-O groups have a dihedral angle of 111.5° between each other as indicated above in Figure 4.13.

Due to the extensive hydrogen bonding, H_2O_2 is a viscous liquid H_2O_2 can act as an oxidizing as well as a reducing agent. It oxidizes to oxygen and reduces to water.

Reducing half-reaction;

$$H_2O_2(aq) + 2H^+(aq) + 2e \longrightarrow 2H_2O(l)$$

Oxidizing half-reaction;

$$H_2O_2(aq) \longrightarrow 2H^+(aq) + O_2(g) + 2e$$

Disproportionation;

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

Reactions of H_2O_2

H_2O_2 as an oxidizing agent;

$$H_2O_2(aq) + 2H^+(aq) + 2I^-(aq) \longrightarrow I_2(aq) + 2H_2O(l)$$

$$H_2O_2(aq) + 2H^+(aq) + 2Fe^{2+}(aq) \longrightarrow 2Fe^{3+}(aq) + 2H_2O(l)$$

H_2O_2 as a reducing agent;

$$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$$

$$Cr_2O_7^{2-}(aq) + 3H_2O_2(aq) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 7H_2O(l) + 3O_2(g)$$

4.6.7 Sulphur containing compounds

Hydrogen sulphide

Hydrogen sulphide, H_2S is a colourless, toxic and acidic gas with the odour of “rotten eggs”. H_2S can be produced by reacting metal sulphides with strong acids. It dissolves in water to produce weak acidic solutions.

Reactions of hydrogen sulphide

H_2S as an acid with strong bases;

$$NaOH(aq) + \text{excess } H_2S(g) \longrightarrow NaHS(aq) + H_2O(l)$$

$$2NaOH(aq) + \text{limited } H_2S(g) \longrightarrow Na_2S(aq) + 2H_2O(l)$$

H_2S reacts with metals as an acid as well as an oxidizing agent;

$$2Na(s) + \text{excess } 2H_2S(g) \longrightarrow 2NaHS(s) + H_2(g)$$

$$2Na(s) + \text{limited } H_2S(g) \longrightarrow Na_2S(s) + H_2(g)$$

$$Mg(s) + H_2S(g) \longrightarrow MgS(s) + H_2(g)$$

H_2S as a reducing agent;

$$2KMnO_4(aq)+3H_2SO_4(aq)+5H_2S(g) \longrightarrow K_2SO_4(aq)+5S(s)+2MnSO_4(aq)+8H_2O(l)$$

$$K_2Cr_2O_7(aq)+4H_2SO_4(aq)+3H_2S(g) \longrightarrow K_2SO_4(aq)+Cr_2(SO_4)_3(aq)+3S(s)+7H_2O(l)$$

$$2H_2S(aq) + SO_2(g) \longrightarrow 3S(s) + 2H_2O(l)$$

Sulphur dioxide

Sulphur dioxide is a colourless gas and soluble in water. Sulphur dioxide can act as an oxidizing and a reducing agent.

Reactions of sulphur dioxide

As an oxidizing agent;

$$2Mg(s) + SO_2(g) \longrightarrow 2MgO(s) + S(s)$$

$$3Mg(s) + SO_2(g) \longrightarrow 2MgO(s) + MgS(s)$$

As a reducing agent;

$$5SO_2(g) + 2KMnO_4(aq) + 2H_2O(l) \longrightarrow K_2SO_4(aq) + 2MnSO_4(aq) + 2H_2SO_4(aq)$$

$$3SO_2(g) + K_2Cr_2O_7(aq) + H_2SO_4(aq) \longrightarrow K_2SO_4(aq) + Cr_2(SO_4)_3 (aq)+ H_2O(l)$$

$SO_2(g) + 2FeCl_3(aq) + 2H_2O(l) \longrightarrow H_2SO_4(aq) + 2FeCl_2(aq) + 2HCl(aq)$

4.6.8 Oxoacids of sulphur

Common oxidation numbers of sulphur are -2, 0, +2, +4 and +6.

Sulphuric acid

Sulphuric acid is a strong diprotic acid. Sulphur trioxide reacts with water to produce sulphuric acid.

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

$$H_2SO_4(aq) + H_2O(l) \longrightarrow HSO_4^-(aq) + H_3O^+(aq)$$

$$HSO_4^-(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + H_3O^+(aq)$$

Concentrated sulphuric acid can act as a dehydrating agent.

$$C_6H_{12}O_6(s) \xrightarrow{\text{conc. } H_2SO_4} 6C(s) + 6H_2O(g)$$

$$C_2H_5OH(l) \xrightarrow{\text{conc. } H_2SO_4} C_2H_4(g) + H_2O(l)$$

Concentrated hot sulphuric acid can act as an oxidizing agent.

With metals,

$$2H_2SO_4(l) + Mg(s) \longrightarrow SO_2(g) + MgSO_4(aq) + 2H_2O(l)$$

$$2H_2SO_4(l) + Cu(s) \longrightarrow SO_2(g) + CuSO_4(aq) + 2H_2O(l)$$

With nonmetals,

$$S(s) + 2H_2SO_4(l) \longrightarrow 3SO_2(g) + 2H_2O(l)$$

$$C(s) + 2H_2SO_4(l) \longrightarrow CO_2(g) + 2SO_2(g) + 2H_2O(l)$$

Dilute H_2SO_4 act as an acid.

$$H_2SO_4(aq) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + 2H_2O(l)$$

$$H_2SO_4(aq) + Mg(s) \longrightarrow MgSO_4(aq) + H_2(g)$$

Dilute sulphuric acid is a strong acid which can protonate to give two H^+ ions to water as shown below.

$$H_2SO_4(aq) + 2H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H_3O^+(aq)$$

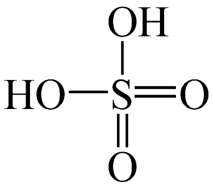


Figure 4.14 Structure of sulphuric acid

Sulphurous acid

Due to the air oxidation of sulphurous acid, it always contains a small amount of sulphuric acid. The reaction of gaseous sulphur dioxide and water produces sulphurous acid. The sulphurous acid reacts with dissolved oxygen in water to produce sulphric acid. Structure of the sulphurous acid is shown below. This acid is a weaker acid than sulphuric acid.

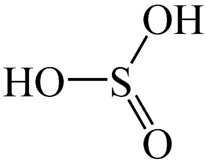


Figure 4.15 Structure of sufurous acid

Thiosulphuric acid

Only the salts of thiosulphuric acid are stable and thiosulphate ion can oxidize as well as reduce.

Thiosulphuric is a weak acid. In aqueous solutions, thiosulphuric acid can decompose to produce a mixture of sulphur containing products.

$$H_2S_2O_3(aq) \longrightarrow S(s) + SO_2(g) + H_2O(l)$$

Thiosulphate ion can act as a reducing agent.

$$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

Structures of thiosulphuric acid and thiosulphate ion are shown below. The oxidation state of the central sulphur atom is +4 where as the terminal sulphur is zero in both structures.

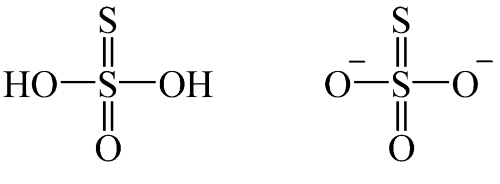


Figure 4.16 Thiosulphuric acid and thiosulphate ion

4.7 Group 17 elements

4.7.1 Group trends

Halogens are reactive and can only be found naturally as compounds. Fluorine is the most electronegative element and exhibits -1 and 0 oxidation states. The halogens other than fluorine form stable compounds corresponding to nearly all values of the oxidation numbers from -1 to +7. However, compounds of bromine with the oxidation state of +7 are unstable. Due to the smaller atomic radius, fluorine can stabilize higher oxidation states of other elements.

