G. C. E. (Advanced Level)

CHEMISTRY

Grade 12

Unit 1: Atomic Structure
Unit 2: Structure and Bonding
Unit 3: Chemical Calculations

Department of Science
Faculty of Science and Technology
National Institute of Education
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Chemistry

Resource Book

Grade 12

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Maharagama

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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.

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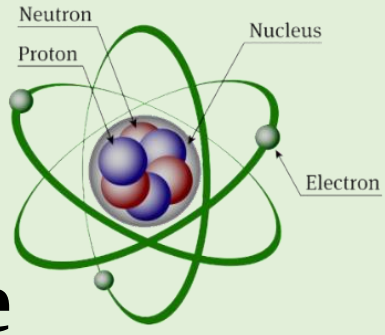
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Introduction

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**.

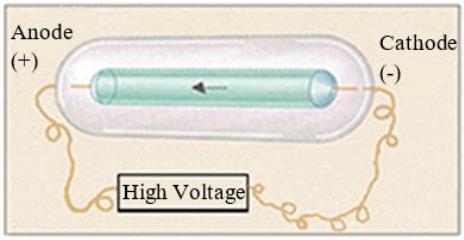


Figure 1.2 A cathode ray tube

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 x 10^8 coulombs per gram (C g^{-1}) for the ratio of the electron's electrical charge to its mass.

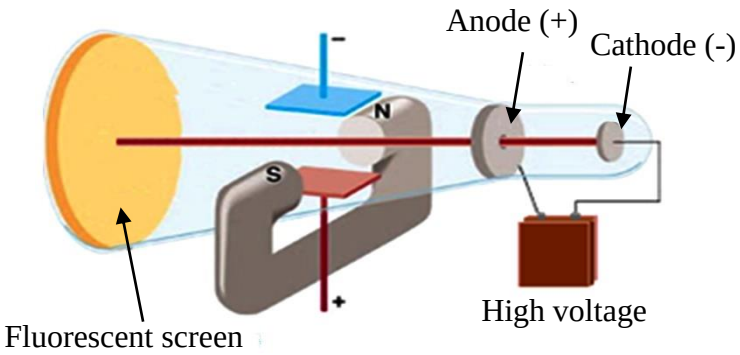


Figure 1.3 Thomson's cathode ray tube

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.

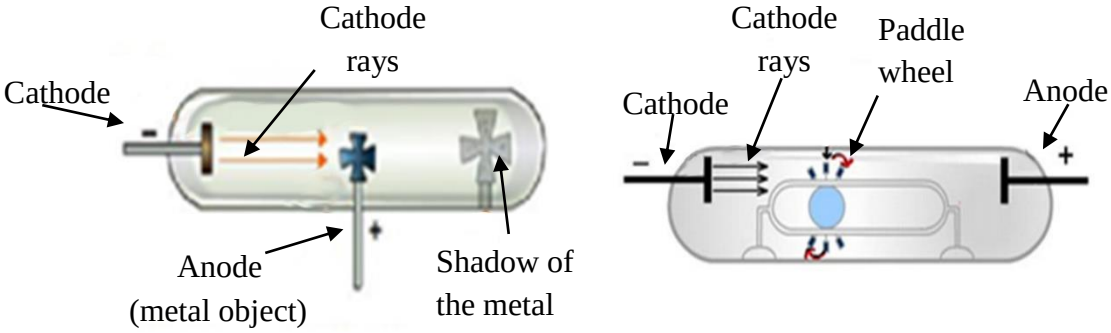


Figure 1.4 Cathode ray properties

- 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.

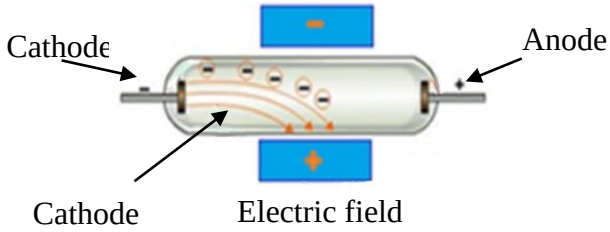


Figure 1.5 Interaction of cathode rays with external electrical fields

- 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.



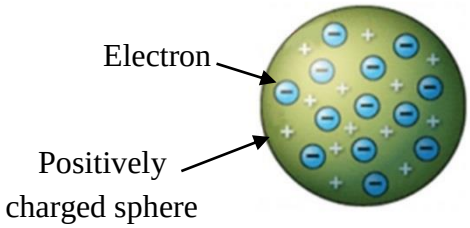
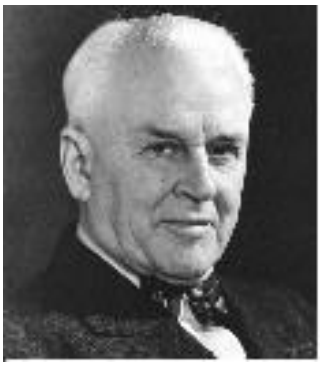


Figure 1.6 J. J. Thomson and his model

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 x 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.

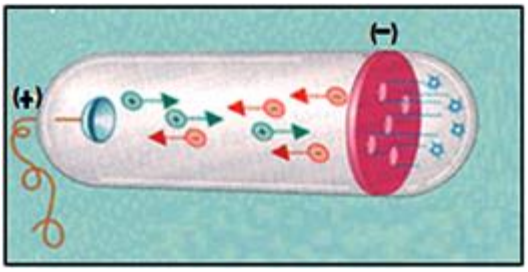


Figure 1.8 A cathode ray tube with a perforated cathode

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 x 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 x 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 towards the positively charged plate. **Beta (β) rays** or **β particles** have the identity of electrons and are deflected towards 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.

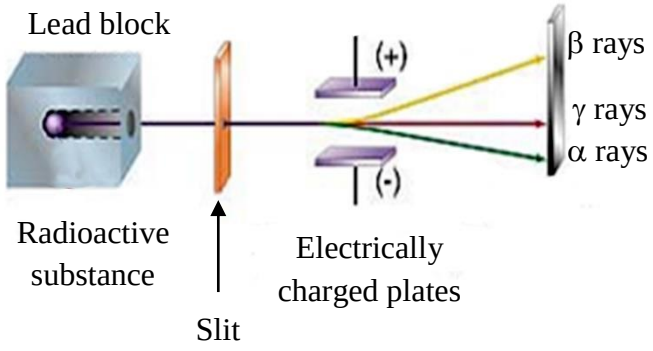
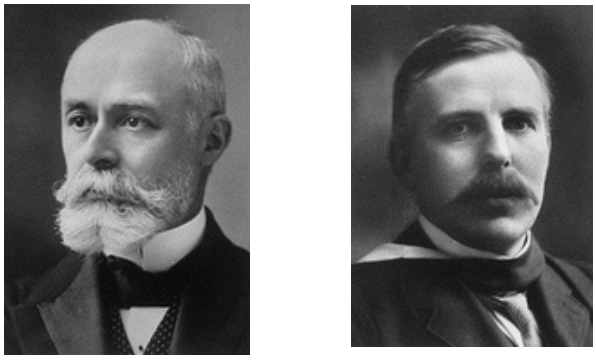


Figure 1.9 Behaviour of alpha (α)**,** beta (β) and gamma (γ) rays in an electric field



(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.

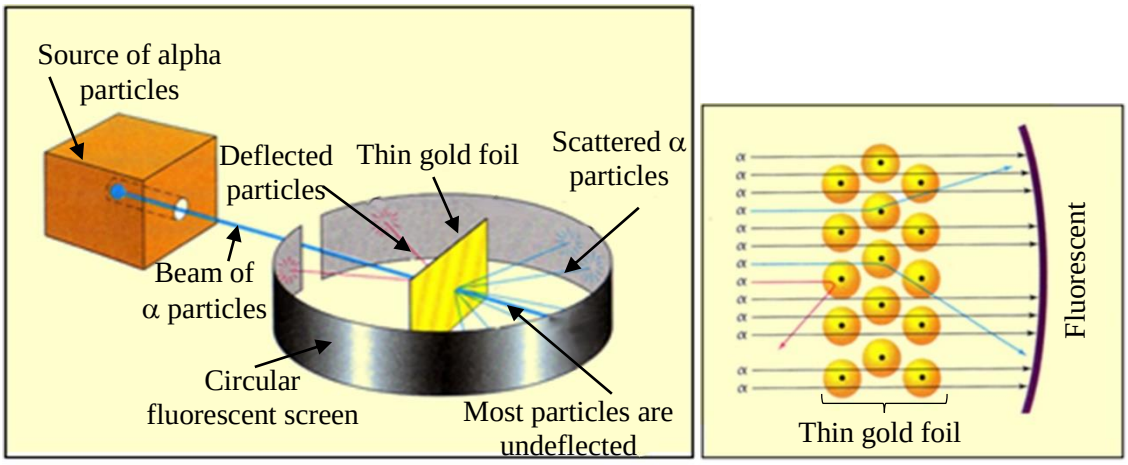


Figure 1.11 Rutherford's gold foil experiment

They observed that the majority of particles penetrated the foil either unreflected 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.

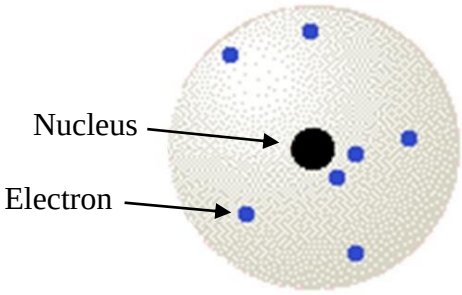
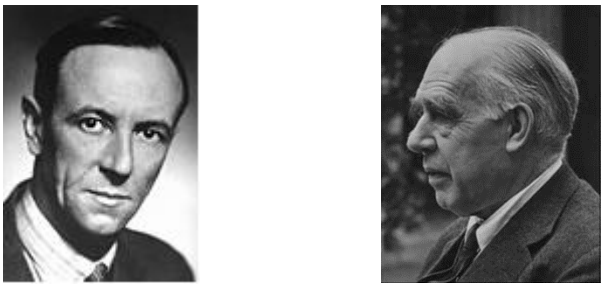


Figure 1.12 Rutherford's model (1911)

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 x 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**.

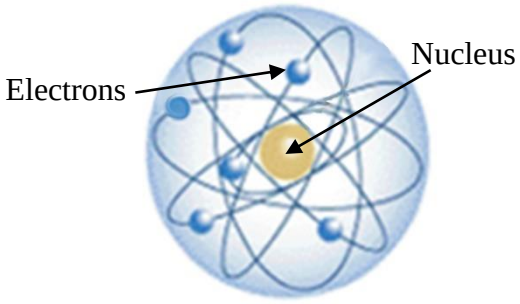


Figure 1.14 The Bohr model

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.

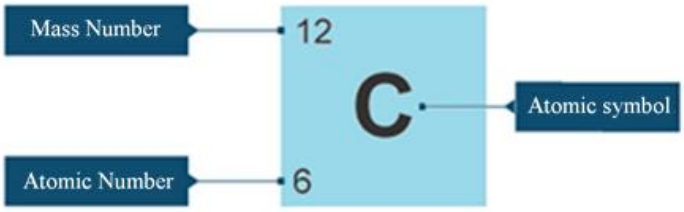


Figure 1.15 Atomic symbol of carbon

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)** $= \frac{12\ \mathrm{g}}{6.02214 \times 10^{23}} \times \frac{1}{12} = 1.66054 \times 10^{-24}\mathrm{g}$

1 u = 1.66054 x 10^{-24} g and 1 g = 6.02214 x 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) x (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 × 12.00 u) + (0.0107 × 13.00335 u) = 12.01 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 x 10^{23} u and 1 mole of atoms = 6.02214 x 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 $\frac{1}{12}$ 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.

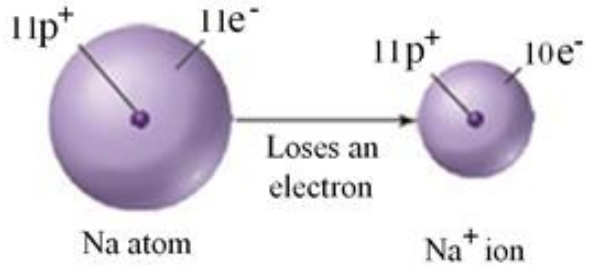


Figure 1.16 Ionization of sodium atom

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

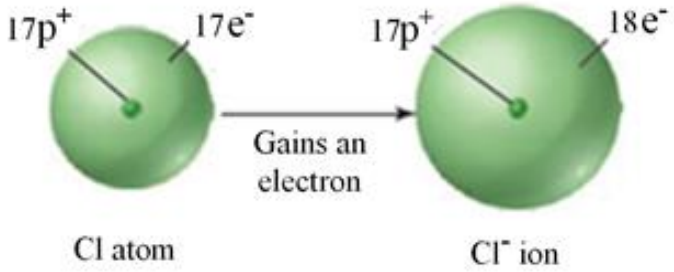


Figure 1.17 Formation of chloride ion

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:

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

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.

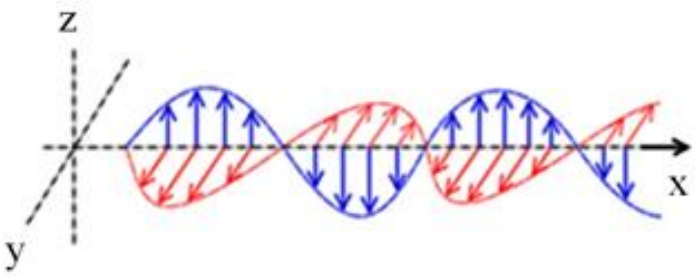


Figure 1.18 Electro-magnetic radiation

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 x10^8 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**,**

$$c = \lambda\nu$$

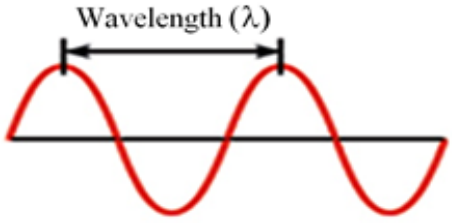


Figure 1.19 An electromagnetic wave

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:

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

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**.

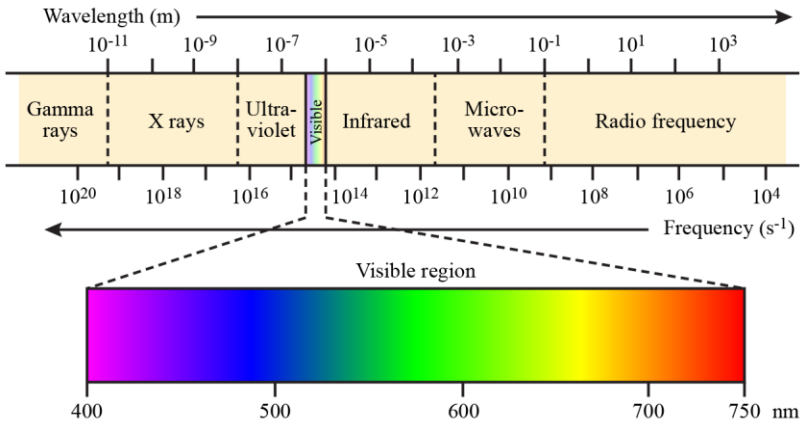


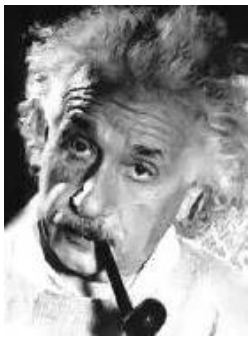
Figure 1.20 The electromagnetic spectrum

1.2.1 Quantization of energy

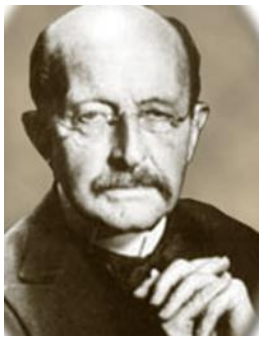
In 1900 a German physicist named **Max Planck (1858–1947)** proposed that energy is quantized; that is the energy can be either released or absorbed by atoms only in discrete quantities of some minimum size. Planck gave the name **quantum** (meaning "fixed amount") to the smallest quantity of energy 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:

$$E = h\nu$$

The constant ***h*** is called **Planck constant** and has a value of 6.626 x 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:

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

$$E = h\nu = (6.626 \times 10^{-34}\ J\ s \times 5.09 \times 10^{14}\ s^{-1})$$
$$= 3.37 \times 10^{-19}\ J$$

If one photon of radiant energy supplies 3.37×10^{-19} J,
Energy of one mole of photons = $(6.02 \times 10^{23}\ mol^{-1})(3.37 \times 10^{-19}\ J)$
$= 2.03 \times 10^{5}\ J\ mol^{-1}$ 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.**

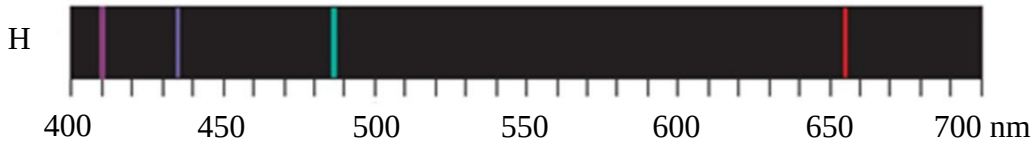


Figure 1.22 Line spectrum of hydrogen

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.

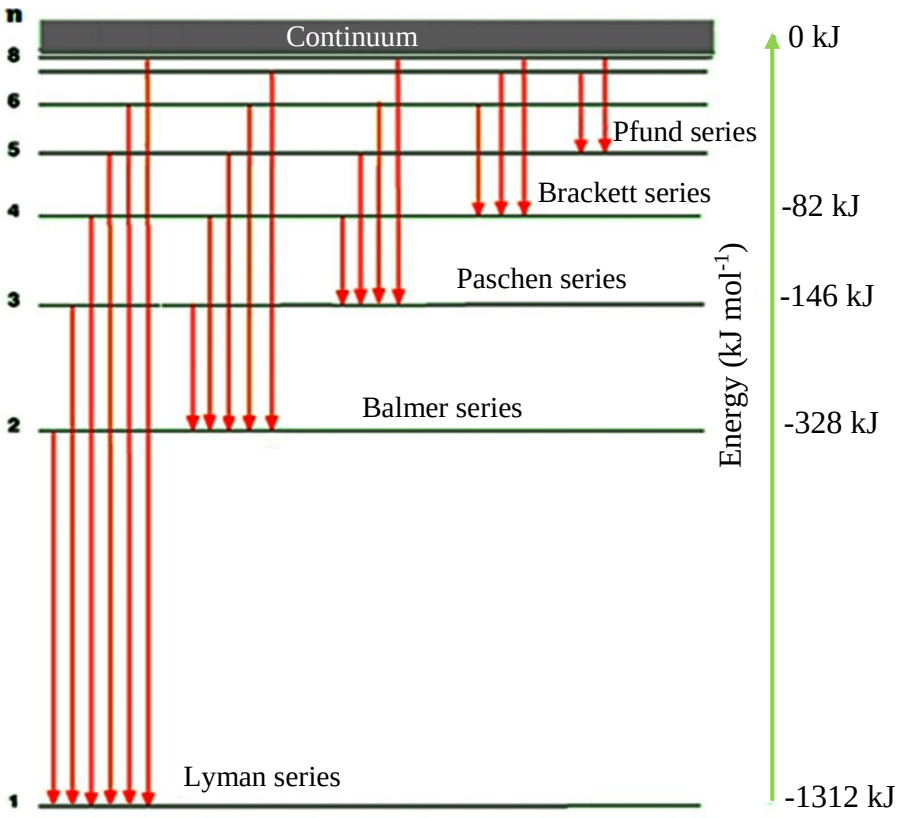


Figure 1.23 Possible electron emissions in hydrogen

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.

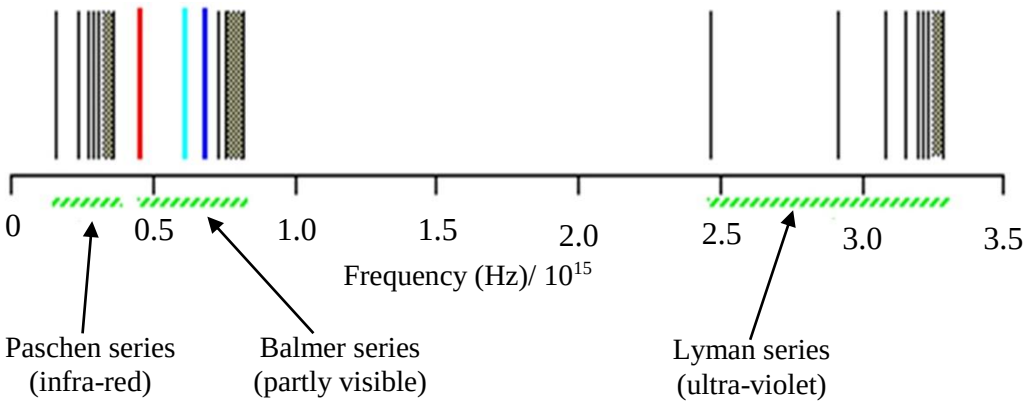


Figure 1.24 (a) The line spectrum of hydrogen

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

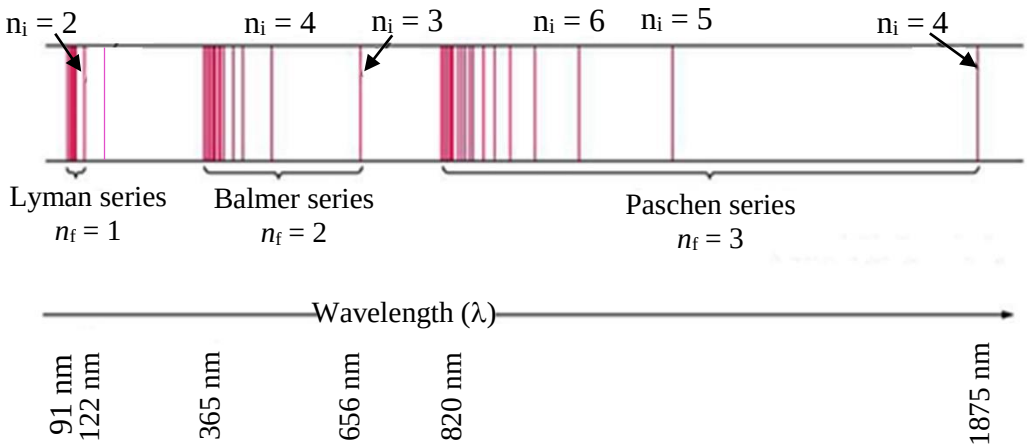


Figure 1.24 (b) The line spectrum of hydrogen

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.

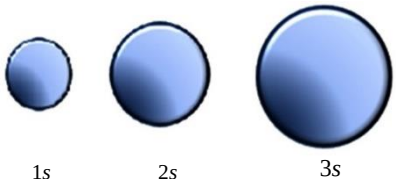


Figure 1.25 Shapes of the *s* orbitals

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.

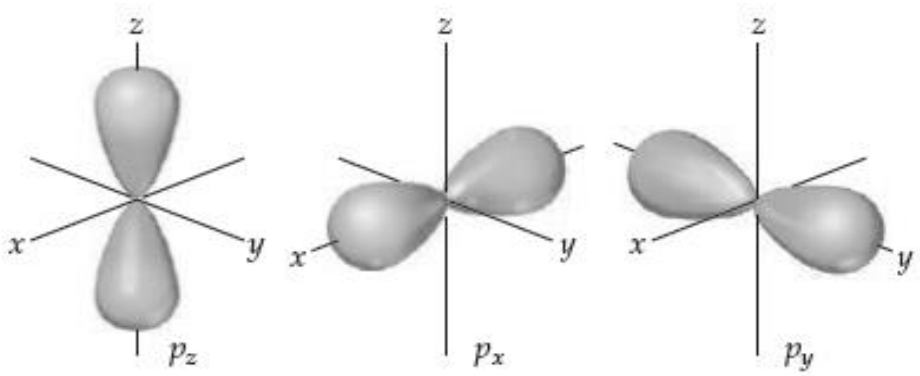


Figure 1.26 Shapes of the *p* orbitals

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* sub shell.

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 3*d* 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').

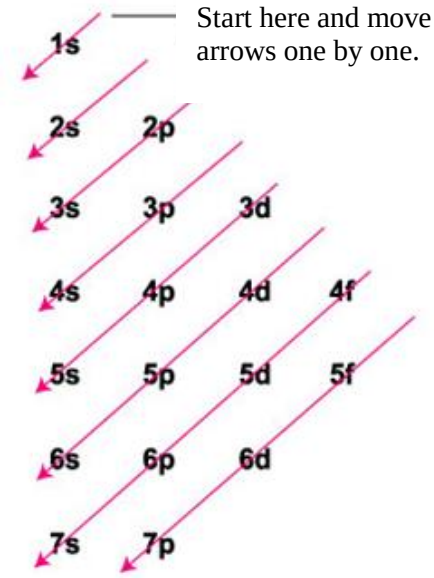


Figure 1.27 Sequence of filling of electrons

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

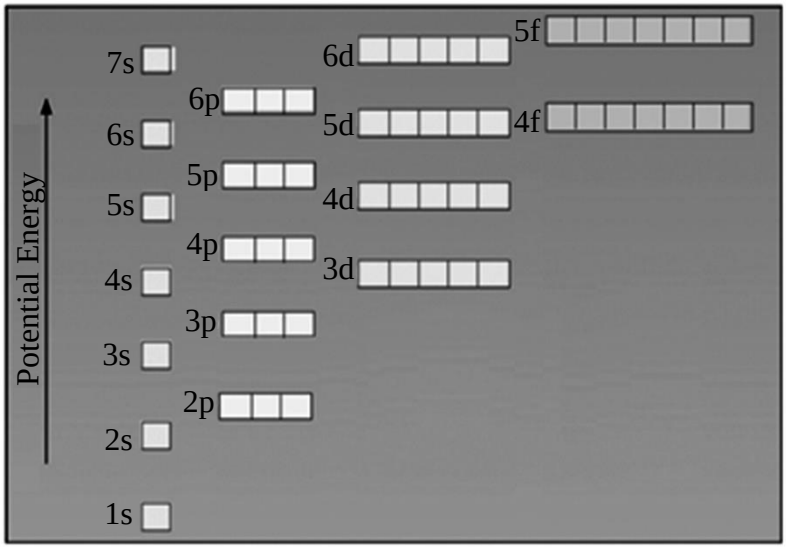


Figure 1.28 Order of the energy levels in an atom

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.

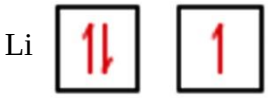
Electrons are distributed among the various orbitals of an atom based on the relative energies of orbitals and the Pauli Exclusion Principle and this distribution is called the **electron configuration** of the atom. The most stable electron configuration, known as the ground state, is that in which 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 $1s^2 2s^1$ and for sodium $1s^2 2s^2 2p^6 3s^1$.

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
		1*s*	2*s*	2*p*	3*s*	
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 $1s^2 2s^2 2p^6 3s^1$. However, the filling of the 2*p* 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 3*s* electron beyond the stable configuration of neon. The configuration of sodium can therefore be abbreviated as $[Ne]3s^1$.

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 $1s^2 2s^2 2p^6 3s^2 3p^3$ or $[Ne]3s^2 3p^3$.

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 $[Ne]3s^2 3p^2$

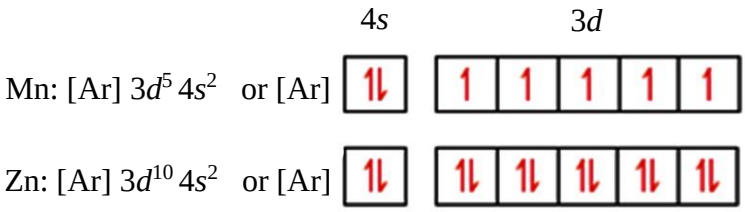
(b)



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*.



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.

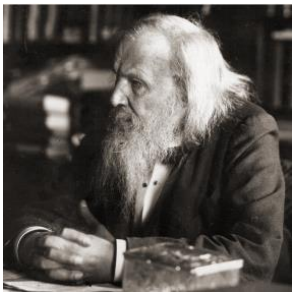
The electron configurations of certain elements appear to deviate from the rules of configuration discussed. For an example, the electron configuration of chromium (element 24) is [Ar]3$d^5$4s^1 rather than [Ar]3$d^4$4s^2 which we might expect. Similarly, the configuration of copper (element 29) is [Ar]3d^{10}4s^1 instead of [Ar]3$d^9$4s^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

-

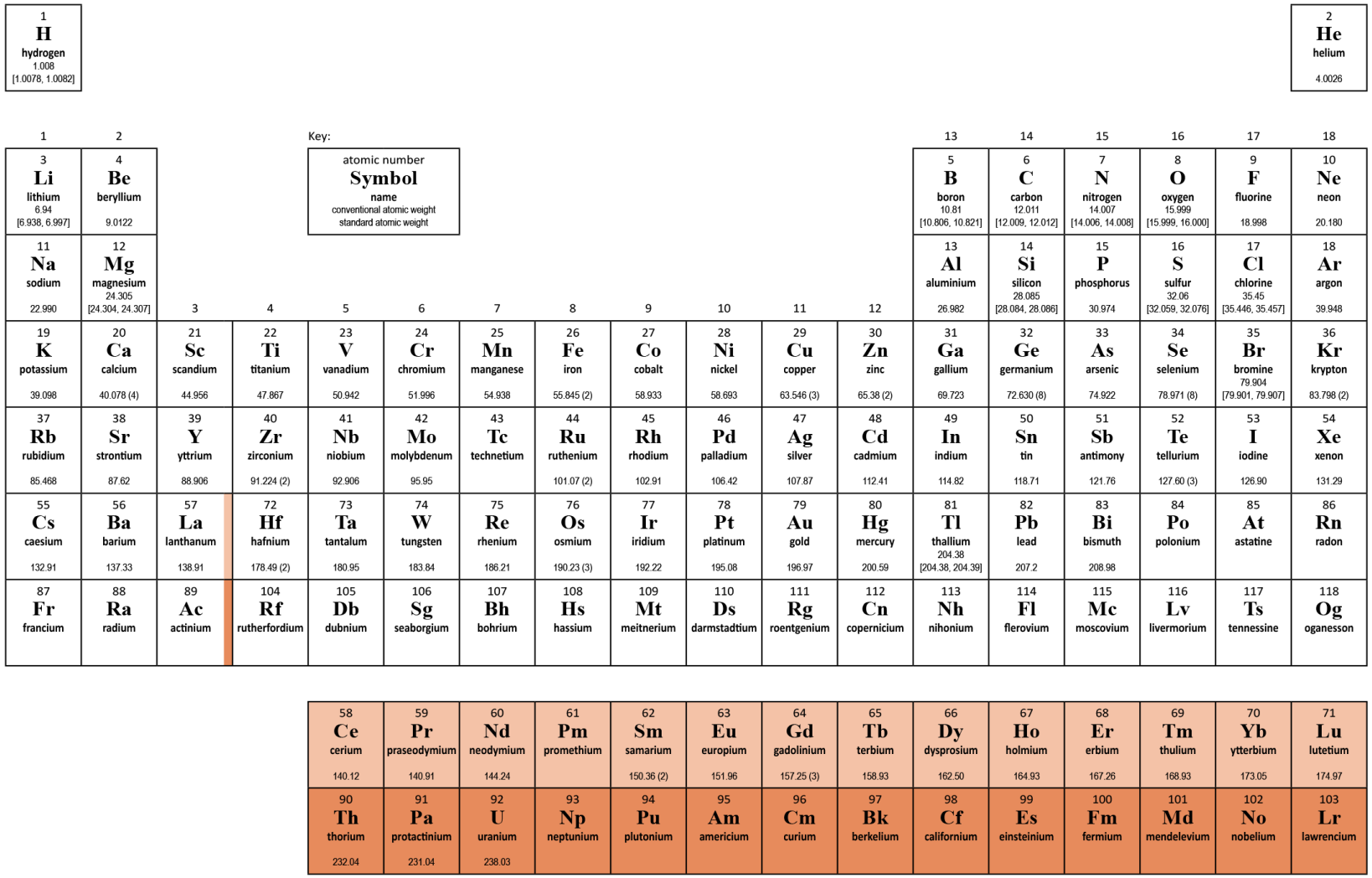


Figure 1.30 The periodic table of elements

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.

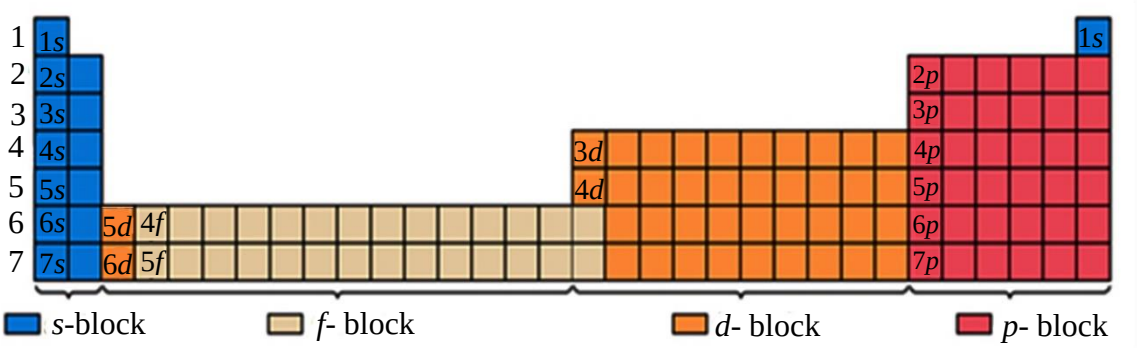


Figure1.31 Regions of the periodic table

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 in general practice group 1 and 10 elements 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. The outer electrons are said to be screened or shielded from the nucleus by the inner electrons close to the nucleus and this phenomenon is hence termed the **screening effect** or **shielding effect** of electrons.

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**, $\boldsymbol{Z_{eff}}$. The effective nuclear charge is always less than the actual nuclear charge ($Z_{eff} < Z$).

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.

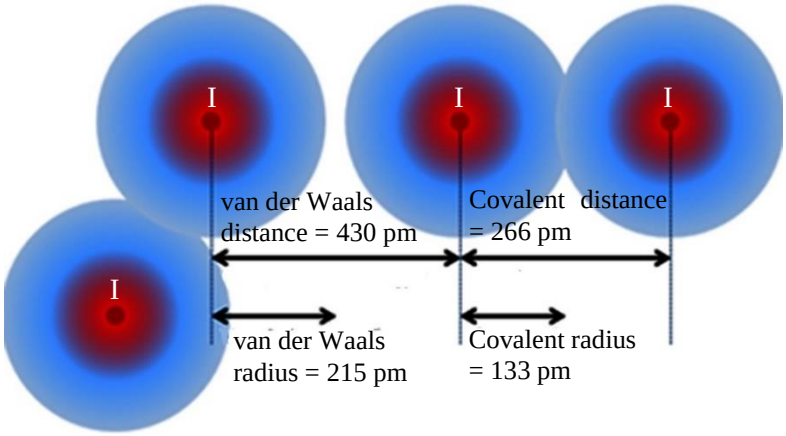


Figure 1.32 Covalent and van der Waals radius for Iodine (I_2)

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**.

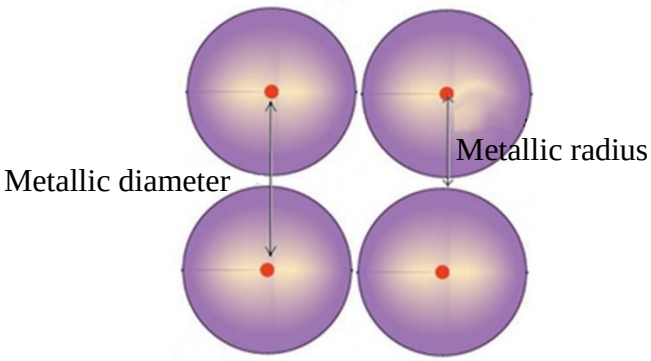


Figure 1.33 The metallic radius

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.

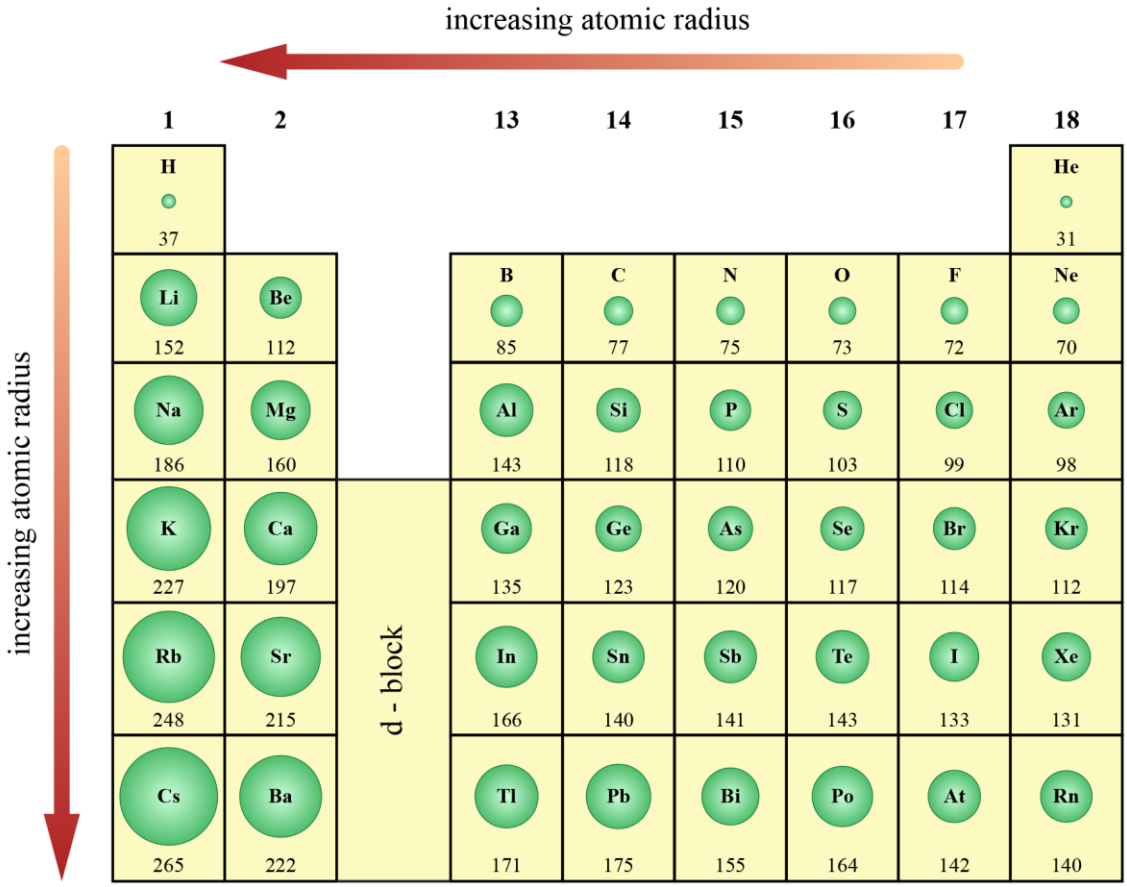


Figure 1.34 (a) Trends in atomic radii in the periodic table in pm

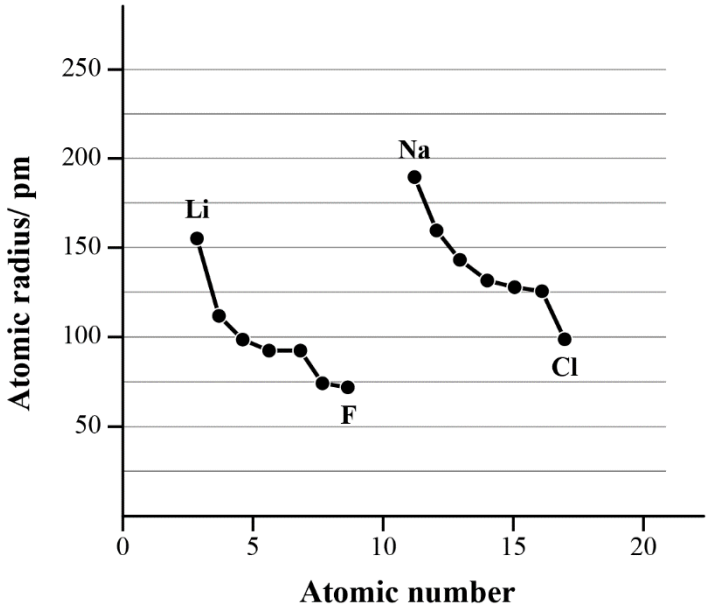


Figure 1.34 (b) Trends in atomic radii in the periodic table

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.

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

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 2*p* electron before it loses its 2*s* electrons.

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

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

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

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

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

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

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 2*p* subshell.

$$F(1s^2 2s^2 2p^5) + e \longrightarrow F^-(1s^2 2s^2 2p^6)$$

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.

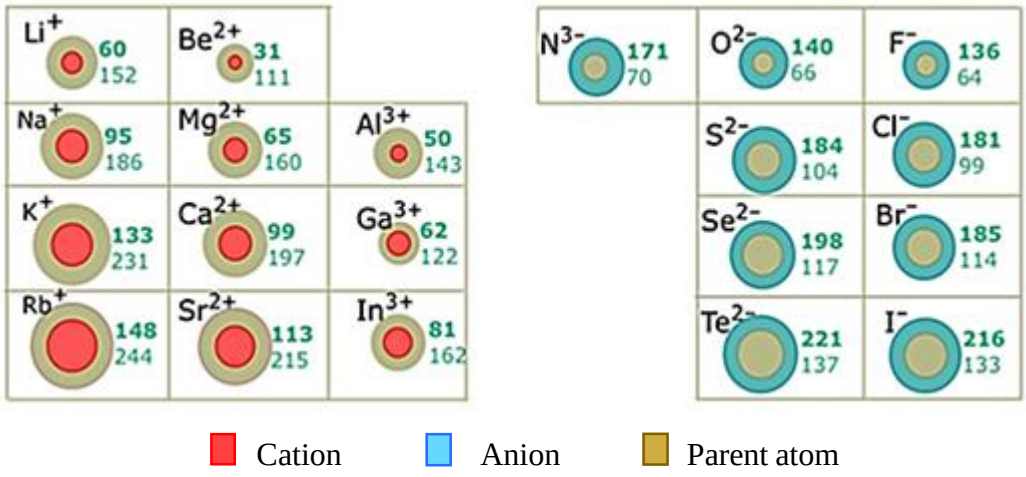


Figure 1.35 Radii of cations and anions compared to parent atoms in pm

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.

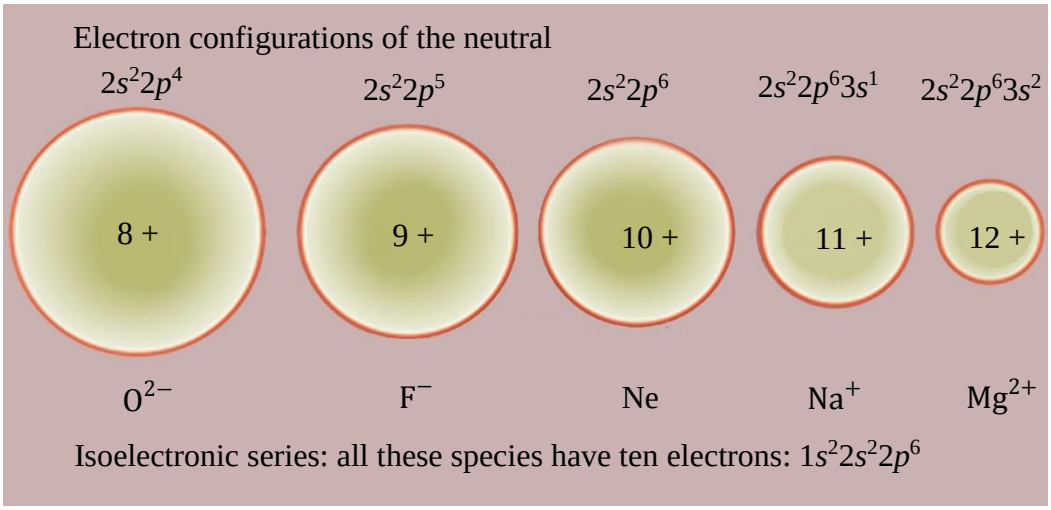


Figure 1.36 Radii in an isoelectronic series

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 ionisation 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 increases 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.

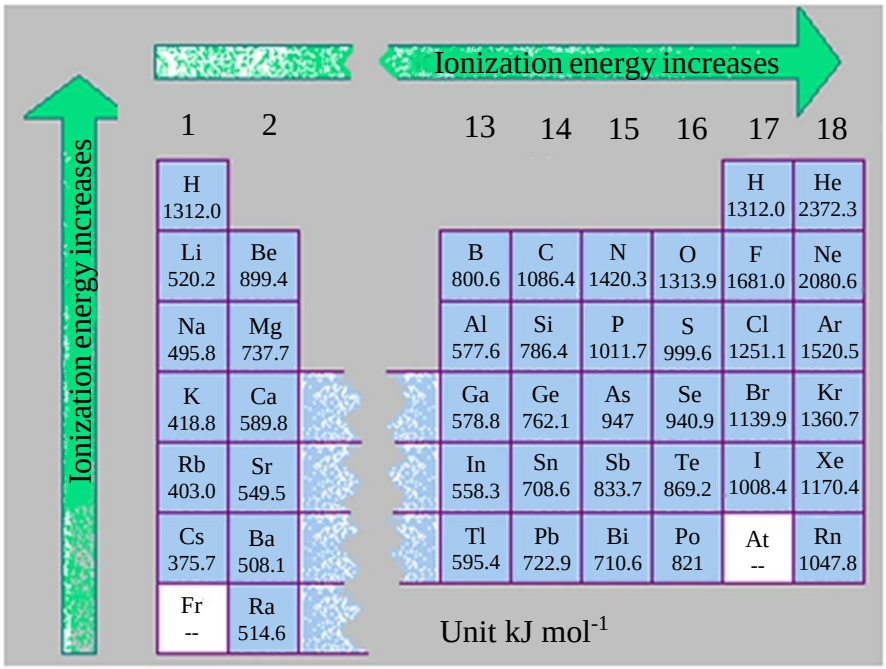


Figure 1.37 Trends in the first ionization energies in the periodic table

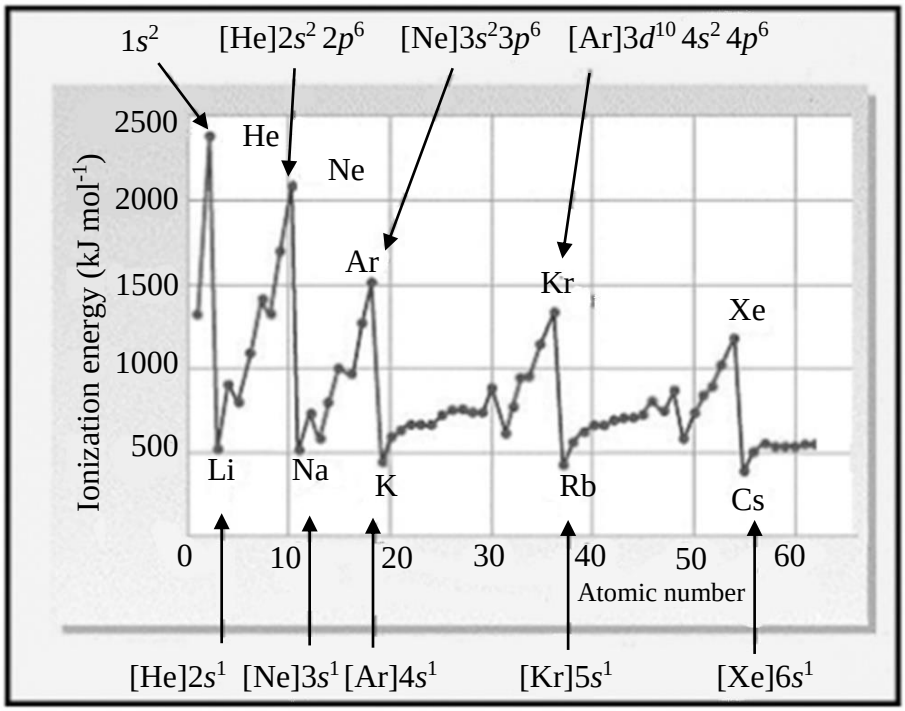


Figure 1.38 Variation of the first ionization energies with atomic number of elements

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* sub shell 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.

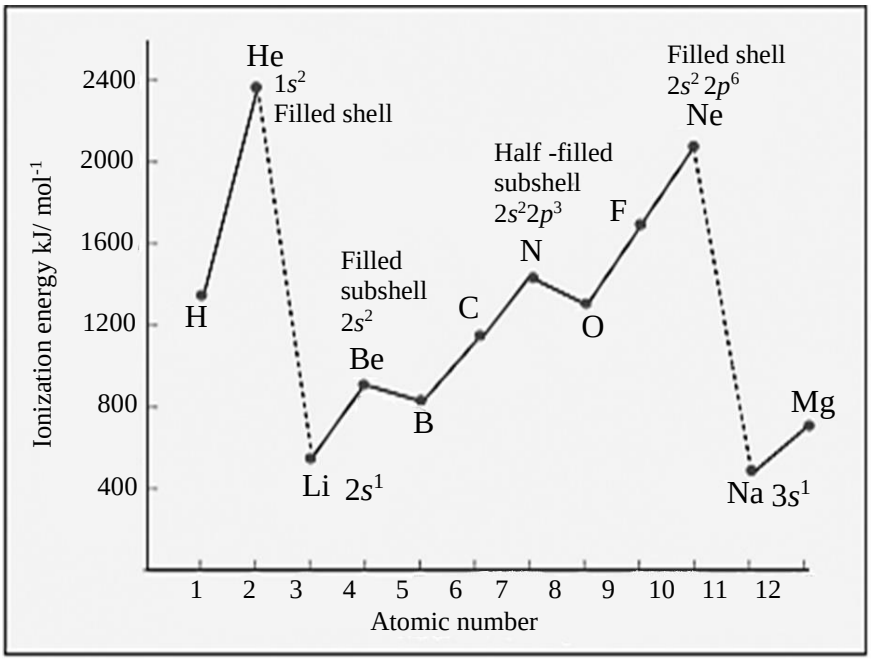


Figure 1.39 Variation of the first ionization energies along the first and second periods

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.

Electron gain energy (ΔE_{EG}) = - 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.

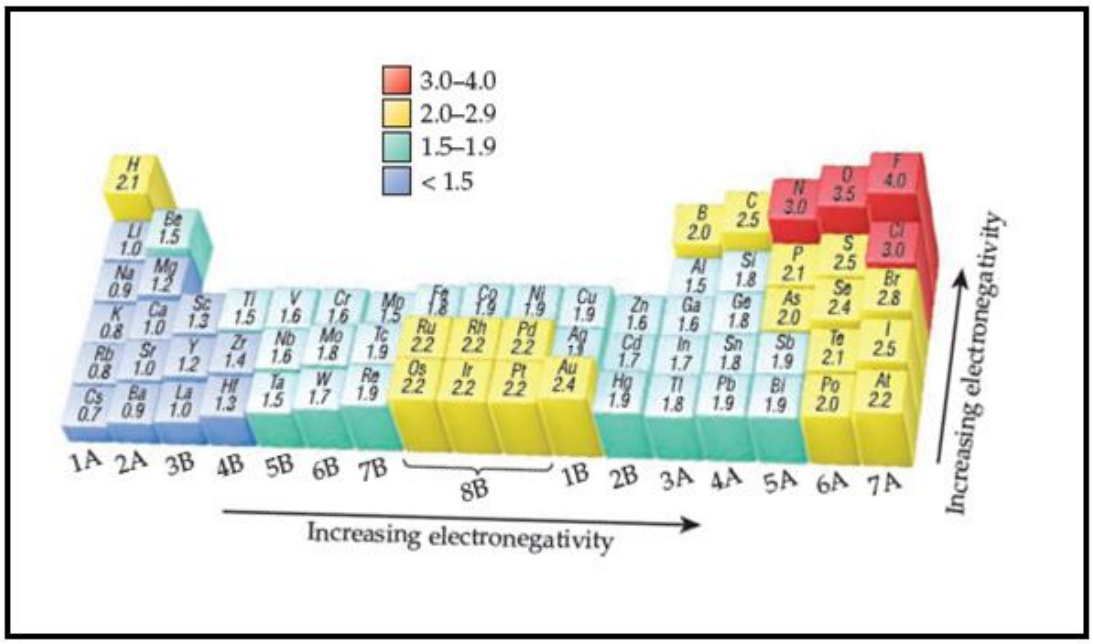
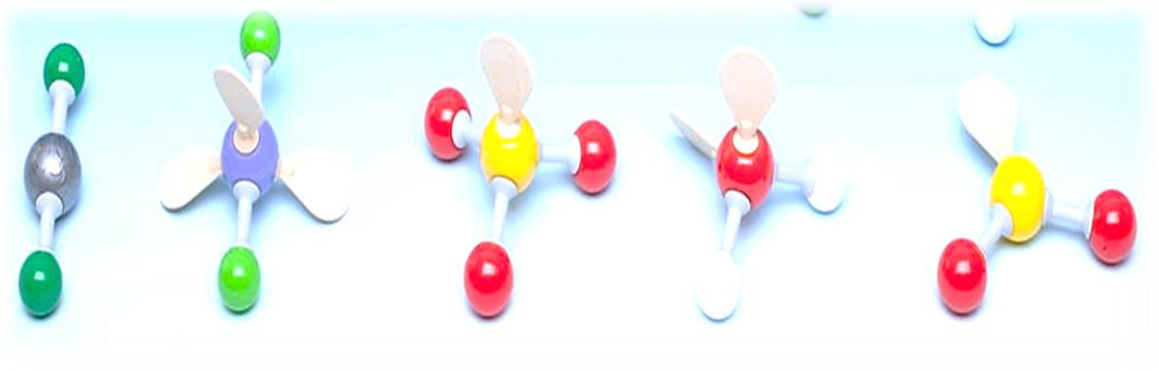


Figure 1.40 Pauling electronegativity values and the trends in the periodic table

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

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2.3 Valance shell electron pair repulsion theory (VSEPR)

- Linear electron pair geometry
- Trigonal planar electron pair geometry
- Tetrahedral electron pair geometry
- Trigonal bipyramid electron pair geometry
- Octahedral electron pair geometry

2.3.1 Hybridization of atomic orbitals

2.3.2 Formation of double and triple bonds

2.3.3 Resonance structures

- Characteristics of resonance
- Formal charges
- Rules to estimate relative stability of resonance structures

2.3.4 Effect of electronegativity and geometry for the polarity of molecules

2.3.5 Dipole moment

2.3.6 Factors affecting the magnitude of electronegativity

2.4 Ionic bonds

2.5 Metallic bonds

2.6 Secondary interactions

- Ion – dipole interactions
- Dipole – dipole interactions Hydrogen bonding
- Ion – induced dipole interactions
- Dipole – induced dipole interaction
- London interactions (forces) (Instantaneous induced dipole – induced dipole interaction)

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.

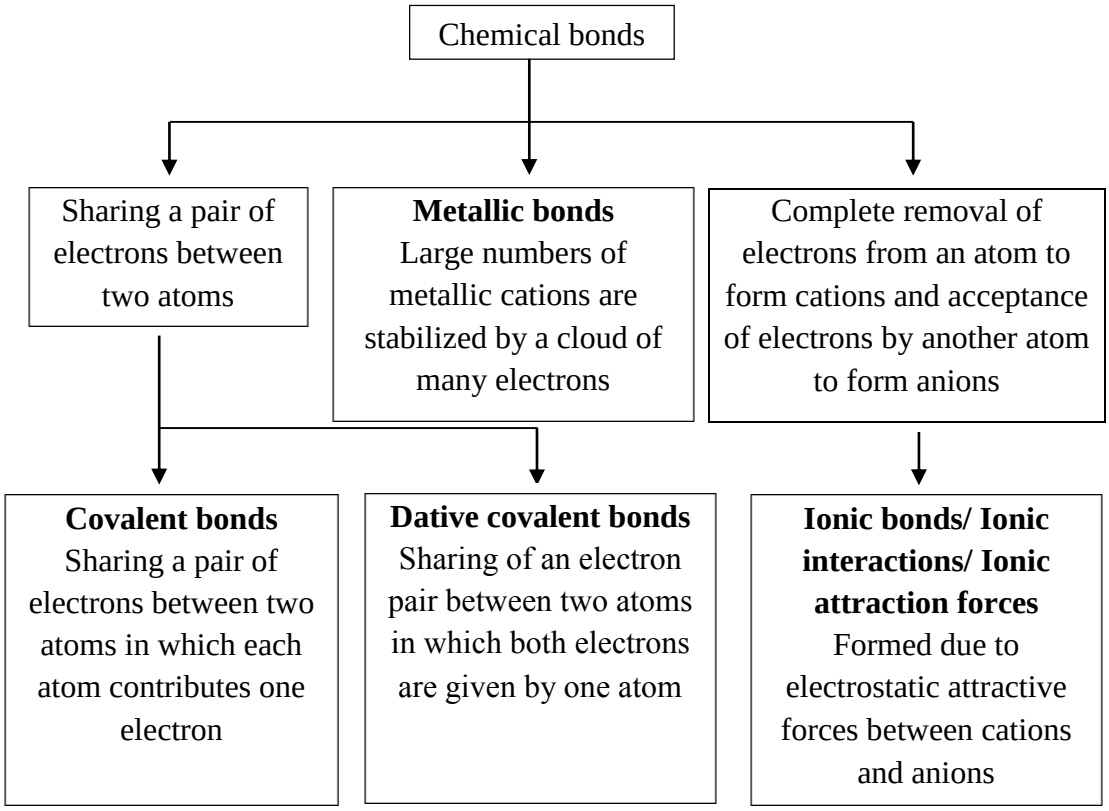


Figure 2.1 Types of chemical bonds

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.

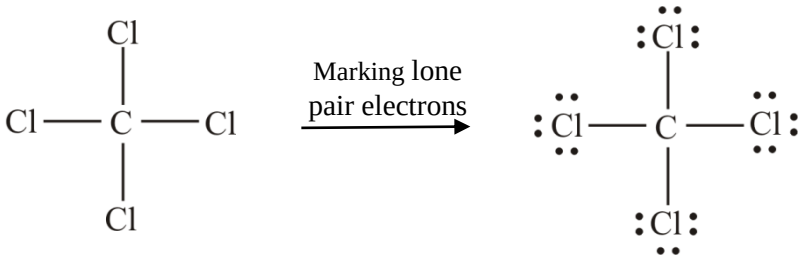


Figure 2.2 Lewis dot-dash structure of CCl_4

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

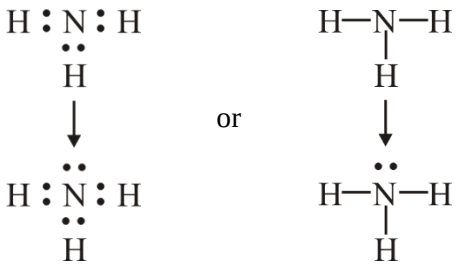


Figure 2.3 Lewis dot-dash structure of NH_3

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.

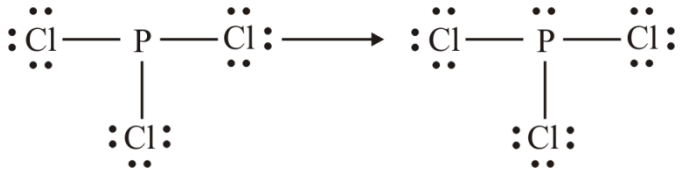
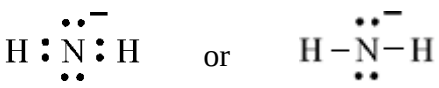


Figure 2.4 Lewis dot-dash structure of PCl_3

(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:

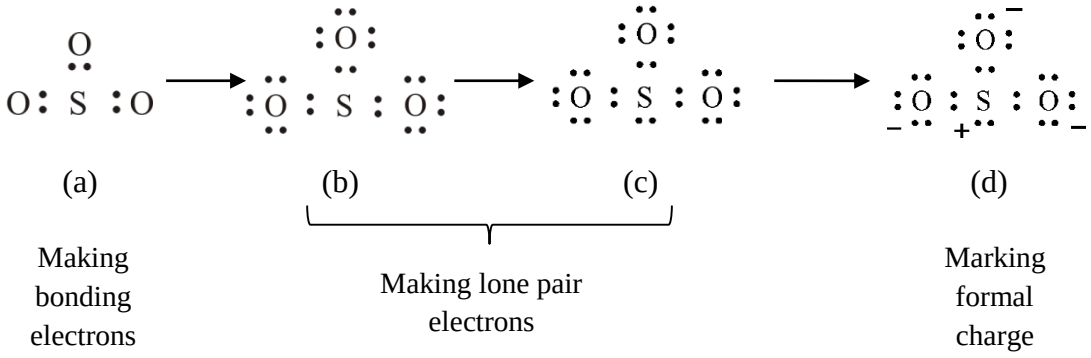


Here the total electron count on the nitrogen atom is 8. Though the nitrogen atom has contributed only 5 electrons, from the Lewis dot diagram, it appears as if the

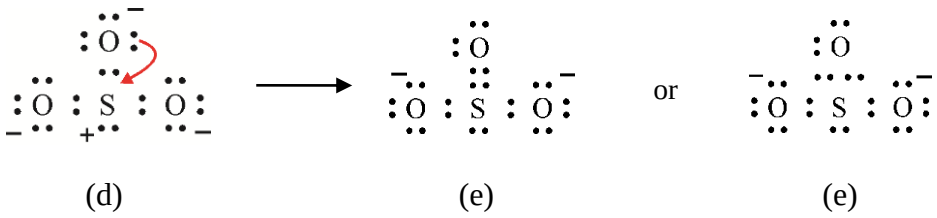
nitrogen has contributed 6 electrons. Since it has one extra electron, (-1) the charge is marked on the nitrogen atom as the formal charge.

(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.

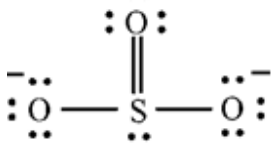


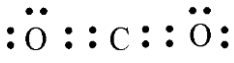
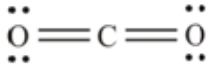
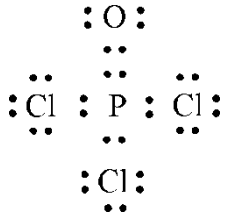
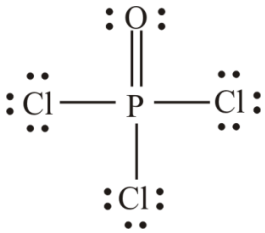
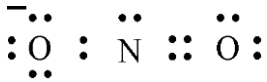
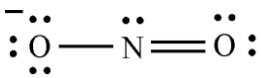
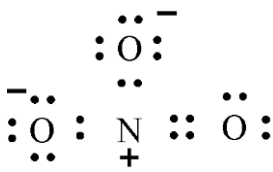
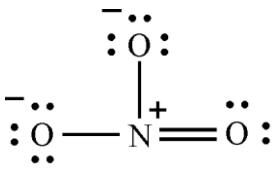
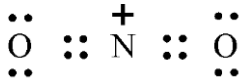
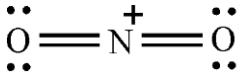
Figure 2.5 Lewis dot dash structure of SO_3^{2-}

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

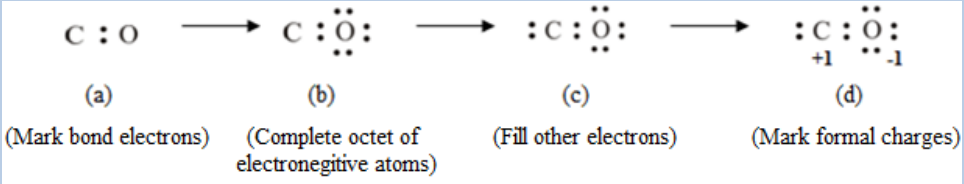
Formula	Number of valance shell electrons	Lewis dot diagram	Lewis dot dash structure
CO_2	16		
$POCl_3$	32		
HCN	10		
NO_2^-	18		
NO_3^-	24		
NO_2^+	16		

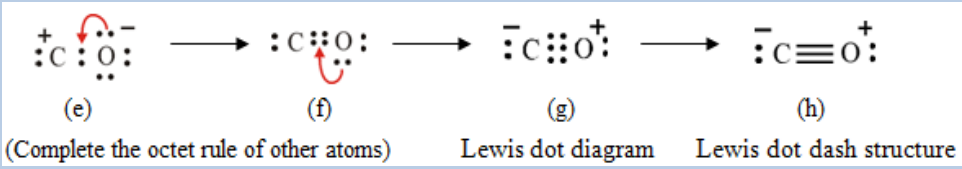
Example 2.1
Draw the Lewis dot diagram and the Lewis structure of carbon monoxide (CO)

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.

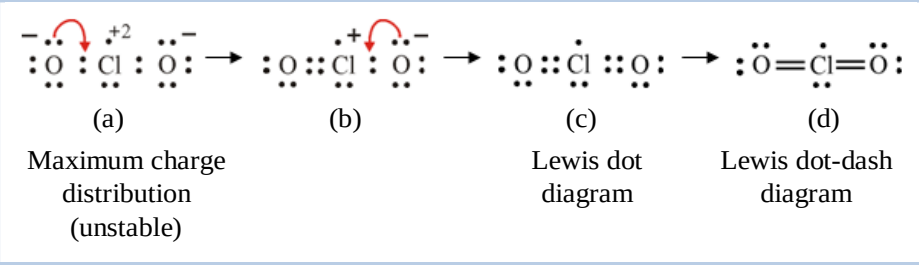




Example 2.2
Draw the Lewis dot diagram and the Lewis dot dash structure for ClO_2.

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.

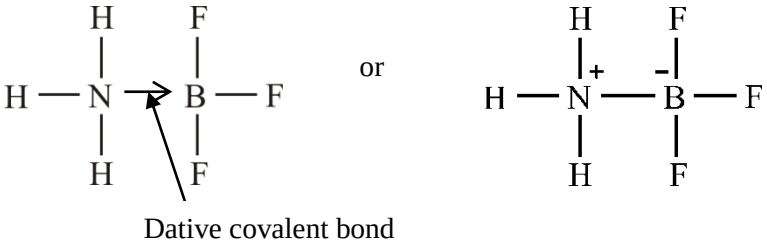


Figure 2.6 Dative covalent bond (H_3N-BF_3)

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.

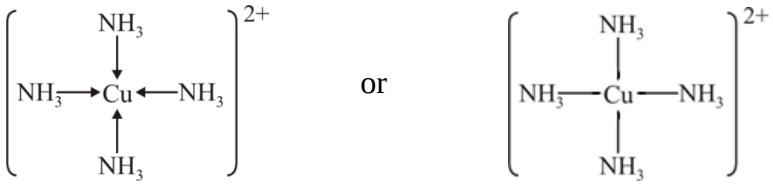


Figure 2.7 Dative covalent bond in $[Cu(NH_3)_4]^{2+}$ complex

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.

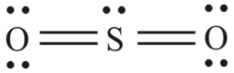
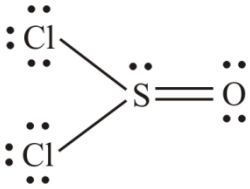
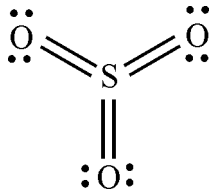
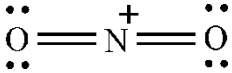
There are three different types of bonding when the number of covalent bonds formed between the central atom and a surrounding atom is considered. These are single bonds, double bonds and triple bonds where double and triple bonds represent multiple bonds. For example, in the CO_2 molecule, double bonds 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
	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.

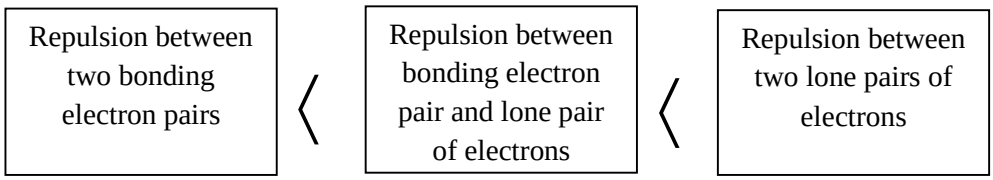
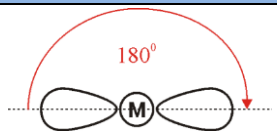
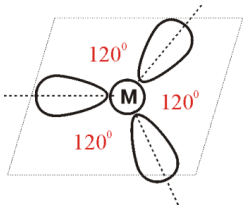
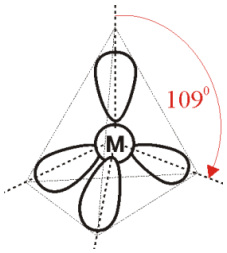
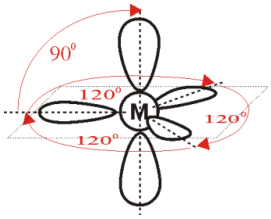
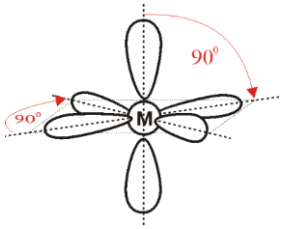


Figure 2.8 Comparison of repulsive forces between bonding and lone pairs of electrons

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.

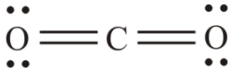
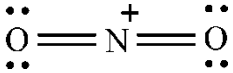
Table 2.3 Electron pair geometry of repulsion units

Repulsion units	Electron pair geometry	
2		Linear
3		Trigonal planar
4		Tetrahedral
5		Trigonal bipyramidal Three repulsive units are on the same plane with 120º 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.

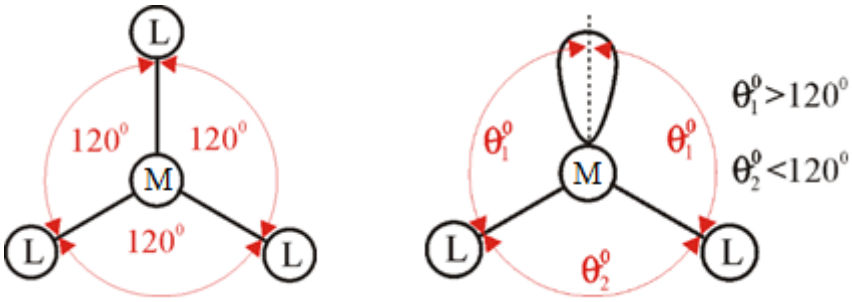
Table 2.4 Molecules/ ions with two repulsion units

Chemical Formula	Lewis dot dash structure	Shape
CO_2		Linear
HCN		Linear
NO_2^+		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



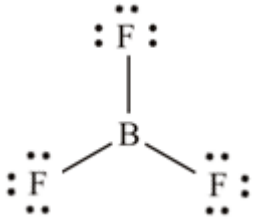
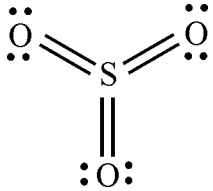
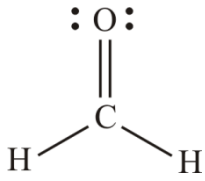
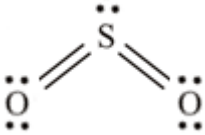
(a) All three repulsive units are bonding

(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.

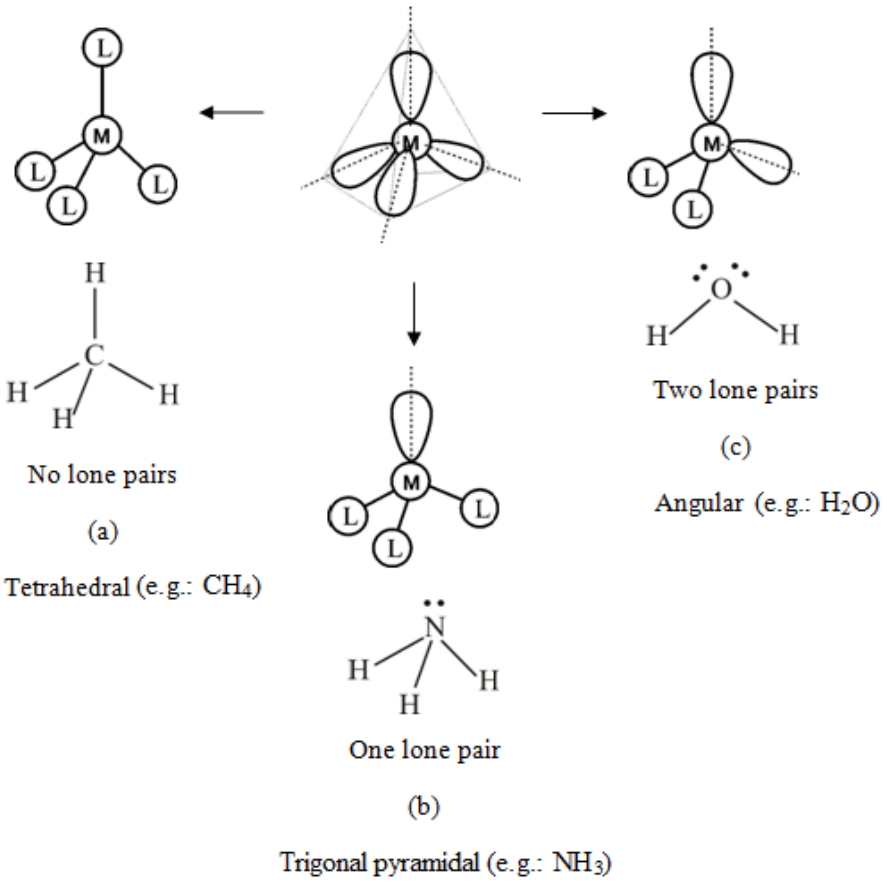
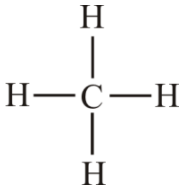
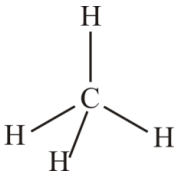
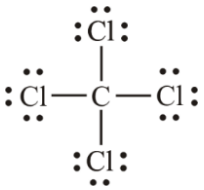
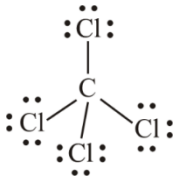
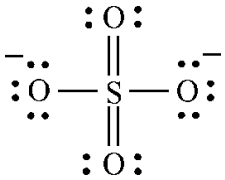
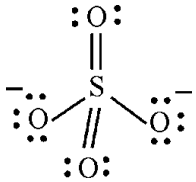


Figure 2.10 Tetrahedral electron pair geometry

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.

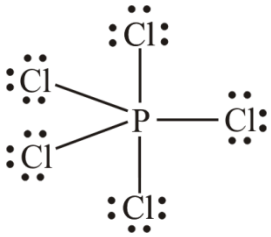
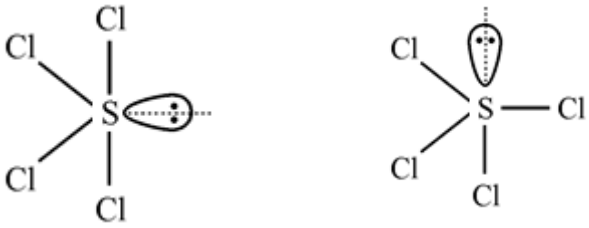


Figure 2.11 Electron pair geometry of PCl_5

- 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.

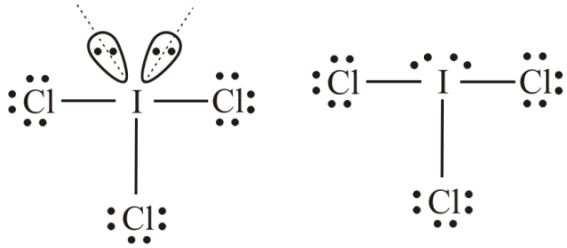


Figure 2.13 Electron pair geometry of ICl_3

- 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.

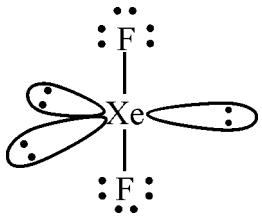


Figure 2.14 Electron pair geometry of XeF_2

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.

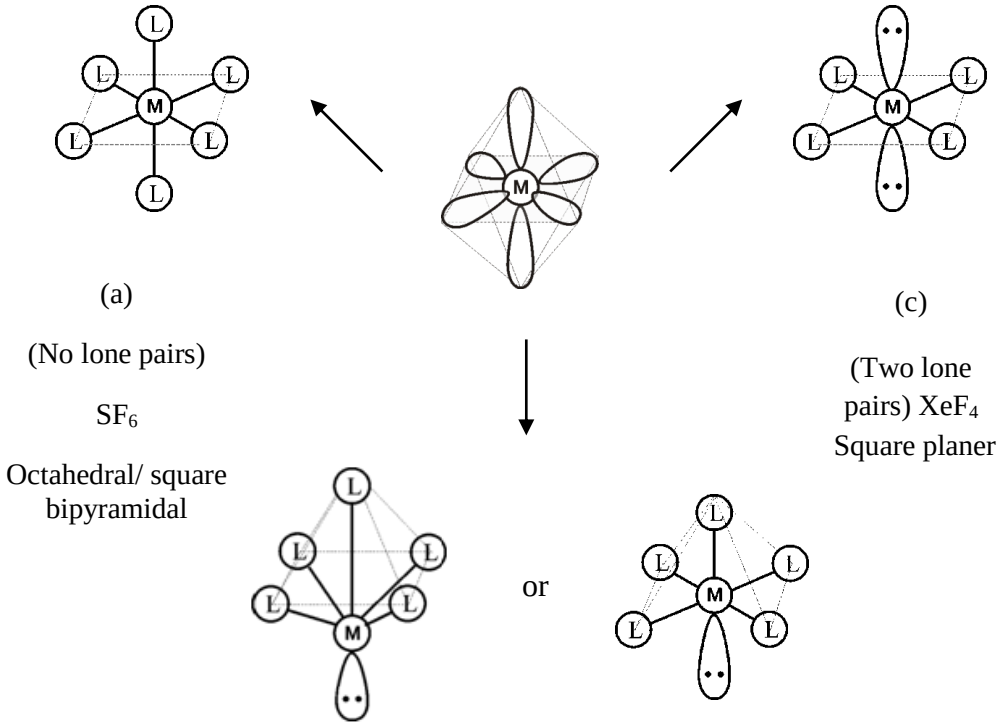


Figure 2.15 Octahedral electron pair geometry

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'.

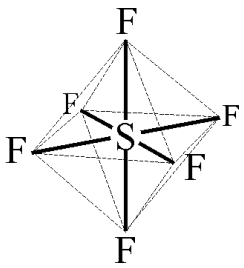
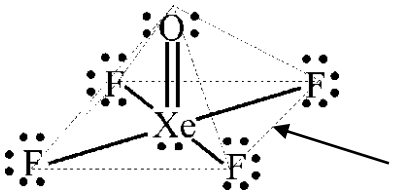


Figure 2.16 Electron pair geometry of SF_6

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.



Imaginary plane where four F atoms are located

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.

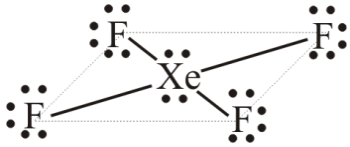


Figure 2.18 Electron pair geometry of XeF_4

Example 2.3

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

(i) SO_3 (ii) CH_2Cl_2

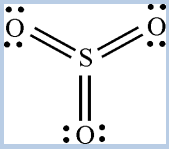
Answer

(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

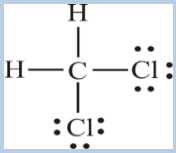
Distribute 14 electrons in order to represent the Lewis dot-dash structure

Total electrons =20

Repulsive units around the central atom = 4

Lone pairs on "C" atom = 0

Shape = tetrahedral



Lewis dot-dash structure

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.

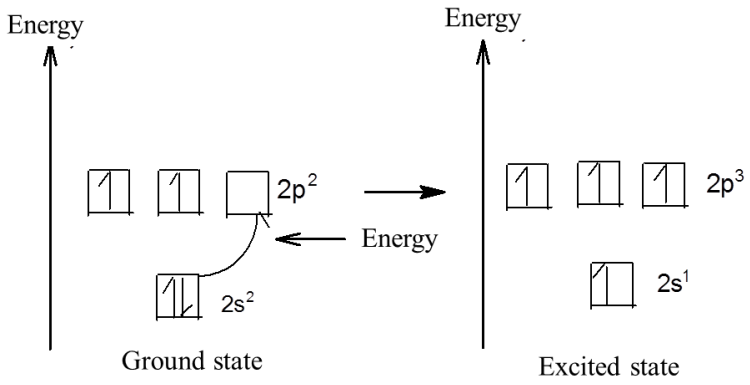


Figure 2.19 Energy level diagram of carbon atom in ground and excited states

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* *a*nd 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^o.

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)

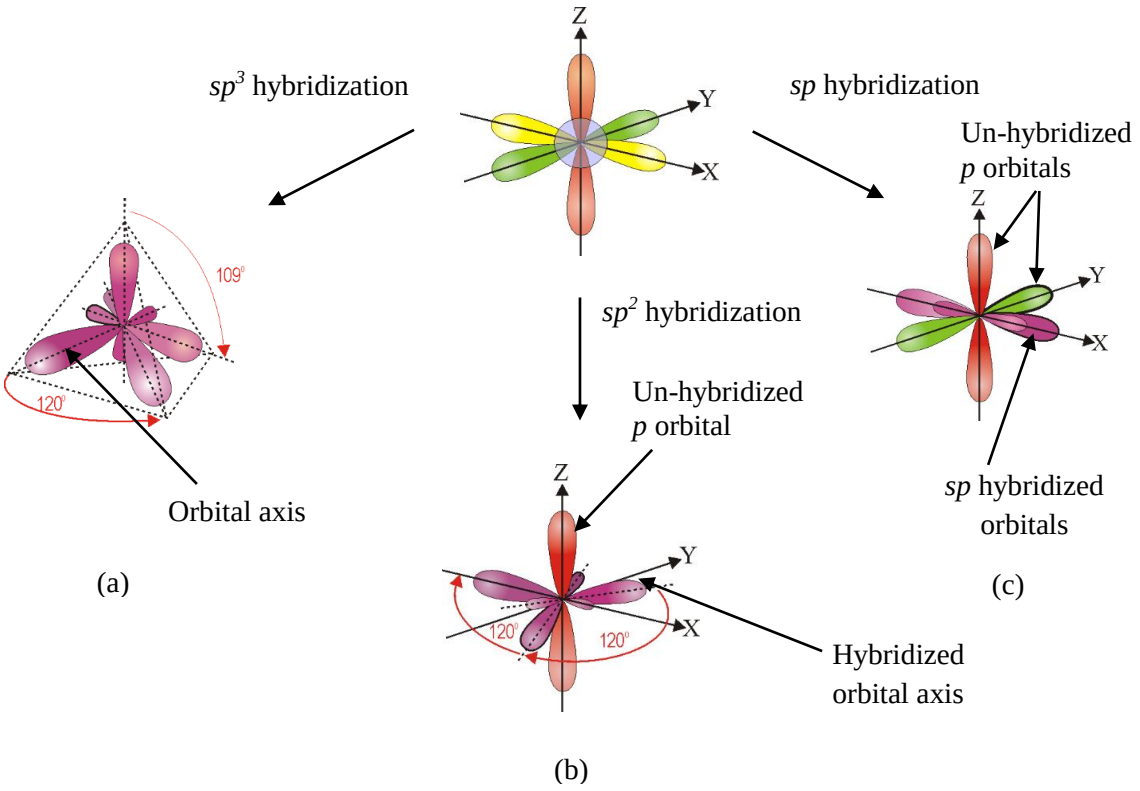
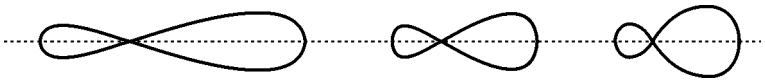


Figure 2.20 sp^3, sp^2 and sp hybridization

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.

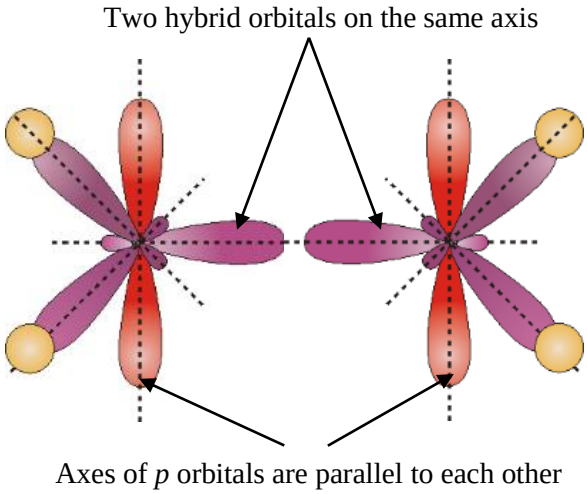


Figure 2.22 sp^2 hybridized orbitals and *p* orbital orientation in C_2H_4

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*.

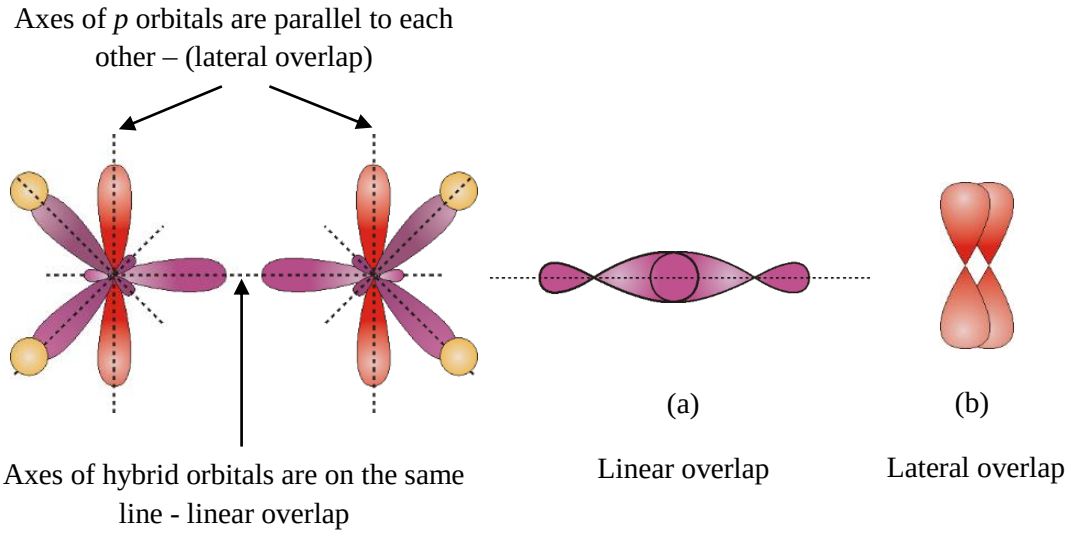
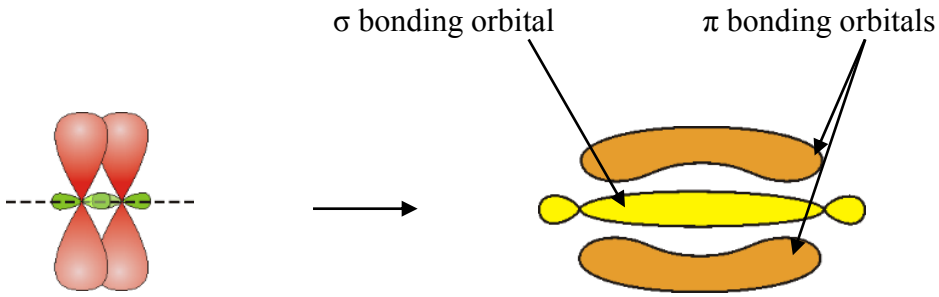


Figure 2.23 Linear and lateral overlap of orbitals in C_2H_4

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



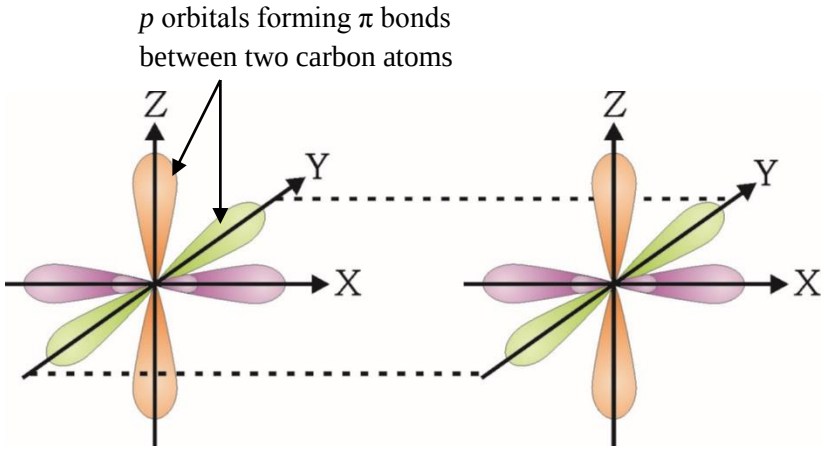
Lateral overlap between *p* orbitals and linear overlap of sp^2 orbitals

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.