Oxidizing ability of halogens decreases down the group. Fluorine is a powerful oxidizing agent. The reactivity of halegons decreases down the group. This can be explained by using the displacement reactions of halegons.

$$Cl_2(aq) + 2Br^-(aq) \longrightarrow 2Cl^-(aq) + Br_2(aq)$$

$$Br_2(aq) + 2I^-(aq) \longrightarrow 2Br^-(aq) + I_2(aq)$$

Fluorine and chlorine are gases with pale yellow and pale green colours respectively at room temperature. Bromine is a red-brown fumming liquid and iodine is a violet-black solid with lustrous effect.

The bond energy of F_2 (155 kJ mol^{-1}) is less than that of Cl_2 (240 kJ mol^{-1}) due to repulsion between the non-bonded electron pairs of fluorine atoms. This is a reason for the high reactivity of fluorine gas. Down the Group 17 bond energies show a gradual decrease (Cl_2 = 240 kJ mol^{-1}, Br_2 = 190 kJ mol^{-1} and I_2 = 149 kJ mol^{-1}).

Table 4.12 Properties of Group 17 elements

	F	**Cl**	**Br**	**I**	****At**
Ground state electronic configuration	$[He]2s^22p^5$	$[Ne]3s^23p^5$	$[Ar]3d^{10}4s^24p^5$	$[Kr]4d^{10}5s^25p^5$	$[Xe]4f^{14}5d^{10}6s^26p^5$
van der Waals radius/ pm	135	180	195	215	-
Ionic radius X^-/ pm	131	181	196	220	-
Covalent radius/pm	71	99	114	133	-
Melting point/ °C	-220	-101	-7.2	114	-
Boiling point/ °C	-188	-34.7	55.8	184	-
Pauling electronegativity	4.0	3.0	2.8	2.5	-
Electron gain enthalpy/ kJ mol^{-1} $X(g) + e \longrightarrow X^-(g)$	-328	-349	-325	-295	-

***Not relevant to the current G. C. E. (A/L) Chemistry Syllabus*

4.7.2 Simple compounds of Group 17

Hydrogen halides

Hydrogen halides are acidic in water. HF has the ability to produce extensive hydrogen bonding, however, HF is a gas (boiling point 20 °C) at room temperature and under atmospheric pressure.

Acidic nature of hydrogen halides in aqueous solutions

For HF; $HF(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$

For other hydrohen halides (HCl, HBr and HI);

$HX(g) + H_2O(l) \longrightarrow H_3O^+(aq) + X^-(aq)$

HF is a weak acid whereas the other hydrogen halides are strong acids in the aqueous medium. HF has the high bond energy (strongest covalent bond), which makes it difficult to dissociate in water to produce H^+ ions readily. The acidic strength of hydrogen halides increases down the Group 17. This can be explained using the same fact mentioned above. Some selected properties of Group 17 hydrogen halides are shown in Table 4.13.

Table 4.13 Selected properties of group 17 hydrogen halides

	HF	HCl	HBr	HI
Melting point/ °C	-84	-114	-89	-51
Boiling point / °C	20	-85	-67	-35
Bond length/ pm	92	127	141	161
Bond dissociation energy/ kJ mol^{-1}	570	432	366	298

Silver halides

Silver halides can be used to identify the halides (chloride, bromide, and iodide) using the colour of the precipitate. Few selected properties are shown below.

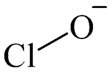
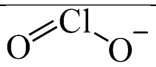
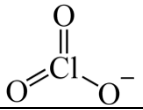
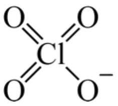
Table 4.14 Silver halides of Group 17 elements

Silver halide	Colour	Solubility in ammonia
AgCl	White	Dissolves in dil. aqueous ammonia
AgBr	Pale yellow	Dissolves in conc. aqueous ammonia
AgI	Yellow	Insoluble in both dil. and conc. aqueous ammonia

Oxides and oxoacids of chlorine

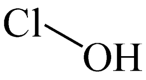
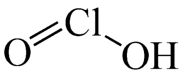
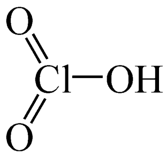
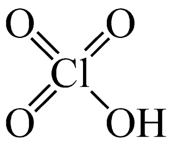
Chlorine forms several oxides and oxoanions with variable oxidation states. Some oxoanions are strong oxidizing agents. Selected oxides of chlorine are shown in Table 4.15.

Table 4.15 Selected oxides and oxoanions of chlorine

Oxidation state	**Formula of oxide**	**Formula of oxoanion**	**Structure of oxoanion**
+1	Cl_2O	ClO^-	
+3	Cl_2O_3	ClO_2^-	
+5	Cl_2O_5	ClO_3^-	
+6	ClO_3 and Cl_2O_6		
+7	Cl_2O_7	ClO_4^-	

Chlorine forms four types of oxoacids. The acidic strength increases with the increasing oxidation number of the chlorine atom. The stuctures and the oxidation states of oxoacids are given in the Table 4.16.

Table 4.16 Structures of oxoacids of chlorine

	$HClO$	**$HClO_2$**	**$HClO_3$**	**$HClO_4$**
Oxidation state	+1	+3	+5	+7
Structure				

Oxidizing power of oxoacids of chlorine is changed as follows.
$HOCl > HClO_2 > HClO_3 > HClO_4$

The oxidation state of chlorine in $HClO$, $HClO_2$, $HClO_3$, $HClO_4$ respectively are +1, +3, +5 and +7. The higher the oxidation state the stronger the acid will be. Therefore the variation of acidic strength is $HClO < HClO_2 < HClO_3 < HClO_4$.

Halides

Most covalent halides react vigorously with water. But CCl_4 does not hydrolyze. Most fluorides and some other halides are inert.

Chlorides of group 14 and 15 elements react with less water as follows.

$$SiCl_4(l) + 2H_2O(l) \longrightarrow 4HCl(aq) + SiO_2(s)$$

$$PCl_5(s) + H_2O(l) \longrightarrow POCl_3(aq) + 2HCl(aq)$$

Chlorides of group 14 and 15 elements react excess water as follows.

$$SiCl_4(l) + 3H_2O(l) \longrightarrow 4HCl(aq) + H_2SiO_3(aq)$$

$$NCl_3(l) + 3H_2O(l) \longrightarrow NH_3(aq) + 3HOCl(aq)$$

$$PCl_3(l) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(aq)$$

$$PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$$

$$AsCl_3(s) + 3H_2O(l) \rightleftharpoons H_3AsO_3(aq) + 3HCl(aq)$$

$$SbCl_3(aq) + H_2O(l) \rightleftharpoons SbOCl(s) + 2HCl(aq)$$

$$BiCl_3(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2HCl(aq)$$

4.7.3 Reactions of chlorine

Chlorine is less reactive than fluorine. Chlorine gas is a strong oxidizing agent. Some reactions of chlorine act as a strong oxidizing agent are given below.

$$2Cu(s) + Cl_2(g) \longrightarrow 2CuCl(s)$$

$$2CuCl(s) + Cl_2(g) \longrightarrow 2CuCl_2(s)$$

$$Fe(s) + Cl_2(g) \longrightarrow FeCl_2(s)$$

$$2FeCl_2(s) + Cl_2(g) \longrightarrow 2FeCl_3(s)$$

excess ammonia, $8NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6NH_4Cl(g)$

excess chlorine, $3Cl_2(g) + NH_3(g) \longrightarrow 3HCl(g) + NCl_3(l)$

Disproportionation reactions of chlorine

Chlorine is simultaneously reduced and oxidized when it reacts with water and bases.

Reaction of chlorine with water;

$$Cl_2(g) + H_2O(l) \longrightarrow HOCl(aq) + HCl(aq)$$

In this reaction, zero oxidation state of chlorine (Cl_2) oxidize to +1 (HOCl) and reduce to -1 (Cl^-).

Reaction with sodium hydroxide;

With cold dilute sodium hydroxide

$Cl_2(g)$ + cold and dil. $2NaOH(aq) \longrightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$

With hot concentrated/ hot dilute sodium hydroxide

$3Cl_2(g)$ + conc. $6NaOH(aq) \xrightarrow{\text{above 80 °C}} 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$

Reactions of oxoanions

ClO^- is stable at low temperatures and disproportionates at high temperature to produce Cl^- and ClO_3^-. However, both BrO^- and IO^- are not stable even at low temperatures and undergo disproportionation.

Disproportionation reactions of hypochlorite

Disproportionation of hypochlorite to produce chlorate and chloride can be written as;

$$3ClO^- \rightleftharpoons ClO_3^- + 2Cl^-$$

Under acidic conditions, HOCl is more stable than ClO^-, which makes disproportionation predominant under basic conditions.

4.8 Group 18 elements

4.8.1 Group trends

All group 18 elements are unreactive monoatomic gasses. Only Xe forms a significant range of compounds. All group 18 elements have positive electron gain enthalpy because an incoming electron needs to occupy an orbital belonging to a new shell.

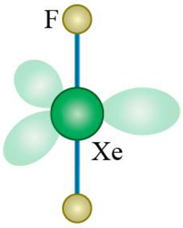
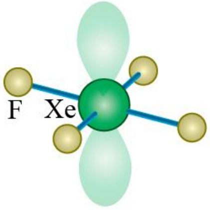
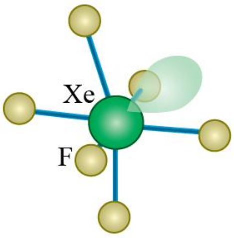
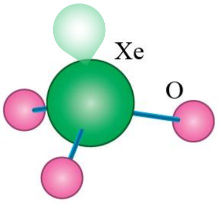
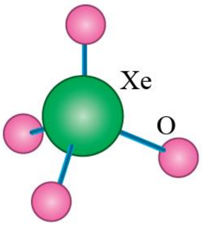
Table 4.17 Properties of Group 18 elements

	He	**Ne**	**Ar**	**Kr**	**Xe**
Ground state electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Xe]4d^{10}5s^25p^6$
Covalent radius/ pm	99	160	192	197	217
1st ionization energy/ kJ mol^{-1}	2373	2080	1520	1350	1170
Electron gain enthalpy/ kJ mol^{-1}	48.2	115.8	96.5	96.5	77.2

4.8.2 Simple compounds of group 18 elements

Compounds of xenon have oxidation numbers of +2, +4, +6 and +8. Xenon reacts directly with fluorine. Some Xe compounds are shown in Table 4.18.

Table 4.18 Some selected compounds of Xe

Oxidation state	Compounds	Structure
+2	XeF_2	
+4	XeF_4	
+6	XeF_6	
+6	XeO_3	
+8	XeO_4	

4.9 Periodic trends shown by *s* and *p* block elements

4.9.1 The valence electron configuration

The valance electron configuration of an element can be predicted from their position in the periodic table.

Group number	1	2	13	14	15	16	17	18
Valance shell electron configuration	ns^1	ns^2	ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6

4.9.2 Metallic character

Metals have lower ionization energies compared to the other elements. Hence, metals can easily release electrons to produce cations. The atomic radii increase and ionization energy decreases when going down a group. Therefore, the metallic nature increases down the group. Also, across a period, atomic radii decrease and ionization energy increases. Therefore, the metallic nature decreases.

The third period shows a gradual increase in melting point and then a decrease across the period. Most abundant elemental form, type of bonding between similar atoms and the melting point of the third period elements are shown below.

Table 4.19 Most abundant elemental form, type of bonding between similar atoms and the melting point of the third period elements

	Na	Mg	Al	Si	P_4	S_8	Cl_2	Ar
Melting point/ °C	98	649	660	1420	44	119	-101	-189
Bonding type	M	M	M	NC	C	C	C	-

Metallic – M, Network covalent – NC, Covalent - C

Acid, base and amphoteric nature of oxides

Across the third period variation of type of bonding in oxides in which the elements are at their highest oxidation number are given below.

Table 4.20 Comparison of the third period oxides

	$Na_2O(s)$	$MgO(s)$	$Al_2O_3(s)$	$SiO_2(s)$	$P_4O_{10}(s)$	$SO_3(g)$	$Cl_2O_7(l)$
Oxidation number	+1	+2	+3	+4	+5	+6	+7
Bonding type	I	I	I	NC	C	C	C
Nature	Strongly B	B	Am	Very weakly A	Weakly A	A	Strong A

Ionic – I, Network covalent – NC, Covalent - C

Basic – B, Amphoteric – Am, Acidic - A

Oxides with the highest oxidation number are considered to compare the chemical nature. The nature from strong basic on the left to strong acidic to the right can be seen. Amphoteric nature can be seen in the middle of the series.

4.9.3 Reactions of third period oxides with water, acids and bases

Oxides of sodium and magnesium react with water to produce hydroxides.

$$Na_2O(s) + H_2O(l) \longrightarrow 2NaOH(aq)$$

$$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(s)$$

As these two oxides are basic, they react with acids to produce salt and water.

$$Na_2O(s) + 2HCl(aq) \longrightarrow 2NaCl(aq) + H_2O(l)$$

$$MgO(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + H_2O(l)$$

Aluminum oxide is amphoteric and it reacts with acids as well as with bases to produce salts.

$$Al_2O_3(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2O(l)$$

$$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \longrightarrow 2Na[Al(OH)_4](aq)$$

SiO_2 is weakly acidic and reacts with strong bases. Also, SiO_2 shows no reaction with water.

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq) + H_2O(l)$$

P_4O_{10}, SO_3, and Cl_2O_7 are acidic and produce acids when dissolved in water. Those reactions are shown below.

$$P_4O_{10}(s) + 6H_2O(l) \longrightarrow 4H_3PO_4(aq)$$

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

$$Cl_2O_7(l) + H_2O(l) \longrightarrow 2HClO_4(aq)$$

These oxides also react with bases to produce salts and water.

$$P_4O_{10}(s) + 12NaOH(aq) \longrightarrow 4Na_3PO_4(aq) + 6H_2O(l)$$

$$SO_3(g) + 2NaOH(aq) \longrightarrow Na_2SO_4(aq) + H_2O(l)$$

$$Cl_2O_7(l) + 2NaOH \longrightarrow 2NaClO_4(aq) + H_2O(l)$$

4.9.4 Acid, base and amphoteric nature of hydroxides and hydrides

Hydroxides of third period show a trend similar to oxides of the same period. The following table shows a comparison of the third period hydroxides.