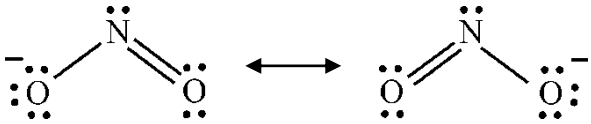
- Axes of p_y orbitals are parallel to each other
- Axes of p_z orbitals are parallel to each other
- Two *sp* hybridized orbitals facing each other in the x axis from a σ bond between the two carbon atoms

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

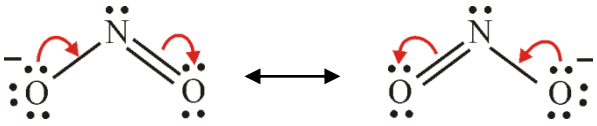
It is possible to draw a number of Lewis structures for a certain molecule or ion. These Lewis structures with the same skeleton or atom positions are called '**Resonance structures**'. The reason is when there are multiple bondings present (double or triple bonds), the position of the π bond and lone 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.



(a) (b)

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.



(a) (b)

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

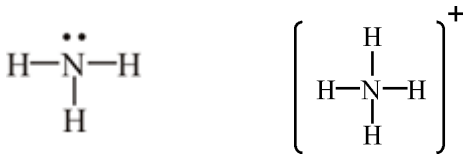
(ii) In a Lewis formula, an atom that has the same number of bonds as its number of valence electrons in the atom, its formal charge is zero.

(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

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

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

Formal charge of N atom in ammonia is zero.

For H atom of NH_3

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

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

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.

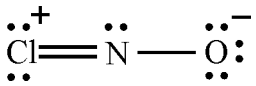
In NH_4^+ the N atom has 4 bonds and no unshared electrons is on the N atom. Hence, formal charge on the N atom of NH_4^+ ion is +1 and formal charge on each H atom is zero. Total of formal charges of NH_4^+ ion is equal to +1 and it is the charge of ammonium ion.

(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.

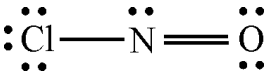
Following examples assign formal charges to the atoms in nitrosyl chloride, NOCl. The Cl atom and the O atom are both bonded to the N atom. Two Lewis formulae that satisfy the octet rule whereas formal charges are not same.

(a) 

For Cl, FC = 7 – (2 + 4) = +1

For N, FC = 5 – (3 + 2) = 0

For O, FC = 6 – (1 + 6) = -1

(b) 

For Cl, FC = 7 – (1 + 6) = 0

For N, FC = 5 – (3 + 2) = 0

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.

Rules to estimate relative stability of resonance structures

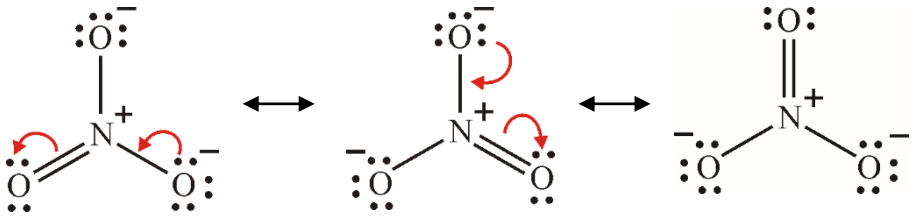
(i) The most stable resonance structure has the least formal charge separation. Thus it contains the greater number of covalent bonds and it contributes mostly to the resonance hybrid. Both maximizing the number of bonds and satisfying the octet rule should be achieved.

(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.

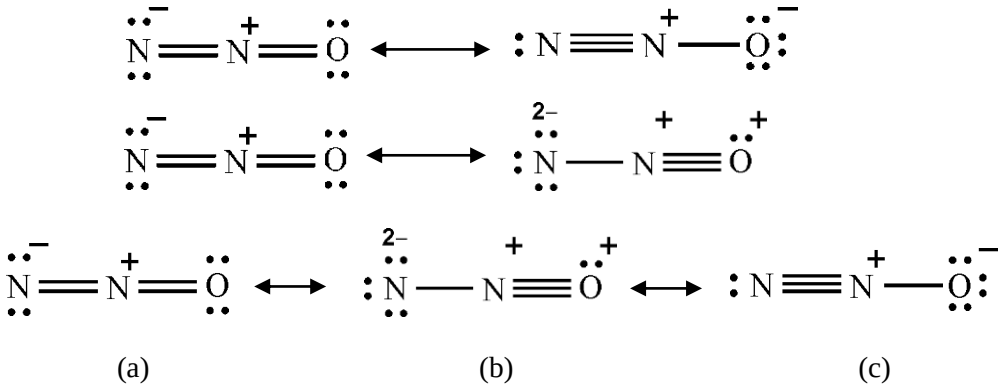


(a) (b) (c)

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.

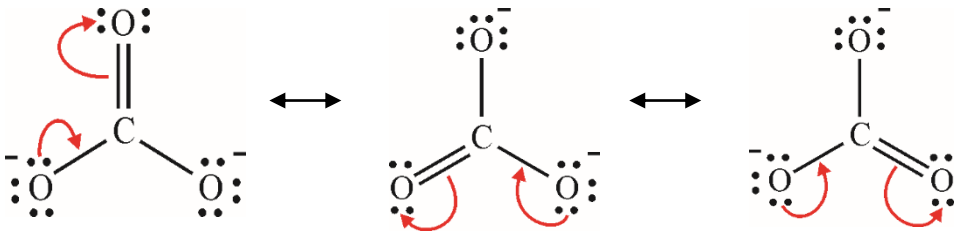


Figure 2.30 Formulation of resonance structures of CO_3^{2-} ion into one another

The corresponding resonance structures of carbonate ion are as follows.

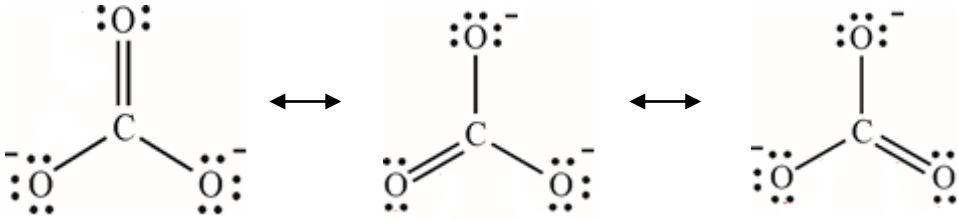
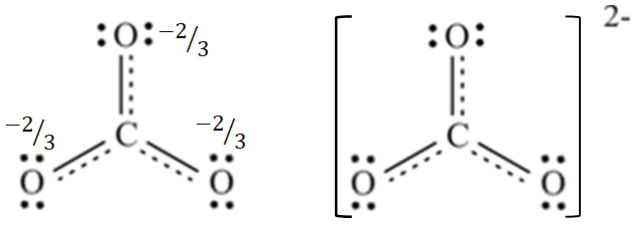


Figure 2.31 Resonance structures of the CO_3^{2-} ion

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).



(a) (b)

Figure 2.32 (a) Resonance hybrid structure of the CO_3^{2-} ion with charges (b) resonance hybrid structure 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.

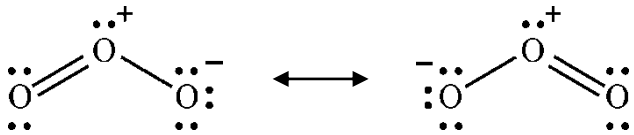


Figure 2.33 Resonance structures of O_3

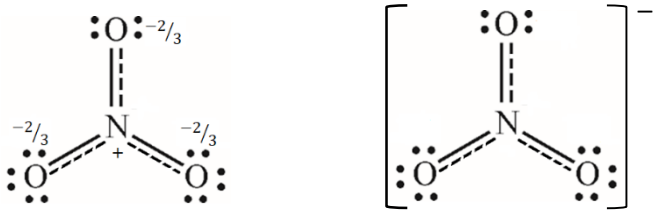
The bond lengths of the two bonds formed by central atom of O_3 molecule with the other two oxygen atoms in O_3 molecule are same and hence the real structure of O_3 is considered a combination of these two. The combination of the two resonance structures (resonance hybrid) of O_3 is illustrated as follows.



(a) (b)

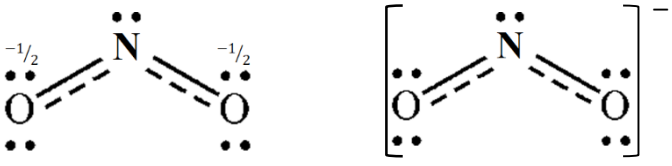
Figure 2.34 (a) Resonance hybrid structure of the O_3 with charges (b) Resonance hybrid structure of the O_3 without charges on terminal/ central atom(s)

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 structure of the NO_3^- with charges (b) Resonance hybrid structure of the NO_3^- without charges on terminal/ central atom(s)



(a) (b)

Figure 2.36 (a) Resonance hybrid structure of the NO_2^- with charges (b) Resonance hybrid structure 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.



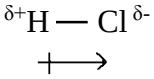
Figure 2.37 CO_2 and CCl_4 molecules

2.3.5 Dipole moment

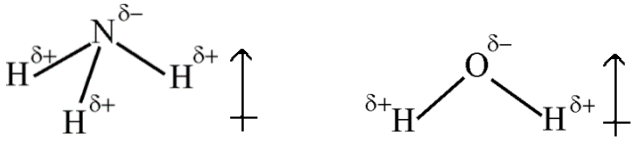
This concept can be clearly understood by taking a molecule with one single bond such as HCl. In a polar molecule, negative pole is created on one end of the molecule, and the positive pole is created on the opposite end of the molecule. Accordingly, in HCl molecule, negative pole is on the Cl atom and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



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



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 Cm.

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} Cm.
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.

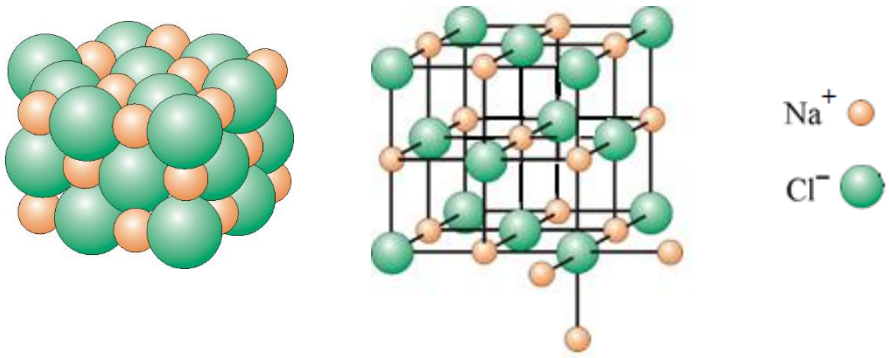
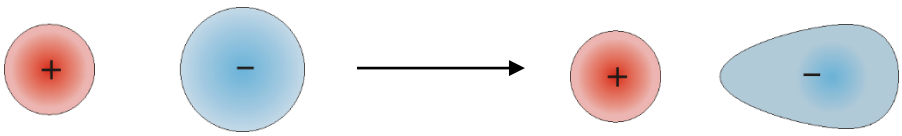


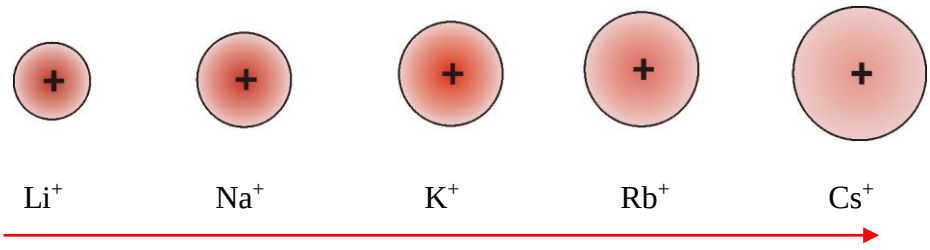
Figure 2.38 Lattice structure of NaCl

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**.

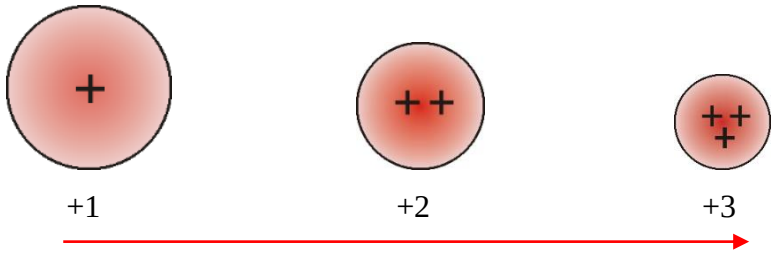


No polarization Polarization of anions

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



Size of the cation increases.
Polarizing power decreases.



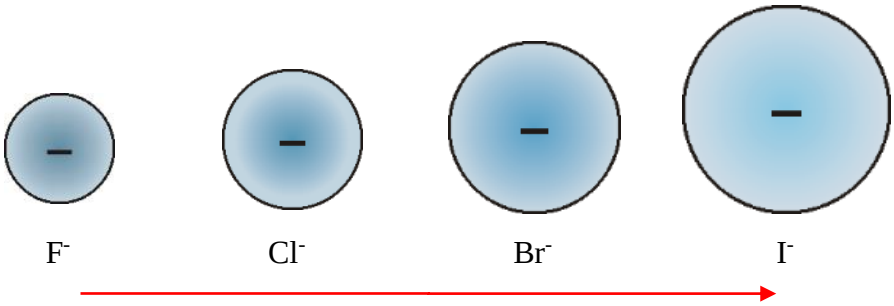
In isoelectronic species:

Charge of the cation increases.

Size of the cation decreases.

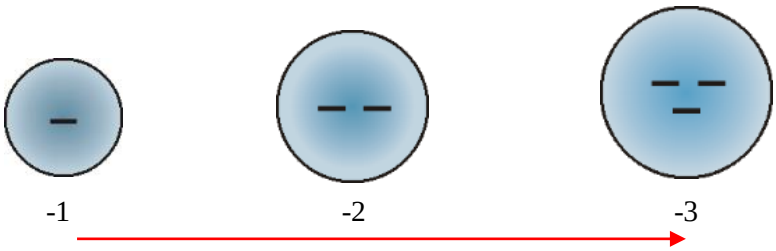
Charge density increases.

Polarizing power increases.



Size of the anion increases.

Polarizability increases.



In isoelectronic species:

Charge of the anion increases.

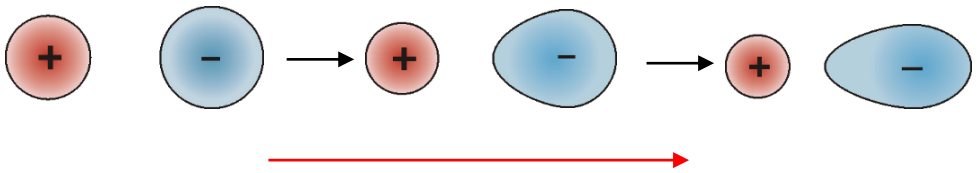
Size of the anion increases.

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 ºC. 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.

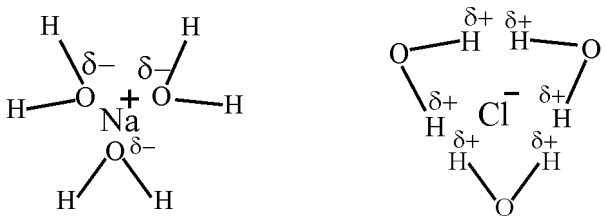


Figure 2.39 Ion dipole interactions formed between H_2O and ions of NaCl

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}.

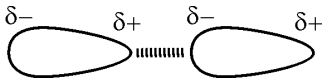


Figure 2.40 Dipole – dipole interactions

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.

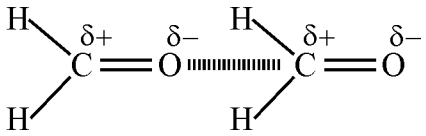


Figure 2.41 Dipole – dipole interactions in formaldehyde

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.

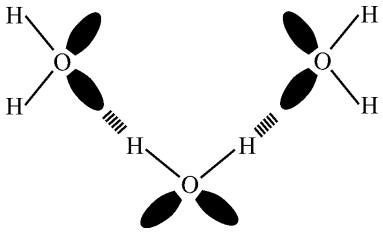


Figure 2.42 Hydrogen bonds in water

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.

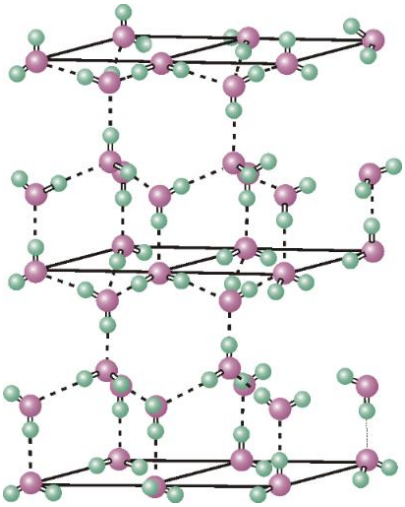


Figure 2.43 Arrangement of H_2O molecules in ice

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.

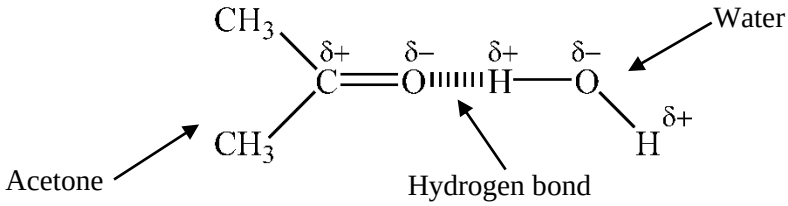


Figure 2.44 Hydrogen bonds in acetone/ water mixture

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.

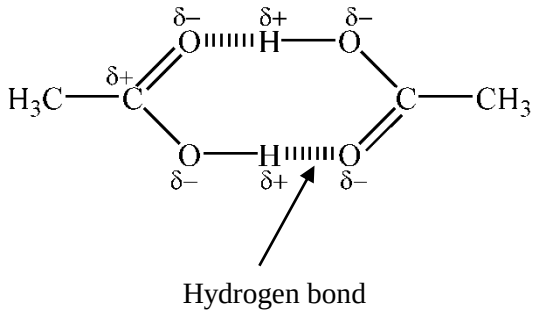
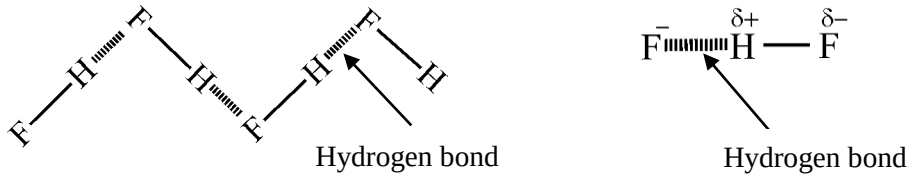


Figure 2.45 Hydrogen bonds in acetic acid

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.

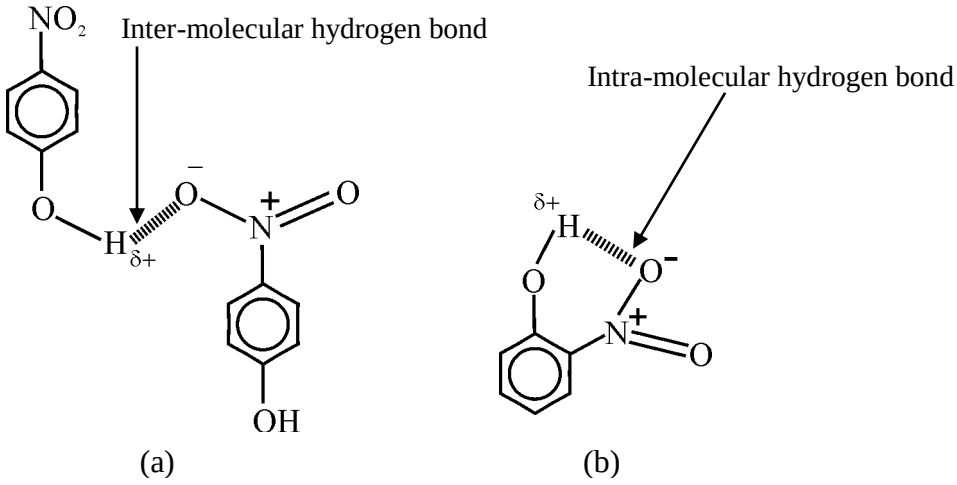


Figure 2.47 Hydrogen bonds in (a) *ortho*-nitrophenol and (b) *para*-nitrophenol

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.

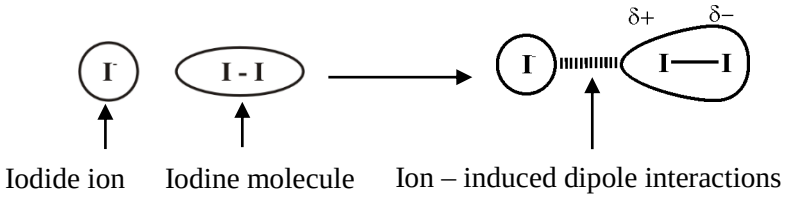


Figure 2.48 Ion –induced dipole interactions

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.

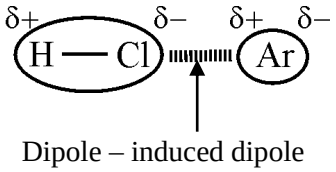


Figure 2.49 Dipole – induced dipole interactions

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.

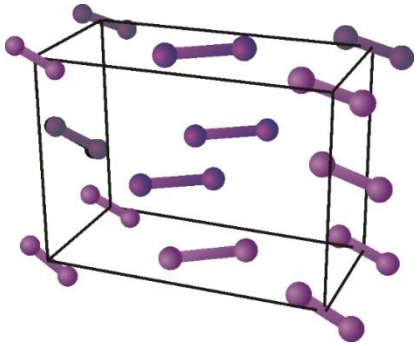


Figure 2.50 Lattice structure of iodine

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.

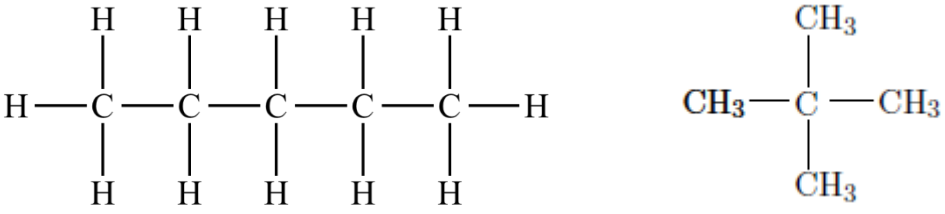
Table 2.7 Variation of boiling points of some simple molecules with dipole moment

Molecule	Molar mass/ g mol^{-1}	Dipole moment/ D	Boiling point/ ^0C	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 ^0C. ICl consists of polar molecules and boils at 97 ^0C almost 40 ^0C 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

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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	H_2O, P_2O_5
	+2	OF_2 only
	-1	peroxides/ O_2^{2-}
	-1 and zero	superoxides/ O_2^-
Hydrogen	+1	H_2O, CH_4
	-1	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

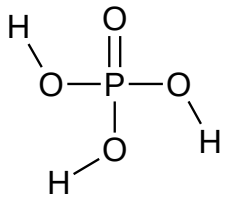
[oxidation number of Ca] + [-2] = 0

Oxidation number of Ca = +2

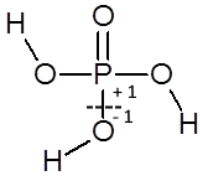
The structural formula of a molecule shows a graphic representation of its molecular structure and how the atoms are arranged. It also can be used to assign the oxidation number to each atom in the molecule using the electronegativity difference between the component atoms. This approach is mainly used 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.

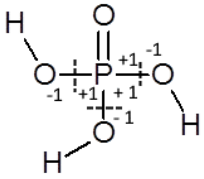
Example 1: Phosphoric acid (H_3PO_4)



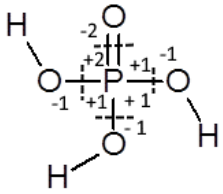
Step 1
Draw the bond structure of the compound.



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.

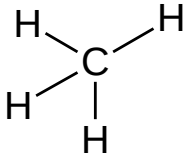


Step 4
Add all the assigned values around the target element.
Phosphorus = (+2)+(+1)+(+1)+(+1) = +5
Oxidation number of the central atom of phosphorus is +5.

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

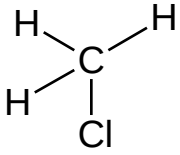
Oxidation number of carbon in compounds in which carbon at the center.

Example 1: Methane (CH_4)



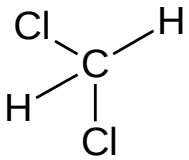
Oxidation number of C = -4

Example 2: Chloromethane (CH_3Cl)



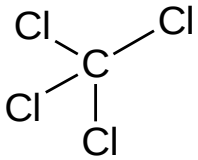
Oxidation number of C = -2

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) $Na(g) \longrightarrow Na^+(g) + e$

$0 \qquad +1$

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

Reduction (Gain of electrons) $Cl_2(g) + 2e \longrightarrow 2Cl^-(g)$

$0 \qquad -1$

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	$^{x}CH_3{}^{y}CH_2{}^{z}CH_3(g)$ + $5O_2(g)$ ⟶	$3CO_2(g)$ + $4H_2O(l)$
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	$^{x}CH_3{}^{y}CH^{z}CH_2(g)$ + $H_2(g)$ ⟶	$^{x}CH_3{}^{y}CH_2{}^{z}CH_3(g)$
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 3.4 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 × 12 u) + (1.11 × 13 u)]

The average atomic mass of natural carbon atom = [(98.89 × 12 u) + (1.11 × 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 × 35 u) + (24.23 × 37 u)]

The average atomic mass of natural chlorine atom = [(75.77×34.97 u)+(24.23×36.97 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,

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

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

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

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}.

molar mass of O = 16.00 g mol^{-1}

molar mass of H_2 = 2 × 1.008 g mol^{-1} = 2.016 g mol^{-1}

molar mass of H_2O = (2 × 1.008 g mol^{-1}) + 16.00 g mol^{-1}

= 18.016 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.

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

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 g mol^{-1} ÷ 49 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 ($n_A + n_B + n_C + \ldots\ldots$).

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

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

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

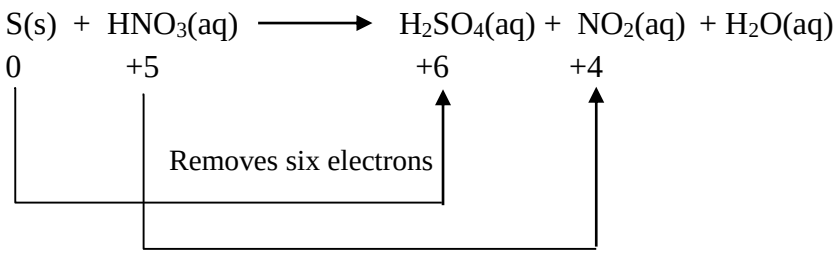
This considers the change in oxidation number and uses them as coefficients of reactants.

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.

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

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



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.

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

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.

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

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.

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

total charge is minus eight — 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.

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

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

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

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

Steps 1, 2 and 3:

$$SO_2(g) \longrightarrow SO_4^{2-}(aq)$$
$$(+4) \qquad\qquad (+6)$$

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.

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

total charge is zero — total charge is minus four

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.

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

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,

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

Simplified equation (balanced ionic equation) is,

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

and the balanced chemical equation is,

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

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 $N_2 \times 3 = 9$ 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 $\times$ 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 $\times$ 2/3 = 6 mol $\times$ 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:

$^{226}_{88}Ra \longrightarrow {}^{4}_{2}He + {}^{222}_{86}Rn$

	Parent nucleus (Radium 226)		Alpha particle		Daughter nucleus (Radon 222)
Mass number :	226	⟶	4	+	222
Atomic number:	88	⟶	2	+	86

Example 2:

$^{7}_{4}Be + {}^{0}_{-1}e \longrightarrow {}^{7}_{3}Li$

	Parent nucleus (Beryllium 7)		Beta particle		Daughter nucleus (Lithium 7)
Mass number :	7	+	0	⟶	7
Atomic number:	4	+	-1	⟶	3

In some nuclear reactions protons ($^{1}_{1}p$) and neutrons ($^{1}_{0}n$) 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 a carefully 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 g cm^{-3}×1000 cm^3 × 36%
= 421.2 g
Number of HCl moles in 1 dm^3 of conc. HCl = 421.2 g ÷ 36.5 g mol^{-1}
Concentration of the conc. HCl acid solution = 11.5 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 mol × 250 cm^3) ÷1000 cm^3
= 0.25 mol

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

The calculation of volume v:
0.25 mol = (11.5 mol × v) ÷ 1000 cm^3
v = 21.7 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 mol = 6 mol × v/1000 cm^3

v = 41.6 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 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 $cm^3 \times 2$

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 mol × 27.00 cm^3/1000 cm^3

= 6.75×10^{-3} mol

The amount of MnO_4^- required = 6.75×10^{-3} mol ÷ 5

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

The calculation of volume v:

6.75×10^{-3} mol ÷5 = 0.6 mol dm^{-3} × v

v = 0.00225 dm^3 = 2.25 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 mol × 233 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

$$\frac{\text{mass of two moles of Fe}}{\text{mass of one mole of } Fe_2O_3} \times 100 = \frac{112\ \text{g}}{160\ \text{g}} \times 100 = 70\%$$

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 $= 1.0 \times 10^3\ \text{g} \times \frac{70\ \text{g}}{100\ \text{g}}$

$= 700$ g

(c) Mass of hematite needed

Mass of Fe_2O_3 $= 1\ \text{kg} \times \frac{100\ \text{g}}{66.4\ \text{g}}$

Mass of hematite ore processed $= 1\text{kg} \times \frac{100\ \text{g}}{66.4\ \text{g}} \times \frac{100\ \text{g}}{70\ \text{g}}$

$= 2.151$ 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) $\text{molality} = \frac{\text{moles of solute}}{\text{mass of solvent (kg)}}$

$$\text{moles of glucose} = \frac{4.0\ \text{g}}{180\ \text{g mol}^{-1}} = 0.022\ \text{mol}$$

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:

$$\text{Moles of } AgNO_3 = \frac{12.70 \text{ g}}{143.32 \text{ g mol}^{-1}} = 0.088 \text{ mol}$$

Number of moles of NaCl + Number of moles of KCl = 0.088 mol

$$0.088 \text{ mol} = \frac{\text{mass of NaCl}}{58.44 \text{ g mol}^{-1}} + \frac{\text{mass of KCl}}{75.55 \text{ g mol}^{-1}}$$

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:

$$0.088 \text{ mol} = \frac{x}{58.44 \text{ g mol}^{-1}} + \frac{(5.48 \text{ g} - x)}{75.55 \text{ g mol}^{-1}}$$

Mass of NaCl = *x* = 4.06 g

$$\text{Mass percentage of NaCl} = \frac{4.06 \text{ g}}{5.48 \text{ g}} \times 100 = 74.01\%$$

Table 3.8 A summary of equations

Equation	Units
$\textbf{Mass fraction of A } (\mathbf{w/w}) = \dfrac{\text{mass of A}}{\text{mass of substance or mixture}}$	-
$\textbf{Volume fraction of A } (\mathbf{v/v}) = \dfrac{\text{volume of A}}{\text{volume of mixture}}$	-
$\textbf{Mole fraction of A } (\boldsymbol{x}\mathbf{A}) = \dfrac{\text{moles of A}}{\text{total moles of mixture}}$	-
$\text{Mass \% of element } x = \dfrac{\text{moles of } \boldsymbol{x} \text{ in formula} \times \text{molar mass of } \boldsymbol{x} \text{ (g mol}^{-1}\text{)}}{\text{molar mass of compound}} \times \mathbf{100}$	-
$\textbf{Mass Percent } (\mathbf{w/w}) = \dfrac{\text{mass of the substance}}{\text{mass of the mixture}} \times \mathbf{100\%}$	-
$\textbf{Volume Percent } (\mathbf{v/v}) = \dfrac{\text{volume of substance}}{\text{volume of mixture}} \times \mathbf{100\%}$	-
$\textbf{Parts per thousand } (\mathbf{ppt}) = \dfrac{\text{mass of substance}}{\text{mass of mixture}} \times \mathbf{10^3}$	-
$\textbf{Parts per million } (\mathbf{ppm}) \dfrac{\text{mass of substance}}{\text{mass of mixture}} \times \mathbf{10^6}$	-
$\textbf{Parts per billion } (\mathbf{ppb}) = \dfrac{\text{mass of substance}}{\text{mass of mixture}} \times \mathbf{10^9}$	-
$\textbf{Molality } (\mathbf{m}) = \dfrac{\text{moles of solute}}{\text{mass of solvent}}$	mol kg^{-1}
$\textbf{Molarity } (\mathbf{M}) = \dfrac{\text{moles of solute}}{\text{volume of solution}}$	mol dm^{-3}
$\textbf{Mole fraction of A } (\mathbf{x_A}) = \dfrac{n_A}{n_A+n_B+n_C+\ldots}$	-

G. C. E. (Advanced Level)

CHEMISTRY

Grade 12

Resource Book

Unit 4: Gaseous State of Matter
Unit 5: Energetics

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

Chemistry

Resource Book

Grade 12

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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.

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1. Gaseous State of Matter

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1.5.1 van der Waals equation

1.5.2 Critical temperature and liquefaction of gases

Introduction

Everything in the universe has a chemical identity. We know that the smallest particle of matter is an atom. "Study of matter and the changes that it undergoes" can simply be understood as the basic definition of chemistry. Usually matter is anything that occupies space and has mass and can be seen and touched (such as soil, water) as well as things we cannot see such as air. Based on the composition and properties, several categories such as substances, mixtures, elements as well as atoms and molecules can be identified. All substances, at least in principle, can exist in three states: solid, liquid and gas. In a solid, particles are held tightly and close together in an ordered structure with a definite shape having a small degree of motion. Particles in a liquid are close together but are not held so tightly in position and can move faster compared to that of solid. Gases differ largely from liquids and solids in the distances between the particles. In a gas, the particles are separated by distances, large compared with the size of the particles allowing them to behave freely. Therefore, the attractive forces between gas particles are very small or negligible and that allows us to consider gas particles individually and some hypotheses are easily predictable depending on the temperature and pressure changes.

1.1 Organization of particles in three principal states and their typical characteristics

Anything that occupies space and has a mass can be called "**matter**". This could be things we can see and touch like trees or things we cannot see like the air we breathe. All matter can be classified broadly into three states **solid, liquid and gas**. Matter can be interconverted among these three states without changing the composition. For an example water in liquid state can be converted to gaseous state (steam) when heated and can be converted to a solid (ice) if cooled.



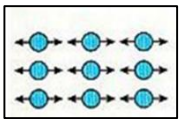
Solid (eg. nail)
Fixed shape
and volume



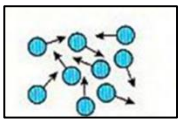
Liquid (eg. water)
No Fixed shape but
has fixed volume



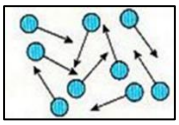
Gas (eg. He balloons)
No fixed shape and no
fixed volume



Solid
Strong interparticle (atoms, molecules or ions) forces. Particles vibrate but cannot move around.



Liquid
Moderate interparticle (atoms, molecules or ions) forces. Particles can move around up to some extent.



Gas
Weak interparticle (atoms, molecules or ions) forces. Particles can move around.

Figure 1.1 Three states of matter

Three states of matter differ based on arrangement and movement of particles. The inter-particle distance is highest in gaseous state and lowest in solids. In liquid state, particles are relatively closer compared to gaseous state, yet not too close compared to the solid state. Therefore, a regular pattern of particles can be seen only in solid state, while both gaseous and liquid state particles show random arrangement. As a result, particles in gaseous state can move fast and freely compared to liquid state particles. However, movement of particles in solids is limited to vibrations. The arrangement and motions of particles in matter result in differences in macroscopic properties such as volume, shape, compressibility and density as indicated in the Table 1.1 below.

Table 1.1 Qualitative comparison of properties of solids, liquids and gases

Property	Solids	Liquids	Gases
Shape	Definite	Take up shape of the container but do not spread throughout the entire volume of the container	Take up the shape of the container and occupy the entire volume of the container
Volume	Definite	Definite	Occupy the volume of the container
Density (ρ)/ g cm^{-3} at 293 K	Have high values eg.: Iron (7.874 g cm^{-3})	Have moderately high values eg.: Water (0.997g cm^{-3})	Have low values eg.: Hydrogen (0.071g cm^{-3})
Compressibility	Extremely hard to compress	Extremely hard to compress	Can compress to a great extent

Note: *Here we say that a liquid takes the shape of the container and we have to think why we get these shapes. Usually, particles of any object is being pulled by a variety of forces such as intermolecular forces, and that's why it has shape. Some given amount (volume) of water in a beaker is being shaped by surface tension resulting from intermolecular forces within the liquid creating a meniscus curve at the edge of the surface, by the force of the walls of the beaker pushing up on it, and by the gravity which is greater than the surface tension, pulling it down. So, it takes the shape of the beaker, with a flat surface on the top. This happens due to the satisfaction of all those different forces. However, in the case that the surface tension is stronger than gravity, the water's surface might not lie flat by taking the shape of the container. Assume that there is no gravity, and so surface tension is very much high. As each part of the surface wants to stay as close as possible to the rest of the surface it tries to minimize the forces within. So, the shape that best allows this is a sphere, because it is the shape that has the minimal surface area for a given volume.*

Matter in one particular state can be converted to another state by heating or cooling. Increase of temperature makes particles move faster and inter-particle distance becomes greater leading to change in state. Accordingly, increase in temperature converts solid state materials to liquid and liquid state materials to gaseous state. The opposite happens with decreasing temperature. Figure 1.2 illustrates how matter can be interconverted among states.

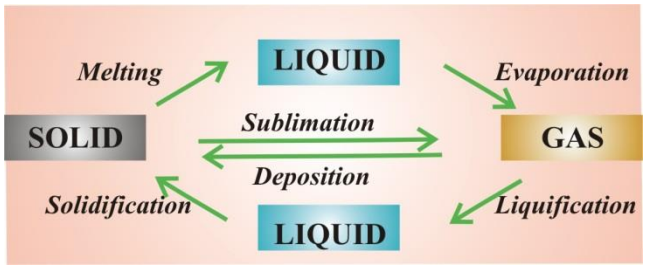


Figure 1.2 Interconversion of states of matter

Example 1.1
In which state of matter are the particles mostly touching but arranged in a random way?

Answer
Liquid State

When we describe the properties of the three states of matter with the help of Table 1.1, motion and arrangement of particles are basically considered. Especially, thermal energy is the energy of a body arising from motion of its atoms or molecules and it is directly proportional to the temperature of the substance. Therefore, it measures the average kinetic energy of the particles of the matter and is thus responsible for movement of particles or the thermal motion.

As we already know, interparticle forces tend to keep the particles together but thermal energy of the particles tends to keep them apart. Therefore the existence of three states of matter can be regarded as a result of balance between interparticle forces and the thermal energy of the particles.

When inter molecular interactions are very weak, molecules do not tend to make liquid or solid unless thermal energy is reduced by lowering the temperature. Gases do not liquefy on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum. However, when thermal energy of molecules is reduced by lowering the temperature, the gases can very easily be liquefied. These behaviours can be explained by Figure 1.3 where we can understand the reversible nature of intermolecular forces and the thermal energy acting on the three states of matter.

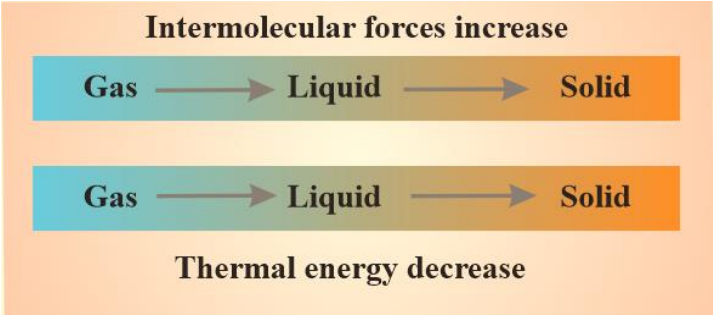


Figure 1.3 Behaviour of three states of matter against intermolecular forces and thermal energy

We have already learnt the cause for the existence of the three states of matter. Now we will learn more about the gaseous state and the laws which govern the behaviour of matter in this state.

1.2 Gaseous state

Let us now focus our attention on the behaviour of substances which exist in the gaseous state under normal conditions of temperature and pressure.

The gaseous state is characterized by the following physical properties as described in Table 1.1.

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.

Simplicity of gas is due to the fact that the forces between their molecules are negligible. Their behaviour is governed by same general laws (will be discussed later), which were discovered as a result of experimental studies. These laws are usually relationships between measurable properties of gases. Some of these properties like pressure, volume, temperature and amount (moles or mass) are very important because relationships between these variables describe *state of the gas* (will be defined in unit 5). Interdependence of these variables leads to the formulation of gas laws.

1.2.1 Gas laws

The gas laws that we are going to discuss are the results of experiments carried out by several scientists on the physical properties of gases. In these experiments, relations among the variables of pressure, temperature, volume and amount of gases are considered and the results provide valuable information on the gaseous state of matter in turn helping the mankind in many ways.

Ideal gas and ideal gas equation

When it is assumed that intermolecular forces do not exist among the molecules of a gas, such a gas is called an **ideal gas.** That is molecules in an ideal gas do not exhibit attraction or repulsion among them. Furthermore, the volume of ideal gas particles is considered negligible when compared to the volume of the container.

The absolute temperature (*T*), pressure (*P*), volume (*V*) and the amount (*n*, moles) of a gas are the factors that affect the behaviour of a gas. *P*, *T*, *V* and *n* are related by the expression;

$$\boldsymbol{PV = nRT}$$

This is known as the **ideal gas equation** or **ideal gas law** where the gas constant *R* is same for every gases. Any gas which obeys the above relationship under any given temperature and pressure is referred to as an **ideal gas**.

The value of the constant *R* for one mole of an ideal gas can be calculated under the conditions of 0 °C and 1 atm as given below: (At 0 °C and 1 atm, the volume of one mole of ideal gas is 22.414 dm^3)

$$R = \frac{P\,V}{n\,T} = \frac{101325\ \text{Pa} \times 22.414 \times 10^{-3}\ \text{m}^3}{1\ \text{mol} \times 273.15\ \text{K}} = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$$

We can see that the ideal gas equation is a relationship among four variables and it describes the state of any gas. Therefore, it is also called **equation of state.**

Calculations based on ideal gas equation

The ideal gas law allows us to determine any one of the quantities volume, pressure, temperature, or moles of the gas when the other three are given. If the amount of moles of the gas is known, we can also calculate its mass using its molar mass. Further it can also be used to determine the density of a gas. It is important to keep in mind that all the other quantities must be in units that match the value used for the ideal gas constant. Usually pressure can be expressed in several units such as atm, Pa, bar, torr, etc. Therefore, in solving these problems it may helpful to use pressure conversions as given in the Table 1.2.

Table 1.2 Pressure units

Pressure unit	Pa	bar	atm	torr/mmHg
1 Pa	1 N m^{-2}	10^{-5}	9.87×10^{-6}	7.5×10^{-3}
1 bar	100,000	1 bar	0.987	750.06
1 atm	101,325	1.01325	1 atm	760
1 torr/mmHg	133.32	1.3332×10^{-3}	1.3158×10^{-3}	1 torr/ 1 mmHg

Example 1.2

The volume of a gas cylinder is 0.950 dm^3. When filled, the cylinder contains liquid propane (C_3H_8) stored under pressure. When the cylinder is empty, it contains some residual propane gas molecules at atmospheric pressure and temperature.

(i) Calculate the number of moles of propane gas remaining in a cylinder when it is empty if the surrounding atmospheric conditions are 25.0 °C and 750 torr (1 torr = 133.32 Pa) (when the internal pressure equals to the external pressure).

(ii) Calculate the mass of propane remaining in the cylinder.

(iii) Calculate the density of remaining propane gas in the cylinder.

Answer

(i) First summarize the given information;

Temperature, T = (25 + 273) K = 298 K

Pressure, P = 750 torr × 133.32 Pa/ 1 torr = 99990 Pa

Volume, V = 0.950 dm^3 = 0.950 × 10^{-3} m^3

Unknown is n

Using $PV = nRT$;

$$n = \frac{PV}{RT} = \frac{99990\ \text{Pa} \times 0.950\ \times 10^{-3}\ \text{m}^3}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}} = 0.038\ \text{mol}$$

(ii) Molar mass of propane(C_3H_8) = 44 g mol^{-1}

Mass of propane = 0.038 mol × 44 g/1 mol = 1.672 g

(iii) Density of propane = mass/volume = 1.672 g/ 0.950 dm^3 = 1.76 g dm^{-3}

When we consider the above example, there are insights into the ideal gas equation that it can be expressed in different forms to estimate mass and density of a given gas with simple modifications as shown below.

$PV = nRT$ and we can write,

$P = \frac{n}{V} RT$

$$\therefore \boldsymbol{P = CRT},$$

where C is the concentration

We can also write $PV = nRT$ as

$$\boldsymbol{PV = \frac{m}{M} RT},$$

where, m is the mass and M is the molar mass of the gas.

Also we can write the above as;

$$P = \frac{1}{M}\left(\frac{m}{v}\right) RT$$

$$\therefore \boldsymbol{P = \frac{d\,RT}{M}}$$

where, d is the density and $d = \frac{m}{v}$

Ideal gas law serves as the basis when deriving several other gas laws under specific conditions.

1.2.2 Boyle law (pressure – volume relationship)

That is the "*pressure of a fixed amount (mass) of gas at constant temperature inversely varies with (or proportional to) the volume of the gas*". This is known as the **Boyle Law** (1627-1691) which was named after **Robert Boyle**, an Irish scientist in the seventeenth century who studied change in volume of a gas when pressure of a gas is varied under constant temperature conditions. Mathematical form of it, is given below.

$$P \propto \frac{1}{V} \quad or \quad P = \frac{k}{V} \; ; \text{ k is a constant}$$

The ideal gas law can be used to derive Boyle law as follows.

$$PV = nRT$$

If the amount of the gas and temperature of the system are kept constant, then the product nT is a constant. Since R is also a constant, then the product, $nRT = k$ (a constant)

$$PV = k$$

It means that "*at constant temperature, the product of pressure and volume of a fixed amount of gas is constant*". This is another way of expressing Boyle law.

If a fixed amount of gas at constant temperature T occupying volume V_1 at pressure P_1 undergoes change, so that volume becomes V_2 and pressure becomes P_2, then according to Boyle law:

$$\boldsymbol{P_1V_1 = P_2V_2}$$

Figure 1.4 shows two conventional ways of graphical representation of Boyle law. Figure 1.4 (a) is the graph of $PV = k$ at different temperatures for the comparison. The value of k for each curve is different because for a given mass of gas, it varies only with temperature. Note that at higher temperatures, curves shift upwards due to the expansion of volume. It should also be noted that volume of the gas doubles if pressure is halved at a constant temperature.

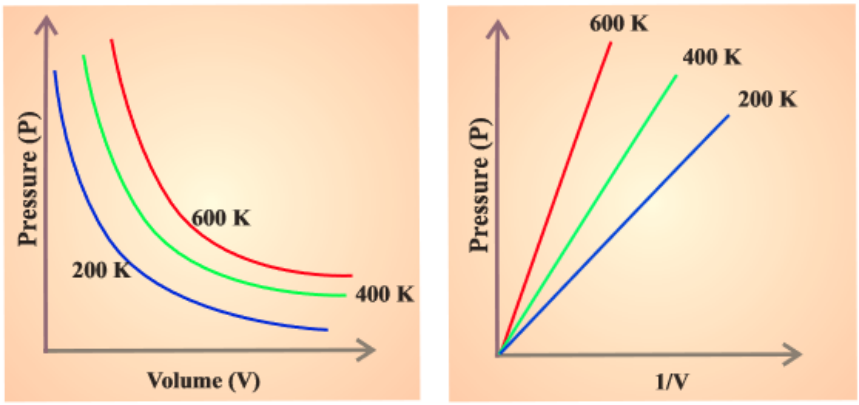


Figure 1.4 Changes in pressure at different constant temperatures with respect to (a) volume (*V*) changes and (b) with *1/V*

Figure 1.4 (b) represents the graph of *P* vs *1/V*. It is a straight line passing through the origin. These plots obtained by the experiments carried out by Boyle, show in a quantitative manner that gases are highly compressible. That is because when a given mass of a gas is compressed, the same number of molecules will occupy a smaller space. This means that gases become denser at high pressures.

Note: *We know that density (d) of a given mass (m) occupying volume (V) is given by; d = m/V. Therefore at constant temperature we can write,* $d = \left(\frac{m}{k/P}\right) = \left(\frac{m}{k}\right) P = k' P$

Example 1.3
Calculate the change in pressure of a gas when the volume is doubled at constant temperature for a known amount of a gas.

Answer

$V_1 = V$, $V_2 = 2V$, $P_1 = P$, $P_2 = ?$
Applying Boyle law: $P_1V_1 = P_2V_2$
$P \times V = P_2 \times 2V$
$P_2 = P/2$

∴New pressure is half the initial pressure.

Example 1.4

A balloon is to be filled with a known amount of hydrogen gas at room temperature. At atmospheric pressure (100 kPa), the gas occupies 2.50 dm^3 volume. What would be the volume of the balloon when the pressure inside is 20 kPa at the same temperature.

Answer

P_1 = 100 kPa, P_2 = 20 kPa, V_1 = 2.5 dm^3, V_2 = *?*

Applying Boyle law: $P_1V_1 = P_2V_2$

100 kPa × 2.5 dm^3 = 20 kPa × V_2

$\therefore V_2$ = 12.5 dm^3

The balloon is filled up to the volume of 12.5 dm^3.

1.2.3 Charles law (temperature – volume relationship)

Investigations by the scientists **Jacques Charles and Joseph Gay-Lussac** have showed that for a fixed amount (mass) of a gas at constant pressure volume of a gas increases on heating and decreases on cooling. It was also found that for each degree change (rise or fall) in temperature, volume of a gas changes (increases or decreases) by a factor of 1/273.15 of the original volume of the gas at 0 °C.

Assume that volumes of the gas at 0 °C and at *t* °C are V_0 and V_t respectively, then we can write,

$$V_t = V_0 + \left(\frac{t}{273.15}\right)V_0 = V_0\left(1 + \frac{t}{273.15}\right) = V_0\left(\frac{273.15 + t}{273.15}\right)$$

At this stage, a new scale of temperature is defined such that ***t*** °C on new scale is given by

$$T_t = 273.15 + t$$

and 0 °C will be given by

$$T_0 = 273.15$$

This new temperature scale is called the **Kelvin temperature scale (K)** or **absolute temperature scale.** -273.15 °C (0 K) is also defined as the thermodynamic zero, which is the lowest theoretically reachable temperature.

By applying this temperature scale, we can rewrite the relation $V_t = V_0\left(\frac{273.15 + t}{273.15}\right)$ as,

$$V_t = V_0\left(\frac{T_t}{T_0}\right)$$

Hence,

$$\frac{V_t}{V_0} = \frac{T_t}{T_0}$$

For a general case when the change occurs from (V_1, T_1) to (V_2, T_2) at constant pressure

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

This can be rearranged as

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

$$\frac{V}{T} = \text{constant or } V = k\,T$$

Therefore, "*the volume of a fixed amount of gas under constant pressure is directly proportional to the absolute temperature of the gas."* This is called **Charles law**.

Further, the ideal gas law can be used to study the effect of temperature on the volume of a gas if the pressure of the system is kept constant for a fixed amount of a gas. The ideal gas law can be rearranged as follows;

$$PV = nRT$$

$$V = nRT/P$$

When the pressure of a fixed mass of gas is constant, $\frac{nR}{P}$ is constant.

$$\therefore \boldsymbol{V \propto T} \text{ or } \boldsymbol{V = kT}$$

According to Charles law for all gases, at any given pressure, graph of volume versus, temperature (in Celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at – 273.15 °C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at – 273.15 °C or 0 K as shown in Figure 1.5.

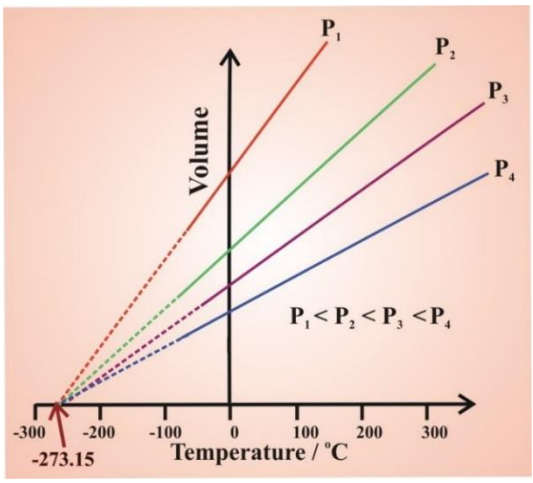


Figure 1.5 Changes in volume of a gas with respect to temperature change at different constant pressures

Example 1.5
Calculate the change in temperature of a gas when the volume is tripled at constant pressure for a known amount of gas moles.

Answer

$V_1 = V, V_2 = 3V, T_1 = T, T_2 = ?$

$V_1/ V_2 = T_1/T_2$

$V/3V = T/T_2$

$T_2 = 3T$

This can further be estimated directly, as the volume is directly proportional to Kelvin temperature T, the new temperature would be thrice the initial value, i.e 3T.

Let's consider the equation $V_t = V_0 \left(\frac{273.15+ t}{273.15}\right)$ and substitute t = -273.15, where we get the volume of the gas equal to zero meaning that the gas will not exist. Therefore, we can understand that all the gases get liquefied before this temperature is reached. The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **absolute zero**.

Example 1.6
A balloon is filled with a known amount of hydrogen gas resulting a volume of 2.0 dm^3 at 23 °C. Calculate the change in volume of a gas when the temperature is increased to 27 °C at the same pressure.

Answer

T_1 = 23 + 273 = 296 K, T_2 = 27 + 273 = 300 K, V_1 = 2.0 dm^3, V_2 = ?
Applying Charles law as the pressure and amount of gas constant,

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

$$\frac{2.0\ \text{dm}^3}{296\ \text{K}} = \frac{V_2}{300\ \text{K}}$$

$$V_2 = 2.03\ \text{dm}^3$$

Therefore, the change in volume is $0.03\ \text{dm}^3$

1.2.4 Avogadro law (amount – volume relationship)

Upon the developments of Boyle and Charles laws, in 1811 Italian scientist Amedeo Avogadro tried to combine conclusions of those with the amount and volume of a gas and postulated a new hypothesis which is now known as Avogadro law. *It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles* (**Avogadro Law**).

i.e. $V \propto n$

or we can write $V = k\,n$

The number of molecules in one mole of a gas has been determined to be 6.022×10^{23} and also known as **Avogadro constant** (denoted as N_A or L).

Avogadro law can be easily understood with the help of the ideal gas law as follows.

$$PV = nRT$$

$$V = \frac{RT}{P} \times n$$

$$V = \frac{RT}{P} \times \frac{N}{N_A} = \frac{RT}{PN_A} \times N$$

Here, N and N_A are the number of molecules of the gas and the Avogadro constant respectively. By applying the above relationships to equal volumes of gases P and Q at the same temperature and pressure,

$$V_P = \frac{RT}{PN_A} \times N_P$$

$$V_Q = \frac{RT}{PN_A} \times N_Q$$

At constant P and T, we can write (as R and N_A are constants)

$$\boldsymbol{V_P / V_Q = N_P / N_Q}$$

Simply it says that for a gas at constant temperature and pressure equal volumes of gases have equal number of molecules. i.e. $V \propto N$

It is useful to understand that the gas laws discussed above can also be used to obtain the ideal gas equation for a given volume V of a gas.

Boyel Law : $V \propto \frac{1}{P} \quad -----(1)$

Charles Law : $V \propto T \quad -----(2)$

Avogardro Law : $V \propto n \quad -----(3)$

The only equation that fulfills (1), (2) and (3) is,

$$V \propto \frac{nT}{P}$$

$$\frac{PV}{n\,T} = k$$

When $k = R$

$$PV = nRT$$

1.2.5 Molar volume (V_m)

Since volume of a gas is directly proportional to the number of moles we can write,

$$\boldsymbol{V_m = \frac{V}{n}}$$

As temperature and pressure are the same, one mole of any gas should occupy the same volume V_m and that can be calculated as,

$$\boldsymbol{V_m = \frac{R\,T}{P}}$$

Therefore, at temperature and standard pressure molar volume (V_m) of any gas should have the same volume. There are two sets of conditions applied for the standard value.

- *In the first set of condition; the temperature is taken as 0 °C (273.15 K) and the standard pressure as 1 atm (101325 Pa). At this standard condition molar volume of an ideal gas or a combination of ideal gases is* ***22.414 dm^3 mol^{-1}****. Molar volume under these conditions is denoted as* $\boldsymbol{V_m^{\ominus}}$**.**

- *In the second set of condition; the ambient temperature is taken as 25 °C (298.15 K) and the standard pressure as 1 atm (101325 Pa). In that case, the molar volume of a gas has the value* ***24.790 dm^3 mol^{-1}****.*

Note: *From Avogadro law we can see that the molar mass (M) of a gas is directly proportional to its density (d).*

V = k n = k (m/M),

therefore M = k (m/V) = k d

Example 1.7

Show that the molar volumes of 1 mole of He and 1 mole of Ne gas at 298 K temperature and 1atm pressure are the same.

Answer

P_{He} = 1 atm = 101325 Pa, T_{He} = 298 K, n_{He} = 1.00 mol, V_{He} = ?

$P_{He}V_{He} = n_{He}RT_{He}$

$V_{He} = n_{He}RT_{He} / P_{He}$

V_{He} = (1 mol × 8.314 J $K^{-1}mol^{-1}$ × 298 K)/ 101325 Pa = 24.4 dm^3

P_{Ne} = 1 atm = 101325 Pa, T_{Ne} = 298 K, n_{Ne} = 1.00 mol, V_{Ne} = ?

$P_{Ne}V_{Ne} = n_{Ne}RT_{Ne}$

$V_{Ne} = n_{Ne}RT_{Ne} / P_{Ne}$

V_{Ne} = (1 mol × 8.314 J $K^{-1}mol^{-1}$ × 298 K)/ 101325 Pa

V_{Ne} = 24.4 dm^3

i.e. at the same temperature and pressure, if number of moles are the same, then different gases will occupy the same volume.

1.2.6 Combined gas law

As all gases behave the same way with respect to pressure, volume, and temperature, if the amount is measured per mole, then the ideal gas expression itself can be written as a ratio useful in the events like when temperature, volume, and pressure of a fixed amount of gas vary from (T_1, V_1, P_1) to (T_2, V_2, P_2). For such an instance we can write,

for the initial condition; $nR = \frac{P_1V_1}{T_1}$

for the final condition; $nR = \frac{P_2V_2}{T_2}$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

This is called the combined gas law.

Example 1.8

At 25 °C and 760 mm Hg pressure, a given amount of a gas occupies a volume of 600 cm^3. What will be its pressure at 10 °C when volume of the gas is 650 cm^3.

Answer

(T_1, V_1, P_1) to (T_2, V_2, P_2) we can write

P_1 = 760 mm Hg = 1 atm = 101325 Pa, V_1= 600 cm^3 = 0.600 dm^3, T_1 = 25 + 273 = 298 K

V_2 = 650 cm^3 = 0.650 dm^3, T_2 = 10 + 273 = 283 K, P_2 = ?

According to Combined gas law; $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$$\frac{760 \text{ mm Hg} \times 600 \text{ cm}^3}{298\ K} = \frac{P_2 \times 650 \text{ cm}^3}{283\ K}$$

P_2 = 666.2 mmHg = 88823 Pa = 88.823 kPa

1.3 Dalton law of partial pressure

In most practical applications we encounter a mixture of gases rather than a single gas. The air we breathe has nitrogen and oxygen gases as major components and a variety of other gases in minute quantities. All of these gases contribute to the total atmospheric pressure.

Also, the pressure that a constituent gas of a mixture of gases would exert if it alone occupies the volume of the mixture at same temperature is defined as the **partial pressure** of that gas. A postulate introduced by Dalton says that *the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.* This is known as **"Dalton law of partial pressures".**

Accordingly, if partial pressures of individual gases in a mixture of gases A, B and C are P_A, P_B and P_C respectively, at constant temperature and constant volume the total pressure $\boldsymbol{P_T}$ of the mixture is given by the following equation.

$$P_T = P_A + P_B + P_C$$

The Dalton law of partial pressure can be derived using ideal gas equation as follows. Consider a mixture of gases A and B with n_A and n_B moles, respectively exerting the total pressure of P_T.

$$PV = nRT$$

For gas A, $n_A = P_AV/RT$ (P_A is the partial pressure of gas A)
For gas B, $n_B = P_BV/RT$ (P_B is the partial pressure of gas B)
For the mixture of gases, $n_T = P_TV/RT$
and $n_T = n_A + n_B$
Therefore, $P_TV/RT = (P_AV/RT) + (P_BV/RT)$

Simplification gives , $\boldsymbol{P_T = P_A + P_B}$
This is the **Dalton law of partial pressures.**

1.3.1 Partial pressure in terms of mole fraction

Suppose at the temperature T, n_A moles of gas A and n_B moles of gas B, are enclosed in a container of volume V, then partial pressures exerted by gases A and B are P_A and P_B respectively while the total pressure is P_T.

Therefore, we can write, $P_A = \frac{n_A RT}{V}$ and $P_B = \frac{n_B RT}{V}$

According to Dalton law, $P_T = P_A + P_B$

Substituting from the above, $P_T = \frac{n_A RT}{V} + \frac{n_B RT}{V} = (n_A + n_B)\frac{RT}{V}$

Dividing the expressions for P_A and P_B separately by P_T, we get;

$$\frac{P_A}{P_T} = \frac{n_A RT/V}{(n_A + n_B) RT/V} = \frac{n_A}{(n_A + n_B)} = x_A \text{ this is the mole fraction of A}$$

Likewise,

$$\frac{P_B}{P_T} = \frac{n_B RT/V}{(n_A + n_B) RT/V} = \frac{n_B}{(n_A + n_B)} = x_B : \text{ this is the mole fraction of B}$$

Therefore, we can write,

$$P_A = x_A P_T \text{ and } P_B = x_B P_T$$

Partial pressure of the constituent gas is equal to the product of total pressure and mole fraction of the gas.

Example 1.9

(i) A mixture of gases contains 0.8 mol of nitrogen gas (N_2) and 0.2 mol of oxygen (O_2). Calculate the partial pressures of the gases if the total pressure is 1.00 atm at a certain temperature.

(ii) When the container is heated and kept at a constant temperature, N_2 gas is reacted with O_2 gas to produce NO_2 gas. At equilibrium the container has 0.7 mol of N_2 gas, 0.15 mol of O_2 gas and 0.1 mol of NO_2 gas. If the partial pressure of N_2 gas is now 0.88 atm, calculate partial pressures of O_2 gas and NO_2 gas.

Answer

(i) $X_{N_2} = \frac{n_{N_2}}{n_{N_2}+n_{O_2}} = \frac{0.8 \text{ mol}}{0.8 \text{ mol}+0.2 \text{ mol}} = 0.8$

$P_{N_2} = X_{N_2} P_T$

$P_{N_2} = 0.8 \times 1.00 \text{ atm}$

$P_{N_2} = 0.8 \text{ atm}$

Similarly for O_2,

$P_{O_2} = 0.2 \text{ atm}$

(ii) $X_{N_2} = \frac{n_{N_2}}{n_{N_2}+n_{O_2}+n_{NO_2}}$ therefore, $X_{N_2} = \frac{0.7 \text{ mol}}{0.7 \text{ mol}+0.15 \text{ mol}+0.1 \text{ mol}} = \frac{0.7}{0.95}$

$P_{N_2} = X_{N_2} P_T$ therefore, $P_T = P_{N_2} / X_{N_2} = \frac{0.88 \text{ atm}}{0.7/0.95} = 1.19 \text{ atm}$

$X_{O_2} = \frac{n_{O_2}}{n_{N_2}+n_{O_2}+n_{NO_2}}$ therefore, $X_{O_2} = \frac{0.15 \text{ mol}}{0.7 \text{ mol}+0.15 \text{ mol}+0.1 \text{ mol}} = \frac{0.15}{0.95}$

$P_{O_2} = X_{O_2} P_T$ therefore, $P_{O_2} = \frac{0.15}{0.95} \times 1.19 \text{ atm} = 0.19 \text{ atm}$

$X_{NO_2} = \frac{n_{NO_2}}{n_{N_2}+n_{O_2}+n_{NO_2}}$ therefore, $X_{NO_2} = \frac{0.10 \text{ mol}}{0.7 \text{ mol}+0.15 \text{ mol}+0.1 \text{ mol}} = \frac{0.10}{0.95}$

$P_{NO_2} = X_{NO_2} P_T$ therefore, $P_{NO_2} = \frac{0.10}{0.95} \times 1.19 \text{ atm} = 0.12 \text{ atm}$

Therefore,

$P_{N_2} = 0.88 \text{ atm}, P_{O_2} = 0.19 \text{ atm}, P_{NO_2} = 0.12 \text{ atm},$

$P_T = 1.19 \text{ atm}$

We apply our knowledge on Dalton law for a mixture of gases assuming that they have the same properties as pure gases, provided that all gases in the mixture are ideal gases thus do not react chemically with each other. However, in practical situations such as chemical reactions involving gases, the procedure used to collect may introduce another gas. For example, a technique often used to collect gases from a chemical reaction is the displacement of water from an inverted container. In this method, a gas is collected in the container by bubbling the gas through a tube into a gas jar filled with water which is placed upside-down in a water trough. So that the gas push all the liquid out from the bottle when it is collected. Here, we assume that the gas does not dissolve in water and does not react with water. However; we do not get the gas which is in the pure state. Instead, the collected gas is a mixture of the gas generated by the reaction and some water vapour formed from evaporation. The amount of water vapour contained in the gas is most readily measured by the pressure it exerts at that temperature, called the **saturated vapour pressure**. Therefore, to determine the pressure exerted by a gas collected in this

way at a specific temperature, it is necessary to subtract the vapour pressure of water from the total pressure of the mixture. Then from the partial pressure of the gas and its volume and temperature, the ideal gas law can be used to calculate the amount of the gas collected. This is illustrated in example 1.10

Example 1.10

Suppose we produce gaseous oxygen by heating $KClO_3(s)$ as shown in the following reaction:

$$2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$$

1.50 dm^3 of O_2 gas is collected over water at 27.0 °C and 760 torr. Saturated vapour pressure of water at 27.0 °C is 26.7 torr.
Calculate the number of moles of O_2 gas produced.

Answer

According to Dalton law, we can write:

$P_{total} = P_{oxygen} + P_{water}$

$\therefore P_{oxygen} = P_{total} - P_{water} = (760 - 26.7)$ torr = 733.3 torr = 97764 Pa

Using the ideal gas equation:

$PV = nRT$ and $n = \frac{PV}{RT} = \frac{97764\ \text{Pa} \times 1.5 \times 10^{-3}\ \text{m}^3}{8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 300\ \text{K}} = 0.058\ \text{mol}$

1.4 Molecular kinetic theory of gases

In the above sections we have gone through and understood the laws related to gaseous state based on experimental observations (Boyle law, Charles law, etc.). By conducting such experiments we can understand how the particular system behaves under different conditions. Though, such observations are made from experiments we then have to know or understand why a system behaves that way. For example, gas laws help us to predict that pressure increases when we compress gases but we need to know what happens in the molecular level when a gas is compressed. Therefore, a theoretical model is needed to explain such events or questions where the theory should help us to understand observations. The theory that attempts to explain the behaviour of gases at the molecular level is known as **"molecular kinetic theory**".

1.4.1 Assumptions of the molecular kinetic theory of an ideal gas

- *Gases are composed of widely separated large number of small particles (molecules or atoms).*

  Because the particles are widely separated, the actual volume of the particles is very small compared to the total volume occupied by the gas. Or in other words the actual volume of the molecules is negligible in comparison to the empty space

between them. This postulate correctly predicts that the volume occupied by a gas is much larger than that of a liquid or a solid, in which the particles are much closer together. Because gas particles are so widely separated, gases have relatively low densities compared to liquids and solids. This assumption explains high compressibility of gases.

- *Each particle in a gas is in random (all possible directions), straight-line motion and undergoes perfectly elastic collisions with another particle or with the walls of the container. Different particles have different speeds.*
  Energy may be transferred from one particle to another, their individual energies may change, but there is no net loss or gain of energy. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

- *The average kinetic energy of gas particles depends only on the absolute temperature.*
  This tells us that the gas particle (molecule or atom) has its own mass and speed because the kinetic energy (*KE*) for a given gas particle is given by the equation

$$KE = \frac{1}{2} m v^2$$

  where *m* is the mass of a gas particle and v is the velocity (or speed). We can see that upon heating a gas at constant volume, the pressure increases. That is because, on heating the gas, kinetic energy of the particles increases and they strike the walls of the container more frequently thus exerting more pressure. As such the relation of kinetic energy of one mole of particle with the temperature is given by the following equation.

$$KE = \frac{3}{2} RT$$

Further, we can make following notes too.

- *Particles of a gas behave independently of one another.*
  Because gas particles are widely separated, they move independently of one another unless they collide. That is, no forces of attraction or repulsion operate among gas particles. We can see that this postulate explains Dalton law of partial pressures. This postulate also explains why gases fill their containers entirely.

- *The pressure of a gas arises from the sum of the collisions of the particles with the walls of the container.*
  This postulate explains Boyle law; at a given temperature, for the same amount of gas, the smaller the volume of the container and hence more collisions occur per unit area. The average distance traveled by a gas particle before a collision is less in a smaller volume. Therefore, more collisions occur in a given area producing greater pressure.

This assumption also predicts that pressure should be proportional to the number of moles of gas particles. The more gas particles, the greater the frequency of collisions with the walls, so the greater the pressure.

1.4.2 Equation of molecular kinetic theory

The equation below is named as the equation of molecular kinetic theory.

$$PV = \frac{1}{3} mN\overline{c^2}$$

This equation now gives pressure, a macroscopic quality, in terms of molecular motion. The significance of the above relationship is that pressure is proportional to the mean-square speed of molecules in a given container at a given temperature. From the equation we can see that when molecular speed increases the pressure exerted on the container increases. $\overline{c^2}$ is defined as the mean square speed of molecules.

1.4.3 Root mean square speed and mean speed

It is worth knowing the definitions of molecular speeds in different forms as follows: When *N* number of molecules in a constant volume container at constant temperature travel with the different speeds of c_1, c_2, ...c_N, it can be written as shown below.

Average speed, $\bar{C} = \frac{c_1 + c_2 + \cdots c_N}{N}$

Mean square speed $\overline{c^2} = \frac{(c_1{}^2 + c_2{}^2 + c_3{}^2 .... + c_N{}^2)}{N}$

Root mean square speed = $\sqrt{\overline{c^2}}$

Molecular kinetic equation can be used to derive equation to show temperature dependence of the mean square speed $\overline{c^2}$. Consider the equation for having N number of particles in volume *V*. We know that, $P = \frac{mN\overline{c^2}}{3V}$ and we can write this as; $PV = \frac{mN\overline{c^2}}{3}$

Since, $N = nN_A$, where N_A is the Avogadro's constant and *n* is the number of moles;

$$PV = \frac{1}{3} mnN_A\overline{c^2}$$

Since, $M = m\,N_A$, then the above equation can be rearranged as, (*M* is the molar mass)

$$PV = \frac{1}{3} n\,M\,\overline{c^2}$$

Substitution of ideal gas law, $PV = nRT$ in the above equation gives,

$$nRT = \frac{1}{3} M\, n\, \overline{c^2}$$

$$\overline{c^2} = \frac{3RT}{M}$$

And hence we can write root mean square speed as;

$$\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}}$$

Example 1.11

Calculate the root mean square speed of H_2 and N_2 gases at 25 ºC.

Answer

T = 25 ºC = 298 K
$M(H_2)$ = 2.0 g mol^{-1} = 0.002 kg mol^{-1}
$M(N_2)$ = 28.0 g mol^{-1} = 0.028 kg mol^{-1}
R = 8.314 J K^{-1} mol^{-1}

For H_2

Substituting in $\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{0.002\ \text{kg mol}^{-1}}} = 1927.8\ \text{m s}^{-1}$

For N_2

Substituting in $\sqrt{\overline{c^2}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 298\ \text{K}}{0.028\ \text{kg mol}^{-1}}} = 515.2\ \text{m s}^{-1}$

From the above example, we can see that heavier molecules move slowly at a given temperature implying that the molecules having higher mass do not have to move as rapidly as lighter molecules to have the same kinetic energy. This kinetic energy directly related to temperature and this can be proved based on the equation of molecular kinetic theory as follows.

We have, $PV = \frac{mN\overline{c^2}}{3}$

Multiply the above equation by 2 and also divide by 2, then we can rearrange the equation as;

$$PV = \frac{mN\overline{c^2}}{3} = \frac{2\,N}{3}\left(\frac{1}{2}\,m\overline{c^2}\right) = nRT$$

$$N\left(\frac{1}{2}\,m\overline{c^2}\right) = \frac{3}{2}nRT$$

And also we can write $\left(\frac{1}{2}\,m\overline{c^2}\right) = \frac{3}{2}\left(\frac{Rn}{N}\right)T = \frac{3}{2}\left(\frac{R}{N_A}\right)T = \frac{3}{2}(k_B)T$

k_B is the Boltzmann constant.

We can then write these as $\frac{1}{2}\,m\overline{c^2}$ is the kinetic energy (KE)

$$\boldsymbol{KE = \frac{3}{2}k_BT} \text{ (per molecule)}$$

$$KE = \frac{3}{2}(k_B)T\,N_A$$

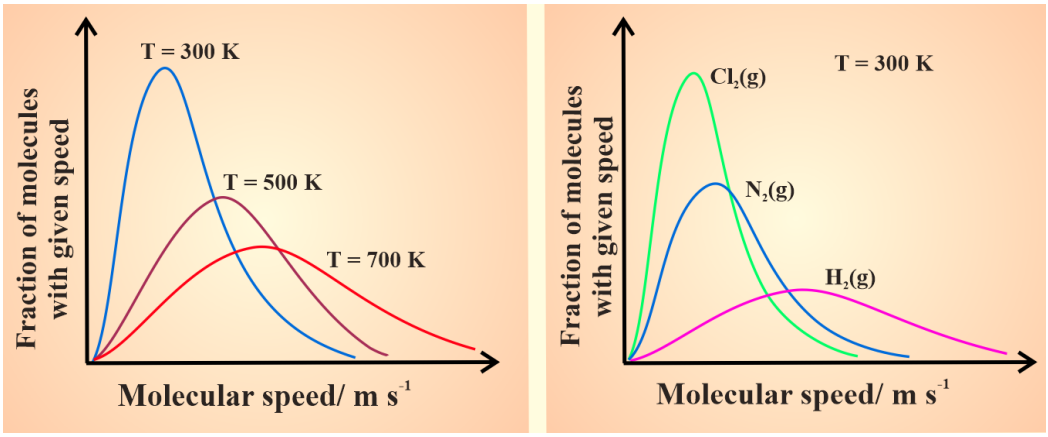
$$KE = \frac{3}{2}\left(\frac{R}{N_A}\right)T\,N_A$$

$$\boldsymbol{KE = \frac{3}{2}RT} \text{ (per mole)}$$

This proves that the kinetic energy of a gas depends only on the Kelvin temperature.

1.4.4 Maxwell- Boltzmann distribution

Although from the above example we have calculated speed of N_2 molecule as 515 m s^{-1}, it does not mean that all the N_2 molecules travel at this speed (as the molecules move in straight line directions, that the motion has vector properties, such that the molecular speeds are expressed in relation). There is a distribution of speeds from zero to values considerably above 515 m s^{-1}. This is because as individual molecules collide and exchange energy, their speeds vary. This speed distribution can be shown as a fraction of molecules travelling with particular speeds as shown in Figure 1.6 and such a distribution is called **Maxwell- Boltzmann distribution of speeds.**

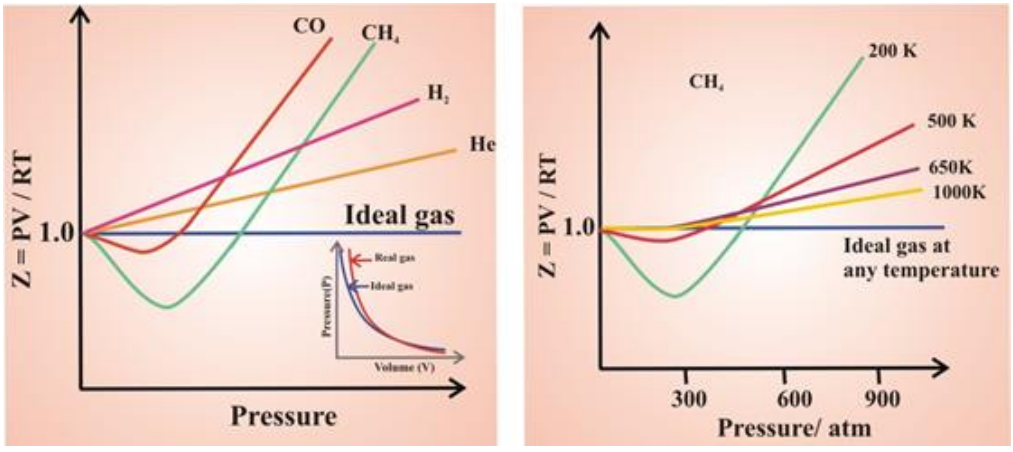


(a) (b)

Figure 1.6 (a) Maxwell- Boltzmann speed distribution for nitrogen gas at different temperatures (b) Speed distribution of three gases at 300 K

1.5 Amendments to ideal gas equation to apply for real gases

For a one mole of an ideal gas we can write $PV = RT$ or in other words $\frac{PV}{RT} = 1$ at a given temperature. When we have a real gas it actually deviates from ideal behaviour to some extent. The quantity, $Z = \frac{PV}{RT}$, called **compressibility factor (coefficient)** is used as one of the measures of this deviation. For example, for a one mole of an ideal gas if we study or analyze the variation of Z with pressure at constant temperature, PV will be constant (Boyle law) and Z *vs* P graph at all pressures will be a straight line parallel to x-axis (pressure - axis). Figure 1.7(a) shows such a plot for several gases at 273 K and Figure 1.7(b) for a one gas at several temperatures.



(a) (b)

Figure 1.7 Variation of compressibility factor for several gases with the comparison of an ideal gas. (a) The variation of Z with pressure at a constant temperature. Inset in (a) shows the Boyle law plot for ideal gas and real gas. (b) is the variation of Z with pressure at different temperatures for CH_4 gas.

From the plots shown in Figure 1.7 (a) it can be seen easily that at constant temperature $\frac{PV}{RT}$ *vs P (Z vs P)* plots for real gases is not a straight line parallel to the *x*-axis (pressure). There is a significant deviation from ideal behaviour. For different types of real gases, two types of curves are resulted. In the curves for hydrogen and helium, the value of *Z* increases as the pressure increases. The second type of plot is seen in the case of other gases like carbon monoxide (CO) and methane (CH_4). In these plots first there is a negative deviation from ideal behavior, the *Z* value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that it starts increasing, crosses the line for ideal gas and increases continuously showing a positive deviation. With these observations it can be found that real gases do not follow ideal gas equation perfectly under all conditions.

This deviation from ideal behaviour can also be understood when pressure versus volume plot is considered which is drawn as an inset in the Figure 1.7(a). In that plot the pressure versus volume data of a real gas is compared with those calculated theoretically. We know that this is the plot of Boyle law (for an ideal gas) and if the real gas follows the same behaviour two plots should coincide. It is clearly apparent that at very high pressures the measured volume is more than the calculated volume and at low pressures, measured and calculated volumes approach close to each other indicating further that low pressure conditions favour the ideal behavior. Thus gases show ideal behavior when the volume occupied is large so that the volume of the molecules can be neglected in comparison to the volume of the container. In other words, the behaviour of the real gas becomes more ideal when pressure is very low and depends upon the nature of the gas and its temperature.

We can further interpret the above behaviour of real gases where Z is less than 1 ($Z < 1$) as a combination of intermolecular interactions and repulsions caused by the significant sizes of the molecules when they become crowded at high pressures. At low pressures but still high for the ideal behaviour intermolecular attractions lower the molar volume and Z value is less than 1. At sufficiently high pressures, molecules tend to become crowded and the volume of the gas particles become large compared to the situation when it would be a point mass. At high temperature (Figure 1.7(b)) intermolecular attractions become less and *PV* factor increases making *Z* values greater than one ($Z > 1$). However deviation from the ideal line is less indicating that the higher temperatures favour the ideality to some extent. Therefore, we can say very low pressures and high temperatures are the favourable conditions for the ideal behaviour of real gases.

If we compare this behaviour of real gases with ideal gases considering these variations in molar volume at a given temperature and pressure, then the relation of compressibility factor Z may be understood. Assume that one mole of a real gas has the volume V_{real} and that for the ideal gas as V_{ideal}. Therefore, we can write;

$$Z = \frac{PV_{real}}{RT}$$

If the gas shows ideal behaviour under the same conditions;

$$PV_{ideal} = RT \text{ (per one mole)}$$

Substituting this in the first equation we get; $Z = \frac{PV_{real}}{PV_{ideal}}$

Therefore, $Z = \frac{V_{real}}{V_{ideal}}$

Therefore, we can see that the compressibility factor *Z* is the ratio of actual molar volume of a gas to the molar volume of it if it behaves as an ideal gas at that temperature and pressure.

Based on this kinds of experiments, it has been found that real gases do not follow Boyle law, Charles law and Avogadro law perfectly under all conditions. Therefore we have to understand; why gases deviate from the ideal behaviour and the conditions under which gases deviate from ideal behaviour.

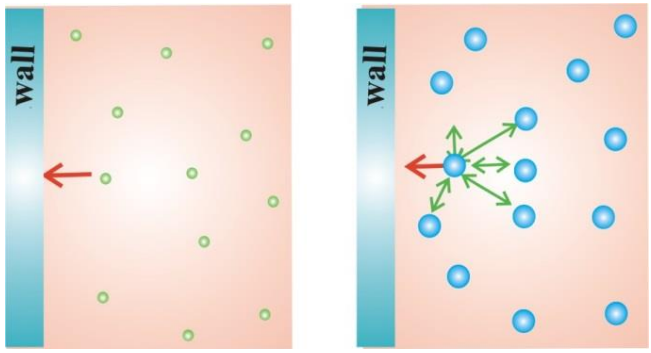
For the first one we can use the assumptions made in the molecular kinetic theory where it was assumed that; there is no force of attraction between the molecules of a gas and volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas.

If there are no interactions among gas molecules, the gas will never liquefy. However, we know that gases do liquefy when cooled and compressed. Once the gases are cooled and compressed the gas molecules will come close and then form liquids. If the volume of a gas molecule is negligible then the pressure versus volume graph of real gas and that of an ideal gas should coincide (see the inset of Figure 1.7 (a) and the behavior shown in the inset help us to understand the deviation of real gases from ideality). But it does not happen therefore, the real gases deviate from ideality.

1.5.1 van der Waals equation

At the beginning of this unit, an ideal gas law, *PV* = *nRT* known as **equation of state** was used to understand the behaviour of gases under different conditions with the measurable variables of *P*,*V*, *T* and *n*. From the above clarifications it can be understood that real gases show deviations from the ideal gas law due to the interactions among molecules and a significant volume of a gas molecule. Therefore, it is necessary to have another kind of equations of state to describe the behaviour of real gases as the measured pressures and volumes would not be the same as those for an ideal gas. Dutch physicist, **J. D. van der Waals** suggested the following which relates pressure and volume of a real gas to the pressure and volume of an ideal gas.

At high pressures molecules of gases are very close to each other and molecular interactions start to operate. Therefore, at high pressures, molecules cannot strike on the walls of the container with full force of impact as these are dragged back by other molecules due to the operation of these molecular attractive forces (a sketch on this behaviour is shown in Figure 1.8 comparing with an ideal gas). This affects the pressure exerted by the molecules on the walls of the container. Thus, the pressure exerted by the real gas is lower than the pressure exerted by the ideal gas under similar conditions.



(a) (b)

Figure 1.8 Comparison of the impact on the wall due to the collision of (a) an ideal gas molecule and (b) a real gas molecule.

As shown in the above figure reduction of pressure of a real gas is due to the intermolecular attractions. As it was found that the number of collisions with the wall in a given time is proportional to the density of the gas, the correction factor to pressure is proportional to the square of the gas amount and inversely proportional to the square of the volume and then the correction factor can be written as $\frac{a\,n^2}{V^2}$ where a is a constant related to magnitude of attractive forces and is independent of temperature and pressure. n and V are the number of moles of the gas and volume of the container respectively. Therefore, the pressure of the system under this condition is given by the following expression.

$$P_{ideal} = P_{real} + \frac{a\,n^2}{V^2}$$

At high pressure, repulsive forces are significant as molecules are almost in contact. Therefore, these repulsive forces cause the molecules to behave as small spheres to minimize the effect and hence results a significant volume occupied by the molecules. Now the ideal volume should be less than the measured volume because instead of moving in volume V, these are now restricted to an effective volume of

$$(V–nb)$$

nb is approximately the total volume occupied by the molecules themselves and b is a constant (volume of one molecule). Having taken into account the corrections for pressure and volume, we can rewrite the equation $PV = nRT$ as,

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

This is called **van-der Waals equation** and *a* and *b* are called **van-der Waals constants**. If we write this equation for one mole of a real gas it takes the following form.

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

1.5.2 Critical temperature and liquefaction of gases

At the beginning of the chapter the importance of the extent of the intermolecular forces to maintain a particular physical state was discussed. Matter can be interconverted between physical states supplying heat or cooling as needed to change the intermolecular distance.

For example, we may think that liquefaction of a gas can be done just by cooling and compression. Though it is correct to some extent, we need more ideas about the behaviour of real gases in accordance with their phase changes.

Note: *This is one of the topics discussed in detail in unit 12 and a little description will be given here as it is important to have a basic idea about the conditions necessary for liquefication of gases.*

For example, such kind of information on the pressure, temperature and volume relations are available for carbon dioxide where it has been found that carbon dioxide can behave as a gas, a liquid and a solid depending on the variations in pressure and temperature.

We know that high temperatures favour the ideal behaviour and a gas cannot be liquefied even at very high pressures. In the case of carbon dioxide, which exists as a gas at high temperatures starts to liquefy at 30.98 °C (304.2 K) when the pressure is below 73 atm. The temperature 30.98 °C is called **critical temperature (T_C)** of carbon dioxide. This is the highest temperature at which liquid carbon dioxide is observed and above this temperature it exists only as a gas. Therefore, we can defined the critical temperature of a substance as the temperature at and above which the vapour of the substance cannot be liquefied, no matter how much pressure is applied. The **critical pressure** of a substance is the pressure required to liquefy a vapour at critical temperature.