Table 4.21 Comparison of the third period hydroxides

	$NaOH$	$Mg(OH)_2$	$Al(OH)_3$	$Si(OH)_4$	$P(OH)_5$	$S(OH)_6$	$Cl(OH)_7$
Stable form				H_2SiO_3	H_3PO_4	H_2SO_4	$HClO_4$
Oxidation number	+1	+2	+3	+4	+5	+6	+7
Bonding type	I	I	C	C	C	C	C
Nature	Strongly B	Weakly B	Am	Very weakly A	Weakly A	Strongly A	Very strongly A

Ionic – I, Network covalent – NC, Covalent - C

Basic – B, Amphoteric – Am, Acidic - A

Nature of hydrides of third period varies from strong bases to strong acids across the period. Amphoteric nature can be seen in the middle of the series.

Table 4.22 Comparison of the third period hydrides

	$NaH(s)$	$MgH_2(s)$	$(AlH_3)_x(s)$	$SiH_4(g)$	$PH_3(g)$	$H_2S(g)$	$HCl(g)$
Oxidation number	+1	+2	+3	-4	-3	-2	-1
Nature of the aqueous solution	Strongly B	Weakly B	Am	Very weakly A	N	Weakly A	Very strongly A
Bonding type	I	I	NC	C	C	C	C

Ionic – I, Network covalent – NC, Covalent - C

Basic – B, Amphoteric – Am, Acidic – A, Neutral - N

Hydrides of sodium and magnesium react with water to produce basic solutions.

$$NaH(s) + H_2O(l) \longrightarrow NaOH(aq) + H_2(g)$$

$$MgH_2(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(s) + 2H_2(g)$$

$$AlH_3(s) + 3H_2O(l) \longrightarrow Al(OH)_3(s) + 3H_2(g)$$

PH_3 is weakly soluble in water and produces a neutral solution. H_2S and HCl are acidic and aqueous solutions are also acidic.

$$H_2S(g) + H_2O(l) \longrightarrow HS^-(aq) + H_3O^+(aq)$$

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

4.9.5 Nature of the halides across the third period

As the electronegativity of elements increases across the period from left to right, the ability of hydrolyzation of chlorides increases accordingly. Corresponding reactions are given below. Chlorides of *s* block elements in the third period are ionic and the *p* block elements are covalent.

Table 4.23 Comparison of the third period chlorides

	$NaCl(s)$	$MgCl_2(s)$	$AlCl_3(s)$	$SiCl_4(l)$	$PCl_5(s)$	$SCl_2(g)$
Oxidation number	+1	+2	+3	+4	+5	+2
Bonding type	I	I	C	C	C	C
Nature of the aqueous solution	N	Very weakly A	A	A	A	A

Ionic – I, Covalent - C

Basic – B, Amphoteric – Am, Acidic – A, Neutral - N

Reactions with water of third period covalent chlorides are,

$$AlCl_3(s) + 7H_2O(l) \longrightarrow [Al(H_2O)_5OH]^{2+}(aq) + 3Cl^-(aq) + H_3O^+(aq)$$

$$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$$

$$PCl_5(s) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$$

$$2SCl_2(l) + 3H_2O(l) \longrightarrow H_2SO_3(aq) + S(s) + 4HCl(aq)$$

Group 15 can be used to understand the variation of properties down the group. Down a group the ionization energy decreases, and the metallic nature increases. Use the information given for the Group 15 and correlate the variation in ionization energies with the increase of metallic properties down the group. Both N and P are nonmetals and produce acidic oxides. However, As and Sb oxides are amphoteric and bismuth oxide is basic.

Reactions with water of group 15 halides are given in the respective section under the halides of group 17.

d Block Elements

Elements in Groups 3 to 12 are collectively classified as *d* block elements. In *d* block elements the last electron gets filled into a *d* orbital. These elements can be categorised into two categories namely transition and non-transition.

4.10 Transition elements

d block elements contain incompletely filled *d* subshell at elemental state or with the ability to form at least one stable ion with incompletely filled *d* subshell are called transition elements. Therefore, *d* block elements producing ions only with d^{10} configurations are considered as non-transition elements.

e.g.: Electronic configurations of Zn : $[Ar]3d^{10}4s^{2}$

Electronic configurations of Zn^{2+}: $[Ar]3d^{10}4s^{0}$

Electronic configuration of Sc : $[Ar]3d^{1}4s^{2}$

Electronic configuration of Sc^{3+} : $[Ar]3d^{0}4s^{0}$

Both Zn and Sc are *d* block elements (last electron is filled to a 3*d* orbital). However, Zn is considered as a non-transition element due to the absence of a partially filled *d* subshell at the elemental stage and Zn^{2+} ion. Sc can be considered as a transition element since Sc contains partially filed d subshell at the elemental stage.

Table 4.24 Comparison of the properties of *d* block elements in fourth period

Group	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Pauling electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6
Atomic radius/pm	162	147	134	128	127	126	125	125	128	137
Covalent radius/pm	144	132	122	118	117	117	116	115	117	125
Ionic radius (M^{2+})/ pm	-	100	93	87	81	75	79	83	87	88

Transition metal ions have less variation in atomic radii across a period than that of the main group elements. Across the period of the transition metals shown in Table 4.23, the atomic radii decrease slightly and then increase. Across the period, to each *d* electron added nuclear charge is also increased by one. The decrease of the atomic radii at the middle of the period (from Sc to Ni) occurs due to the predominance of attraction power of nuclear charge increase than the repulsion among the electrons. However, at the end of the period (Cu and Zn), radii of the atoms increase due to greater repulsion among electrons as electrons are paired in *d* orbitals.

4.10.1 Occurrence

Elements on the left of the 3*d* series (fourth period *d* block elements) exist commonly in the nature as metal oxides and cations combined with anions.

Few examples are shown below.

Table 4.25 Occurrence of some fourth period *d* block elements

Element	**Example**
Ti	$FeTiO_3$ (Ilmenite) and TiO_2 (Rutile)
Fe	Fe_2O_3 (Hematite), Fe_3O_4 (Magnetite) and $FeCO_3$ (Siderite)
Cu	$CuFeS_2$ (Copper Pyrite)

4.10.2 Properties of fourth period *d* block elements

Oxidation states and ionization energies

Except Sc and Zn in the fourth period *d* block elements, others can form stable cations with multiple oxidation states. The multiplicity of the oxidation state is due to the varying number of *d* electrons participate in bonding. Both Zn (+2) and Sc (+3) only produce ions with a single oxidation state, and these ions do not contain partially filled *d* orbitals. Electron configuration and the oxidation states of *d* block elements are shown in Table 4.26. Sc forms only Sc^{3+} ions. Except in Sc, +2 oxidation number can be seen in all the other elements since electrons in 4*s* orbital get removed due to ionization before electrons in 3*d* orbitals. Reason for this is that the 4*s* orbital with two electrons in the outermost shell experiences a lesser effective nuclear charge than that of electrons in the 3*d* orbital.

As a result of the $3d^{10}4s^1$ configuration, Cu can form +1 oxidation number commonly. However, Cr^+ is extremely rare and unstable even though Cr has $3d^54s^1$ configuration.

The highest possible oxidation number that a d block element can show is the sum of 4*s* and 3*d* electrons. Transition metals are also capable of producing variable oxidation states similar to *p* block elements and show the ability to interconvert among their oxidation states. Therefore, they can act as oxidizing as well as reducing agents.

First five elements achieve the maximum possible oxidation state by losing all 4*s* and 3*d* electrons. With the filling of more 3*d* electrons, towards the right end of the period, the 3*d* orbitals become greater in energy as the nuclear charge of the atom increases. This makes *d* electrons are harder to remove. The most common oxidation state for these elements is +2 due to the loss of 4*s* electrons.

Reactivity

d block elements do not react with the water while *s* block elements react with water vigorously. The 4*s* electrons of the *d* block elements are tightly bound to the nucleus due to the higher nuclear charge than that of the *s* block elements. First ionization energy of *d* block elements lies between the values of those of *s* and *p* block elements.

Table 4.26 Electronic configuration and oxidation states of *d* block elements

Element	**Ground state configuration**			**Oxidation states**
		3*d*	4*s*	
Sc	[Ar]$3d^1 4s^2$	[↑][ ][ ][ ][ ]	[↑↓]	+3
Ti	[Ar]$3d^2 4s^2$	[↑][↑][ ][ ][ ]	[↑↓]	(+2), +3, +4
V	[Ar]$3d^3 4s^2$	[↑][↑][↑][ ][ ]	[↑↓]	(+2), (+3), +4, +5
Cr	[Ar]$3d^5 4s^1$	[↑][↑][↑][↑][↑]	[↑]	+2, +3, (+4), (+5), +6
Mn	[Ar]$3d^5 4s^2$	[↑][↑][↑][↑][↑]	[↑↓]	+2, +3, +4, (+5), (+6), +7
Fe	[Ar]$3d^6 4s^2$	[↑↓][↑][↑][↑][↑]	[↑↓]	+2, +3, (+4), (+5), (+6)
Co	[Ar]$3d^7 4s^2$	[↑↓][↑↓][↑][↑][↑]	[↑↓]	+2, +3, (+4)
Ni	[Ar]$3d^8 4s^2$	[↑↓][↑↓][↑↓][↑][↑]	[↑↓]	+2, (+3), (+4)
Cu	[Ar]$3d^{10} 4s^1$	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑]	+1, +2, (+3), (+4)
Zn	[Ar]$3d^{10} 4s^2$	[↑↓][↑↓][↑↓][↑↓][↑↓]	[↑↓]	+2

**Less common states are shown in brackets.*

Ionization energies of fourth period *d* block elements are higher than that of the *s* block elements in the same period. The first ionization energies of *d* block elements are increase slightly across the period when move from left to the right of the period. Variation of the first ionization energy across the *d* block is less than that of *s* and *p* block elements. Increase in the nuclear charge across the fourth period *d* block elements expect to be increase the first ionization energies due to the greater attraction towards the nucleus by the 4*s* electrons. However, in all *d* block elements, extra electrons are inserted in to the 3*d* orbital moving from left to right across the period, and these *d* electrons shield the 4s electrons from the inward attraction of the nucleus. Because of these two counter effects, the ionization energy of *d* block elements increases slightly across the period. Successive ionization energies of the fourth period *d* block elements are shown in the table given below.

Table 4.27 Successive ionization energies of fourth period *d* block metals, K and Ca.**

Element	1st ionization energy/ kJ mol^{-1}	2nd ionization energy/ kJ mol^{-1}	3rd ionization energy/ kJ mol^{-1}
K	418	3052	
Ca	589	1145	4912
Sc	631	1235	2389
Ti	658	1310	2652
V	650	1414	2828
Cr	653	1496	2987
Mn	717	1509	3248
Fe	759	1561	2957
Co	758	1646	3232
Ni	737	1753	3393
Cu	746	1958	3554
Zn	906	1733	3833

** For K, only first and second ionization energies are given to understand the energy increase due to removal of an electron from an inner orbital.

First ionization energies of *d* block elements are higher than those of *s* block elements in the same period. This explains the less reactivity of *d* block elements than the *s* block elements.

All *d* block elements are metals because 4*s* electrons in *d* block elements can be released easily to form cations. Metallic character of the *d* block elements increases down the group.

All *d* block elements in the fourth period are solids with high melting and boiling points. Melting and boiling points of *d* block elements are extremely high as compared to those of *s* and *p* block elements. *d* block elements are moderately reactive.

Except metal ions with $3d^0$ and $3d^{10}$ configurations, *d* block metal compounds produce characteristic colours. This means transition metal ion complexes can produce coloured compounds. Most *d* block metal ions form complex compounds.

Electronegativity

Table below provides the electronegativity of *d* block elements and can be used to understand the variation of electronegativity of *d* block elements in the fourth period. Electronegativity increases with the atomic number. However, Mn and Zn are deviated from the trend due to their stable electron configuration. Due to the higher nuclear charge, *d* block elements have higher electronegativity than that of the *s* block elements.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronegativity	1.3	1.5	1.6	1.6	1.5	1.8	1.8	1.8	1.9	1.6

When an atom exhibits variable oxidation states, the higher oxidation state has higher electronegativity.

Catalytic properties

Most transition metals and compounds can act as catalysts due to the presence of partially filled and empty *d* orbitals. This makes *d* orbitals to accept or donate electrons. This property that makes them effective components of catalysts. Pd for hydrogenation, Pt/Rh for oxidation of ammonia to nitrogen oxide, and V_2O_5 for oxidation of SO_2 to SO_3 and $TiCl_3/Al(C_2H_5)_6$ for the polymerization of ethene are some examples for the use of *d* block element and its compound as a catalyst. Some popular organic reactions such as alkylation and acylation are done in the presence of transition metal ion as the catalyst.

Colours of transition metal ions

Aqueous solutions of many transition metal ions can absorb radiation in the visible region of the electromagnetic spectrum to produce various colours. This ability is due to the presence of partially filled *d* subshells. In contrast, metal ions of *s* block are colourless because these ions have completely filled subshells. The following Table shows some of the colours of transition metal ions and oxoanions in aqueous solutions. For example, $[Co(H_2O)_6]^{2+}$ is pink, $[Mn(H_2O)_6]^{2+}$ pale pink. In contrast, aqueous solutions of Sc^{3+} and Zn^{2+} are colourless due to the unavailability of partially filled *d* orbitals. Also, ions with d^0 or d^{10} configuration are coloureless when in an aqueous solution. Colours of MnO_4^- and CrO_4^{2-} are not due to the electron transition of electrons among the *d* orbitals. Colours of some elected oxoanions are given in **Table 4.28**.

Table 4.28 Colours of *d* block metal ions and oxoanions in aqueous solutions. The number of 3*d* and 4*s* electrons are shown in brackets next to the metal ion.

Ion	Colour	Ion	Colour
Sc^{3+} (d^0 s^0)	Colourless	Fe^{3+}(d^5 s^0)	Brown yellow
Ti^{4+}(d^0 s^0)	Colourless	Fe^{2+}(d^6 s^0)	Pale green
Cr^{3+}(d^3 s^0)	Blue violet	Co^{2+}(d^7 s^0)	Pink
Mn^{2+}(d^5 s^0)	Pale pink	Ni^{2+}(d^8 s^0)	Green
		Cu^{2+}(d^9 s^0)	Blue
		Cu^{+}(d^{10} s^0)	Colourless
		Zn^{2+}(d^{10} s^0)	Colourless
Oxoanion	**Colour**	**Oxoanion**	**Colour**
MnO_4^-	Purple	CrO_4^{2-}	Yellow
MnO_4^{2-}	Green	$Cr_2O_7^{2-}$	Orange

4.10.3 Oxides of *d* block elements

First four elements form oxides by removing all valence electrons. Unlike main group elements, transition elements produce different oxidation states. Some *d* block elements can form oxides in which metal atom presence with two different oxidation numbers. Both Mn_3O_4 and Fe_3O_4 are examples for binary oxides (which are formed with two oxidation numbers). Mn_3O_4 is a mixture of Mn(II) and Mn(III) . Also, Fe_3O_4 is a mixture of Fe(II) and Fe(III) .