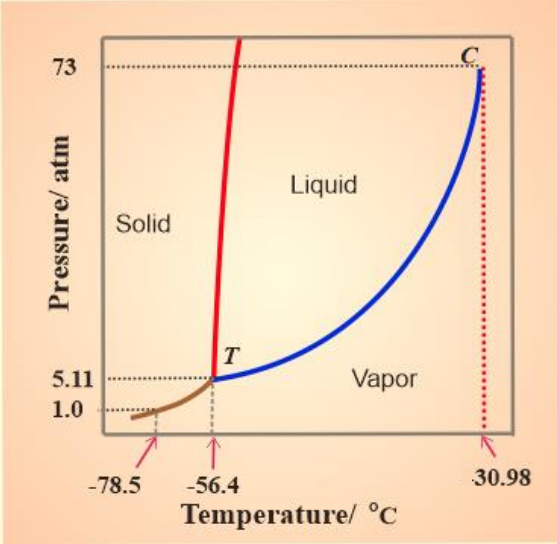


Figure 1.9 Phase diagram of CO_2

Table 1.3 A summary of equations

Gas law	Equation	Parameters kept constant
Ideal gas law	$PV = nRT$	None
Boyle law	$P = k/V$	n and T
Charles law	$V = kT$	n and P
Avogadro law	If $V_A = V_B$ then $N_A = N_B$	P and T
Molecular kinetic equation	$PV = \frac{1}{3} mN\overline{c^2}$	
Average speed	$\bar{C} = \frac{c_1 + c_2 + \cdots c_N}{N}$	
Mean square speed	$\overline{c^2} = \frac{({c_1}^2 + {c_2}^2 + {c_3}^2 \ldots . + {c_N}^2)}{N}$	
Mean square speed	$\overline{c^2} = \frac{3RT}{M}$	
Dalton law of partial pressures	$P_A = x_A P_T$ $P_T = P_A + P_B + P_C$	
Compressibility factor	$z = \frac{PV}{RT}$	for one mole of gas
van der Waals equation	$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$	



2. Energetics

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- Standard enthalpy change of solvation, ΔH_{sol}^θ
- Standard enthalpy change of hydration, ΔH_{hyd}^θ
- Standard enthalpy change of dissolution, $\Delta H_{dissolution}^\theta$
- Standard enthalpy change of sublimation, ΔH_{sub}^θ
- Standard enthalpy change of evaporization, ΔH_{evap}^θ
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- Gibbs free energy (*G*) and spontaneity of a reaction

Introduction

This unit discusses the study of the role or changes of energy in the form of heat. Almost all chemical reactions absorb or release energy, generally in the form of heat. It is important to understand the distinction between thermal energy and heat. **Heat** is *the transfer of thermal energy between two bodies that are at different temperatures* and we often speak of "heat flow" from a hot object to a cold one. Although the term "heat" by itself implies transfer of energy when describing the energy changes that occur during a process, we customarily talk of "heat absorbed" or "heat released". **Thermochemistry** is *the study of heat change in chemical reactions* and when considering thermochemical events they are usually in reference to a state of standard state.

This chapter is concerned with the study of energy changes at the molecular level and the consequences to the changes of that system. In this regard, the basic terms appearing in thermochemistry must first be defined and understood. The significance of mathematical symbols "+" and "-" specified with the energy change must also be understood in respect of the amount of energy produced or supplied and this will be used to explain types of reactions such as endothermic and exothermic reactions. Thereafter, the discussion will move into the definition of enthalpies of different chemical events/reactions and expanded to the standard state. The basic laws in thermochemistry (Hess Law) will be used to perform calculations for chemical events as appropriate. Finally, the tendency for the occurrence of a reaction will be discussed with entropy, enthalpy and Gibbs free energy relation ($\Delta G = \Delta H - T\Delta S$) and hence to the spontaneity of reactions.

2.1 Basic terms in thermochemistry and thermodynamics

2.1.1 System, surrounding and boundary

It is useful to define and understand important terms that are used to define and explain the basic concepts and laws of thermochemistry.

- **System**
  A thermochemical system is defined as any portion of matter or universe under consideration which is separated from the rest of the universe. (or simply the object under study is defined as the system).

- **Surroundings**
  Everything in the universe (or the rest) that is not a part of the system and can interact with it is called surroundings (or simply everything outside the system).

- **Boundary**
  It is anything (for example wall of flask) which separates the system from its surroundings.



Figure 2.1 Schematic representation of a system, surroundings and boundary

2.1.2 Types of systems

There are different types of systems which can be defined depending on the interactions/processes between the system and the surroundings.

- **Open system**
  A system is said to be open if it can exchange both energy and matter/ mass with its surroundings. For example, an open bottle containing an aqueous salt solution represents an open system. Here, matter and heat can be added or removed simultaneously or separately from the system to its surroundings or separately from the surroundings to the system.

- **Closed system**
  A system which permits the exchange of energy but not matter/ mass, across the boundary with its surroundings is called a closed system. For example, a liquid in equilibrium with its vapour in a sealed bottle represents a closed system since the sealed container may be heated or cooled to add or remove energy from its contents while no matter (liquid or vapour) can be added or removed.

- **Isolated system**
  A system which can exchange neither energy nor matter with its surroundings is called an isolated system. For example, a sample in a sealed thermos flask with walls made of insulating materials represents an isolated system.

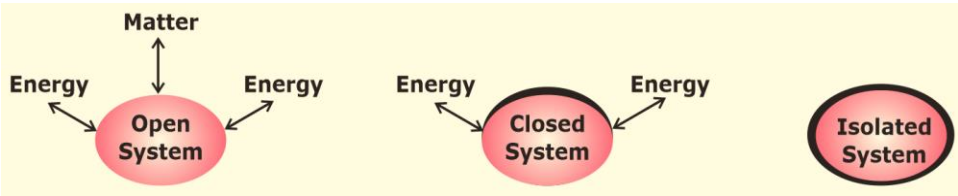


Figure 2.2 Schematic view of **(**a) open, (b) closed and (c) isolated systems

- **Homogeneous and heterogeneous systems**
  A system is said to be **homogeneous** if the physical states of all its matter are uniform. For example mixtures of gases, mixtures of completely miscible liquids, etc.

A system is said to be **heterogeneous**, if its contents do not possess the same physical state (phase). For example, immiscible liquids, solid in contact with an immiscible liquid, solid in contact with a gas, etc.

2.1.3 Properties of a system

- **Microscopic properties**
  A system is called a microscopic system if it is roughly of atomic dimensions i.e. on the atomic or molecular scale the properties must be determined by an indirect method(s) such as kinetic energy, speed, etc. of atoms/molecules in a closed container.

- **Macroscopic properties**
  The properties which are associated with bulk or macroscopic state of the system such as pressure, volume, temperature, concentration, density, viscosity, surface tension, refractive index, colour, etc. are called macroscopic properties.

Macroscopic properties of a system can be divided into two types.

- **Extensive properties**
  The properties that depend on the amount or size of a system (extent of a system) are called extensive properties. (For example, volume, number of moles, mass, energy, internal energy etc.). The value of the extensive property is equal to the sum of extensive properties of smaller parts into which the system is divided. Suppose masses $\mathbf{m_1}$ g, $\mathbf{m_2}$ g and $\mathbf{m_3}$ g are mixed in a system. Then the total mass of the system is equal to ($\mathbf{m_1}$+$\mathbf{m_2}$+$\mathbf{m_3}$) g. Thus mass is an extensive property.

- **Intensive properties**
  The properties that are independent of the amount or size of the system (extent of a system) are known as intensive properties. (For example, refractive index, surface tension, density, temperature, boiling point, freezing point, etc.), of the system. These properties do not depend on the number of moles of the substance in the system.

  If any extensive property is expressed per mole (mol^{-1}) or per gram (g^{-1}) or per cm^3 (cm^{-3}) or per cm^2 (cm^{-2}), it becomes an intensive property. For example, mass, volume, heat capacity are extensive properties while density, molar volume, specific heat capacity are intensive properties.

2.1.4 State of a system

A system is said to be in a particular physical state when specific values of the macroscopic properties of the system are known. For example, the gaseous state of matter can be described by parameters pressure (P), volume (V) and temperature (T) etc. The values of these parameters change when the matter is in liquid state. Thus, the

state of a system is defined by specific measurable macroscopic properties of the system.

The **initial state** of system refers to the starting state of the system before any kind of interaction with its surroundings.

The **final state** of system refers to the state after the interaction of system with its surroundings. A system can interact with its surroundings by means of exchange of matter, heat, energy or all.

The variables like P, V, T and composition (or amount of moles or 'n') that are used to describe the state of a system are called **state variables** or **state functions**. When the state of the system changes, the values of the state variables of the system also change. Thus, state functions depend only on the initial state and the final state of the system and not on how the changes occur. Also, if the values of state functions of a system are known, all other properties like mass, viscosity, density, etc. of the system become specified. For specifying a state of the system, it is not necessary to know all the state variables, since they are interdependent and only a few of them (state variables) are sufficient.

Standard state

It is needed to refer to a reference pressure or the standard pressure denoted by P^{Θ} at a specified temperature when heat changes in a system is considered. The standard pressure has a constant value in any given application. The IUPAC recommended the value for P^{Θ} as 1 atm (101325 Pa). (Note that there is no defined standard temperature, however, 298 K is used sometimes as specified.) A standard state of a pure substance is a particular reference state appropriate for the phase and is described by intensive variables. For example, standard state of solid iron is pure iron at 1 atm and at a given temperature (500 K). Standard conditions are denoted by adding the superscript Θ to the symbol of the quantity (ΔH^{Θ}, ΔG^{Θ}, ΔS^{Θ} etc.) It has to be noted that when solutions are involved, a concentration is 1 mol dm^{-3}.

- **Spontaneous processes**

  These are occurring on their own accord. For example heat flow from a hotter end of a metal rod to a colder end. In these processes, the transformation of the system from the initial, to the final state is favourable in a particular direction only. Many of the spontaneous processes are natural processes and are also, irreversible processes.

- **Non-spontaneous processes**
  These are not occurring on their own accord. For example, although carbon burns in air evolving heat to form carbon dioxide, on its own carbon does not catch fire and an initial heat supply is required.

- **Reversible process**
  In a reversible process the series of changes carried out on the system during its transformation from initial to final state may be possibly reversed in an exact manner. This is possible when the changes are carried out very slowly in many smaller steps on the system during its change from initial to final state. Under such conditions the initial and final states of the system become reversible completely. For example, when ice melts a certain amount of heat is absorbed. The water formed can be converted back to ice if the same amount of heat is removed from it.

- **Irreversible process**
  An irreversible process is one which cannot be retraced to the initial state without making a permanent change in the surroundings. Many of the spontaneous processes are irreversible in nature. For example biological ageing is an irreversible process. Water flowing down a hill on its own accord is an irreversible process.

2.1.5 Enthalpy (*H*)

Most of the physical and chemical changes take place or are carried out under the constant pressure conditions. For example in the laboratory, reactions are generally carried out in beakers, flasks, or test tubes that remain open to their surroundings and hence to a pressure of approximately one atmosphere (1 atm, ~10^5 Pa). To quantify the heat flow into or out of a system in a constant pressure process, chemists use a property called **enthalpy,** represented by the symbol ***H***. i.e. at constant pressure chemist use the relation, heat change equals to enthalpy change. Enthalpy is an extensive property; its magnitude depends on the amount of the substance present. It is impossible to determine the enthalpy of a substance, so it is the change in enthalpy, ΔH, that we actually measure.

The **enthalpy change of reaction,** ΔH**,** *is the difference between the total enthalpies of the products and the total enthalpies of the reactants.*

$$\Delta H = H_{(products)} - H_{(reactants)}$$

2.1.6 Heat

As the enthalpy is equal to the heat (q) at constant pressure, we may consider the measurement of heat changes. In the laboratory heat changes in physical and chemical processes are measured with a calorimeter, a closed container designed specifically for this purpose. To estimate heat changes we first need to have an understanding of specific heat and heat capacity.

Specific heat and heat capacity

The **specific heat (*c*)** of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius. The **heat capacity (*C*)** of a substance is the amount of heat required to raise the temperature of a given quantity of the substance by one degree Celsius. Specific heat is an intensive property, whereas heat capacity is an extensive property. The relationship between the heat capacity and specific heat of a substance is

$$C = m\,c$$

where, m is the mass of the substance in grams.
Note: *sometimes* ***s*** *is used to denote specific heat.*

For example, the specific heat of water is 4.184 J g^{-1} $°C^{-1}$ and the heat capacity of 100.0 g of water is (100.0 g) × (4.184 J g^{-1} $°C^{-1}$) = 418.4 J $°C^{-1}$.

Note: *Specific heat has the units* J g^{-1} $°C^{-1}$ *(or* J g^{-1} K^{-1}*) and heat capacity has the units* J $°C^{-1}$ *(or* J K^{-1}*).*

Knowing the specific heat, the mass of a substance and the change in the sample's temperature Δt (temperature in °C) or ΔT (temperature in K), the amount of heat (Q) that has been absorbed or released in a particular process can be calculated by the equation;

$$Q = m\,c\Delta t \quad \text{or} \quad Q = m\,c\Delta T$$

where m is the mass of the sample and Δt is the temperature change i.e. $\Delta t = t_{final} - t_{initial}$
The sign convention for q is the same as that for enthalpy change; q is positive for endothermic processes and negative for exothermic processes.

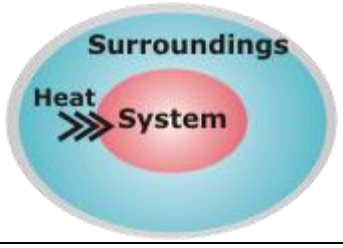
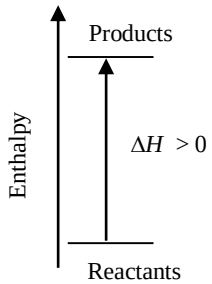
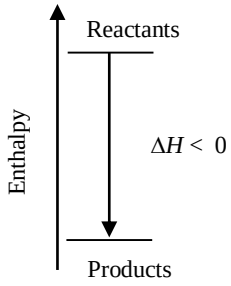
2.2 Enthalpy changes and standard enthalpy changes associated with different thermochemical processes/ reactions

ΔH represents the heat given off or absorbed during a reaction. The enthalpy of reaction can be positive or negative, depending on the process. Enthalpy change is directly proportional to the amounts of substances in a system.

2.2.1 Exothermic and endothermic processes

When a thermodynamic process is a chemical reaction or a physical transformation, it is classified as either exothermic or endothermic depending on the nature of heat change involved in the overall process. These two processes are differentiated as follows:

Table 2.1 Comparison between endothermic and exothermic processes

Endothermic processes	Exothermic processes
A process that transforms a system from initial to final state by absorption of heat is called an endothermic process.	A process that transforms a system from initial to final state by evolution of heat is called an exothermic process.
The final state of the system possesses higher energy than the initial state. The energy needed is absorbed as heat by the system from the surroundings. Example: Dissolving ammonium chloride in water.	The final state of the system possesses lower energy than the initial state. The excess energy is released as heat to the surrounding. Example: All combustion processes are exothermic.
Generally in a physical transformation which is endothermic, heat is supplied to bring about the change from initial to final state. Example: melting of a solid by supplying heat is an endothermic process.	If the physical transformation is exothermic heat is removed to bring about the change from the initial to final state. Example: Freezing of a liquid at its freezing point is an exothermic process.
Reactant + Energy(Heat) → Products $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + 90\ kJ \rightarrow NO(g)$	Reactant → Products + Energy(Heat) $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) + 242\ kJ$
	
For an endothermic process (heat absorbed by the system from the surroundings), ΔH is positive (that is, $\Delta H > 0$)	For an exothermic process (heat released by the system to the surroundings), ΔH is negative (that is, $\Delta H < 0$)
	

Heat effects measured at constant pressure indicate changes in enthalpy of a system. Using calorimeters operating at constant pressure, the enthalpy change of a process can be measured directly.

Standard enthalpy changes

The measured enthalpy change for a reaction has a unique value only if the initial state (reactants) and final state (products) are precisely described. If we define a standard state (10^5 Pa pressure and a temperature of interest) for the reactants and products, we can then say that the standard enthalpy change is the enthalpy change in a reaction in which the reactants and products are in their standard states. This so-called **standard enthalpy of reaction** is denoted with a degree symbol, ΔH^θ. Although temperature is not a part of the definition of a standard state, it still must be specified in tabulated values because it depends on temperature. The standard temperature values given in this text are all 298.15 K or 25 °C unless otherwise stated.

Simply, we can say;

The standard enthalpy change of a reaction is the enthalpy change which occurs when the given quantities in a reaction react under standard conditions to form products in the standard state.

2.2.2 Thermochemical equations

A balanced chemical equation together with standard conventions adopted and including the value of ΔH (or ΔH^θ) of the reaction is called a thermochemical equation. The following conventions are necessarily adopted in a thermochemical equation.

(i) The coefficients in a balanced thermochemical equation refer to number of moles of reactants and products involved in the reaction.

(ii) The enthalpy change of a reaction has unit **kJ mol^{-1}** and will remain as it is, even if more than one mole of the reactant or product are involved but with only the magnitude changing.

(iii) When a chemical reaction is reversed the value of ΔH is reversed in sign with the magnitude remaining the same.

(iv) Physical states of all species is important and must be specified in a thermochemical equation since ΔH (or ΔH^θ) depends on states (phases) of reactants and products.

(v) If the thermochemical equation is multiplied throughout by a number, the enthalpy change is also be multiplied by the same number.

(vi) The negative sign of ΔH^θ indicates an exothermic reaction and a positive sign of ΔH^θ indicates an endothermic reaction.

Example:

Consider the following reactions.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ $\quad\quad$ $\boldsymbol{\Delta H^\theta = -483.7\ kJ\ mol^{-1}}$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$ $\quad\quad$ $\boldsymbol{\Delta H^\theta = -571.6\ kJ\ mol^{-1}}$

First reaction in the above thermochemical equations can be interpreted in several ways.

- 483.7 kJ given off per mole of the reaction*****
- 483.7 kJ given off per 2 moles of $H_{2(g)}$ consumed
- 483.7 kJ given off per mole of $O_{2(g)}$ consumed

- 483.7 kJ given off per 2 moles of water vapour formed

ΔH^{θ} tells how much the enthalpy change would be, if the number of moles reacting is the same as the stoichiometric coefficients.

*** *Note:*** *In this case, 483.7 kJ mol^{-1}means that 483.7 kJ of heat is evolved when 2 moles of hydrogen gas were to react with 1 mole of oxygen gas to form 2 moles of gaseous water*

Sometimes the above reaction is written as;

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \qquad \mathbf{\Delta H^{\theta} = - 483.7\ kJ}$$

*** *Note:*** *In this case, 483.7 kJ of heat is evolved when a defined extent of reaction occurs as written and gives the units in* ***kJ****. Extent of reaction has the unit of mol. For the above reaction ;* $\mathbf{\Delta H = \Delta H^{\theta} \times mol = - 483.7\ kJ\ mol^{-1} \times mol = - 483.7\ kJ}$

For example if we write the reaction as;

$$4H_2(g) + 2O_2\ (g) \rightarrow 4H_2O(g)$$

then we write ΔH of the reaction as $2 \times \Delta H^{\theta}$ **= - 967.4 kJ**

That means the original ΔH^{θ} value has to be multiplied by 2 or in other words the value of ΔH is multiplied by the amount (mol) of substance reacting. Therefore, instead of the extent of reaction, we can use the actual amount of substance of any species reacting, divided by its stoichiometric coefficient in the simplest balanced chemical equation. Hence for the above reaction we get (for oxygen),

$$\Delta H = - 483.7\ kJ\ mol^{-1} \times \left(\frac{2\ mol}{1}\right) = - 967.4\ kJ$$

If we are giving only ΔH^{θ}, then it would equals to - 967.4 kJ mol^{-1}

If we write the equations as;

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \mathbf{\Delta H_f^{\theta} = -285.8\ kJ\ mol^{-1}}$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g) \qquad \mathbf{\Delta H_f^{\theta} = -241.85\ kJ\ mol^{-1}}$$

We can see that the enthalpy values are halves of the above values.

The above equations describe the combustion of hydrogen gas to water in a general sense. The first reaction can be considered the formation reaction of liquid water and the second reaction the formation of water vapour. The negative sign of ΔH indicates that they are exothermic reactions.

The reaction which is exothermic in the forward direction is endothermic in the reverse direction and vice-versa. This rule applies to both physical and chemical processes.

$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ $\quad \Delta H^\theta = +571.6$ **kJ mol^{-1}**

$2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$ $\quad \Delta H^\theta = +483.7$ **kJ mol^{-1}**

2.2.3 Enthalpy diagrams

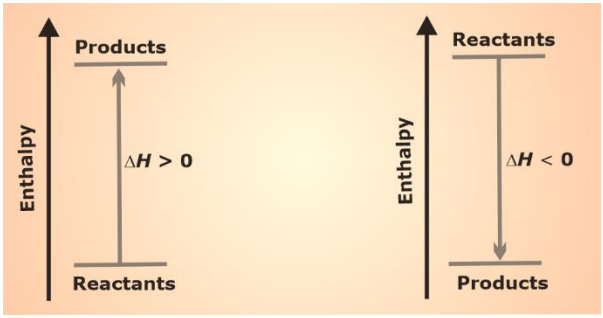
Consider the following reaction.

$C_{12}H_{22}O_{11}(s) + 12\ O_2(g) \rightarrow 12\ CO_2(g) + 11\ H_2O(l)$ $\quad \Delta H^\theta = -5650$ **kJ mol^{-1}**

The negative sign of ΔH^θ in the above equation means that the enthalpy of the products is lower than that of the reactants. This decrease in enthalpy appears as heat evolved to the surroundings. The combustion of sucrose is an exothermic reaction.

$N_2(g) + O_2(g) \rightarrow 2NO(g)$ $\quad \Delta H^\theta = 180.50$ **kJ mol^{-1}**

In the above reaction the products have a higher enthalpy than the reactants so ΔH^θ is positive. To produce this increase in enthalpy, heat is absorbed from the surroundings. The reaction is endothermic. An **enthalpy diagram** is a diagrammatic representation of enthalpy changes in a process. Figure 2.3 below shows how exothermic and endothermic reactions can be represented through such diagrams as are already shown in the Table 2.1).



(a) (b)

Figure 2.3 Enthalpy diagrams of **(**a) endothermic and (b) exothermic processes

2.2.4 Enthalpy changes and standard enthalpy changes

- **Standard enthalpy change of formation, ΔH_f^θ**

The **standard enthalpy of formation,** ΔH_f^θ of a substance is the enthalpy change that occurs in the formation of one mole of the substance in the standard state from the reference forms of the elements in their standard states. The reference forms of the elements in all but a few cases are the most stable forms of the elements at one atm (101325 Pa) and the given temperature. The θ symbol denotes that the enthalpy change is a standard enthalpy change, and the subscript "*f* " signifies that the reaction is one in which a substance is formed from its elements. Because the formation of the most stable form of an element from itself is no change at all that is *the standard enthalpy of a pure element in its reference form is 0.*

For example, listed below are the most stable forms of some elements/ compounds at 298.15 K, the temperature at which thermochemical data are commonly tabulated.

$Na(s)$, $H_2(g)$, $N_2(g)$, $O_2(g)$, $C(s, graphite)$, $Br_2(l)$

Example :

One may concern the situation with carbon. In addition to graphite, carbon also exists naturally in the form of diamond. However, because there is a measurable enthalpy difference between them, they cannot both be assigned $\Delta H_f^\theta = 0$

$$C(s, graphite) \rightarrow C(s, diamond)\ ; \Delta H_f^\theta = 1.9\ kJ\ mol^{-1}.$$

We choose as the reference form the more stable form, the one with the lower enthalpy. Thus, we assign $\Delta H^\circ_{f(graphite)} = 0$.

The physical state of the product of the formation reaction must be indicated explicitly if it is not the most stable one at 25 °C and 1 atm pressure

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\quad\quad$ $\boldsymbol{\Delta H_f^\theta = -285.8\ kJ\ mol^{-1}}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(g)$ $\quad\quad$ $\boldsymbol{\Delta H_f^\theta = -241.8\ kJ\ mol^{-1}}$

Note that the difference between these two $\boldsymbol{\Delta H_f^\theta}$ values is just the heat of vapourization ($44\ kJ\ mol^{-1}$) of water.

We often use standard enthalpies of formation in a variety of calculations and the first thing we must do is to write the chemical equation to which a ΔH_f^θ value applies, as illustrated in following examples in the text.

The standard enthalpy of formation of formaldehyde (HCHO) is -108 $kJ\ mol^{-1}$ at 298 K and the chemical equation below shows this event.

$$H_2(g) + \frac{1}{2}O_2(g) + C(graphite) \rightarrow HCHO(g) \quad\quad \boldsymbol{\Delta H_f^\theta = -108\ kJ\ mol^{-1}}$$

Before going to discuss some examples it is worth defining standard enthalpies of some chemical reactions/events.

- **Standard enthalpy change of combustion, $\boldsymbol{\Delta H_c^\theta}$**

It is the enthalpy change when one mole of an element or a compound in the standard state undergoes complete combustion with excess oxygen (or one may say air) in the standard state to give the products in the standard state.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\quad\quad$ $\boldsymbol{\Delta H^\theta_{c[C_3H_8(g)]} = -2219.9\ kJ\ mol^{-1}}$

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad\quad$ $\boldsymbol{\Delta H^\theta_{c[C(s)]} = -393.5\ kJ\ mol^{-1}}$

- **Standard enthalpy change of bond dissociation, ΔH_D°**

It is the enthalpy change when a gaseous compound in the standard state undergoes dissociation to gaseous atoms or components in the standard state by breaking a mole of bonds.

$H_2(g) \rightarrow 2H(g)$ $\quad \Delta H_D^\theta = 432 \text{ kJ mol}^{-1}$

$CH_4(g) \rightarrow CH_3(g) + H(g)$ $\quad \Delta H_D^\theta = 428 \text{ kJ mol}^{-1}$

$CH_3(g) \rightarrow CH_2(g) + H(g)$ $\quad \Delta H_D^\theta = 441 \text{ kJ mol}^{-1}$

$CH_2(g) \rightarrow CH(g) + H(g)$ $\quad \Delta H_D^\theta = 454 \text{ kJ mol}^{-1}$

$CH(g) \rightarrow C(g) + H(g)$ $\quad \Delta H_D^\theta = 344 \text{kJ mol}^{-1}$

Therefore the bond dissociation energy change of methane is the mean value of the above four enthalpy values.

Mean standard enthalpy change of bond dissociation of $CH_4(g)$ $= \frac{(428 + 441 + 454 + 344) \text{ kJ mol}^{-1}}{4}$

$= 416.75 \text{ kJ mol}^{-1}$

- **Standard enthalpy change of neutralization, ΔH_{neu}^θ**

It is the enthalpy change when a mole of an aqueous H^+ ions and a mole of an aqueous OH^- ions in the standard state react to form a mole of liquid water.

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ $\quad \Delta H_{neu}^\theta = -57 \text{ kJ mol}^{-1}$

- **Standard enthalpy change of solvation, ΔH_{sol}^θ**

It is the enthalpy change when a mole of gaseous ions in the standard state changes into a solution to form 1.0 mol dm^{-3}.

$M^{n+}(g) + \text{solvent} \rightarrow M^{n+}(\text{solvent})$

- **Standard enthalpy change of hydration, ΔH_{hyd}^θ**

It is the enthalpy change when a mole of gaseous ions in the standard state changes into a solution with water with the concentration of 1.0 mol dm^{-3}.

$Na^+(g) + \text{water} \rightarrow Na^+(aq)$ $\quad \Delta H_{hyd}^\theta = -406 \text{ kJ mol}^{-1}$

- **Standard enthalpy change of dissolution, $\Delta H_{dissolution}^\theta$**

It is the enthalpy change when a mole of a substance in the standard state dissolved in a solvent to form a solution with the concentration of 1.0 mol dm^{-3} (a saturated solution formed by a sparingly soluble salt).

$NaCl(s) + \text{water} \rightarrow NaCl(aq)$ $\quad \Delta H_{dissolution}^\theta = 1 \text{ kJ mol}^{-1}$

- **Standard enthalpy change of sublimation, ΔH^{θ}_{sub}**

It is the enthalpy change when a mole of a solid element or a mole of a solid compound in the standard state converts completely into a gas at its standard state.

$Ca(s) \rightarrow Ca(g)$ $\quad\quad$ $\mathbf{\Delta H^{\theta}_{sub} = 193\ kJ\ mol^{-1}}$

- **Standard enthalpy change of evaporization, ΔH^{θ}_{evap}**

It is the enthalpy change when a mole of a liquid compound or an element in the standard state converts into a mole of gaseous compound or element at its standard state.

$Br_2(l) \rightarrow Br_2(g)$ $\quad\quad$ $\mathbf{\Delta H^{\theta}_{evap} = 30.91\ kJ\ mol^{-1}}$

- **Standard enthalpy change of fusion, ΔH^{θ}_{fus}**

It is the enthalpy change when a mole of a solid compound or an element in the standard state converts into a mole of liquid compound or element at its standard state.

$Al(s) \rightarrow Al(l)$ $\quad\quad$ $\mathbf{\Delta H^{\theta}_{fus} = 10.7\ kJ\ mol^{-1}}$

- **Standard enthalpy change of atomization, ΔH^{θ}_{at}**

It is the enthalpy change when an element in the standard state converts into a one mole of gaseous atoms at the standard state.

$\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$ $\quad\quad$ $\mathbf{\Delta H^{\theta}_{at} = 121\ kJ\ mol^{-1}}$

- **Standard enthalpy change of first ionization, ΔH^{θ}_{IE1}**

It is the enthalpy change when a mole of a gaseous mono-positive ions at standard state are formed by removing an electron from each atom that is most weakly bonded to the nucleus from a mole of gaseous atoms of an element in standard state.

$Na(g) \rightarrow Na^{+}(g) + e$ $\quad\quad$ $\mathbf{\Delta H^{\theta}_{IE1} = 496\ kJ\ mol^{-1}}$

- **Standard enthalpy change of electron gain, ΔH^{θ}_{EG}**

It is the enthalpy change when a mole of gaseous mono-negative ions are formed by gaining electrons to a mole of gaseous atom at the standard state.

$Cl(g) + e \rightarrow Cl^{-}(g)$ $\quad\quad$ $\mathbf{\Delta H^{\theta}_{EG} = -349\ kJ\ mol^{-1}}$

- **Standard lattice dissociation enthalpy change of an ionic compound, ΔH^{θ}_{L}**

It is the enthalpy change when one mole of a solid ionic compound is converted to its gaseous positive and negative ions at the standard state.

$NaCl(s) \rightarrow Na^{+}(g) + Cl^{-}(g)$ $\quad\quad$ $\mathbf{\Delta H^{\theta}_{L} = +788\ kJ\ mol^{-1}}$

2.2.5 Indirect determination of ΔH ($\Delta H^{\ominus}$): Hess Law

One of the reasons that the enthalpy concept is so useful is that a large number of heat of reaction can be calculated from a small number of measurements. The following features of enthalpy change make this possible.

ΔH is an extensive property and is also a function of state. Consider the standard enthalpy change of formation of $NO_{(g)}$ from its elements at 25 °C.

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H^{\ominus} = \mathbf{180.50\ kJ\ mol^{-1}}$$

To express the enthalpy change in terms of one mole of $NO_{(g)}$ we divide all coefficients and the value $\Delta H^{\ominus}$ by two.

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g) \qquad \mathbf{\Delta H^{\ominus} = 90.25\ kJ\ mol^{-1}}$$

$\Delta H^{\ominus}$ changes sign when a process is reversed as the change in a function of state reverses sign. Thus, for the decomposition of one mole of $NO_{(g)}$, standard enthalpy change is $\mathbf{-90.25\ kJ\ mol^{-1}}$ which is the negative value of the enthalpy for the formation of one mole of $NO_{(g)}$.

$$NO(g) \rightarrow \tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \qquad \mathbf{\Delta H^{\ominus} = -90.25\ kJ\ mol^{-1}}$$

An example for Hess Law of constant heat summation:

The standard enthalpy change for the formation of $NO_2(g)$ from $N_2(g)$ and $O_2(g)$ can be found as follows.

$$\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H^{\ominus} = ?$$

We can think of the reaction as proceeding in two steps: First we form $NO_{(g)}$ from $N_2(g)$ and $O_{2(g)}$, and then $NO_{2(g)}$ from $NO_{(g)}$ and $O_{2(g)}$.When the thermochemical equations for these two steps are added together with their individual and distinctive $\Delta H^{\ominus}$ values, we get the overall equation and $\Delta H^{\ominus}$ value that we are seeking.

$$\tfrac{1}{2}N_2(g) + \tfrac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H^{\ominus} = 90.25\ kJ\ mol^{-1} \quad \text{------ (1)}$$

$$NO(g) + \tfrac{1}{2}O_2(g) \rightarrow NO_2(g) \qquad \Delta H^{\ominus} = -57.07 kJ\ mol^{-1} \quad \text{------ (2)}$$

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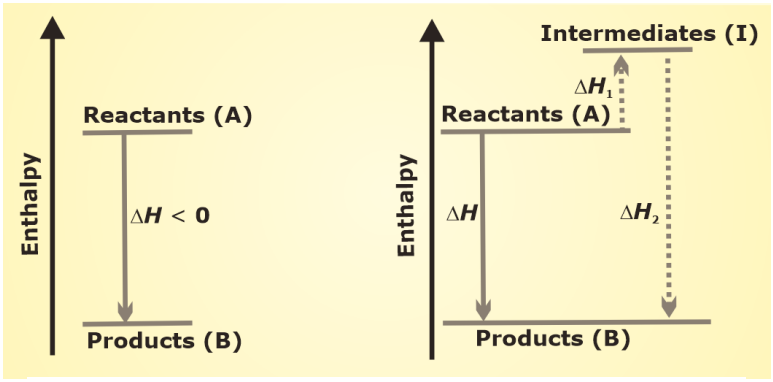
(1) + (2), $\mathbf{\tfrac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g)} \qquad \mathbf{\Delta H^{\ominus} = +33.18}\ kJ\ mol^{-1}$

As of the above example the **Hess law** states the principle we used: i.e.

> *If a process occurs in stages or steps (even if only hypothetically), the enthalpy change for the overall process is the sum of the enthalpy changes for the individual steps.*

In other words, Hess law is simply a consequence of the state function property of enthalpy. Regardless of the path taken in going from the initial state to the final state, ΔH (or ΔH^{θ} if the process is carried out under standard states) has the same value or it is independent of the route.

This concept can also be illustrated by an enthalpy diagram and a thermochemical cycle as described in Figure 2.4 and 2.5 respectively.



(a) (b)

Figure 2.4 Enthalpy changes for an exothermic reaction using two different ways of getting from reactants A to products B. (a) direct conversion and (b) two-step process involving some intermediates

Figure 2.4 describes the statement of Hess Law, that is, if you convert reactants A into products B, the overall enthalpy change will be exactly the same whether you do it in one step or two steps or many steps. In either case, the overall enthalpy change must be the same, because it is governed by the relative positions of the reactants and products on the enthalpy diagram.

Calculations can also be done by setting them out as enthalpy diagrams as above, but there is a much simpler way of doing it which needs a cycle to understand the process as below where the conversion of reactant A to product B is considered in two routes.

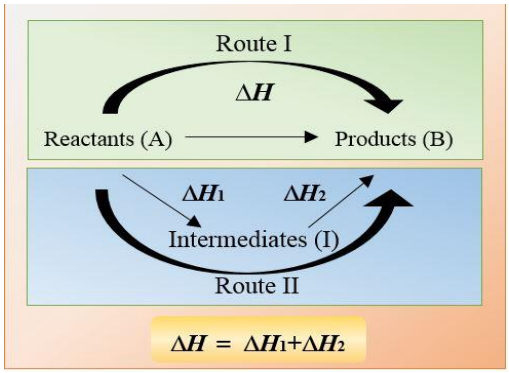


Figure 2.5 Thermochemical cycle

When we write the thermochemical cycle it is important to follow the instructions given below.

First write the chemical reaction in which the enthalpy change needs to find and write ΔH over the top of the arrow. Then include the other reactions with thermodynamic information to the same diagram to make a thermochemical cycle (Hess law cycle), and write the known enthalpy changes over the arrows for each of the other reactions. Find two routes around the diagram, always going with the flow of the various arrows. There must be no arrows going in the opposite direction.

In addition, it is necessary to multiply the known enthalpy values by a number of moles involved in a particular reaction. For example, standard enthalpy changes of combustion starts with one mole of the substance (carbon) burning and the enthalpy value should be multiplied by the number of carbon atoms involved in the reaction (see the example given below). Remember that this should also be included when the problem is solved with the equations.

Example:
Suppose we want the standard enthalpy change for the following reaction.

$$3C(s) + 4H_2(g) \rightarrow C_3H_8(g) \qquad \Delta H^{\ominus} = \ ?$$

Now we have a question that how should we proceed? If we try to get graphite and hydrogen to react, but it will not go to completion. Furthermore, the product will not be limited to propane and several other hydrocarbons will form as well. The fact is that we cannot directly measure ΔH^{θ} for reaction above. Instead, we must resort to an indirect calculation from ΔH^{θ} values that can be established by experiment. Here is where Hess law is of greatest value. It permits us to calculate ΔH^{θ} values that we cannot measure directly.

To determine an enthalpy change with Hess law, we need to combine the appropriate chemical equations. A good starting point is to write chemical equations for the given combustion reactions based on one mole of the indicated reactant. Considering that the products of the combustion of carbon–hydrogen–oxygen compounds are $CO_2(g)$ and $H_2O(l)$ we can find the path to solve the problem as follows.

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$ $\Delta H^\theta = -2219.9$ kJ mol^{-1} (a)

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\theta = -393.5$ kJ mol^{-1} (b)

$\frac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l)$ $\Delta H^\theta = -285.8$ kJ mol^{-1} (c)

Reverse of the reaction (a).

$3CO_2(g) + 4H_2O(l) \rightarrow C_3H_8(g) + 5O_2(g)$ $\Delta H^\theta = 2219.9$ kJ mol^{-1} (a)′

Considering the reactants of the reaction of interest, $C_{(s)}$ and $H_{2(g)}$, to get the proper number of moles of each, we must multiply equation (b) by three and equation (c) by four.

$3C(s) + 3O_2(g) \rightarrow 3CO_2(g)$ $\Delta H^\theta = 3(-393.5$ kJ mol$^{-1}) = -1180.5$ kJ mol^{-1} (b)′

$2O_2(g) + 4H_2(g) \rightarrow 4H_2O(l)$ $\Delta H^\theta = 4(-285.8$ kJ mol$^{-1}) = -1143.2$ kJ mol^{-1} (c)′

Here is the overall change we have described: 3 mol of C(s) and 4 mol of $H_{2(g)}$ have been consumed, and 1 mol of $C_3H_{8(g)}$ has been produced. This is exactly what is required. We can now combine the three modified equations by summing them up (i.e. (a)′ + (b)′ + (c)′)

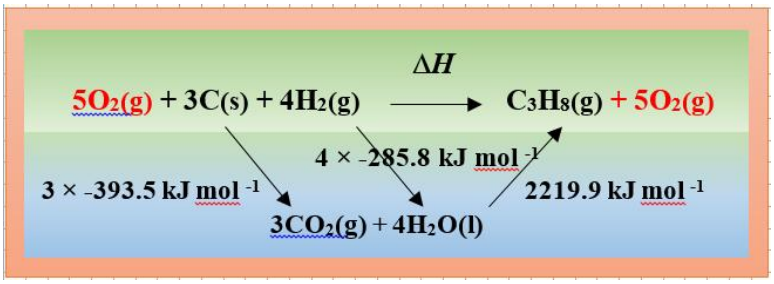
~~$3CO_2(g)$~~ ~~$+ 4H_2O$~~$(l) \rightarrow C_3H_8(g) +$ ~~$5O_2(g)$~~ $\Delta H^\theta = 2219.9$ kJ mol^{-1} (a)′

$3C(s) +$ ~~$3O_2(g) \rightarrow 3CO_2(g)$~~ $\Delta H^\theta = 3(-393.5$ kJ mol$^{-1}) = -1180.5$ kJ mol^{-1} (b)′

~~$2O_2(g)$~~ $+ 4H_2(g) \rightarrow$ ~~$4H_2O$~~(l) $\Delta H^\theta = 4(-285.8$ kJ mol$^{-1}) = -1143.2$ kJ mol^{-1} (c)′

$3C(s) + 4\,H_2(g) \rightarrow C_3H_8(g)$ $\Delta H^\theta = -103.8$ kJ mol^{-1}

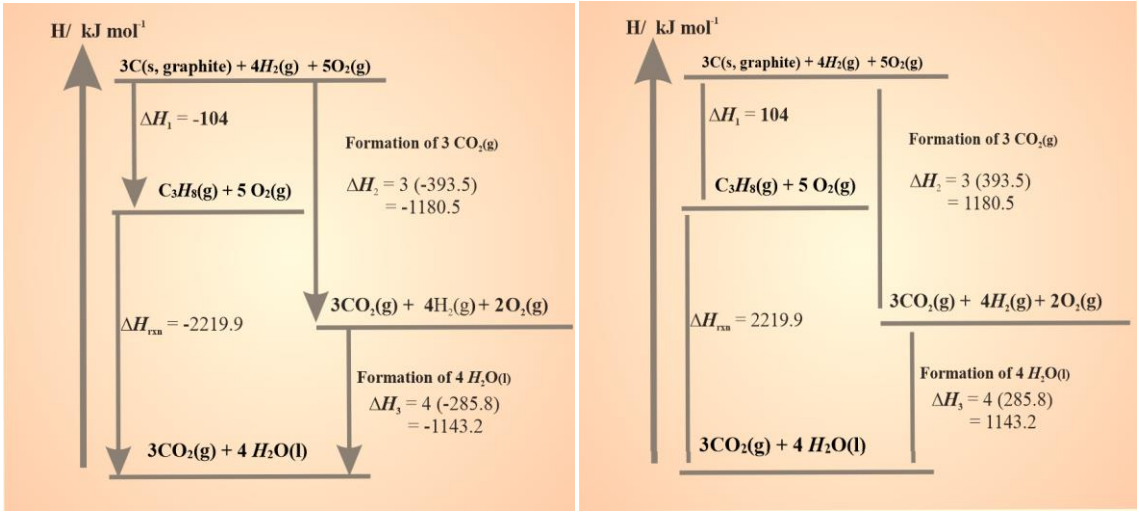
Solving the above with a thermochemical cycle:



$\Delta H = 3(-393.5$ kJ mol$^{-1}) + 4(-285.8$ kJ mol$^{-1}) + 2219.9$ kJ mol^{-1} = **-103.8 kJ mol^{-1}**

Representation and solving of the above with an enthalpy diagram:

In the enthalpy diagrams we have drawn, we have not written any numerical values on the enthalpy axis. This is because we cannot determine absolute values of enthalpy, *H*. However, enthalpy is a function of state, so changes in enthalpy, *ΔH* have unique values. We can deal just with these changes. Nevertheless, as with many other properties, it is still useful to have a starting point, a zero value.



(a) (b)

Figure 2.6 Enthalpy diagram for $3C(s) + 4H_2(g) \rightarrow C_3H_8(g)$ reaction. (a) represents each process with the enthalpy values with respect to the direction of reaction. (b) shows the enthalpy-gap and we can decide the sign according to the direction of the reactions wanted.

Standard enthalpies of reaction

We have learned that if the reactants and products of a reaction are in their standard states, the enthalpy change is the standard enthalpy change, which we can denote as ΔH^o or ΔH^{θ}_{rxn}. One of the primary uses of standard enthalpies of formation is in calculating standard enthalpies of reaction.

Example 2.1

Calculate the standard enthalpy of reaction for the decomposition of sodium bicarbonate, a side reaction that occurs when baking soda is used in baking by using Hess law.

$$\mathbf{2\ NaHCO_3(s) \rightarrow\ Na_2CO_3(s) + H_2O(\mathit{l}) + CO_2(g)} \quad \boldsymbol{\Delta H^{\theta}_{rxn} = ?}$$

Answer:

From Hess law, we see that the following four equations yield the above equation when added together.

$2NaHCO_3(s) \rightarrow 2Na(s) + H_2(g) + 2C(graphite) + 3O_2(g)$ $\quad \Delta H^{\theta} = -2\Delta H^{\theta}_{f[NaHCO_3(s)]}$ (a)

$2Na(s) + C(graphite) + \frac{3}{2}O_2(g) \rightarrow Na_2CO_3(s)$ $\quad \Delta H^{\theta} = \Delta H^{\theta}_{f[Na_2CO_3(s)]}$ (b)

$\frac{1}{2}O_2(g) + H_2(g) \rightarrow H_2O(l)$ $\quad \Delta H^{\theta} = \Delta H^{\theta}_{f[H_2O(l)]}$ (c)

$C(graphite) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^{\theta} = \Delta H^{\theta}_{f[CO_2(g)]}$ (d)

$$2NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O(\mathit{l}) + CO_2(g) \quad \boldsymbol{\Delta H^{\theta}_{rxn} = ?}$$

Equation (a) is the reverse of the equation representing the formation of two moles of $NaHCO_3(s)$ from its elements. This means that $\Delta H^{\ominus}$ for reaction (a) is the negative of twice $\Delta H^{\ominus}_{f[NaHCO_3(s)]}$. Equations (b), (c) and (d) represent the formation of one mole each of $Na_2CO_3(s)$, $H_2O(l)$ and $CO_2(g)$. Thus, we can express the value of $\Delta H^{\ominus}$ for the reaction;

$$\Delta H^{\ominus}_{rxn} = \Delta H^{\ominus}_{f[Na_2CO_3(s)]} + \Delta H^{\ominus}_{f[H_2O(l)]} + \Delta H^{\ominus}_{f[CO_2(g)]} + (-2\Delta H^{\ominus}_{f[NaHCO_3(s)]})$$

$= (-1130.68 \text{ kJ mol}^{-1}) + (-187.78 \text{ kJ mol}^{-1}) + (-393.51 \text{ kJ mol}^{-1}) + (1901.62 \text{ kJ mol}^{-1})$

$= \mathbf{189.65 \text{ kJ mol}^{-1}}$ **(**For **2 moles** of $NaHCO_3(s)$)

$= \mathbf{94.825 \text{ kJ mol}^{-1}}$ **(**For **1 mole** of $NaHCO_3(s)$)

We can use the enthalpy diagram to visualize the Hess law procedure and to show how the state function property of enthalpy enables us to arrive at the equation above.

Imagine the decomposition of sodium bicarbonate taking place in two steps. In the first step, suppose a vessel contains 2 mol of $NaHCO_3(s)$ which is allowed to decompose into 2 mol Na(s), 2 mol C(graphite), and 3 mol of $O_2(g)$ as in equation (a) above. In the second step, recombine 2 mol Na(s), 2 mol C(graphite), 1 mol of $H_2(g)$ and 3 mol of $O_2(g)$ to form the products according to equations (b), (c) and (d) above.

Step 1: $2 \times [NaHCO_3(s) \rightarrow Na(s) + 1/2H_2(g) + C(\text{graphite}) + 3/2O_2(g)]$

$\mathbf{\Delta H^{\ominus} = 2\times (-\Delta H^{\ominus}_f[NaHCO_3(s)]) = (2 \text{ mol})[-(-950.81 \text{ kJ mol}^{-1})]}$

Step 2: $2Na(s) + C(\text{graphite}) + 3/2O_2(g) \rightarrow Na_2CO_3(s)$

$\mathbf{\Delta H^{\ominus} = \Delta H^{\ominus}_f[Na_2CO_3(s)] = (1 \text{ mol } Na_2CO_3)(-1130.68 \text{ kJ mol}^{-1})]}$

$C(\text{graphite}) + O_2(g) \rightarrow CO_2(g)$

$\mathbf{\Delta H^{\ominus} = \Delta H^{\ominus}_f\ [CO_2(g)] = (1 \text{ mol } CO_2)(-393.51 \text{ kJ mol}^{-1})]}$

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(l)$

$\mathbf{\Delta H^{\ominus} = \Delta H^{\ominus}_f\ [H_2O(l)] = (1 \text{ mol } H_2O)(-187.78 \text{ kJ mol}^{-1})]}$

Because enthalpy is a state function and the change of any state function is independent of the path chosen, the enthalpy change for the overall reaction is the sum of the standard enthalpy changes of the individual steps as shown in the above equation according to Hess law. Therefore, the above procedure is a specific application of the following more general relationship for a standard enthalpy of reaction.

$$\Delta H^{\ominus}_{rxn} = \sum \nu_p H^{\ominus}_{f[\text{products}]} - \sum \nu_r H^{\ominus}_{f[\text{reactants}]}$$

where ν_p and ν_r are the stoichiometric coefficients of products and reactants, respectively. The enthalpy change of the reaction (ΔH^{θ}_{rxn}) (sometimes written as ΔH^{θ}_{r}) is the sum of terms for the products minus the sum of terms for the reactants.

Simply for example, consider the hypothetical reaction

$$a\,A + b\,B \rightarrow c\,C + d\,D \qquad \Delta H^{\theta}_{rxn} = \ ?$$

where *a*, *b*, *c* and *d* are stoichiometric coefficients. For this reaction ΔH°_{rxn} is given by

$$\Delta H^{\theta}_{rxn} = \left[\, c\,\Delta H^{\theta}_{f[\mathrm{C}]} + \ d\,\Delta H^{\theta}_{f[\mathrm{D}]}\right] - \left[\, a\,\Delta H^{\theta}_{f[\mathrm{A}]} + \ b\,\Delta H^{\theta}_{f[\mathrm{B}]}\right]$$

In order to use the above equation to calculate ΔH^{θ}_{rxn}, we must know the ΔH^{θ}_{f} values of the compounds that take part in the reaction. To determine these values we can apply the direct method or the indirect method.

The Direct Method;

This method of measuring ΔH^{θ}_{f} works for compounds that can be readily synthesized from their elements. Suppose we want to know the enthalpy, ΔH^{θ}_{rxn} for the combustion of $C_2H_6(g)$. We must measure or know the ΔH^{θ}_{f} values of $C_2H_6(g)$, $O_2(g)$, $CO_2(g)$ and $H_2O(l)$ in their standard states.

Example 2.2

Calculate ΔH^{θ}_{rxn} for the combustion of $C_2H_6(g)$ using the direct method

Answer:

The reaction is;

$$C_2H_6(g) + \tfrac{7}{2}O_2(g) \rightarrow 2CO_2(g) + 3H_2O\ (l)$$

$$\Delta H^{\theta}_{rxn} = [2\Delta H^{\theta}_{f[CO_2(g)]} + \ 3\Delta H^{\theta}_{f[H_2O(l)]}] - [\,\Delta H^{\theta}_{f[C_2H_6(g)]} + \tfrac{7}{2}\Delta H^{\theta}_{f[O2(g)]}]$$

$$= 2\times\text{-393.5 kJ mol}^{-1} + 3\times\text{-285.8 kJ mol}^{-1} - (\text{-84.7 kJ mol}^{-1} + \tfrac{7}{2}\times 0.0\ \text{kJ mol}^{-1})$$

$$= \mathbf{-1559.7\ kJ\ mol^{-1}}$$

The Indirect Method;

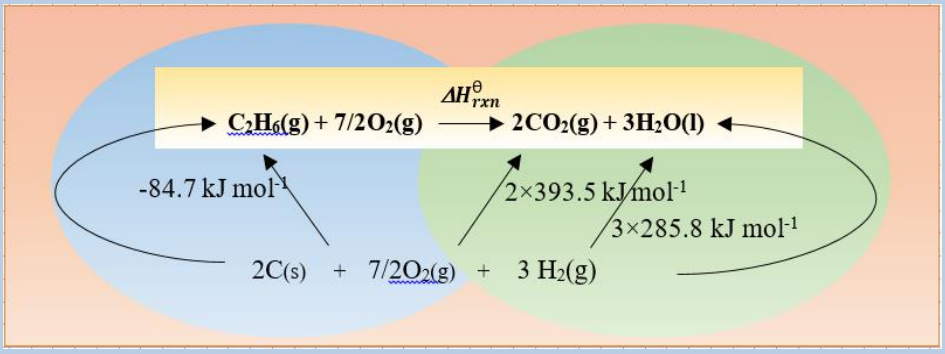
In many cases or reactions, compounds cannot be directly synthesized from their elements. In some cases, the reaction proceeds too slowly, or side reactions produce substances other than the desired compound. In these cases ΔH^{θ}_{f} can be determined by an indirect approach of Hess law as described earlier.

Example 2.3
Calculate ΔH^{θ}_{rxn} for the combustion of $C_2H_6(g)$ using the indirect method

Answer:
This is use of simple Hess Law cycles that you are likely to come across.

In the cycle below, this reaction has been written horizontally, and the enthalpy of formation values are added to complete the cycle.

Hess law cycle for the reaction of C_2H_6 with O_2.



And now for the calculation we can write down all the enthalpy changes which make up the two routes, and equate.

$$-84.7 \text{ kJ mol}^{-1} + \Delta H^{\theta} = 2 \times -393.5 \text{ kJ mol}^{-1} + 3 \times -285.8 \text{ kJ mol}^{-1}$$

$$\Delta H^{\theta} = \mathbf{-1559.7 \text{ kJ mol}^{-1}}$$

2.3 Lattice enthalpy or enthalpy of formation of an ionic compound: Born-Haber cycle

We can predict which elements are likely to form stable ionic compounds based on ionization energy and electron gain enthalpy. Ionization energy and electron gain enthalpy are defined for processes occurring in the gas phase, but at 100 kPa (1 atm) and 25 °C all ionic compounds are solids. The solid state is a very different environment because each cation in a solid is surrounded by a specific number of anions, and vice versa. Thus the overall stability of a solid ionic compound depends on the interactions of all these ions and not merely on the interaction of a single cation with a single anion. A quantitative measure of the stability of any ionic solid is its **lattice (dissociation) enthalpy,** defined as *the enthalpy change when one mole of a solid ionic compound is completely separated into its gaseous ions.*

Lattice (dissociation) enthalpy cannot be measured directly. However, if we know the structure and composition of an ionic compound, we can calculate the compound's lattice enthalpy by using **Coulomb law,** which states that *the potential energy (E) between two ions is directly proportional to the product of their charges and inversely proportional to the distance of separation between them (will not discuss here).*

We can also determine lattice enthalpy indirectly, by assuming that the formation of an ionic compound takes place in a series of steps. This procedure, known as the **Born-Haber cycle,** *relates lattice enthalpies of ionic compounds to ionization energies, electron gain energies and other atomic and molecular properties.* Basically, it is based on Hess law. The Born-Haber cycle defines the various steps that precede the formation of an ionic solid. We will illustrate its use to find the lattice (dissociation) enthalpy of lithium fluoride. Consider the reaction between lithium and fluorine.

$$Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s) \qquad \Delta H^{\theta}_{rxn} = ?$$

The standard enthalpy change for this reaction is -594.1 kJ mol^{-1} which is the standard enthalpy of formation of LiF. Considering the formation of LiF from its elements through five separate steps as described below. This pathway facilitates to analyze the energy (enthalpy) changes in ionic compound formation, with the help of Hess law.

1. Sublimation step to convert solid lithium to lithium vapour

$Li(s) \rightarrow Li(g)$ $\qquad \boldsymbol{\Delta H^{\theta}_{sub} = \Delta H^{\theta}_{1} = 155.2\ kJ\ mol^{-1}}$

2. Atomization of $F_2(g)$ to F(g)

$\frac{1}{2}F_2(g) \rightarrow F(g)$ $\qquad \boldsymbol{\Delta H^{\theta}_{at} = \Delta H^{\theta}_{2} = 75.3\ kJ\ mol^{-1}}$

3. Ionization of gaseous Li atoms

$Li(g) \rightarrow Li^{+}(g) + e$ $\qquad \boldsymbol{\Delta H^{\theta}_{IE1} = \Delta H^{\theta}_{3} = 520\ kJ\ mol^{-1}}$

4. Formation of F^- by capturing an electron

$F(g) + e \rightarrow F^{-}(g)$ $\qquad \boldsymbol{\Delta H^{\theta}_{EG} = \Delta H^{\theta}_{4} = -328\ kJ\ mol^{-1}}$

5. Combination between $Li^+(g)$ and $F^-(g)$

$Li^{+}(g) + F^{-}(g) \rightarrow LiF(s)$ $\qquad \boldsymbol{\Delta H^{\theta}_{5} = x\ kJ\ mol^{-1}}$

The lattice dissociation enthalpy of LiF is defined as

$LiF(s) \rightarrow Li^{+}(g) + F^{-}(g)$ $\qquad \boldsymbol{\Delta H^{\theta}_{L} = -\Delta H^{\theta}_{5} = -x\ kJ\ mol^{-1}}$

The value of ΔH^{θ}_{5} can be calculated by the following procedure. As the overall reaction has the standard enthalpy change, ΔH°_{rxn} of -594.1 kJ mol^{-1}, we can write,

$$\Delta H^{\theta}_{rxn} = \Delta H^{\theta}_{1} + \Delta H^{\theta}_{2} + \Delta H^{\theta}_{3} + \Delta H^{\theta}_{4} + \Delta H^{\theta}_{5}$$

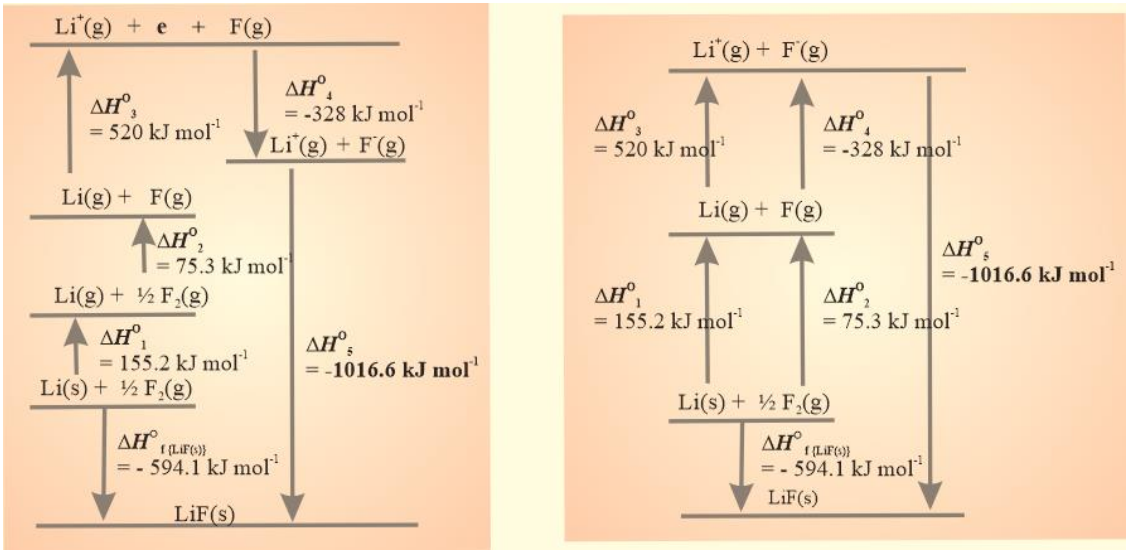
and by summing up reactions of 5 steps we get the overall reaction as ;

$$Li(s) + \frac{1}{2}F_2(g) \rightarrow LiF(s)$$

Therefore, -594.1 kJ mol^{-1} = 155.2 kJ mol^{-1}+75.3 kJ mol^{-1}+520 kJ mol^{-1}+(-328 kJ mol^{-1}) + ΔH^{θ}_{5}

ΔH_5^θ = -1016.6 **kJ mol^{-1}** and hence the lattice dissociation enthalpy of LiF(s) is **1016.6 kJ mol^{-1}**

The Figure 2.7 below summarizes the Born-Haber cycle for LiF. Steps 1, 2 and 3 all require the input of energy. On the other hand, steps 4 and 5 release energy. Because ΔH_5^θ is a large negative quantity, the lattice dissociation enthalpy of LiF is a large positive quantity, which accounts for the stability of solid LiF. The greater the lattice dissociation enthalpy means that the more stable the ionic compound which exists. Keep in mind that lattice dissociation enthalpy is *always* a positive quantity because the separation of ions in a solid into ions in the gas phase is an endothermic process.



(a) (b)

Figure 2.7 Born-Haber cycle of the above system (ΔH_5^θ = -1016.6 kJ mol^{-1} and hence the lattice dissociation enthalpy of LiF(s) is 1016.6 kJ mol^{-1}). In (a) each process is shown separately while (b) show respective processes together.

2.4 Spontaneity of chemical reactions

Spontaneous processes; An important part of experimental chemistry deals with spontaneous reactions, that is, reactions that take place without having to continually supply energy from outside the system. Or we can describe that as once a spontaneous reaction starts it will go to completion until either the reactants are consumed or it enters a state of equilibrium if the products are not removed. It is also important to remember that the term spontaneous does not necessarily mean a fast reaction rate. Time is not a part of the thermodynamic definition of a spontaneous process. A spontaneous process may or may not happen immediately, or at all.

For example, the conversion of diamond to graphite is a spontaneous process at 25 °C and a pressure of 100 kPa, even though this process is so slow that it cannot be observed in a human life time.

One goal of thermodynamics is to predict whether a reaction will take place when a given set of reactants is brought together. Thermodynamics only tells us whether or not the reaction will occur, but it tells us nothing about how fast.

The release of heat by a reaction was once thought to be an indication that the reaction was spontaneous. The sign of the enthalpy change, ΔH or ΔH^{θ} , by itself is not an adequate guide to spontaneity because while some spontaneous reactions are known to be exothermic (ΔH^{θ} is -ve), many endothermic reactions (ΔH^{θ} is +ve) are known to be spontaneous as well.

In addition to the heat absorbed or released in a spontaneous process, another factor called entropy must be considered. **Entropy** is a *measure of the disorder or randomness of a system.* The entropy *(S)* is a state function that increases in value as the disorder or randomness of the system increases. Entropy has the units **J K^{-1} mol^{-1}.**

A number of factors contribute to the entropy of a substance, such as the physical state, temperature, molecular size, intermolecular forces, and mixing. Here at this stage it is simply described with physical state and temperature.

Gases tend to have the highest entropies because the motion of gas particles is highly random. Liquids tend to have higher entropies than solids, which are much more restricted in their motions. At room temperature, one mole of $CO_{2(g)}$ has a much higher entropy than one mole of liquid water, which has a higher entropy than one mole of solid copper metal. The entropy of a substance increases with temperature because the translational and rotational motions of the molecules increase with temperature. Water at 50 °C is higher in entropy than water at 25 °C.

Standard entropy change of a chemical reaction

The standard entropy change of a reaction is denoted by the symbol ΔS°_{rxn}. It can be calculated from standard molar entropy (entropy content of one mole of substance under a standard state) values where each standard molar entropy value is multiplied by the stoichiometric coefficient in the balanced chemical equation.

$$\Delta S^{\theta}_{rxn} = \Sigma S^{\theta}(\text{products}) - \Sigma S^{\theta}(\text{reactants})$$

ΔS^{θ}_{rxn} is the entropy change when pure (unmixed) reactants in their standard states are converted to pure (unmixed) products in their standard states. The sign of ΔS^{θ}_{rxn} can often be estimated by taking into account the stoichiometry of a reaction and the

physical states of reactants and products. If the total number of moles of gas increases when going from reactants to products, we can predict that the sign of ΔS^{θ}_{rxn} is positive. The entropy of products is higher than that of reactants. Conversely, if the number of moles of gaseous products is less than the number of moles of gaseous reactants then the sign of ΔS^{θ}_{rxn} is negative.

Example 2.4

Hydrogen and oxygen react to form water vapor in a spontaneous reaction.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

Predict the sign of the entropy change for this reaction and calculate ΔS^{θ}_{rxn} at 25 °C.

Answer:

When hydrogen and oxygen gas react to form water vapour, three moles of gas are converted into two moles of gas, for every mole of reaction. The total number of moles of gas decreases, so ΔS^{θ}_{rxn} for this reaction should be negative.

Using standard molar entropy values to calculate the standard entropy;

$\Delta S^{\theta}_{rxn} = S^{\theta}$ *(products)* $- S^{\theta}$ *(reactants)*

$= (2\text{ mol})(S^{\theta}\,[H_2O(g)]) - \{(2\text{ mol})(S^{\theta}\,[H_2(g)]) + (1\text{ mol})(S^{\theta}\,[O_2(g)])\}$

$= (2)(188.8\text{ J K}^{-1}\text{ mol}^{-1}) - \{(2)(130.7\text{ J K}^{-1}\text{ mol}^{-1}) + (1)(205.1\text{ J K}^{-1}\text{ mol}^{-1})\}$

$= -88.9\text{ J K}^{-1}\text{mol}^{-1}$

The entropy change for this reaction is negative, as predicted based on the reaction stoichiometry.

For a reaction to occur spontaneously, both enthalpy, ΔH°_{rxn} and entropy, ΔS°_{rxn} should be considered. As we know, for a reaction we can simply say that the decrease in enthalpy and increase in entropy favour the reaction and hence the reaction occurs spontaneously. In addition following combinations can also be considered under some conditions of temperature.

ΔH^{θ}_{rxn} −ve, $\Delta S^{\theta}_{rxn} + ve$	Spontaneous at all temperatures
ΔH^{θ}_{rxn} +ve, $\Delta S^{\theta}_{rxn} + ve$	Spontaneous at high temperatures
ΔH^{θ}_{rxn} −ve, $\Delta S^{\theta}_{rxn} - ve$	Spontaneous at low temperatures
ΔH^{θ}_{rxn} +ve, $\Delta S^{\theta}_{rxn} - ve$	Not spontaneous at all temperatures (Reverse reaction is spontaneous)

Gibbs free energy *(G)* and spontaneity of a reaction

As we have seen, the spontaneity of a reaction is determined by both the entropy and enthalpy change of the system. The **Gibbs free energy (*G*)**, or simply free energy, is a state function that combines enthalpy and entropy, where *T* is the absolute temperature. *G* is defined as follows:

$$G = H - TS$$

For a reaction occurring at constant temperature, the change in free energy is,

$$\Delta G = \Delta H - T\,\Delta S$$

For a reaction occurring at constant temperature and at standard state the change in free energy is,

$$\Delta G^{\theta}_{rxn} = \Delta H^{\theta}_{rxn} - T\,\Delta S^{\theta}_{rxn}$$

Note: *Sometimes* ΔG^{θ}_{rxn} *indicated as* ΔG^{θ}_{r}.

- A reaction that is at **equilibrium** has $\Delta G^{\theta}_{rxn} = 0$. There will be no net change in either the forward or reverse direction. For a spontaneous reaction at constant temperature and pressure, $\Delta G^{\theta}_{rxn} < 0$, and for non-spontaneous reaction $\Delta G^{\theta}_{rxn} > 0$.

Example 2.5

Carbon monoxide and oxygen gas react to form carbon dioxide.

$$CO(g) + \tfrac{1}{2}\,O_2(g) \rightarrow CO_2(g)$$

Calculate the standard free energy change for this reaction at 25°C from ΔH^{θ}_{rxn} and ΔS^{θ}_{rxn}.

($\Delta H_f^{\theta}[CO_2(g)] = -393.5$ kJ mol^{-1}, $\Delta H_f^{\theta}[CO(g)] = -110.5$ kJ mol^{-1}, $S^{\theta}[CO_2(g)] = 213.7$ J mol^{-1} K^{-1}, $S^{\theta}[CO(g)] = 197.7$ J mol^{-1} K^{-1}, $S^{\theta}[O_2(g)] = 205.1$ J mol^{-1} K^{-1})

Answer:

Using the standard heats of formation calculate first the enthalpy change for this reaction under standard state conditions.

$$\Delta H^{\theta}_{rxn} = \Delta H_f^{\theta}(\text{products}) - \Delta H_f^{\theta}(\text{reactants})$$
$$= \Delta H_f^{\theta}[CO_2(g)] - \Delta H_f^{\theta}[CO(g)] - \tfrac{1}{2}\,\Delta H_f^{\theta}[O_2(g)]$$
$$= -393.5 \text{ kJ mol}^{-1} - (-110.5 \text{ kJ mol}^{-1}) - 0 \text{ kJ mol}^{-1}$$
$$= -283.0 \text{ kJ mol}^{-1}$$

Using standard entropy values calculate the entropy change for this reaction under standard state conditions.

ΔS^{θ}_{rxn} = S^{θ} (products) − S^{θ} (reactants)
= S^{θ} [CO_2(g)] − S^{θ} [CO(g)] − ½ S^{θ} [O_2(g)]
= 213.7 J mol^{-1} K^{-1} − (197.7 J mol^{-1} K^{-1}) − (½)(205.1 J mol^{-1} K^{-1})
= −86.6 J mol^{-1} K^{-1}

***Note**: ΔS^{θ}_{rxn} is negative, as predicted by the stoichiometry: 1.5 moles of gas forms 1 mole of gas.*

Calculate ΔG^{θ}_{rxn} using

$\Delta G^{\theta}_{rxn} = \Delta H^{\theta}_{rxn} - T\,\Delta S^{\theta}_{rxn}$
= −283.0 kJ mol^{-1} − (298 K)(−86.6 J mol^{-1} K^{-1})(1 kJ/1000 J)
= −257 kJ mol^{-1}

ΔG^{θ}_{rxn} is negative. Therefore, the reaction occurs spontaneously.

Table 2.2 A summary

Relationships		**Units**
Enthalpy change of reaction	$\Delta H = \Sigma\, \nu_p H_{(\text{products})} - \nu_r \Sigma\, H_{(\text{reactants})}$	kJ mol^{-1}
Standard enthalpy change of a reaction	$\Delta H^{\theta}_{rxn} = \sum \nu_p H^{\theta}_{f[\text{products}]} - \sum \nu_r H^{\theta}_{f[\text{reactants}]}$ (Where ν_p *and* ν_r are the stoichiometric coefficients of products and reactants)	kJ mol^{-1}
Hess Law	If a process occurs in stages or steps (even if only hypothetically), the enthalpy change for the overall process is the sum of enthalpy changes for the individual steps. In other words, Hess law is simply a consequence of the state function property enthalpy. Regardless of the path taken in going from the initial state to the final state, ΔH (or ΔH^{Θ}) if the process is carried out under standard conditions) has the same value or it is independent of the route.	
Standard entropy change for a reaction	$\Delta S^{\theta}_{rxn} = \Sigma\, \nu_p S^{\theta}$ (products) $- \Sigma\, \nu_r S^{\theta}$ (reactants)	J K^{-1} mol^{-1}
Standard change in free energy	$\Delta G^{\theta}_{rxn} = \Delta H^{\theta}_{rxn} - T\,\Delta S^{\theta}_{rxn}$	kJ mol^{-1}
Spontaneity of a reaction	Spontaneous at all temperatures	ΔH^{θ}_{rxn} -ve $\Delta S^{\theta}_{rxn} + ve$
	Spontaneous at high temperatures	ΔH^{θ}_{rxn} +ve $\Delta S^{\theta}_{rxn} + ve$
	Spontaneous at low temperatures	ΔH^{θ}_{rxn} -ve $\Delta S^{\theta}_{rxn} - ve$
	Not spontaneous at all temperatures (Reverse reaction is spontaneous)	ΔH^{θ}_{rxn} +ve $\Delta S^{\theta}_{rxn} - ve$
	Spontaneous	$\Delta G^{\theta}_{rxn} < 0$
	Not spontaneous	$\Delta G^{\theta}_{rxn} > 0$
	Equilibrium	$\Delta G^{\theta}_{rxn} = 0$

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G. C. E. (Advanced Level)

CHEMISTRY

Grade 12

Unit 6: Chemistry of *s*, *p* and *d* Block Elements

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Grade 12

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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.

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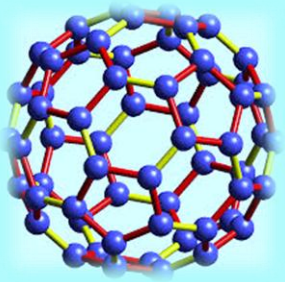
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Introduction

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 $KCl \cdot MgCl_2 \cdot 6H_2O$ (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	60	95	133	148	169
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 in inorganic chemistry, it is not always essential to indicate the physical state of 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
Gently	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 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.

$$4LiNO_3(s) \xrightarrow{\Delta} 2Li_2O(s) + 4NO_2(g) + O_2(g)$$

$$2KNO_3(s) \xrightarrow{\Delta} 2KNO_2(s) + O_2(g)$$

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.

$$2NaHCO_3(s) \xrightarrow{\Delta} Na_2CO_3(s) + H_2O(g) + CO_2(g)$$

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.

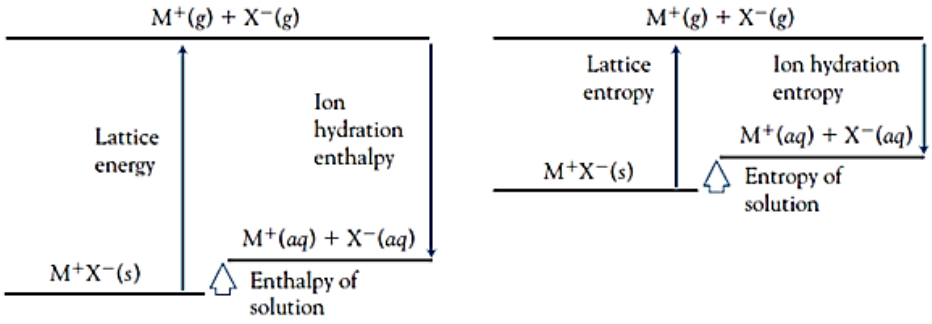


Figure 4.1 Enthalpy and entropy cycles for the solvation process

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 – Crimson red Sodium – Yellow

Rubidium – Red-violet Caesium – Blue - violet

Potassium – Lilac

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 ($CaCO_3{\cdot}MgCO_3$). Magnesite ($MgCO_3$), kieserite ($MgSO_4{\cdot}H_2O$) and carnallite ($KMgCl_3{\cdot}6H_2O$) are

examples of minerals with magnesium. Fluoroapatite [$3(Ca_3(PO_4)_2)\cdot CaF_2$] and gypsum ($CaSO_4\cdot 2H_2O$) 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	160	197	215	224
Melting point/ °C	1560	923	1115	1040	973
Radius of M^{2+}/ pm	30	65	99	113	135
1st ionization energy/ kJ mol^{-1}	899	736	589	594	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 alkaline earth Group 2 elements

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.

$$2Mg(NO_3)_2(s) \longrightarrow 2MgO(s) + 4NO_2(g) + O_2(g)$$

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.

$$MCO_3 \longrightarrow MO + CO_2$$

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.

$$Ca(HCO_3)_2(aq) \longrightarrow CaCO_3(s) + CO_2(g) + H_2O(l)$$

4.2.4 Solubility of Group 2 salts

Solubility of Group 2 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	$[He]2s^2 2p^1$	$[Ne]3s^2 3p^1$	$[Ar]3d^{10} 4s^2 4p^1$	$[Kr]4d^{10} 5s^2 5p^1$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^1$
Metallic radius/ pm	-	143	153	167	171
Covalent radius/ pm	88	130	122	150	155
Melting point/ °C	2300	660	30	157	304
Radius of M^{3+}/ pm	27	53	62	80	89
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) 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) : $4Al + O_2 \longrightarrow 2Al_2O_3$

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).

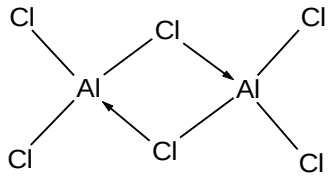


Figure 4.2 Structure of gaseous Al_2Cl_6

4.4 Group 14 elements

4.4.1 Group trends

Due to the formation of covalent bond network structure, the 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 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]$2s^2 2p^2$	[Ne]$3s^2 3p^2$	[Ar]$3d^{10} 4s^2 4p^2$	[Kr]$3d^{10} 5s^2 5p^2$	[Xe]$4f^{14} 5d^{10} 6s^2 6p^2$
Metallic radius/ pm	-	-	-	158	175
Covalent radius/ pm	77	118	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) lattice 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.

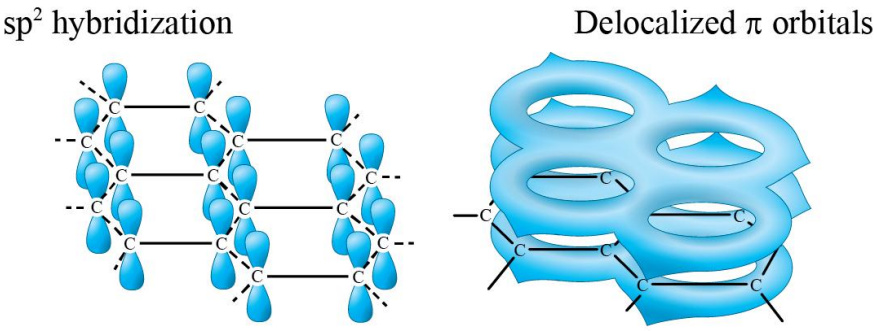
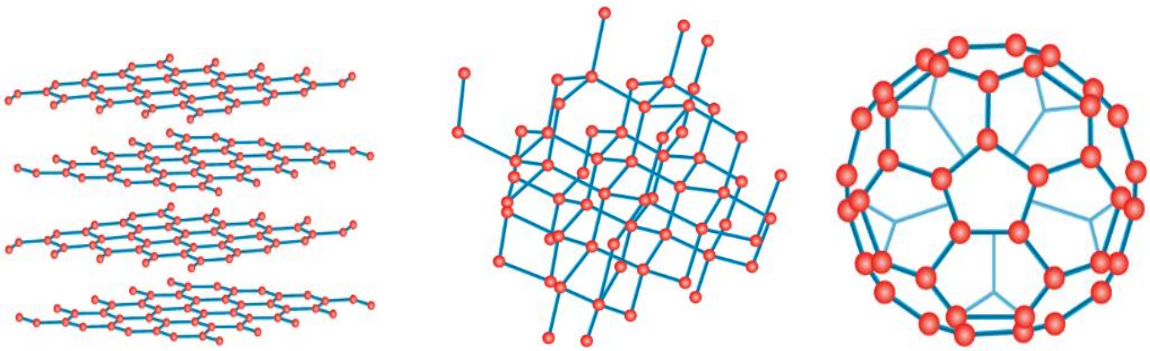


Figure 4.3 Delocalizing π bonds of graphite

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.

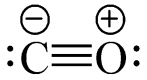


Figure 4.5 The Lewis structure of CO

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.

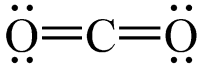


Figure 4.6 The Lewis structure of CO_2

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.

$$CO_2(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq)$$

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq)$$

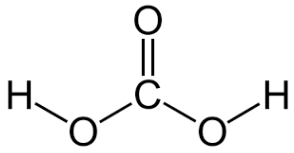


Figure 4.7 The bond structure of H_2CO_3

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	$[He]2s^2 2p^3$	$[Ne]3s^2 3p^3$	$[Ar]3d^{10} 4s^2 4p^3$	$[Kr]3d^{10} 5s^2 5p^3$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^3$
Metallic radius/ pm	-	-	-	-	182
Covalent radius/ pm	75	110	122	143	152
Melting point/ °C	-210	44 (white) 590 (red)	613	630	271
Pauling electronegativity	3.0	2.2	2.2	2.0	2.0

***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.

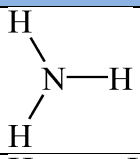
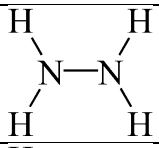
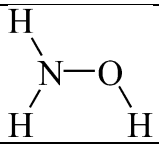
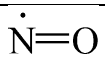
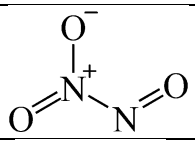
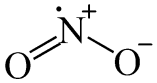
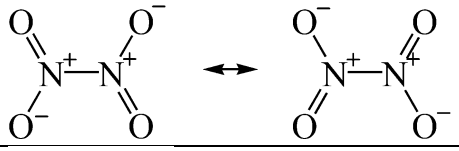
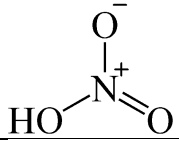
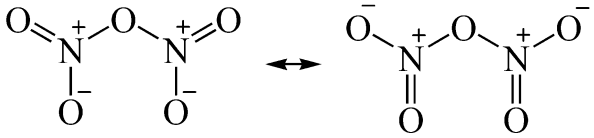
$$3Mg(s) + N_2(g) \xrightarrow{\triangle} Mg_3N_2(s)$$

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	
+1	Dinitrogen monoxide	N_2O	
+2	Nitrogen monoxide	NO	
+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.

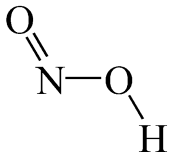


Figure 4.8 The bond structure of nitrous acid

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.

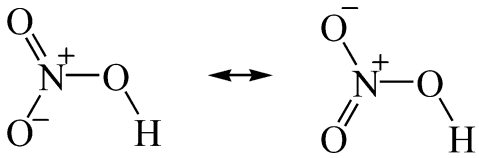


Figure 4.9 The bond structure of nitric acid

Due to the light-induced decomposition, nitric acid produces oxygen and nitrogen dioxide.

$$4HNO_3(aq) \xrightarrow{h\nu} 4NO_2(g) + O_2(g) + 2H_2O(l)$$

Due to this reason concentrated nitric acid is stored in brown colour glass bottles in laboratories.

Oxidizing and reducing 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 amonia.

$NH_4Cl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + NH_3(g) + H_2O(l)$

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.

$\text{excess ammonia, } 2NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6HCl(g)$

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.

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

$NH_3(g) + HCl(g) \longrightarrow NH_4Cl(s)$ 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.

$2NO_3^-(aq) + 4H_2SO_4(l) + 6Fe^{2+}(aq) \longrightarrow 6Fe^{3+}(aq) + 2NO(g) + 4SO_4^{2-}(aq) + 4H_2O(l)$

$Fe^{2+}(aq) + NO(g) \longrightarrow [Fe(NO)]^{2+}(aq)$ 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 true metals. 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 for 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	$[He]2s^2 2p^4$	$[Ne]3s^2 3p^4$	$[Ar]3d^{10} 4s^2 4p^4$	$[Kr]4d^{10} 5s^2 5p^4$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^4$
Ionic radius X^{2-}/ pm	140	184	198	221	-
Covalent radius/ pm	73	103	117	137	140
Melting point/ °C	-218	113(α)	217	450	254
Pauling electronegativity	3.4	2.6	2.6	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.

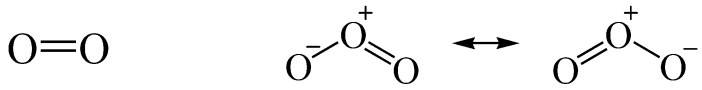
The observed varation in bond length of covalent hydrides is due to the increase of size of the central atom. Therefore, bond length increases down the group.

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.

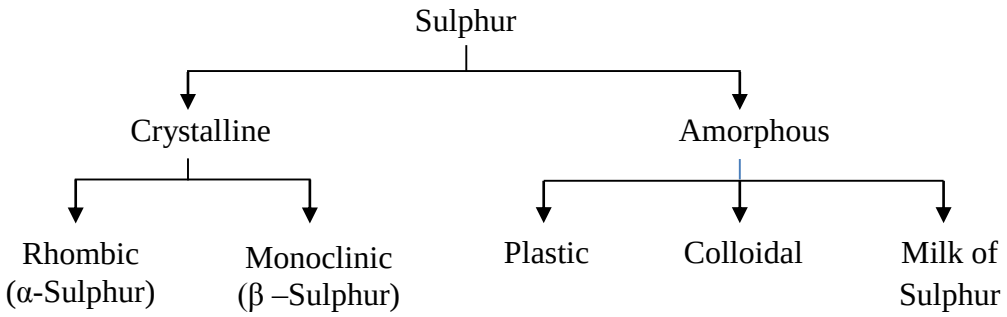
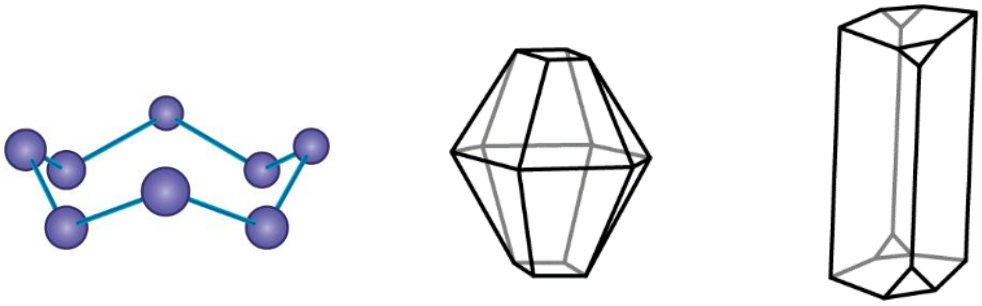


Figure 4.11 Classification of sulphur

Unlike oxygen, sulphur forms single bonds with itself rather than double bonds. The most commonly occurring allotrope is rhombic sulphur which is referred 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

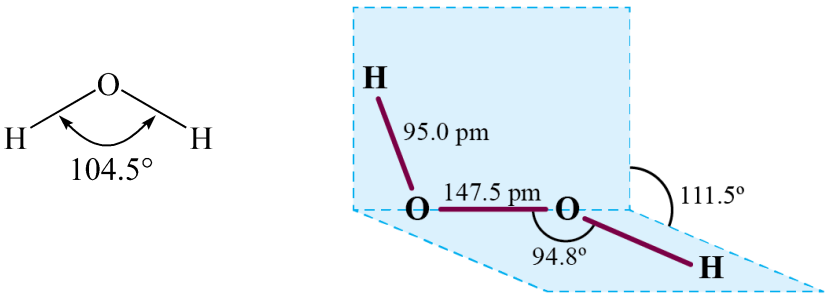
Crystalline form of rhombic and monoclinic sulphur consist of S_8 rings in the shape of crown. These can be packed together in two different ways to form rhombic crystals and to form needle shaped monoclinic crystals as shown above. Below 95 °C the rhombic form is the most stable allotropic form of sulphur.

Amorphous sulphur is an elastic form of sulphur which is obtained by pouring melted sulphur into water. Sudden cooling of molten sulphur with open chains 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 amphoteric 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;

$$NaOH(aq) + \text{excess } H_2S(g) \longrightarrow NaHS(s) + H_2O(l)$$

$$2NaOH(aq) + \text{limited } H_2S(g) \longrightarrow Na_2S(s) + 2H_2O(l)$$

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.

$$H_2SO_4(aq) + 2H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H_3O^+(aq)$$

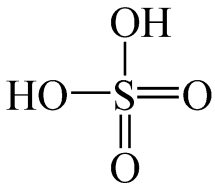


Figure 4.14 Structure of sulphuric acid

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.

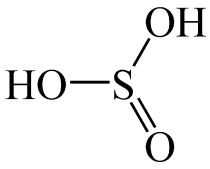


Figure 4.15 Structure of sufurous acid

Thiosulphuric acid

Only the salts of thiosulphuric acid are stable and thiosulphate ion can oxidize as well as reduce to give sulphur and sulphur dioxide as its products. 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.

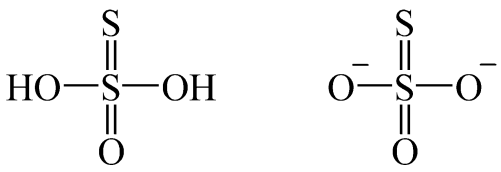


Figure 4.16 Thiosulphuric acid and thiosulphate ion

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	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar]3d^{10} 4s^2 4p^5$	$[Kr]4d^{10} 5s^2 5p^5$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^5$
van der Waals radius/ pm	135	180	195	215	-
Ionic radius X^-/ pm	133	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	3.2	3.0	2.7	-
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.

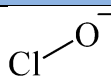
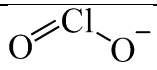
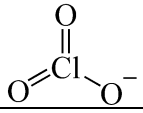
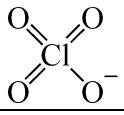
Table 4.14 Silver halides of Group 17 elements

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

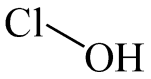
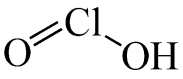
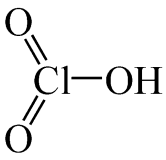
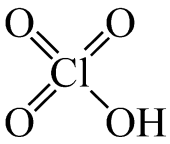
Chlorine forms several oxides and oxoanions with variable oxidation states. Some oxoanions are strong oxidizing agents. Selected oxides of chlorine are shown in Table 4.15.

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		ClO_2^-	
+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 changed as follows.
HClO > $HClO_2$ > $HClO_3$ > $HClO_4$

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.

$$SiCl_4(l) + 2H_2O(l) \longrightarrow 4HCl(aq) + SiO_2(s)$$

$$PCl_5(l) + H_2O(l) \longrightarrow POCl_3(aq) + 2HCl(aq)$$

Chlorides of group 14 and 15 elements react excess water as follows.

$$SiCl_4(l) + 3H_2O(l) \longrightarrow 4HCl(aq) + H_2SiO_3(aq)$$

$$NCl_3(l) + 3H_2O(l) \longrightarrow NH_3(aq) + 3HOCl(aq)$$

$$PCl_3(l) + 3H_2O(l) \longrightarrow H_3PO_3(aq) + 3HCl(aq)$$

$$PCl_5(l) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$$

$$AsCl_3(s) + 3H_2O(l) \rightleftharpoons H_3AsO_3(aq) + 3HCl(aq)$$

$$SbCl_3(aq) + H_2O(l) \rightleftharpoons SbOCl(s) + 2HCl(aq)$$

$BiCl_3(aq) + H_2O(l) \rightleftharpoons BiOCl(s) + 2HCl(aq)$

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, $8NH_3(g) + 3Cl_2(g) \longrightarrow N_2(g) + 6HCl(g)$

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

$Cl_2(g) + \text{cold and dil. } 2NaOH(aq) \longrightarrow NaCl(aq) + NaOCl(aq) + H_2O(l)$

With hot concentrated/ hot dilute sodium hydroxide

$3Cl_2(g) + \text{conc. } 6NaOH(aq) \xrightarrow{\text{above 80 °C}} 5NaCl(aq) + NaClO_3(aq) + 3H_2O(l)$

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.

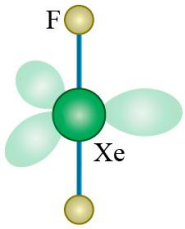
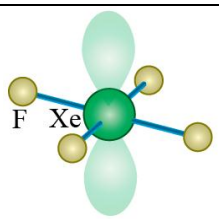
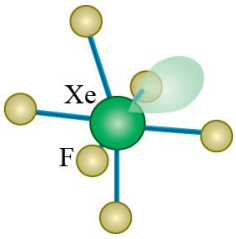
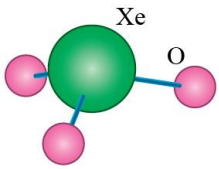
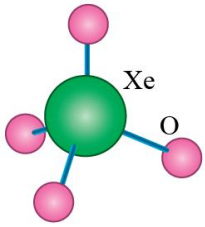
Table 4.17 Properties of Group 18 elements

	He	Ne	Ar	Kr	Xe
Ground state electronic configuration	$1s^2$	$[He]2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]3d^{10}4s^24p^6$	$[Xe]4d^{10}5s^25p^6$
Atomic radius/ pm	99	160	192	197	240
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.

$$Na_2O(s) + H_2O(l) \longrightarrow NaOH(aq)$$

$$MgO(s) + 2H_2O(l) \longrightarrow Mg(OH)_2$$

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.

$$SiO_2(s) + 2NaOH(aq) \longrightarrow Na_2SiO_3(aq)$$

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 the 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	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

	$NaCl(s)$	$MgCl_2(s)$	$AlCl_3(s)$	$SiCl_4(l)$	$PCl_5(g)$	$SCl_2(g)$
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,

$$AlCl_3(s) + H_2O(l) \longrightarrow [Al(H_2O)_5OH]^{2+}(aq) + H_3O^+(aq)$$

$$SiCl_4(l) + 2H_2O(l) \longrightarrow SiO_2(s) + 4HCl(aq)$$

$$PCl_5(g) + 4H_2O(l) \longrightarrow H_3PO_4(aq) + 5HCl(aq)$$

$$2SCl_2(g) + 3H_2O(l) \longrightarrow H_2SO_3(aq) + S(s) + 4HCl(aq)$$

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 filed *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 filed *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	1.9	1.9	1.9	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) exit 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 (Haematite), 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 *3d* 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 $3d^5 4s^1$ 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 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 filed and empty *d* orbitals. This makes d orbitals to accept or donate electrons. This property 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)	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 depends on the oxidation number. The change in the bonding type explains the basis in the acid-base behaviour of metal oxides. For the compounds with high oxidation numbers have covalent bonding characteristics are acidic and the compounds 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	
MnO_2	Amphoteric	+4	moderate oxidation state
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.

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

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^{6+} to Cr^{3+} happens only in acidic medium. In acidic medium, CrO_4^{2-} ions will dimerized and 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.

$$Cr_2O_7^{2-}(aq) + 3H_2S(g) + 8H^+(aq) \longrightarrow 2Cr^{3+}(aq) + 3S(s) + 7H_2O(l)$$

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

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

$$Cr_2O_7^{2-}(aq) + conc.14HCl(aq) \longrightarrow 2Cr^{3+}(aq) + 3Cl_2(g) + 8Cl^-(aq) + 7H_2O(l)$$

In CrO_4^{2-}, oxidation number Cr is +6. Therefore it can act as an oxidizing agent. Under acidic conditions, Cr(IV) can be reduced to Cr(III).

$$8H^+(aq) + CrO_4^{2-}(aq) + 3e \longrightarrow Cr^{3+}(aq) + 4H_2O(l)$$

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 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, $[Ni(NH_3)_6]Cl_2$ consists of 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.

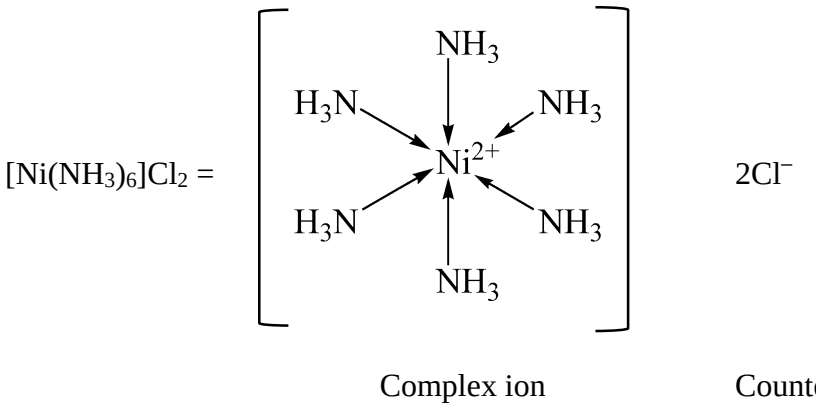


Figure 4.17 A coordination compound

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.

The charge of the complex	=	Oxidation number of the central metal atom or the ion	+	Total charge of all ligands

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:

The charge of the complex	=	Oxidation number of the central metal atom or the ion	+	Total charge of all ligands

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 the 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. The 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.: $[CuC1_4]^{2-}$ 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 tetrachlorocoboltate(II)

Coordination number

The 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. The 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)	Fe(II)	Co(II)	Ni(II)	Cu(II)
$[Mn(H_2O)_6]^{2+}$	$[Fe(H_2O)_6]^{2+}$	$[Co(H_2O)_6]^{2+}$	$[Ni(H_2O)_6]^{2+}$	$[Cu(H_2O)_6]^{2+}$
Pink	Pale-green	Pink	Green	Pale-blue

2. The oxidation state of the central metal ion

Mn(II)	Mn(III)	Fe(II)	Fe(III)
$[Mn(H_2O)_6]^{2+}$	$[Mn(H_2O)_6]^{3+}$	$[Fe(H_2O)_6]^{2+}$	$[Fe(H_2O)_6]^{3+}$
Pale-pink	Violet	Pale-green	Yellow

Colour of $[Fe(H_2O)_6]^{3+}$ is depend on the anion

3. Nature of the ligand

H_2O	OH^-	NH_3	Cl^-
$[Co(H_2O)_6]^{2+}$	$[Co(OH)_4]^{2-}$	$[Co(NH_3)]^{2+}$	$[Co(Cl)_4]^-$
Pink	Deep-blue	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 4.33 Metal complexes and colours

Metal	Nature of the ligand			
	$H_2O(l)$	$OH^-(aq)$	$NH_3(aq)$	$Cl^-(aq)$
Cr	$[Cr(H_2O)_6]^{3+}$ Violet	$Cr(OH)_3$ Blue-green ppt (precipitate)	$Cr(OH)_3$ Blue-green ppt	$[CrCl_6]^{3-}$ Blue-violet
Mn	$[Mn(H_2O)_6]^{2+}$ Pale pink	$Mn(OH)_2$ White/ cream colour ppt	$Mn(OH)_2$ White/ cream colour ppt	$[MnCl_4]^{2-}$ Greenish 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 With excess OH^- $[Co(OH)_4]^{2-}$ Deep-blue	$[Co(NH_3)_6]^{2+}$ 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 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.

$$[Co(H_2O)_6]^{2+}(aq) + 2OH^-\,(aq) \longrightarrow Co(OH)_2(s) + 6H_2O(l)$$

$Co(OH)_2$ is a pink precipitate. With excess concentrated hydroxide ion solutions, a deep blue solution is formed.

$$Co(OH)_2(s) + 2OH^-(aq) \longrightarrow [Co(OH)_4]^{2-}(aq)$$

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 yellow colour $[Co(NH_3)_6]^{2+}$ complex ion. However due to the auto-oxidation, $[Co(NH_3)_6]^{2+}$ complex convert to a brown colour $[Co(NH_3)_6]^{3+}$. Because of this, the solution appears as yellowish-brown solution.

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 deep 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 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 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 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 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 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, 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, 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, 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.

$$Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow [Zn(OH)_4]^{2-}(aq)$$

The colourless solution turns into a white precipitate, then with excess base, the precipitate dissolves to form a colourless solution.

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. The 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+}

Oxidation of Cr^{3+} to yellow colour solution of CrO_4^{2-}

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-}.

$$Cr^{3+}(aq) + 3NaOH \longrightarrow Cr(OH)_3(s) + 3Na^+(aq)$$

$$2Cr(OH)_3(s) + 3H_2O_2(aq) \longrightarrow 2CrO_4^{2-}(aq) + 4H_2O(l) + 4H^+(aq)$$

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G. C. E. (Advanced Level)

CHEMISTRY

Grade 12

Resource Book

Unit 07. Basic concepts of organic chemistry
Unit 08. Hydrocarbons and halohydrocarbons
Unit 09. Oxygen containing organic compounds
Unit 10. Nitrogen containing organic compounds

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Faculty of Science and Technology
National Institute of Education
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Resource Book
Grade 12

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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

A Note to Students from the Authors

This book has been written to specifically cover the contents of the Organic Chemistry units of the G.C.E. (A/L) Chemistry syllabus. The core content of the syllabus is concerned with the characteristic reactions of selected classes of compounds. Modern Organic Chemistry is founded on the basic idea that the chemical behavior of a compound can be accounted for by its structure. The book emphasizes the application of a limited number of fundamental concepts to rationalize and understand all the reactions covered. Simple descriptions of mechanisms are given and explained where relevant. Only the reactions specified in the syllabus are covered, and for any given reaction only the main product/products are considered. Experimental conditions are given only if they are critical.

The authors hope that the book will be useful to students to understand and appreciate organic chemistry, and to move away from rote memorization of isolated facts. This will build a solid foundation for more advanced study if the student wishes to do so.

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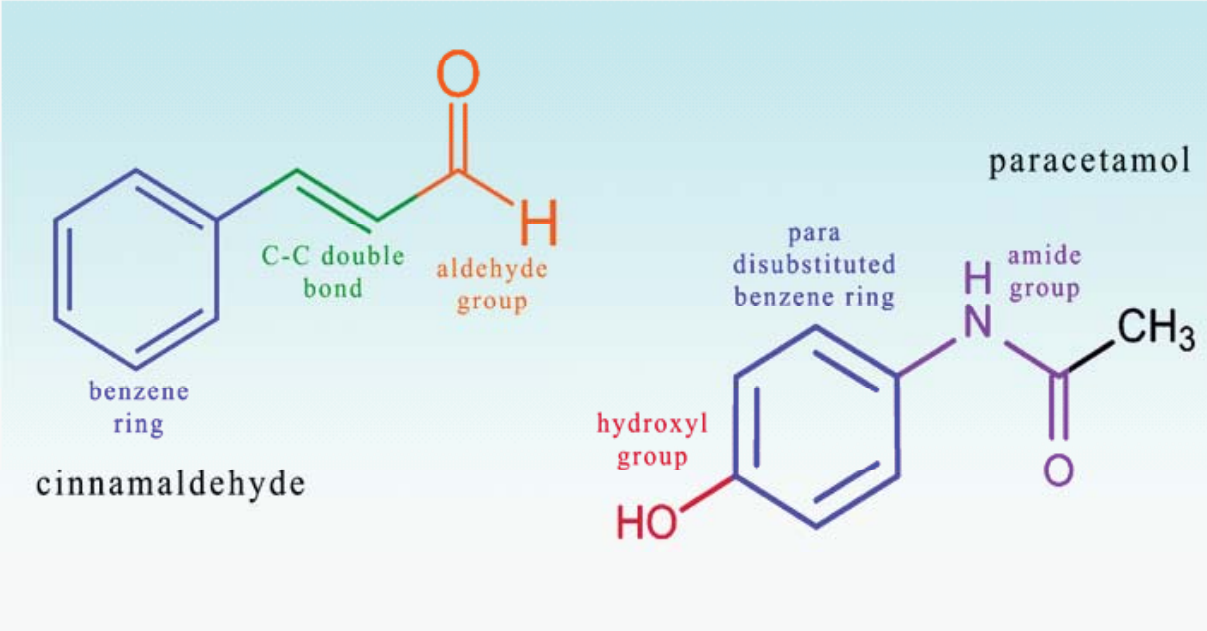
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Introduction

Organic Chemistry is the chemistry of compounds of carbon. In these compounds, carbon atoms form the skeleton or backbone of the molecule. In addition to carbon, organic compounds usually contain hydrogen. Oxygen, nitrogen, sulphur, phosphorus and halogens are also found in certain organic compounds. These compounds can be natural or synthetic. Organic compounds form an essential component of all living organisms and play a central role in metabolic processes. Organic compounds also form an essential component in many of the materials that are essential for our daily life such as food, plastic items, textiles, cosmetics and medicines. The variety and number of compounds formed by carbon is very large compared to the compounds formed by other elements in the periodic table.

1.1 Organic chemistry in day to day life

Organic compounds are associated with nearly every aspect of our existence. For example:

Food components: Carbohydrates, fats, proteins
Plastic materials: PVC, polythene, polystyrene, polyesters, nylon
Medicines: Paracetamol, aspirin, penicillin, amoxicillin
Fuels: Petrol, diesel, kerosene, LP gas

1.1.1 Why carbon can form a large number of organic compounds with vast structural diversity? Uniqueness of carbon

Carbon-carbon and carbon-hydrogen bonds are the predominant bonds found in organic compounds. Between two C atoms strong single bonds, double bonds and triple bonds can be formed. The small electronegativity difference between C and H also leads to the formation of C–H covalent bonds. The presence of 4 electrons in its valence shell enables it to form 4 covalent bonds which include carbon-carbon double bonds and triple bonds. Due to these reasons, carbon is capable of forming linear and branched chains and rings leading to compounds with diverse carbon skeletons. As carbon can also form bonds with O, N, S, P and halogens, this leads to the formation of an enormous variety of organic compounds having a wide range of molecular weights. When compared to Si which is also in the fourth group of the periodic table to which C belongs, the C–C and C–H bonds possess higher bond energies than Si–Si and Si–H bonds. Some bond energies relevant to the discussion above are shown in **Table 1.1.**

Table 1.1 Bond energies of some bonds with C and Si

Bond	Bond energy/ kJ mol^{-1}
C–C	346
C=C	610
C≡C	835
C–H	413
Si–Si	226
Si–H	318

1.2 Diversity of organic compounds in terms of functional groups

Some organic compounds contain only C and H as the constituent elements. They are known as hydrocarbons. On the basis of the structure, hydrocarbons are divided into two main groups called aliphatic and aromatic. Hydrocarbons consisting of only open carbon chains are called as acyclic aliphatic hydrocarbons while those with cyclic carbon chains are called alicyclic hydrocarbons. The aliphatic hydrocarbons are classified as alkanes, alkenes, and alkynes. The cyclic organic compounds which are stabilized by forming a cyclic delocalized cloud of π electrons are called aromatic compounds. Benzene which is indicated by the molecular formula C_6H_6 is the simplest of aromatic hydrocarbon compounds. The classification of hydrocarbons is shown in the **Figure 1.1** with common examples of each type.

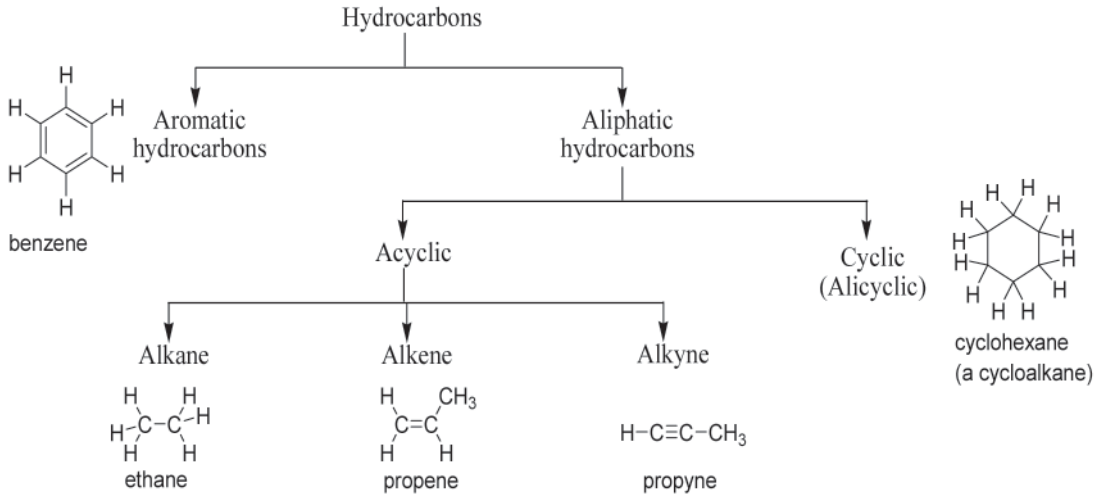
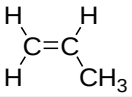
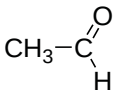
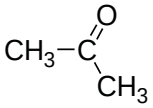
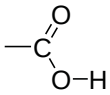
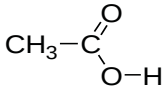
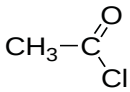
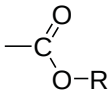
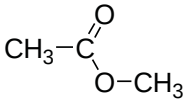
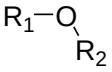
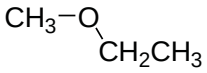
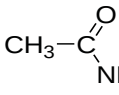
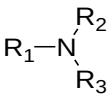


Figure 1.1 Classification of hydrocarbons

Note: *Cycloalkanes, cycloalkenes and cycloalkynes are not included in the current G.C.E. (A/L) syllabus*.

Compounds are classified according to the functional groups present in their molecules. A functional group is a group of atoms in a molecule where most of its reactions take place. Apart from the carbon-carbon double bond and carbon-carbon triple bond, a functional group contains one or more heteroatoms such as nitrogen and oxygen. Common functional groups and the names of the corresponding homologous series are given in **Table 1.2.**

Table 1.2 Functional groups in organic compounds

Functional group	Name of the homologous series		Example with name	
	Alkene			propene
—C≡C—	Alkyne		H−C≡C−H	ethyne
—OH	Alcohol		CH_3CH_2−OH	ethanol
	Aldehyde			ethanal
	Ketone			propanone
	Carboxylic acid			ethanoic acid
	Acid halide	X = Cl; acid chloride X = Br; acid bromide		ethanoyl chloride
	Ester			methyl ethanoate
	Ether			ethylmethyl ether
	Amide			ethanamide
	Amine		CH_3CH_2−NH_2 CH_3CH_2−NH(−CH_3)	ethylamine ethylmethylamine
—C≡N	Nitrile		CH_3CH_2−C≡N	propanenitrile
—X	Alkyl halide	X = Cl; alkyl chloride X = Br; alkyl bromide X = I; alkyl iodide	CH_3CH_2−Cl CH_3CH_2−Br	chloroethane bromoethane

Note: *Alkenes, alkynes, ethers and alkyl halides are not considered as functional groups in the IUPAC nomenclature system.*

1.2.1 Classes of compounds with functional groups containing heteroatoms

1.2.1.1 Alcohol

Alcohols are compounds containing a hydroxyl group (–OH) attached to an alkyl group. Some examples are given in **Figure 1.2.**

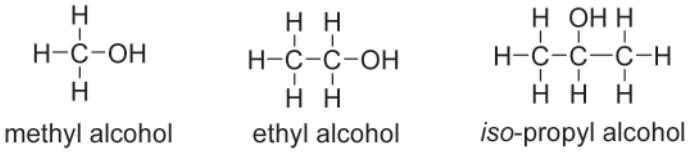


Figure 1.2 Some examples for alcohols

Note: *An alkyl group is formally derived from an alkane by the removal of a hydrogen atom.*

1.2.1.2 Ethers

Ethers are compounds containing an oxygen atom attached to two alkyl groups. Some examples are given in **Figure 1.3.**

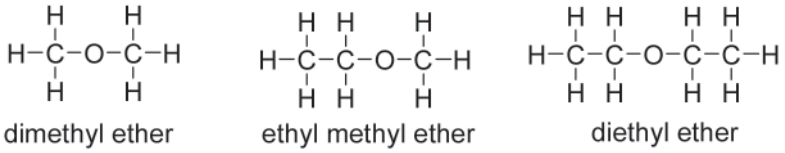


Figure 1.3 Some examples for ethers

1.2.1.3 Aldehyde

Aldehydes are compounds containing a carbonyl (C=O) group attached to an H atom. Some examples are given in **Figure 1.4.**

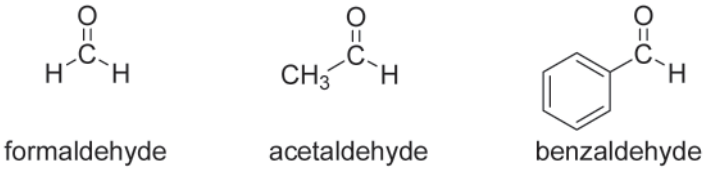


Figure 1.4 Some examples for aldehydes

1.2.1.4 Ketones

Ketones are compounds containing a carbonyl (C=O) group attached to two carbon atoms each of which may belong to an alkyl or aryl group. Some examples are given in **Figure 1.5.**

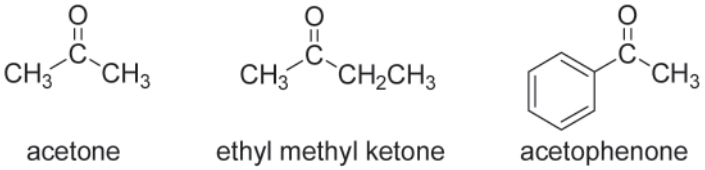


Figure 1.5 Some examples for ketones

1.2.1.5 Alkyl halides

Alkyl halides are compounds containing a halogen atom bonded to an alkyl group. Some examples are given in **Figure 1.6.**

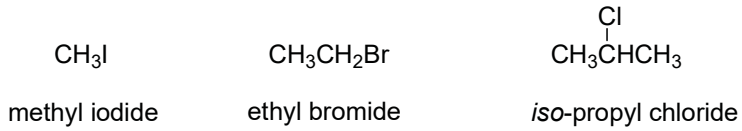


Figure 1.6 Some examples for alkyl halides

Note: *Compounds containing a halogen atom joined to an aromatic ring are called aryl halides.*

1.2.1.6 Carboxylic acids

Carboxylic acids are compounds containing the carboxylic acid (COOH) group. Some examples are given in **Figure 1.7.**

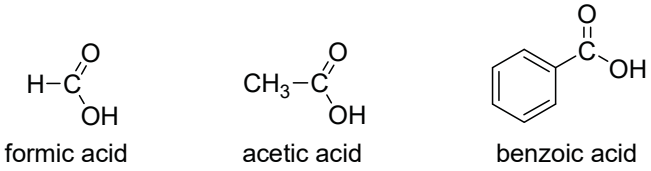


Figure 1.7 Some examples for carboxylic acids

1.2.1.7 Acid halides, esters and amides (derivatives of carboxylic acids)

Acid halides are compounds containing the COX group where X is a halogen atom. Esters are compounds containing the COOR group and amides are compounds containing the $CONH_2$ group. Some examples are given in **Figure 1.8.**

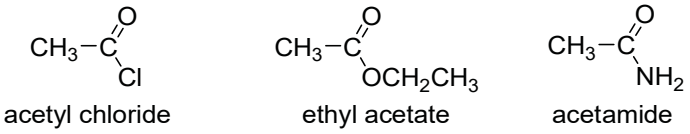


Figure 1.8 Some examples for derivatives of carboxylic acids

Note: *Acid halides, esters and amides are derived by replacing the OH group in the COOH group by halogen, OR and NH_2 groups respectively.*

1.2.1.8 Amines

Amines are compounds derived formally from ammonia by replacing its H atoms either by alkyl groups or aryl groups. Some examples are given in **Figure 1.9.**

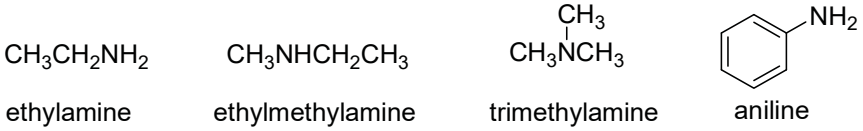


Figure 1.9 Some examples for amines

1.3 IUPAC nomenclature of organic compounds

The set of rules for systematic nomenclature of organic compounds which is now in practice evolved through several international conferences and are known as International Union of Pure and Applied Chemistry rules (IUPAC rules). Therefore, this system of nomenclature is called the IUPAC nomenclature system. In addition to the IUPAC nomenclature many common organic compounds are known by trivial (non-systematic) names. Some examples are given at the end of this section.

1.3.1 IUPAC nomenclature

The IUPAC nomenclature system is governed by a large number of rules. In our discussion we will limit ourselves to understand the most important ones which can be used to name more common types of organic compounds. The most important feature of the IUPAC system would be that it will allow us to give one name to a given organic compound and to write only one structure for a given IUPAC name.

In this system, all the compounds with heteroatoms such as O, N, halogen, are considered to be derived from the corresponding hydrocarbon. Therefore, as a start, let us look at how hydrocarbons are named according to the IUPAC system of nomenclature.

1.3.2 Alkane hydrocarbons

All the names of saturated hydrocarbons end with the suffix **-ane.** The stem of the hydrocarbon name denotes the number of carbon atoms present in the longest carbon chain. Learning the stems is like learning to count in Organic Chemistry. Stem names up to 6 carbon atoms are given in **Table 1.3.**

Table 1.3 Stem names of hydrocarbons having up to six carbon atoms

Carbon Number	Stem name	Name of hydrocarbon	Structure
1	meth-	methane	CH_4
2	eth-	ethane	CH_3CH_3
3	prop-	propane	$CH_3CH_2CH_3$
4	but-	butane	$CH_3CH_2CH_2CH_3$
5	pent-	pentane	$CH_3CH_2CH_2CH_2CH_3$
6	hex-	hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$

Before we consider little more complex hydrocarbons, let us look at how we can name alkyl groups.

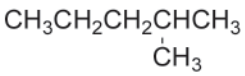
When we formally remove a H atom from an alkane an alkyl group is obtained. The name of an alkyl group ends with the suffix **-yl**. When the terminal H atom of an unbranched hydrocarbon is removed the unbranched alkyl group is formed. Some examples are given in **Table 1.4**.

Table 1.4 Some examples of alkyl groups

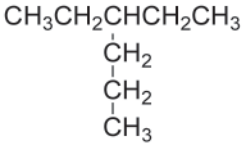
Hydrocarbon		Alkyl group	
$H–CH_3$	methane	$–CH_3$	methyl
$H–CH_2CH_3$	ethane	$–CH_2CH_3$	ethyl
$H–CH_2CH_2CH_3$	propane	$–CH_2CH_2CH_3$	propyl

1.3.3 Nomenclature of branched chain alkanes

Branched chain alkanes can be considered the hydrocarbons which have alkyl groups attached to its longest carbon chain. Let us go through the steps involved in naming of branched chain alkanes taking the following examples.

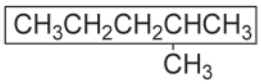


(1)



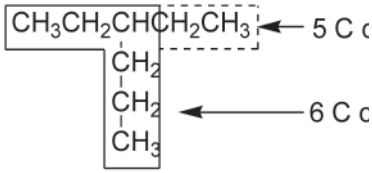
(2)

Step 1. Identify the longest continuous chain of carbon atoms and derive the hydrocarbon name.



(1)

5 Carbon atoms – pentane

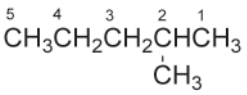


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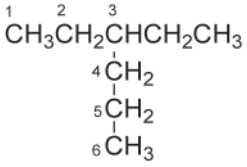
6 C atoms - hexane

Note: *A methyl group is attached to one of the C atoms of compound 1 and an ethyl group is attached to one of the C atoms of compound 2. A group that replaces an H atom of the hydrocarbon chain is called a substituent group. Therefore methyl group in compound 1 and ethyl group in compound 2 are substituents.*

Step 2. Number the carbon atoms of the longest continuous carbon chain such that the C atom bearing the substituent group gets the lowest possible number.



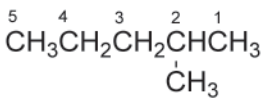
(1)



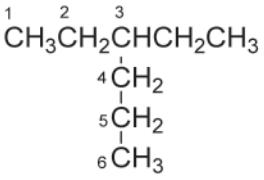
(2)

Note: *The carbon chain of compound 1is numbered from right to left. If the carbon chain of this compound is numbered from left to right, the carbon atom to which the methyl group is attached will be assigned number 4 which is a higher number than 2.*

Step 3. Use the number obtained by applying the above step (2) to designate the location of the substituent. Write the name of the compound by placing the hydrocarbon name (name of the parent hydrocarbon) at last preceded by the substituent group with the number designating its location. Numbers are separated from words by a hyphen while numbers are separated by commas.

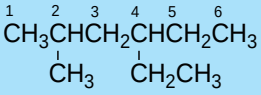
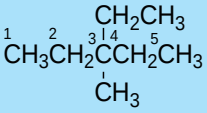


(1)
2-methylpentane

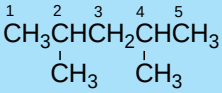
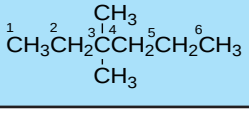


(2)
3-ethylhexane

When two or more substituents are present they should get the lowest possible numbers designating their location on the longest carbon chain. The substituent groups should be placed alphabetically in the IUPAC name. Let us take two more examples.

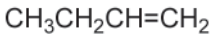
		
Longest hydrocarbon chain	Six - hexane	Five - pentane
Substituents and their location	2-methyl, 4-ethyl	3-methyl, 3-ethyl
IUPAC name	4-ethyl-2-methylhexane	3-ethyl-3-methylpentane

When two or more substituents are identical, they are indicated by the prefixes, di- (2), tri- (3), tetra- (4) etc. Every substituent should be given the number that shows its location on the longest carbon chain.

		
Longest hydrocarbon chain	Five - pentane	Six - hexane
Substituents and their location	2-methyl, 4-methyl	3-methyl, 3-methyl
IUPAC name	2,4-dimethylpentane	3,3-dimethylhexane

1.3.4 Nomenclature of alkene and alkyne hydrocarbons

Alkenes contain carbon-carbon double bonds. According to IUPAC nomenclature, the suffix -ane is replaced by suffix -ene in alkenes with the number designating the location of the double bond in the parent hydrocarbon. Let us go through the steps involved in naming alkenes taking some examples.

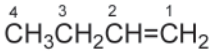


(3)

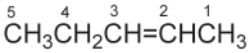


(4)

Step 1. Identify the longest continuous carbon chain including the carbon-carbon double bond. Number the carbon chain such that the double bond carbons get the lowest possible numbers.

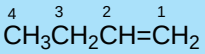
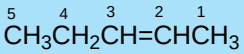


(3)

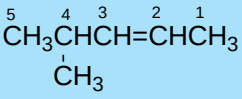
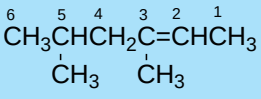


(4)

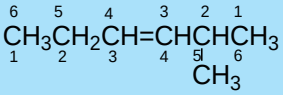
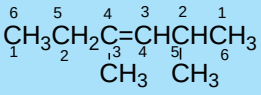
Step 2. Build the IUPAC name by placing the name representing the carbon number and suffix -ene with the lowest number designated to the location of the double bond.

	 (3)	 (4)
Longest carbon chain	Four - but	Five – pent
Double bond location	1,2	2,3
IUPAC name	but-1-ene (1-butene)	pent-2-ene (2-pentene)

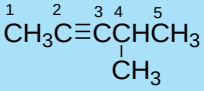
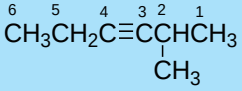
Step 3. When substituents are present, they are placed in as prefixes along with the number designated to indicate their location in the longest carbon chain containing the double bond.

		
Longest carbon chain	Five - pent	Six - hex
Double bond location	2,3	2,3
Parent hydrocarbon name	pent-2-ene (2-pentene)	hex-2-ene (2-hexene)
Substituents with location	4-methyl	3-methyl, 5-methyl
IUPAC name	4-methylpent-2-ene (4-methyl-2-pentene)	3,5-dimethylhex-2-ene (3,5-dimethyl-2-hexene)

If the double bond gets the same set of numbers when the chain is numbered from either sides of the carbon chain, then the numbering should be done such that substituents get the lowest possible numbers.

		
Longest carbon chain	Six - hex	Six - hex
Double bond location	3, 4	3, 4
Parent hydrocarbon name	hex-3-ene (3-hexene)	hex-3-ene (3-hexene)
Substituents with location	2-methyl	2-methyl, 4-methyl
IUPAC name	2-methylhex-3-ene (2-methyl-3-hexene)	2,4-dimethylhex-3-ene (2,4-dimethyl-3-hexene)

Alkynes contain carbon-carbon triple bonds. They are named by replacing suffix **-ane** of alkane by suffix **-yne.** The rest follows similar to nomenclature of alkenes.

		
Longest carbon chain	Five - pent	Six - hex
Triple bond location	2, 3	3, 4
Parent hydrocarbon name	pent-2-yne (2-pentyne)	hex-3-yne (3-hexyne)
Substituents with location	4-methyl	2-methyl
IUPAC name	4-methylpent-2-yne (4-methyl-2-pentyne)	2-methylhex-3-yne (2-methyl-3-hexyne)

Let us now summarize the basic principles of naming hydrocarbons according to the IUPAC system. **This will be the foundation for the naming of compounds containing functional groups.**

(i) All the compounds are considered to be derived from the hydrocarbon containing the longest carbon chain.

(ii) When a double bond or a triple bond is present, the longest carbon chain should be chosen to include the double bond or the triple bond.

(iii) A suitable suffix (-ane, -ene or -yne) is added to the stem name which denotes the number of carbon atoms (parent hydrocarbon).

(iv) When double bonds or triple bonds are absent, the carbon atoms carrying substituents are given the lowest possible numbers.

(v) When a double bond or a triple bond is present it is given the lowest possible number.

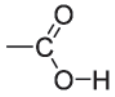
(vi) Substituent names are placed as prefixes to the parent hydrocarbon name in the alphabetical order.

1.3.5 IUPAC nomenclature of compounds other than hydrocarbons

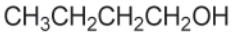
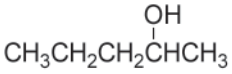
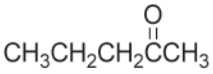
In this section nomenclature of compounds containing other functional groups **(Table 1.2)** will be discussed. This also follows the principles we have already discussed. In addition we now need a class name (suffix) to designate the functional group present in the molecule.

Let us take class names (suffixes) **(Table 1.5)** of some functional groups and study how these principles should be applied in naming compounds with one functional group.

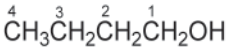
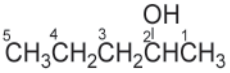
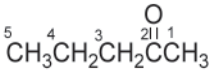
Table 1.5 Class names of some functional groups

Functional group	Name of the homologous series	Class name (Suffix)
—OH	Alcohol	-ol
	Aldehyde	-al
	Ketone	-one
	Carboxylic acid	-oic acid

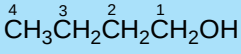
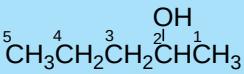
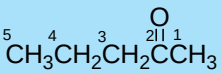
Let us now go through the steps involved in naming the following compounds.

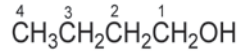
1. Identify the longest continuous carbon chain containing the functional group and number the carbon atoms of the carbon chain such that the C atom bearing the functional group gets the lowest possible number.

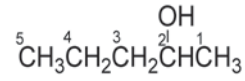
2. Derive the parent hydrocarbon name which shows the number of C atoms and whether it is saturated or contains a double bond or a triple bond.

					
4 C atoms:	but	5 C atoms:	pent	5 C atoms:	pent
Saturated hydrocarbon chain:	ane	Saturated hydrocarbon chain:	ane	Saturated hydrocarbon chain:	ane
but + ane; butane		pent + ane; pentane		pent + ane; pentane	

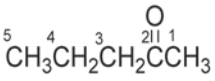
3. Write the name of the compound by placing the hydrocarbon name deleting the last letter ‘e’ (name of the parent hydrocarbon) followed by the suffix identifying the functional group with the number designating its location.



butane + 1-ol
butan-1-ol (1-butanol)



pentane + 2-ol
pentan-2-ol (2-pentanol)



pentane + 2-one
pentan-2-one (2-pentanone)

The IUPAC names derived above give the following information:

(i) The number of C atoms in the longest continuous carbon chain (pent, but etc.).

(ii) The saturated nature of the carbon chain (-an-)

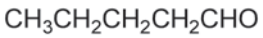
(iii) The functional group present in the molecule and its position (1-ol, 2-ol or 2-one).

Note:*The hydroxyl group (OH) of alcohols can be positioned on any carbon atom including the terminal carbon atom of the carbon chain while the carbonyl group (C=O) of ketones cannot be positioned at the terminal carbon atom of the carbon chain. Thus in naming alcohols and ketones the number designating the location of the functional group has to be stated.*

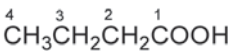
The carbonyl group (C=O) of the aldehydes and the carboxylic acids are always positioned at the terminal carbon atom of the carbon chain. Therefore it is not necessary to state the number designating their location.

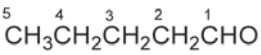
Let us take the following two examples.



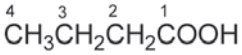


1. Identify the longest continuous carbon chain containing the functional group and number the carbon atoms of the carbon chain such that the C atom of the functional group gets number 1.

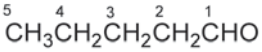




2. Derive the parent hydrocarbon name which shows the number of C atoms and whether it is saturated or contains a double bond or a triple bond.

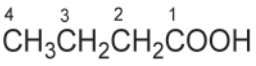


4 C atoms and saturated hydrocarbon (but + ane)

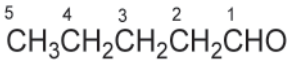


5 C atoms and saturated hydrocarbon (pent + ane)

3. Write the name of the compound by placing the hydrocarbon name deleting the last letter ‘e’ (name of the parent hydrocarbon) followed by the suffix identifying the functional group. Because aldehyde functional group and carboxylic acid functional group always get number 1, the number is not stated in the name.

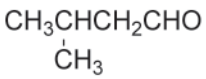


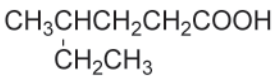
butane + oic acid
butanoic acid



pentane + al
pentanal

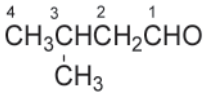
Let us now take few examples containing alkyl substituents attached to the longest continuous carbon chain. Recall that aldehyde and carboxylic acid functional groups are always positioned at the terminal of the carbon chain. Hence the C of these two functional groups is given number 1 when numbering.

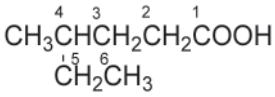




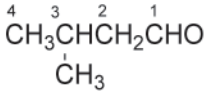
Let us go through the steps involved in naming the above examples.

1. Identify the longest continuous carbon chain containing the functional group and number the carbon atoms of the carbon chain such that the C atom of the functional group gets number 1.

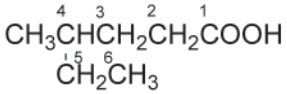




2. Derive the parent hydrocarbon name which shows the number of C atoms and whether it is saturated or contains a double bond or a triple bond.

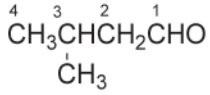


4 C atoms and saturated hydrocarbon (but + ane)

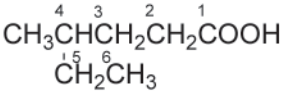


6 C atoms and saturated hydrocarbon (hex+ ane)

3. Identify the substituent groups with the location.

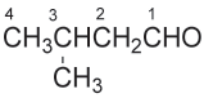


3-methyl

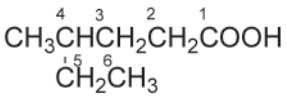


4-methyl

4. Build the IUPAC name of the compound by placing the hydrocarbon name deleting the last letter 'e' (name of the parent hydrocarbon) followed by the suffix identifying the functional group. Place the substituent names with their locations as prefixes. When there are several substituents they should be placed in the alphabetical order.

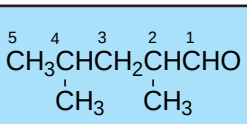
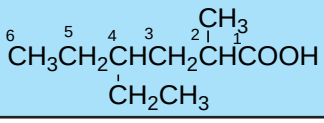


3-methyl+butane+al
3-methylbutanal



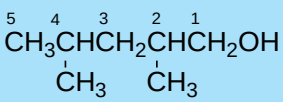
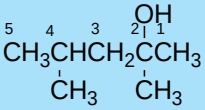
4-methyl+hexane+oic acid
4-methylhexanoic acid

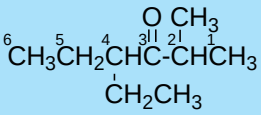
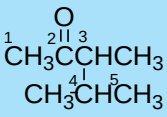
Let us take two more examples.

		
Longest carbon chain	5C – pent	6C - hex
Parent hydrocarbon name	pentane	hexane
Functional group (with location)	1-al	1-oic acid
Substituents with locations	2-methyl, 4-methyl	2-methyl, 4-ethyl
IUPAC name	2,4-dimethylpentanal	4-ethyl-2-methylhexanoic acid

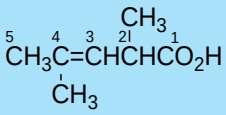
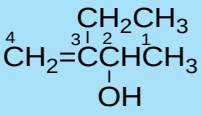
Carbon chains of compounds containing functional groups that can be placed on any carbon atom (such as alcohols and ketones) should be numbered such that the functional group gets the lowest possible number. Rest of the steps discussed will then be followed to build the IUPAC name.

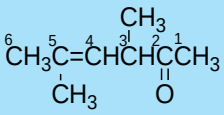
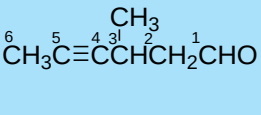
Let us take few examples.

		
Longest carbon chain	5C atoms - pent	5C atoms - pent
Parent hydrocarbon name	pentane	pentane
Functional group (with location)	OH at C-1 (1-ol)	OH at C-2 (2-ol)
Substituents with locations	2-methyl, 4-methyl	2-methyl, 4-methyl
IUPAC name	2,4-dimethylpentan-1-ol 2,4-dimethy- lpentanol	2,4-dimethylpentan-2-o1 2,4-dimethyl-2-pentanol

		
Longest carbon chain	6C atoms - hex	5C atoms - pent
Parent hydrocarbon name	hexane	pentane
Functional group (with location)	C=O at C-3 (3-one)	C=O at C-2 (2-one)
Substituents with locations	2-methyl, 4-ethyl	3-methyl, 4-methyl
IUPAC name	4-ethyl-2-methylhexan-3-one 4-ethyl-2-methyl-3-hexanone	3,4-dimethylpentan-2-one 3,4-dimethyl-2-pentanone

When the compound contains a double bond or a triple bond (a multiple bond), the longest chain must contain both the functional group and the multiple bond. Accordingly the parent hydrocarbon will be either an alkene or an alkyne. Rest of the steps discussed will then be followed to build the IUPAC name. Let us take a look at few examples.

		
Longest carbon chain	5C atoms - pent	4C atoms - but
Functional group with location	oic acid	2-ol
Double/triple bond with location	3-ene	3-ene
Parent hydrocarbon name	pent-3-ene	but-3-ene
Substituents with locations	2-methyl, 4-methyl	3-ethyl
IUPAC name	2,4-dimethylpent-3-enoic acid 2,4-dimethyl-3-pentenoic acid	3-ethylbut-3-en-2-ol 3-ethyl-3-buten-2-ol

		
Longest carbon chain	6C atoms - hex	6C atoms - hex
Functional group with location	2-one	al
Double/triple bond with location	4-ene	4-yne
Parent hydrocarbon name	hex-4-ene	hex-4-yne
Substituents with locations	3-methyl, 5-methyl	3-methyl
IUPAC name	3,5-dimethylhex-4-en-2-one	3-methylhex-4-ynal
	3,5-dimethyl-4-hexen-2-one	3-methyl-4-hexynal

1.3.6 IUPAC nomenclature of compounds containing more than one functional group

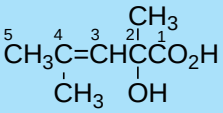
There are many organic compounds containing several functional groups. Recall that in the foregoing discussion you learnt that compounds are named according to their functional group. In the IUPAC nomenclature system, functional groups are arranged in a priority order. When there are two functional groups in a molecule, the compound is named according to the functional group that gets the highest priority. The functional group with the highest priority is called the principal functional group. The remaining functional group is considered as a

substituent. When a functional group is considered as substituent, it is given a different name to be used as a prefix. The carbon chain is numbered so that the principal functional group gets the lowest possible number. Class names and substituent names of some functional groups are given in **Table 1.6** in the order of their priority.

Table 1.6 Class names and substituent names of some functional groups in their priority order

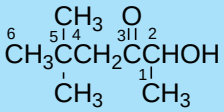
Functional group	Name of the homologous series	Substituent name (prefix)	Class name (suffix)
-COOH	Carboxylic acid	-	oic acid
-COOR	Ester	-	oate
-COCl	Acid chloride	-	oyl chloride
$-CONH_2$	Amide	-	amide
-CN	Nitrile	cyano	nitrile
-CHO	Aldehyde	formyl	al
-CO-	Ketone	oxo	one
-OH	Alcohol	hydroxy-	ol
$-NH_2$	Amine	amino	amine
-F		fluoro-	-
-Cl		chloro-	-
-Br		bromo-	-
-I		iodo-	-
$-NO_2$		nitro	-

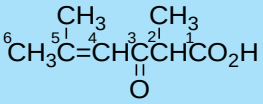
Note: *alkene (C=C) as "ene" and alkyne (C≡C) as "yne" are used as suffixes.*



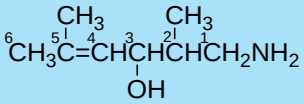
Longest carbon chain	5C atoms - pent
Functional group with highest priority and its location	oic acid
Double/triple bond with location	3-ene
Parent hydrocarbon name	pent-3-ene
Substituents with locations	2-hydroxy, 2-methyl, 4-methyl
IUPAC name	2-hydroxy-2,4-dimethylpent-3-enoic acid 2-hydroxy-2,4-dimethyl-3-pentenoic acid

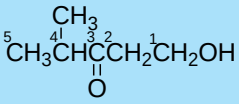
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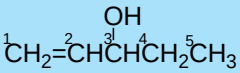
	
Longest carbon chain	6C atoms - hex
Functional group with highest priority and its location	3-one
Double/triple bond with location	none
Parent hydrocarbon name	hexane
Substituents with locations	2-hydroxy, 5,5-dimethyl
IUPAC name	2-hydroxy-5,5-dimethylhexan-3-one 2-hydroxy-5,5-dimethyl-3-hexanone

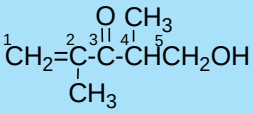
	
Longest carbon chain	6C atoms - hex
Functional group with highest priority and its location	oic acid
Double/triple bond with location	4-ene
Parent hydrocarbon name	hex-4-ene (4-hexene)
Substituents with locations	3-oxo, 2-methyl, 5-methyl
IUPAC name	2,5-dimethyl-3-oxohex-4-enoic acid 2,5-dimethyl-3-oxo-4-hexenoic acid

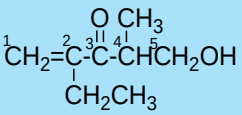
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Longest carbon chain	6C atoms - hex
Functional group with highest priority and its location	3-ol
Double/triple bond with location	4-ene
Parent hydrocarbon name	hex-4-ene (4-hexene)
Substituents with locations	1-amino, 2,5-dimethyl
IUPAC name	1-amino-2,5-dimethylhex-4-en-3-ol 1-amino-2,5-dimethyl-4-hexen-3-ol

	
Longest carbon chain	5C atoms - pent
Functional group with highest priority and its location	3-one (when numbered from either side) In such a case, the direction of numbering is chosen so as to give the lowest possible numbers to the substituent groups.
Parent hydrocarbon name	pentane
Substituents with locations	1-hydroxy, 4-methyl
IUPAC name	1-hydroxy-4-methylpentan-3-one 1-hydroxy-4-methyl-3-pentanone

	
Longest carbon chain	5C atoms - pent
Functional group with highest priority and its location	3-ol (when numbered from either side) In this case, we should give the lowest possible number to the double bond.
Double/triple bond with location	1-ene
Parent hydrocarbon name	pent-1-ene (1-pentene)
Substituents with locations	none
IUPAC name	pent-1-en-3-ol 1-penten-3-ol

	
Longest carbon chain	5C atoms - pent
Functional group with highest priority and its location	3-one (when numbered from either side). The lowest possible number should be given to the double bond. Recall how the substituted alkene and alkynes were named.
Double/triple bond with location	1-ene
Parent hydrocarbon name	pent-1-ene (1-pentene)
Substituents with locations	5-hydroxy, 2,4-dimethyl
IUPAC name	5-hydroxy-2,4-dimethylpent-1-en-3-one 5-hydroxy-2,4-dimethyl-1-penten-3-one

	
Longest carbon chain	5C atoms - pent (not hex; the carbon chain should include the C=C).
Functional group with highest priority and its location	3-one
Double/triple bond with location	1-ene
Parent hydrocarbon name	pent-1-ene (1-pentene)
Substituents with locations	5-hydroxy, 2-ethyl, 4-methyl
IUPAC name	2-ethyl-5-hydroxy-4-methylpent-1-en-3-one 2-ethyl-5-hydroxy-4-methyl-1-penten-3-one

Let us now summarize the stepwise approach to build the IUPAC name of a compound (other than hydrocarbons).

1. Identify the longest hydrocarbon chain which includes the functional group having the highest priority (principal functional group) (Table 1.6) and any double or triple bonds.
2. Number the hydrocarbon chain:
   a. Such that the principal functional group gets the lowest possible number.
   b. If the principal functional group gets the same number when the hydrocarbon chain is numbered from different directions, then the direction giving the lowest possible number to the multiple bond is chosen.
   c. If the principal functional group gets the same number when the hydrocarbon chain is numbered from different directions and multiple bonds are absent, then the direction giving the lowest possible numbers to the substituents is chosen.
3. Derive the hydrocarbon name using the name designated for the number of C atoms and suffix for the saturation or unsaturation with its position number (ane, ene or yne).
4. Add the suffix designating the principal functional group.
5. Add prefixes designating the substituent groups along with their position numbers.
6. Then build the IUPAC name as follows:

Prefix	+	**Hydrocarbon name**	+	**Suffix**
Substituent groups with position numbers		Number of C atoms and suffix for the saturation or unsaturation with its position number		Class name of the principal functional group

Trivial Names

Prior to the development of systematic nomenclature organic compound were known by trivial (common) names. As the trivial names of common compounds are still used by chemists it is advisable to be familiar with these names. Trivial names of some common compounds and their corresponding IUPAC names are given in **Table 1.7.**

Table 1.7 Trivial names of some common compounds and their IUPAC names.

Compound	Trivial name	IUPAC name
CH_3COOH	acetic acid	ethanoic acid
CH_3CHO	acetaldehyde	ethanal
CH_3COCH_3	acetone	propanone
CH_3CN	acetonitrile	ethanenitrile
$HC{\equiv}CH$	acetylene	ethyne
$CHCl_3$	chloroform	trichloromethane
$HOCH_2CH_2OH$	ethylene glycol	ethane-1,2-diol
$HCHO$	formaldehyde	methanal
$HCOOH$	formic acid	methanoic acid

1.4 Isomerism

Isomerism is the existence of different compounds that have the **same molecular formula.** Different compounds having the same molecular formula are called isomers. Isomers can be subdivided into constitutional isomers and stereoisomers.

1.4.1 Constitutional (structural) isomerism

Isomers that differ from the order in which the constituent atoms are connected to each other are called **constitutional isomers.** Hence they have different structural formulae. A few examples of constitutional isomers are shown in **Table 1.8**.

Table 1.8 Some examples of constitutional isomers

Molecular formula	Constitutional isomers		
C_5H_{12}	$CH_3CH_2CH_2CH_2CH_3$	$CH_3CH(CH_3)CH_2CH_3$	$CH_3C(CH_3)_2CH_3$
C_3H_8O	$CH_3CH_2CH_2OH$	$CH_3CH(CH_3)OH$	$CH_3CH_2OCH_3$
C_4H_8O	$CH_3CH_2CH_2C(H)=O$	$CH_3CH(CH_3)C(H)=O$	$CH_3CH_2C(CH_3)=O$

Constitutional isomers are generally subdivided into *chain isomers, position isomers and functional group isomer*s. These subdivisions are not exclusive and can overlap.

Chain isomers: Chain isomers are those which have different hydrocarbon chains for same molecular formula **(Figure 1.10).**

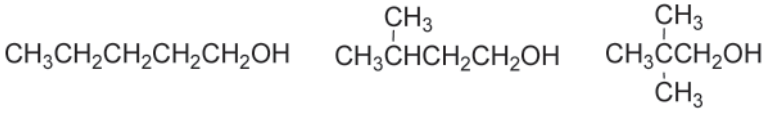
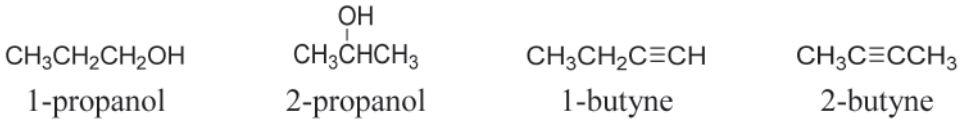


Figure 1.10 Chain isomers for the molecular formula $C_5H_{12}O$

Position isomers: Position isomers are those which have the same functional group and/or substituents in different positions in the same carbon chain **(Figure 1.11)**.



Position isomers for the molecular formula C_3H_8O

Position isomers for the molecular formula C_4H_6

Figure 1.11 Examples of position isomers

Functional group isomers: Functional group isomers are those which have different functional groups in compounds having the same molecular formula **(Figure 1.12).**



Functional group isomers for the molecular formula C_3H_8O

Functional group isomers for the molecular formula C_3H_6O

Figure 1.12 Examples of functional group isomers

Chain isomerism, position isomerism and functional group isomerism can overlap. Take a look at the isomers which have been drawn for the molecular formula C_4H_8O **(Figure 1.13)**.

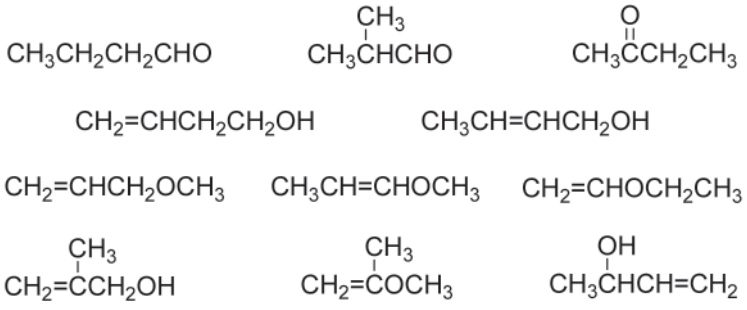


Figure 1.13 Constitutional isomers for the molecular formula C_4H_8O

1.4.2 Stereoisomerism

Stereoisomerism is the existence of compounds whose structures differ from each other only in the orientation of bonds in three-dimensional space. **Stereoisomers** have the same structural formulae. They have the same connectivity: their constituent atoms are connected in the same order but differ in the manner in which atoms or groups are arranged in three-dimensional space. Therefore their structures cannot be **superimposed** on each other even though they have the same molecular and structural formulae. Pair of stereoisomers whose three-dimensional structures are mirror images of each other are **enantiomers** of each other. Pairs of stereoisomers whose three-dimensional structures are not mirror images of each other are **diastereomers** of each other.

The different types of isomers described above and their classification is shown in **Figure 1.14.**

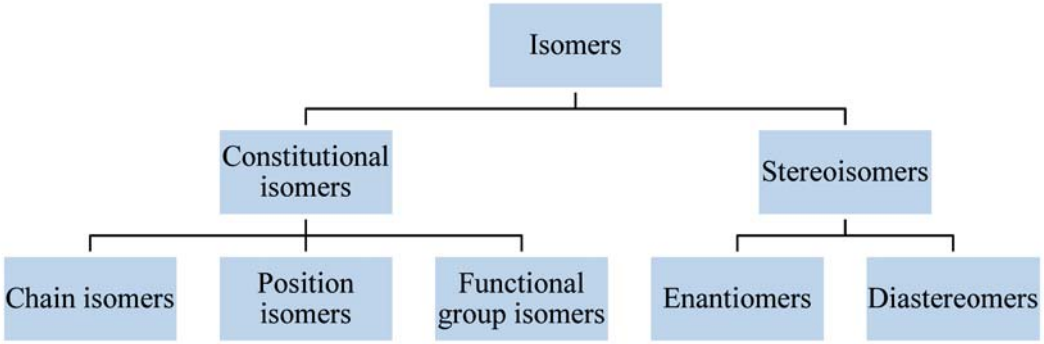
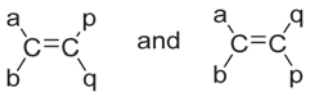


Figure 1.14 Classification of isomers

Diastereomerism

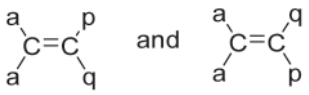
Geometric isomerism is one occasion where diastereomerism is seen. A C=C double bond consists of a σ-bond and a π-bond. Due to the π bond, the two carbon atoms cannot freely rotate about the σ-bond. Both alkene carbon atoms and the four atoms attached to them are all in one plane. For geometrical isomers to exist, the two groups attached to each carbon atom of the double bond should not be identical. In such an instance it is possible to have two compounds which differ from each other in the spatial arrangements of the groups joined to the two carbon atoms. These two compounds cannot be superimposed on each other and cannot interconvert by rotation around the carbon-carbon bond axis (due to the π-bond). Such compounds are known as geometrical isomers.

For example,



are diastereoisomers because the structures cannot be superimposed on each other.

However,



are the same because the structures can be superimposed on each other.

***Cis* and *trans* nomenclature**

In alkenes the words *cis* and *trans* are used to indicate the geometrical relationship of two groups attached to different carbon atoms in the same double bond. Consider a plane passing through the C=C which is perpendicular to the plane of the molecule (See Figure 1.15). If the two groups are on the same side of this plane, then the relationship is *cis*. Observe that in **Figure 1.15** the two H-atoms are *cis* to each other and the two methyls are also *cis* to each other.

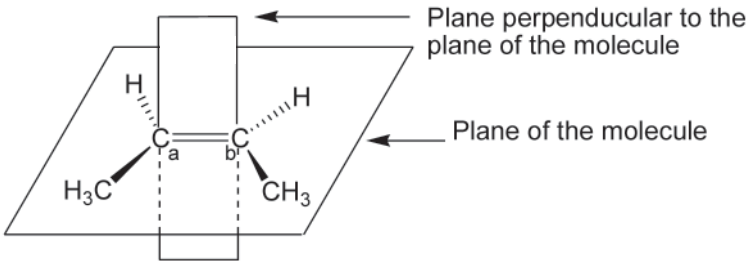


Figure 1.15 *cis*-2-butene showing the plane perpendicular to the plane of the molecule

If the two groups are on opposite sides of the plane then the relationship is *trans.* Observe that H atom on C_a is *trans* to the methyl group on C_b (see **Figure 1.16**).

Note that the geometrical isomer of *cis*-2-butene is *trans*-2-butene in which the two methyl groups are *trans* to each other (the two H atoms are also *trans* to each other).

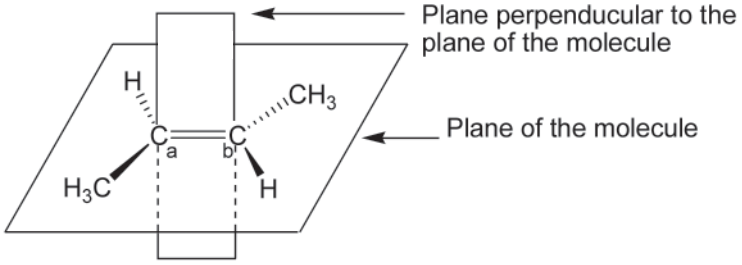


Figure 1.16 *trans*-2-butene

Enantiomerism

Isomers which are mirror images of each other are known as enantiomers (see **Figure 1.17**). A compound having a carbon atom which is joined to four different groups shows enantiomerism. Such a carbon atom is known as an asymmetric or chiral carbon atom. When plane polarized light is passed through a solution containing only one enantiomer, the plane of polarization rotates.

One enantiomer rotates the plane of polarization in one direction and the other enantiomer in the opposite direction. As the enantiomers rotate the plane of polarization, they are also known as optical isomers. Compounds which rotate the plane of plane polarized light are known as optically active compounds.

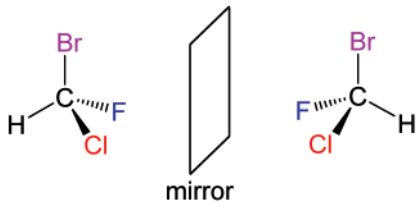
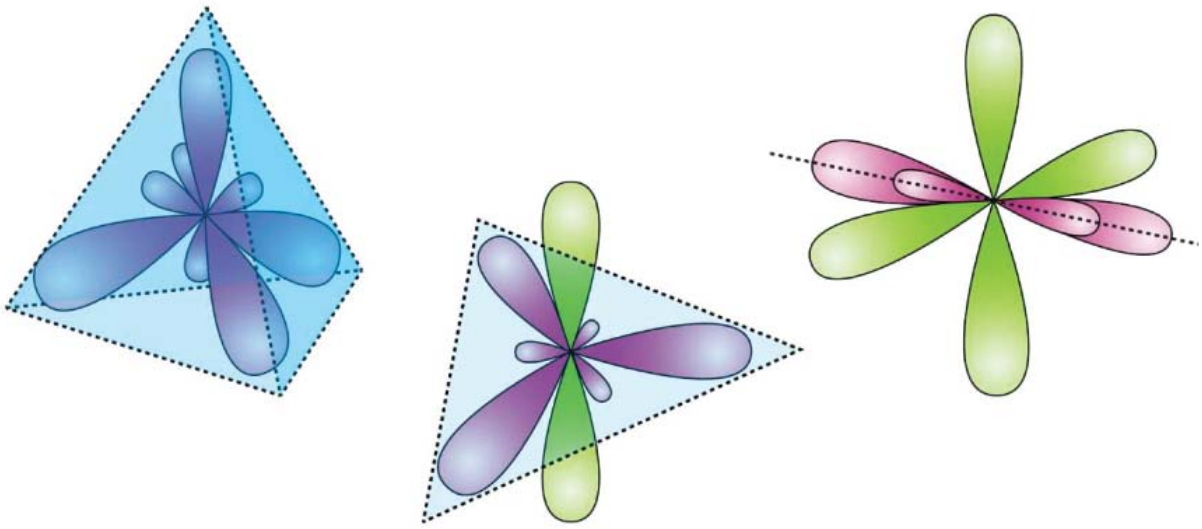


Figure 1.17 Enantiomers of bromochlorofluoromethane

Observe that the above mirror images of each other are not superimposable.

Note: *Stereoisomers which are not mirror images of each other are known as diastereomers. Therefore geometrical isomers are diastereomers.*



2. Hydrocarbons & Halohydrocarbons

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Introduction

Hydrocarbons are compounds containing only carbon and hydrogen. We have already discussed that aliphatic hydrocarbons are classified as alkanes, alkenes and alkynes. Halohydrocarbons are compounds containing one or more halogen atoms in addition to carbon and hydrogen.

2.1 Structure, physical properties and nature of bonds of aliphatic hydrocarbons

Alkane hydrocarbons are saturated hydrocarbons. Only carbon-hydrogen and carbon-carbon single bonds are found in these compounds. Methane (CH_4) is the simplest alkane hydrocarbon and it contains only one carbon atom. There are four hydrogen atoms attached to this carbon atom by four single bonds. The alkane which contains two carbon atoms is ethane (C_2H_6). In ethane the two carbons are bonded to each other with a single bond and each of these carbon atoms is bonded to three hydrogen atoms. The alkane with three carbon atoms is propane (C_3H_8). It will be noticed that the formula of ethane differs from that of methane by CH_2, and that the formula of propane differs from that of ethane also by CH_2. If two consecutive members of a series of compounds differ only by a CH_2 unit, such a series of compounds is called a homologous series.

A homologous series is a series of compounds with similar chemical properties which share the same general formula in which consecutive members of a series of compounds differ only by a CH_2 unit. The general formula of an alkane is C_nH_{2n+2} (where n = 1, 2, 3, ...) and all alkanes except cyclic alkanes follow this general formula.

2.1.1 Properties of alkanes

An alkane molecule is non-polar or very weakly polar. The attractive forces between two non-polar molecules are the dispersion forces. While the first few members of the series are gases at room temperature, the higher members are liquids and solids. As a result of increase in surface area down the series, dispersion forces also increase. While this leads to the aforesaid variation in the physical states of hydrocarbons, it also results in increase of the boiling points and melting points of unbranched hydrocarbons with the increase in molecular weight **(Table 2.1).**

Table 2.1 Melting points, boiling points and densities of some straight chain alkanes, showing regular increase of the property with the carbon number

Name	Formula	Melting point/ °C	Boiling point/ °C	Density (at 20 °C)/ g cm^{-3}
methane	CH_4	-183	-162	
ethane	CH_3CH_3	-172	-88.5	
propane	$CH_3CH_2CH_3$	-187	-42	
butane	$CH_3(CH_2)_2CH_3$	-138	-0.5	
pentane	$CH_3(CH_2)_3CH_3$	-130	36	0.626

Name	Formula	Melting point/ °C	Boiling point/ °C	Density (at 20 °C)/ g cm^{-3}
hexane	$CH_3(CH_2)_4CH_3$	-95	69	0.659
heptane	$CH_3(CH_2)_5CH_3$	-90.5	98	0.659
octane	$CH_3(CH_2)_6CH_3$	- 57	126	0.659
nonane	$CH_3(CH_2)_7CH_3$	- 54	151	0.718
decane	$CH_3(CH_2)_8CH_3$	- 30	174	0.730

With branching of the carbon chain the surface area of a molecules decreases and consequently dispersion forces become weaker and the boiling point decreases. As can be seen from the data given in **Table 2.2** the boiling points of alkanes with five carbon atoms decrease with the increase in branching of the carbon chain.

Table 2.2 Reduction of boiling points of isomeric pentanes as the branching occurs

Compound	Boiling point/ °C
pentane	36
2-methylbutane	28
2,2-dimethylpropane	9

2.1.2 Structure of alkanes

Let us consider the bonding of the simplest alkane, methane (CH_4). The carbon atom forms four covalent bonds with four hydrogen atoms. A covalent bond is formed by the overlap of two orbitals of two different atoms, each of which contains one electron. As the carbon atom in its ground state has only two *p* orbitals (p_x and p_y) containing one electron each, it could form only two covalent bonds at right angles to each other (recall that electronic configuration of C in its ground state is $1s^2\,2s^2\,2p^2$). If the two electrons in the 2*s* orbital are unpaired and one electron is promoted to the p_z orbital, then the carbon atom would have four orbitals, each containing one electron to form four bonds to four hydrogen atoms. The energy required to unpair and promote an electron could be compensated by the energy released by the formation of two extra bonds.

However, this overlap would result in a CH_4 molecule where three of the C–H bonds will be at right angles to each other and one C-H bond will not have any directionality. This would lead to a methane molecule which would have two types of C–H bonds. In order to explain the fact that in methane all four C–H bonds are equivalent, the 2*s* orbital and the three 2*p* orbitals are considered to be mixed with each other, to generate four equivalent orbitals pointing to the apices of a tetrahedron **(Figure 2.1)**.

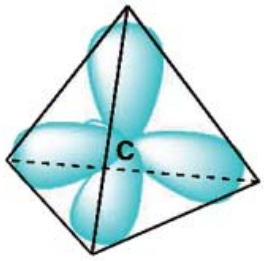


Figure 2.1 Shape and arrangement of sp^3 hybrid orbitals of carbon

The mixing of orbitals to generate new orbitals is termed 'hybridization'. The new orbitals are termed hybrid orbitals to differentiate them from pure atomic orbitals. In methane, the four hybrid orbitals of carbon are called sp^3 hybrid orbitals as one *s* orbital and three *p* orbitals are mixed to generate them. Such carbon atoms are referred to as **'*sp*^{3} hybridized carbon'**. The energy of the sp^3 hybrid orbitals lies between the energy of the *s* orbital and the *p* orbitals **(Figure 2.2)**.

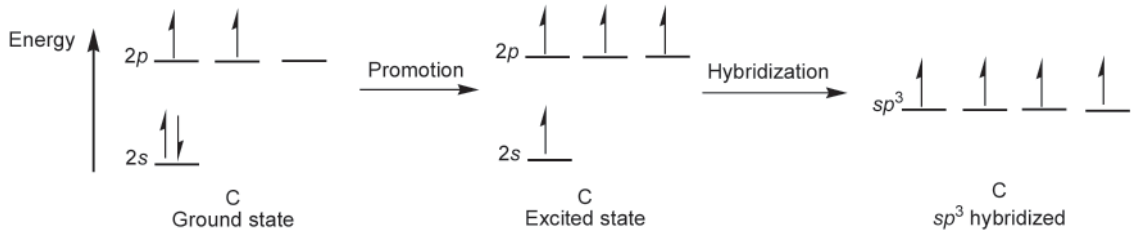


Figure 2.2 Graphical representation of hybridization of carbon in methane

In methane each of these four sp^3 hybridized orbitals overlap with *s* orbital of H atoms and forms four C–H bonds. The angle between any of these two C–H bonds is 109.5° and the four H atoms of methane are located at the apices of a tetrahedron **(Figure 2.3)**.

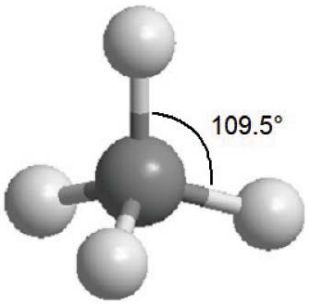


Figure 2.3 Tetrahedral shape of methane (CH_4) molecule

All carbon atoms joined to four other atoms in any organic compound are considered sp^3 hybridized. In alkanes, the carbon-hydrogen bonds are formed by the overlap of a sp^3 hybrid orbital of carbon with a 1*s* orbital of hydrogen while the carbon-carbon bonds are formed by the overlap of two sp^3 hybrid orbitals of two carbon atoms **(Figure 2.4)**.

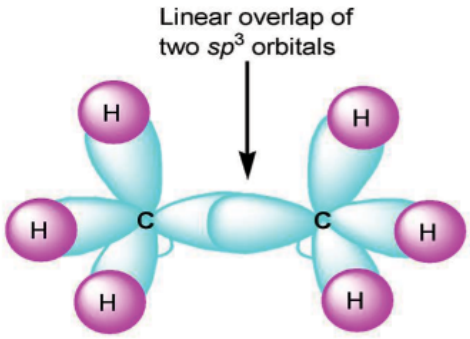


Figure 2.4 Structure of ethane showing overlap of orbitals to form C–C and C–H bonds

The overlap of the two sp^3 orbitals to form the carbon-carbon bond takes place along the direction of the orbitals. Such an overlap is called a **linear overlap** and results in the formation of a **σ bond.**

2.1.3 Properties of alkenes and alkynes

Both alkene and alkyne hydrocarbons are unsaturated compounds. Alkenes contain at least one carbon-carbon double bond while alkynes contain at least one carbon-carbon triple bond. Acyclic alkenes with one double bond but without any other functional group form the homologous series of alkenes with the general formula C_nH_{2n}. Alkynes with one triple bond and without any other functional group form the homologous series of alkynes with the general formula C_nH_{2n-2}.

Carbon-carbon double bond of an alkene and carbon-carbon triple bond in alkyne are stronger and shorter than a carbon-carbon single bond **(Table 2.3)**.

Table 2.3 Bond energies and bond lengths of carbon-carbon single, double and triple bonds

Bond	Bond energy/ kJ mol^{-1}	Bond length/ pm
C–C	347	154
C=C	611	133
C≡C	839	120

Alkenes show boiling points very similar to those of alkanes with the same number of C atoms. Ethene, propene and the isomeric butenes are gases at room temperature. All the rest are liquids. As with alkanes, boiling points of alkenes increase with the increase of molecular mass (chain length). Intermolecular forces of alkenes become stronger with increase in the size of the molecules. As the polarity of alkynes is also low, their physical properties are very similar to those of the corresponding alkanes and alkenes.

2.1.4 Structure of alkenes

Ethene (C_2H_4) is the simplest alkene. It contains a carbon-carbon double bond. Each carbon atom in ethene is sp^2 hybridized and forms three equivalent sp^2 hybrid orbitals which lie in the same plane and point to the three corners of an equilateral triangle **(Figure 2.5)**. The unhybridized *p* orbital lies perpendicular (90º) to this plane.

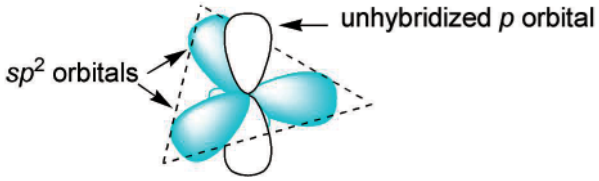


Figure 2.5 Shape and arrangement of sp^2 hybrid orbitals an unhybridized *p* orbital of carbon

These sp^2 orbitals are formed by mixing of the 2*s* orbital with two 2*p* orbitals leaving one unhybridized *p* orbital **(Figure 2.6)**.

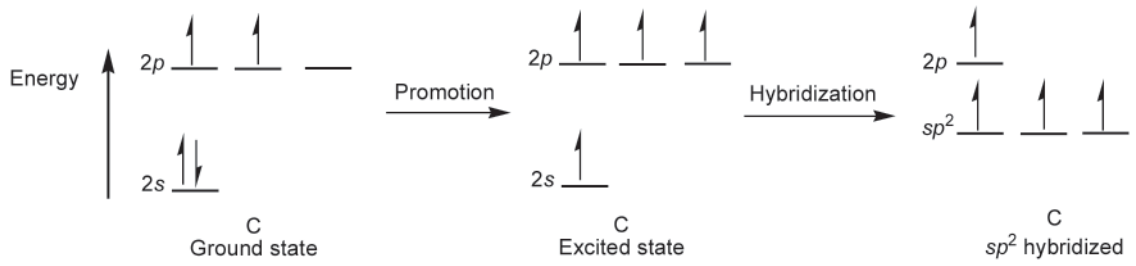


Figure 2.6 Graphical representation of sp^2 hybridization of carbon in ethane

In ethene each carbon uses two sp^2 orbitals to form two C–H bonds each. The remaining sp^2 orbital in each carbon is used to form a carbon-carbon σ bond by linear overlap. The unhybridized *p* orbitals of each carbon atom which are parallel to each other overlap laterally to form another carbon-carbon bond. This bond formed by the lateral overlap of *p* orbitals is called a π bond. All alkenes contain a carbon-carbon double bond which consists of a σ bond and a π bond. The π bond is weaker than the σ bond **(Figure 2.7)**.

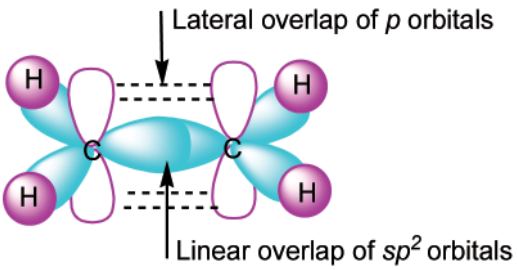


Figure 2.7 Structure of ethene showing overlap of orbitals to form C–C and C–H bonds

The 2 carbon atoms used to form the double bond and the four atoms attached directly to them lie in the same plane. The angle between any two atoms attached to the sp^2 hybridized carbon will be 120° **(Figure 2.8).**

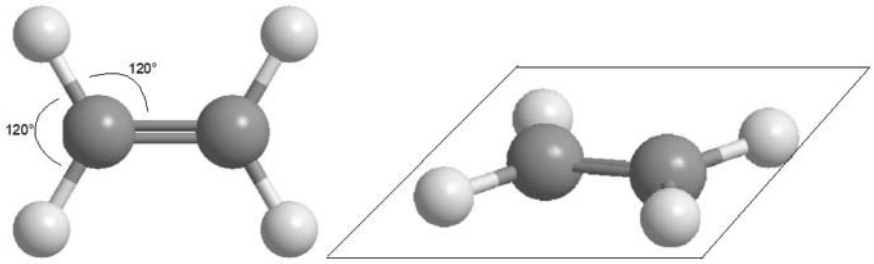


Figure 2.8 Planar shape of ethene (C_2H_4) molecule

2.1.5 Structure of alkynes

Ethyne (C_2H_2) is the simplest alkyne. It contains a carbon-carbon triple bond. Each carbon atom in ethyne is *sp* hybridized and forms two equivalent *sp* hybrid orbitals which lie in the same straight line and point in opposite directions **(Figure 2.9)**. The two unhybridized *p* orbitals lie perpendicular (90º) to each other and to these two *sp* orbitals.

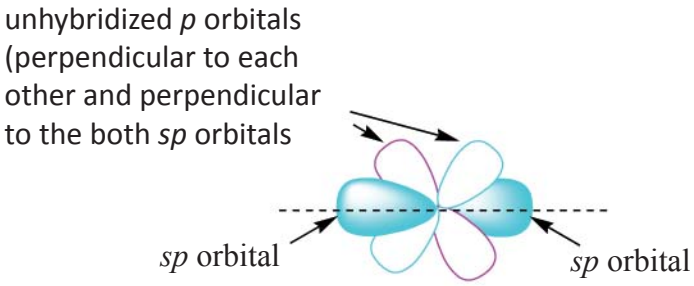


Figure 2.9 Shape and arrangement of *sp* hybrid orbital and unhybridized *p* orbitals of carbon

These *sp* orbitals are formed by mixing of the *2s* orbital with one *2p* orbital leaving two unhybridized *p* orbitals **(Figure 2.10)**.

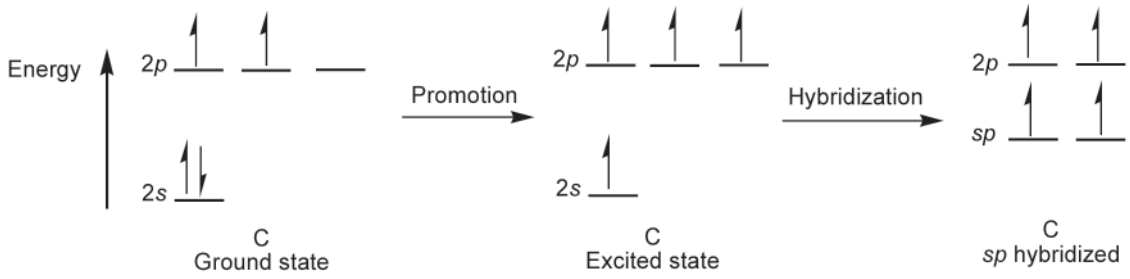


Figure 2.10 Graphical representation of *sp* hybridization of carbon in ethyne

In ethyne each carbon uses one *sp* orbital to form a C–H bond each. The remaining *sp* orbital in each carbon is used to form a carbon-carbon σ bond by linear overlap. The two unhybridized

p orbitals of each carbon atom overlap laterally to form another two carbon-carbon bonds (two π bonds). Thus all alkynes contain a carbon-carbon triple bond which consists of a σ bond and two π bonds **(Figure 2.11)**.

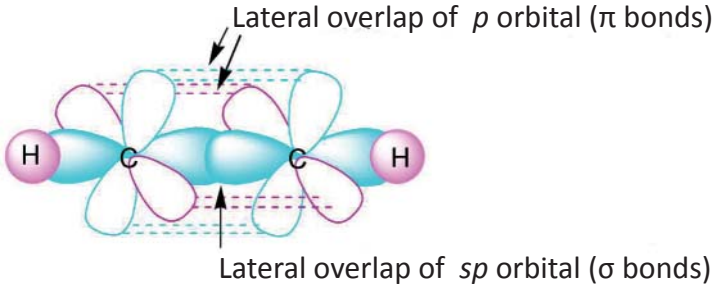


Figure 2.11 Structure of ethyne showing overlap of orbitals to form C–C and C–H bonds

The 2 carbon atoms used to form the triple bond and the two atoms attached directly to them lie in the same straight line. The angle between the two atoms attached to the *sp* hybridized carbon will be 180° **(Figure 2.12)**.

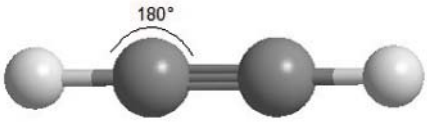


Figure 2.12 Linear shape of ethyne (C_2H_2) molecule

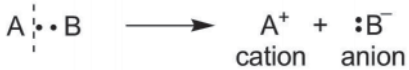
2.2 Chemical reactions of alkanes, alkenes and alkynes in terms of their structures

Covalent bond cleavage during organic reactions

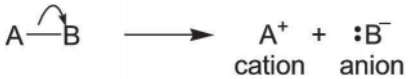
Any organic reaction involves the cleavage (breaking) and formation of covalent bonds. Bond cleavage can take place in two different ways.

(i) Heterolytic cleavage

In heterolytic cleavage the two electrons involved in the bond will remain with one of the atoms (the more electronegative atom). This will result in a positively charged species (cation) and a negatively charged species (anion).

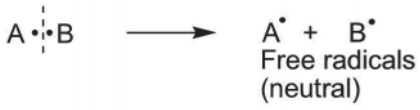


When writing mechanisms, heterolytic cleavage is shown by a curved arrow which indicates the movement of a pair of electrons.



(ii) Homolytic cleavage

In homolytic cleavage the two electrons involved in the bond will be equally divided such that one electron will remain with each atom. This will result in two neutral species each having one unpaired electron. Such species are called free radicals.



When writing mechanisms, homolytic cleavage is shown by a pair of fishhooks. Each fishhook indicates the movement of a single electron.



2.2.1 Reactions of alkanes

In alkanes all the bonds are either C–C or C–H bonds. Because the polarity of those C–C and C–H bonds is low, alkanes do not have atoms which bear high positive (electron deficient) or negative charges (electron rich). Therefore, they do not react with common polar reagents such as OH^-, CN^-, H^+ under normal conditions.

2.2.1.1 Chlorination of alkanes

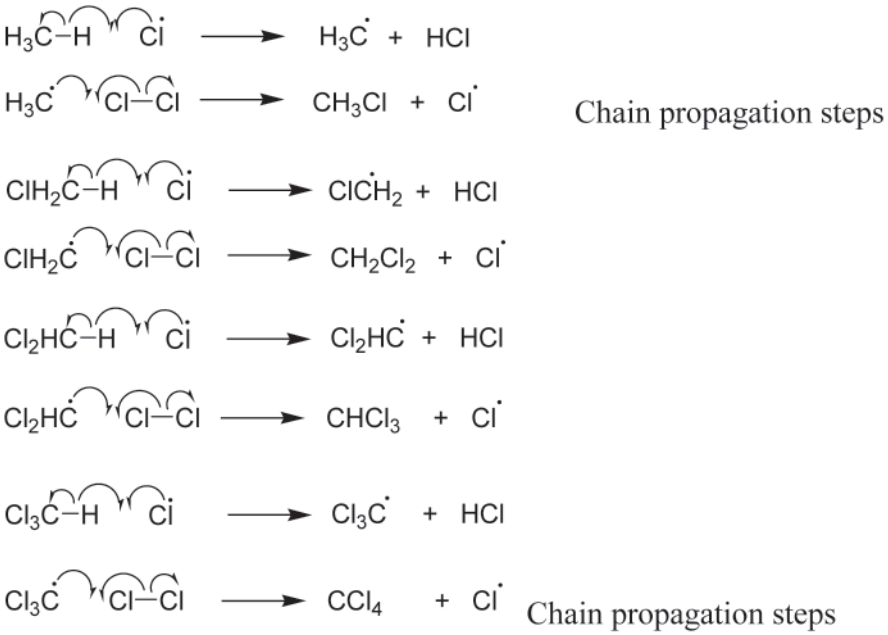
Although alkanes do not react with common polar reagents, they tend to react with free radicals by homolytic cleavage of C–H bonds. For example, alkanes react with reagents such as chlorine and bromine free radicals (Cl atoms and Br atoms) which can be generated by the homolytic cleavage Cl_2 and Br_2. This can be achieved by irradiation of Cl_2 or Br_2 with ultra-violet light. Thus, methane in the presence of ultra-violet light reacts with Cl_2 to give a mixture of chloromethanes, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4. These products are formed by a sequence of reactions where the product of one reaction, becomes the starting material for the subsequent reaction of the sequence. Such reactions are called **chain reactions**.

The mechanism of the reaction is given below. The first step of the reaction is the formation of chlorine free radicals by the homolysis of the covalent bond between two chlorine atoms. This is called the **chain initiation step**.



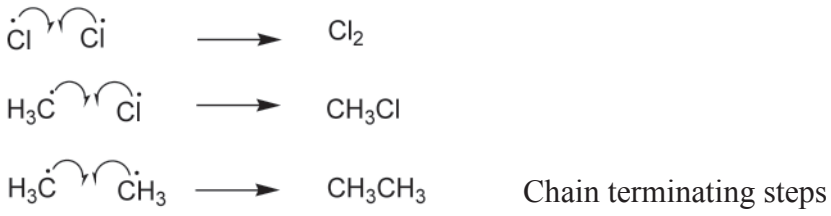
Chain initiation step

The chlorine free radical reacts with CH_4 to produce methyl free radical ($\bullet CH_3$). The methyl free radical reacts with another molecule of chlorine (Cl_2) producing CH_3Cl and $Cl^\bullet$. The chlorine radical produced in this step can react either with a molecule of CH_4 or a molecule of CH_3Cl to produce the corresponding carbon free radicals as shown in the reaction sequence given below.



These steps are called **chain propagation steps.** In these chain propagation steps, free radicals are used and are also generated. Therefore the reaction sequence can proceed without stopping until all the H atoms in CH_4 are replaced by Cl. The carbon free radicals produced in this reaction sequence are called **reactive intermediates** in the free radical chlorination of methane.

A chain reaction can be stopped by **chain terminating reactions**. There are many chain terminating reactions (steps) that can occur during a chain reaction. In these chain terminating reactions the radicals are used but not generated. A few such chain terminating reactions are shown below.



It should be noted that, as free radical chlorination (and bromination) of alkanes produces a mixture of products, it is of limited use in the synthesis of chloro or bromo hydrocarbons in the laboratory.