4.10.4 Chemistry of some selected *d* block oxides

Chromium and manganese oxides

Properties of an oxide depend on the oxidation number. The bonding type depend on the oxidation number. The change in the bonding type explains the basis in the acid-base behaviour of metal oxides. For the oxides with high oxidation numbers have covalent bonding characteristics are acidic and the oxides with low oxidation numbers have ionic bonding characteristics are basic.

Table 4.29 Acid-base nature of chromium oxides

Oxide	Acid-base nature	Oxidation number	
CrO	Weakly basic	+2	Low oxidation state
Cr_2O_3	Amphoteric	+3	Moderate oxidation state
CrO_2	Weakly acidic	+4	
CrO_3	Acidic	+6	High oxidation state

Generally, if the metal is in a lower oxidation state, the oxide is basic. Also, if the metal is in a moderate oxidation state, the oxide is amphoteric and metal oxides with higher oxidation state are acidic. This explains why the compounds in **Tables 4.29** and **4.30** with lower oxidation states are more metallic while compounds with higher oxidation states are more non-metallic in properties.

Table 4.30 Acid-base nature of manganese oxides

Oxide	Acid-base nature	Oxidation number	
MnO	Basic	+2	Low oxidation state
Mn_2O_3	Weakly basic	+3	Moderate oxidation state
MnO_2	Amphoteric	+4	
MnO_3	Weakly acidic	+6	
Mn_2O_7	Acidic	+7	High oxidation state

Reactions of some selected oxoanions of chromium

The yellow coloured chromate ion exists in neutral or basic conditions. Under the acidic conditions, it is converted to the orange coloured dichromate ion.

$$2\,CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Even without partially filled *d* subshells (Cr at +6 oxidation state), both chromate and dichromate produce colours due to the electron charge transfer between Cr and O ligands. However, the explanation of this phenomena is not a part of the current syllabus.

The reduction of $Cr_2O_7^{2-}$ to Cr^{3+} happens only in acidic medium. In acidic medium, CrO_4^{2-} ions will be converted into $Cr_2O_7^{2-}$ ions. Therefore in acidic medium Cr^{6+} present only as $Cr_2O_7^{2-}$.

Some important redox reactions of chromium oxoanions are given below.

$$Cr_2O_7^{2-}(aq) + 3H_2S(g) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O(l)$$

$$Cr_2O_7^{2-}(aq) + 3SO_2(g) + 2H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_2O(l)$$

$$Cr_2O_7^{2-}(aq) + 6Fe^{2+}(g) + 14H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 6Fe^{3+}(aq) + 7H_2O(l)$$

$$Cr_2O_7^{2-}(s) + \text{conc. } 14HCl(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cl_2(g) + 8Cl^-(aq) + 7H_2O(l)$$

In CrO_4^{2-}, oxidation number Cr is +6. Therefore it can act as an oxidizing agent. Under acidic conditions, Cr(VI) can be reduced to Cr(III).

Reactions of manganese oxides and oxoanions

$KMnO_4$ is a purple solid. Colour of MnO_4^- is due to the electron transfer process between central Mn atom and O ligands. Under acidic conditions, permanganate ion can act as a strong oxidizing agent. Colours of MnO_2 and $KMnO_4$ are given below.

Table 4.31 Colours of MnO_2 and $KMnO_4$

Compound	Colour
MnO_2	Dark brown/ black
$KMnO_4$	Purple

Some important redox reactions of MnO_4^- are given below.

Under acidic conditions:

$2MnO_4^-(aq) + 5H_2O_2(l) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5O_2(g) + 8H_2O(l)$

$2MnO_4^-(aq) + 5H_2S(g) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5S(g) + 8H_2O(l)$

$2MnO_4^-(aq) + 5SO_2(g) + 2H_2O(l) \longrightarrow 2Mn^{2+}(aq) + 5SO_4^{2-}(aq) + 4H^+(aq)$

$MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \longrightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq)+ 4H_2O(l)$

$2MnO_4^-(aq) + 10I^-(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(aq) + 8H_2O(l)$

$2MnO_4^-(aq) + 5NO_2^-(aq) + 6H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 5NO_3^-(aq) + 3H_2O(l)$

$2MnO_4^-(aq) + \text{conc. } 16HCl(aq) \longrightarrow 2Mn^{2+}(aq) + 5Cl_2(g) + 6Cl^-(aq) + 8H_2O(l)$

$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

In all these reactions, under acidic conditions, MnO_4^- reduces to Mn^{2+}.

Under dilute alkaline/ neutral conditions:

$2MnO_4^-(aq) + I^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + IO_3^-(aq) + 2OH^-(aq)$

$2MnO_4^-(aq) + 3SO_3^{2-}(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + 3SO_4^{2-}(aq) + 2OH^-(aq)$

4.10.5 Coordination compounds of transition metal ions

Transition metal ions typically form coordination compounds. These coordination compounds consist of complex ions. These complex ions are built with a central metal ion and two or more surrounding monodentate ligands (there are ligands that form more than one bond with the central metal ion). For example, $[Ni(NH_3)_6]Cl_2$ is consist with the complex ion of $[Ni(NH_3)_6]^{2+}$ and the counter ion of Cl^- (Figure 4.17).

Ligands (Lewis bases) can donate electrons to the central metal ion (Lewis acid) to form dative bonds with it.

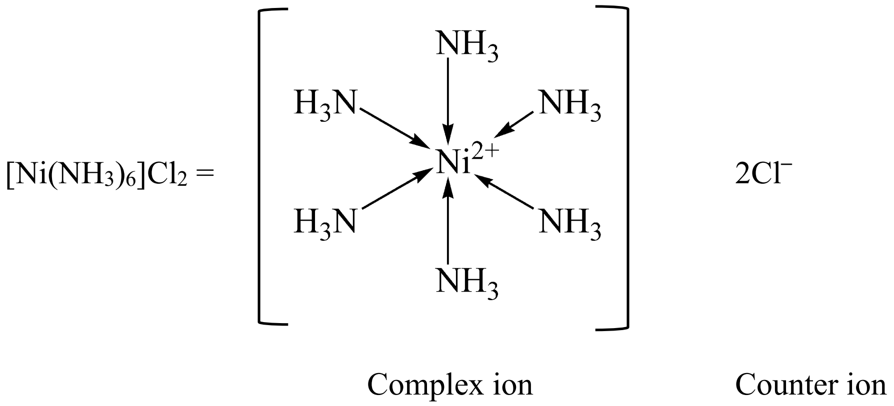


Figure 4.17 A coordination compound

In this example, ammonia molecules are bonded as ammine ligands to the central metal ion of Ni^{2+}. The charge of the complex ion can be easily determined using the following equation.

$$\begin{array}{ccccc} \text{The charge of the} & & \text{Oxidation number of} & & \text{Total charge of} \\ \text{complex} & = & \text{the central metal atom} & + & \text{all ligands} \\ & & \text{or the ion} & & \end{array}$$

Determination of oxidation number of the central metal ion

The following method can be used to determine the oxidation number of the central metal ion of a coordination complex.

Example 6.1

Calculate the oxidation number of the central metal ion in $[Ni(H_2O)_3Cl_3]^-$ complex ion.

Answer:

$$\begin{array}{ccccc} \text{The charge of the} & & \text{Oxidation number of} & & \text{Total charge} \\ \text{complex} & = & \text{the central metal atom} & + & \text{of all ligands} \\ & & \text{or the ion} & & \end{array}$$

Charge of the complex ion = - 1

Charges of the ligands = three H_2O molecules: $3 \times 0 = 0$,

three Cl^- ions: $3(-1) = -3$

Using the equation;

-1 = Oxidation number of Ni + 0 + (-3)

Oxidation number of Ni = +2

4.10.6 Nomenclature of simple complex ions and compounds

Name of a metal complex provides information about the complex such as oxidation state of the central metal ion, types of ligands and the number. The rules used to write the name of a complex ion is proposed by IUPAC are given below.

Naming of ligands

Name of an anion acting as a ligand in the complex ion can be obtained by removing last letter of the anion name and adding '*o*' letter to the end. Neutral molecules acting as ligands are usually given the name of the molecule. However, there are some exceptions and those are not discussed in the current G. C. E. (A/L) Chemistry syllabus.

Anionic ligands		**Neutral ligands**	
Cl^-	chlorido	NH_3	ammine
Br^-	bromido	H_2O	aqua
CN^-	cyanido	CO	carbonyl
OH^-	hydroxido		

Number of a particular ligand is indicated by prefixes. The used prefixes are *di* – two, *tri* – three, *tetra* – four, *penta* – five, *hexa* – six, etc.

Naming of complex cations

Name of the complex ion must be written as a single word with no space and must only be written using lower case English letters. Oxidation number of the metal ion is indicated by Roman numerals within parentheses at the end of the metal name.

e.g.:	$[Ni(NH_3)_6]^{2+}$	hexaamminenickel(II) ion
	$[Cu(NH_3)_4]^{2+}$	tetraamminecopper(II) ion
	$[Cr(H_2O)_6]^{3+}$	hexaaquachromium(III) ion

Complex anions

For negatively charged complex ions (complex anions) the suffix '*ate*' must be used after the name of the metal.

e.g.:	$[CuCl_4]^{2-}$	tetrachloridocuprate(II) ion
	$[CoCl_4]^{2-}$	tetrachloridocobaltate(II) ion

Table 4.32 Names used for metals in anionic complexes

Metal	Name used in anionic complexes	Metal	Name used in anionic complexes
Cr	chromate	Co	cobaltate
Cu	cuprate	Fe	ferrate
Mn	manganate	Ni	nickelate
Ag	argentate	Hg	mercurate
Au	aurate		

Name of a complex compound must have the name of the cation first and the anion name second. These two names must be separated by a space.

e.g.: $[Ni(NH_3)_6]Cl_2$ - hexaamminenickel(II) chloride

$Na_2[CoCl_4]$ - sodium tetrachloridocobaltate(II)

Coordination number

Number of coordination bonds formed between the central metal ion and ligands is defined as coordination number. Since some ligands can form more than one coordination bond with the central metal ion, it is incorrect to define the coordination number as the number of ligands coordinated to the central metal ion. The coordination number depends on the size, charge, nature of ligands and the electronic configuration of the central metal ion.

Table 4.33 Common coordination numbers of *d* block ions

M^+	Coordination number	M^{2+}	Coordination number	M^{3+}	Coordination number
Cu^+	2, 4	Mn^{2+}	4, 6	Sc^{3+}	6
		Fe^{2+}	6	Cr^{3+}	4,6
		Co^{2+}	4, 6	Co^{3+}	4,6
		Ni^{2+}	4, 6		
		Cu^{2+}	4, 6		
		Zn^{2+}	4, 6		

4.10.7 Factors affecting the colour of the complexes

Transition metal atoms and ions can produce coloured complexes. Colour of these complexes depends on the following factors. Examples which reflect the effect these factors are given in Table 4.34.

1. Central metal ion
2. Oxidation state of the central metal ion
3. Nature of the ligands

Table 4.34 Colours of transition metal ion complexes depends on the factors

1. Central metal ion

Mn(II)	Ni(II)	Cu(II)
$[Mn(H_2O)_6]^{2+}$	$[Ni(H_2O)_6]^{2+}$	$[Cu(H_2O)_6]^{2+}$
Pale-pink	Green	Pale-blue

2. Oxidation state of the central metal ion

Co(II)	Co(III)	Fe(II)	Fe(III)
$[Co(H_2O)_6]^{2+}$	$[Co(H_2O)_6]^{3+}$	$[Fe(H_2O)_6]^{2+}$	$[Fe(H_2O)_6]^{3+}$
Pink	Blue	Pale-green	Yellow-brown

3. Nature of the ligand

H_2O	NH_3	Cl^-
$[Co(H_2O)_6]^{2+}$	$[Co(NH_3)_6]^{2+}$	$[CoCl_4]^-$
Pink	Yellowish-brown	Blue

Ability to form coloured compounds is a unique property of the transition metal elements. Colours of some common metal complexes are given in Table 4.33.

Table 4.35 Metal complexes and colours

Metal	**Nature of the ligand**			
	H_2O(l)	**OH^-(aq)**	**NH_3(aq)**	**Cl^-(aq)**
Cr	$[Cr(H_2O)_6]^{3+}$ Blue-violet	$Cr(OH)_3$ Blue-green ppt (precipitate)	$Cr(OH)_3$ Blue-green ppt	
Mn	$[Mn(H_2O)_6]^{2+}$ Pale pink	$Mn(OH)_2$ Off white/ cream colour ppt	$Mn(OH)_2$ Off white/ cream colour ppt	$[MnCl_4]^{2-}$ Yellow
Fe	$[Fe(H_2O)_6]^{2+}$ Pale-green $[Fe(H_2O)_6]^{3+}$ Yellow-brown	$Fe(OH)_2$ Dirty green ppt $Fe(OH)_3$ Reddish-brown ppt	$Fe(OH)_2$ Dirty green ppt $Fe(OH)_3$ Reddish-brown ppt	$[FeCl_4]^-$ Yellow
Co	$[Co(H_2O)_6]^{2+}$ Pink	$Co(OH)_2$ Pink ppt	$[Co(NH_3)_6]^{2+}$ Yellowish-brown $[Co(NH_3)_6]^{3+}$ Brownish-red	$[CoCl_4]^{2-}$ Blue
Ni	$[Ni(H_2O)_6]^{2+}$ Green	$Ni(OH)_2$ Green ppt	$[Ni(NH_3)_6]^{2+}$ Blue	$[NiCl_4]^{2-}$ Yellow
Cu	$[Cu(H_2O)_6]^{2+}$ Pale blue	$Cu(OH)_2$ Blue ppt	$[Cu(NH_3)_4]^{2+}$ Deep blue	$[CuCl_4]^{2-}$ Yellow
Zn	$[Zn(H_2O)_6]^{2+}$ Colourless	$Zn(OH)_2$ White ppt With excess OH^- $[Zn(OH)_4]^{2-}$ Colourless	$[Zn(NH_3)_4]^{2+}$ Colourless	$[ZnCl_4]^{2-}$ Colourless

Reactions of $[Cr(H_2O)_6]^{3+}$

With aqueous NH_3, the blue-violet colour $[Cr(H_2O)_6]^{3+}$ aqueous solution will be turned into a blue-green gelatinous precipitate.

$$[Cr(H_2O)_6]^{3+} + 3NH_3\,(aq) \longrightarrow Cr(OH)_3(s) + 3NH_4^+(aq) + 3H_2O(l)$$

Reactions of $[Co(H_2O)_6]^{2+}$

With strong base (NaOH); the pink colour $[Co(H_2O)_6]^{2+}$ aqueous solution turns into pink precipitate.

$$[Co(H_2O)_6]^{2+}(aq) + 2OH^-\,(aq) \longrightarrow Co(OH)_2(s) + 6H_2O(l)$$

With NH_3

$$[Co(H_2O)_6]^{2+}(aq) + 6NH_3(aq) \longrightarrow [Co(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

Initially the pink colour $[Co(H_2O)_6]^{2+}$ forms a pink colour $Co(OH)_2$ precipitate with limited amount of concentrated NH_3 and on further addition of concentrated NH_3 it forms a yellowish-brown colour $[Co(NH_3)_6]^{2+}$ complex ion. However due to the auto-oxidation, $[Co(NH_3)_6]^{2+}$ complex convert to a brownish-red colour $[Co(NH_3)_6]^{3+}$. Because of this, the solution appears a mixture of above two colours.