2.2.2 Reactions of alkenes

The reactions of alkenes take place at the carbon-carbon double bond. Carbon-carbon double bond is formed from a σ bond and a π bond. The double bond of an alkene is an electron rich area due to the presence of the pi-electron cloud above and below the plane of the alkene. Therefore it can attract a species which can accept a pair of electrons. Such species are electron deficient and are known as **electrophiles**.

As each of the doubly bonded C atoms is bonded only to three atoms, they are unsaturated and another atom can be attached (added) to each of these two carbon atoms during a reaction.

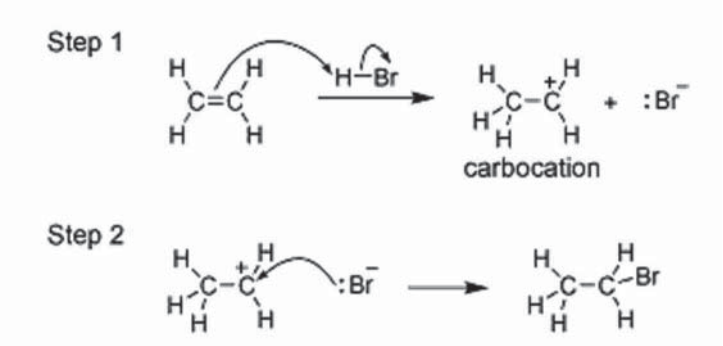
Therefore the typical reactions of alkenes are **electrophilic addition reactions**. Let us study the electrophilic addition reaction with its mechanism, using a few examples.

2.2.2.1 Addition of hydrogen halides (HCl, HBr or HI)

The electron deficient pole of a hydrogen halide molecule is H (eg. $H^{\delta+}$– $Br^{\delta-}$). This acts as an electrophile and reacts initially with the double bond. During the reaction the H-Br bond breaks releasing a Br- ion. Thus, the H reacts as if it was a H^+ ion and forms a bond with carbon using the two electrons from the π-bond.

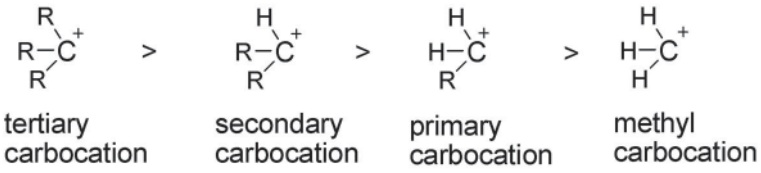
During these electrophilic addition reactions, intermediate carbocations are formed *(Carbocations are electron deficient positively charged trivalent carbon species).*

Let us look at the mechanism of addition of HBr to ethene. The reaction proceeds in two steps.

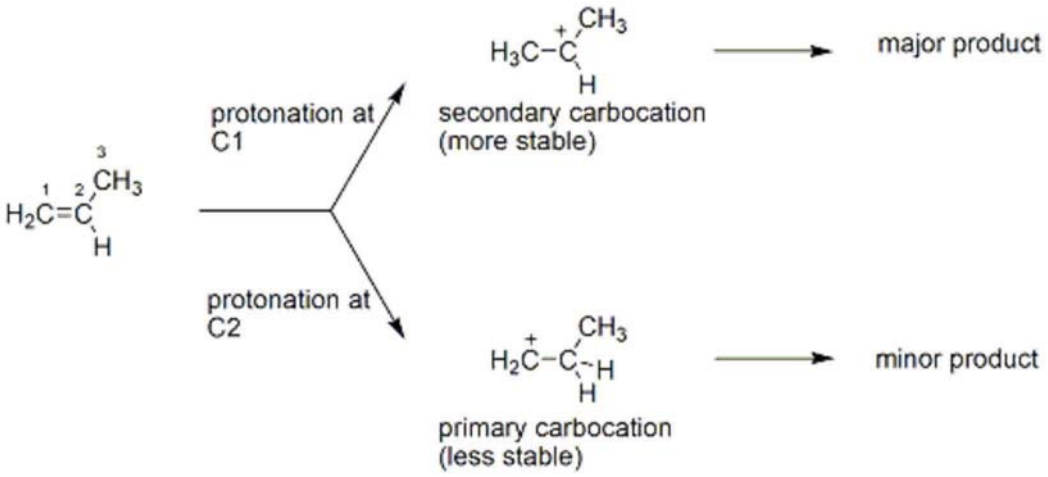


Carbocations are classified as primary, secondary and tertiary carbocations depending on the number of hydrogen atoms attached to the positively charged carbon atom.

Stability of these carbocations follows the order shown below.

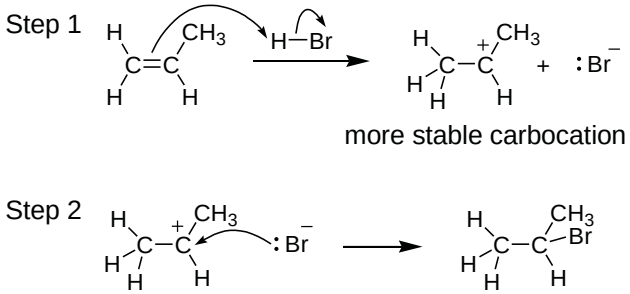


When alkyl groups are attached to the positively charged C atom of the carbocation, stability of the carbocation increases. The reason for this is the release of electrons by the alkyl groups through C–C bonds towards the positively charged carbon atom to which they are attached. This results in spreading the positive charge thereby stabilizing the ion. When asymmetrically substituted alkenes undergo electrophilic addition reactions with hydrogen halides, two different carbocations can be formed after the bonding of the electrophile (H^+). The more stable of these two carbocations forms more easily. Let us take addition of HBr to propene as an example.

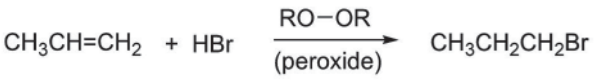


The more stable carbocation is obtained when the electrophile gets attached to the carbon atom to which the higher number of hydrogen atoms is attached. This is the explanation for 'Markovnikov's rule' which states that when a protic acid HX adds to an asymmetric alkene, the H adds to the carbon atom bonded to the higher number of H atoms.

The mechanism of addition of HBr to propene can be shown as follows.



Hydrogen bromide adds in the opposite way to this rule (anti-Markovnikov addition) when there are peroxides in the reaction medium (i.e. the H adds to the carbon bonded to the lower number of H atoms). The reason for this is that in the presence of peroxides the reaction between hydrogen bromide (HBr) and the alkenes takes place via a free radical mechanism and not the ionic mechanism described above. *A description of the mechanism of this reaction is not expected.* It is to be noted that the direction of addition of HCl and HI is not changed in the presence of peroxides.

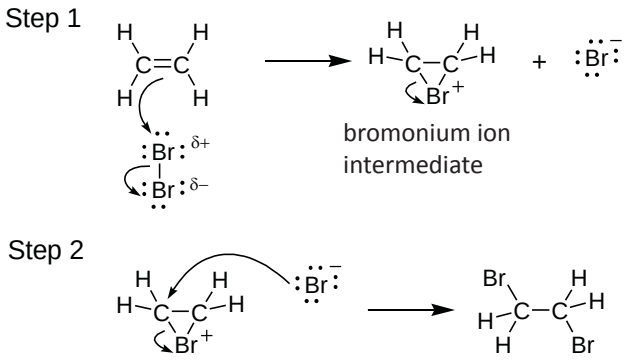


2.2.2.2 Addition of bromine to alkenes

Bromine is a not a polar molecule, but polarity is induced in it during the reaction with alkenes. When a bromine molecule approaches the electron rich double bond, a dipole is induced with the Br atom closer to the pi-bond having a partial positive charge. In the first step of the reaction, this Br atom reacts with the double bond and forms a bromonium ion, which is a three membered cyclic intermediate with a positive charge on the Br atom.

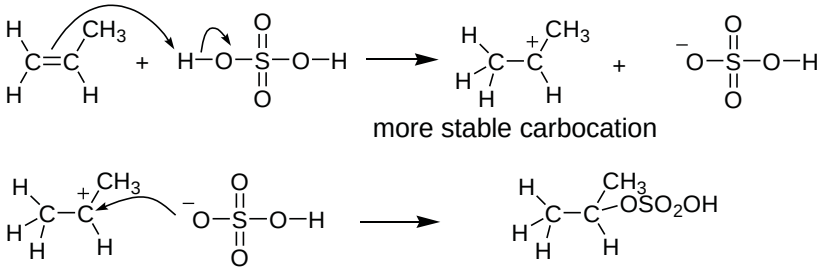
In the second step of the reaction, a bromide ion (Br^-) acting as a nucleophile, forms a bond to one of the carbon atoms bonded to Br^+. The bond formed by that carbon atom to Br^+ is broken during this step, giving an open chain structure again.

The mechanism is as follows.

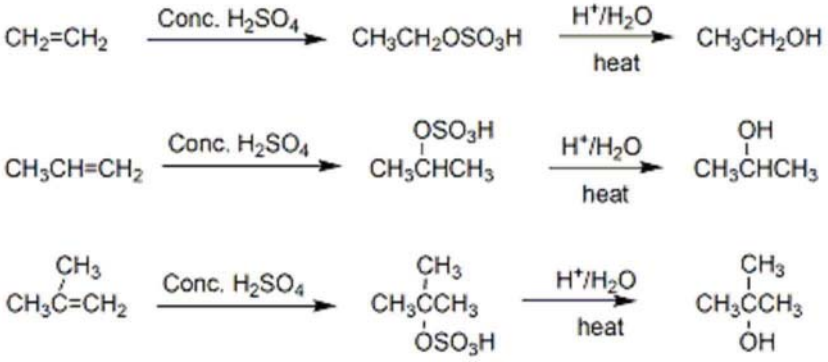


2.2.2.3 Addition of sulphuric acid and the hydrolysis of the addition product

Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphates. The reaction is an electrophilic addition reaction and proceeds *via* a carbocation intermediate as in the case of the addition of HBr.



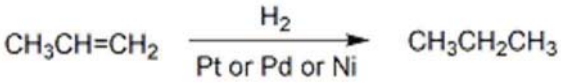
The reaction is carried out by passing the gaseous alkene through cold concentrated H_2SO_4 or stirring the liquid alkene with the cold concentrated H_2SO_4. When the solutions of alkyl hydrogen sulphates are diluted with water and heated, they undergo hydrolysis to give an alcohol bearing the same alkyl group as the original alkyl hydrogen sulphate. Let us look at few examples of this reaction.



It is seen that the final product of this sequence of reactions is the alcohol that would be obtained by the Markovnikov addition of water (H-OH) to the alkene. The same products can be obtained directly by the direct addition of water to alkenes in the presence of dilute sulphuric acid. However the preparation of ethanol by direct addition of water to ethylene is difficult under laboratory conditions.

2.2.2.4 Catalytic addition of hydrogen (Hydrogenation)

In the presence of catalysts such as finely powdered Pt, Pd or Ni, alkenes react with hydrogen to produce alkanes.



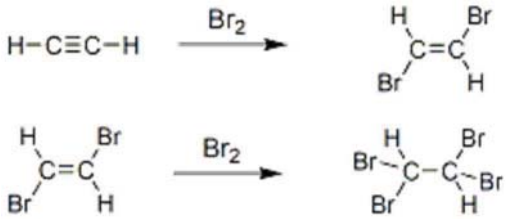
2.2.2.5 Reaction of alkenes with cold, alkaline, dilute potassium permanganate

Alkenes react with cold, alkaline, dilute $KMnO_4$ solution to produce diols (glycols). When this reaction takes place the purple colour of permanganate is disappeared and a brown precipitate of MnO_2 is formed. This reaction is used as a test for unsaturation (carbon-carbon double bonds and triple bonds). This is named as Baeyer test for unsaturation. However easily oxidisable substances such as aldehydes will also answer this test.

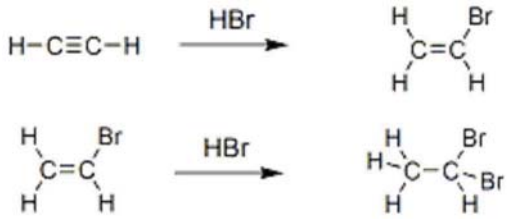
2.2.3 Reactions of alkynes

Alkynes have a triple bond which consists of one sigma bond and two π bonds. Alkynes also undergo electrophilic addition reactions with reagents that add to alkenes. The two pi-bonds react independently of each other.

2.2.3.1 Addition of bromine

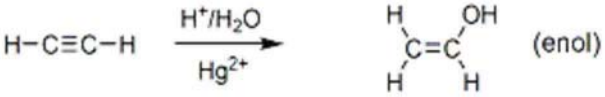


2.2.3.2 Addition of hydrogen halides

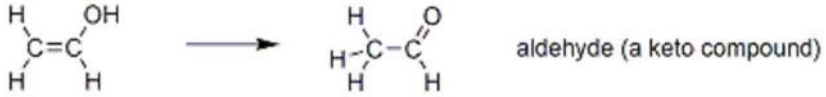


2.2.3.3 Addition of water

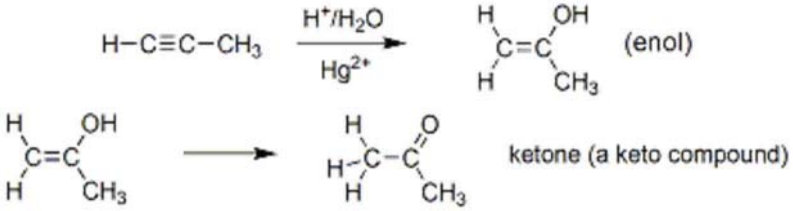
In the presence of Hg^{2+} and dilute H_2SO_4, one molecule of water adds to an alkyne producing an enol. A molecule containing a hydroxyl group attached to a carbon atom in a carbon-carbon double bond is known as an **enol.**



Enols are unstable and rapidly rearrange to a more stable keto form (aldehydes or ketones)

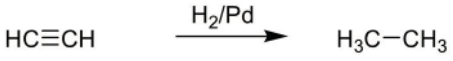


The addition of water to alkynes takes place according to the Markovnikov's rule as shown below by the reaction of propyne.

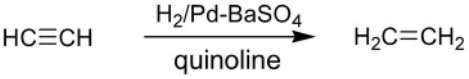


2.2.3.4 Catalytic addition of hydrogen (Hydrogenation)

Alkynes react with hydrogen in the presence of catalysts such as Pt, Pd or Ni to give alkanes.



During this reaction the alkyne is first reduced to the alkene which is further reduced to the alkane under the reaction conditions. The reaction can be stopped at the alkene stage by using a less active catalyst. Very often, Pd catalyst deposited on $BaSO_4$ deactivated (poisoned) by quinoline is used.



2.2.4 Acidic nature of alkynes with terminal hydrogen

The triple bond C atoms are *sp* hybridized. A C-H bond involving a triple bond carbon is formed by the linear overlap of a *sp* orbital of C and a *s* orbital of H.

Since a *sp* orbital has more *s* character (50% *s* character) than sp^2 or sp^3 orbitals, the bonding electrons in the C–H bond of alkynes are closer to the carbon nucleus than in the case of C–H bonds in alkenes and alkanes. Therefore the H attached to a triple bond carbon has a higher acidity than the H in alkene or alkane C–H bonds. However, the acidity of H attached to terminal alkynes is less than that of water and alcohol.

The H of a terminal alkyne can react as H^+ with strong bases such as $NaNH_2$ and active metals such as Na. The resulting acetylide anion is stable because the two non-bonded electrons (negatively charged) are close to the carbon nucleus (positively charged).

$$H_3C-C\equiv C-H \xrightarrow{Na} H_3C-C\equiv C^- Na^+ + H_2$$

$$H_3C-C\equiv C-H \xrightarrow{NaNH_2} H_3C-C\equiv C^- Na^+ + NH_3$$

Terminal alkynes react with certain heavy metal ions such as Ag^+ and Cu^+ to form insoluble metal acetylides. These two reactions can be used to identify terminal alkynes.

$$H_3C-C\equiv C-H \xrightarrow{NH_3/Cu_2Cl_2} H_3C-C\equiv C-Cu\downarrow$$

$$H_3C-C\equiv C-H \xrightarrow{NH_3/AgNO_3} H_3C-C\equiv C-Ag\downarrow$$

2.3 The nature of bonding in benzene

The molecular formula of benzene is C_6H_6 which indicates that it is an unsaturated compound. Under normal conditions benzene does not answer the tests for unsaturation. Therefore, benzene cannot have a structure similar to that of a simple alkene or an alkyne.

2.3.1 Structure of benzene

The structure proposed for benzene by Kekulé contained a six-membered ring of carbon atoms with alternating three double and three single bonds **(Figure 2.13)**.

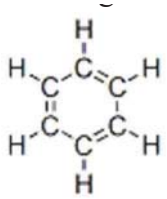
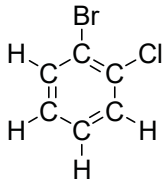


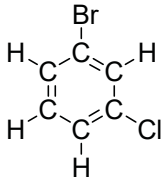
Figure 2.13 Structure of benzene proposed by Kekulé in 1865

This structure was based on the evidence available regarding the relationships of aromatic isomeric compounds. No isomer has been found for any mono-substituted benzene (C_6H_5X; X= $-CH_3$, $-C_2H_5$, -OH, -Cl, -Br, -CHO etc.), implying that all six atoms in benzene are equivalent. Therefore substitution at any one carbon atom will always give a single compound.

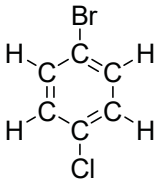
It was found that there are three isomeric disubstituted benzenes. Kekulé proposed structures with 1,2-disubstitution, 1,3-disubstitution and 1,4-disubstitution **(Figure 2.14)**, later named as -*ortho,* -*meta* and -*para* isomers.



1,2-bromochlorobenzene
(*ortho*-bromochlorobenzene)



1,3-bromochlorobenzene
(*meta*-bromochlorobenzene)



1,4-bromochlorobenzene
(*para*-bromochlorobenzene)

Figure 2.14 Three isomeric disubstituted benzenes

However these structures implied that two distinct *ortho*- disubstituted benzenes are possible, depending on whether the substituted carbons are separated by a double bond or a single bond. Since two different *ortho*- isomers have never been found, Kekulé proposed that benzene molecule could be represented by two equivalent structures which are in equilibrium **(Figure 2.15)** so that single and double bonds continually interchange positions.



Figure 2.15 Proposed rapid equilibrium of two equivalent structures of *ortho*-bromochlorobenzene

This proposal explains that benzene has two possible structures and that both of them exist at room temperature. However, no experimental evidence has been found for the existence of two such structures for benzene.

Further the bond length between any two adjacent carbon atoms in benzene is the same. The carbon-carbon bond length of benzene is 1.39×10^{-10} m which is in-between the length of a carbon-carbon double bond (1.34×10^{-10} m) and the length of a carbon-carbon single bond (1.54×10^{-10} m).

The structure of benzene is now considered to be a resonance hybrid of two structures as given in **Figure 2.16**.

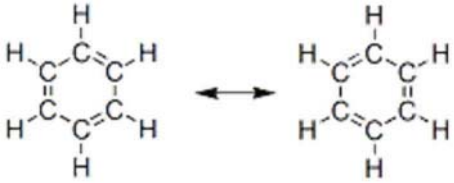


Figure 2.16 Resonance structures of benzene

For convenience, the resonance hybrid of benzene is written as shown below.



Take note of the difference between the resonance sign (the double headed arrow) and the equilibrium sign. In an equilibrium, the compounds shown by structures really exist while in the concept of a resonance hybrid, none of the compounds represented by the structures really exist. They are drawn because there is no other way of representing the real molecule. Each structure contributes to the real structure of the compound. The extent of contribution depends on the relative stability of each resonance structure with the more stable structure making a larger contribution to the real structure. In the case of benzene, both structures have the same stability and contribute equally.

All C atoms of benzene are sp^2 hybridized. Each carbon bears an unhybridized *p* orbital which can overlap with the unhybridized *p* orbitals on either sides of it **(Figure 2.17)**. From this, a cyclic delocalized electron cloud common to all six carbon atoms is formed. Hence, the real structure of benzene is considered to be a hybrid of two Kekulé structures. The real structure of benzene with delocalized electrons is more stable than the hypothetical Kekulé structure with three double bonds. The concept of resonance is used when there are delocalized electrons to be depicted using conventional structures which are drawn using localized bonds.

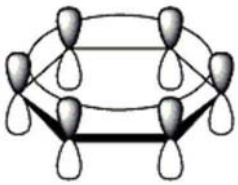
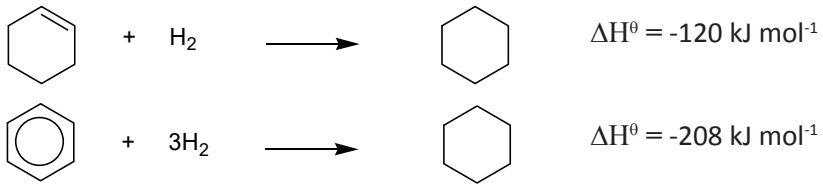


Figure 2.17 Benzene showing lateral overlap of *p* orbitals forming a cyclic delocalized electron cloud

2.3.2 Stability of benzene

The data for the standard enthalpy of hydrogenation helps to illustrate the stability of a benzene molecule.



Since the standard enthalpy of hydrogenation of cyclohexene (six-membered cyclic hydrocarbon with one double bond) is -120 kJ mol^{-1}, the standard enthalpy of hydrogenation of benzene should be 3 x -120 kJ mol^{-1} = -360 kJ mol^{-1} if it possesses three double bonds similar to alkenes. The standard enthalpy of hydrogenation of benzene is found to be -208 kJ mol^{-1}, which is -152 kJ mol^{-1}

less than the expected value for the hydrogenation of three double bonds **(Figure 2.18)**. Hence, benzene is more stable than its Kekulé structure by an amount equal to (360-208) = 152 kJ mol^{-1}. This stability is due to the cyclic delocalization of six pi-electrons, and is termed the resonance stabilization (or aromatic stabilization) energy of benzene.

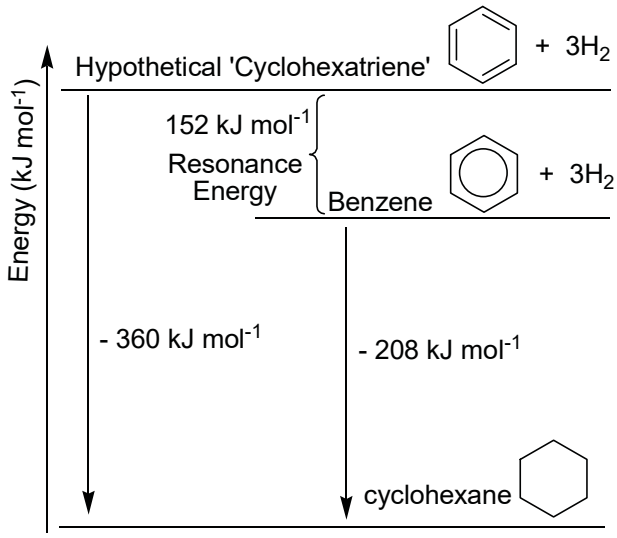


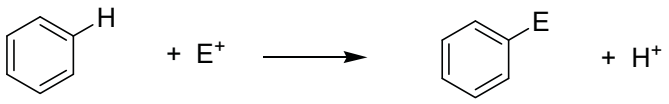
Figure 2.18 Standard enthalpies of hydrogenation of benzene and hypothetical cyclohexatriene.

2.4 Characteristic reactions of benzene exemplifying its stability

Benzene contains loosely bound delocalized electron cloud on both faces of the planar benzene molecule. This makes benzene ring electron rich and hence reactive toward electrophiles, similar to alkenes. As we have discussed, benzene shows extra stability due to this delocalization of electrons. Therefore benzene does not easily undergo reactions which destroy this cyclic delocalization. Hence the characteristic reactions of benzene are electrophilic substitution reactions and not electrophilic addition reactions as in the case of alkenes.

2.4.1 Electrophilic substitution reactions of benzene

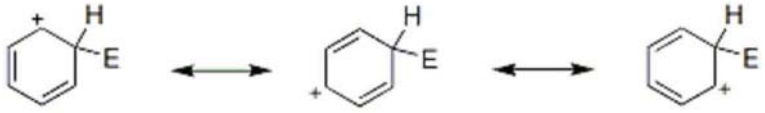
In electrophilic substitution reactions, hydrogen atoms attached to the benzene ring are substituted by electrophiles (E^+).



The first step in this reaction is the formation of a bond between the electrophile (E^+) and a carbon atom in the benzene ring giving rise to a carbocation (arenium ion). This step is very similar to the first step of the electrophilic addition of HBr to an alkene.

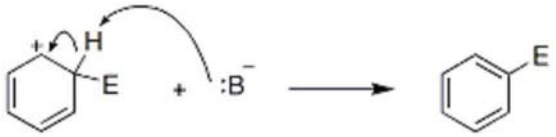


The intermediate carbocation thus formed is stabilized by the delocalization of the positive charge by conjugation with the two π bonds. This can be shown by resonance as follows.



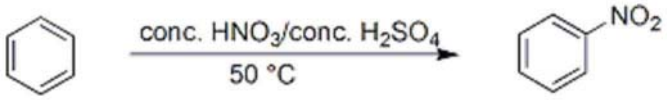
However, in going from benzene to the above carbocation the cyclic delocalization of π electrons is broken, and the aromatic stabilization energy is lost. It is energetically more favourable for the intermediate carbocation to lose a proton and re-establish the cyclically delocalized electron cloud, than to react with a nucleophile and give an addition product as in the case of alkenes.

The proton is usually taken up by one of the bases ($B:^-$) present in the reaction mixture. Thus, the result is the substitution of a H atom on the benzene ring with E.

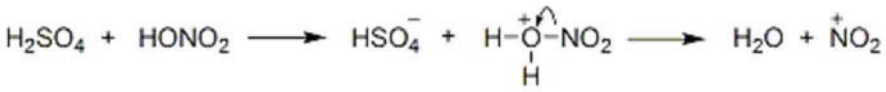


2.4.1.1 Nitration

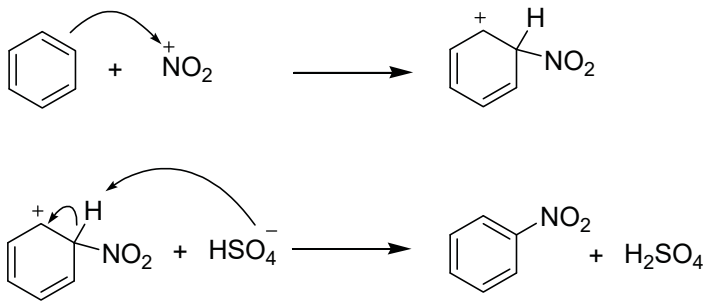
Benzene reacts with a mixture of conc. HNO_3 and conc. H_2SO_4 to give nitrobenzene which is formed by the substitution of H by a nitro group.



The electrophile in this reaction is $^+NO_2$ which is generated in the medium by the dehydration of nitric acid by sulphuric acid as follows.

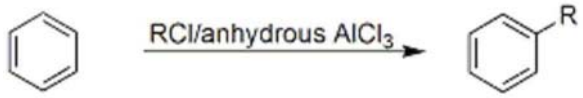


The $^+NO_2$ ion reacts with benzene and in the final step the proton is removed by the hydrogensulphate (bisulphate) ion which act as the base.



2.4.1.2 Friedel - Crafts alkylation

Benzene reacts with alkyl halides in the presence of a Lewis acid such as anhydrous $AlCl_3$ to give alkyl benzene, in which a H attached to the benzene is substituted by an alkyl group.



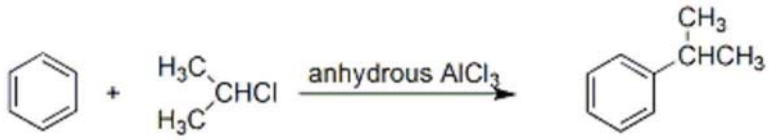
In the case of secondary and tertiary halides (see section 8.6) the electrophile of this reaction is R^+, and is generated in the first step by the reaction between alkyl halide and the Lewis acid.



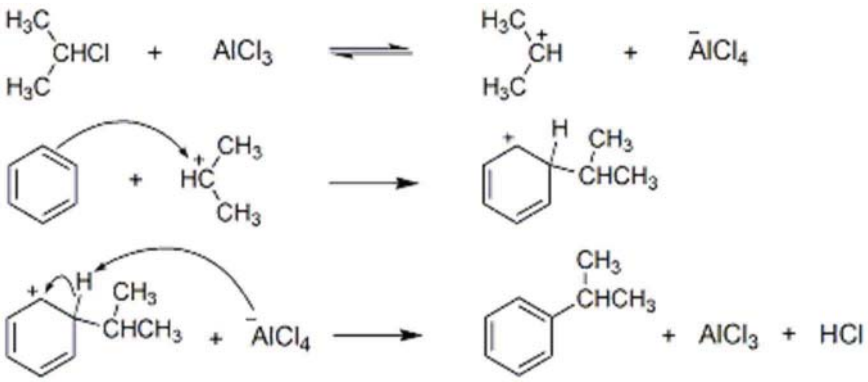
In the final step a proton is removed by $AlCl_4^-$.



Let us see an example.



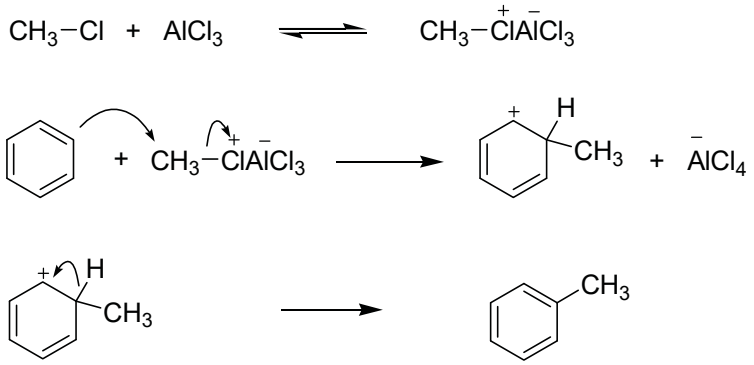
The mechanism of this reaction is as follows.



As you can see the first step of this reaction is formation of carbocation from the alkyl halide. In the second step benzene interacts with this carbocation to form an arenium ion. Removal of proton takes place in the final step restoring the aromatic stability in the product.

In cases where RX is a primary alkyl halide (eg. CH_3Cl) the species actually reacting with the benzene molecule may not be R^+, but be a R-Cl molecule polarized by coordination to $AlCl_3$, which will transfer R^+ to the benzene molecule during the reaction by cleavage of the R-Cl bond.

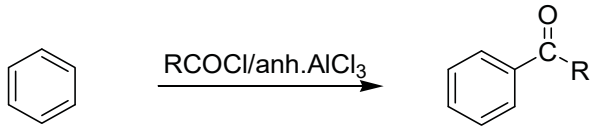
The possible mechanism is as follows.



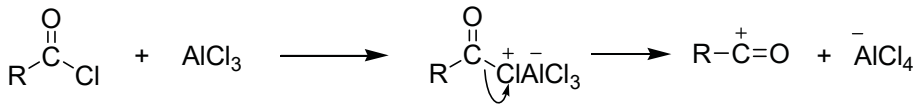
The Friedel - Crafts alkylation does not take place in mono substituted benzenes where the substituent group has a stronger electron attracting ability than halogen. (eg. nitrobenzene).

2.4.1.3 Friedel - Crafts acylation

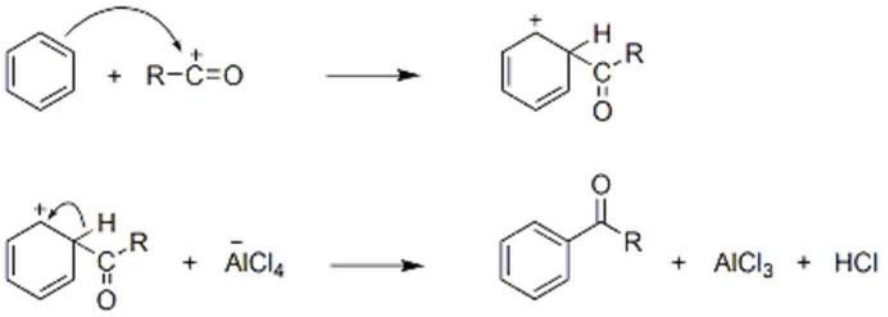
Benzene reacts with acid chlorides in the presence of a Lewis acid such as anhydrous $AlCl_3$, giving acyl benzene, in which a H is substituted by an acyl group.



The electrophile in this reaction is acylium ion (RCO^+). This is formed in the first step by reacting $AlCl_3$ with acyl chloride as follows.

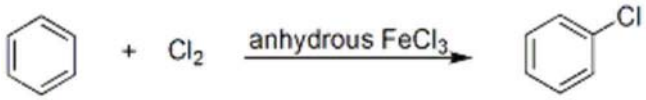


In the step 2, the acylium ion reacts with benzene to form an arenium ion and in the final step a proton is removed restoring the aromatic stability.

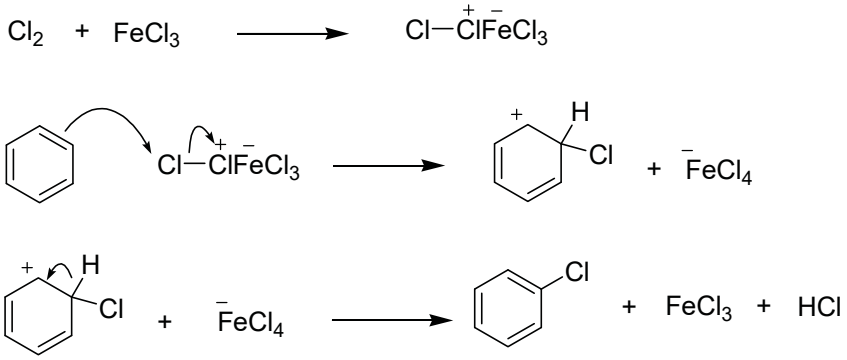


2.4.1.4 Halogenation

When benzene reacts with Cl_2 or Br_2 in the presence of a Lewis acid such as $FeCl_3$, $FeBr_3$, $AlCl_3$ or $AlBr_3$, under anhydrous conditions, substitution by a halogen atom takes place in the benzene ring.

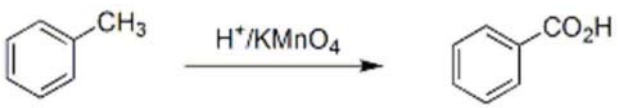


The effective electrophile in the above reaction is Cl^+. It is transferred to the benzene ring from the complex during the reaction. Proton is removed in the last step restoring the aromatic stability.



2.4.2 Resistance of benzene ring towards oxidation

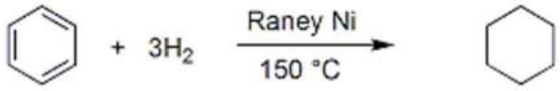
Benzene does not get oxidized by normal oxidizing agents like $H^+/KMnO_4$ due to its stability. However, the alkyl group in alkyl substituted benzene can be oxidized by $H^+/KMnO_4$ to a carboxylic acid group. $H^+/K_2Cr_2O_7$ can also be used for this oxidation.



Tertiary alkyl groups do not get oxidized under the conditions in which primary and secondary alkyl groups get oxidized. More vigorous conditions under which tertiary alkyl groups can be oxidized also result in cleavage of the benzene ring.

2.4.3 Resistance of benzene ring towards hydrogenation

Although benzene does not undergo electrophilic addition reactions, like alkenes, it can undergo addition of hydrogen in the presence of suitable catalysts at higher temperatures in comparison to alkenes.



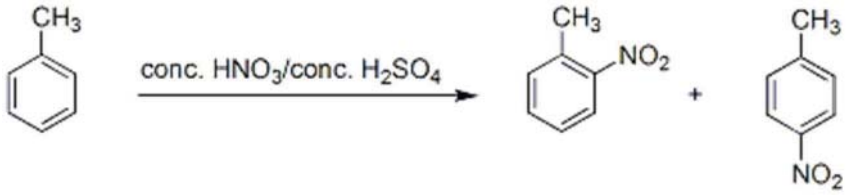
2.5 Directing ability of substituent groups of mono substituted benzene

When a monosubstituted benzene undergoes an electrophilic substitution reaction, the place where the second substituent group attaches will be determined by the nature of the first substituent group. Substituent groups can be categorized into two basic types.

2.5.1 Ortho para directing groups

eg. -OH, -R, -NH_2, -NHR, -OCH_3, halogens

Other than halogen, the *ortho para* directing groups activate the benzene ring towards electrophilic substitution by making it more electron rich than benzene.

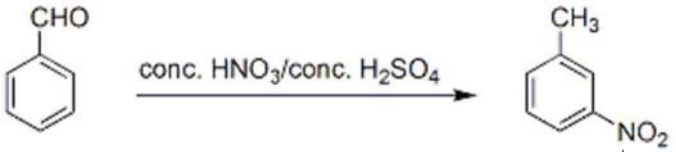


ortho para

2.5.2 Meta directing groups

eg. - NO_2, -CHO, -COR, -COOH, -COOR

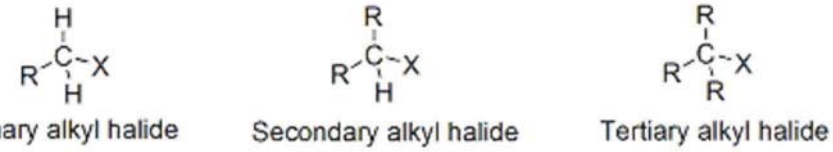
Meta directing groups deactivate the benzene ring towards electrophilic substitution by withdrawing electrons from it.



meta

2.6 Structure and reactions of alkyl halides

Alkyl halides are classified as primary, secondary or tertiary depending on the number of H atoms attached to the carbon atom which carries the halogen atom.



Primary alkyl halide Secondary alkyl halide Tertiary alkyl halide

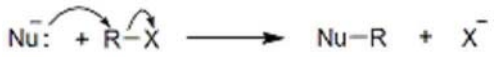
Alkyl halides are polar compounds. Although they are polar, the solubility of alkyl halides in water is very low. One reason for this is that they do not form hydrogen bonds with water.

Due to the higher electronegativity of the halogen atom relative to the carbon atom, the carbon-halogen bond is polarized. As a result, there is a deficiency of electrons in that carbon atom. Therefore, it is possible that nucleophiles attack this position. Nucleophiles are basic, electron rich reagents which can utilize a pair of electrons to form a bond with an electron deficient carbon atom.

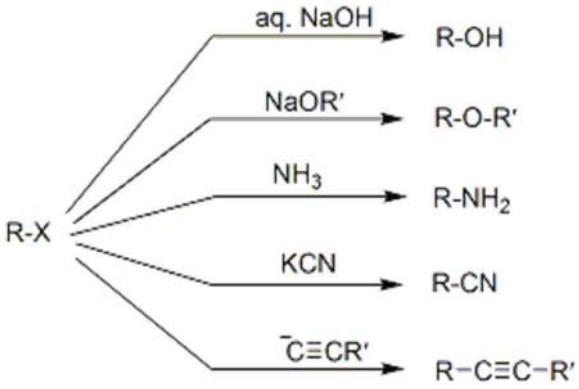
A few common examples are:

$\bar{O}H$ $\bar{O}R$ $\bar{N}H_2$ $\bar{C}N$ $RC\equiv\bar{C}$ H_2O NH_3

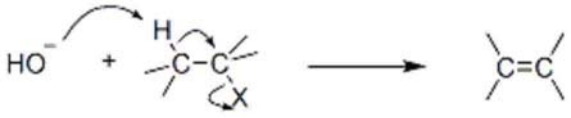
Characteristic reactions of alkyl halides are nucleophilic substitution reactions. During nucleophilic substitution reaction, the carbon atom forms a new bond with the nucleophile and the halogen atom leaves as a halide ion.



Let us look at some examples:



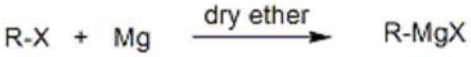
As a nucleophile possesses a pair of electrons, any nucleophile can also act as a base by forming a bond with H^+. Therefore, when an alkyl halide is reacted with a reagents such as: OH^-, OR^-, it can also undergo an elimination reaction by the mechanism shown below.



In this reaction, instead of reacting OH^- group as a nucleophile with carbon, it reacts as a base and removes a H^+ from the carbon atom adjacent to the carbon atom bearing halogen. The hydrogen atoms attached to the carbon atom adjacent to the carbon atom bearing the halogen atoms, have a low acidity due to the polarization of the C-X bond. Thus substitution and elimination are competing reactions in alkyl halides. The balance between substitution and elimination is influenced by the solvent used in the reaction. In the laboratory, aqueous KOH is used when substitution is desired, and ethanolic KOH is used when elimination is desired.



Alkyl halides react with Mg in the medium of **dry ether** to form **Grignard reagents.** Grignard reagents are organometallic reagents.



When an alkyl halide forms a Grignard reagent the polarity of the carbon atom originally joined to halogen, changes as shown below.

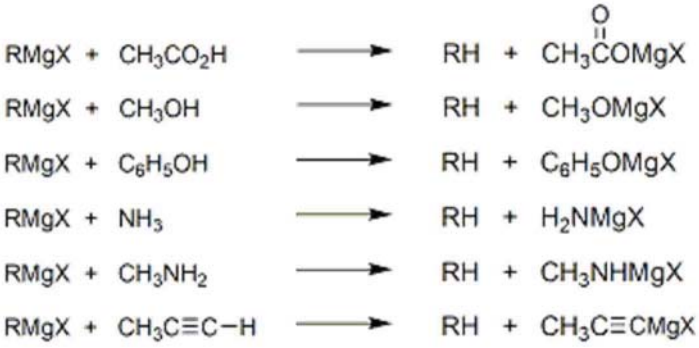


Thus, an electron deficient carbon atom is converted to an electron rich carbon atom. In fact, the alkyl group attached to Mg can utilize the pair of electrons in the C-Mg bond and behave as a strong base as well as a strong nucleophile.

Therefore Grignard reagents cannot be prepared or used in organic reactions in the presence of compounds which have even weakly acidic H atoms, including water.



The strong basic character of the Grignard reagent can be shown by the following reactions.



The last reaction of the above list is the reaction of a Grignard reagent with a terminal alkyne. Note that the product is also another Grignard reagent. This reaction can be used to prepare acetylenic Grignard reagents.

2.7 Nucleophilic substitution reactions of alkyl halides in terms of the timing of bond making and bond breaking steps

During reactions, bonds are broken and new bonds are formed. Nucleophilic substitution reactions of alkyl halides involve the breaking of a carbon-halogen bond and the formation of a carbon-nucleophile bond. To study the mechanism of nucleophilic substitution reactions of alkyl halides the time interval between bond breaking and bond making steps can be considered.

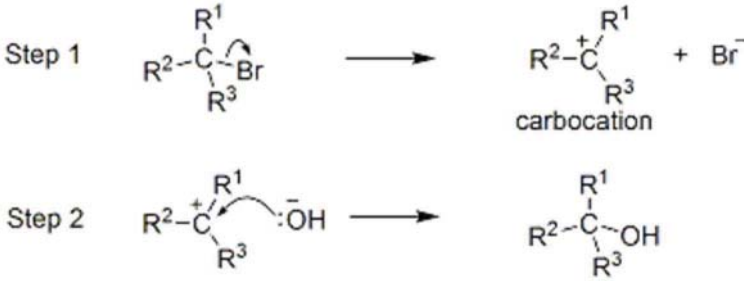
When the breaking of the C-X bond and the formation of the new bond to the nucleophile takes place simultaneously, the nucleophilic substitution reaction of the alkyl halide takes place as a one-step reaction.

Accordingly, for the reaction of an alkyl bromide with the hydroxyl ion, the one-step reaction can be presented as follows.



When the breaking of the C-X bond takes place at first and then the formation of the new bond to the nucleophile takes place, the nucleophilic substitution reaction of the alkyl halide takes place as a two-step reaction.

Accordingly, the reaction that takes place by two steps can be presented as follows



The reaction that takes place by two steps goes through a carbocation intermediate. On considering the stability of the carbocation formed, the tertiary alkyl halides (R^1, R^2, R^3 = alkyl) which are able to form a more stable tertiary carbocations tend to undergo nucleophilic substitution in two steps. The primary alkyl halides (R^1, R^2 = H, R^3 = H or alkyl) tend to undergo nucleophilic substitution reactions in one step as the primary carbocations they form are less stable.

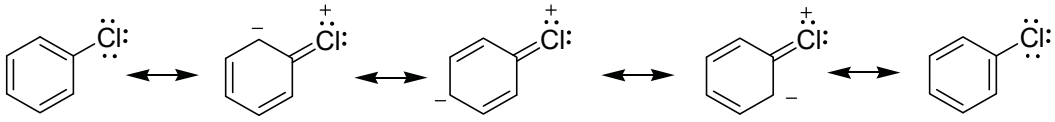
Generally, both pathways are taken by the secondary alkyl halides (R^1 = H, R^2, R^3 = alkyl) to extents which depend on the reaction conditions.

Vinyl and phenyl carbocations are unstable and therefore, vinyl halides and aryl halides they do not react by the two step pathway. They also do not react by the one step pathway because the C-X bond is stronger than in alkyl halides due to its double bond character. This can be shown by resonance.

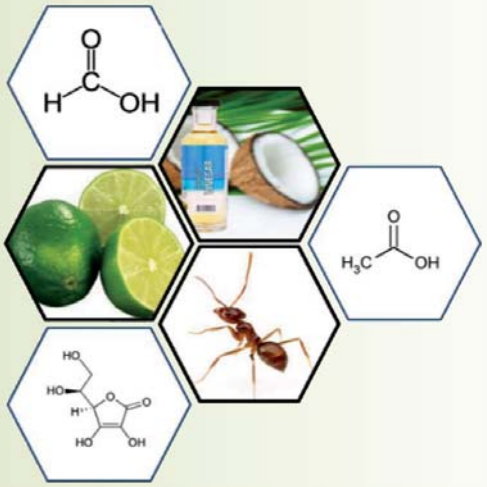
Resonance structures of vinyl halide:



Resonance structures of chlorobenzene:



3. Oxygen Containing Organic Compounds



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3.2.2	Reactions involving cleavage of the O-H bond	3.5.2.3	Reduction of carboxylic acids with $LiAlH_4$
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		3.6.3.2	Reduction with $LiAlH_4$

Introduction

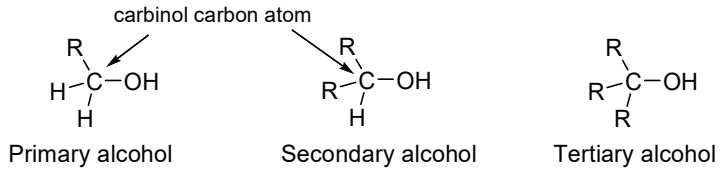
The common oxygen containing organic compounds includes alcohols, phenols, ethers, carbonyl compounds (aldehydes and ketones) and carboxylic acids and carboxylic acid derivatives (esters, amides and acid halides). Alcohols are compounds containing OH group attached to aliphatic carbon atom while phenols are aromatic compounds in which an OH group is attached to a benzene ring. Aldehydes, ketones, carboxylic acids and carboxylic acid derivatives all contain a carbonyl (C=O) group. These classes of compounds differ from each other based on the nature of the two groups attached to the carbonyl carbon.

3.1 Structure, properties and reactions of alcohols

Alcohols are compounds containing an O–H group attached to a sp^3 hybridized carbon atom. Alcohols with one OH group are called monohydric alcohols while those with two, three, four etc. are called dihydric alcohols, trihydric alcohols, tetrahydric alcohols etc. Compounds with many OH groups are commonly called polyhydric alcohols. Our discussion will be mainly confined to monohydric alcohols.

3.1.1 Classification of monohydric alcohols

Similar to the alkyl halides monohydric alcohols are classified into three types depending on the number of H atoms attached to the carbon atom bearing the OH group (carbinol carbon atom) as primary (2 H atoms), secondary (1 H atom) and tertiary (no H atoms attached) as shown below.



3.1.2 Physical properties

In alcohols the O–H bond is polarized as $R–O^{\delta-}–H^{\delta+}$. Hence, inter-molecular hydrogen bonds are formed between alcohol molecules **(Figure 3.1)**.

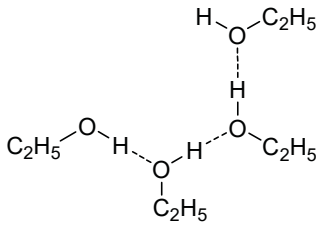


Figure 3.1 Intermolecular H-bonding in ethanol

Because of these relatively strong intermolecular bonds, the boiling points of alcohols have higher values compared to the alkanes and ethers with comparable relative molecular masses **(Table 3.1)**. The boiling point increases in going down the series of alcohols. Similar to alkanes, branching of the alkyl part of the molecule leads to a reduction of boiling point.

Table 3.1 Boiling points of alcohols, ethers and alkanes of comparable relative molecular masses

Compound	Structural formula	Relative molecular mass	Boiling point/ °C
ethanol	CH_3CH_2OH	46	78
dimethyl ether	CH_3OCH_3	46	–25
propane	$CH_3CH_2CH_3$	44	–42
1-propanol	$CH_3CH_2CH_2OH$	60	97
2-propanol	$(CH_3)_2CHOH$	60	83
ethylmethyl ether	$CH_3CH_2OCH_3$	60	11
butane	$CH_3CH_2CH_2CH_3$	58	0
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99
2-methyl-2-propanol	$(CH_3)_3COH$	74	82
diethyl ether	$CH_3CH_2OCH_2CH_3$	74	35
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	88	138
ethyl propyl ether	$CH_3CH_2CH_2OCH_2CH_3$	88	64
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86	68

Alcohols with low relative molecular masses are soluble in water. The solubility of alcohols in water is due to the OH group which can forms H - bonds with water molecules. The non-polar alkyl group in the alcohol molecule is a hindrance to the solubility in water. In going down the homologous series of alcohols the size of the non - polar alkyl group gradually increases relative to the OH group. Accordingly the solubility of alcohols in water gradually decreases **(Table 3.2).**

Table 3.2 Boiling points and solubility (in water) of some long chain alcohols

Alcohol	Structural formula	Boiling point/ °C	Solubility (g/ 100g H_2O)
methanol	CH_3OH	65	∞
ethanol	CH_3CH_2OH	78	∞
1-propanol	$CH_3CH_2CH_2OH$	82	∞
1-butanol	$CH_3(CH_2)_2CH_2OH$	118	7.9
1-penatanol	$CH_3(CH_2)_3CH_2OH$	138	2.3
1-hexanol	$CH_3(CH_2)_4CH_2OH$	158	0.6
1-heptanol	$CH_3(CH_2)_5CH_2OH$	176	0.2
1-octanol	$CH_3(CH_2)_6CH_2OH$	195	0.05

∞ - Miscible in any proportion.

3.1.3 Reactions of alcohols

Alcohols undergo reactions involving cleavage of O–H bond and cleavage of C–O bond.

3.1.3.1 Reactions involving cleavage of O-H bond

(a) *Reaction with sodium (and other alkali metals)*

Alcohols show acidic behaviour because of the polarization of the O–H bond and react with sodium liberating hydrogen and forming sodium alkoxides. The alkoxide ion is a strong nucleophile and also a strong base.

$$RO{-}H + Na \longrightarrow RO^{-} + H_2$$

However alcohols are not acidic enough to give a substantial reaction with sodium hydroxide to give sodium alkoxide. Thus the equilibrium shown below lies essentially on the side of the alcohol. Hence alcohols are weaker acids than water.

$$ROH + NaOH \rightleftharpoons RO^{-}Na^{+} + H_2O$$

(b) *Reaction with carboxylic acid (Acylation of alcohols to give esters)*

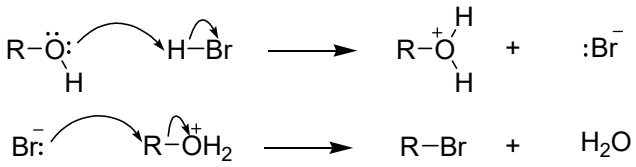
Alcohols react with carboxylic acids to form esters (esterification reaction). Concentrated H_2SO_4 acid acts as a catalyst for this esterification reaction.

$$C_2H_5OH + CH_3COOH \underset{}{\overset{\text{conc. } H_2SO_4/\text{heat}}{\rightleftharpoons}} CH_3COOC_2H_5 + H_2O$$

3.1.3.2 Nucleophilic substitution reactions involving cleavage of C-O bond

(a) *Reaction with hydrogen halides* (HBr or HI)

Alcohols undergo nucleophilic substitution reaction with HBr or HI to give the corresponding alkyl bromides or alkyl iodides. Protonation of the O atom in the presence of acid (HBr or HI), converts the -OH group into a better leaving group (H_2O).



This is a nucleophilic substitution reaction. In this reaction Br^- ion acts as the nucleophile and the leaving group is H_2O.

Alcohols react with HCl only in the presence of Lewis acids or acids.

The Lucas test to distinguish primary, secondary and tertiary alcohols makes use of this fact. In this reaction, ROH is converted to RCl. $ZnCl_2$which is a Lewis acid acts as the catalyst in this reaction. Because alkyl halides are insoluble in water, as the reaction proceeds the reaction mixture becomes cloudy and turbid. The time taken for the turbidity to appear, after the mixing of reagents, can be used to distinguish between primary, secondary and tertiary alcohols. Under the given reaction conditions the above nucleophilic substitution reaction takes place in two steps. Tertiary alcohols form stable

intermediate tertiary carbocations and therefore, tertiary alcohols in the presence of the Lucas reagent form turbidity in a very short time. Secondary alcohols take longer time to produce turbidity and primary alcohols react very slowly.

(b) *Reaction with phosphorus trihalides* (PCl_3 or PBr_3)

Alcohols react with PCl_3 and PBr_3 to give alkyl chlorides and alkyl bromides respectively.

$$3\ ROH + PCl_3 \longrightarrow 3\ RCl + H_3PO_3$$
$$3\ ROH + PBr_3 \longrightarrow 3\ RBr + H_3PO_3$$

(c) *Reaction with phosphorus pentachloride* (PCl_5)

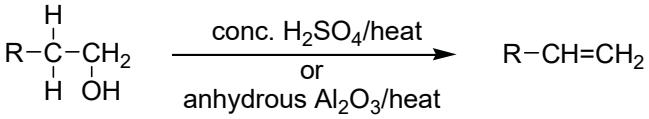
Alcohols react with PCl_5 to give alkyl chlorides.

$$ROH + PCl_5 \longrightarrow RCl + POCl_3 + HCl$$

Reactions of alcohols with phosphorous halides described in (b) and (c) above are also nucleophilic substitution reactions where the halide ion acts as the nucleophile.

3.1.3.3 Elimination reaction

Alcohols undergo an elimination reaction when heated with conc. H_2SO_4 or when heated with alumina to a higher temperature. The reaction is the dehydration of alcohols, in which a molecule of water is eliminated from an alcohol. During this reaction an alkene is formed as the product.

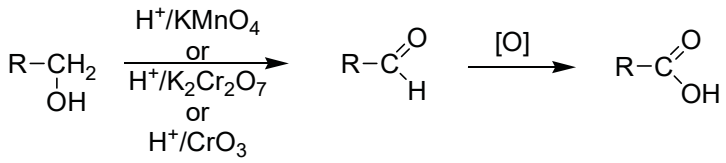


3.1.3.4 Oxidation of alcohols

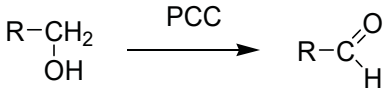
Alcohols can be oxidized with several oxidizing agents. The product of oxidation depends on whether the alcohol is primary, secondary or tertiary. Oxidation of alcohols can be carried out with $H^+/KMnO_4$ or $H^+/K_2Cr_2O_7$ or H^+/CrO_3.

(a) *Oxidation of primary alcohols*

Primary alcohols are oxidized to carboxylic acids through the corresponding aldehyde with the above oxidizing reagents.

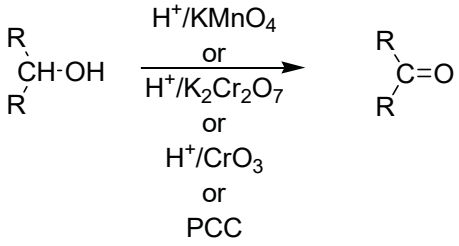


The oxidation reaction will be stopped at the stage where aldehyde is formed when pyridinium chlorochromate $[C_5H_5NH]^+[CrO_3Cl]^-$ (PCC) is used.



(b) *Oxidation of secondary alcohols*

Secondary alcohols are oxidized to give ketones with any of the above reagents.



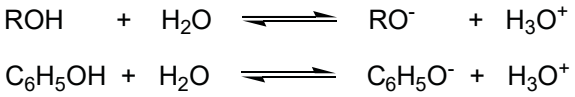
(c) *Oxidation of tertiary alcohols*

Generally the tertiary alcohols do not undergo oxidation under conditions that primary and secondary alcohols are oxidized.

3.2 Structure, properties and reactions of phenols

3.2.1 Acidity of phenols

Aromatic compounds, in which an OH group is joined directly to a carbon atom of a benzene ring, are called phenols. Alcohols and phenols dissociate in aqueous solutions as shown below.



Phenols are more acidic than alcohols. This means that in the above equilibria, the equilibrium point for phenols is more towards the right than alcohols. The reason for this is that the stability of phenoxide ion relative to phenol is greater than the stability of the alkoxide ion relative to the alcohol. This can be understood by considering the resonance structures for phenol and its anion.

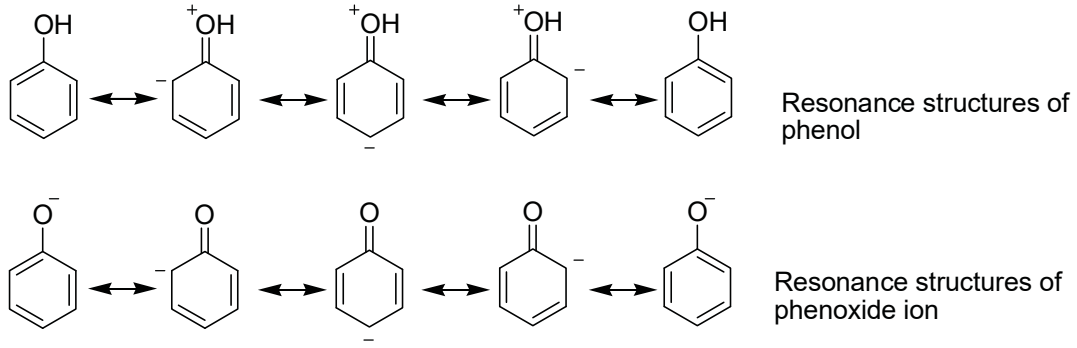


Figure 3.2 Resonance structures of phenol and phenoxide ion

The stabilization of the anion by resonance is greater than the stabilization of the phenol because unlike in the phenol there is no charge separation in the resonance structures of the anion **(Figure 3.2).** There is no corresponding resonance stabilization of alcohol or its anion.

3.2.2 Reactions involving cleavage of the O-H bond

The higher acidity of phenols is confirmed by the following examples. Unlike alcohols, phenols react with NaOH to give sodium phenoxide. However, neither phenols nor alcohols are acidic enough to react with $NaHCO_3$ and evolve CO_2.

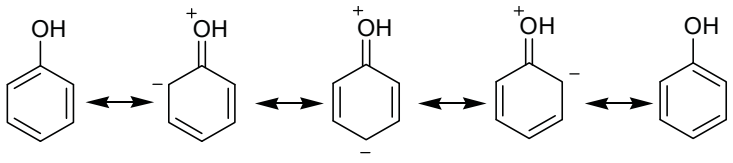
$$2\ C_6H_5OH + 2Na \longrightarrow 2\ C_6H_5O^-\ Na^+ + H_2$$

$$C_6H_5OH + NaOH \longrightarrow C_6H_5O^-\ Na^+ + H_2O$$

3.2.3 Non-occurrence of nucleophilic substitution reactions by breaking C-O bond

Unlike alcohols phenols do not undergo nucleophilic substitution reactions. Neither the one step nor the two step mechanism takes place because,

(a) The C–O bond is shorter (sp^2 hybridized C atom) and stronger (double bond nature) due to delocalization of lone pair of electrons on the oxygen atom into the benzene ring. This can be shown by resonance.



(b) Phenyl cation is unstable.

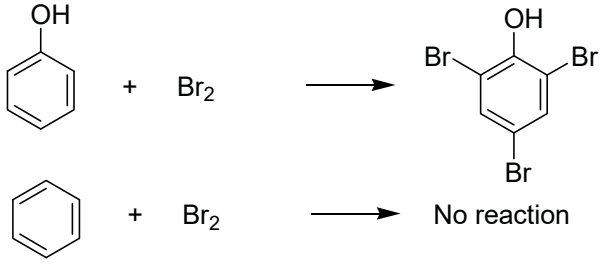
3.3 Reactivity of the benzene ring in phenols

The benzene ring in phenol is electron rich compared to benzene due to the delocalization of a lone pair of electrons on the oxygen atom over the benzene ring in phenol. Therefore the benzene ring in phenol is more reactive towards electrophilic reagents than benzene itself. The O–H group of phenol directs the electrophilic substitution to the *ortho* and *para* positions with respect to the phenolic OH group.

When the electrophilic substitution reactions of phenol are compared with the corresponding reactions of benzene along with the relevant conditions, it is clear that the benzene ring of phenol is more reactive towards electrophiles. Consider the following examples.

3.3.1 Reaction of phenol with Br_2

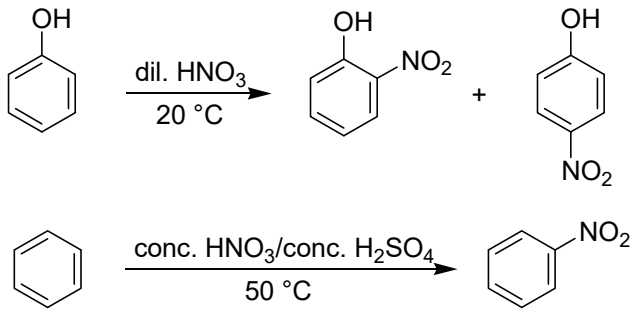
Phenol reacts readily with bromine to form 2,4,6-tribromophenol while benzene does not react with bromine.



When this reaction is carried out with bromine water 2,4,6-tribromophenol is observed as a white precipitate.

3.3.2 Nitration of phenol

Nitration occurs even with dilute HNO_3 at 20 °C while benzene requires conc. HNO_3/conc. H_2SO_4 and higher temperatures for nitration.



It should be noted that Friedel-Crafts alkylation reactions cannot be carried out with phenols because of the complex formation between Friedel-Crafts catalyst and phenols.

3.4 Structure, properties and reactions of aldehydes and ketones

Both aldehydes and ketones contain the carbonyl (C=O) functional group. In aldehydes the carbonyl carbon is attached to an H atom and an alkyl or aryl (aromatic) group. However, the simplest aldehyde, formaldehyde (methanal) has two H atoms attached to the carbonyl carbon. In ketones each of the groups attached to the carbonyl carbon is either an alkyl group or an aryl group. The carbonyl C atom is sp^2 hybridized and the three atoms attached to it lie in one plane (trigonal planar). The carbon oxygen double bond consists of a σ bond and a π bond.

3.4.1 Physical properties

Boiling points of aldehydes and ketones are higher than those of alkanes of comparable relative molecular masses due to the presence of intermolecular dipole-dipole interactions. However their boiling points are lower than alcohols of comparable relative molecular masses as they do not form intermolecular H-bonds **(Table 3.3)**.

Table 3.3 Boiling points and water solubility of aldehydes, ketones, alcohols and alkanes of comparable relative molecular masses

Compound	Structural formula	Relative molecular mass	Boiling point/ °C	Water Solubility (g/100 mL)*
ethanal	CH_3CHO	44	21	∞
ethanol	CH_3CH_2OH	46	78	∞
propane	$CH_3CH_2CH_3$	44	–42	none
propanal	CH_3CH_2CHO	58	49	16
propanone	CH_3COCH_3	58	56	∞
1-propanol	$CH_3CH_2CH_2OH$	60	97	∞
2-propanol	$(CH_3)_2CHOH$	60	83	∞
butane	$CH_3CH_2CH_2CH_3$	58	0	none
butanal	$CH_3CH_2CH_2CHO$	72	76	7
2-butanone	$CH_3COCH_2CH_3$	72	80	26
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118	7.9
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99	29
pentane	$CH_3CH_2CH_2CH_2CH_3$	72	36	none
penatanal	$CH_3CH_2CH_2CH_2CHO$	86	103	1
2-pentanone	$CH_3COCH_2CH_2CH_3$	86	102	6
1-pentanol	$CH_3CH_2CH_2CH_2CH_2OH$	88	138	2.3
hexane	$CH_3CH_2CH_2CH_2CH_2CH_3$	86	68	none

∞ - Miscible in any proportion.

However aldehydes and ketones can participate in intermolecular H-bonding with water **(Figure 3.3).** Therefore aldehydes and ketones with relatively lower molecular masses are soluble in water **(Table 3.3)**.

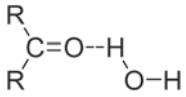


Figure 3.3 Intermolecular H-bonding of aldehydes and ketones with water

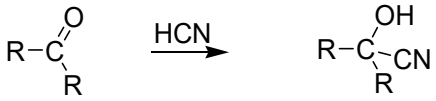
3.4.2 Reactions of aldehydes and ketones

The carbonyl group is a polar group because of the electron negative O atom ($^{\delta+}C=O^{\delta-}$). Hence the C atom is electron deficient and can react with a nucleophile. The C atom is unsaturated because it is attached only to three atoms. It can therefore form a new bond with a nucleophile. During this process the two π electrons are transferred to the oxygen atom which thereby acquiring a negative charge. This negative charge is neutralized by the attachment of a positively charged species (very often a proton). Therefore the characteristic reactions of aldehydes and ketones are nucleophilic addition reactions.

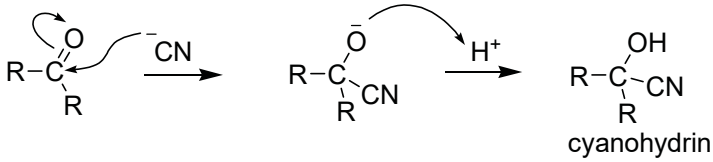
3.4.3 Nucleophilic addition reactions

3.4.3.1 Addition of HCN to aldehydes and ketones

Addition of HCN to aldehydes and ketones is a nucleophilic addition reaction. This is carried out by adding a dilute mineral acid into a mixture of the carbonyl compound and an aqueous solution of sodium cyanide. Here the CN^- ion acts as the nucleophile.

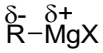


Mechanism of the reaction is as follows.

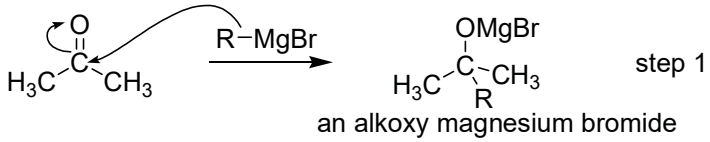


3.4.3.2 Reaction with Grignard reagents

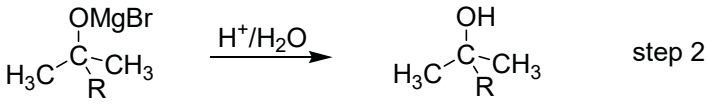
In Grignard reagents the C–Mg bond is polarized as follows.



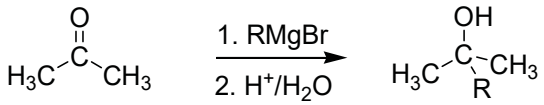
Therefore the R group of the Grignard reagent together with the electron pair of R–Mg bond reacts as a nucleophile with the carbonyl carbon. This leads to the formation of an alkoxy magnesium halide.



Hydrolysis of the alkoxy magnesium halide gives the corresponding alcohol. This is carried out by an aqueous acid.



The overall reaction is as follows:

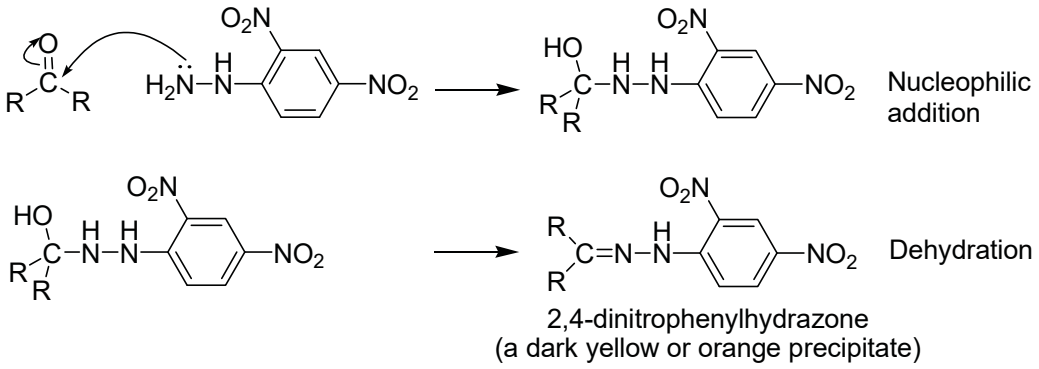


All aldehydes except formaldehyde give secondary alcohols whereas ketones give tertiary alcohols with Grignard reagents. Formaldehyde gives primary alcohols.

Grignard reagents are prepared and reacted with aldehydes and ketones under anhydrous conditions. Hence the formation of the alkoxy magnesium halide and its hydrolysis are two distinct steps.

3.4.3.3 Reaction with 2,4-dinitrophenylhydrazine (2,4-DNP or Brady reagent)

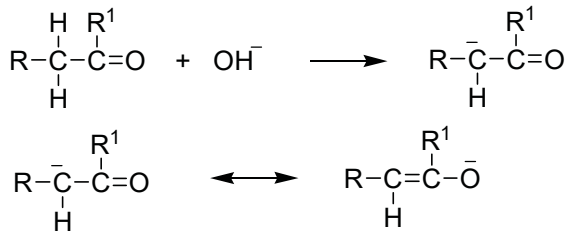
In this reaction, nucleophilic addition of 2,4-dinitrophenylhydrazine to the aldehyde or ketone takes place first. Then a water molecule is eliminated from the intermediate product to form the final product, which is a 2,4-dinitrophenylhydrazone.



Although this reaction takes place in two steps as shown above, the hydroxy product first obtained by the nucleophilic addition cannot be isolated under the reaction conditions and dehydrates to give the final product. This reaction is used to identify aldehydes and ketones.

3.4.4 Self-condensation reactions of aldehydes and ketones

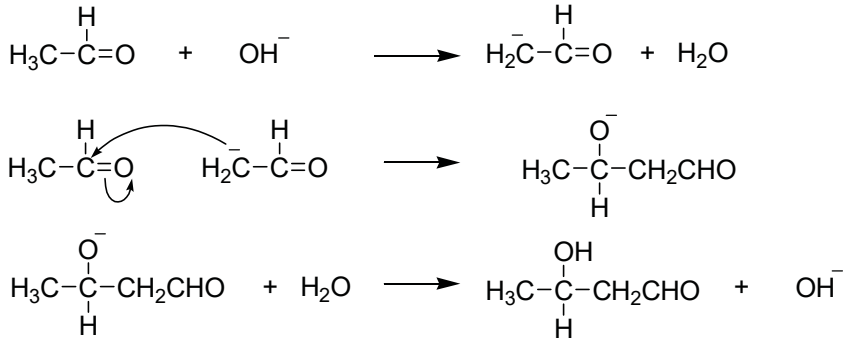
Due to the strong electron withdrawing nature of the carbonyl group, H atoms attached to the carbon atoms directly bound to the carbonyl carbon (the α-H) become acidic. This α-H can be abstracted as a proton by a base (e.g.: OH^-). The carbanion so formed is stabilized by resonance as shown below.



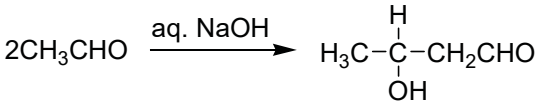
This carbanion reacts as a nucleophile and attacks the carbon atom of the carbonyl group of an un-ionized aldehyde molecule. Hence aldehydes and ketones with α-hydrogens undergo base catalyzed self-condensation reactions.

Let us see some examples.

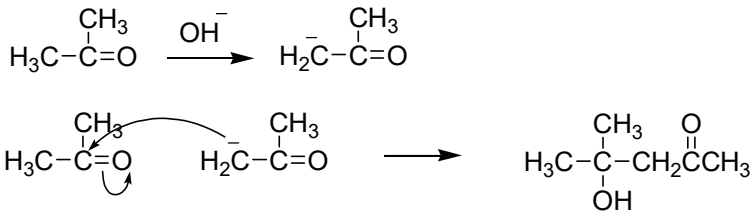
Reaction of acetaldehyde in the presence of aqueous NaOH



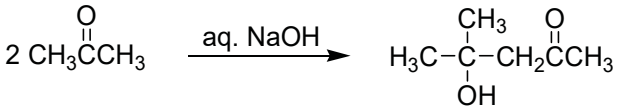
The overall reaction is:



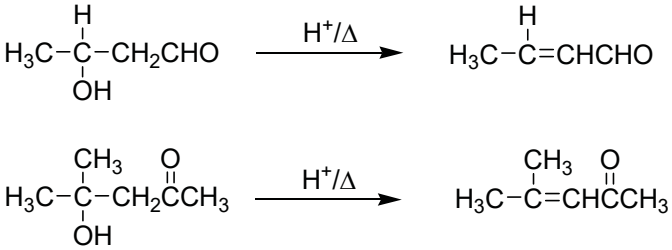
Condensation of acetone in the presence of aqueous NaOH



The overall reaction is:

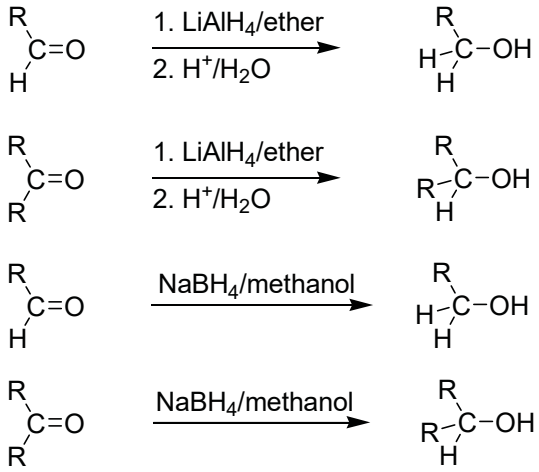


The addition products obtained above undergo dehydration easily when heated with acids.



3.4.5 Reduction of aldehydes and ketones by lithium aluminium hydride ($LiAlH_4$) or sodium borohydride($NaBH_4$)

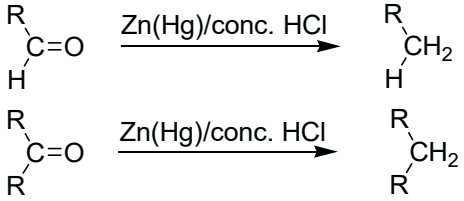
Aldehydes are reduced to primary alcohols with $LiAlH_4$ or $NaBH_4$ while ketones are reduced to give secondary alcohols. In these reductions both $LiAlH_4$ and $NaBH_4$ provide hydride ions (H^-). The hydride ion reacts with the carbonyl C as a nucleophile. Thus these reductions can be considered as nucleophilic addition reactions.



Note that $LiAlH_4$ is too reactive to be used in the presence of water or methanol.

3.4.6 Reduction of aldehydes and ketones by Zn(Hg)/ conc.HCl (Clemmenson reduction)

In this reduction reaction, C=O group is reduced to a methylene (CH_2) group. Thus, both aldehydes and ketones can be converted to hydrocarbons.

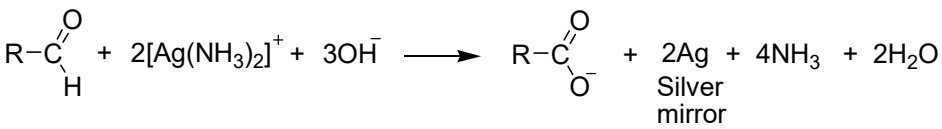


3.4.7 Oxidation of aldehydes

Aldehydes are oxidized to carboxylic acids by oxidizing agents such as acidified potassium dichromate, acidified chromic oxide or acidified potassium permanganate and even by mild oxidizing agents such as Tollen reagent and Fehling solution. In acidic medium aldehydes are oxidized to carboxylic acids while with Tollen and Fehling solution, which are alkaline, the product is a salt of the carboxylic acid. Ketones do not undergo oxidation with these reagents.

3.4.7.1 Oxidation by Tollens reagent

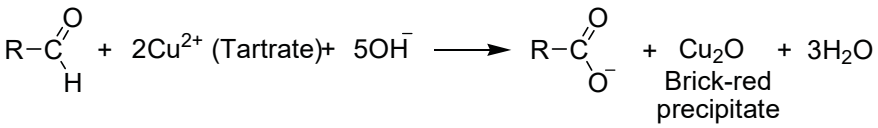
Tollens reagent, is a solution containing Ag^+ in the form $[Ag(NH_3)_2]^+$. During the oxidation of aldehydes to carboxylic acids, Ag^+ ions are reduced to metallic silver giving a silver mirror in the test tube.



Oxidation of aldehydes by Tollens reagent or the silver mirror test is used to distinguish between aldehydes and ketones.

3.4.7.2 Oxidation by Fehling solution

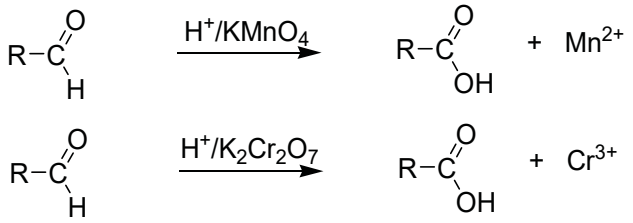
A solution of Copper (II) tartrate in aqueous NaOH is known as Fehling solution. This is a dark blue solution. When a few drops of an aldehyde are added to this reagent and heated, the blue colour of the solution gradually disappears and a brick red precipitate of cuprous oxide is formed.



Aldehydes and ketones can be distinguished from each other by reacting with Fehling solution.

3.4.7.3 Oxidation by acidified potassium dichromate or acidified chromic oxide or acidified potassium permanganate

Aldehydes get oxidized to carboxylic acids by reacting with oxidizing agents such as acidified potassium dichromate or acidified chromic oxide or acidified potassium permanganate.



The pink colour of $H^+/KMnO_4$ solution becomes colourless in the presence of an aldehyde while the orange colour of $H^+/ Cr_2O_7^{2-}$ solution turns green. By using these reagents aldehydes and ketones can be distinguished from each other.

Since ketones do not contain an H atom attached to the C=O group, they do not undergo oxidation with these oxidizing reagents.

However strong oxidizing agents like potassium permanganate can oxidize ketones when heated. During this oxidation carbon-carbon bonds are broken resulting in the decomposition of the ketone.

3.5 Structure, properties and reactions of carboxylic acids

Carboxylic acids are compounds containing carboxyl (COOH) group which consists of a C=O and OH groups **(Figure 3.4)**. Carboxylic acids are generally more acidic than other organic compounds containing OH groups but weaker than the common mineral acids.

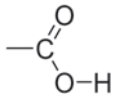


Figure 3.4 Structure of the carboxyl group

3.5.1 Physical properties

Carboxyl group is a polar functional group. Due to the polarity of C–O and O–H groups it forms intermolecular hydrogen bonds. Carboxylic acids are capable of forming dimeric structures in which carboxylic acid molecules are attached by hydrogen bonds as pairs **(Figure 3.5)**.

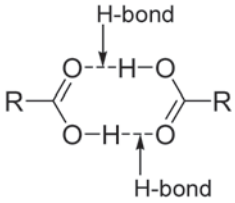


Figure 3.5 Dimeric structure of carboxylic acids due to H-bonding

Due to these reasons carboxylic acids show higher boiling points than the alcohols, aldehydes and ketones with comparable relative molecular masses **(Table 3.4)**.

Table 3.4 Boiling points of some carboxylic acids, alcohols, aldehydes and ketones of comparable relative molecular masses

Compound	Structural formula	Relative molecular mass	Boiling point/ °C
methanoic acid	HCO_2H	46	100
ethanol	CH_3CH_2OH	46	78
ethanal	CH_3CHO	44	20
ethanoic acid	CH_3CO_2H	60	118
1-propanol	$CH_3CH_2CH_2OH$	60	97
2-propanol	$(CH_3)_2CHOH$	60	83
propanal	CH_3CH_2CHO	58	49
propanone	$(CH_3)_2C=O$	58	56
propanoic acid	$CH_3CH_2CO_2H$	74	141
1-butanol	$CH_3CH_2CH_2CH_2OH$	74	118
2-butanol	$CH_3CH(OH)CH_2CH_3$	74	99
butanal	$CH_3CH_2CH_2CHO$	72	75
butanone	$CH_3COCH_2CH_3$	72	80

Carboxyl group can form H-bonds with water. Therefore carboxylic acids of C_1 to C_4 dissolve well in water. When the number of carbon atoms increases solubility decreases. Aromatic

carboxylic acids are water insoluble and exist as solid crystalline substances. Almost all the carboxylic acids are soluble in organic solvents.

3.5.2 Comparison of the reactivity pattern of -COOH group with >C=O group in aldehydes and ketones and -OH group in alcohols and phenols

Similar to alcohols, the O–H group of carboxylic acids also undergoes reactions involving cleavage of both C–O bond and O–H bond.

3.5.2.1 Reactions involving cleavage of the O–H bond

Carboxylic acids are acidic. They react with alkali metals such as sodium and potassium, alkali such as NaOH and KOH and bases such as Na_2CO_3 and $NaHCO_3$.

$$2\,RCOOH + 2\,Na \longrightarrow 2\,RCOO^-Na^+ + H_2$$

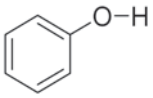
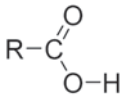
$$RCOOH + NaOH \longrightarrow RCOO^-Na^+ + H_2O$$

$$2\,RCOOH + Na_2CO_3 \longrightarrow 2\,RCOO^-Na^+ + CO_2 + H_2O$$

$$RCOOH + NaHCO_3 \longrightarrow RCOO^-Na^+ + CO_2 + H_2O$$

A comparison of the reactions of alcohols, phenols and carboxylic acids with sodium, sodium hydroxide and sodium bicarbonate is given in the **Table 3.5.**

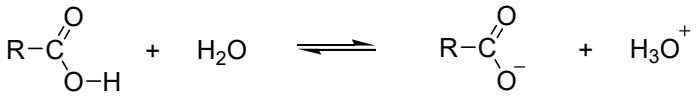
Table 3.5 Reactions of alcohols, phenols and carboxylic acids with sodium, sodium hydroxide, sodium carbonate and sodium bicarbonate

Compound	Reaction with		
	Metallic Na	**aq. NaOH**	**aq. Na_2CO_3 or $NaHCO_3$**
	Liberates H_2 gas forming RO^-Na^+	No reaction	No reaction
	Liberates H_2 gas forming $C_6H_5O^-Na^+$	Dissolves in aq. NaOH forming a solution of $C_6H_5O^-Na^+$	No reaction
	Liberates H_2 gas forming $RCOO^-Na^+$	Dissolves in aq. NaOH forming a solution of $RCOO^-Na^+$	Dissolves in aq. Na_2CO_3 or aq. $NaHCO_3$ forming a solution of $RCOO^-Na^+$ and liberating CO_2 gas

Thus the acidic strengths of alcohols, phenols and carboxylic acids vary as follows.

Alcohols < Phenols < Carboxylic acids

In aqueous medium carboxylic acids exist in the following equilibrium.



The equilibrium point of the above equilibrium is more shifted towards the right side relative to the corresponding equilibrium attained by the phenols. The reason for this is that the stabilization of the carboxylate ion relative to the carboxylic acid is greater than the stabilization of the phenoxide ion relative to phenol. Both the carboxylate ion and carboxylic acid are stabilized by resonance **(Figure 3.6)** as in the case of phenoxide ion and phenols **(Figure 3.2)**.



Resonance structures of a carboxylic acid

Resonance structures of a carboxylate anion

Figure 3.6 Resonance structures of a carboxylic acid and a carboxylate anion

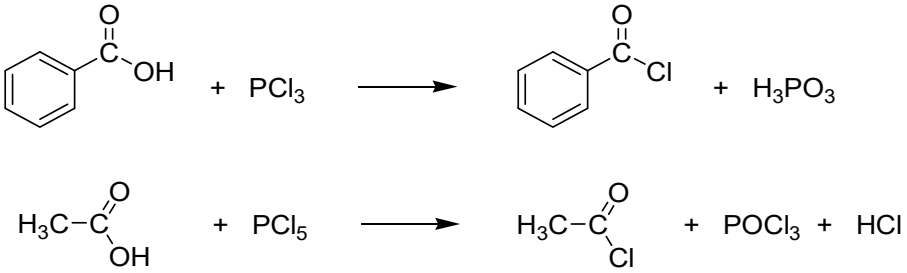
The stabilization of the carboxylate anion by resonance is greater than the stabilization of the acid because unlike in the acid there is no charge separation in the resonance structures of the anion **(Figure 3.6)**.

The higher acidity of the carboxylic acids can be explained by the fact that the carboxylate ion is stabilized by the delocalization of the negative charge between two equivalent electronegative oxygen atoms in contrast to the delocalization of the negative charge on oxygen and carbon atoms in phenoxide anion.

3.5.2.2 Reactions involving cleavage of the C–O bond

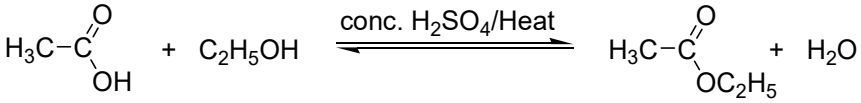
(a) *Reaction with PCl_3 or PCl_5*

Carboxylic acids react with PCl_3 or PCl_5 giving carboxylic acid chlorides.

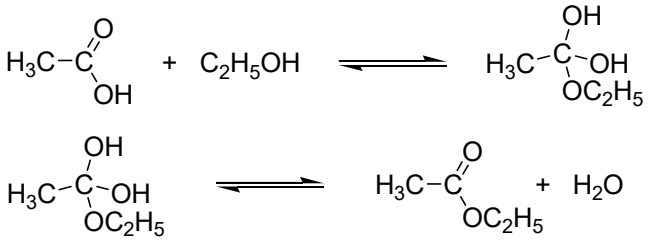


(b) *Reaction with alcohols*

Carboxylic acids react with alcohols in the presence of acid catalyst to give esters.



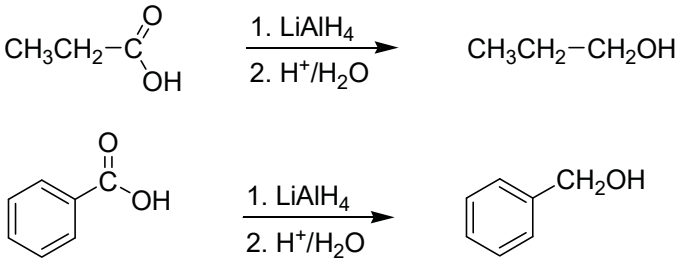
Although the above reaction appears to be a simple nucleophilic substitution reaction (OH being replaced by OC_2H_5) it actually involves first the nucleophilic addition of the C_2H_5OH molecule across the C=O to give a tetrahedral intermediate. Under acidic condition of the reaction this intermediate loses a molecule of water to give the ester.



Note: *Please also see the discussion in the* ***Section 3.6.***

3.5.2.3 Reduction of carboxylic acids with $LiAlH_4$

Carboxylic acids react with $LiAlH_4$ which is a powerful reducing agent to give alcohols. Note that carboxylic acids and their derivatives are not reduced by $NaBH_4$ which is a less powerful reducing agent than $LiAlH_4$.



3.6 Reactions of carboxylic acid derivatives

It is instructive to compare the reactions of carboxylic acid derivatives and carboxylic acids with those of aldehydes and ketones **(Figure 3.7)**.