With conc. HCl, pink colour solution turns into a blue colour solution.

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \longrightarrow [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

Reactions of $[Ni(H_2O)_6]^{2+}$

With a strong base, the green colour $[Ni(H_2O)_6]^{2+}$ aqueous solution turns into a green precipitate.

$$[Ni(H_2O)_6]^{2+}(aq) + 2OH^-\,(aq) \longrightarrow Ni(OH)_2(s) + 6H_2O(l)$$

With excess $NH_3(aq)$, the green colour $[Ni(H_2O)_6]^{2+}$ solution turns into a blue solution.

$$[Ni(H_2O)_6]^{2+}(aq) + 6NH_3\,(aq) \longrightarrow [Ni(NH_3)_6]^{2+}(aq) + 6H_2O(l)$$

With concentrated HCl, green colour solution turns into a yellow colour solution.

$$[Ni(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \longrightarrow [NiCl_4]^{2-}(aq) + 6H_2O(l)$$

Reactions of $[Mn(H_2O)_6]^{2+}$

With strong base, pale pink colour $[Mn(H_2O)_6]^{2+}$ aqueous solution turns to a off white / cream colour precipitate.

$$[Mn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow Mn(OH)_2(s) + 6H_2O(l)$$

With aqueous NH_3, the pale pink colour solution turns into a off white/ cream colour precipitate.

$$[Mn(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \longrightarrow Mn(OH)_2(s) + 2NH_4^+(aq) + 4H_2O(l)$$

Reactions of $[Fe(H_2O)_6]^{3+}$

With strong base, yellow-brown colour $[Fe(H_2O)_6]^{3+}$ aqueous solution turns into a reddish-brown precipitate.

$$[Fe(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \longrightarrow Fe(OH)_3(s) + 6H_2O(l)$$

With aqueous NH_3, yellow-brown colour $[Fe(H_2O)_6]^{3+}$ aqueous solution turns into a reddish-brown precipitate.

$$[Fe(H_2O)_6]^{3+}(aq) + 3NH_3(aq) \longrightarrow Fe(OH)_3(s) + 3NH_4^+(aq) + 3H_2O(l)$$

Reactions of $[Cu(H_2O)_6]^{2+}$

With strong base, the pale blue colour $[Cu(H_2O)_6]^{2+}$ aqueous solution turns into a blue precipitate.

$$[Cu(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow Cu(OH)_2(s) + 6H_2O(l)$$

With a limited amount of aqueous NH_3, pale blue colour solution turns into a blue precipitate.

$$[Cu(H_2O)_6]^{2+}(aq) + 2NH_3(aq) \longrightarrow Cu(OH)_2(s) + 2NH_4^+(aq) + 4H_2O(l)$$

With excess aqueous NH_3, pale blue colour solution turns into a deep blue colour complex.

$$[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq) + 6H_2O(l)$$

With concentrated HCl, pale blue colour solution turns into a yellow colour solution.

$$[Cu(H_2O)_6]^{2+}(aq) + 4Cl^-(aq) \longrightarrow [CuCl_4]^{2-}(aq) + 6H_2O(l)$$

Reactions of $[Zn(H_2O)_6]^{2+}$

With limited amount of strong base, colourless $[Zn(H_2O)_6]^{2+}$ aqueous solution turns into a white precipitate.

$$[Zn(H_2O)_6]^{2+}(aq) + 2OH^-(aq) \longrightarrow Zn(OH)_2(s) + 6H_2O(l)$$

With excess strong base; white precipitate turns into a colourless clear solution.

$$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow [Zn(OH)_4]^{2-}(aq)$$

4.10.8 Importance of *d* block elements

1. Transition metals are good conductors (Au, Ag and Cu), and are also malleable, ductile, and lustrous. Transition metals can be mixed together to produce alloys since they have similar atomic sizes. These alloys are used since the ancient time for various purposes. Production of alloys can change the properties of metals.
2. Cobalt isotope ^{60}Co is widely used as a radiation source in radiotherapy.
3. Transition metal atoms and ions are used to develop compounds with catalytic properties that are widely used in different industries as catalyst.
4. Since transition metals can form various coloured compounds, they are used as pigments for the production of paint. They are also used to produce coloured glasses and glass bottles.
5. *d* block elements such as Ni and Cd are used to produce rechargeable batteries.
6. They are used in the production of compounds such as cadmium telluride (CdTe) and copper indium diselenide in photovoltaic cells. Solar cell is an example for a photovoltaic cell.

4.10.9 Identification tests for selected cations of *d* block elements

1. Fe^{2+}

   Formation of $KFe[Fe(CN)_6]$, a dark-blue precipitate of with $K_3[Fe(CN)_6]$, can be used to identify Fe^{2+}.

   $$Fe^{2+}(aq) + K_3[Fe(CN)_6](aq) \longrightarrow KFe[Fe(CN)_6](s) + 2K^+(aq)$$

2. Fe^{3+}

   Formation of $Fe_4[Fe(CN)_6]_3$, Prussian-blue complex of with $K_4[Fe(CN)_6]$, can be used to identify Fe^{3+}.

   $$4Fe^{3+}(aq) + K_4[Fe(CN)_6](aq) \longrightarrow Fe_4[Fe(CN)_6]_3(s) + 4K^+(aq)$$

   Formation of red colour, $[Fe(SCN)(H_2O)_5]^{2+}$ complex with a slightly acidic NH_4SCN solution, can be used to identify Fe^{3+}.

   $$[Fe(H_2O)_6]^{3+} + NH_4SCN(aq) \longrightarrow [Fe(SCN)(H_2O)_5]^{2+} + NH_4^+(aq)$$

3. Cr^{3+}

Addition of excess of sodium hydroxide to a Cr^{3+} solution followed by a few milliliters of 6% hydrogen peroxide form a yellow colour solution of CrO_4^{2-}.

$$Cr^{3+}(aq) + 3NaOH(aq) \longrightarrow Cr(OH)_3(s) + 3Na^+(aq)$$

$$4OH^-(aq) + 2Cr(OH)_3(s) + 3H_2O_2(aq) \longrightarrow 2CrO_4^{2-}(aq) + 8H_2O(l)$$

Reference:

Atkins, P. Overton, T. *Shriver and Atkins' Inorganic Chemistry*, 5th Edition, 2010.

Brown, T. E. LeMay, H. E. Bursten, B. E. *Chemistry: The Central Science,* 13th Edition, 2015

Prakash, S. *Advanced Inorganic Chemistry*, 2000

Sodhi, G. S. *Principle of Inorganic Chemistr,* 2nd Edition, 2015

Svehla, G. *Vogel's Qualitative Inorganic Analysis*, 6th Edition, 1987

Tuli, G. D. Madan, R. D Malik, W. U *Selected Topics in Inorganic Chemistry,* 5th Edition, 2014

NOMENCLATURE OF INORGANIC CHEMISTRY (IUPAC Recommendations 2005)

Rayner-Canham, Geoff *Descriptive Inorganic Chemistry*, 6th Edition, 2013.

Lee, J. D. *Concise inorganic chemistry*, 5th Edition, 1996.