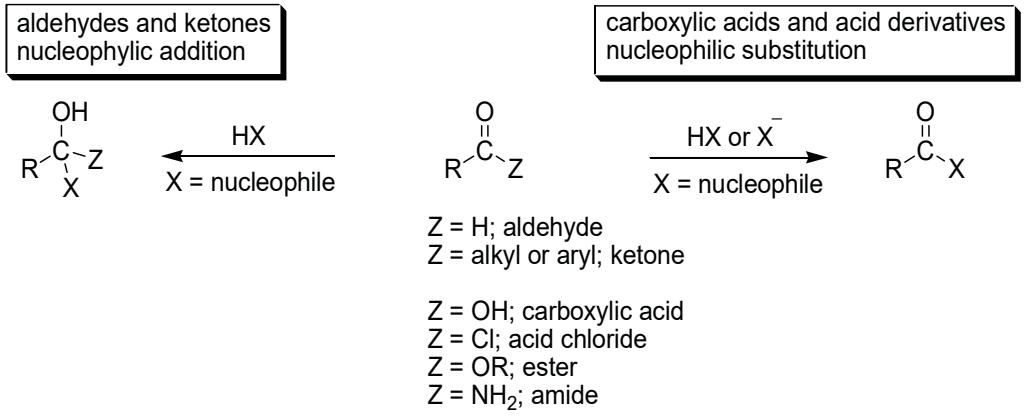


Figure 3.7 Comparison of characteristic reactions of aldehydes/ ketones with those of carboxylic acids and their derivatives

The essential difference is that in contrast to aldehydes and ketones, the Z group in carboxylic acid derivatives and carboxylic acids is capable of behaving as a leaving group. That is in reactions involving heterolytic cleavage of C–Z bond, Z leaves with the electron pair of the bond.

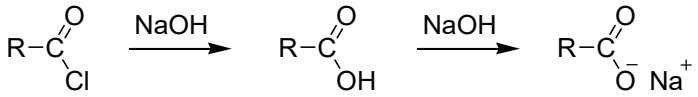
As in the case of aldehydes and ketones the first step of the reaction is the attack of a nucleophile on the carbonyl carbon of acids and acid derivatives with the opening of the carbon oxygen double bond to give a tetrahedral intermediate. This is followed by re-formation of the carbon oxygen double bond with the loss of Z as Z^- under basic or neutral conditions or as ZH under acidic conditions.

Thus the carbon atom regains its trigonal geometry and the overall reaction is the substitution of Z with a nucleophile. This reaction pathway is not available in aldehydes and ketones as H, alkyl and aryl do not behave as leaving group.

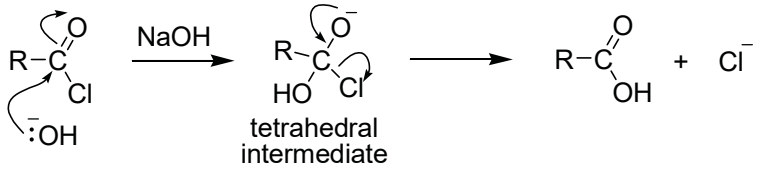
3.6.1 Reactions of acid chlorides

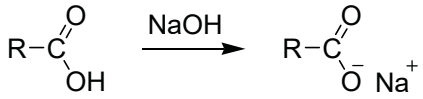
3.6.1.1 Reaction with aqueous sodium hydroxide

Acid chlorides react with aqueous NaOH to form the corresponding carboxylic acid which reacts with excess NaOH to form its sodium salt.



The mechanism of the reaction is as follows.

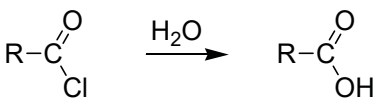




In the above reaction the OH^- is the nucleophile and Cl^- is the leaving group.

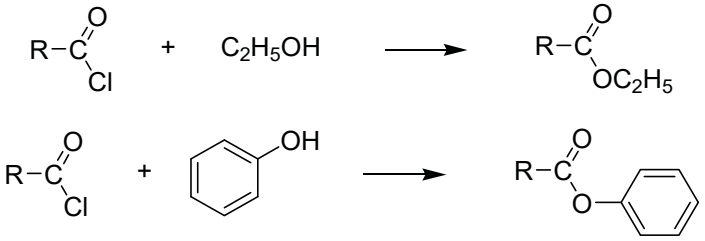
3.6.1.2 Reaction with water

Acid chlorides react with water by a similar mechanism to form the corresponding carboxylic acid.



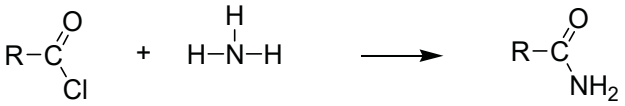
3.6.1.3 Reaction with alcohols and phenols

Acid chlorides react with alcohols and phenols to form alkyl esters and phenyl esters respectively.

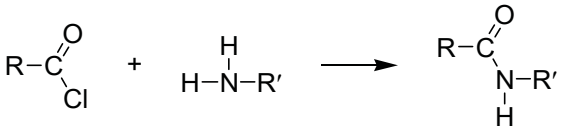


3.6.1.4 Reaction with ammonia and primary amines

Acid chlorides react with ammonia to form primary amides.



Acid chlorides react with primary amines to form secondary amides.

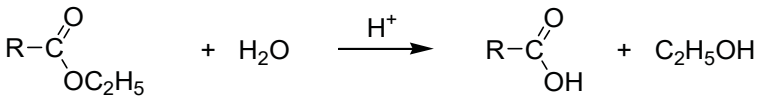


Note: *Amides are classified as primary amides when two H atoms are attached to the N atom. If one H atom is replaced by an alkyl group, it is classified as a secondary amide and if both H atoms are replaced by two alkyl groups the amide is classified as tertiary amide.*

3.6.2 Reactions of esters

3.6.2.1 Reaction with dilute mineral acids

Esters react with dilute acids and give corresponding carboxylic acid and the alcohol as the products. In this reaction water acts as the nucleophile and the ester undergoes hydrolysis. This reaction also goes through the same tetrahedral intermediate involved in the formation of esters as given in **Section 3.5.2.2** (b).



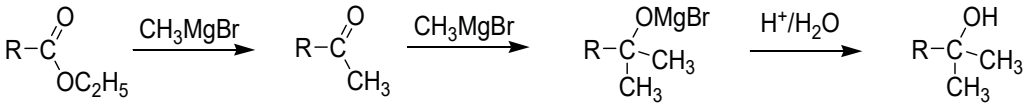
3.6.2.2 Reaction with aqueous sodium hydroxide

Esters when reacted with aqueous NaOH form the sodium salt of corresponding carboxylic acid and the alcohol. The mechanism of this reaction is similar to the mechanism of the reaction of acid chlorides with NaOH **(Section 3.6.1.1)**.



3.6.2.3 Reaction with Grignard reagent

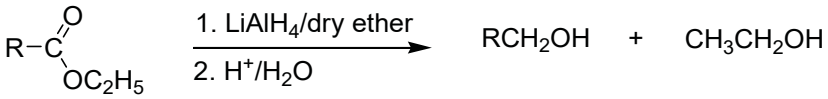
Esters react with Grignard reagents to give tertiary alcohols. In this reaction, the ester is first converted to a ketone which reacts rapidly with the Grignard reagent again to give the tertiary alcohol as the product.



Note that as ketones react faster than esters with Grignard reagents it is not possible to stop the reaction at the ketone stage.

3.6.2.4 Reduction by $LiAlH_4$

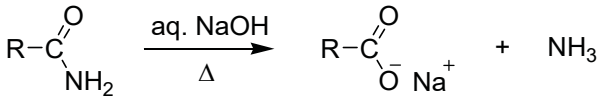
Esters react with $LiAlH_4$ and reduce to give alcohols.



3.6.3 Reactions of amides

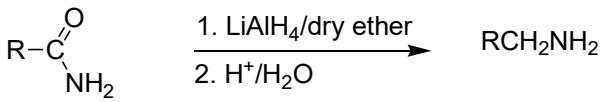
3.6.3.1 Reaction with aqueous sodium hydroxide

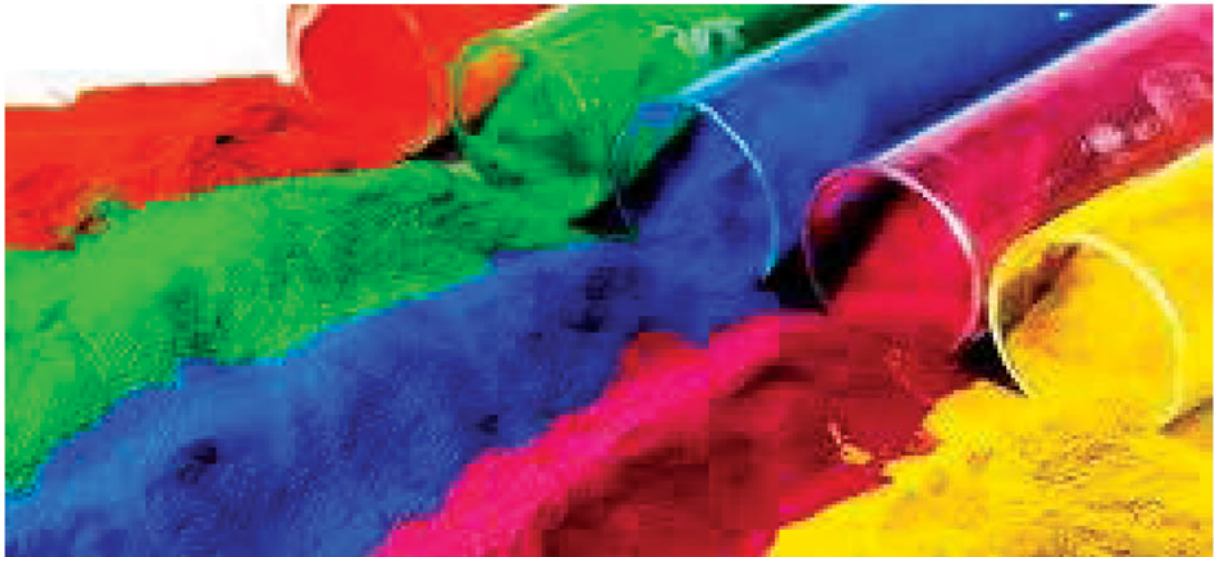
When amides are warmed with an aqueous solution of NaOH, the sodium salt of the corresponding carboxylic acid is formed with liberation of gaseous NH_3.



3.6.3.2 Reduction with $LiAlH_4$

Amides are reduced to the corresponding primary amine with $LiAlH_4$.





4. Nitrogen Containing Organic Compounds

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4.3.2 Reactions in which the diazonium ion acts as an electrophile

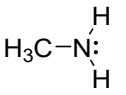
Introduction

Common organic compounds containing N includes amines and amides. Reactions of amides have been discussed under derivatives of carboxylic acids because of the presence of acyl group which are common to all derivatives of carboxylic acids. In this unit properties and reactions of amines in relation to their structures will be discussed. Amines can be defined as compounds where alkyl or aryl groups are attached to nitrogen in place of hydrogen atoms in ammonia.

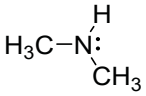
4.1 Structure, properties and reactions of primary amines and aniline

4.1.1 Classification of amines

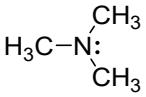
Unlike in alkyl halides and alcohols, amines are classified as primary, secondary and tertiary according to the number of alkyl or aryl groups attached to the hetero atom (N in amines). The compounds in which an alkyl or an aryl group is attached in place of one of the three hydrogen atoms in ammonia are called primary amines. The compounds in which two groups, each of which could be an alkyl or aryl group are attached in place of two atoms of hydrogen in ammonia are called secondary amines and the compounds in which three such groups are attached in place of the three atoms of hydrogen are called tertiary amines.



methylamine
(primary amine)

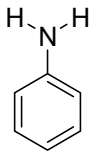


dimethylamine
(secondary amine)

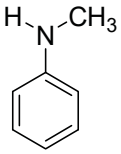


trimethylamine
(tertiary amine)

The compounds in which at least one aryl group (aromatic ring) is attached to the nitrogen atom are called aromatic amines.



aniline
(primary aromatic amine)

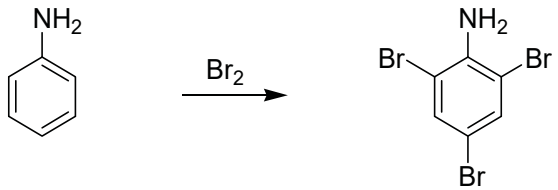


N-methylaniline
secondary aromatic amine

The simplest aromatic amine is the one with NH_2 attached to a benzene ring (aniline)

4.1.2 Reactivity of the benzene ring of aniline

Similar to phenol, aniline readily reacts with bromine to give 2,4,6-tribromoaniline because the $-NH_2$ group activates the benzene ring towards electrophilic substitution.



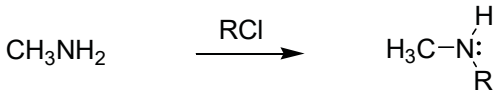
When this reaction is carried out with bromine water 2,4,6-tribromoaniline is observed as a white precipitate.

4.1.3 Reactions of primary amines

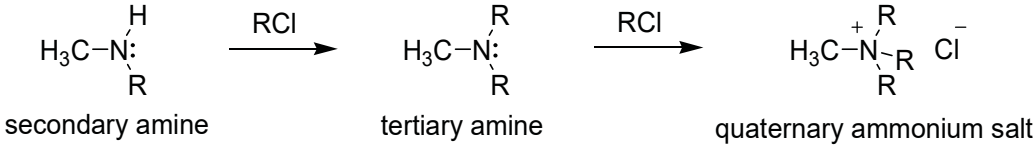
Amines can act as nucleophiles as the N atom contains a lone pair of electrons. The following are some of the reactions of primary amines with various reagents where the amine acts as a nucleophile.

4.1.3.1 Reaction of amines with alkyl halides

Primary amines react with alkyl halides to give secondary amines.



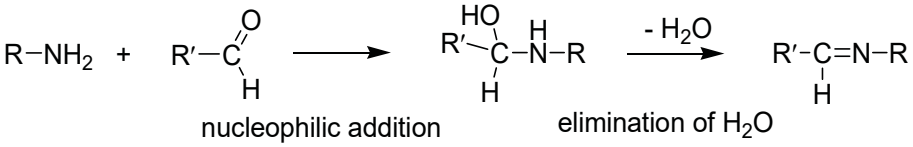
These secondary amines too have a lone pair of electrons on N atom and hence can further react with alkyl halide to form tertiary amines. Thus formed tertiary amine can react with alkyl halide further, because it also has a lone pair of electrons, to give a quaternary ammonium salt.



Therefore the reaction between primary amine and alkyl halides give a mixture of products.

4.1.3.2 Reaction of amines with aldehydes and ketones

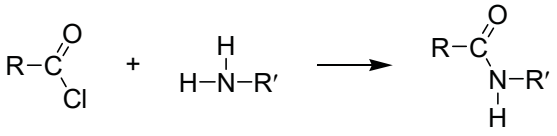
Amines show nucleophilic addition followed by elimination with aldehydes and ketones. The products are called imines.



This reaction corresponds to the reaction of aldehydes and ketones with the 2,4-dinitrophenylhydrazine (Brady reagent).

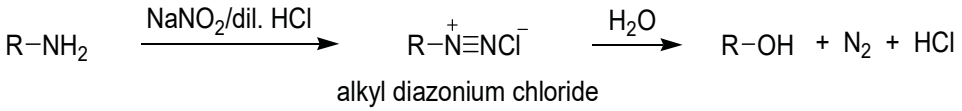
4.1.3.3 Reaction of amines with acid chlorides

Primary amines react with acid chlorides to give secondary amides.



4.1.3.4 Reaction of amines with nitrous acid ($NaNO_2$/HCl)

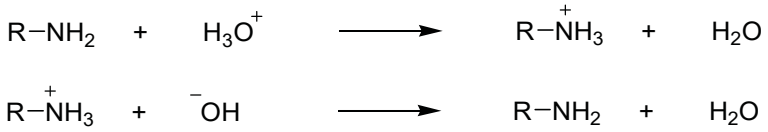
Primary amines react with nitrous acid to form diazonium salts. As alkyl diazonium salts are unstable they rapidly convert to alcohols with the evolution of nitrogen gas.



Aromatic diazonium salts formed from aromatic amines are more stable than alkyl diazonium salts.Therefore solutions of aromatic diazonium salts may be obtained at low temperatures.

4.2 Basicity of amines

Aliphatic amines are basic and the basicity is comparable to that of ammonia. Aqueous mineral acids or carboxylic acids convert amines into their salts. These salts react readily with hydroxide ions to regenerate the amine.



4.2.1 Basicity of amines versus alcohols

Nitrogen is less electronegative than oxygen. Therefore it has a higher tendency to donate lone pair of electrons than oxygen. On the other hand, nitrogen atom can bear a positive charge more easily than oxygen due to its lower electronegativity when compared to oxygen. Therefore the stability of the alkyl ammonium ion relative to the amine is more than the stability of the alkyl oxonium ion relative to the alcohol. Hence, amines are more basic than alcohols.

4.2.2 Basicity of primary aliphatic amines and aniline

Aliphatic primary amines are more basic than aniline. In aniline the lone pair of electrons on the nitrogen is delocalized on to the aromatic ring by resonance **(Figure 4.1)**. Therefore it is not easily available to a proton. Due to this reason aniline show lower basicity than primary aliphatic amines.

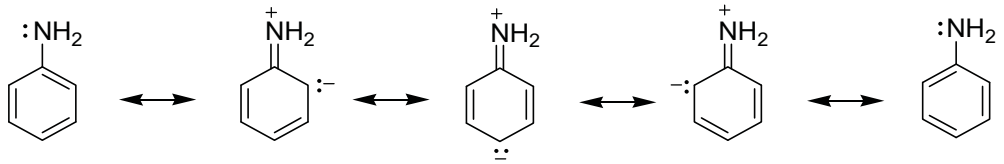


Figure 4.1 Resonance structures of aniline

4.2.3 Basicity of amines compared to amides

Amides are less basic than amines. It is because the pair of electrons on the nitrogen of the amide group is delocalized on to the carbonyl group by resonance **(Figure 4.2)** making them less available to a proton than is the lone pair of electrons on the N atom of amines.

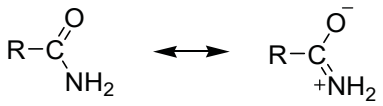
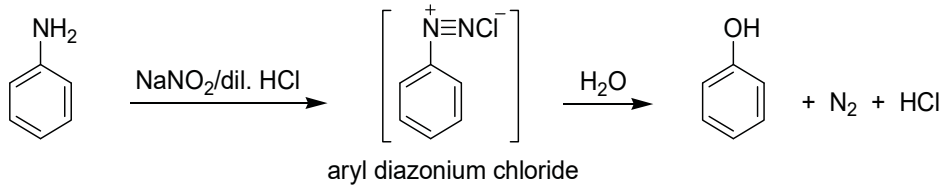


Figure 4.2 Resonance structures of amides

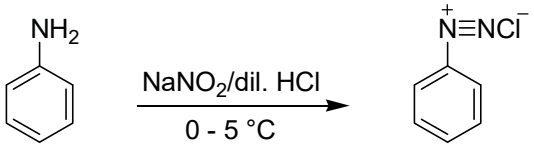
4.3 Reactions of aromatic diazonium salts

Aromatic amines such as aniline when reacted with nitrous acid ($NaNO_2$/HCl) give aromatic diazonium salts which undergo decomposition at room temperature to give phenols.



Aromatic diazonium salts are more stable than aliphatic diazonium salts. Therefore, when this reaction is carried out at low temperatures, the conversion of the aromatic diazonium salt to the phenol can be slowed down, and the diazonium salt can be isolated.

Therefore aromatic diazonium salts are prepared by the treatment of aromatic primary amines with an aqueous solution of $NaNO_2$ in the presence of dilute mineral acid such as dil. HCl or dil. H_2SO_4 at low temperature (0 – 5 °C). Since diazonium salts slowly decompose even at these temperatures, the solutions of diazonium salts are used immediately after preparation for any desired reaction.

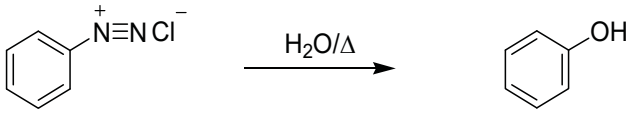


Diazonium salts undergo a large number of reactions. They can be divided into two classes: **replacement** of the diazonium group by another atom or a group; and **coupling** in which diazonium ion act as an electrophile and the nitrogen atoms are retained in the product.

4.3.1 Reactions in which the diazonium group is replaced by another atom or a group

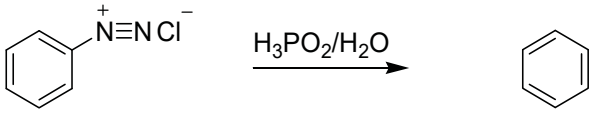
4.3.1.1 Reaction of diazonium salts with water

When aqueous solutions of diazonium salts are heated, phenols are formed.



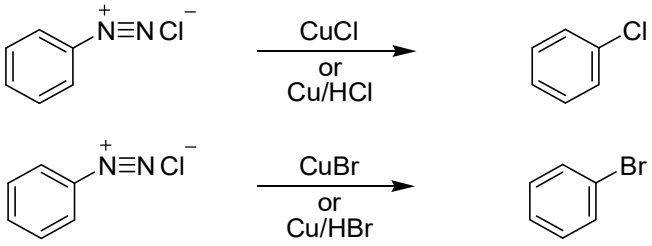
4.3.1.2 Reaction of diazonium salts with hypophosphorous acid (H_3PO_2)

When diazonium salts are treated with hypophosphorous acid (H_3PO_2), the diazonium group is replaced by an H atom.



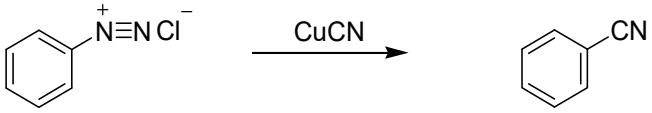
4.3.1.3 Reaction of diazonium salts with CuCl and CuBr

When diazonium salts are reacted with CuCl or CuBr, the corresponding aromatic halide is formed. This reaction can also be carried out with copper powder and hydrogen halide (Cu/HCl or HBr) instead of copper(I) halide.



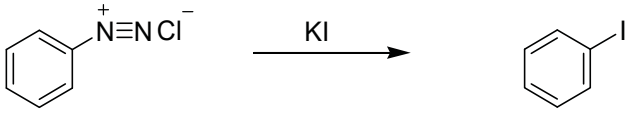
4.3.1.4 Reaction of diazonium salts with CuCN

When diazonium salts are reacted with CuCN, the diazonium group is replaced by CN group.



4.3.1.5 Reaction of diazonium salts with KI

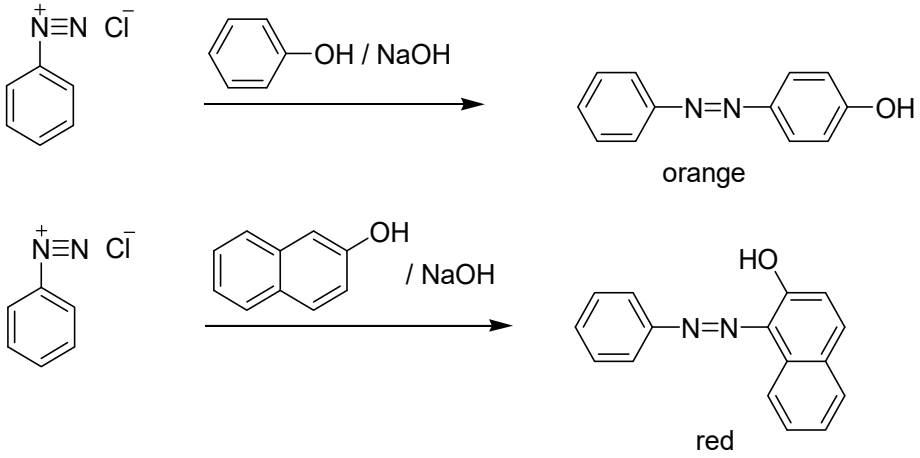
When diazonium salts are reacted with KI, the diazonium group is replaced by I.



4.3.2 Reactions in which the diazonium ion acts as an electrophile

Aryl diazonium ions can participate as electrophiles as it contains a positive charge on N. They react with phenols under alkaline conditions.

Benzene diazonium chloride reacts with phenol in the presence of aqueous NaOH to give an orange coloured compound, and with β-naphthol (2-naphthol) in the presence of aqueous NaOH to give a red coloured compound.



Reference:

Morrison, R. T. and Boyd, R. N. (2010) *Organic Chemistry*: Pearson.

Solomons, T. W. G. and Fryhle C. B. (2011) *Organic Chemistry*: John Wiley and Sons Inc.

G. C. E. (Advanced Level)

CHEMISTRY

Grade 13

Resource Book

Unit 11: Chemical Kinetics
Unit 12: Chemical Equilibrium
Unit 13: Electrochemistry

Department of Science
Faculty of Science and Technology
National Institute of Education
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Chemistry

Resource Book

Grade 13

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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.

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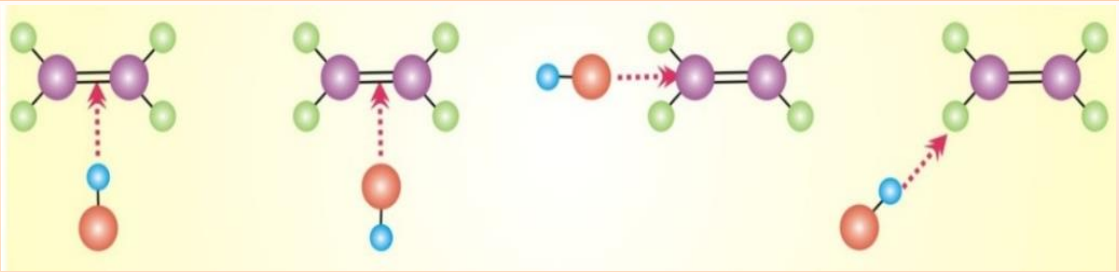
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1. Chemical Kinetics

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1.11 Energy profiles of reactions

Introduction

In the previous units for example, unit 4 and 5 described the basic aspects of behavior of molecules depending on their physical state and energy requirements for the reaction to occur. Though, we know that the amounts of reactants and products and their molecular nature yet, we have not focused quantitatively on "How fast is the reaction proceed" and requirements to be satisfied to occur a chemical reaction. In this regard the present unit addresses and focuses on the field of *kinetics* where the rates of reactions are concerned. We examine the rate of a reaction, the factors that affect it, the theories that explain those effects, and the stepwise changes reactants undergo as they transform into products. This unit also introduce some general ideas about reaction rates and overview key factors that affect them—concentration/ pressure, physical state, catalyst and temperature. Further, express rate through a rate law and determine its components and see how concentrations change as a reaction proceeds and discuss the meaning of half-life. In addition, we discuss about reaction mechanisms, noting the steps a reaction goes through and picturing the chemical species that exists as reactant bonds are breaking and product bonds are forming.

1.1 Concept of chemical kinetics

We have gained some idea about chemical reactions in unit 5 (energetics). Chemistry is mainly concerned with changes occurring in nature or in substances of interest. Such changes are depicted in a simple way by an equation which is considered a chemical reaction. In the study of any chemical reaction we try to find out the followings.

(a) The feasibility of a chemical reaction, which can be predicted by thermodynamics. For example, energy changes associated with a reaction are expressed by thermodynamic quantities such as ΔH, ΔG, ΔS and we know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible. This also gives us in which direction the reaction occurs.

(b) Extent of a reaction, which explains how far a reaction proceeds to give the desired products and this can be determined from chemical equilibrium (unit 12). This can be quantified with the knowledge of the equilibrium constant.

Along with these, there is another equally important aspect for a given reaction worth paying attention; that is how fast a reaction occurs or the rate of a reaction and factors controlling the rate of a reaction. In this case, time taken by a reaction to reach some known point (extent) has to be studied. Further, how the conversion of reactants to products occurs: that is the mechanism of the reaction has to be known. All these questions can be answered by a branch of chemistry, which deals with the study of reaction rates and their mechanisms, called "chemical kinetics".

If a reaction is to occur, it must be both thermodynamically and kinetically favoured under given conditions such as temperature and pressure of the system. These are relative terms: the reaction must be thermodynamically favoured enough to form the amount of the product desired, and it must be kinetically favoured enough to be completed within the

desired time period. For example, nuclear reactions occur very fast (in a fraction of a second) and the conversion of graphite to diamond takes millions of years. This is because it has an enormous activation energy that must be overcome before the reaction may proceed. We must also consider the mechanism of the reaction which is a sequence of events at the molecular level that controls the speed and the desired products of the reaction. Therefore, studying the rates of reactions is very important in many fields. These factors of thermodynamics and kinetics can be simply shown schematically in Figure 1.1 below.

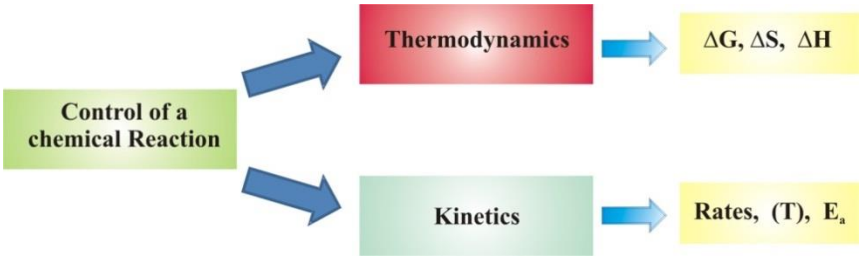


Figure 1.1 Controlling chemical reactions in view of thermodynamics and kinetics

Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions which can alter the reaction rates. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. In these studies, investigations in measurable quantities such as amounts reacted or formed and the rates of consumption or formation come under macroscopic level. At the molecular level, the reaction mechanisms involving orientation, velocities and energy of molecules undergoing collisions have to be considered. These parameters are somewhat hard to measure.

When we consider chemical processes, many chemical processes such as explosive reactions take place in a fraction of a second while the rusting of iron may take a very long time, sometimes in centuries for completion. Ionic reactions in solution, for example the reaction between NaCl(aq) and $AgNO_3$(aq) giving a white precipitate of silver chloride occurs within a very short (but measurable with some advanced techniques) time. In chemical kinetics, at this stage we actually study the rates of reactions which are neither so fast nor so slow. Usually, a chemical reaction involves breaking of bonds in the reactant molecules and making of bonds in the product molecules and it is easy to understand that a reaction that involves breaking of weak bond(s) is faster than a one involving breaking of strong bond(s) at a given temperature. Ionic compounds such as strong electrolytes in solution remain completely ionized and hence in any ionic reaction, no bond is broken. Therefore, an ionic reaction is fast. Different reactions, as they involve variety of bonding in respect of the strength of the bonds to be broken, occur at different rates. Reactions which involve less bond rearrangements are generally faster than those which involve considerable bond rearrangements at a given temperature. Chemical kinetics or reaction kinetics is the study of rates of chemical processes. Chemical kinetics includes

investigations of how different experimental conditions can influence the speed of a chemical reaction and gives information about the mechanisms of reactions and transition states, as well as the construction of mathematical models (rate equations) that can describe the characteristics of a chemical reaction. With this it may worth to categorize reactions with respect to their rates as described below.

Very fast (Instantaneous) reactions

These reactions are so fast and occur as soon as the reactants are bought together. These reactions involve ionic species and are thus known as ionic reactions. There are many reactions occurring on the surfaces of catalysts. They are much faster and usually take place in 10^{-12} to 10^{-18} seconds in the time scale. It is almost impossible to determine the rates of these reactions with conventional techniques. However, there are advanced techniques available with ultra-fast laser spectroscopy which in further allow us even to follow electron transfer processes. Some examples we can consider for these very fast reactions are;

Formation of a precipitate of AgCl when highly concentrated solutions of silver nitrate and sodium chloride are mixed:

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

Neutralisation of a strong acid with a strong base when their aqueous solutions are mixed:

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

Very slow reactions

There are certain reactions which occur in extremely slow rates or sometimes never happen at the room temperature. It is therefore, difficult to study the kinetics of such reactions. Examples:

Reaction between hydrogen and oxygen at room temperature: This is highly explosive at high temperatures (~ 1000 K).

Reaction between carbon and oxygen; coke does not catch fire spontaneously in air and remains unreacted.

Moderate reactions

Between the above two extremes, there is a large number of reactions which take place at moderate and measurable rates at room temperature and these allow us to study chemical kinetics under laboratory conditions. Some common examples are given below.

Decomposition of hydrogen peroxide:

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

Decomposition of nitrogen pentoxide:

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

Hydrolysis of an ester:

$$CH_3COOC_2H_5(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + C_2H_5OH(aq)$$

Inversion of sucrose in aqueous solution:

$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$

Reaction between nitrogen dioxide and carbon monoxide:

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Reaction between nitric acid and thiosulfate:

$Na_2S_2O_3(aq) + 2HNO_3(aq) \rightarrow S(s) + 2NaNO_3(aq) + SO_2(g) + H_2O(l)$

Reaction between ferric chloride and potassium iodide:

$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

Reaction between calcium carbonate and hydrochloric acid:

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

The rates of chemical processes can be decreased or increased by changing conditions under which they occur. For example, very slow reaction at room temperature; $CO + 2H_2 \rightarrow CH_3OH$, can be speeded up by maintaining temperature around 400 ^oC, pressure about 300 atm and using a catalyst. The decay of food items can be slowed down by reserving them in refrigerators.

In the study of chemical kinetics, we can predict the rate of a particular reaction under given conditions and that conditions can be adjusted or optimized to make the reactions occur at a desired rate. This is useful in industry to accelerate the formation of industrial products and to predict the mechanism of the reaction.

1.2 Rate of a reaction

Different reactions can occur at different rates. Reactions that occur slowly have a low rate of reaction and reactions that occur quickly have a high rate of reaction. As mentioned above, for example, the chemical change of graphite to diamond and weathering of rocks are very slow reactions; it has a low rate of reaction. Explosions and nuclear reaction are very fast reactions: they have a high rate of reaction.

In general, a reaction can be represented as follows.

$$\text{Reactants} \rightarrow \text{Products}$$

When the reaction proceeds, reactants are consumed while products are formed. As a result, the speed of a reaction or the rate of a reaction can be defined as the change in amount (concentration) of a reactant or product in unit time. That is;

(i) the rate of decrease in amount/ concentration of any one of the reactants, or

(ii) the rate of increase in amount/ concentration of any one of the products at a constant temperature.

Consider a hypothetical reaction at a constant temperature and also assume that the volume of the system remains constant.

$$A \rightarrow B$$

In general, it is more convenient to express the reaction rate in terms of the change in amount with time at a constant temperature. For the reaction above let's consider that at the time t_i *(not at t = 0)* the initial amount of A is $(n_A)_i$ moles and after some time t_t, the amount of A is $(n_A)_t$ moles. Therefore, the change in amount of A within the time interval (t_t - t_i) is [$(n_A)_t$ - $(n_A)_i$] moles.

$\therefore$ The rate of change in the amount of A $= \frac{[(n_A)_t - (n_A)_i]}{t_t - t_i} = \frac{\Delta(n_A)}{\Delta t}$

Similarly for the product B we can write,

The rate of change in amount of B $= \frac{[(n_B)_t - (n_B)_i]}{t_t - t_i} = \frac{\Delta(n_B)}{\Delta t}$

In the above, $\Delta(n_A)$; change in amount of the reactant has a negative sign because $(n_A)_t < (n_A)_i$. It is important to note that the change in amount in any chemical process is considered to be a positive quantity. Hence in the case of change in amount in a reactant we use a negative sign. So, the rate of change in amount is always a positive quantity. Therefore, the rate of the above reaction can be written as,

$$\text{Rate} = -\frac{\Delta(n_A)}{\Delta t} = \frac{\Delta(n_B)}{\Delta t}$$

With the above understanding, the rate of a reaction can easily be correlated with the change in amount of either reactant(s) or product(s) of the reaction as the rate of consumption of the reactants or formation of the products.

In this simple description, the rate depends upon the change in amount of reactants or products and the time taken for that change to occur. Thus, the variation of the rate of the reaction A $\rightarrow$ B can be illustrated as shown in Figure 1.2.

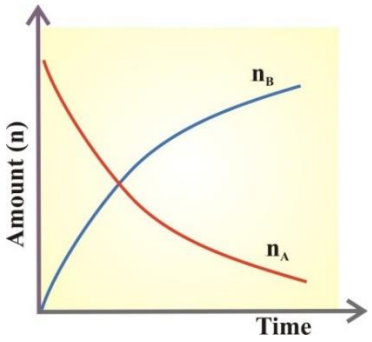
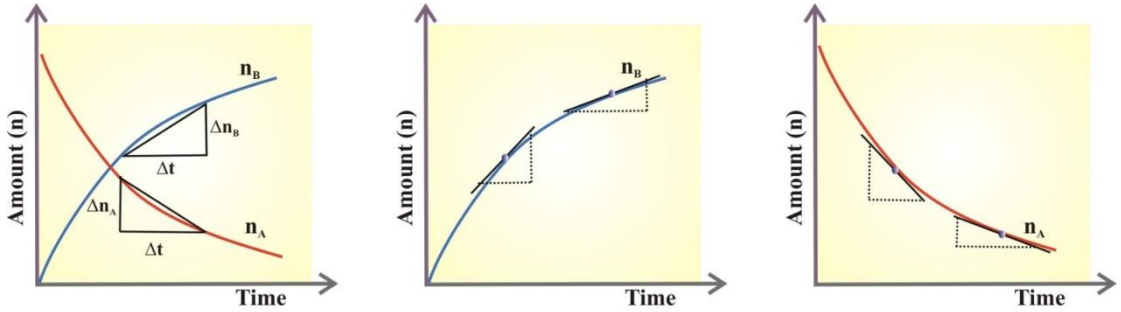


Figure 1.2 The rate of reaction A $\rightarrow$ B; is the decrease of n_A and increase of n_B with time at a constant temperature. It has to be noted that the rate of the reaction has decreased over the time.

In a mathematical point of view, this quantity $-\frac{\Delta(n_A)}{\Delta t}$ or $\frac{\Delta(n_B)}{\Delta t}$ can be represented as depicted in Figure 1.3(a) where the rate of the reaction is given by the change in amount

$\Delta(n_A)$ *or* $\Delta(n_B)$ over the time interval Δt and usually this rate is defined as *average rate*. Usually the rate changes at a very small time and hence to calculate the rate over the time interval $\boldsymbol{\Delta t}$, the rates at each time within the interval has to be averaged. The rate at a given instance of time is the slope of the tangent drawn to the curve showing the variation of amount with time as shown in Figures 1.3 (b) and (c) for the product B and reactant A, respectively. It is noted that the slope for the rate of change in amount of A (reactant) is negative indicating that the amount decreases with the time and therefore, we use a negative sign in front of the slope when the rate is calculated. It also shows that the rate also decreases with time as the slope decreases with the time because the reactant is consumed during the progress of reaction.



(a) (b) (c)

Figure 1.3 The rate of reaction A → B; **(a)** Description of rate as the change in amount Δn over time period Δt. The definition of rate as the slope of the tangent drawn to the curve showing the variation of amount of the product B with time **(b)** and the reactant A with time **(c)**. In **(c)**, negative slope indicates that the amount of reactants is decreasing over the time. It is also shown in **(b)** and **(c)** that the rate of the reaction decreases with the time as the slope of the tangent decreases.

In the above we have gone through a very basic idea about the description of reaction rate in which the change in amount (number of moles) is considered the measure of the quantity. If we consider the volume of the container in which the reactions occurs as *V* and *it does not change during the progress of reaction* then we can define the rate of the reaction as the change in amount of either reactant(s) or product(s) per unit time per unit volume. If the volume *V* of the system in which the reaction is carrying out is constant, we can write the rate as,

$$\text{Rate} = \frac{\Delta(n_A)}{V\,\Delta t} = \frac{\Delta(C_A)}{\Delta t} \quad \because \ {}^{(n_A)}/_{V} = C_A : \text{concentration}$$

Thus we can then express the rate of the reaction as the change in concentration of either reactant(s) or product(s) per unit time as: $\text{Rate} = -\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$.

We can therefore, replace the amount in y-axis in the plots of Figures 1.2 and 1.3 with the concentration and hereafter, we use the concentration to represent the change in quantity of a given reaction as shown in Figure 1.4.

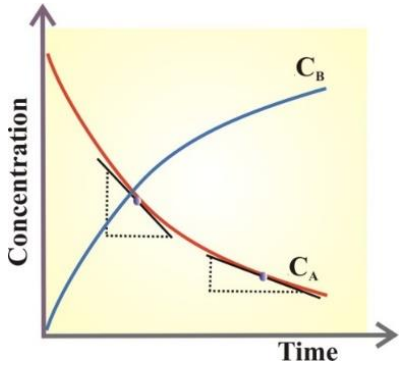


Figure 1.4 The rate of reaction A → B; description of rate as the change in concentration over the time. Rate decreases with the time as is evident from the decrease in the slope of the curve.

We can also see in this plot that the reaction slows down as it proceeds (not the case with reactions) indicating that the reaction rate depends on the concentration of A available to react. Note that when [A] is large, the slope of the curve is steep and hence the reaction is fast. Later in the reaction, [A] is much smaller, and so is the slope. Hence the reaction slows down as A is used up showing that there is a concentration dependence of rate.

Units of rate:

As the rate is defined as the change in concentration at a given time, the units will be **mol dm^{-3} s^{-1}** (if the time is measured in seconds). This unit can easily be applied for the reactions in solutions. When the gas phase reactions are concerned we have to measure the concentrations as partial pressures. Therefore, the units will be **Pa s^{-1}** (or atm s^{-1}).

It can further be understood that the reaction rate will be equal (proportional) to the reciprocal of time (1/t) if the time taken to occur a given change in a reaction is monitored.

For a reaction A → B, we write the rate as;

$$\text{Rate} = -\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$$

If the change occurred is a constant and the time taken for that change is t, we write,

$$\text{Rate} = \frac{\text{constant}}{t}$$

or

$$\text{Rate } \alpha \ \frac{1}{t}$$

1.3 Reaction rate and stoichiometry

As shown in section 1.2, the rate of a simple reaction of the type A $\rightarrow$ B at a constant temperature and in a closed rigid vessel (constant volume) can be expressed either as the rate of decrease in concentration of A, $-\frac{\Delta(C_A)}{\Delta t}$ or as the rate of increase in concentration of B, $\frac{\Delta(C_B)}{\Delta t}$. In this reaction we see that one mole of A gives one mole of B, so that the rate can be given as are equal giving $-\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$. Now let us consider a reaction when 2 moles of A giving one mole of B.

$$2A \rightarrow B$$

Because two moles of A are consumed to produce one mole of B, the rate of consumption of A would be twice the rate of production of B. Therefore, we can express the rate of the reaction as;

$$-\frac{1}{2}\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$$

Or we write the same as,

$$-\frac{1}{2}\frac{\Delta[\mathrm{A}]}{\Delta t} = \frac{\Delta[\mathrm{B}]}{\Delta t}$$

Therefore, in general for a reaction: aA + bB $\rightarrow$ cC + dD

We can write,

$$\textbf{Rate} = -\frac{\mathbf{1}}{\boldsymbol{a}}\frac{\Delta[\mathbf{A}]}{\Delta \boldsymbol{t}} = -\frac{\mathbf{1}}{\boldsymbol{b}}\frac{\Delta[\mathbf{B}]}{\Delta \boldsymbol{t}} = \frac{\mathbf{1}}{\boldsymbol{c}}\frac{\Delta[\mathbf{C}]}{\Delta \boldsymbol{t}} = \frac{\mathbf{1}}{\boldsymbol{d}}\frac{\Delta[\mathbf{D}]}{\Delta \boldsymbol{t}}$$

Example 1.1

Consider the decomposition of $H_2O_{2(aq)}$ occurring in a 1.0 dm^3 rigid container at a given temperature according to the following reaction.

$$2H_2O_{2(aq)} \rightarrow 2H_2O(l) + O_2(g)$$

Write the rate of the above reaction in terms of both reactants and products.

Answer

Assuming that the reaction proceeds according to the stoichiometry as shown in the **Figure 1.5**, plot the variations in concentrations of each species in the reaction mixture over the time.

According to the stoichiometry of the reaction; 2 moles of $H_2O_{2(aq)}$ give 2 moles of $H_2O(l)$ and one mole of $O_2(g)$. As the volume of the container is 1.0 dm^3:

Initial concentrations; $H_2O_{2(aq)}$: $H_2O(l) : O_2(g) = 2.0 : 0.0 : 0.0$ mol dm^{-3}

Final concentrations; $H_2O_{2(aq)}$: $H_2O(l) : O_2(g) = 0.0 : 2.0 : 1.0$ mol dm^{-3}

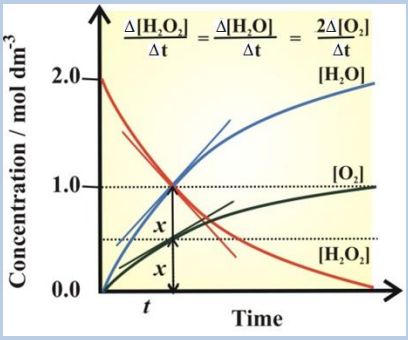


Figure 1.5 The variation of concentrations of the species in reaction $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ at a given temperature

Rate of the reaction can be written as;

$$\text{rate} = -\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t} \quad \text{or} \quad \frac{-\Delta[H_2O_2]}{\Delta t} = \frac{\Delta[H_2O]}{\Delta t} = 2\frac{\Delta[O_2]}{\Delta t}$$

It has to be noted that the above graphs were drawn with the accurate scale according to the stoichiometry and rate of the reaction. Therefore, from the plots after time *t* the rates (slopes) can be calculates as:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = -\frac{(-)2x}{t} = \frac{2x}{t}; \frac{\Delta[H_2O]}{\Delta t} = \frac{2x}{t} \text{ and } \frac{\Delta[O_2]}{\Delta t} = \frac{x}{t}$$

This clearly implies the definition of the rate of this reaction. Therefore, we can understand that the rates of reactions can be experimentally determined or estimated.

Example 1.2

Write the rates of following reactions in terms of both reactants and products.

(i) $Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

(ii) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Answer

(i) $$\text{Rate} = -\frac{\Delta[Na_2CO_3(aq)]}{\Delta t} = -\frac{1}{2}\frac{\Delta[HCl]}{\Delta t} = \frac{1}{2}\frac{\Delta[NaCl]}{\Delta t} = \frac{\Delta[CO_2(g)]}{\Delta t}$$

(ii) $$\text{Rate} = -\frac{\Delta[N_2(g)]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

Example 1.3

$N_2O_5(g)$ decomposes as follows:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

It was found that in a closed rigid vessel at a particular instant the rate of decomposition of $N_2O_5(g)$ was 3.0×10^{-7} mol dm^{-3} s^{-1} at a constant temperature. Write the rates of formation of (i) $NO_2(g)$ and (ii) $O_2(g)$.

Answer

We can write the rate of the reaction as;

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5(g)]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2(g)]}{\Delta t} = \frac{\Delta[O_2(g)]}{\Delta t}$$

(i) $\frac{1}{2} \times 3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1} = \frac{1}{4}\ \frac{\Delta[NO_2(g)]}{\Delta t}$

$$\frac{\Delta[NO_2(g)]}{\Delta t} = 6.0 \times 10^{-7}\ \text{mol dm}^{-3}\text{s}^{-1}$$

(ii) $\frac{1}{2} \times 3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1} = \frac{\Delta[O_2(g)]}{\Delta t}$

$$\frac{\Delta[O_2(g)]}{\Delta t} = 1.5 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Example 1.4

In the reaction taking place in a closed rigid container at a constant temperature:

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

the rate of formation of NO(g) was found to be 2.0×10^{-4} mol dm^{-3} s^{-1}.

Write the rates of (i) the reaction and (ii) the consumption of NOBr(g).

Answer

We can write; $\text{Rate} = -\frac{1}{2}\frac{\Delta[NOBr(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO(g)]}{\Delta t} = \frac{\Delta[Br_2(g)]}{\Delta t}$

(i) $\therefore$ rate of the reaction $= \frac{1}{2} \times 2.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

$$= 1.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

(ii) $\frac{1}{2}\frac{\Delta[NOBr(g)]}{\Delta t} = 1.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

$$\therefore \frac{\Delta[NOBr(g)]}{\Delta t} = 2.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Example 1.5

At a given time, the rate of the following reaction with respect to C_2H_4 is 0.20 mol dm^{-3} s^{-1}. Write the rate of the reaction with respect other species in the reaction.

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

Answer

Rate of the reaction:

$$\text{Rate} = -\frac{\Delta[C_2H_4(g)]}{\Delta t} = -\frac{1}{3}\frac{\Delta[O_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[CO_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O(g)]}{\Delta t}$$

Given that, $\frac{\Delta[C_2H_4(g)]}{\Delta t} = 0.20 \text{ mol dm}^{-3} \text{ s}^{-1}$

$$\frac{\Delta[O_2(g)]}{\Delta t} = 3 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 3 \times 0.20 \text{ mol dm}^{-3} \text{ s}^{-1} = 0.60 \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\frac{\Delta[CO_2(g)]}{\Delta t} = 2 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 2 \times 0.20 \text{ mol dm}^{-3} \text{ s}^{-1} = 0.40 \text{ mol dm}^{-3} \text{ s}^{-1}$$

$$\frac{\Delta[H_2O(g)]}{\Delta t} = 2 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 2 \times 0.20 \text{ mol dm}^{-3} \text{ s}^{-1} = 0.40 \text{ mol dm}^{-3} \text{ s}^{-1}$$

From the above examples we can see that the rate of a reaction is not directly equal to either the rate of disappearance of reactants or the rate of appearance of products.

Therefore, for a reaction taking place at constant temperature and constant volume, rate of the reaction is given by;

$$\textbf{Rate} = \frac{1}{\nu_j}\frac{\Delta[J]}{\Delta t}$$

$\boldsymbol{\nu_j}$ is the stoichiometric coefficient of the substance ***J***. $\boldsymbol{\nu_j}$ is negative for reactants and positive for products.

Example 1.6

Consider the reaction, A $\rightarrow$ 2B, which was started with the initial concentration of 0.50 mol dm^{-3} of reactant A. It drops to 0.00 mol dm^{-3} in 10 seconds. During this time the concentration of B increased from 0.00 mol dm^{-3} to 1.00 mol dm^{-3}. Calculate the rate of this reaction as follows.

Answer

We can write the rate of the reaction as; Rate $= \frac{1}{\nu_j}\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$

$$= -\frac{(0.00-0.50)\text{mol dm}^{-3}}{10\text{ s}}$$

$$= 0.05\text{ mol dm}^{-3}\text{ s}^{-1}$$

or

$$\text{Rate} = \frac{1}{\nu_j}\frac{\Delta[B]}{d\,t} = \frac{1}{2}\frac{\Delta[B]}{\Delta t} = \frac{1}{2}\times\frac{(1.00-0.00)\text{ mol dm}^{-3}}{10\text{ s}}$$

$$= 0.05\text{ mol dm}^{-3}\text{ s}^{-1}$$

Example 1.7

The decomposition of A at 300 K in a solution with constant volume can be followed by monitoring the concentration of A. Initially (at t = 0), the concentration of A is 2.00 mol dm^{-3} and after 180 seconds, it is reduced to 1.64 mol dm^{-3}. The reaction takes place according to the equation

$$2A(aq) \rightarrow 4B(aq) + C(aq)$$

Calculate the rate of this reaction.

Answer

$\Delta A = 1.64 - 2.00 = -0.36$ mol dm^{-3}

$\therefore -\Delta A = 0.36$ mol dm^{-3}

According to the reaction,

Rate = ½ $[\Delta[A]/\Delta t]$ = ½ × 0.36 mol dm^{-3}/ 180 s

$= 1.0 \times 10^{-3}$ mol dm^{-3} s^{-1}

1.4 Experimental techniques to determine the rates of reactions

As from the example 1.1 and other calculations, we know that the reaction rates are experimentally determined quantities and therefore it is necessary to understand that how the rate of a reaction, is obtained experimentally. In this context, we know to determine the rate of a reaction we have to monitor the concentration of the reactant (or product) as a function of time. That is, in order to determine the rate of a particular reaction, it is necessary to follow either the rate of decrease in concentration of a reactant(s), or the rate of increase in concentration of a product, by choosing an appropriate experimental method at a constant temperature. We can categorize the techniques as non-disruptive and disruptive. In non-disruptive techniques, this is done through a measurement of a rapidly determinable physical property of the reaction mixture. For example, for reactions in solutions, the concentration of a species can often be measured by spectrophotometric techniques if coloured species are involved. If ions are involved, the change in concentration can also be detected by an electrical conductance measurement. Reactions involving gases are monitored by pressure measurements under the constant volume.

Spectrophotometric methods

This is usually employed when at least one of the species involved in the reaction is coloured and its absorbance is monitored as a function of time at a suitable wavelength obtained from the absorption spectrum of either a reactant or a product. As the absorbance is directly proportional to the concentration of the particular species, the rate of the reaction can be monitored by these absorbance measurements as a function of time.

Methods involving the measurement of change in total pressure

As we know, the total pressure of a gas-phase reaction occurring in rigid container at any time will be the sum of the partial pressures of all the gaseous reactants and products. Thus if the stoichiometry of the reaction is known, this can be used to determine either the rate of decrease of a reactant or the rate of increase of a product as a function of the measured total pressure.

Electrical conductance/ conductivity method

Consider, for example, the reaction:

$$R_1COOR_2(aq) + OH^-(aq) \rightarrow R_1COO^-(aq) + R_2OH(aq)$$

The conductivity of hydroxyl ions is much higher than that of the other ions such as ethanoate ions ($R_1 = C_2H_5$). Also the conductivity depends on the concentration of ions and hence, measurement of the conductance is an appropriate method for following the rate of loss of hydroxyl ions in the above process where the decrease in conductivity will be observed.

Optical rotation method

This method is suitable for reactions where the optical activity of the products is different from those of the reactants. For example hydrolysis of sucrose gives glucose and fructose with different optical rotations. An instrument called "polarimeter" is used for the optical rotation measurements. As the optical rotation is related to the concentration, measurement of the optical rotation will then be related to the rate of the reaction.

Refractive index method

This method is especially useful for liquid-phase reactions where the refractive index of reaction mixture changes in the course of the reaction due to increase in the products and decrease in the reactants.

Gas evolution method

If there is one gaseous product in a reaction, the gas evolved can be collected and its volume measured as a function of time. For example, the decomposition of calcium carbonate proceeds by producing CO_2 gas.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

For these types of reactions, the rate can be determined from a measurement of the volume of gas evolved during the reaction (you will practice such in a laboratory under this unit).

Disruptive techniques: Chemical analysis method

In chemical analysis method, a required sample of the reaction mixture is taken out and analyzed, for example, titration to estimate the acid liberated during the hydrolysis of an ester. In the method of chemical analysis, to obtain the composition of the reaction mixture at a given time it is necessary to ensure that no further reaction takes place between sampling and analysis. This is usually achieved by lowering the temperature (quenching) of the mixture immediately after sampling.

1.5 Factors affecting the rate of a chemical reaction

Usually a balanced chemical equation is used to describe the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed in a chemical reaction. As we have some idea from the previous sections, this balanced equation gives us no information about how fast a given reaction will occur. Such information is obtained by studying the chemical kinetics or rates of a reaction. The rate of the reaction depends on various factors: reactant concentrations, temperature, physical nature and surface areas of reactants, catalyst properties and solvent. By studying the kinetics of a reaction, it is possible to gain insights into how to control reaction conditions to achieve a desired outcome.

It is easy to get an idea that the rate of a chemical reaction can be increased by:
Increasing the concentration of a solution or raising the pressure (for a gas phase reaction), increasing the temperature of the reaction system, increasing the surface area of a solid

and by adding a catalyst. In addition to these, solvent used in an experiment to dissolve solute (reactant) can also affect the rate of reaction.

Insight into these can be understood by considering the basic requirements necessary to satisfy to occur a chemical reaction based on collision theory as discussed below.

1.6 Uses molecular kinetic theory (Collision Theory) to explain the effect of factors affecting the rate of chemical reactions

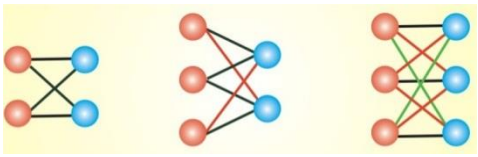
1.6.1 Collision theory

As we know from unit 4 (gaseous state of matter), collision theory explains the motion of molecules, their kinetic energy and how pressure changes in a system accordingly. Now it is easy to understand that for a reaction to occur the molecules must collide all the time and some fraction- but not all of those collisions will lead to transformation of the reactants to the products. This simply means that all the collisions will not result products. For example, at 1 atm and 20 °C, the $N_{2(g)}$ and $O_{2(g)}$ molecules in 1 cm^3 of air experience about 10^{27} collisions per second. If all that was lead for a reaction atmosphere would consist of almost all NO; but only traces are present. This indicates that the number of collisions can't be the only factor which determines the occurrence of a reaction and a reaction rate. Therefore, following must be satisfied to occur a chemical reaction:

1. The molecules must come into contact leading to a collision.
2. They must collide with enough energy to overcome an energy barrier. This minimum energy required is called the activation energy for the reaction.
3. They must collide in favorable orientation that allows the necessary bond-breaking and forming needed to transform the reactants to the products.

Collision:

According to kinetic molecular theory, the reactant molecules are considered to be hard spheres. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency *(Z)*. In its basic form, collision theory deals with one-step reactions, those in which two particles collide and form products: A + B $\rightarrow$ products. Suppose we have only two particles of A and two of B confined in a vessel.



(a) (b) (c)

Figure 1.6 Increase in number of collisions with concentration of the reactants A and B in a constant volume of the reaction mixture. **(a)** Two molecules of A and two molecules of B can undergo four collisions. Likewise, in **(b)** when there are three molecules of A and 2 molecules are present total of six (3 × 2) collisions result. Three molecules of each A and B results nine (3 × 3) collisions as in **(c)**. Note that though the number of collision probabilities could predict like this, all the collisions may not result the product of the reaction.

Figure 1.6 shows that four A-B collisions are possible when there are two A and two B molecules. If we have three A and two B molecules, then there are six possible collisions and likewise when there are three A and three B molecules, we have nine possible collisions. Therefore, it can be noted that this probability of collision shows that the number of collisions depends on the *product* of the numbers of reactant particles, not their sum. Thus, collision theory explains that how the rate of a chemical reaction depends on the number of collisions per unit time per unit volume which in turn explains how the increase in concentration increases the reaction rate. Usually, this collision requirement has a large effect on what media are chosen to perform chemical reactions. Solids tend to be very slow reactors because only the atoms on the surface can have collisions with other atoms of other molecules. That's why the rusting of iron is very slow. Most reactions are done either in solution or in the gas phase where freedom of movement of the reactant molecules allows them to easily come into contact. Therefore, the more collisions per unit time per unit volume at a given temperature, the faster is the reaction rate.

Collision orientation

It is easy to understand that in a situation involving two molecules they can only react together when they come into contact with each other. In this encounter, they first have to collide, and then they *may* react. This means that though the molecules collide with each other and all the collisions may not result the product. Reactant molecules must collide with a favorable orientation and they must have necessary activation energy to yield the desired product and such collisions are called *effective collisions.* The reaction rate increases with the increase in number of effective collisions and it is in turn proportional to the total number of collisions.

Example:

Consider the single-step decomposition reaction of BrNO given below.

$$2BrNO(g) \rightarrow 2NO(g) + Br_2(g)$$

Now let's see the way the two molecules of BrNO arrange in space as depicted in Figure 1.7. To form $Br_2(g)$ as a product, two Br atoms of the two molecules of BrNO should approach along the same line as shown in the first two collisions. However, if those molecules line up as depicted in third collision, there is no way to collide two Br atoms and hence the collision orientation would not produce the products in the reaction. Therefore, the proper line of approach or the direction of colliding reactant molecules control the rate of reaction.

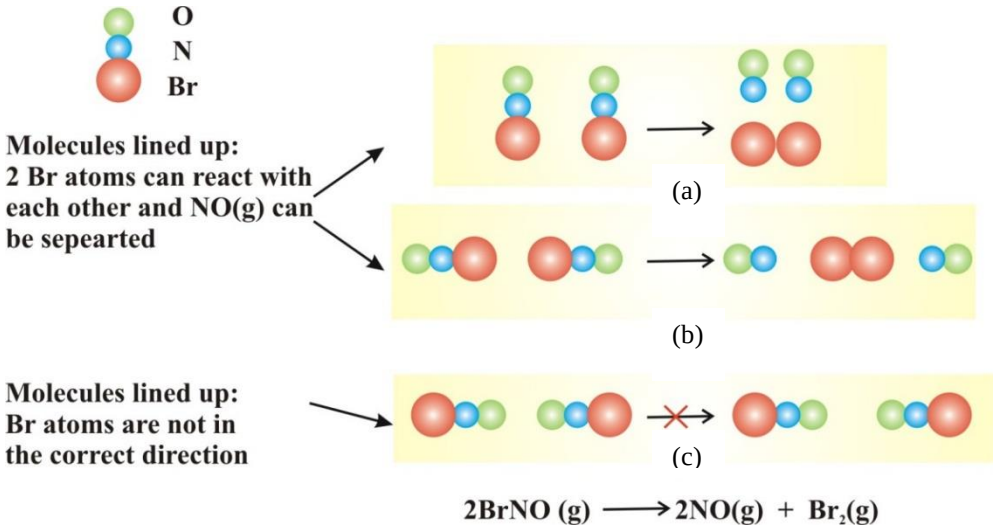
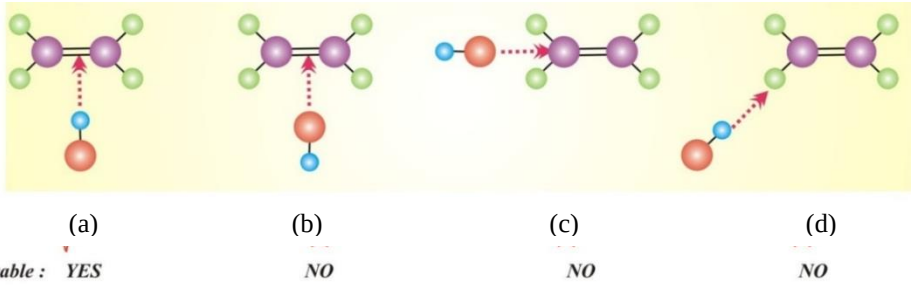


Figure 1.7 Different orientations of collisions between two BrNO molecules. In **(a)** and **(b)**, two molecules lined up properly and result the formation of a Br_2 molecule and two NO molecules. In **(c)** though the molecules lined up, Br atoms are not in the favourable sides/directions to collide and to for in the products.

Consider another single-step reaction between ethene and HCl to produce chloroethane.

$$CH_2{=}CH_2(g) + HCl(g) \rightarrow CH_3CH_2Cl(g)$$

As a result of the collision between the two molecules, the C = C double bond is converted into a single bond attaching hydrogen atom to one of the carbons and a chlorine atom to the other. The desired product of the reaction is only possible if the hydrogen end of the H-Cl bond approaches the carbon-carbon double bond. C = C has a high electron density around it and if the Cl atom approaches it, the Cl atom is repelled leading to no products. The collisions leads to the products and the other possible collisions the collisions which do not lead to products are compared in Figure 1.8.



$$CH_2{=}CH_2(g) + HCl(g) \rightarrow CH_3CH_2Cl(g)$$

Figure 1.8 Possible orientations of collisions between $CH_2{=}CH_2$ and HCl molecules. In **(a)** hydrogen atom of HCl oriented towards the C=C bond and as the C=C bond has negative charge, this collision favours the product. In **(b)**, Cl atom of HCl is repelled thus the reaction is not favoured. In **(c)** and **(d)** product is not favoured.

Surmounting the activation energy barrier

We know that a sample of reactant molecules in motion will have a Boltzmann distribution of molecular kinetic energies. Some molecules will have high energy; some low; many with intermediate energies. Figure 1.9 shows Boltzmann plots for a set of reactants at two different temperatures. Only those reactant molecules with energies greater than a certain minimum (threshold) energy called the ***activation energy, E_a*** (to the right of the plot) will be able to yield products. Because a greater fraction of molecules in the high temperature sample exceed the activation energy, the high-temperature sample will have more effective collisions and will experience a faster reaction rate compared to the sample at low temperature.

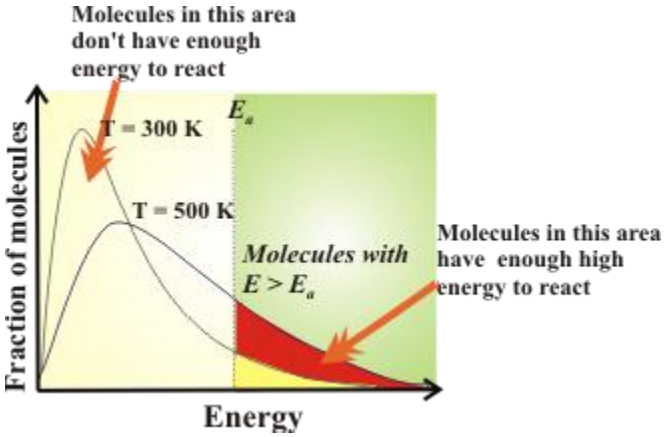


Figure 1.9 The effect of temperature on the distribution of collision energies. At higher temperature fraction of molecules having energy more than the activation energy increases leading to higher reaction rates.

When a favorable collision occurs between molecules overcoming the forces of interactions among the molecules, first an unstable molecule cluster, called the activated complex (transition state) is formed. The life time of the activated complex is very short and transformed to the products (or may break into the reactants again). The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reaction. The energy diagram for this with the example of the decomposition of BrNO(g) is shown in Figure 1.10 More details on this will be discussed later.

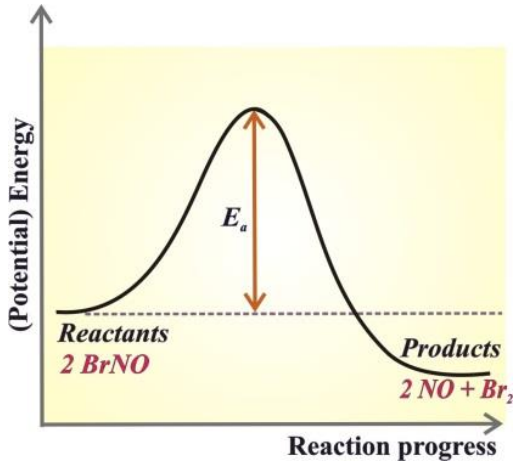


Figure 1.10 Energy diagram in which the activation energy (E_a) is depicted

For example, in the decomposition reaction $2BrNO(g) \rightarrow 2NO(g) + Br_2(g)$, of BrNO(g) two Br-N bonds need to be broken and one Br-Br bond needs to be formed. The energy required to break a Br-N bond is about 243 kJ mol^{-1} and hence this energy must be required to occur the reaction. Based upon the collision model, the energy comes from the kinetic energy of the molecules and once the molecules collide, the kinetic energy is transferred into potential energy which breaks the bonds and rearranges the atoms.

As a summary we can see that a chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after an effective collision and then they can go to the right side of the curve and consequently change into products. If the activation energy for a reaction is low, the fraction of effective/ favourable collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of collisions and the number of effective collisions per unit time per unit volume will increase and hence the rate of reaction will increase.

Concentration effects

In a chemical reaction of the type A + B → *Products:* reactant molecules of A and B (atoms, or ions) come into contact and converted into products. If there is no contact, the reaction rate will be zero. If the number of molecules per unit volume is increased the reaction rate increases as the collisions between them increase. This means that the reaction rate usually increases as the concentration of the reactants increases. In reactions involving liquids or gases, increasing the concentration of the reactants increases the rate of reaction. In a few cases, increasing the concentration of one of the reactants may not have an effect of the rate (Details of this is discussed in a latter section). The reaction between solid $CaCO_3$ and HCl acid can be used to demonstrate this concentration effect:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The rate of reaction can be altered by changing the concentration of the acid. (Also size of the calcium carbonate chips can be changed and it comes under the physical nature of the reactant). In this reaction it has been observed that if the $CaCO_3$ chips are large and in excess, then only a small fraction of the solid reacts. The rate will decrease over time as the hydrochloric acid is consumed because the concentration of HCl decreases over the time. Therefore, the rate of reaction can be monitored by measuring the pH of the solution, the decrease in the mass of calcium carbonate, or the increase in the volume of carbon dioxide. The easiest way is the volume measurement of the evolved CO_2 as it is the only gaseous species formed. In a particular experiment if we allow to react a known amount of $CaCO_3$ separately with a known volume of (~ 100 cm^3) of 0.50, 1.00 and 2.00 mol dm^{-3} HCl solutions, and monitor the volume of CO_2 formed with the time, following results could be observed (Figure 1.11).

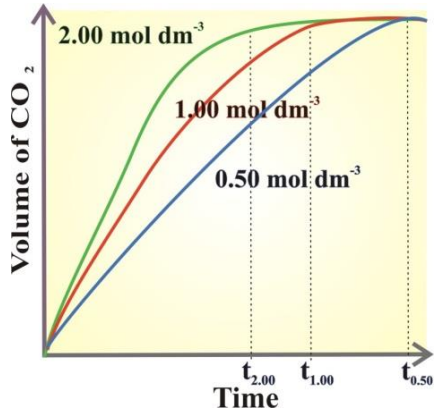


Figure 1.11 The variation in time for the generation of a constant volume of $CO_2(g)$ with the concentration of HCl in a reaction $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ at a given temperature.

From the above graph it can be seen that the time taken to produce a constant volume of CO_2 gas decreases ($t_{2.00} < t_{1.00} < t_{0.50}$) with the increasing concentration of HCl. That

is the rate of the reaction increases with the increasing concentration of HCl. The reason for this increased rate is explained by the collision theory. At high concentrations collisions per unit time per unit surface area of ($CaCO_3$) among reactants increase and hence the rate of the reaction.

Though the reaction rate increases with concentration, it has to be noted that in certain type of reactions (multi-step) this phenomenon does not exist. For example, consider a reaction which occurs in a series of steps having widely different rates where some of the steps are fast and some of them are slow.

Suppose two reactants A and B react together to give product P in the following two steps:

$$A_{(aq)} \rightarrow X_{(aq)} \quad : \textbf{\textit{slow}}$$

$$B_{(aq)} + X_{(aq)} \rightarrow P \; : \textbf{\textit{fast}}$$

In the above reaction overall rate of the reaction is controlled by the ***slow*** step in which **A** makes X. This is described as the ***rate determining step*** of the reaction.

If the concentration of A is increased, it is clear that the rate of that step increases as described above. However, if the concentration of B is increased, of course, the rate of the step increases but that does not make any impact on the overall rate of the reaction because that the step happens very fast as soon as any X is formed. Therefore, in such a multi-step reaction, increase in the concentration of a particular reactant which involves in the fast step does not show any impact on the reaction rate. Nucleophilic substitution reactions are some of the examples for this type of reactions.

Pressure effects

Increasing the pressure of a reaction involving gaseous reactants increases the rate of reaction. Changing the pressure of a reaction involving only solids or liquids has no effect on the rate. For example, in the manufacture of ammonia by the Haber process, the rate of reaction is increased by the use of very high pressures. Increasing the pressure of a gas is exactly the same as increasing its concentration for a given mass of gas as can be understood from the *ideal gas equation* as follows.

$$PV = nRT$$

For a given mass of gas, we can rearrange the above equation as;

$P = \frac{n}{V} RT = C\,RT$ for a given volume at a constant temperature. As a product *(RT)* is a constant at constant temperature, pressure is directly proportional to the concentration. It is clear that when the pressure is increased collision between two different particles or two of the same particles increases and hence the rate of reaction. This is true for the systems with the both reacting molecules are in gaseous state at constant volume, or whether one is a gas and the other is a solid as described in the Figure 1.11.

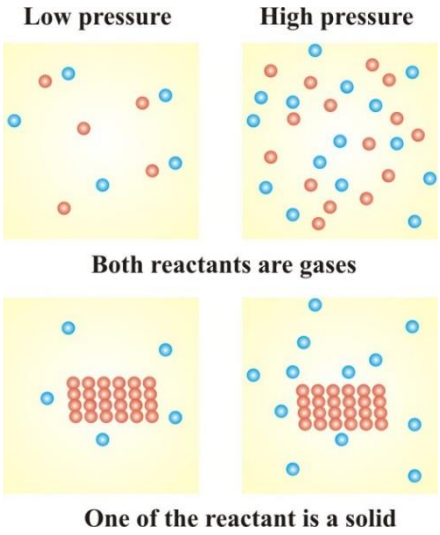


Figure 1.12 Effect of the pressure: Increase in pressure increases the concentrations of gaseous reactants.

Temperature effects

It has been understood that changing the temperature affects the rate of a reaction. As described in the above with the Maxwell-Boltzmann distribution of molecular energies in a gas increase in the temperature leads the rate of reaction to increase. For many reactions (not for all reactions) happening at around the room temperature, the rate of reaction approximately doubles for every 10 °C rise in temperature. Some reactions are virtually instantaneous (very fast). Examples are precipitation reactions from participant ions in solution to make an insoluble solid, or the reaction between hydrogen ions from an acid and hydroxide ions from an alkali in solution. So heating one of these would not make any acceptable or significant difference in the rate of the reaction.

As described in Unit 4 (gaseous state of matter) the increase in temperature of a system increases the average kinetic energy of its constituent molecules/particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time (per unit volume). This leads to increase the fraction of molecules processing energy for productive collisions (or in other words, exceeds the activation energy of the reaction). Both of these factors increase the reaction rate. Hence, the reaction rate of all (most) reactions increases with increasing temperature. Details of this will be discussed in a latter section. Conversely, the rate of reactions decreases with decreasing temperature. For example, refrigeration slows down the growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce.

In addition, in the systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the

presence of dilute sulfuric acid and at temperatures around 100 °C, ethanol is converted to diethyl ether:

$$2CH_3CH_2OH(aq) \xrightarrow{H_2SO_4} CH_3CH_2OCH_2CH_3(aq) + H_2O(l)$$

At 180 °C, however, a completely different reaction occurs, which produces ethylene as the major product:

$$CH_3CH_2OH(aq) \xrightarrow{H_2SO_4} C_2H_4(g) + H_2O(l)$$

Physical nature of the reactants

Consider a reaction of two reactant molecules in the same liquid phase. They collide more frequently than when one or both reactants are solids (or when they are in different immiscible liquid phases). If the reactant molecules are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time per unit volume depends on concentration and temperature. If the reaction is heterogeneous, the reactants are in two different phases (solid/gas), and collisions between the reactants can occur only at the interface between the two phases. The number of collisions between reactants per unit time per unit volume is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. Usually rates of reactions depend on the physical state as Gaseous state > Liquid state > Solid state. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

In automobile engines, surface area effect on the reaction rate is used. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided iron burns slowly (or not at all), but spraying finely divided dust into a flame produces a vigorous reaction.

In the case of solid reactant, a more finely powdered solid reacts faster than the same mass present as a single lump because the powdered solid has a greater surface area than the single lump.

For example in the calcium carbonate and hydrochloric acid reaction in the laboratory you can observe that the powdered calcium carbonate reacts much faster with dilute hydrochloric acid than if the same mass was present as lumps of marble or limestone.

In the catalytic decomposition of hydrogen peroxide solid manganese(IV) oxide is often used as the catalyst. Oxygen is given off much faster if the catalyst is present as a powder than as the same mass of granules.

For example, in a reaction between magnesium metal and a dilute hydrochloric acid involves collision between magnesium atoms and hydrogen ions. The surface area of the

metal here also affects the rate of the reaction. Fine magnesium powder causes evolution of hydrogen gas more rapidly than the magnesium strip.

Not only the physical nature as described earlier but nature of chemical bonds in reactants affects the rate.

Consider the following two reactions:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ …… (a)

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ …… (b)

The first reaction (a) is faster than the second because in the first reaction only N = O bond is to be broken where as in the second reaction (b) four C-H bonds are to be broken.

Similarly consider another example of two similar reactions:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ ……... (c)

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ ……..... (d)

NO bond is weaker than CO bond, hence is broken easily. Thus reaction (c) is faster than (d).

Solvent effects

The nature of the solvent can also affect the reaction rates. The same reaction occurring in different solvents shows different rates depending on the polarities of solvents used.

When the reaction occurs in the same solvent, viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time per unit volume. Thus the reaction rates decrease with increasing solvent viscosity.

Catalyst effects

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate by changing the path of the reaction without undergoing a net chemical change itself. For example, the reaction $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$ is very slow at room temperature and can be speeded up by introducing a catalyst. In addition, the decomposition of hydrogen peroxide in the presence of catalyst occurs in much more rapidly compared to the rate of that reaction without a catalyst. Because most catalysts are specific to certain reactions, they often determine the product of a reaction by accelerating only one of several possible reactions that could occur. In particular reactions with a catalyst the increase in concentration of the reactants sometimes may not increase the rate of reaction. For example, when a small amount of finely powdered solid catalyst is used in a reaction with a high enough concentration of reactant in solution the catalyst surface is totally covered up with reacting particles. Increasing the concentration of the solution even more

cannot make any effect because the catalyst is already working at its maximum capacity. Details of these effects on the reaction rate and mechanisms will be discussed in a separate section.

1.7 Controlling the rate of a reaction by appropriately manipulating the concentration of reactants

1.7.1 Expressing the rate of a reaction: Average, instantaneous and initial rates

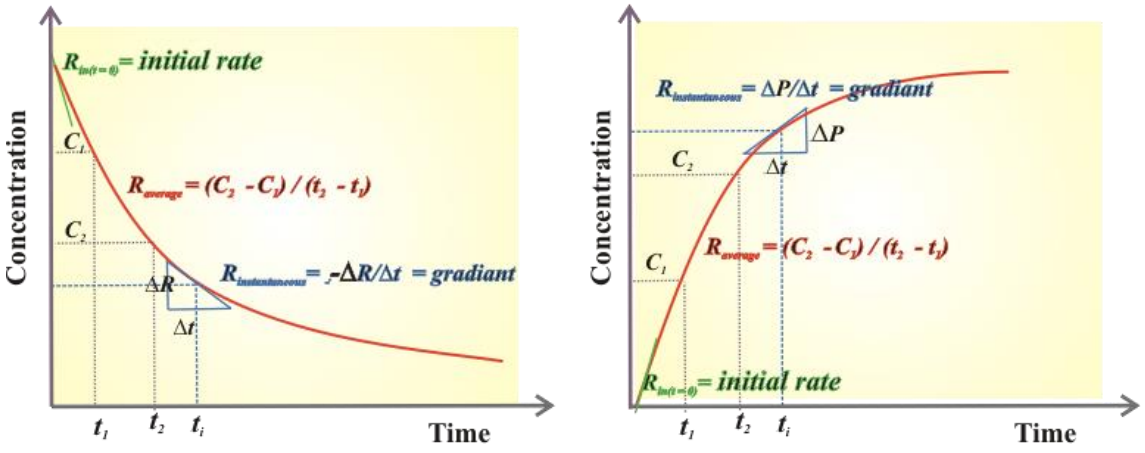
As described earlier *the rate varies as a reaction proceeds.* Consider the following hypothetical gas phase reaction between **A** and **B**.

$$A(g) + B(g) \rightarrow C(g)$$

For every molecule of **A**, a molecule of **B** reacts and hence [**A**] and [**B**] decrease at the same rate and we can write:

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{\Delta t}$$

Assume that the reaction is started with a known [A] in a closed vessel at 298 K and the concentration of is manured A at 10 second intervals after adding B. The obtained data can be plotted as shown in Figure 1.13. Rate *decreases* during the progress of the reaction because the *reactant* concentration decreases with the time (As **A** molecules react, the number of effective collisions decreases and hence the rate). If we plot the concentration of the products with the time the opposite curve will result. With the help of the plot of concentration vs time, following three types of rates can be defined.



(a) (b)

Figure 1.13 Definitions and graphical expression of reaction rates; average, instantaneous and initial rates: (a); change in rate for the reactants and (b); change in rate for the products. Note that the quantity of rate takes negative sign (as the slope is negative) and that for the products is positive. Therefore, in the calculations rate of consumption of reactants is multiplied by (-1).

Average rate

Over a given period of time, the **average rate** is the slope of the line joining two points along the curve. The average rate over the first 100 s time interval is the change in concentration during that time interval divided by the time taken. For example, when $C_1 = 3.50 \times 10^{-5}$ and $C_2 = 0.50 \times 10^{-5}$ mol dm^{-3},

$$\text{Rate}_{0-100} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,0.50 \times 10^{-5} - \ 3.50 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,100 - 0\,]s}$$
$$= \ 3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

This shows that during the first 100 s of the reaction, [A] decreases with the *average* of 3.0×10^{-7} mol dm^{-3} each second. However, this does not imply that the rate at any point along the curve is 3.0×10^{-7} mol dm^{-3} s^{-1}. We can clearly understand that the slope of the curve decreases with the time and hence the rate (average) should also decrease.

That means the rate over shorter intervals may be lower or higher than the average. In the above estimation in whole 100 s interval the decrease in [A] does not show the rate over any shorter time period. This *change* in reaction rate is evident when we calculate the average rate over two shorter periods. For example, in the first 10 s the average rate is given by ($C_1 = 3.50 \times 10^{-5}$ and $C_2 = 3.00 \times 10^{-5}$ mol dm^{-3});

$$\text{Rate}_{0-10} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,3.00 \times 10^{-5} - \ 3.50 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,10 - 0\,]s}$$
$$= \ 5.0 \times 10^{-7}\text{mol dm}^{-3}\ \text{s}^{-1}$$

Likewise the average rate in the 50-60 s interval is when $C_1 = 1.00 \times 10^{-5}$ and $C_2 = 0.75 \times 10^{-5}$ mol dm^{-3}.

$$\text{Rate}_{50-60} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,0.75 \times 10^{-5} - \ 1.00 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,60 - 50\,]\ \text{s}}$$
$$= \ 2.50 \times 10^{-7}\text{mol dm}^{-3}\ \text{s}^{-1}$$

Instantaneous rate

Average rate which is a constant for the time interval interested cannot be used to predict the rate of a reaction at a particular instant. So, to express the rate at a particular instant of time the instantaneous rate is determined. Rate of the reaction at a certain time is called as an instantaneous rate. The slope of a line tangent to the curve at any point gives the instantaneous rate at that time.

For example, the instantaneous rate at 50.0 s is;
To calculate this it is necessary to calculate the slope of the tangent line drawn to the curve at 50.0 s. Related points considered are (65, 1.25 $\times 10^{-5}$) and (35, 0.75 $\times$ 10^{-5})

$$\text{Rate}_{50} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{[(0.75 - 1.25)\times 10^{-5}]\ \text{mol dm}^{-3}}{[\,65 - 35\,]\text{s}} = 1.70 \times 10^{-7}\text{mol dm}^{-3}\ \text{s}^{-1}$$

It is very clear that the instantaneous rate is different from the average rate and in general, we use the term *reaction rate* to mean *instantaneous* reaction rate.

Initial rate

The instantaneous rate at the moment the reactants are mixed (that is, at $t = 0$) is the **initial rate.** Initial rate is calculated from the slope of the line tangent to the curve at $t = 0$ s (Figure 1.13). Measurements of initial rates is usually used in chemical kinetics to find other kinetic parameters.

When there is a reversible reaction the use of initial rate poses some complications. As a reaction proceeds in the *forward* direction (products $\rightarrow$ reactants), product increases, causing the *reverse* reaction (products $\rightarrow$ reactants), to occur more quickly. To find the overall (net) rate, we would have to calculate the difference between the forward and reverse rates. But, for the initial rate, $t = 0$, so product concentrations are negligible. So the rate of the reverse reaction would not affect the estimations.

As such in the simple way the initial rate or the instantaneous rate at t = 0, occurs when reactants have just been mixed and before any product accumulates.

1.7.2 Effect of concentration on reaction rate

Rate law

From the above section it is known that the frequency of effective collisions controls reaction rates. The more effective collisions mean the faster the rate. There are two ways to increase the frequency of collisions between molecules: increase the number of molecules in a constant volume at a given temperature or increase the kinetic energy of them by raising temperature. Increasing the number of molecules in a constant volume means the increase in concentration.

As was explained previously, for many reactions involving liquids or gases, increasing the concentration of the reactants increases the rate of reaction due to the increase in collision frequency. In some cases, increasing the concentration of one of the reactants may not affect the rate and also doubling the concentration of one of the reactants may not double the rate of the reactions always. Therefore, it is necessary to understand the behavior of concentration dependence of the reaction rate quantitatively with some models.

Consider a simple reaction;

$$A \rightarrow B$$

We can write,

$$\text{Rate } \alpha \text{ [A]}$$
$$\therefore \text{ Rate} = k \text{ [A]}$$

where ***k*** is the proportionality constant and is called the "**rate constant".** The above expression is called the **rate law expression** or **rate law** of the reaction A $\rightarrow$ B. In this reaction we can say that the rate of the reaction is proportional to the concentration of A. If we assure that doubling the concentration of A doubles the rate and we can then write the rate law as;

$$\text{Rate} = k\,[A]^1 = k[A]$$

Consider the following decomposition reaction.

$$NH_4NCO_{(aq)} \rightarrow (NH_2)_2CO_{(aq)}$$

It has been experimentally found that the rate of the above reaction is proportional to the above square of the $NH_4NCO_{(aq)}$ concentration. That is when the concentration of $NH_4NCO_{(aq)}$ is doubled the rate will quadruple. Therefore, the rate law for the reaction can be written as,

$$\text{Rate} = k\,[NH_4NCO_{(aq)}]^2$$

From the above it can be noted that there are three parts appear in the rate law;

***k:* rate constant;** For a given reaction it has a number and (appropriate) units. Rate constant is different for different reactions and is different for the same reaction at different temperatures.

[$NH_4NCO_{(aq)}$]: the concentration of the reactants; If more than one reactant is present, any or all of them may be present in the equation. Sometimes it is the case that one or more reactants will not be appearing in the rate law.

2: the order of the reaction with respect to the relevant reactant; This is more often an integer like 1,2. but fractions are also possible sometimes. If the order is one, 1 is not written in the rate law expression. The order of the reaction can also be more than 2. However, they are not included in this discussion.

Experimentally derived rate laws for two reactions are given below.

$2NO_{(g)} + O_{2(g)} \rightarrow NO_{2(g)}$: Rate = $k\,[NO_{(g)}]^2[O_{2(g)}]$

$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$: Rate = $k\,[NO_{2(g)}]^2$

Now consider a general reaction between reactants A and B;

$$aA + bB \rightarrow \textit{Products}$$

The rate law for the reaction can be written as,

$$\text{Rate} = \boldsymbol{k}\,[A]^{x}[B]^{y}$$

From the above examples concentrations of **A** and **B** have to be raised to some power ***x*** and **y** to show how they affect the rate of the reaction. These powers are called the **orders of the reaction** with respect to **A** and **B**. The sum of *x* and y, **(*x* + y)** is called as the **overall order** of the reaction.

> *i.e the sum of powers of the concentration terms of the reactants written in the rate law expression is called the overall order of that chemical reaction.*

If the order of reaction with respect to **A** is 0 (zero), this means that the concentration of **A** doesn't affect the rate of the reaction. Mathematically, any number raised to the power zero is equal to 1. That is why that particular concentration term disappears from the rate equation.

> *Therefore, rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.*

Let's consider some examples of observed rate laws and note the reaction orders.
For the reaction between NO and H_2 gases,

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

the rate law is

$$\text{Rate} = k\,[NO(g)]^2\,[H_2(g)]$$

This reaction is second order with respect to NO. And, even though $H_{2(g)}$ has the stoichiometric coefficient of 2 in the balanced equation, the reaction is first order with respect to $H_{2(g)}$. It is third order overall.

For the reaction between nitrogen monoxide and ozone,

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

the rate law is

$$\text{Rate} = k\,[NO(g)]\,[O_3(g)]$$

This reaction is first order with respect to $NO_{(g)}$ and first order with respect to $O_3(g)$, thus it is second order overall.

For the hydrolysis of 2-bromo-2-methylpropane,

$$(CH_3)_3CBr(l) + H_2O(l) \rightarrow (CH_3)_3COH(l) + HBr(aq)$$

the rate law is

$$\text{Rate} = k\,[(CH_3)_3CBr(l)]$$

This reaction is first order with respect to 2-bromo-2-methylpropane and zero order with respect to $H_2O(l)$, despite its coefficient of 1 in the balanced equation. If we want to note that water is a reactant, we can write the rate law as follows.

$$\text{Rate} = k\,[(CH_3)_3CBr(l)]\,[H_2O(l)]^0$$

This is a first order reaction overall.

The above examples give an important point:

> *Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation and must be determined experimentally. Although the rate constant is really a number with appropriate units, when describing a general rate law, we usually just write* ***k*** *but any value is true only at one temperature.*

The rate of a reaction is always expressed in terms of mol dm^{-3} s^{-1}. We can classify the reactions as *zeroth, first, second, etc.* order reactions. Assuming time is measured in seconds, The corresponding units of the *rate constant can be derived* as follows.

Zero order reactions

Consider the reaction; A $\rightarrow$ products

If the reaction is zero order, the rate law is,

$$\text{Rate} = k$$

The units of k must be the same as that of rate, **mol dm^{-3} s^{-1}.**

First order reactions

Consider the reaction; A $\rightarrow$ products

If the reaction is first order, the rate law is,

Rate = k [A]

Units of k; $= \frac{\text{Rate}}{[A]} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}} = \mathbf{s^{-1}}$.

Second order reactions

Consider a reactions A $\rightarrow$ products or A + B $\rightarrow$ products

If the reaction is second order, the rate law is,

Rate = k $[A]^2$ or Rate = k [A][B]

Units of k; $= \frac{\text{Rate}}{[A]^2} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol}^2\,\text{dm}^{-6}} = \mathbf{mol^{-1}\,dm^3\,s^{-1}}$.

Example 1.8

Methyl acetate reacts with hydroxide ion according to the following equation.

$$CH_3COOCH_3(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + CH_3OH(aq)$$

The rate law is;

$$\text{Rate} = k\,[CH_3COOCH_3(aq)][OH^-(aq)]$$

What is the order of reaction with respect to each reactant, and the overall reaction order?

Answer

Because there are no superscripts to the right of each concentration term in the rate law, it means they are each first order. The reaction is first order in $CH_3COOCH_3(aq)$ and first order in $OH^-(aq)$. It is second order overall (1 + 1 = 2).

For example let's consider experimentally derived rate laws for the following reactions;

$2NO(g) + O_2(g) \rightarrow NO_2(g)$: Rate = $k\,[NO(g)]^2[O_2(g)]$

The reaction is second order with respect to $NO(g)$ *and first order with respect to* $O_2(g)$. *Overall order of the reaction is 3.*

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$: Rate = $k\,[NO_2(g)]^2$

The reaction is second order with respect to $NO_2(g)$ *and zero order with respect to* $CO(g)$. *Overall order of the reaction is 2.*

Example 1.9

Identify the reaction order from each of the following rate constants.

Answer

(i) $k = 5.6 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$

The unit of second order rate constant is $dm^3\ mol^{-1}\ s^{-1}$

$\therefore k = 5.6 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$ *represents the second order reaction.*

(ii) $k = 3 \times 10^{-4}\ s^{-1}$.

The unit of a first order rate constant is s^{-1}

$\therefore k = 3 \times 10^{-4}\ s^{-1}$ *represents the first order reaction.*

Table 1.1 summarizes the difference in rate of a reaction and rate constant to avoid the confusion between them.

Table 1.1 The difference in rate of a reaction and rate constant

Rate of reaction	Rate constant
It is the speed of conversion of reactants into products.	It is a proportionality constant.
It is measured as the rate of decrease of concentration of reactants or the rate of increase of concentration of products with time.	It is equal to the rate of reaction when the concentration of each of the reactants is unity.
It depends upon the initial concentration of reactants.	It is independent of the initial concentration of the reactants. It has a constant value for a given reaction at a fixed temperature.

1.7.3 Graphical representation of change in rate with concentration for zero, first and second order reactions

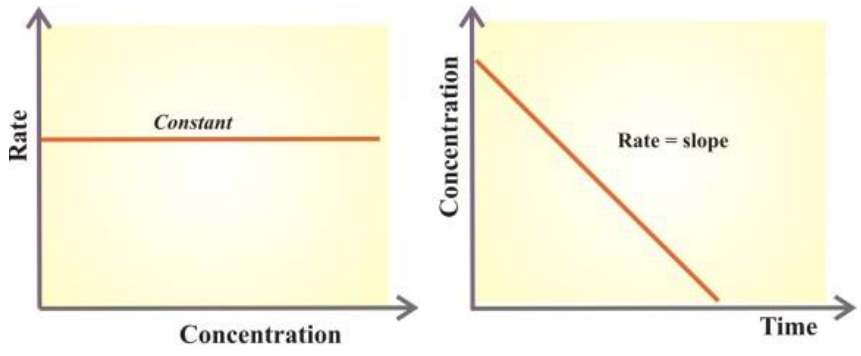
Zero order reactions

Zero order reactions means that the rate of the reaction is independent of the concentration of the reactants or we can say that the rate is proportional to zeroth power of the concentration of reactants. Consider the reaction,

$$A \rightarrow \text{Products}$$

$$\text{Rate} = k[A]^0 = k$$

Therefore, for any given concentration of A, the rate does not change implying that the rate is a constant with the concentration. Hence the plot of rate against the concentration is a horizontal straight line as shown in Figure 1.14 (a). In other words, the change in concentration over the time is a constant which can be obtained from the slope of the graph of concentration over the time as shown in Figure 1.14(b).



(a) (b)

Figure 1.14 (a) Variation of reaction rate over the concentration of the reactant and (b) Variation of concentration of the reactant over the time for a zero-order reaction.

The behaviour of the zero order reaction can be treated as follows too.
Consider a reaction:

$$A + B \rightarrow \text{Products}$$

Rate of the reaction is,

$$\text{Rate} = k\,[A]^a[B]^b$$

Assume that the concentration of B is very high and change in its concentration is negligible during the course of reaction. Therefore, the rate of reaction can be written as,

$$\text{Rate} = k'\,[A]^a \quad \text{where } k' = k\,[B]^b$$

As the reaction is zero order with respect to A, Rate $= k' =$ constant

Therefore, the graph of rate verses the concentration is again a horizontal straight line as described above.

Some photochemical reactions and a few heterogeneous reactions are examples for zero-order reactions. Such reactions are not common.

Photochemical reaction between hydrogen and chlorine:

$$H_2\,(g) + Cl_2\,(g) \xrightarrow{h\nu} 2HCl\,(g)$$

This photochemical reaction is a zero-order reaction. The reaction is studied by placing H_2 and Cl_2 gases over water. The rate of reaction is studied by noting the rate at which water rises in the vessel due to dissolving of HCl formed. The rate of rise of water is the same as the rate of disappearance of H_2 and Cl_2, i.e., the concentration of the gaseous phase will not change with time, although the quantities will change.

Decomposition of $N_2O_{(g)}$ on a hot platinum surface:

$$N_2O(g) \rightarrow N_2(g) + 1/2\ O_2(g)$$

Rate $= k\,[N_2O]^0 = k$ or,

$$\frac{\Delta[N_2O]}{\Delta t} = k$$

Decomposition of $NH_3(g)$ in the presence of molybdenum or tungsten is a zero-order reaction.

$$2NH_3(g) \xrightarrow{Mo} N_2(g) + 3H_2(g)$$

The surface of the catalyst is almost completely covered by NH_3 molecules. The adsorption of gas on the surface cannot be changed by increasing the pressure or

concentration of NH_3. Thus, the concentration of gas phase remains constant although the product is formed. Therefore, this reaction has zero order kinetics.
Other examples for zero order reactions are:
Iodination of acetone in the presence of $H^+(aq)$ ions:

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} ICH_2COCH_3(aq) + HI(aq)$$

Experimentally found that the rate equation of this reaction does not containing $[I_2]$ factor, i.e.,

$$\text{Rate} = k\,[CH_3\,COCH_3(aq)\,][H^+(aq)]$$

Indicating that the reaction is zero order with respect to $[I_2(aq)]$

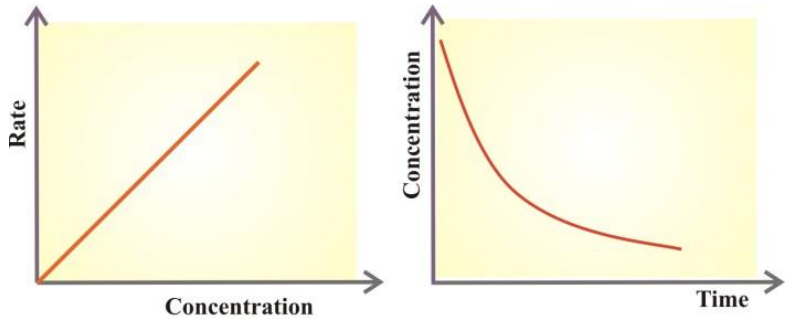
Characteristics of zero order reactions
The concentration of the reactants decreases linearly with time.
The time required for the reaction to be complete, i.e., time at which [A] is zero is given by;

$$t_{\,completion} = \frac{[A]_0}{k} = \text{(Initial concentration)/ (Rate constant)}$$

First order reactions
In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant. For example, considering the same reaction; A $\rightarrow$ products

$$\text{Rate} = k\,[A]$$

This takes the form; $y = mx$ and the graph of rate against the concentration will be a straight line going through the origin (0,0) as shown in Figure 1.15(a). The plot of the variation of concentration over the time will be a curve as shown in Figure 1.15(b).



(a) (b)

Figure 1.15 **(a)** Variation of reaction rate over the concentration of the reactant (gradient = rate constant) and **(b)** Variation of concentration of the reactant over the time for a first-order reaction.

Let us consider this in another way.
We can write,

$$\text{Rate} = k\,[\text{A}]$$

Taking log of both sides; $\log(\text{Rate}) = \log[\text{A}] + \log(k)$

Therefore, the graph of log (Rate) against log[A] will be $\boldsymbol{y = mx + c}$ type having the slope of one (1) and the intercept of log (k) as shown in Figure 1.17 (will be shown later).

As discussed previously, the rate constant of a first order reaction has only (inverse) time unit. It has no concentration unit. This means that the numerical value of k for a first order reaction is independent of the unit in which concentration is expressed. ($k = \frac{\text{rate}}{\text{concentration}} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}}$)Therefore, even if the concentration unit is changed the numerical value of k for a first order reaction will remain unchanged. However, it would change with the change in time unit. Say, k is 6.0×10^{-3} min^{-1}, then it can also be written as 1.0×10^{-4} s^{-1} .i.e. The numerical value of k has changed.

Following are some examples for the first order reactions.

Decomposition of H_2O_2(aq) in aqueous solution

$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

Hydrolysis of methyl acetate in the presence of mineral acids

$$CH_3COOCH_3(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + CH_3OH(aq)$$

Inversion of cane sugar in the presence of mineral acids

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H^+} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

Decomposition of ammonium nitrite in aqueous solution

$$NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O(l)$$

Hydrolysis of diazo derivatives

$$C_6H_5N{=}NCl(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

In the cases where gas phase reactions are considered, it is necessary to use pressure terms instead of concentration terms in the rate law. For example, a reaction $A(g) \rightarrow B(g) + C(g)$ is a first order reaction. If the initial (at t = 0) pressure of the system is P_1 and the pressure of the system changed to P_2 after time t, it is necessary to understand the way we write the rate law of the reaction.

In this case we can assume that the partial pressure of A is decreased by -x due to its decomposition and hence the pressures built up by each of B and C would be +x. Therefore we can construct the system as follows.

	$A(g) \rightarrow$	$B(g) +$	$C(g)$
Initial	P_1	0	0
At time *t*	P_1-x	x	x

Therefore, total pressure at time t = $(P_1-x) + x + x = P_1 + x = P_2$

$\therefore x = P_2 - P_1$

t Pressure of A at t = $P_1-x = P_1 -(P_2 - P_1) = 2P_1 - P_2$

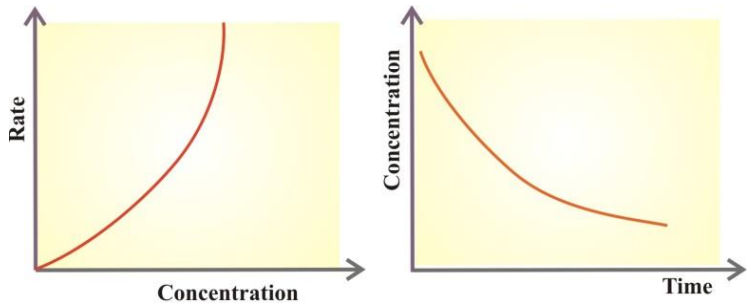
Thus these pressure terms can be used for the estimation of orders and rate constants of the reactions.

Second order reactions

In this class of reactions, the rate of the reaction is proportional to the second power of the concentration of the reactant or if the concentration of the respective reactant is doubled the rate will be quadrupled. For example, considering the same reaction; A $\rightarrow$ products

$$\text{Rate} = k\,[\text{A}]^2$$

This takes the form; $y = mx^2$ and the graph of rate against the concentration will be a upward-curve passes through the origin (0,0) as shown in the Figure 1.16(a). The variation of concentration against time will be a curve; however, slope would be higher than that for the first order plot as seen in Figure 1.16(b).



(a) (b)

Figure 1.16 (a) Variation of reaction rate over the concentration of the reactant and (b) Variation of concentration of the reactant over the time for a second-order reaction.

Let us consider this in another way,

We can write,

$$\text{Rate} = k\,[\text{A}]^2$$

Taking log of both sides; $\log(\text{Rate}) = 2\log[\text{A}] + \log(k)$

Therefore, the graph of log(rate) against log[A] will be $\boldsymbol{y = mx + c}$ type having the slope of two (2) and the intercept of log*(k)*. As a summary Figure 1.17 compares the above cases in order to understand the differences in zeroth, first and second order reactions easily.

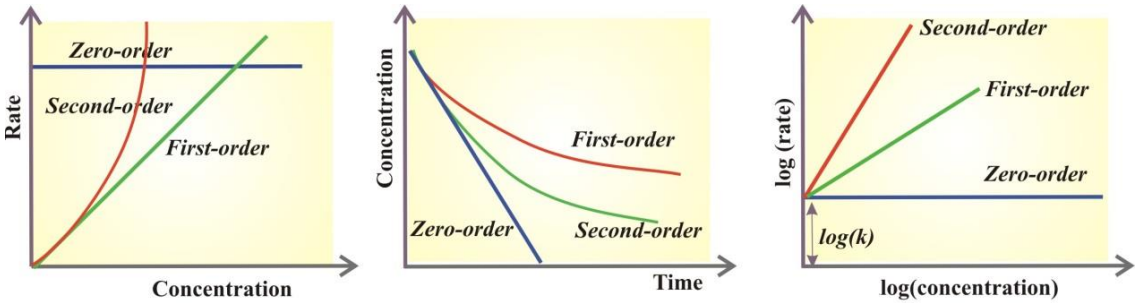


Figure 1.17 Comparison of first order, second order and zero order reactions; **(a)** Variation of reaction rate with concentration. The plot is a horizontal line for the zero order reaction because the rate does not change no matter what the value of [A]. The plot is an upward-sloping line for the first order reaction because the rate is directly proportional to [A]. The plot is an upward-sloping curve for the second order reaction because the rate increases exponentially with [A]. **(b)** Variation of concentration over time. The decrease in [A] does not change as time goes on for a zero order reaction. The decrease slows down as time goes on for a first order reaction. The decrease is even more for a second-order reaction. **(c)** Variation of log(rate) with log(concentration). The plot is a horizontal line for the zero order reaction. The plot is a straight line with the slope one for the first order reaction and the plot is a straight line with the slope two for a second order reaction.

Example 1.10

Consider the following first order reaction.

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

At 328 K, when the concentration of $N_2O_5(g)$ was 2.00×10^{-2} mol dm^{-3} the rate of the decomposition was found to be 1.00×10^{-2} mol dm^{-3}s^{-1}. Calculate the first order rate constant of the reaction at 328 K.

Answer

$$\text{Rate} = k\,[\text{A}] = 1.00 \times 10^{-2}\ \text{mol dm}^{-3}\ s^{-1}$$

$$\therefore k = \frac{1.00 \times 10^{-2}\ mol\ dm^{-3}\ s^{-1}}{2.00 \times 10^{-2}\ mol\ dm^{-3}} = 0.50\ s^{-1}$$

Example 1.11

Consider the reaction between oxygen and nitrogen monoxide.

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

Rate law of the reaction is $\text{rate} = k\ [O_{2(g)}]\ [NO(g)]^2$ at 300 K.

When the concentrations of $O_2(g)$ and $NO(g)$ were 1.00×10^{-2} and 2.00×10^{-2} mol dm^{-3}, respectively, the rate was found to be 3.20×10^{-3} mol dm^{-3} s^{-1} at 300 K. Calculate the rate constant for the reaction at 300 K.

Answer

$$k = \frac{\text{rate}}{[O_{2(g)}]\ [NO(g)]^2}$$

$$= \frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{[1.00 \times 10^{-2}\text{mol dm}^{-3}]\ [2.00 \times 10^{-2}\ \text{mol dm}^{-3}]^2}$$

$$k = 8.00 \times 10^2\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

Example 1.12

Consider the hypothetical reaction given below at a given temperature.

$$aA + bB \rightarrow cC + dD$$

In a particular experiment carried out at a given temperature, the rate of the reaction was found to be 5.00×10^{-4} mol dm^{-3} s^{-1} when the concentrations of A and B are 1.00×10^{-5} mol dm^{-3} and 2.00 mol dm^{-3} respectively. It has also been observed that the rate doubles as the concentration of A is doubled. Calculate the rate constant of the reaction.

Answer

For the reaction we can write the rate law as,

$$\text{rate} = k\ [A]^x\ [B]^y$$

It is given that the rate doubles as the concentration of A is doubled. Therefore, we can conclude/find that the reaction is first order with respect to A. Next, it is necessary to understand the dependence of rate on the concentration of B, which is much higher than the concentration of A (1.00×10^{-5} <<< 2.00 mol dm^{-3}). Thus, it is evident that the reaction rate does not depend on the concentration of B, or assuming that [B] remains unchanged during the reaction. Now the rate law of the reaction can be rewritten as,

$$\text{Rate} = k'\ [A]$$

$$k' = \frac{5.00 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{1.00 \times 10^{-5}\ \text{mol dm}^{-3}} = 50\ \text{s}^{-1}$$

Following example gives an idea about the relation between order and the concentration of the reactants. Consider a hypothetical reaction,

$$aA + bB \rightarrow cC + dD$$

and the rate low of the reaction is given by; Rate = k [A][B]^2

(a) Consider that the initial concentrations of both A and B are 1.0 mol dm$^{-,3}$

Rate$_1$ = k [1.0][1.0]^2 mol ^{3}dm^{-9} = k mol ^{3}dm^{-9}

If the concentration of A is doubled while keeping the concentration of B constant at 1.0 mol dm^{-3},

Rate$_2$ = k [2.0][1.0]^2 mol ^{3}dm^{-9} = 2k mol ^{3}dm^{-9}

i.e. The rate is doubled when the concentration of A is doubled revealing that the reaction is first order with respect to A.

(b) If the concentration of B is doubled while keeping the concentration of A constant at 1.0 mol dm^{-3},

Rate$_3$ = k [1.0][2.0]^2 mol ^{3}dm^{-9} = 4k mol ^{3}dm^{-9}

i.e. The rate is quadrupled when the concentration of B is doubled revealing that the reaction is second order with respect to B.

1.7.4 Methods to determine the order of a reaction and rate constant (Rate law)

From the above last two examples, when a concentration of one reactant is in large excess compared to the other reactant it has been assumed that the concentration of that reactant can be considered a constant during the course of reaction. This postulate can be used to investigate the kinetics of reactions involving more than one reactant and the experiments can be designed as such.

There are two fundamentally different approaches to this; follow a particular reaction all the way through, and process the results from that single reaction or investigate the change occurred in the *initial rate* of the reaction as concentrations of the reactants are changed. In the first approach experiments are carried out by keeping the concentrations of all the reactants except one is in large excess. Thus for example, for the reaction:

$$aA + bB \rightarrow cC + dD$$

The rate law is: Rate = k [A]$^{\boldsymbol{x}}$[B]$^{\boldsymbol{y}}$

Let B to be in large excess relative to [A]$_o$, so that [B] can be considered constant during a course of reaction. Thus we may write:

Rate = k' [A]$^{\boldsymbol{x}}$

where:

k' = k [B]$^{\boldsymbol{y}}$

By taking logarithm of both sides we get:

$$\log(\text{Rate}) = \boldsymbol{y} \log[\text{A}] + \log(k')$$

which is the equation of a straight line and by plotting log(Rate) against log[A] with gradient **y** and intercept of log(*k*`), the order and the rate constant of the reaction would be estimated.

The process can then be repeated by letting A in excess to determine ***x*** and *k*.

Method of initial rates

As we know, the rate laws are not derived from the reaction equation and are derived from experimental data. The method of initial rates is an experimental method to investigate the kinetics of reaction leading to find the rate constant and orders of a given reaction, in which a reaction is run multiple times with different initial concentrations of each reactant. The initial rate of each experiment is compared with the initial concentrations of the reactants to determine its order. The method is most often performed in the following way:

In a simple way of initial rate experiments involve measuring the time taken for some easily measurable or recognizable event that happens very early in a reaction. This could be the time taken for, say, to liberate a *given volume* of a gas, to from a measurable amount of a *precipitate* or for a *colour change* to occur. Further, some *titrations* can be performed by stopping a reaction after a given period of time.

Then the concentration of one of the components of the reaction is changed, keeping everything else such as the concentrations of other reactants, the total volume of the solution and the temperature and so on constant. Then the time taken for the same event to take place has to be measured with that new concentration. This has to be repeated for a range of concentrations of the substance interested in. It is worth to cover a reasonably wide range of concentrations, taking perhaps five or more different concentrations varying from the original one down to half of it or less.

This means that for each reactant, it is needed to run at least a pair of reactions in which that reactant's concentration is doubled (changed) while all other reactant concentrations and conditions are held constant. This isolates the effect on rate to that single reactant.
Most often one of three things happens to the initial rate when the reactant concentration is doubled:

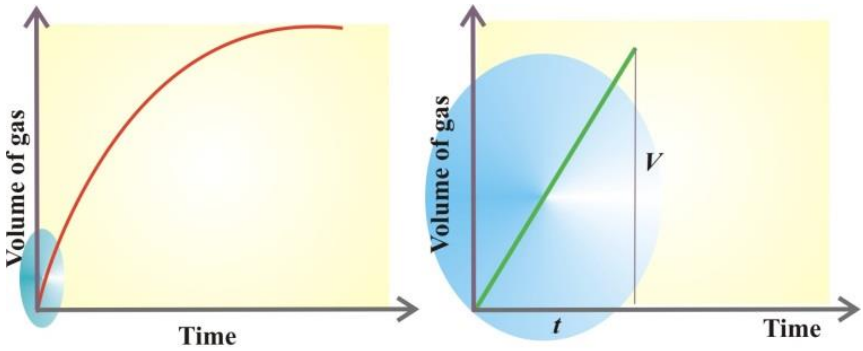
(a) The rate does not change: This means that the rate is independent of that reactant. The reaction is zero order with respect to that reactant.
(b) The rate doubles: This means that the rate is proportional to the concentration of that reactant. The reaction is first order with respect to that reactant.

(c) The rate quadruples: This means that the rate is proportional to the square of the concentration of that reactant. The reaction is second order with respect to that reactant.

Once the order for each reactant is found, take any of the experiments and substitute in concentration values and the measured rate to determine the numerical value of the rate constant *k.*

Exploration of the results from initial rate experiments

Consider a simple example of an initial rate experiment in which a gas being produced. This could be a reaction between a metal and an acid, for example, or the catalytic decomposition of hydrogen peroxide. Assume that the volume of the evolved gas being measured with the time and that can be shown as a plot of volume of gas given off against time as shown in the Figure 1.18.



(a) (b)

Figure 1.18 Measuring the volume of an evolved gas in an initial rate experiment. (**a)** Change in volume over the time, volume increases very fast at the beginning and slows down when the reaction progresses. (**b)** Expanded view of the shaded area of **(a)** Increase in volume at the very beginning of the reaction is linear and therefore it is possible to measure the time taken to produce a constant volume of gas by varying the concentration of the desired reactant at a given temperature.

We know that a measure of the rate of the reaction at any point is found by measuring the slope of the graph. Since we are interested in the initial rate, it is necessary to find the slope at the very beginning (say at *t ~0 s).* Of course, it is impossible to observe some changes at the time = 0, and therefore, we measure the time taken for a given/constant change to happen in the system (like a constant volume). However, since the concentration of the species at the very beginning is almost the initial concentration, it is assumed that during the event measured, the change in concentration of that particular reactant is negligible.

In the Figure 1.18(a), variation of volume over time in the entire range shows a curve. By enlarging the circled area, i.e. enlarging the very beginning of the first curve, it can be seen that it is approximately a straight line at that point (Figure 1.18(b)). That is a reasonable approximation once very early stage in the reaction is considered. This can also be obtained by drawing a tangent line to the curve at the $t \sim 0$. The slope in this case is simply V/t. Now suppose the experiment is carried out again with different (lower) concentrations of the reagent and the time taken to evolve the same volume of the gas is measured at the very beginning of the reaction as earlier. Following types of graphs as shown in Figure 1.19 would result for the formation of a constant volume of a gas in which different time measurements could be obtained.

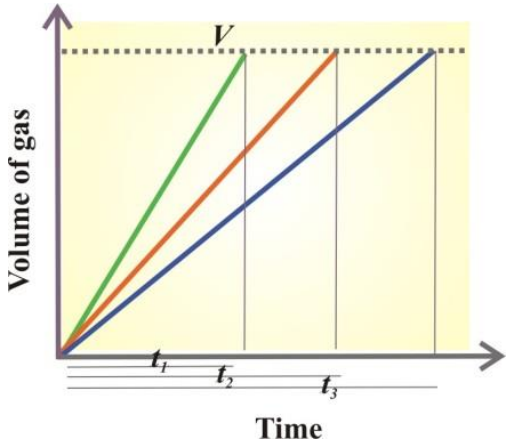


Figure 1.19 Measuring time taken to produce a constant volume of a gas with different concentrations of the reactant in an initial rate experiment. When there is no linearity at the beginning of the reaction, gradient of the tangent has to be determined.

From these experiments the initial rates (in terms of volume of gas produced per second) can be deduced as:

Experimet 1 : Initial rate$_1$ = V/t_1
Experimet 2 : Initial rate$_2$ = V/t_2

In the above two experiments as the time taken to evolve a constant volume (V) of a gas is measured it is easy to compare the initial rates obtained. It is clear from the above two that the initial rate is inversely proportional to the time taken and therefore;

$$\text{Initial rate} \propto \frac{1}{t}$$

Thus, normal in experiments of this type, $\frac{1}{t}$ can be used as a measure of the initial rate without any further calculations. Therefore, the initial rates measured by varying concentrations of respective reactant(s) can be used to determine the orders of reactions

and finally the value of the rate constant. Following examples give some insight into this type of experiments.

Example:

Consider a hypothetical reaction at a given temperature:

$$A + 2B \rightarrow C + D$$

The rate law, expressed in general terms, is

$$\text{Rate} = k[A]^m[B]^n$$

To find the values of **m** and **n**, a series of experiments was carried out in which one reactant concentration was changed while the other was kept constant. The initial rate measured in each case is shown in the table shown below. Using the data given in the table calculate the values of ***m, n*** and ***k.***

Table 1.2 Data set for calcultion

Experiment	Initial [A]/ mol dm^{-3}	Initial [B]/ mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	2.5×10^{-2}	3.0×10^{-2}	1.75×10^{-3}
2	5.0×10^{-2}	3.0×10^{-2}	3.50×10^{-3}
3	2.5×10^{-2}	6.0×10^{-2}	3.50×10^{-3}

1. *Finding m, the order with respect to A*

   By comparing experiments 1 and 2, in which [A] doubles and [B] is constant, we can obtain m. First, take the ratio of the general rate laws for these two experiments:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k\,[A]_1^m\,[B]_1^n}{k[A]_2^m\,[B]_2^n}$$

   In experiments 1 and 2, $[B]_1$ and $[B]_2 = 3.0 \times 10^{-2}$ mol dm^{-3} and *k* is a constant as the temperature is constant.

   Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[A]_1^m}{[A]_2^m}$$

$$\frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{3.50 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}} = \frac{(2.5 \times 10^{-2}\ \text{mol dm}^{-3})^m}{(5.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^m$$

$$\therefore\ \boldsymbol{m = 1}$$

   Thus, the reaction is first order *with respect to* A, because when [A] doubles, the rate doubles.

2. *Finding n, the order with respect to B.*
   Comparing experiments 3 and 1 in which [A] is held constant and [B] doubles:

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{k\,[\text{A}]_1^m\,[\text{B}]_1^n}{k[\text{A}]_3^m\,[\text{B}]_3^n}$$

   In experiments 1 and 3, $[\text{A}]_1$ and $[\text{A}]_3 = 2.5 \times 10^{-2}$ mol dm^{-3} and *k* is a constant as the temperature is constant.
   Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{[\text{B}]_1^n}{[\text{B}]_3^n}$$

$$\frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{3.50 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}} = \frac{(3.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}{(6.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^n$$

$$\therefore\ \boldsymbol{n = 1}$$

   Thus, the reaction is also first order with respect to B, because when [B] doubles, the rate doubles.
   Therefore the rate law of the reaction is

$$\text{Rate} = k\,[\text{A}][\text{B}]$$

   The value of k can be obtained by substituting appropriate values in the rate expression as for the experiment 1 ;

$$1.75 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1} = k\,(2.5 \times 10^{-2})(3.0 \times 10^{-2})\ \text{mol}^2\ \text{dm}^{-6}$$

$$k = \frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{7.50 \times 10^{-4}\ \text{mol}^2\ \text{dm}^{-6}} = 2.3\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

Note: What would be the initial rate of the above reaction if the concentrations of both A and B are doubled at the same time?
When both [A] *and* [B] *doubled, the rate should quadruple to* $7.00 \times 10^{-3}\ mol\ dm^{-3}s^{-1}$ *and therefore, that confirms the rate law derived from the experiment.*

Note especially, that while the order with respect to B is 1, the coefficient of B in the balanced equation is 2. Thus, as mentioned earlier, reaction orders must be determined from experiment.

Example 1.13

Consider the real reaction between oxygen and nitrogen monoxide at 300 K.

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

The general rate law is,

$$\text{Rate} = k\,[O_2(g)]^m[\,NO(g)]^{\,n}$$

Using the data given in the table below derive the rate law of the reaction at 300 K.

Experiment	Initial $[O_2(g)]$ or $[O_2(g)]_0$/ mol dm^{-3}	Initial $[NO(g)]$ or $[NO(g)]_0$/ mol dm^{-3}	Initial rate mol dm^{-3} s^{-1}
1	1.0×10^{-2}	2.0×10^{-2}	3.20×10^{-3}
2	2.0×10^{-2}	2.0×10^{-2}	6.40×10^{-3}
3	1.0×10^{-2}	4.0×10^{-2}	12.80×10^{-3}
4	3.0×10^{-2}	2.0×10^{-2}	9.60×10^{-3}

$[O_2(g)]_0$ and $[NO(g)]_0$ are the initial concentrations.

Answer

1. Finding m, the order with respect to $O_2(g)$.

   By comparing experiments 1 and 2, in which $[O_2(g)]$ doubles and $[NO(g)]$ is constant, we can obtain m. First, take the ratio of the general rate laws for these two experiments:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k\,[O_2]_1^m\,[NO]_1^n}{k[O_2]_2^m\,[NO]_2^n}$$

   In experiments 1 and 2, $[NO]_1 = [NO]_2 = 2.0 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

   Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[O_2]_1^m}{[O_2]_2^m}$$

$$\frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{6.40 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}} = \frac{(1.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}{(2.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^m$$

$$\therefore\ \boldsymbol{m = 1}$$

   Thus, the reaction is first order with respect to O_2, because when $[O_2(g)]$ doubles, the rate doubles.

   Experiment 4 also supports the value of m (m =1); rate increases thrice when the concentration is increased by three times.

2. Finding n, the order with respect to NO(g).

Comparing experiments 1 and 3 in which $[O_2]$ is held constant and [NO] doubles:

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{k\,[O_2]_1^m\,[NO]_1^n}{k[O_2]_3^m\,[NO]_3^n}$$

In experiments 1 and 3, $[O_2]_1$ and $[O_2]_3 = 1.0 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{[NO]_1^n}{[NO]_3^n}$$

$$\frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{12.8 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}} = \frac{(2.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}{(4.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^n$$

$$\therefore\ \boldsymbol{n = 2}$$

Thus, the reaction is second order with respect to NO, because when [NO] doubles, the rate increases four times.

Therefore the rate law of the reaction is

$$\text{Rate} = k\,[O_2(g)]\,[\,NO(g)]^2$$

Note: In some cases we may not have exactly simplifying numbers in this calculations. For example if the initial rate of the experiment 1 is 3.10×10^{-3} mol dm^{-3}s^{-1}, then we get $\frac{3.10 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{6.40 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}} = 0.485$ and hence

$0.485 = \left(\frac{1}{2}\right)^m = (0.500)^m$.

This can be solved by taking log as;

log (0.485) = *m* log *(0.500)*

$$m = \frac{\log(0.485)}{\log(0.500)} = 1.04 \text{ or } m = \frac{\log(0.500)}{\log(0.500)} = 1 \ (as\ 0.485 \sim 0.500)$$

As m has to be an integer, m =1

The value of k can be obtained by substituting appropriate values in the rate expression as for the experiment 1.

$$3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1} = k\,(1.0 \times 10^{-2})(2.0 \times 10^{-2})^2\ \text{mol}^3\ \text{dm}^{-9}$$

$$k = \frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{4.0 \times 10^{-6}\ \text{mol}^3\ \text{dm}^{-9}} = 8.00 \times 10^2\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$$

In addition to the above type of calculations, the data obtained by several experiments can be plotted as a plot of $\frac{1}{t}$ against the varying concentrations of the reactant. If the reaction is first order with respect to that substance, then straight line will result. That's because in a first order reaction, the rate is proportional to the concentration.

If the plot is a curve, then it isn't first order. It *might* be second order (or some sort of fractional order).

The best way for this analysis with several data of initial rates is constructing a *log graph*. As previously discussed, for a reaction involving A, with an order of ***n*** with respect to A, the rate equation is:

$$\textbf{Rate} = k\,[\text{A}]^n$$

Taking the log of each side of the equation, you get:

$$\log(\text{Rate}) = n \log[\text{A}] + \log k$$

Therefore the plot of log(Rate) against log[A], would give a straight line with slope *n*, that is the order of the reaction. The intercept of the plot is log(*k)* and hence *k* can be obtained.

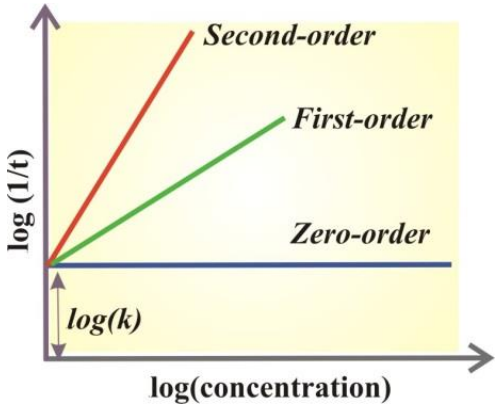


Figure 1.20 Shapes of graphs that could be obtained from initial rate experiments (Figure 1.17(a) can also be obtained)

Some kind of laboratory experiments can be designed and carried out by measuring time measurements to occur for a constant extent of the reaction and then by plotting the appropriate graphs, the order of the reaction(s) can be deduced. Following are some examples which are included in your practical manual.

Thiosulphate-acid reaction

Addition of dilute nitric acid (HNO_3) to sodium thiosulphate ($Na_2S_2O_3$) solution at room temperature results in a slow formation of a pale yellow precipitate of sulphur through the following reaction.

$$Na_2S_2O_3(aq) + 2HNO_3(aq) \rightarrow S(s) + 2NaNO_3(aq) + SO_2(g) + H_2O(l)$$

In this system, there is a simple, but very effective, way of measuring the time taken for a small fixed amount of sulphur precipitate to form. As a precipitate is formed in the reaction, it is possible to measure the time taken to form a fixed amount of precipitate under different concentrations of reactants at a given temperature as follows.

Keep a flask or small beaker on a piece of paper with a cross mark (X) drawn on it, and then look down through the reaction mixture until the cross disappears. First, put a known amount of thiosulphate solution in to a beaker and then add a small amount of dilute acid solution with known different concentrations and measure the time it takes for the cross to disappear (Detailed experiment is discussed in your practical manual). In this experiment, the actual concentration of the sodium thiosulphate does not have to be known because in each case, its relative concentration can be estimated with the total volume of the reaction mixture. The solution with 40 cm^3 of sodium thiosulphate solution plus 10 cm^3 of water has a concentration which is 80% of the original one, for example. The one with 10 cm^3 of sodium thiosulphate solution plus 40 cm^3 of water has a concentration which is 20% of the original one.

After collecting data on the time measurements, the data can be plotted as the variation of 1/t with the thiosulphate concentration and from that the reaction order with respect to the reactant thiosulphate can be deduced. In addition to this, the effect of temperature on the reaction rate could also be investigated as described in the practical manual.

Iodine clock experiments

There are several reactions given the name "iodine clock". They are all reactions which give iodine as one of the products and help measure the time taken for the formation of constant amount of iodine. This is the simplest of them, because it involves the most familiar reagents. For example, kinetics of the reaction of the oxidation of iodide ions by hydrogen peroxide under acidic conditions can be monitored by such “iodine clock” experiments. In the acidic medium iodide ions reacts with hydrogen peroxide as follows.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

In this reaction the amount of iodine ($I_{2(aq)}$) produced can be monitored by using starch when a small amount has been formed. Iodine reacts with starch solution to give a deep blue colored complex turning the solution blue. If a little volume (few drops) of starch solution is added to the reaction mixture initially, as soon as the first trace of iodine was formed, the solution would turn blue. However, just the addition of starch will not help to follow the kinetics as the colour change occurs instantaneously. Therefore, another way to remove the iodine produced is used. As iodine also reacts with sodium thiosulphate solution that can be used to consume some iodine produced.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

If a very small known amount of sodium thiosulphate solution is added to the reaction mixture (including the starch solution), it will react with the iodine that is initially produced, and so the iodine will not affect the starch and no blue colour is displayed. However, when that small amount of sodium thiosulphate has been used up, there is nothing to stop the next bit of iodine produced from reacting with the starch. The mixture suddenly goes blue and the time taken to appear the blue colour can be measured for different experimental conditions.

In this experiment, effect of changing the hydrogen peroxide concentration, or the iodide ion concentration, or the hydrogen ion concentration - each time, keeping everything else constant would let you find the orders with respect to each reactant taking part in the reaction.

Note that a similar experiment is included in the practical manual to follow the kinetics of the reaction;

$$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$$

In addition to the above - mentioned reactions, the method of initial rate can be used to monitor the kinetics of the catalytic decomposition of hydrogen peroxide by monitoring the volume of oxygen gas produced at a given temperature.
Above examples show that the kinetics of reactions can be investigated by carefully designed experiments. It has to be noted that following requirements must be fulfilled once such experiments are carried out.

(i) Controlling the temperature of the system with a good thermostat (this will be learnt during practical) as rates change (exponentially) with temperature.
(ii) Choosing an accurate timing device.
(iii) An appropriate method for determining the concentration of reactant or product. This can be done through a measurement of a rapidly determinable physical property of the reaction mixture.

Following the course of a single reaction

Rather than doing a whole set of initial rate experiments, information about orders of reaction can also be obtained by following a particular reaction from start to finish.

There are two different ways to do this. Withdraw samples of the mixture at intervals and find out how the concentration of one of the reagents is changing by doing an appropriate titrations. Or by measuring some physical property of the reaction which changes as the reaction proceeds - for example, refractive index, absorbance, etc. Then the set of values obtained for concentration can be plotted against time and the rates of reaction at different points need to be extracted from the graph. Finally, by plotting log(rate) against log(concentration) the order of reaction can be estimated.

Half-life of a reaction ($t_{1/2}$)

As the reaction proceeds, the concentration of the reactant(s) decreases and another measure of the rate of reaction relating the concentration to the time is the half-life. The concept of half-life is useful for describing the rough speed of a reaction. The half-life of a reaction is the time it takes for the consumption of reactants by half of the initial amount. In other words, the half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $\mathbf{t_{1/2}}$ and this is affected by temperature. This can be represented by the Figure 1.21.

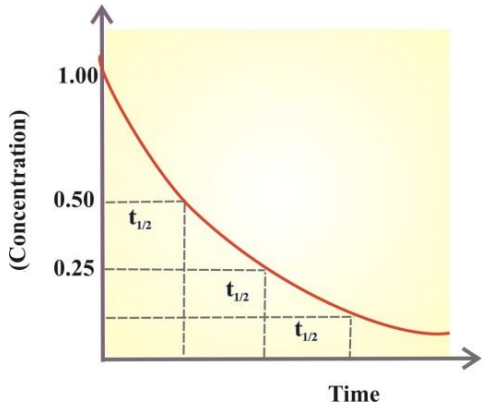


Figure 1.21 Definition of half-life (for a first order reaction)

For example, consider the first order decomposition of hydrogen peroxide. The table below shows the concentration of H_2O_2 in increments of 600 min.

Table 1.3 Concentration of H_2O_2 in increments of 600 min

Time/ min	Number of half-lives	Fraction remaining	$[H_2O_2]$/ mol dm^{-3}
0	0	1	0.020
600	1	1/2	0.010
1200	2	1/4	0.005
1800	3	1/8	0.0025
2400	4	1/16	0.0013
3000	5	1/32	0.00065

Note that in the first 600 min, the concentration drops from 0.020 mol dm^{-3} to 0.010 mol dm^{-3}. That is, it drops in half. The half-life of the reaction is therefore 600 min. Then, when another 600 min passes (from t = 600 to t = 1200) and the concentration drops in half again: from 0.010 mol dm^{-3} to 0.0050 mol dm^{-3} the half-life is still 600 min. Successive half-lives produce reaction mixture with concentration fractions of 1/2, 1/4, 1/8, 1/16 and 1/32 as shown in the table.

Half-life of a first order reaction

Half-life of a first order reaction is given by, $\mathbf{t_{1/2}} = \frac{0.693}{k}$ *

k is the rate constant.

Since k is a constant for a given reaction at a given temperature and the expression does not contains any concentration term, the half-life of a first order reaction is a constant independent of initial concentration of reactant**.**

This means that if we start with 2.00 mol dm^{-3}, and of a reactant reacting with first order kinetics and after 20 minute it is reduced to 1.00 mol dm^{-3}, and the half-life of the reaction will be 20 minutes. In other words, during the first 20 minutes 50% of the reaction completes, then in 40 minutes 75%, in 60 minutes 87.5% and so on. This can also be understood from the Figure 1.21.

Example 1.14

A certain first-order reaction has a half-life of 20.0 minutes.

(i) Calculate *k* for the reaction.

(ii) How much time is required for this reaction to be 75% complete?

Answer

(i) Half-life of a first order reaction is given by $\mathbf{t_{1/2}} = \frac{0.693}{k}$.

$$20.0 \text{ min} = \frac{0.693}{k}$$

$$k = \frac{0.693}{20 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

(ii) If the reaction is 75% complete that means there is 25% of the reactant is left or the reaction has occurred up to the second half life cycle. Therefore, the time taken to complete the reaction by 75% is two-half-lives, i.e 40 min.

Show that in a first order reaction, time required for completion of 99.9% is 10 times the half-life ($t_{1/2}$) of the reaction.

When 99.9% is completed the remaining amount is 0.100 % or 0.001

The value of remaining concentration after 10 half-life cycles

Can be written as $\frac{1}{2^n} = \frac{1}{2^{10}} = \frac{1}{1024} = 0.001$

Therefore, the time required for the completion of 99.9% of a first order reaction is 10 times the half-life.

Half-life of a zero order reaction is given by;

$$t_{1/2} = \frac{[A]_0}{2k} \ *$$

$[A]_0$ is the initial concentration. Therefore, half-life of the zero-order reaction depends on the initial concentration.

* *Derivation of this equation will not be tested at the G. C. E. (A/L) Chemistry examination.*

1.8 The effect of the physical nature (surface area) on the reaction rate

In the section 1.1 a little description on the effect of the physical nature of the reactant on the rate has been given. When the reactions involve solid reactants, increasing the surface area by turning the solid into a fine powder enhances the rate of reaction due the increase in the number of collisions between reacting particles.

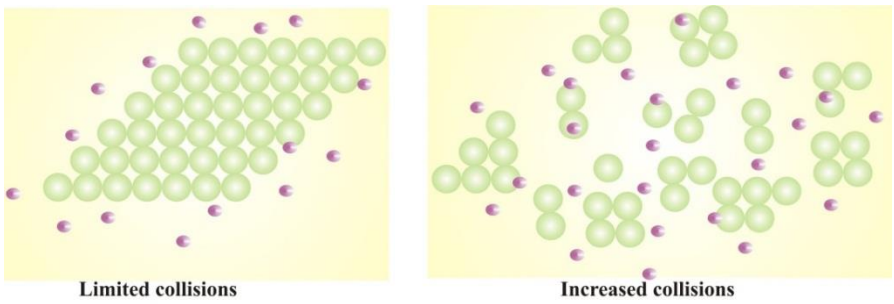
As described earlier, rates of reactions depend on the physical nature as Gaseous state > Liquid state > Solid state. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase. In the case of solid reactant, the more finely powdered solid reacts faster than the same mass present as a single lump because the powdered solid has a greater surface area than the single lump.

For example in the reaction between calcium carbonate and hydrochloric acid you can observe in the laboratory that powdered calcium carbonate reacts much faster with dilute hydrochloric acid than the same mass of marble or limestone in lumps.

In the catalytic decomposition of hydrogen peroxide solid manganese(IV) oxide is often used as the catalyst. Oxygen is given off much faster if the catalyst is present as a powder than when the same mass of it is present as granules.

In these cases with increasing surface area of the solid, the frequency of collisions increases and the rate of the reaction thus increases.

For example, the reaction between magnesium metal and a dilute hydrochloric acid involves collision between magnesium atoms and hydrogen ions. The effect of surface area can be understood by the Figure 1.22.



(a) (b)

Figure 1.22 Effect of particle size on the reaction rate; (a) A particle has a little area to collide with the reactant molecules, molecules collide only with the outer surface. (b) When the solid sample with the same number of atoms is powdered to fine particles, surface area for the collisions with reactant molecules increases and hence the rate of reaction.

1.9 Effect of catalysts on the rate of reactions

Increasing the rate of a reaction has many advantages in industry. Higher temperatures can speed up a reaction, but energy for industrial processes is costly and many organic and biological substances are heat sensitive. More commonly, by far, a reaction is accelerated by a **catalyst,** a substance that increases the rate *without* being consumed. Thus, only a small, non stoichiometric amount of the catalyst is required to speed the reaction.

A catalyst is a substance that accelerates a reaction but undergoes no net chemical change. *It functions by providing an alternative path with lower activation energy of the reaction and avoids the slow, rate-determining step of the unanalyzed reaction, and results in a higher reaction rate at the same temperature*.

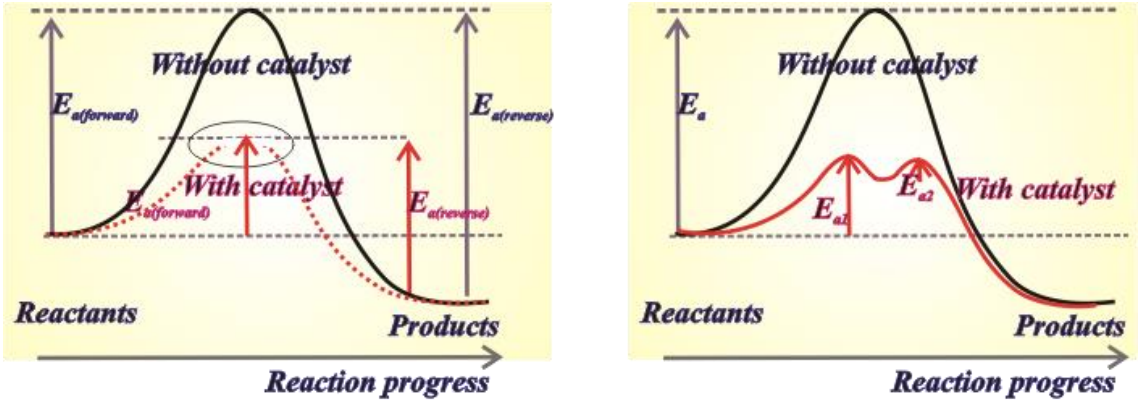
As we know, there are two basic types of catalysts namely heterogeneous and homogeneous catalyst. Heterogeneous catalyst is in a different phase (for example, a solid catalyst for a gas-phase reaction). A homogeneous catalyst is a one that is in the same phase as the reaction mixture (for example, acid catalyzed reactions in aqueous solution).

The following examples elaborates the function of a catalyst on the reaction rate. The activation energy for the decomposition of hydrogen peroxide in solution is 76 kJ mol^{-1} and the reaction is slow at room temperature. When a little amount of iodide ions is added, the activation energy falls to 57 kJ mol^{-1}, and the rate constant increases by a factor of 2000.

In addition, enzymes (categorized as biological catalysts), are very specific and can have a dramatic effect on the reactions they control. The activation energy for the acid

hydrolysis of sucrose is 107 kJ mol^{-1} but the enzyme saccharase reduces it to 36 kJ mol^{-1}, corresponding to an acceleration of the reaction by a factor of 1012 at body temperature (310 K).

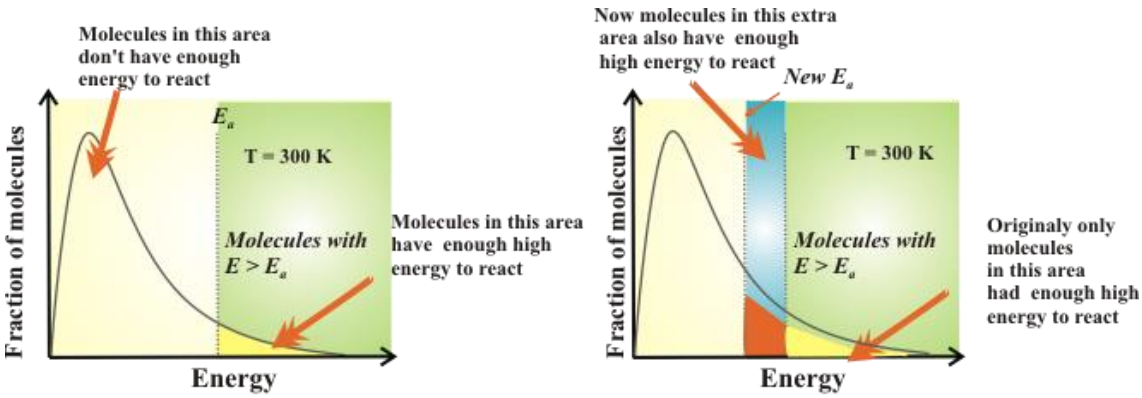
There are some substances which decrease the rate of reaction and such substances are called inhibitors. Obviously, the substances accelerating the rate will be a catalyst. Catalyst are generally foreign substances but sometimes one of the product formed may act as a catalyst. Such a catalyst is called an "auto catalyst" and the phenomenon is called auto catalysis. The function of the catalyst on the reaction rate can be depicted as illustrated in the Figure 1.23



(a) (b)

Figure 1.23 Comparison of the reaction profiles with and without a catalyst. The addition of a catalyst to a reaction increases the rate by providing a new, lower-energy alternative pathway. **(a)** Reaction goes through a different mechanism and **(b)** for example reaction goes through two transition states.

In a chemical reaction collisions result products only if the particles collide with a certain minimum energy or the activation energy for the reaction. The position of activation energy can be marked on a Maxwell-Boltzmann distribution curve as illustrated in Figure 1.24(a).



(a) (b)

Figure 1.24 Comparison of Maxwell - Boltzmann distributions with and without a catalyst at 300 K (same temperature). The addition of a catalyst to a reaction increases the rate by increasing the fraction of molecules having enough energy to react through an alternative pathway by increasing the collision frequency and hence the rate of the reaction.

Only those particles represented by the area to the right of the activation energy will react when they collide. The great majority does not have enough energy, and will simply bounce apart. Therefore, to increase the rate of a reaction it is necessary to increase the number of effective collisions by increasing the fraction of molecules with enough energy. In one way, this can be done by providing an alternative pathway for the reaction to happen with lower activation energy. In other words, the activation energy should be moved to the lower energy side (left) of the Maxwell Boltzmann distribution as shown in Figure 1.24(b). Adding a catalyst to a reaction has exactly this effect on activation energy. i.e. a catalyst provides an alternative path for the reaction with a lower activation energy compared to the un-catalyzed reaction as depicted in Figure 1.23.

It is very important to note that;

> *"A catalyst provides an alternative path for the reaction with lower activation energy." It does not "lower the activation energy of the reaction".*

This means that the original value of the activation energy of the reaction remains the same and the new catalyzed-path has lower activation energy. It is just like going through a tunnel without climbing a mountain.

1.10 Uses of reaction mechanisms to describe the rate of chemical reactions

In any chemical reaction or change, some bonds are broken and new bonds are formed. Usually, these changes such as bond breaking/ formation and rearrangements are too complicated to happen simply in one stage. Instead, the reaction may involve a series of steps one after the other. A reaction mechanism describes the one or more steps involved in the reaction in a way which makes it clear exactly how the various bonds are broken and formed.

A chemical reaction that takes place in one and only one step i.e., all that occurs in a single step is called an **elementary reaction**.

A chemical reaction occurring in a sequence of two or more steps is called a multi-step or complex reaction. As described above, the sequence of steps through which a multi-step reaction takes place is called the reaction mechanism. Each step in a mechanism is an elementary reaction. Reaction mechanisms cannot be calculated or predicted; instead, all reaction mechanisms must be determined experimentally.

Therefore, a chemical reaction in which one or more chemical species react directly to form products in a single step reaction and with a single transition state is called an elementary reaction. In this elementary reaction the molecules collide exactly as the stoichiometric equation of the reaction.

Further, in an elementary reaction no reaction intermediates are involved. Also their presence is not a requirement to describe the chemical reaction on a molecular scale.

1.10.1 Molecularity of a reaction

The molecularity of an elementary reaction is defined as the minimum number of molecules, atoms or ions of the reactant(s) required for the reaction to occur and is equal to the sum of the stoichiometric coefficients of the reactants in the balanced chemical equation.

In general, molecularity of a simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.

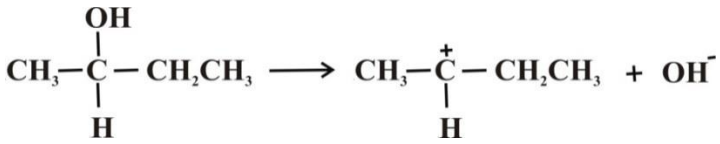
When multi-step reaction mechanism is written, the minimum number of reacting particles (molecules, atoms or ions) that comes together or collide in the **rate determining step** to form a product or products is called the molecularity of a reaction.

Therefore, chemical reactions can be categorized simply by the number of reacting species in an elementary step. A reaction is **unimolecular** when only a single reactant molecule is involved and is **bimolecular** when two reactant molecules are involved. For example, in a **unimolecular reaction**, a single molecule decomposes itself or changes its atoms into a new arrangement, as in the isomerization of cyclopropane to propene. In

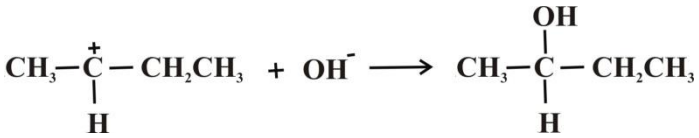
a **bimolecular reaction**, a pair of molecules collides and exchange energy while atoms or groups of atoms undergo some other kind of change getting converted into a product or products.

Molecularity is a theoretical concept; it cannot be zero, negative, fractional, infinite and imaginary.

Consider a following reaction in which a bond breaking step involves a single entity breaking up into two pieces. The C-O bond breaks. A single reactant forms two products. Because only one reactant molecule is involved, this step is unimolecular.



The following **bond forming step** which involves bringing two molecular fragments together to form a single product, a C-O bond is formed. Two reactants form a single product. Because two reactant molecules are involved, this step is **bimolecular**.



Usually, there are few reactions with termolecular elementary behaviour as the collision of three molecules at the same time is somewhat difficult (However, such reactions occur through multi steps).

1.10.2 Examples of single step reactions

Many chemical reactions are simple events that occur in a single step. Acid-base reactions mostly occur in a single step. The protonation of ammonia by a hydronium ion involves the transfer of an H^+ ion from H_3O^+ to NH_3. This single step is a concerted bond-breaking and forming process.

$$H_3O^+(aq) + NH_3(aq) \rightarrow H_2O(l) + NH_4^+(aq)$$

The reaction occurs via a single step involving two species and is called as **bimolecular elementary reaction**.

The decomposition of $N_2O_4(g)$ is a single bond breaking step.

$$N_2O_4(g) \rightarrow 2NO_2(g)$$

The reaction occurs via a single step involving one species and is called as **unimolecular elementary reaction**.

Followings examples show some elementary reactions with different molecularities.

Table 1.4 Elementary reactions with different molecularities

Reaction	Molecularity
$PCl_5 \rightarrow PCl_3 + Cl_2$	Unimolecular
$2HI \rightarrow H_2 + I_2$	Bimolecular
$NO + O_3 \rightarrow NO_2 + O_2$	Bimolecular
$2SO_2 + O_2 \rightarrow 2SO_3$	Termolecular
$2CO + O_2 \rightarrow 2CO_2$	Termolecular
$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$	Termolecular

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g.

$4HBr(aq) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)$

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

In the first reaction molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions do not occur in a single step and involve two or more steps; each step has its own molecularity not greater than three. Following describes the basic features of reactions which occurs through multistep.

1.10.3 Multistep reactions

Chemical processes that occur in a series of elementary steps has their own set of rules.

(i) The overall reaction is the sum of the elementary reaction steps.

(ii) A species that is formed in one step and then used up in a later step is an **intermediate**.

(iii) A species that is used in one step and increase the rate of the reaction, then regenerated in a later step is acting as a **catalyst**.

(iv) Neither intermediates nor catalysts are seen in the overall reaction rate law.

Example 1:

The decomposition of ozone takes place in two steps.

Step 1: $O_3(g) \rightarrow O_2(g) + O(g)$; unimolecular, bond breaking

Step 2: $O_3(g) + O(g) \rightarrow 2O_2(g)$: bimolecular, bond forming and breaking

As learned in Unit 5, the idea of adding a series of reactions to give a net reaction is used here to determine the overall reaction that takes place in a series of steps.

In this case, O(g) is present on both sides.

Step 1: $O_3(g) \rightarrow O_2(g) + O(g)$

Step 2: $O_3(g) + O(g) \rightarrow 2O_2(g)$

$2\ O_3(g) + O(g) \rightarrow 3\ O_2(g) + O(g)$

$\therefore$ Overall reaction: $\mathbf{2\ O_3(g) \rightarrow 3\ O_2(g)}$

In this example, it can be seen that the O(g) atom formed in the step 1 is consumed in the step 2 and it doesn't appear in the overall reaction. That doesn't mean that it does not exist at least for a little while. A chemical species that is formed in one step of a mechanism and then used in a later step is called an intermediate. Intermediates never appear in the overall reaction equation. Sometimes they can be observed while the reaction progresses, but other times they are formed and used up so quickly and are not seen.

Example 2:

The decomposition of hydrogen peroxide in the presence of iodide ion occurs in two steps.

Step 1. $H_2O_2(aq) + I^-(aq) \rightarrow IO^-(aq) + H_2O(l)$; bimolecular

Step 2. $IO^-(aq) + H_2O_2(aq) \rightarrow I^-(aq) + H_2O(l) + O_2(g)$: bimolecular

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

In this case, the $IO^-(aq)$ ion is formed in the first step and then consumed in the second step. $IO^-(aq)$ is an intermediate in this reaction. Conversely, $I^-(aq)$ ion is used in the first step and then regenerated in the second step. Therefore, $I^-(aq)$ act as a catalyst in this reaction

Example 3:

Chlorofluorocarbons break down in the upper atmosphere to give chlorine atoms. These are involved in the breakdown of ozone via the following mechanism.

Step 1. $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$

Step 2. $ClO(g) + O_3(g) \rightarrow Cl(g) + O_2(g)$

Overall reaction: $2O_3(g) \rightarrow 2O_2(g)$

Reactions in step 1 and 2 are both bimolecular. Cl(g) is a reactant in the Step 1, but is regenerated in Step 2. Cl is therefore a catalyst. ClO is generated in Step 1, but is consumed in Step 2. ClO is therefore an intermediate.

1.10.4 The rate laws of elementary reactions

The rate law for elementary reactions can deduced directly from their molecularity. For example, the rate law of a unimolecular elementary reaction is first-order with respect to the reactant. Consider the reaction where P denotes products (several different species may be formed).

$$A \rightarrow P$$

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k\,[A]$$

A unimolecular elementary reaction is first-order because the number of A molecules that decays in a short interval is proportional to the number available to decay. Therefore the rate of decomposition of A is proportional to its molar concentration.

An elementary bimolecular reaction has a second-order rate law:

$$2A \rightarrow P$$

$$\text{Rate} = k\,[A]^2$$

Or we can write the reaction as;

$$A + B \rightarrow P$$

$$\text{Rate} = k\,[A][B]$$

A bimolecular elementary reaction is second order because its rate is proportional to the rate at which the reactant species meet, which in turn is proportional to their concentrations. Therefore, if we consider that a reaction is a single-step, bimolecular process, we can write down the rate law.

Note that the converse of this rule does not follow, that is, for example *second order rate law does not imply that the reaction is bimolecular.* Also, care must be taken to ensure that the reaction /step that we are considering is really elementary. For example, the reaction

$H_2(g) + I_2(l) \rightarrow 2HI(g)$ may look simple, but it is not elementary, and in fact, it has a very complex reaction mechanism, and hence the rate law cannot be deduced by merely looking the reaction.

With the above descriptions, for an elementary reaction of the general type;

$$aA + bB \rightarrow cC + dD$$

rate law is written as,

$$\text{Rate} = k\,[A]^a\,[B]^b$$

The order of an elementary reaction with respect to a given reactant is exactly same as the stoichiometric coefficient. Therefore, for the above elementary reaction, order with respect to the reactant A is ***a*** and the order with respect to the reactant B is ***b.*** The overall order of the reaction is (***a + b).***

It is very important to understand the difference between molecularity and reaction order:

The ***reaction order*** is an empirical quantity, and obtained from the experimental rate law.

The ***molecularity*** refers to an elementary reaction proposed as an individual step in a mechanism.

The following table summarizes some examples.

Table 1.5 Summary of molecularity

Molecularity	Elementary step	Rate law
Unimolecular	A → Products	Rate = k [A]
Bimolecular	A + A → Products	Rate = k $[A]^2$
Bimolecular	A + B → Products	Rate = k [A] [B]
Termolecular	A + A + A → Products	Rate = k $[A]^3$
Termolecular	A + A + B → Products	Rate = k $[A]^2$[B]
Termolecular	A + B + C → Products	Rate = k [A][B][C]

1.10.5 Reaction mechanisms and the rate law

As described earlier, a species acting as an intermediate or a catalyst does not appear in the rate law. Then it is necessary to understand how the rate law is derived for such systems. Usually, in a mechanism there are some steps that occur very slowly and some other steps that occur very rapidly. The overall rate of a reaction is controlled by the rate of the slowest step. The slowest step of a reaction is known as the **rate determining step (RDS)**. Therefore, in experiments, when the rates are measured, the rate of the rate determining step is actually measured as long as there is a lot of differences among the rates of the various steps.

Consider the following example; in which the reaction occurs in two steps. First the reactant A is transformed into another species B; then in the next step it acts as a reactant which is transformed into the desired product P.

$$A \xrightarrow{k_1} B$$

$$B \xrightarrow{k_2} P$$

k_1 and k_2 are the rate constants of respective steps.

Assume that $k_2 >> k_1$. In such a case, whenever a molecule B is formed, it decays rapidly to P indicating that the rate of the reaction depends only on the first step and that the step would be the rate determining step of the reaction.

Consider another example in which the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ occurs through following mechanism.

$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g)$: slow; rate determining step

$NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g)$: fast

In this reaction the first step is the rate determining step and hence we can say that the rate of reaction depends only on the rate constant k_1. This can further be proven from the experiments in determining the empirical rate law of the reaction. The empirical rate law of the reaction is

$$\text{Rate} = k\,[NO_2]^2$$

i.e. the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is 2nd order with respect to $NO_2(g)$ and zero-order with respect to CO(g).

In the mechanism given above NO_3 functions as a **reaction intermediate,** which is formed and used up during the reaction. Even though it does not appear in the overall balanced equation, a reaction intermediate is essential for the reaction to occur. Intermediates are less stable than the reactants and products.
Rate laws for the two elementary steps written above are;

$$\text{Rate}_1 = k_1\,[NO_2]^2$$

$$\text{Rate}_2 = k_2\,[NO_3][CO]$$

Three key points to notice about this mechanism are

(i) If $k_1 = k$, the rate law for the rate-determining step (step 1) becomes identical to the observed rate law.

(ii) Because the first step is slow, $[NO_3]$ is low. As soon as any NO_3 forms, it is consumed by the fast second step, so the reaction takes as long as the first step does.

(iii) CO does not appear in the rate law (reaction order = 0) because it takes part in the mechanism *after* the rate-determining step.

Example:
Consider the reaction between nitrogen dioxide and fluorine as an example:

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

The experimental rate law is that it is first order in NO_2 and in F_2.
$\therefore$ Rate = $k\,[NO_2(g)]\,[F_2(g)]$

The accepted mechanism is

Step 1; $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$: slow; rate determining

Step 2; $NO_2(g) + F(g) \rightarrow NO_2F(g)$: fast

Note that here the free fluorine atom is a reaction intermediate.

Let us consider the mechanism and how the rate law of the reaction is explained.
Sum of the two elementary reaction steps is the overall balanced equation.

Step 1; $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$

Step 2; $NO_2(g) + F(g) \rightarrow NO_2F(g)$

Overall reaction: $\mathbf{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)}$

And both steps are bimolecular.
The rate laws for the elementary steps are:

$Rate_1 = k_1 [NO_2(g)] [F_2(g)]$

$Rate_2 = k_2 [NO_2(g)] [F(g)]$

It can be seen that the step 1 is the rate-determining step, and with $k_1 = k$, it is the same as the overall rate law.

In this mechanism it has to be noted that the second molecule of NO_2 is involved *after* the rate-determining step, so it does not appear in the overall rate law.

From the above examples it can be noted that though the reaction proceeds through several steps, rate law of the reaction follows the rate determining step (slowest step) of the mechanism.

Consider the reaction between 2-bromo-2-methylpropane with hydroxide (OH^-) ions:

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

In the overall reaction the bromine atom is replaced by an OH group.
The first step that happens is that the carbon-bromine bond breaks to give ions via a unimolecular reaction;

$$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + :Br^- \ : \textit{slow}$$

Carbon-bromine bonds are reasonably strong, so this is a slow change. If there is a high concentration of hydroxide ions, the positive ions will combine with them and this step of the reaction will be very fast. A new covalent bond is made between the carbon and the oxygen, using one of the lone pairs on the oxygen atom via a bimolecular (fast) reaction;

$$(CH_3)_3C^+ + :OH^- \rightarrow (CH_3)_3COH \ : \textit{fast}$$

The mechanism shows that the reaction takes place in two steps and describes exactly how those steps happen in terms of bonds being broken or made. It also shows that the steps have different rates of reaction; one slow and one fast.

The emperical rate law of the above reaction has been found to be as follows,

$$\text{Rate} = k[(CH_3)_3CBr]$$

The reaction is first order with respect to the $(CH_3)_3CBr$, and zero order with respect to the hydroxide ions. The concentration of the hydroxide ions does not affect the rate of the overall reaction.

If the hydroxide ions were taking part in the slow step of the reaction, increasing their concentration would speed up the reaction. Since its concentration does not seem to matter, they must be taking part in a later fast step.

Increasing the concentration of the hydroxide ions will speed up the fast step, but that will not not have a noticeable effect on the overall rate of the reaction as that is governed by the speed of the slow step.

Example: *Predicting a suitable mechanism*
Suppose an elementary bimolecular reaction between A and B which was experimentally found to be first order with respect to both A and B.
So the rate equation is:
Rate = k [A][B]

Let us consider the following two mechanisms;
Mechanism 1

$$A \rightarrow C + D \; ; slow$$
$$B + C \rightarrow E \; ; fast$$

Mechanism 2

$$A + B \rightarrow D + E \; ; slow$$

In this case, the reaction is first order with respect to both A and B, so one molecule of each must be taking part in the slow step. That means, mechanism 2 is the possible one.

Mechanism 1 must be wrong. One molecule of A is taking part in the slow step, but no B. The rate equation for that would be:
Rate = k[A]

1.10.6 Consecutive (elementary) reactions

As noted from the above reaction steps/mechanisms, the reaction which goes through an intermediate can be expressed as,

$$A \overset{k_1}{\rightarrow} I \overset{k_2}{\rightarrow} P$$

The above reaction is defined as a consecutive unimolecular reaction because one reactant is involved in each step and the first step is the rate determining step of the reaction. For such a process:

(i) The concentration of A decreases through unimolecular decomposition of A, and is not replenished. Thus we have the rate equation

$$\text{Rate} = -k_1[A]$$

(ii) The intermediate I is formed from A at a rate k_1[A], and decreases through decay to P at rate k_2[I]. This event happens very fast.
(iii) The product P is formed from I at a fast rate k_2[I], and it does not decrease.

Therefore, from these it can be simply noted that

(i) The concentration of the reactant A decreases with time;
(ii) The concentration of the intermediate I rises to a maximum and then falls to zero within a short time interval;
(iii) The concentration of the product P rises from zero to some value depending on the stoichiometry of the reaction.

These can be illustrated as shown in the Figure 1.25.

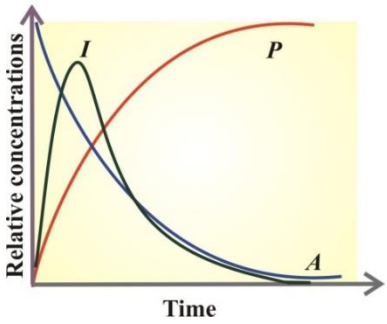


Figure 1.25 The concentrations of A, I, and P in the consecutive reaction $A \xrightarrow{k_1} I \xrightarrow{k_2} P$. Intermediate I is formed and consumed in the next step making its concentration zero with the time.

We can look at the above in another direction as follows.

The reaction $A \xrightarrow{k_1} I \xrightarrow{k_2} P$ occurs in two steps.

Step 1; $A \xrightarrow{k_1} I$

Step 2; $I \xrightarrow{k_2} P$

Overall reaction: $A \xrightarrow{k} P$

From the above we can deduce how the concentrations of A, I, and P will change over time. It is important to consider the relative rates of each step to understand the variation in concentrations of the species participating in the reaction. In any case, the concentration of A will decrease as the reaction proceeds, and the concentration of the product P will increase. But what would be the concentration of the intermediate, I? It is formed in one step and consumed in another. Its concentration must be zero at the start of the reaction, and must be zero when the reaction is complete, but non-zero in between. This is best observed by examining concentration-time curves. Figure 1.26 shows concentration-time curves of these species in three cases.

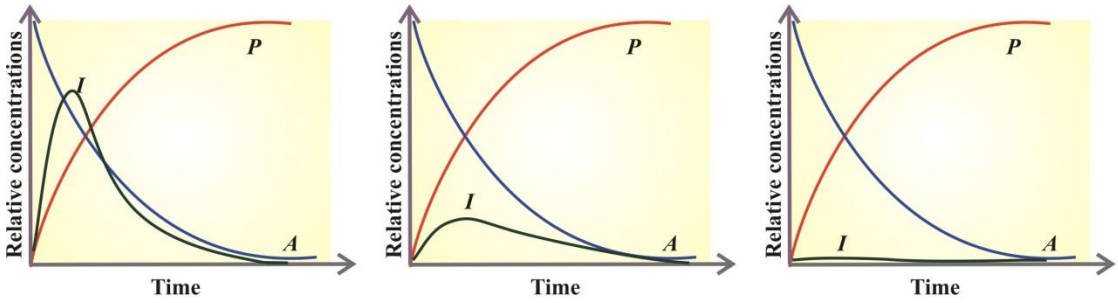


Figure 1.26 **(a)** Step 1 faster than Step 2. **(b)** Step 2 a little faster than Step 1. (c) Step 2 much faster than Step1.

In (a) the first step is somewhat faster than the second step. Initially, as A → I occurs, the rate of formation of I is greater than its rate of consumption in Step 2. So, the concentration of I increases over time. Then, as reactant A is depleted and the concentration of I increases, the rate of formation of I decreases and its rate of consumption increases. At this point, the concentration of I starts to decrease. Eventually the concentrations of both A and I drop to near zero as the reaction nears completion. (b) shows a case where Step 2 is somewhat faster than Step 1. In this case, I is consumed more quickly and its concentration does not build up as much as in (a). (c) shows a case where Step 2 is much faster than Step 1. In this case, I is consumed almost instantly as it is formed. The concentration of I never rises to an appreciable level and I may never be concentrated enough to observe in an experiment.

If a case like (c) occurs, it is important to know that the intermediate ever existed or not. Additional experiments can be designed to show that the intermediate was present, even if not directly observed. One of the methods is the addition of another reagent that would react with the postulated intermediate and observing the expected product. Then we can have evidence for the existence of the intermediate.

1.10.7 Cases where a pre-equilibrium exists in a mechanism

Example 1:

Suppose the mechanism for a reaction $A + B \rightarrow P$

$$A \rightleftharpoons I \; ; fast$$

$$I + B \rightarrow P \; : slow$$

This time the slow step is the second step and the intermediate I reaches an equilibrium with the reactants A and B. This mechanism involves a **pre-equilibrium**, in which an intermediate is in equilibrium with the reactants.

A pre-equilibrium arises when the rates of formation of the intermediate and its decay back into reactants are much faster than its rate of formation of the products.

The rate of the reaction will be governed by the slow step, and so the rate equation of the slow step is : Rate = k [B] [I]

In the rate law the concentration of the intermediate I is appearing and however, it is known that I is in equilibrium with A. Therefore the equilibrium constant K_c for the first step is;

$$K_c = \frac{[\mathrm{I}]}{[\mathrm{A}]}$$
$$\therefore \ [\mathrm{I}] = K_c[\mathrm{A}]$$

Therefore the rate of the reaction is:

$$\text{Rate} = k\ [\mathrm{B}]\ K_c\ [\mathrm{A}] = k\ K_c\ [\mathrm{A}][\mathrm{B}]$$

This can further be modified with the relation between rate constants and equilibrium constant of the reaction. If the rate constants for the forward and backward reactions are k_f and k_r, respectively, we can write;

$$K_c = \frac{k_f}{k_r}$$

Finally,

$$\therefore \text{Rate} = k\ \frac{k_f}{k_r}[\mathrm{A}][\mathrm{B}]$$
$$\text{Rate} = k'\ [\mathrm{A}][\mathrm{B}]$$

The above shows that the rate law is similar to that of an elementary bimolecular reaction.

Consider another example.

Suppose the mechanism for a reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{I}\ ; fast$$
$$\mathrm{I} + \mathrm{A} \rightarrow \mathrm{P}\ : slow$$

The overall reaction is ; $2\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$

The rate of the reaction will be governed by the slow step, so the rate equation of the slow step is : Rate = k [A] [I]

In the rate law the concentration of the intermediate I is appears. However, it is known that I is in equilibrium with A and B, so the equilibrium constant K_c for the first step is;

$$K_c = \frac{[\mathrm{I}]}{[\mathrm{A}][\mathrm{B}]}$$
$$\therefore \ [\mathrm{I}] = K_c[\mathrm{A}][\mathrm{B}]$$
$$\therefore \ Rate \ = kK_c[\mathrm{A}][\mathrm{A}][\mathrm{B}]$$
$$\therefore Rate = k'[\mathrm{A}]^2[\mathrm{B}]$$

The rate law obeys the termolecular elementary reaction.

Example 2:

The gas phase reaction between $H_2(g)$ and $I_2(g)$ is one example for the above type of reactions.

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

This has a fas*t* pre-equilibrium step in which molecular iodine converts to atoms.

$$I_2(g) \rightleftharpoons 2I(g)$$

Then that atomic iodine reacts with molecular hydrogen to form HI in a slow second step.

$$H_2(g) + 2I\,(g) \rightarrow 2HI(g)$$

The rate of the reaction is governed by the slow step, so the rate equation of the slow step is: $\text{Rate} = k\,[H_2(g)]\,[I(g)]^2$

In the rate law, the concentration of the intermediate, I appears. However, it is known that I is in equilibrium with $I_2(g)$. Therefore the equilibrium constant $\boldsymbol{K_c}$ for the first step is;

$$K_c = \frac{[I(g)]^2}{[I_2(g)]}$$

$$\therefore\ [I(g)]^2 = K_c[I_2(g)]$$

$$\therefore\ \text{Rate} = kK_c[I_2(g)][H_2(g)]$$

$$\therefore \text{Rate} = k'[I_2(g)][H_2(g)]$$

Therefore, the rate of reaction depends on the concentrations of both $I_2(g)$ and $H_2(g)$.

Example 3:

In this example in which the first step of the reaction is a *fast* and *reversible*. Consider the oxidation of nitrogen monoxide given below.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The observed rate law is

$$\text{Rate} = k\,[NO(g)]^2\,[O_2(g)]$$

the reaction has the mechanism;

Step 1 : $NO(g) + O_2(g) \rightleftharpoons NO_3(g)$: fast

Step 2 : $NO_3(g) + NO(g) \rightarrow 2NO_2(g)$: slow; rate determining step

The sum of the above two steps gives the overall reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ and both steps are bimolecular.

Rate law for the slow step is;

$$\text{Rate} = k\,[NO_3(g)]\,[NO(g)]$$

For the step 1, equilibrium constant is,

$$K_c = \frac{[NO_3(g)]}{[NO(g)][O_2(g)]}$$
$$\therefore [NO_3(g)] = K_c[NO(g)][O_2(g)]$$
$$\therefore \text{Rate} = kK_c[NO(g)][O_2(g)][NO]$$
$$\text{Rate} = k'[NO(g)]^2[O_2(g)]$$

This derived rate law is constant with the empirical rate law given earlier. Therefore, the mechanism of the reaction is correct.

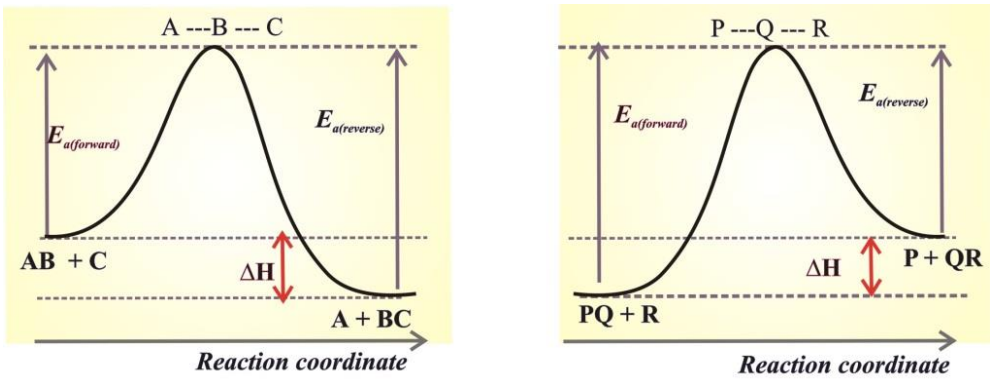
1.11 Energy profiles of reactions

First, consider an elementary reaction which occurs through a single step A → products. As described in earlier sections about the requirements to be satisfied for a chemical reaction to occur when two molecules approach each other, repulsion between their electron clouds continually increase, so they slow down as some of their kinetic energy is converted to potential energy. If they collide, but the energy of the collision is *less* than the activation energy, the molecules bounce off from each other.

According to Maxwell-Boltzmann distribution, however, in a fraction of collisions in which the molecules are moving fast enough, *their kinetic energies push them together with enough force to overcome the repulsions and surmount the activation energy.* Usually in this fraction of sufficiently energetic collisions, the molecules are oriented effectively. In those cases, nuclei in one molecule attract electrons in the other, atomic orbitals overlap, electron densities shift, and some bonds lengthen and weaken while others shorten and strengthen. At some point during this smooth transformation, *a species with partial bonds exists* that is neither a reactant nor a product. This very unstable species, called the **transition state** (or **activated complex**) exists only at the instant of highest potential energy. Thus, *the activation energy of a reaction is used to reach the transition state.* Reaching the transition state does not guarantee that a reaction will proceed to products because *a transition state can change in either direction*. In this case, if the new bond continues to strengthen, products form; but, if the existing bond becomes stronger again, the transition state reverts to reactants.

A useful way to depict these events is with a reaction energy diagram or energy profile which plots how potential energy changes as the reaction proceeds from reactants to products (the *reaction progress or reaction coordinate*). The diagram shows the relative energy levels of reactants, products, and transition state, as well as the forward and reverse activation energies and the enthalpy of reaction. Simply the energy profiles can be depicted for single step exothermic and endothermic reactions as shown in Figure 1.27 considering some hypothetical reactions given below.

AB + C → A + BC: ΔH < O and PQ + R → P + QR : ΔH > O.



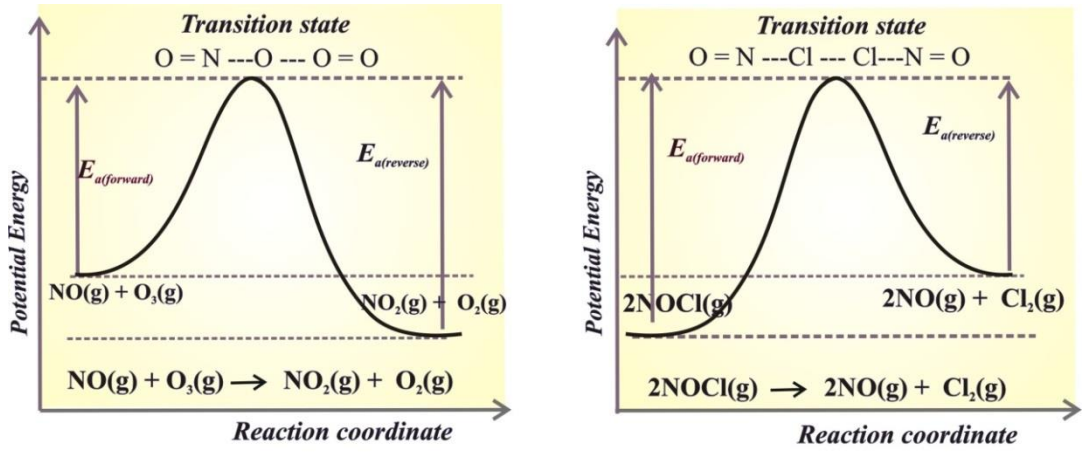
(a) (b)

Figure 1.27 Energy profiles for **(a)** exothermic and **(b)** endothermic reactions going through a single transition state.

Figure 1.27(a) shows that, overall, the reaction is exothermic. The products have lower energy than the reactants, so energy is released when the reaction happens. It also shows that the molecules have to possess enough energy (activation energy) to get the reactants over the "activation energy barrier".

For an endothermic reaction, a simple energy profile is shown in Figure 1.27(b).

For example, following two reactions occur through a single step with a single transition state. The reaction; $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ is exothermic while the reaction $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$ is endorthermic. Their transition states are also shown along with the potential energy in Figure 1.28.



(a) (b)

Figure 1.28 Energy profiles for two gas-phase reactions of **(a)** exothermic and **(b)** endothermic nature. In each case, the structure of the transition state is predicted from the orientations of the reactant atoms that must become bonded in the product.

As another example, the reaction below shows a reaction in which a bromine atom of bromoethane is being replaced by an OH group to produce ethanol.

$$CH_3Br(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq)$$

In the reaction one of the lone pairs of electrons on the negatively charged oxygen in the OH^- ion is attracted to the carbon atom with the bromine attached.

As the bromine is more electronegative than carbon, and so the electron pair in the C-Br bond is slightly closer to the bromine. The carbon atom becomes slightly positively charged and the bromine slightly negative. As the hydroxide ion approaches the slightly positive carbon, a new bond starts to be set up between the oxygen and the carbon. At the same time, the bond between the carbon and bromine starts to break as the electrons in the bond are repelled towards the bromine.

At some point, the process is exactly half complete. The carbon atom now has the oxygen half-attached, the bromine half-attached, with three other groups still there and then the process undergo completion. The structure in which the bonds are half-made and half-broken is the **transition state**, and is at the maximum potential energy.

It has to be noted that the transition state is entirely unstable. Any tiny change in either direction will send it either forward to make the products or back to the reactants again. There is no anything special about a transition state except that it has this maximum energy.

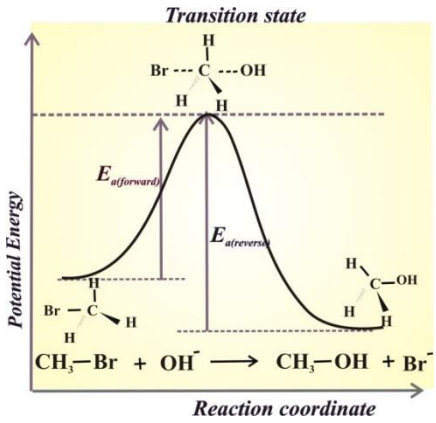


Figure 1.29 Energy profile for the reaction $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

Example 1.15

The reaction, $O_3(g) + O(g) \rightarrow 2O_2(g)$ has the activation energy of 19 kJ mol^{-1} for the forward reaction and the ΔH for the reaction is -392 kJ mol^{-1}. Draw an energy profile for the reaction with approximate relative positions of the species. Estimate the activation energy for the backward reaction.

Answer

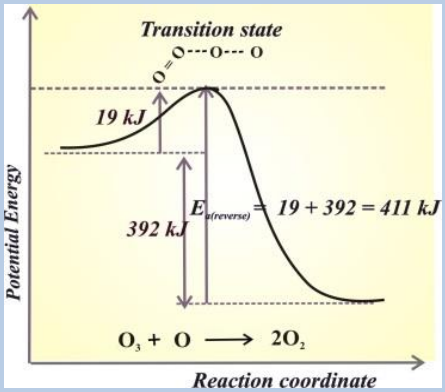


Figure 1.30 Energy profile for the reaction $O_3(g) + O(g) \rightarrow 2O_2(g)$.

Calculation of the activation energy of the backward reaction is indicated in the figure and the postulated structure of the transition state is also drawn.

Energy profiles for reactions which go via an intermediate

In this case, consider the following reaction which goes through an intermediate.

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

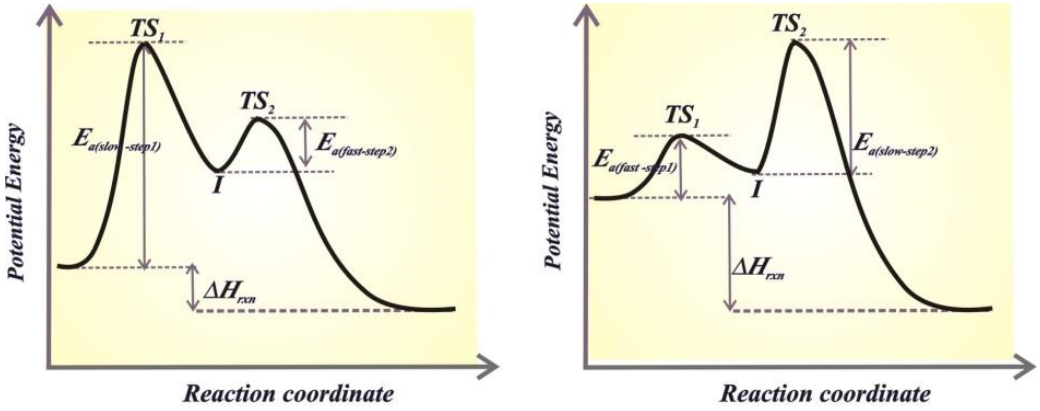
In the overall reaction the bromine atom is replaced by an OH group.
As mentioned earlier the reaction occurs via two steps as follows.

$$(CH_3)_3CBr \rightleftharpoons (CH_3)_3C^+ + :Br^- \quad : \text{slow}$$

$$(CH_3)_3C^+ + :OH^- \rightleftharpoons (CH_3)_3COH \quad : \text{fast}$$

The main difference in this case is that the positively charged ion can actually be detected in the mixture. It is very unstable, short-lived and soon reacts with a hydroxide ion (or picks up its bromide ion again). But, it does have a real presence in the system. The stability (however temporary and slight) of the intermediate is shown by the fact that there are small activation barriers to its conversion either into the products or back into the reactants again.

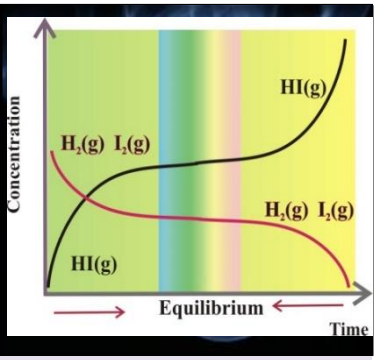
Notice that the barrier on the product side of the intermediate is lower than that on the reactant side meaning the fast second step as shown in Figure 1.30(a). That means, there is a greater chance of it to find the extra bit of energy to convert into products. It would need a greater amount of energy to convert back to the reactants again. The "TS_1" and "TS_2" both represent transition states between the intermediate and either the reactants or the products. During either conversion, there will be some arrangement of the atoms which causes an energy maximum.



(a) (b)

Figure 1.31 Energy profiles for two reactions, each of which has a two-step mechanism. **(a)** The reaction starts with a slow step, and **(b)** The reaction starts with a fast step. Both overall reactions are exothermic. Note these key points: Each step in the mechanism has its own peak with the transition state at the top. The intermediates are reactive, unstable species, so they are higher in energy than the reactants or product. The slow (rate-determining) step (step 1 in (**a)** and step 2 in (**b**) has a larger E_a than the other step.

2. Chemical Equlibrium



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Introduction

In the previous units, we have analyzed key questions about chemical reactions: What happens, how fast and by what mechanism does it happen? It is very much needed to know that "to what extent does it happen?" The stoichiometry of the balanced chemical equation, and the kinetics of the reaction explain the answers to first two questions respectively, and in this unit we look for the answer to the question, how far does a reaction proceed toward completion before it reaches a state of **equilibrium** a state in which the concentrations of reactants and products no longer change. This state is reached when the concentrations of reactants and products remain constant over time. Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either the reactants or products. This stage of the system is the dynamic equilibrium and the rates of the forward and reverse reactions become equal. At this dynamic equilibrium stage it is recognized that there is no change in macroscopic properties such as pressure, colour of the solution, or concentration of the solution at a constant temperature. However, at the atomic level, atoms, ions, and/or molecules are in constant reaction. When a system is a gas partial pressures are used to represent the amounts of substances present in the equilibrium condition.

The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations/pressures of reactants, temperature, etc. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called ionic equilibrium. Finally, the equilibrium in gas-liquid systems will be discussed.

2.1 The concept of equilibrium

Consider a chemical reaction between reactants **A** and **B** to form products **C** and **D.** After allowing sufficient period of time for the reaction, upon analyses, when **A** and **B** are absent in the reaction mixture, the reaction is understood to be completed and only the presence of **C** and **D** will be detected. That reaction can be written as,

$$A + B \rightarrow C + D \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

In this reaction, the reverse reaction to form back the reactants never occurs even when the reaction vessel is a closed one. Reactions which go to completion and never proceed in the reverse direction are called **irreversible reactions**.

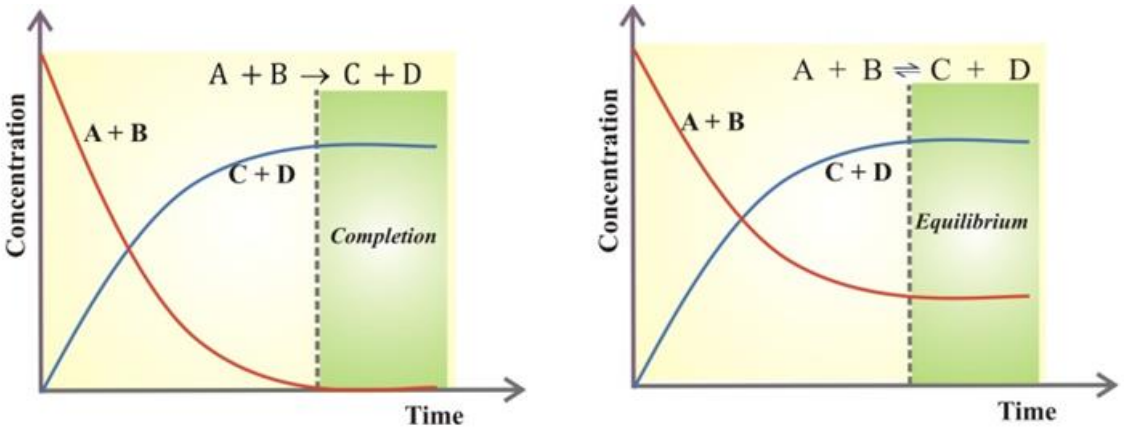
However, even after allowing sufficient period of time for reaction, when the presence of **A** and **B** are always detected along with **C** and **D**, then such reactions are understood to be never completed. i.e. Initially the reaction proceeds to form **C** and **D** until a certain period of time and with further increase in the reaction time, **C** and **D** molecules start to

produce back **A** and **B** and in such a way, the reaction mixture always contains **A, B, C** and **D** for any length of time until external factors like temperature, pressure, catalyst etc. are applied. Reactions which never proceed to completion in both forward and backward direction are called **equilibrium reactions** (*or reversible reactions*) and the system is said be reached an **equilibrium state**. A mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**. And the chemical equation of such reactions are represented as,

$$A + B \rightleftharpoons C + D \quad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

To indicate that the reaction can proceed in both forward and reverse directions, we write the balanced equation with two arrows, ⇌, one pointing from reactants to products and the other pointing from products to reactants.

These two cases of completion of reaction and reaching a reaction to an equilibrium state can be represented graphically as shown in the Figure 2.1 below.



(a) (b)

Figure 2.1 Change in concentrations of reactants and products over the time **(a)** for an irreversible and **(b)** equilibrium reactions at a given temperature

At the start of a reversible reaction, first reaction proceeds in the forward direction to form products. Once the product concentration increases with time they begin to react back to form reactant molecules. Therefore, the chemical equilibrium may be defined as the state of a reversible reaction when the two opposing reactions occur at the **same rate** and the concentration of reactants and products do not change with time. The true equilibrium of a reaction can be attained from both sides proving that the chemical equilibrium is a dynamic process. This nature can be illustrated for the reaction (2) with the help of Figure 2.2**.** It has to be noted that the equilibrium concentrations of reactants are different from their initial concentrations.

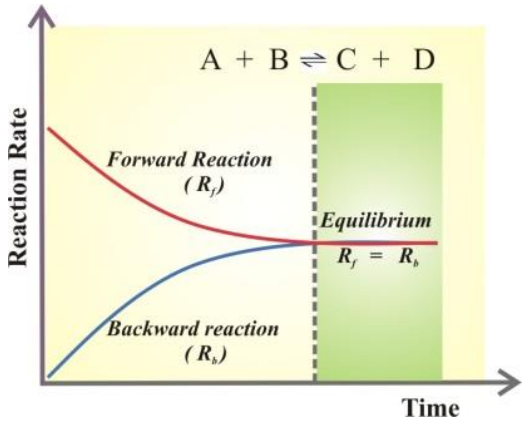


Figure 2.2 When the two rates become equal at a given temperature, an equilibrium state is attained with equalizing the rates of forward and backward reactions and there are no further changes in concentrations.

When a reversible reaction attains equilibrium it appears that the concentrations of individual reactants and that of the products remain constant with time. Actually, the reactant molecules are always reacting to form the product molecules. When the product molecules are able to react with themselves under the same experimental condition to form the same amount of reactants simultaneously (at the same time) in an equal rate of the forward reaction, then the process is a ceaseless phenomenon. Thus chemical equilibrium is **dynamic** when the forward and reverse reactions take place **endlessly and simultaneously with equal rates**. Therefore a chemical equilibrium is called a **dynamic equilibrium**. Hence, we can understand that;

(i) When a chemical equilibrium is established in a closed container at constant temperature, the concentrations of various species like reactants and products remain unchanged.

(ii) Equilibrium can be initiated from either side**.** The state of equilibrium of a reversible reaction can be arrived at whether we start from reactants or products.

(iii) Equilibrium cannot be attained in an open container. Only in a closed container, a reaction can be considered to attain equilibrium since no part of reactants or products should escape out. In an open container, gaseous reactants or products may escape so that no possibility of attaining equilibrium exists. Equilibrium can be attained when all the reactants and products are in contact with each other.

The phenomenon discussed above can be understood by the following example. Consider a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide ($N_2O_4(g)$) to nitrogen dioxide ($NO_2(g)$). $NO_2(g)$ is responsible for the brown color we associate with smog. In a sealed vessel containing $N_2O_4(g)$, the red-brown colour of $NO_2(g)$ appears. Therefore the reaction can be followed

visually because the product ($NO_2(g)$) is coloured, whereas the reactant ($N_2O_4(g)$) is colourless.

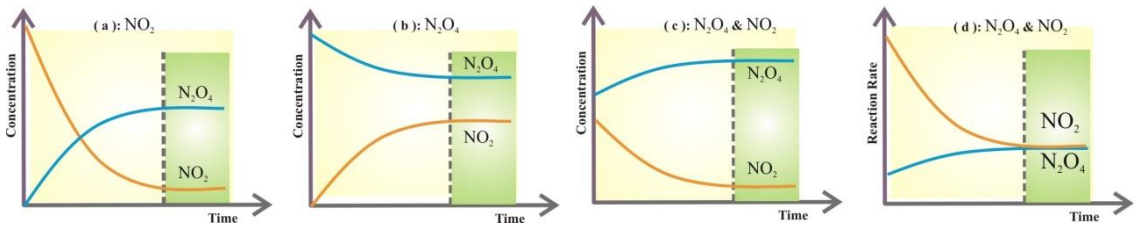
$$N_2O_{4(g)} \rightleftharpoons 2\,NO_{2(g)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

This system can be used to understand the reversible nature of a reaction which attains equilibrium in three ways.

(i) When gaseous $N_2O_4(g)$ is injected into an evacuated flask brown colour appears immediately, indicating the formation of $NO_2(g)$ molecules. The colour intensifies with the time as the dissociation of $N_2O_4(g)$ continues until eventually equilibrium is reached and remains at a constant intensity. At this point, the concentrations of both $N_2O_4(g)$ and $NO_2(g)$ remain constant.

(ii) We can also bring about an equilibrium state by starting with pure $NO_2(g)$. As some of the $NO_2(g)$ molecules combine to form $N_2O_4(g)$, the colour fades and remains at constant intensity once the equilibrium is attained.

(iii) Another way to create this equilibrium state is to start with a mixture of $NO_2(g)$ and $N_2O_4(g)$ and monitor the system until the color stops changing. The important thing to keep in mind is that at equilibrium, the conversions of $N_2O_4(g)$ to $NO_2(g)$ and $NO_2(g)$ to $N_2O_4(g)$ are still going on. We do not see a colour change because the two rates are equal, i.e. the removal of $NO_2(g)$ molecules takes place as fast as the production of $NO_2(g)$ molecules, and $N_2O_4(g)$ molecules are formed as quickly as they dissociate. Figure 2.3 summarizes these three situations.



(a) (b) (c) (d)

Figure 2.3 $N_2O_4(g) \rightleftharpoons NO_2(g)$ equilibrium system: **(a)** Initially, the system contains gaseous $NO_2(g)$ and no gaseous $N_2O_4(g)$. The concentration of $NO_2(g)$ decreases with time as the concentration of $N_2O_4(g)$ increases. **(b)** Initially the system contains gaseous $N_2O_4(g)$ and no gaseous $NO_2(g)$. The concentration of $N_2O_4(g)$ decreases with time as the concentration of $NO_2(g)$ increases. **(c)** Initially a mixture of $NO_2(g)$ and $N_2O_4(g)$ is present. Note that even though equilibrium is reached in all cases, the equilibrium concentrations of $NO_2(g)$ and $N_2O_4(g)$ are not the same. **(d)** Rates of forward and backward reactions in the mixture described in (c). Note also that even though the values of concentrations are not marked variation in concentrations are in parallel with the stoichiometry of the reaction.

When there is a change in the state of occurrence of matter, then a physical transformation is said to have occurred. The equilibrium concepts are also applicable to physical state transformations of matter and some examples are discussed below.

2.1.1 Equilibrium in physical processes

The characteristics of a system at equilibrium are better understood if we examine some physical processes. The most familiar examples are **phase transformation processes**, e.g.: solid ⇌ liquid, liquid ⇌ gas, solid ⇌ gas etc.

Solid-liquid equilibrium

Here, the solid and the liquid forms of a substance co-exist at characteristic temperature and pressure. At 1 atm and at the melting point of a substance, there is a solid-liquid equilibrium existing. For example, the solid-liquid equilibrium of water at 273 K (0 °C),

$$H_2O(l) \rightleftharpoons H_2O(s)$$

occurs at atmospheric pressure (1 atm, 101325 Pa). Here, both the liquid and ice exist together. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. At the boundary between liquid and solid, molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K. It is obvious that ice and water are in equilibrium only at a particular temperature and pressure. "*For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance"*. In this example, we can see that the system is in dynamic equilibrium and at the melting point of ice or freezing point of water, the rate of melting of ice equals to the rate of freezing of water so that the amount of ice and water remains constant. It has to be noted that with change in pressure, the temperature at which this equilibrium onsets changes.

Liquid-vapour equilibrium

Here, the solid and the vapour forms of a substance co-exist at a characteristic temperature and pressure in a closed system. At 1 atm and at the boiling point of a substance, there is a liquid- vapour equilibrium existing. For example, the liquid- vapour equilibrium of water at 373 K (100 °C),

$$H_2O(l) \rightleftharpoons H_2O(g)$$

occurs at atmospheric pressure. Here, both the liquid and vapour exist together. This can be demonstrated by a simple experiment by putting a watch glass containing certain amount of water in previously evacuated and dried box connected with a barometer (pressure-meter) at 100 °C. It will be observed that the mercury level in the right limb of

the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases. Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water molecules into the gaseous phase inside the box. The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained at which the rate of evaporation equals the rate of condensation.

At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the "*equilibrium vapour pressure*" of water (or just vapour pressure of water); vapour pressure of water increases with temperature.

Here "*the vapour and the liquid forms of a substance exist simultaneously at 1 atm pressure and at a characteristic temperature called the boiling point*". For example, at 1 atm pressure, 100 °C is the boiling point of water, and both liquid water and water vapour (steam) exist simultaneously, provided the vapour does not escape.

Solid - vapour equilibrium

If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After a certain time, the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as, $I_2(s) \rightleftharpoons I_2(g)$

Solid-solid equilibrium

When a substance existing in a particular crystalline solid transforms to another crystalline form retaining its solid nature at a characteristic temperature called the transition temperature with both the solid forms coexisting at 1 atm pressure, it is said to be in solid-solid equilibrium. For example, solid sulphur exhibits equilibrium with rhombic to monoclinic forms at its transition temperature.

$$S(\text{rhombic}) \rightleftharpoons S(\text{monoclinic})$$

2.1.2 Equilibrium in chemical processes

Homogeneous equilibrium

Chemical equilibrium exists in two types, homogeneous and heterogeneous. In a chemical reaction existing in equilibrium, if all the reactants and products are present in the same phase, a homogeneous equilibrium is said to have occurred. For example,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2\,NH_3(g)$$

Here all the reactants and products exist in the gaseous state. This is an example of a gas-phase equilibrium.

A chemical equilibrium in which all the reactants and products are in the liquid phase referred to as liquid equilibrium. For example,

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

Both gas phase and liquid phase equilibria are collectively called homogeneous equilibria.

Heterogeneous equilibrium

In a chemical equilibrium, if the reactant and product species are in different phases then heterogeneous equilibrium is said to have occurred.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

Here, when the reaction is carried out in a closed vessel, the equilibrium state is established.

2.1.3 Law of chemical equilibrium and equilibrium constant

It is important to know the relationship between the concentrations of reactants and products in an equilibrium mixture, how to determine equilibrium concentrations from initial concentrations and what factors can be exploited to alter the composition of an equilibrium mixture? Two Norwegian Chemists, Guldberg and Waage, studied experimentally a large number of equilibrium (reversible) reactions. In 1864, they postulated a generalization called the **law of mass action**. It states that: "the rate of a chemical reaction is proportional to the active masses of the reactants". By the term `active mass', it is meant the molar concentration i.e., mol dm^{-3}. At a fixed temperature the rate of a reaction is determined by the number of collisions between the reactant molecules present in a unit volume and hence its concentration, which is generally referred to as the active mass.

Consider a reaction,

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C + D$$

According to the law of mass action;

Rate of forward reaction: $R_f = k_f$ [A] [B]

Rate of backward reaction: $R_r = k_r$ [C] [D]

[A], [B], [C] and [D] are the molar concentrations of A,B,C and D at equilibrium, respectively.

k_f and k_r are the rate constants of forward and backward reactions, respectively.

At equilibrium, $R_f = R_r$

Therefore we can write, k_f [A] [B] = k_r [C] [D]

And $$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

At any specific temperature $\frac{k_f}{k_r}$ is a constant since both k_f and k_r are constants. The ratio $\frac{k_f}{k_r}$ is called **equilibrium constant** and is represented by the symbol $\boldsymbol{K_c}$. The subscript `**c**' indicates that the value is in terms of concentration of reactants and products. The equation (I) may be written as

$$K_C = \frac{[C][D]}{[A][B]}$$

i.e. *for a reversible reaction in equilibrium at constant temperature, a certain ratio of reactant and product concentrations has a constant value,* $\boldsymbol{K_c}$ *(the equilibrium constant).*

2.1.4 Equilibrium law and equilibrium constant expression for a reaction

For example in the study of analysis of experimental data by changing the initial concentrations of $NO_{2(g)}$ and $N_2O_{4(g)}$ in a $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ system at 25°C some interesting pattern is seen: Analysis of the equilibrium concentration data shows that although the ratio $[NO_{2(g)}]/[N_2O_{4(g)}]$ gives random values, the ratio $[NO_{2(g)}]^2/[N_2O_{4(g)}]$ gives a nearly constant value. i.e.

$$K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$$

is a constant at a given temperature.

Likewise, similar kind of results was observed for the $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ reaction giving the ratio $[HI]^2/[H_2]\,[I_2]$ as a constant. With this type of findings in many equilibrium systems at given temperature, we can derive a generalized form for the equilibrium expression of a reaction:

$$aA + bB \rightleftharpoons cC + dD$$

where a, b, c, and d are the stoichiometric coefficients for the reacting species A, B, C, and D,

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where $\boldsymbol{K_c}$ is the equilibrium constant. The general definition of the equilibrium constant may thus be stated as:

The product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.

For example, consider the equilibrium constant expression for the reaction,

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

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\ [H_{2(g)}]^3}$$

If we write the chemical equation in the reverse direction, the new equilibrium constant expression is the reciprocal of the original expression and the new equilibrium constant ' is the reciprocal of the original equilibrium constant . (The prime distinguishes $K_c^{`}$ from K_c.). i.e.

$$K_c^{`} = \frac{[N_{2(g)}]\ [H_{2(g)}]^3}{[NH_{3(g)}]^2} = \frac{1}{K_c}$$

Because the equilibrium constants K_c and $K_c^{`}$ have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant. Further, it has to be noted that the physical states of the species appearing in the equilibrium constant expressions must be indicated for each as shown above.

Example 2.1

The following concentrations were measured for an equilibrium mixture of $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3\,(g)}$ at 500 K: $[N_2] = 3.0 \times 10^{-2}$ mol dm^{-3}, $[H_2] = 4.0 \times 10^{-2}$ mol dm^{-3} and $[NH_3] = 2 \times 10^{-3}$ mol dm^{-3}. Calculate the equilibrium constants for both forward and reverse reactions at 500 K.

Answer

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3\,(g)}$

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\ [H_{2(g)}]^3}$$

$$K_c = \frac{(2 \times 10^{-3})^2\ (\text{mol dm}^{-3})^2}{(3 \times 10^{-2})(4 \times 10^{-2})^3(\text{mol dm}^{-3})^4} = 2.083\ \text{mol}^{-2}\text{dm}^6$$

$$K_c^{`} = \frac{[N_{2(g)}]\ [H_{2(g)}]^3}{[NH_{3(g)}]^2} = \frac{(3 \times 10^{-2})(4 \times 10^{-2})^3(\text{mol dm}^{-3})^4}{(2 \times 10^{-3})^2\ (\text{mol dm}^{-3})^2}$$

$$= 0.48\ \text{mol}^2\text{dm}^{-6}$$

or

$$K_c^{`} = \frac{1}{K_c} = \frac{1}{2.083\ \text{mol}^{-2}\text{dm}^6} = 0.48\ \text{mol}^2\text{dm}^{-6}$$

Note: *See the change in magnitude as well as the units when the equilibrium constant is defined in two opposite directions in the reaction.The equilibrium constant for a reaction written in reverse is the inverse of the equilibrium constant for the reaction as written originally.*

2.1.5 Extent of reaction

If ***K*** *(either* K_c *or* K_p *which pertains to the gas phase reactions)* is much greater than 1 (that is, $K >>> 1$), the equilibrium will lie to the right and favours the products. That is concentration of products is higher than that of reactants. Conversely, if the equilibrium constant is much smaller than 1 (that is, $K <<< 1$), the equilibrium will lie to the left and favours the reactants, i.e. concentration of reactants is higher than that of products. Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), indicating they are neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products.

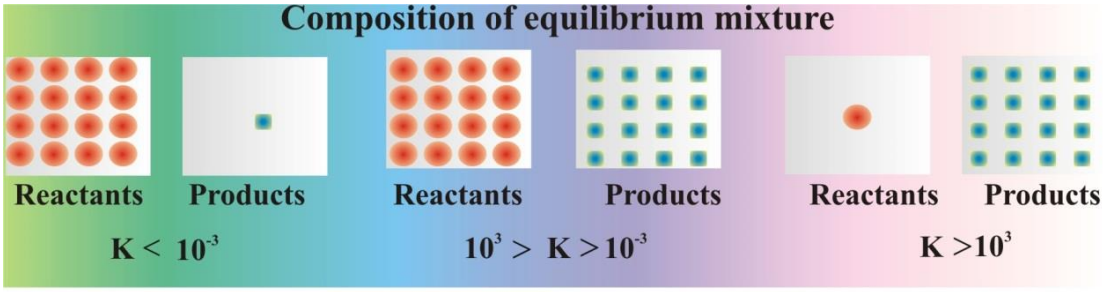


Figure 2.4 Representation of the extent and equilibrium position of a reaction with respect to the magnitude of equilibrium constant, ***K***

Figure 2.4 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as ***reactants ⇌ products***. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants when $k_f >> k_r$, ***K*** is a large number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f << k_r$, ***K*** is a very small number, and the reaction produces almost no products as written. Systems with $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium. i.e.

- If, $K_c > 10^3$, products predominate over reactants. If it is very large, the reaction proceeds nearly to completion.
- If, $K_c < 10^3$, reactants predominate over products. If it is very small, the reaction proceeds hardly at all.
- If, $10^3 \geq K_c \geq 10^{-3}$, appreciable concentrations of both reactants and products are present.

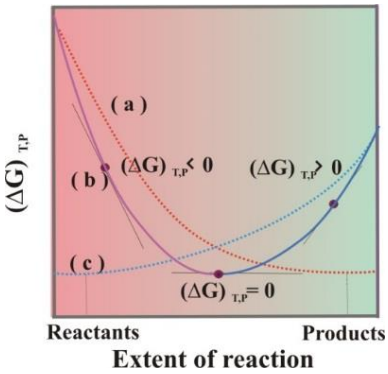


Figure 2.5 Representation of a spontaneous reaction towards minimum Gibbs function at equilibrium at given temperature and pressure. As the reaction proceeds the slope of the Gibbs function changes. Equilibrium point corresponds to the zero slope.

In addition to the simple description used in Figure 2.4 to understand the position of equilibrium, this equilibrium concept can further be understood by the knowledge of thermochemistry described in unit 05 to explain the spontaneity of reactions. In Figure 2.5, curve (a) shows that the position of equilibrium lies close to products indicating that the reaction goes to completion where Gibbs energy difference $(\Delta G)_{T,P} < 0$. The curve (b) represents the state of equilibrium consisting of significant amounts of both reactants and products in the mixture where $(\Delta G)_{T,P} = 0$. In curve (c) we can see that the position of equilibrium lies close to the reactants where $(\Delta G)_{T,P} > 0$, or the reaction is non-spontaneous.

> ***Note:*** *Here $(\Delta G)_{T,P}$ means the value of free energy change per change in number of moles ($(\Delta G)_{T,P}/\Delta n$). However, for a given reaction the use of $(\Delta G)_{T,P} = \Delta H - T\,\Delta S$ gives the standard free energy change of the complete reaction (i.e ΔG_r^o). In general, ΔG_r of a given reaction at a given temperature is given by; $\Delta G_r = \Delta G_r^o + RT\,lnQ$, and we know that at equilibrium, $\Delta G_r = 0$ indicating that any reaction has its own (characteristic) ΔG_r^o value. In other words, for a reaction at a given temperature, $\Delta G_r^o \neq 0$, or $\Delta G_r^o = -RTlnK$. (This is just for the clarification and the equation here is not tested in G.C.E (A/L) examination)*

The description of Figure 2.5 can also be represented by the following three diagrams in Figure 2.6 for understanding better about the Gibbs energy changes in a spontaneous chemical reaction, a reaction that goes to completion and a reaction that never proceeds to products.

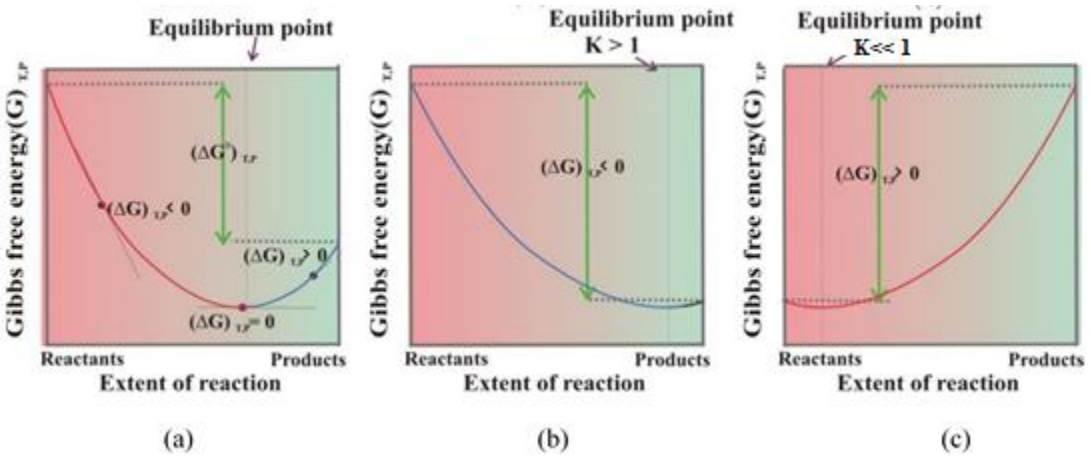


Figure 2.6 Details of Figure 2.5 **(a)** Variation of Gibbs free energy with composition for a reaction with spontaneous tendency. **(b)** A reaction which goes to a completion in which the equilibrium point lies very close to products ($K > 1$) and **(c)** A reaction which never reaches completion or a reaction which has no tendency to form products in which the equilibrium point lies very close to reactants ($K << 1$).

From the Figure 2.6 we can note that;

The equilibrium position, or how close to products or reactants the reaction will go is defined by the magnetude and sign of ΔG_r^θ.

$\Delta G_r^\theta < 0$ *: products are favoured.*

$\Delta G_r^\theta \approx 0$ *: neither reactants nor products are favoured and the system is at equilibrium.*

$\Delta G_r^\theta > 0$ *: reactants are favoured.*

2.1.6 Different forms of writing equilibrium constant expression

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, when the equation for the reaction $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ with the equilibrium constant K is written as $NO_2 \rightleftharpoons 1/2\ N_2O_4$, the equilibrium constant K''; can be written as follows.

$$K = \frac{[N_2O_4(g)]}{[NO_2(g)]^2}$$

$$K'' = \frac{[N_2O_4(g)]^{1/2}}{[NO_2(g)]}$$

We can see that the K'' and K has the relation, $\boldsymbol{K'' = (K)^{1/2}}$ and according to the law of mass action, each concentration term in the equilibrium constant expression is raised to a power equal to its stoichiometric coefficient. Thus if you double a chemical equation throughout, the corresponding equilibrium constant will be the square of the original

value; if you triple the equation, the equilibrium constant will be the cube of the original value, and so on.

In general, if all the coefficients in a balanced chemical equation are subsequently multiplied by ***n****, then the new equilibrium constant is the original equilibrium constant is raised to the* n^{th} *power.*

Example 2.2

At 800 K, equilibrium constant ***K*** for the reaction $N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$ is 0.25. What is the equilibrium constant K'' for the reaction $\frac{1}{2}N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3(g)$ at 800 K?

Answer

We can write

$$K = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\ [H_{2(g)}]^3}$$

$$K'' = \frac{[NH_{3(g)}]}{[N_{2(g)}]^{1/2}[H_{2(g)}]^{3/2}} = K^{1/2} = (0.25)^{\frac{1}{2}} = 0.50$$

2.1.7 Equilibrium constant in gaseous systems

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, $\boldsymbol{K_c}$ for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressures.

As we know, at constant temperature the pressure ***P*** of a gas is directly related to the concentration in **mol dm^{-3}** of the gas; that is, $P = (n/V)\,RT$ *or* $P = CRT$. Thus, for the equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, we can write,

$$\boldsymbol{K_p} = \frac{(P_{NO_{2(g)}})^2}{(P_{N_2O_{4(g)}})}$$

Where $P_{NO_{2(g)}}$ and $P_{N_2O_{4(g)}}$ are the equilibrium partial pressures (in Pa) of $NO_2(g)$ and $N_2O_4(g)$, respectively. The subscript in $\boldsymbol{K_p}$ indicates that equilibrium concentrations are expressed in terms of pressure. In general, $\boldsymbol{K_c}$ is not always equal to $\boldsymbol{K_p}$, since the partial pressures of reactants and products are not equal to their concentrations expressed in **mol dm^{-3}**. At a constant temperature, a simple relationship between $\boldsymbol{K_p}$ and $\boldsymbol{K_c}$ can be derived as follows. First, let us consider the following equilibrium in the gas phase:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

We can write,

$$\boldsymbol{K_c} = \frac{[HI(g)]^2}{[I_2(g)]\ [H_2(g)]}$$

$$\boldsymbol{K_p} = \frac{(P_{HI(g)})^2}{(P_{H_2(g)})\ (P_{I_2(g)})}$$

Applying ***P = CRT*** relation, we can write,
$P_{HI(g)} = [HI(g)]\ RT$, $P_{H_2(g)} = [H_2(g)]\ RT$ and $P_{I_2(g)} = [I_2(g)]\ RT$ and substituting these in

$$\boldsymbol{K_p} = \frac{(P_{HI(g)})^2}{(P_{H_2(g)})\ (P_{I_2(g)})} = \frac{[HI(g)]^2(RT)^2}{[I_2(g)](RT)\ \ [H_2(g)](RT)} = \frac{[HI(g)]^2(RT)^{(2-2)}}{[I_2(g)]\ \ [H_2(g)]} = \boldsymbol{K_c}$$

In this example, ***Kp = Kc*** i.e., both equilbrium constants are equal. However, this is not always the case. For example in reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$,

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)]\ \ [H_2(g)]^3} \text{ and } K_p = \frac{(P_{NH_3(g)})^2}{(P_{N_2(g)})\ \ (P_{H_2(g)})^3}$$

Assuming ideal behaviour,

$$K_p = \frac{[NH_3(g)]^2(RT)^2}{[N_2(g)](RT)[H_2(g)]^3(RT)^3}$$
$$= \frac{[NH_3(g)]^2(RT)^{(2-4)}}{[N_2(g)][H_2(g)]^3}$$
$$= \frac{[NH_3(g)]^2(RT)^{(-2)}}{[N_2(g)][H_2(g)]^3}$$

and hence we can write,

$$K_p = K_c\ (RT)^{-2}$$

With the impression derived from the above two examples, we can now consider a general case for a gas phase reaction, $aA(g) \rightleftharpoons bB(g)$,

$$K_c = \frac{[B(g)]^b}{[A(g)]^a} \text{ and } K_p = \frac{(P_{B(g)})^b}{(P_{A(g)})^a}$$

where P_A and P_B are the partial pressures of A and B. Assuming ideal gas behavior in a closed rigid container of volume V dm^3 at temperature T (K),
$P_AV = n_ART$ and $P_BV = n_BRT$.

Therefore we can write
$P_A = C_ART$ and $P_B = C_BRT$ and when the C_A and C_B are expressed in mol dm^{-3},

$P_A = [A]RT$ and $P_B = [B]RT$ substituting in K_p expression above,

$$K_p = \frac{([B]RT)^b}{([A]RT)^a} = \frac{[B]^b}{[A]^a}(RT)^{b-a} = K_c\ (RT)^{b-a}$$

$$= K_C\ (RT)^{\Delta n}, where\ \Delta n = b - a$$

$$\boldsymbol{K_p = K_c\ (RT)^{\Delta n}}$$

As a summary we can write the relation between $\boldsymbol{K_P}$ and $\boldsymbol{K_C}$ for a reaction,
aA + bB ⇌ cC + dD as,

$$\boldsymbol{K_p = K_c\ (RT)^{(c+d)-(a+b)} = K_c\ (RT)^{\Delta n}}$$

$\Delta n =$ amount of moles of gaseous products - amount of moles of gaseous reactants

In general, $K_p \neq K_c$ except in the special case(s) as shown above for the example with $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ system in which $\Delta n = 0$.

Note: *It is general practice not to include units for the equilibrium constant. In thermodynamics, K is defined as having no units because every concentration (molarity) or pressure (atm/ Pa) term is actually a ratio to a standard value, which is 1 mol dm^{-3} or 1 atm/ 101325 Pa (~ 100 kPa). This procedure eliminates all units but does not alter the numerical parts of the concentration or pressure. Consequently, K has no units.*

However, in the case when every concentration (molarity) or pressure (atm/ Pa) term is not a ratio to the standard value, that procedure will append appropriate units for the equilibrium constant(s) .

i.e. Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1bar ($P^\ominus = 1$ atm, 100 kPa). Therefore a pressure of 400 kPa in standard state can be expressed as 400 kPa/100 kPa = 4, which is a dimensionless number. Standard state ($C^\ominus$) for a solute in a solution is 1.0 mol dm^{-3}. All concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Though the equilibrium constants are considered dimensionless/ unitless quantities, in this text we consider the concentrations and pressures with their respective units unless the standard state is mentioned.

The value of equilibrium constant K_c can be calculated by substituting the concentration terms in **mol dm^{-3}** and for K_p partial pressure can be substituted in **Pa, kPa, bar** or **atm**. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are the same.

For the reactions,

$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, K_c and K_p have no unit.

$N_2O_{4(g)} \rightleftharpoons 2NO_{2\,(g)}$, K_c has unit **mol dm^{-3}** and K_p has unit **Pa**.

Example 2.3

Methane gas (CH_4) reacts with hydrogen sulfide gas at 1000 K to yield H_2 and carbon disulfide as $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$

What are the value of K_P and K_C at 1000 K if the partial pressures in an equilibrium mixture at 1000 K are 0.20×10^5 Pa of CH_4, 0.25×10^5 Pa of H_2S, 0.52×10^5 Pa of CS_2 and 0.10×10^5 Pa of H_2?

Answer

$$K_p = \frac{\left(P_{H_2(g)}\right)^4 \left(P_{CS_2(g)}\right)}{\left(P_{CH_4(g)}\right) \left(P_{H_2S(g)}\right)^2} = \frac{(0.1\ \text{Pa})^4\ (0.52\ \text{Pa})}{(0.20\ \text{Pa})\ \ (0.25\ \text{Pa})^2}\ (1.0 \times 10^5\ \text{Pa})^2$$

$$= 4.2 \times 10^{-3} \times 10^{10}\ Pa^2 = 4.2 \times 10^7\ Pa^2$$

$K_p = K_c\,(RT)^{\Delta n}$

$\Delta n = 5 - 3 = 2$

Therefore, $K_p = K_c\,(RT)^2$ *and* $K_c = \frac{K_P}{(RT)^2}$

$$K_c = \frac{K_P}{(RT)^2} = \frac{4.2 \times 10^7\ \text{Pa}^2}{(8.314\ \text{J K}^{-1}\ \text{mol}^{-1} \times 1000\ \text{K})^2} = \frac{4.2 \times 10^7\ (10^{-3}\ \text{J dm}^{-3})^2}{(8314\ \text{J mol}^{-1})^2}$$

$$= 6 \times 10^{-7}\ \text{mol}^2\ \text{dm}^{-6}$$

However, if the partial pressures are defined as $P/P^{\ominus}$*, where* $P^{\ominus}$ *is the standard pressure of 1 atm or* 1.0×10^5 *Pa, we will have*

$$K_p = \frac{\left(\frac{P_{H_2(g)}}{P^{\ominus}}\right)^4 \left(\frac{P_{CS_2(g)}}{P^{\ominus}}\right)}{\left(\frac{P_{CH_4(g)}}{P^{\ominus}}\right) \left(\frac{P_{H_2S(g)}}{P^{\ominus}}\right)^2} = \frac{(0.1)^4\ (0.52)}{(0.20)\ \ (0.25)^2} = 4.2 \times 10^{-3}$$

Consider the ionization of acetic acid (CH_3COOH) in water as another example for a homogeneous equilibrium.

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

The equilibrium constant is; $K_c^{`} = \frac{[CH_3COO^-(aq)]\ \ [H_3O^+(aq)]}{[CH_3COOH(aq)]\ \ [H_2O(l)]}$

Here, liquid water, $H_2O(l)$ is present as a medium for the reaction. In 1 dm^3 (1 L, or 1000 g of water, there are 1000 g/(18 g mol^{-1}) or 55.5 moles, of water. Therefore, the "concentration" of water or $[H_2O(l)]$ is 55.5 mol dm^{-3}. This is a large quantity compared to the concentrations of other species in solution (usually 1 mol dm^{-3} or smaller), and we

can assume that it does not change appreciably during the course of a reaction. Thus we may treat [$H_2O(l)$] as a constant. Therefore, we can write the equilibrium constant as;

$$K_c = \frac{[CH_3COO^-(aq)]\ [H_3O^+(aq)]}{[CH_3COOH(aq)]}$$

Where, $K_c = K_c^{`}\,[H_2O(l)]$

2.1.8 Heterogeneous equilibria

Equilibrium in a system having more than one phase is called a heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of a heterogeneous equilibrium.

$$H_2O(l) \rightleftharpoons H_2O(g)$$

In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution is a heterogeneous equilibrium.

$$Ca(OH)_2(s) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). Let us consider thermal decomposition of calcium carbonate as an example for heterogeneous chemical equilibrium.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Considering the stoichiometric equation, we can write,

$$K_c^{`} = \frac{[CaO(s)]\,[CO_2(g)]}{[CaCO_3(s)]}$$

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids.The reference states for pure solids and liquids are those forms stable at 100 kPa/1 atm, which are assigned an activity (effective mass) of **1**. i.e. the "concentration" of a solid, like its density, is an intensive property and does not depend on how much of the substance is present.

In the above example, since [$CaCO_{3(s)}$] and [$CaO_{(s)}$] are both constants, the modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K_c = [CO_{2(g)}],$$

where,

$$K_c = K_c^{`}\ \frac{[CaCO_3(s)]}{[CaO(s)]}$$ is a constant.

Likewise we can write $K_p = P_{CO_2(g)}$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that for pure water it is about 55.5 mol dm^{-3} and for pure ethanol it is about 17 mol dm^{-3}). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

In the reaction,

$$Hg(l) + Hg^{2+}(aq) \rightleftharpoons Hg_2^{2+}(aq)$$

$$K_c` = \frac{[Hg_2^{2+}(aq)]}{[Hg^{2+}(aq)][Hg(l)]} \text{ and we can write,}$$

$$K_c = \frac{[Hg_2^{2+}(aq)]}{[Hg^{2+}(aq)]} \text{ where, } \quad K_c = K_c` [Hg(l)]$$

In this case, it's not appropriate to write an expression for $\boldsymbol{K_p}$ because none of the reactants and products is a gas.

In summary, it is clear that in a systems of a heterogeneous equilibrium, pure solids or liquids must be present for the equilibrium to exist, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. In the reaction below, we can see that though a solid reactant is present and liquid water is produced, the equilibrium constant expression does not contain both.

$$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$$

$$K_C = \frac{[AgNO_3(aq)]^2}{[HNO_3(aq)]^2}$$

Note: *The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.*

2.1.9 Equilibrium constant expressions for multi-step reactions

It is essential to know the equilibrium constant for a reaction that has not been previously studied or the desired reaction occurs in several steps. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated or available values of the other reactions.

For example, consider the system A + B ⇌ E + F in which the products formed in the first reaction, C and D, react further to form products E and F. At equilibrium we can write two separate equilibrium constants for the reactions,

$$A + B \rightleftharpoons C + D$$
$$C + D \rightleftharpoons E + F$$
$$K_c` = \frac{[C][D]}{[A][B]} \text{ and } K_c" = \frac{[E][F]}{[C][D]}$$

We can see that the sum of the two reactions results the overall reaction and hence,

$$A + B \rightleftharpoons C + D$$
$$C + D \rightleftharpoons E + F +$$
$$\overline{A + B \rightleftharpoons E + F}$$

The equilibrium constant for the overall reaction is,

$$K_c = \frac{[E][F]}{[A][B]}$$

We can see that the expression of K_c is the product of $K_c`$ and $K_c"$

$$K_c` K_c" = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]}$$

Therefore,

$$K_c = K_c` K_c"$$

Note: *If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.*

For example, let's consider the reaction of $N_2(g)$ with $O_2(g)$ to give $NO_2(g)$ at 100 °C. The reaction normally occurs in two distinct steps. In the first reaction (I), $N_2(g)$ reacts with $O_2(g)$ to give NO(g). The NO(g) produced then reacts with additional $O_2(g)$ to give $NO_2(g)$ as in reaction (II). Assume also that the concentrations are measured with respect to the standard molarity i.e. $C^{\ominus}$ = 1.0 mol dm^{-3}.

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$: $K_c` = 2.0 \times 10^{-25}$ ……(I)

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$: $K_c" = 6.4 \times 10^{9}$ ……(II)

Summing reactions (I) and (II) gives the overall reaction:

$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$ K_c = ?

$$K_c` = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]} = 2.0 \times 10^{-25} \text{ and } K_c" = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]} = 6.4 \times 10^{9}$$

$$K_c` \times K_c" = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]} \times \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]} = \frac{[NO_2(g)]^2}{[O_2(g)]^2[N_2(g)]} = K_c$$

Therefore, $K_c = K_c^{`} \times K_c^{"} = (2.0 \times 10^{-25})(6.4 \times 10^{9}) = 1.28 \times 10^{-15}$

Note: *The relation among equilibrium constants of multi-step reactions can also be understood by the principles of chemical kinetics as described in Unit 11.*

Consider the above example of the reaction A + B ⇌ E + F.
Suppose the same reaction has a mechanism with two elementary steps.

$$A + B \underset{k`_r}{\overset{k`_f}{\rightleftharpoons}} C + D$$

$$C + D \underset{k"_r}{\overset{k"_f}{\rightleftharpoons}} E + F$$

We can write, $K_c^{`} = \frac{k`_f}{k`_r} = \frac{[C][D]}{[A][B]}$ and $K_c^{"} = \frac{k"_f}{k"_r} = \frac{[E][F]}{[C][D]}$

$$K_c^{`}K_c^{"} = \frac{k`_f}{k`_r} \times \frac{k"_f}{k"_r} = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]} = K_c$$

In summary the followings are the key points to remember.

- *The equilibrium constant is a constant at a given temperature, or it depends on the temperature.*
- *The concentrations of the reacting species in the condensed phase are expressed in* **mol dm^{-3}**. *In the gaseous phase, the concentrations can be expressed in* **mol dm^{-3}** *or in* **Pa** (atm). $\boldsymbol{K_c}$ *is related to* $\boldsymbol{K_p}$ *by a simple equation of*

$$\boldsymbol{K_p = K_c (RT)^{\Delta n}}$$

  - *The concentrations of pure solids, pure liquids (in heterogeneous equilibria), and solvents (in homogeneous equilibria) do not appear in the equilibrium constant expressions.*
  - *The equilibrium constant (*$\boldsymbol{K_c}$ *or* $\boldsymbol{K_p}$*) is a dimensionless quantity when the standard condition is used.*
  - *In quoting a value for the equilibrium constant, we must specify the balanced equation and the temperature.*
  - *If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.*
  - *The value of* **K** *also depends on how the equilibrium equation is balanced. According to the law of mass action, each concentration term in the equilibrium constant expression is raised to a power equal to its stoichiometric coefficient. Thus if you double a chemical equation throughout, the corresponding equilibrium constant will be the square of the original value; if you triple the equation, the equilibrium constant*

will be the cube of the original value, and so on. i.e. In general, if all the coefficients in a balanced chemical equation are subsequently multiplied by ***n****, then the new equilibrium constant is the original equilibrium constant raised to the* n^{th} *power.*

2.1.10 Predicting the direction of reaction and calculations based on equilibrium constant

We have seen that the equilibrium constant for a given reaction can be calculated from known equilibrium concentrations. Given the equilibrium constant and the initial concentrations of reactants, we can calculate the concentration of one or more substances at equilibrium only if the temperature does not change. In general, the *magnitude of the* equilibrium constant helps us to predict the direction in which a reaction mixture will proceed to achieve equilibrium and to calculate the concentrations of reactants and products once the equilibrium is reached. These uses of the equilibrium constant will be explored in this section.

Predicting the direction of a reaction

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the **reaction quotient** ***Q*** by substituting the initial concentrations in the equilibrium constant expression. The reaction quotient, ***Q*** (Q_C with molar concentrations and Q_p with partial pressures) is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_C are not necessarily to be equilibrium values.

For a general reaction:

$$aA + bB \rightleftharpoons cC + dD$$

$$Q_c = \frac{[C]_t^c[D]_t^d}{[A]_t^a[B]_t^b}$$

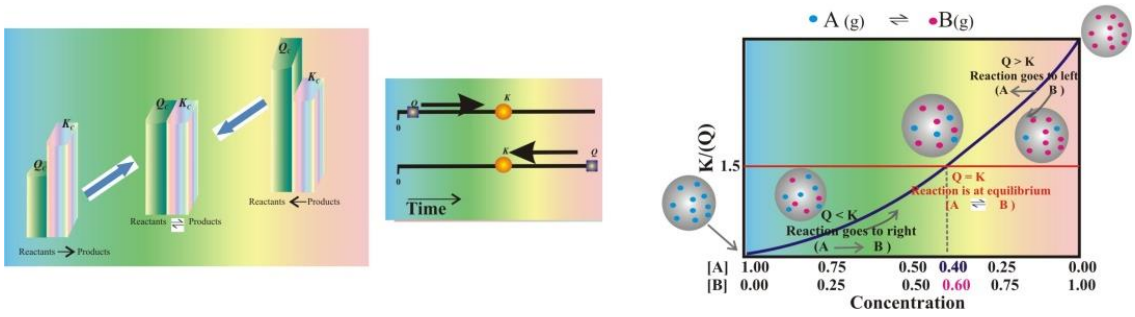
Here subscript ***t*** means that the concentrations are measured at an arbitrary time ***t*** and not necessarily at equilibrium. The reaction quotient ***Q*** is useful because it helps us predict the direction of reaction by comparing the values of Q_c and K_c. If Q_c is less than K_c $(Q_c < K_c)$, movement toward equilibrium increases by converting reactants to products (that is, net reaction proceeds from left to right). If Q_c is greater than K_c $(Q_c > K_c)$, movement toward equilibrium decreases by converting products to reactants (that is, net reaction proceeds from right to left). If Q_c equals K_c $(Q_c = K_c)$, the reaction mixture is already at equilibrium, and no net reaction occurs. Thus, we can make the following generalizations concerning the direction of the reaction:

- $Q_c > K_c$*: The ratio of initial concentrations of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system*

proceeds from right to left (consuming products, forming reactants) to reach equilibrium.

- $Q_c = K_c$*: The initial concentrations are equilibrium concentrations. The system is at equilibrium.*
- $Q_c < K_c$*: The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.*

This can be illustrated by the conceptual diagram shown in Figure 2.7.



(a) (b) (c)

Figure 2.7 Different views for the interpretation of the magnitudes of *K* and *Q*: **(a)** compares the magnitudes of *K* and *Q*, **(b)** indicates the way that how the direction or equilibrium position of the reaction tends to move with the relative size of *Q* and **(c)** compares the composition of the reaction mixture at diferent positions where it can be noted that at equilibrium, $Q = K = 1.5$ with the presence of appropriate number of reactant and product molecules in the reaction mixture.

Example 2.4

The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the composition of reaction mixture is [A] = [B] = [C] = 3×10^{-4} mol dm^{-3}. In which direction will the reaction proceed?

Answer

For the reaction the reaction quotient Q_c is given by,

$$Q_c = \frac{[B][C]}{[A]^2} = (3 \times 10^{-4})(3 \times 10^{-4}) / (3 \times 10^{-4})^2 = 1$$

$Q_c > K_c$

Therefore, the reaction will proceed in the reverse direction.

Example 2.5

At elevated temperatures, methane ($CH_4(g)$) reacts with water to produce hydrogen and carbon monoxide as:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

Equilibrium constant for the reaction is $K = 2.4 \times 10^{-4}$ at 900 K. If, 1.2×10^{-2} moles of CH_4, 8.0×10^{-3} moles of H_2O, 1.6×10^{-2} moles of CO and 6.0×10^{-3} moles of H_2 are placed in a 2.0 dm^3 closed rigid reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O?

Answer

First let's find the initial concentrations of the substances present.
For example, we have 1.2×10^{-2} moles of CH_4 in a 2.0 dm^3 container, so
$[CH_4(g)] = 1.2 \times 10^{-2}$ mol/ 2.0 $dm^3 = 6.0 \times 10^{-3}$ mol dm^{-3}

Similarly, we can calculate $[H_2O(g)] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[CO(g)] = 8.0 \times 10^{-3}$ mol dm^{-3}, and $[H_2(g)] = 3.0 \times 10^{-3}$ mol dm^{-3}.

$$Q_c = \frac{[CO_{(g)}][H_2(g)]^3}{[CH_4(g)][H_2O(g)]}$$

$$= \frac{(8 \times 10^{-3})\ (3 \times 10^{-3})^3}{(6 \times 10^{-3})(4 \times 10^{-3})}$$

$$= 9.0 \times 10^{-6}$$

$$Q_c < K\ (2.4 \times 10^{-4})$$

Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4.

Example 2.6

A mixture of 1.5 mol of N_2, 2.0 mol of H_2, and 8.0 mol of NH_3 is introduced into a 20.0 dm^3 closed rigid reaction vessel at 500 K. At this temperature, the equilibrium constant for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, is 1.7×10^2. Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Answer

The initial concentration of $[N_2(g)]$ is $1.5/20 = 7.5 \times 10^{-2}$ mol dm^{-3}. Similarly, $[H_2(g)] = 1.0 \times 10^{-1}$ mol dm^{-3} and $[NH_3(g)] = 4.0 \times 10^{-1}$ mol dm^{-1}. Substituting these concentrations into the Q expression gives

$$Q_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}][H_{2(g)}]^3} = \frac{(4 \times 10^{-1})^2}{(7.5 \times 10^{-2})(1.0 \times 10^{-1})^3}$$

$$= 2.1 \times 10^4$$

Because Q_c does not equal to K_c, the reaction mixture is not at equilibrium.

$$Q_c > K_c$$

Net reaction will proceed from right to left, decreasing the concentration of NH_3 and increasing the concentrations of N_2 and H_2 until $Q_c = K_c$.

With the knowledge from above examples, we can simply explain how Q_c varies with time as shown in Figure 2.8.

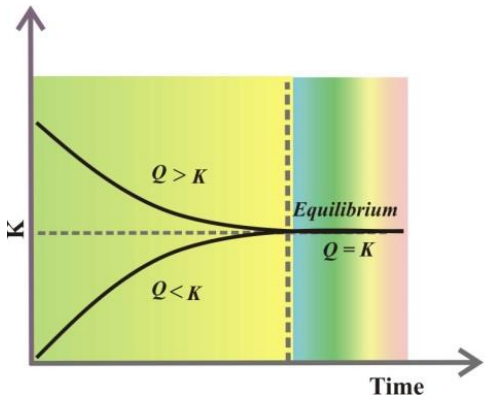


Figure 2.8 The figure explaining the variation of Q over time: If the initial Q is less than K it increases with time favouring the forward reaction; if it is greater than K, it decreases with time favouring the backward reaction until the condition is reached at which $Q = K$.

With the help of Figures 2.5 and 2.8, we can note that;

Before equilibrium, $\Delta G < 0$ and $Q < K$. The reaction is spontaneous in the forward direction.

At equilibrium, $\Delta G = 0$ and $Q = K$.
Beyond the equilibrium position, $\Delta G > 0$ and $Q > K$. The reaction is spontaneous in the reverse direction.

Note: *The reaction quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction.*

2.1.11 Calculating equilibrium concentrations

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

(a) *the initial concentration,*
(b) *the change in concentration (x) on going to equilibrium, and*
(c) *the equilibrium concentration.*

In constructing the table, define *x (or α)* as the concentration (mol dm^{-3})(or degree of dissociation) of one of the substances that reacts when going to equilibrium, and then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of *x*.

Step 3. Substitute the equilibrium concentrations into the equilibrium expression for the reaction and solve for *x*. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense. Calculate the equilibrium concentrations from the calculated value of *x*.

Example 2.7

The equilibrium constant K_C for the reaction of $H_2(g)$ with $I_2(g)$ is 64.0 at 800 K:

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

If 1.00 mol of $H_2(g)$ is allowed to react with 1.00 mol of $I_2(g)$ in a 10.0 dm^3 closed-rigid-reaction vessel at 800 K, what are the concentrations of $H_2(g)$, $I_2(g)$, and HI(g) at equilibrium? What is the composition of the equilibrium mixture in moles?

Answer

The initial concentrations are $[H_2(g)] = [I_2(g)] = 1.00 \text{ mol}/10.0 \text{ dm}^3$
$= 0.10 \text{ mol dm}^{-3}$.

For convenience, define an unknown, x, as the concentration (mol dm^{-3}) of $H_2(g)$ that reacts. According to the balanced equation for the reaction, x mol dm^{-3} of $H_2(g)$ reacts with x mol dm^{-3} of $I_2(g)$ to give $2x$ mol dm^{-3} of HI(g). This reduces the initial concentrations of $H_2(g)$ and $I_2(g)$ from 0.10 mol dm^{-3} to $(0.10 - x)$ mol dm^{-3} at equilibrium.

These can be summarized in a table under the balanced equation:

	$H_2(g)$	+	$I_2(g)$	⇌	$2HI(g)$
Initial/ mol dm^{-3}	0.1		0.1		0
Change/ mol dm^{-3}	$-x$		$-x$		$+2x$
Equilibrium/ mol dm^{-3}	$(0.10 - x)$		$(0.10 - x)$		$2x$

The equilibrium constant, $K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$

Substituting the values; $64.0 = \frac{(2x)^2}{(0.10-x)(0.10-x)} = \frac{(2x)^2}{(0.10-x)^2} = [\frac{2x}{0.10-x}]^2$

Taking square roots of both sides: $\pm 8.0 = \frac{2x}{(0.10-x)}$

Taking + 8.0; $0.80 - 8x = 2x$

$x = 0.08 \text{ mol dm}^{-3}$

(If we take $-8.0 = \frac{2x}{(0.10-x)}$; we get $x = 0.13 \text{ mol dm}^{-3}$ which is unacceptable as the initial concentration is 0.10 mol dm^{-3})

$\therefore [H_2(g)] = [I_2(g)] = 0.02 \text{ mol dm}^{-3}$ and $[HI(g)] = 0.16 \text{ mol dm}^{-3}$

$\therefore$ The composition in moles: $H_2(g) = I_2(g) = 0.02 \text{ mol dm}^{-3} \times 10.0 \text{ dm}^3 = 0.2 \text{ mol}$

And $HI(g) = 1.6 \text{ mol}$

Example 2.8

For the same reaction and temperature as in the previous example, suppose that the initial concentrations of $H_{2(g)}$, $I_{2(g)}$, and $HI_{(g)}$ are $0.006 \text{ mol dm}^{-3}$, $0.004 \text{ mol dm}^{-3}$, and 0.02 mol dm^{-3} respectively. Calculate the concentrations of these species at equilibrium.

Answer

As the initial concentrations do not correspond to the equilibrium concentrations, let *x* be the depletion in concentration (mol dm^{-3}) of $H_2(g)$ and $I_2(g)$, at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be *2x*.

	$H_2(g)$	+	$I_2(g)$	⇌	$2HI(g)$
Initial/ mol dm^{-3}	0.006		0.004		0.02
Change/ mol dm^{-3}	$-x$		$-x$		$+2x$
Equilibrium/ mol dm^{-3}	$(0.006 - x)$		$(0.004 - x)$		$(0.02 + 2x)$

The equilibrium constant, $K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} = 64 = \frac{(0.02 + 2x)^2}{(0.006 - x)(0.004 - x)}$

Multiplication gives us a quadratic equation;

$60x^2 - 0.72x + 11.34 \times 10^{-4} = 0$

This is of the type: $ax^2 + bx + c = 0$ and its solutions for x is given by,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

By applying this to the quadratic equation we have, we get x = 0.01 mol dm^{-3} or 0.002 mol dm^{-3}. The value 0.01 mol dm^{-3} is unacceptable as the equilibrium concentration cannot be higher than the initial concentration. Therefore the accepted value of x is 0.002 mol dm^{-3}.

Now the equilibrium concentrations are:

$[H_2(g)] = (0.006 - 0.002) = 0.004 \text{ mol dm}^{-3}$

$[I_2(g)] = (0.004 - 0.002) = 0.002 \text{ mol dm}^{-3}$

$[HI(g)] = (0.02 + 0.004) = 0.024 \text{ mol dm}^{-3}$

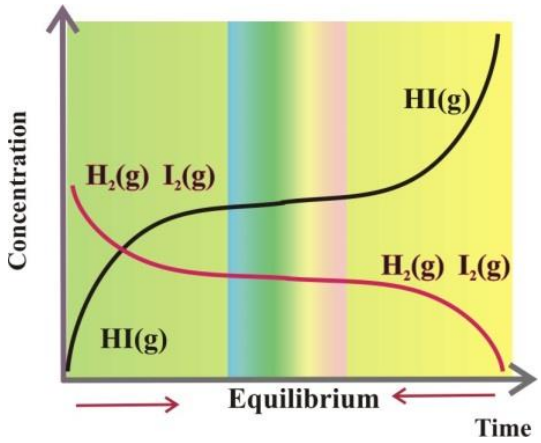


Figure 2.9 Chemical equilibrium in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ can be attained from either direction. This explains that the reaction can start from either side (right and left) with a mixture of $H_2(g)$ and $I_2(g)$ or with HI(g). When it starts with $H_2(g)$ and $I_2(g)$ mixture eventually those decrease in amount while the amount of HI(g) increases. In the other way, if the reactions starts with HI(g), amounts of $H_2(g)$ and $I_2(g)$ increase with the time while the amount of HI(g) decreases.

Example 2.9

0.15 moles of N_2O_4 gas was placed in a 1.0 dm^3 closed rigid reaction vessel at 400 K and allowed to attain the equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. The total pressure at equilibrium was found to be 9.0×10^5 Pa. Calculate partial pressures of each and hence K_p and K_C at equilibrium.

Answer

Assuming ideal behaviour for $N_2O_4(g)$;

$PV = nRT$

$P_{N_2O_4} = 0.15 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 400 \text{ K} \approx 5.0 \times 10^5 \text{ Pa}$

Therefore, initial pressure = 4.98×10^5 Pa

Consider the reaction,

	N_2O_4 (g)	$\rightleftharpoons$	$2NO_2$
Initial Pressure/ Pa:	5.0×10^5		0
Pressure change/ Pa:	x		$2x$
Pressure at equilibrium/ Pa:	$(5.0 \times 10^5 - x)$		$2x$

At equilibrium, total pressure; $P_{total} = P_{N_2O_4} + P_{NO_2}$

$$9.0 \times 10^5 \text{ Pa} = [(5.0 \times 10^5 - x) + 2x] \text{Pa}$$

$$x = 4.0 \times 10^5 \, Pa$$

$$P_{N_2O_4} = 1.0 \times 10^5 \text{ Pa} \text{ and } P_{NO_2} = 8.0 \times 10^5 \text{ Pa}$$

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(8.0 \times 10^5 \text{ Pa})^2}{(1.0 \times 10^5 \text{ Pa})} = 6.4 \times 10^6 \text{ Pa}$$

$$K_p = K_c (RT)^{\Delta n}; \text{and } \Delta n = 2 - 1 = 1$$

$$K_c = \frac{K_p}{(RT)} = \frac{6.4 \times 10^6 \text{ Pa} \times 10^{-3}}{8.314 \times 400 \text{ J mol}^{-1}} = 1.9 \text{ mol dm}^{-3}$$

Example 2.10

The reduction of iron(II) oxide by carbon monoxide gives iron metal and carbon dioxide. The equilibrium constant K_p for the reaction at 1000 K is 0.25.

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

What are the equilibrium partial pressures of CO(g) and $CO_2(g)$ at 1000 K if the initial partial pressures are $P_{CO(g)} = 1.0 \times 10^5$Pa and $P_{CO_2(g)} = 0.50 \times 10^5$Pa. Comment on the value calculated.

Answer

We can calculate equilibrium partial pressures from initial partial pressures and In the same way that we calculate equilibrium concentrations from initial concentrations and substitute partial pressures for concentrations.

	$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$	
Initia pressure/ Pa	1.0×10^5	0.50×10^5
Change pressure/ Pa	$-x$	$+x$
Equilibrium pressure (Pa)	$(1.0 \times 10^5 - x)$	$(0.50 \times 10^5 + x)$

$$K_P = \frac{(P_{CO_2(g)})}{(P_{CO(g)})} = 0.25 = \frac{(0.50 \times 10^5 + x)}{(1.0 \times 10^5 - x)}$$

$$0.25 \times 10^5 - 0.25x = 0.50 \times 10^5 + x$$

$$x = -0.20 \times 10^5 \text{ Pa}$$

$$\therefore P_{CO(g)} = 1.20 \times 10^5 \text{ Pa}$$

$$P_{CO_2(g)} = 0.30 \times 10^5 \text{ Pa}$$

A negative value for x means that the reaction goes from products to reactants to reach equilibrium. This makes sense because the initial reaction quotient, $Q_p = \frac{0.5}{1.0} = 0.5 > K_p$: is greater than the equilibrium constant, i.e. the net reaction always goes from products to reactants (right to left).

We can confirm this by the re-calculation of K_P using the derived values for $P_{CO(g)}$ and $P_{CO_2(g)}$. We get $K_p = \frac{0.30 \times 10^5 \text{ Pa}}{1.20 \times 10^5 \text{ Pa}} = 0.25$. So that the above given reaction proceeds to the left.

Example 2.11

The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) in the presence of a catalyst to give ethane (C_2H_6) is:

$H_2(g) + C_2H_4(g) \rightleftharpoons C_2H_6(g)$.

Equilibrium constant of the reaction $K_c = 9.6 \times 10^{18}$ at 25 °C. If a mixture of 0.200 mol dm^{-3} $H_2(g)$ and 0.155 mol dm^{-3} $C_2H_4(g)$ is maintained at 25 °C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Answer

Very large value of K_c shows that the reaction goes to completion. i.e. As the amount of $H_2(g)$ (0.200 mol dm^{-3}) is higher than the amount of $C_2H_4(g)$ (0.155 mol dm^{-3}), it is clear that all the $C_2H_4(g)$ is consumed to produce 0.155 mol dm^{-3} of $C_2H_6(g)$. Therefore the remaining amount of $H_2(g)$ is (0.200 -0.155) mol dm^{-3}= 0.045 mol dm^{-3}. As the K_c of the forward reaction is very large, the equilibrium constant for the reverse reaction should be very small. On this basis we can consider that the reverse reaction occurs in which the amount of $C_2H_6(g)$ consumed is x and the following equilibrium is built-up.

	$H_2(g)$	+	$C_2H_4(g)$	⇌	$C_2H_6(g)$
Initial/ mol dm^{-3}	0.045		0.0		0.155
Change/ mol dm^{-3}	$+ x$		$+ x$		$- x$
Equilibrium/ mol dm^{-3}	$(0.045+x)$		x		$0.155 - x$

$$K_c = \frac{[C_2H_6(g)]}{[H_2(g)][C_2H_4(g)]} = 9.6 \times 10^{18} = \frac{(0.155 - x)}{(0.045+x)x} \approx \frac{(0.155)}{(0.045)x} \quad \text{(since } x \text{ is very small)}$$

$$x = 3.6 \times 10^{-19} \text{ mol dm}^{-3}$$

$[H_2(g)] = 0.045$ mol dm^{-3}
$[C_2H_4(g)] = 3.6 \times 10^{-19}$ mol dm^{-3}
$[C_2H_6(g)] = 0.155$ mol dm^{-3}

We can check and confirm the answer by substituting the values in K_c expression.

$$K_c = \frac{[C_2H_6(g)]}{[H_2(g)][C_2H_4(g)]} = \frac{0.155}{0.045\ (3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

i. e. the assumptions made are correct.

2.1.12 Factors affecting the equilibrium

From the above discussions we now know that the chemical equilibrium is a balance between forward and reverse reactions at a constant temperature in a closed rigid system. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. When we say that an equilibrium position shifts to the right, for example, we mean that the net reaction is now from left to right or vice-versa. Variables that can be controlled experimentally are concentration, pressure, volume, and temperature. Here, we will examine how each of these variables affects a reacting system at equilibrium. The qualitative effect of the above

variables on the composition of an equilibrium mixture can be predicted using a principle first described by the French chemist Henri-Louis Le Chātelier.

Le Chātelier's principle:
Change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

This is applicable to all physical and chemical equilibria.

Effect of concentration change
In general, when equilibrium is disturbed by the addition/removal of any reactant/ product, Le Chatelier's principle predicts that:

- The concentration stress of an *added* reactant/product is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a *removed* reactant/product is relieved by net reaction in the direction that *replenishes* the removed substance.

or in other words:
"When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration change".

Let us consider the reaction,

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

If $H_{2(g)}$ is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein $H_{2(g)}$ is consumed, i.e., more of $H_{2(g)}$ and $I_{2(g)}$ react to form $2HI_{(g)}$ and finally the equilibrium shifts to right (forward). This is in accordance with the Le Chātelier's principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture. Figure 2.10 illustrates the system.

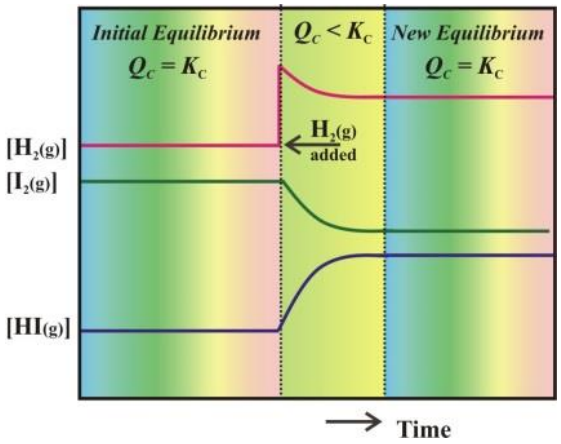


Figure 2.10 Effect of addition of H_2 on the change of concentration for the reactants and products in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

This behaviour can be explained in terms of the reaction quotient, $\boldsymbol{Q_c}$

$$Q_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

Addition of hydrogen at equilibrium results in the increase in the magnitude of the denominator which in turn decreases the value of Q_c below K_c. Thus, in order to release this stress, more $H_2(g)$ will be consumed making the forward reaction predominant. Therefore, the system will readjust with time making the forward reaction to move forward to attain a new equilibrium. Similarly, we can understand that the removal of a product also boosts the forward reaction and increases the concentration of the products.

Another simple system that can be tested experimentally in the laboratory is the equilibrium in Iron(III) -thiocyanate system. $[Fe(SCN)_3]$ dissolves readily in water to give a red solution. The red colour is due to the presence of hydrated $[FeSCN]^{2+}$ ion. The equilibrium between undissociated $[FeSCN]^{2+}$ and the Fe^{3+} and SCN^- ions is given by

$$\underset{red}{[FeSCN]^{2+}(aq)} \rightleftharpoons \underset{pale\ yellow}{Fe^{3+}(aq)} + \underset{colourless}{SCN^-(aq)}$$

Once we add some sodium thiocyanate (NaSCN) to this solution, the stress applied to the equilibrium system increases the concentration of $SCN^-(aq)$. To relieve this stress, some $Fe^{3+}(aq)$ ions react with the added $SCN^-(aq)$ ions, and the equilibrium shifts from right to left by deepening the red colour of the solution. Similarly, if we add $Fe^{3+}(aq)$ ions to the original solution, the red colour would also deepen because the additional $Fe^{3+}(aq)$ ions shift the equilibrium from right to left.

Further, if we write the above equilibrium as;

$$Fe^{3+}(aq) \quad + \quad SCN^{-}(aq) \quad \rightleftharpoons \quad [FeSCN]^{2+}(aq)$$
pale yellow *colourless* *red*

This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove $Fe^{3+}(aq)$ or $SCN^{-}(aq)$ ions. For example, oxalic acid ($H_2C_2O_4$), reacts with $Fe^{3+}(aq)$ ions to form the stable complex ion $[Fe(C_2O_4)_3]^{3-}$, thus decreasing the concentration of free $Fe^{3+}(aq)$. In accordance with the Le Chatelier's principle, the concentration stress of removed $Fe^{3+}(aq)$ is relieved by dissociation of $[Fe(SCN)]^{2+}$ to replenish the $Fe^{3+}(aq)$ ions. Because the concentration of $[Fe(SCN)]^{2+}$ decreases, the intensity of red color decreases.

This effect can be explained by the reactions shown below.

$$3H_2C_2O_4(aq) + Fe^{3+}(aq) \rightarrow [Fe(C_2O_4)_3]^{3-}(aq) + 6H^{+}(aq)$$

and

$$[FeNCS]^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + SCN^{-}(aq)$$

Addition of aq. $HgCl_2$ also decreases red colour because $Hg^{2+}(aq)$ reacts with $SCN^{-}(aq)$ ions to form the stable complex ion $[Hg(SCN)_4]^{2-}$. Removal of free $SCN^{-}(aq)$ shifts the equilibrium from right to left to replenish $SCN^{-}(aq)$ ions. Addition of potassium KSCN on the other hand increases the colour intensity of the solution as it shift the equilibrium to right.

$$HgCl_2(aq) + 4SCN^{-}(aq) \rightarrow [Hg(SCN)_4]^{2-}(aq) + 2Cl^{-}(aq)$$

and

$$[FeNCS]^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + SCN^{-}(aq)$$

Example:

Let's consider the following equilibrium system in the Haber process for the synthesis of ammonia:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_C = 0.291 \text{ at } 700 \text{ K}$$

Suppose we have an equilibrium mixture of 0.50 mol dm^{-3} $N_2(g)$, 3.00 mol dm^{-3} $H_2(g)$, and 1.98 mol dm^{-3} $NH_3(g)$ at 700 K and that we disturb the equilibrium by increasing the $N_2(g)$ concentration to 1.50 mol dm^{-3}. Le Châtelier's principle tells us that the reaction will occur to relieve the stress of the increased concentration of $N_2(g)$ by converting some of the $N_2(g)$ to $NH_3(g)$. It is clear that the number of gaseous molecules decreases in the forward direction allowing the release in the stress. i.e. as the $N_2(g)$ concentration decreases, the $H_2(g)$ concentration must also decrease and the $NH_3(g)$ concentration must increase in accordance with the stoichiometry of the balanced equation.

These changes can be explained by the following Figure 2.11.

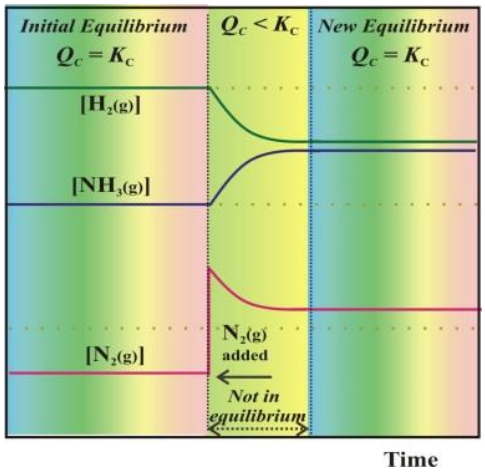
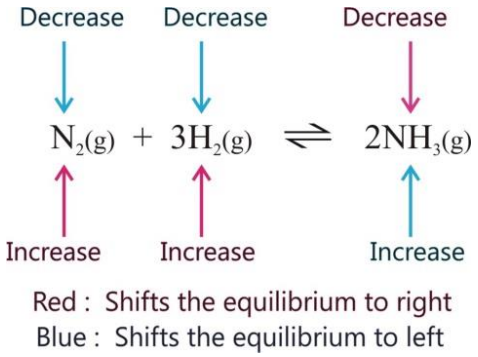


Figure 2.11 Effect of addition of N_2 on the change of concentration for the reactants and products in the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Now we can understand that once the rules of Le Châtelier's principle are applied to the equilibrium, the yield of ammonia is increased by an increase in the $N_{2(g)}$ or $H_{2(g)}$ concentration or by a decrease in the $NH_{3(g)}$ concentration and the sketch below gives us a kind of summary on the effect on the equilibrium position.



Sketch 1 An increase in the $N_2(g)$ or $H_2(g)$ concentration or a decrease in the $NH_3(g)$ concentration shifts the equilibrium from left to right. A decrease in the $N_2(g)$ or $H_2(g)$ concentration or an increase in the $NH_3(g)$ concentration shifts the equilibrium from right to left.

Though Le Châtelier's principle gives us to predict changes in the composition of an equilibrium mixture with the applying stress, it does not explain *why* those changes occur. However, we can understand the effect by considering the reaction quotient $\boldsymbol{Q_c}$. For the initial equilibrium mixture of 0.50 mol dm^{-3} $N_{2(g)}$, 3.00 mol dm^{-3} $H_2(g)$, and 1.98 mol dm^{-3} $NH_3(g)$ at 700 K, $\boldsymbol{Q_c}$ equals the equilibrium constant $\boldsymbol{K_c}$ (0.291) because the system is at equilibrium:

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_{2(g)}]^3} = \frac{[1.98]^2}{[0.5][3.0]^3} = 0.29 = K_c$$

When we disturb the equilibrium by increasing the $N_2(g)$ concentration to 1.50 mol dm^{-3}, the denominator of the equilibrium constant expression increases and Q_c decreases to a value less than K_c :

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{[1.98]^2}{[1.5][3.0]^3} = 0.0968 < K_c$$

For the system to move to a new state of equilibrium, Q_c must increase; that is, the numerator of the equilibrium constant expression must increase and the denominator must decrease. This implies that the net conversion of $N_2(g)$ and $H_2(g)$ to $NH_3(g)$ occurs just as predicted by Le Châtelier's principle. When the new equilibrium is established as shown in Figure 2.11, the concentrations are 1.31 mol dm^{-3} $N_2(g)$, 2.43 mol dm^{-3} $H_2(g)$, and 2.36 mol dm^{-3} $NH_3(g)$, and Q_c again equals K_c :

$$Q_c = \frac{[2.36]^2}{[1.31][2.43]^3} = 0.29 = K_c$$

Example:

Applying Le Châtelier's principle to solid ⇌ gas systems:

The reaction of iron(III) oxide with carbon monoxide occurs in a blast furnace when iron ore is reduced to iron metal:

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(l) + 3CO_2(g)$$

Let's use Le Châtelier's principle to predict the direction of the net reaction when an equilibrium mixture is disturbed by:

(a) Adding Fe_2O_3
(b) Removing CO_2
(c) Removing CO; while accounting for the change using the reaction quotient *Qc*.

(a) Because Fe_2O_3 is a pure solid, its concentration is equal to 1 and does not change when more Fe_2O_3 is added. Therefore, there is no concentration stress and the original equilibrium is undisturbed.

(b) Le Châtelier's principle predicts that the concentration stress of CO_2 removed will be relieved by net reaction shift from reactants to products to replenish CO_2.

(c) Le Châtelier's principle predicts that the concentration stress of CO removed will be relieved by net reaction shift from products to reactants to replenish CO. The reaction quotient is;

$$Q_c = \frac{[CO_2(g)]^3}{[CO(g)]^3}$$

When the equilibrium is disturbed by reducing [CO], Q_c increases, so that $Q_c > K_c$. For the system to move to a new state of equilibrium, Q_c must decrease; that is, $[CO_2]$ must decrease and [CO] must increase. Therefore, the net reaction goes from products to reactants, as predicted by Le Châtelier's principle.

Example 1:

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:

$$PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g)$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2(g)]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of $CO_2(g)$ at equilibrium, regardless of the ratio or the amounts of the solids present. This can be understand by Figure 2.12, which shows a plot of $[CO_2(g)]$ versus the amount of solid $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to $CO_2(g)$ because the amount of $PbCO_3$ is not sufficient to give a $CO_2(g)$ concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only $CO_2(g)$ and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2(g)] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the $CO_2(g)$ concentration: so the graph is a horizontal line. Thus any $CO_2(g)$ concentration that is not on the horizontal line represents a non-equilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough $PbCO_3$ and PbO are present. For example, the point labelled as **A** in Figure 2.12, the concentration of $CO_2(g)$ lies above the horizontal line, so it corresponds to a $[CO_2(g)]$ that is greater than the equilibrium concentration of $CO_2(g)$ ($Q > K$). To reach equilibrium, the system must decrease $[CO_2(g)]$, which it can do only by reacting $CO_2(g)$ with solid PbO to form solid $PbCO_3$. Thus the reaction will proceed to the left side, until $[CO_2(g)] = K$. Conversely, the point labelled as **B** in the figure, the concentration of gaseous $CO_2(g)$ lies below the horizontal line, so it corresponds to a $[CO_2(g)]$ that is less than the equilibrium concentration of $CO_2(g)$ ($Q < K$). To reach equilibrium, the system must increase $[CO_2(g)]$, which it can do only by decomposing solid $PbCO_3$ to form $CO_2(g)$ and solid PbO. The reaction will therefore proceed to the right as written, until $[CO_2(g)] = K$.

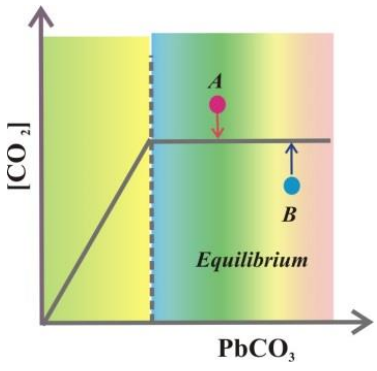


Figure 2.12 Initially the concentration of $CO_2(g)$ increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to $CO_2(g)$ and solid PbO. Once the $CO_2(g)$ concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2(g)]$, as long as the temperature remains constant.

Example 2:

The reduction of cadmium oxide by hydrogen giving metallic cadmium and water vapour exhibits a manner which further gives us much understanding about the Le Châtelier's principle.

$$CdO(s) + H_2(g) \rightleftharpoons Cd(s) + H_2O(g)$$

Equilibrium constant K_c is $[H_2O(g)]/ [H_2(g)]$. For example, if $[H_2O(g)]$ is doubled at equilibrium, then $[H_2(g)]$ must also be doubled for the system to remain at equilibrium. A plot of $[H_2O(g)]$ versus $[H_2(g)]$ at equilibrium is a straight line with a slope of K_c . Again, only those pairs of concentrations of $H_2O(g)$ and $H_2(g)$ that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a non-equilibrium state. In such cases, the reaction will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 2.13 lies below the line, indicating that the $[H_2O(g)]/ [H_2(g)]$ ratio is less than the ratio of an equilibrium mixture ($Q < K$). Thus the reaction will proceed to the right as written, consuming $H_2(g)$ and producing $H_2O(g)$, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 2.13 lies above the line, indicating that the $[H_2O(g)]/ [H_2(g)]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction will proceed to the left as written, consuming $H_2O(g)$ and producing $H_2(g)$, which causes the concentration ratio to move down and to the right toward the equilibrium line.

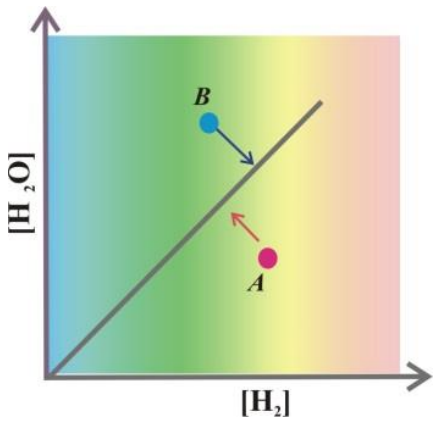


Figure 2.13 For any equilibrium concentration of $H_2O(g)$, there is only one equilibrium concentration of $H_2(g)$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O(g)]$ at equilibrium requires a large $[H_2(g)]$ and vice versa. In this case, the slope of the line is equal to K_c.

Changes in pressure and volume

To illustrate how an equilibrium mixture is affected by a change in pressure as a result of a change in the volume, let's return to the Haber synthesis of ammonia. The balanced equation for the reaction has 4 moles of gas on the reactant side of the equation and 2 moles on the product side:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad K_c = 0.29 \text{ at } 700 \text{ K}$$

What happens to the composition of the equilibrium mixture if we increase the pressure by decreasing the volume? (the pressure of an ideal gas is inversely proportional to the volume at constant temperature and constant number of moles of gas). According to Le Châtelier's principle, net reaction will occur in the direction that relieves the stress of the increased pressure, which means that the number of moles of gas must decrease. Therefore, we predict that the net reaction will proceed from left to right because the forward reaction converts 4 moles of gaseous reactants to 2 moles of gaseous products. In general, Le Châtelier's principle predicts that

- *An increase in pressure by reducing the volume will bring about net reaction in the direction that decreases the number of moles of gas.*
- *A decrease in pressure by expanding the volume will bring about net reaction in the direction that increases the number of moles of gas.*

To see why Le Châtelier's principle works for pressure (volume) changes, let's look again at the reaction quotient for the equilibrium mixture of 0.50 mol dm^{-3} $N_2(g)$, 3.00 mol dm^{-3} $H_2(g)$ and 1.98 mol dm^{-3} $NH_3(g)$ at 700 K, where Q_c equals the equilibrium constant $\boldsymbol{K_c}$ (0.291) because the system is at equilibrium:

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{[1.98]^2}{[0.5][3.0]^3} = 0.29 = K_c$$

If we disturb the equilibrium by reducing the volume by a factor of 2, we not only double the total pressure, we also double the partial pressure and thus the molar concentration of each reactant and product (molarity = $n/V = P/RT$) . Because the balanced equation has more moles of gaseous reactants than the gaseous products, the increase in the denominator of the equilibrium constant expression is greater than the increase in the numerator and the new value of Q_c is less than the equilibrium constant.

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]} = \frac{[3.96]^2}{[1.0][6.0]^3} = 0.073 < K_c$$

For the system to move to a new state of equilibrium, Q_c must increase, which means that the net reaction must go from reactants to products, as predicted by Le Châtelier's principle. In practice, the yield of ammonia in the Haber process is increased by running the reaction at high pressure, typically 130 – 300 atm.

Effect of inert gas addition

If the volume is kept constant by doing the experiment in a closed-rigid container and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substances involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction

Effect of temperature change

Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, $\boldsymbol{Q_c}$ no longer equals the equilibrium constant, $\boldsymbol{K_c}$ due to the change in equilibrium position and that does not change the value of equilibrium constant. However, when a change in temperature occurs, the value of equilibrium constant, $\boldsymbol{K_c}$ is changed. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- *The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.*
  We can write the reaction as: *reactants ⇌ products + heat ($\Delta H < 0$)*
- *The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.*
  We can write the reaction as : reactants + heat ⇌ products ($\Delta H > 0$)

According to above reactions, heat can be thought of as a product in an exothermic reaction and as a reactant in an endothermic reaction. Increasing the temperature of a system corresponds to adding heat. Le Chatelier's principle predicts that an exothermic reaction will shift to the left (toward the reactants) if the temperature of the system is increased (heat is added). Conversely, an endothermic reaction will shift to the right (toward the products) if the temperature of the system is increased. If a reaction is thermochemically neutral ($\Delta H_{rxn} = 0$), then a change in temperature will not affect the equilibrium composition.

Example:

We can examine the effects of temperature on the dissociation of $N_2O_4(g)$ to $NO_2(g)$, for which ΔH = +58 kJ mol^{-1}. This reaction can be written as follows:

$$58\ \text{kJ} + \text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$$

$$K_\text{c} = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]}$$

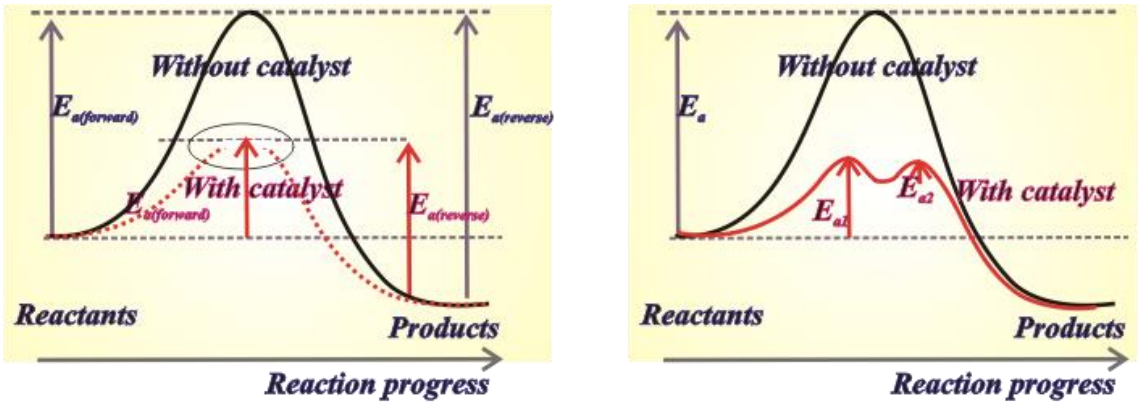
Increasing the temperature (adding heat to the system) is a stress that will drive the reaction to the right. Thus increasing the temperature increases the ratio of $NO_{2(g)}$ to $N_2O_{4(g)}$ at equilibrium, which increases equilibrium constant ***K***.

The effect of increasing the temperature on a system at equilibrium can be summarized as follows: increasing the temperature increases the magnitude of the equilibrium constant for an endothermic reaction, decreases the equilibrium constant for an exothermic reaction, and has no effect on the equilibrium constant for a thermally neutral reaction.

In summary, three types of stresses can alter the composition of an equilibrium system: adding or removing reactants or products, changing the total pressure or volume, and changing the temperature of the system. A reaction with an unfavourable equilibrium constant can be driven to completion by continually removing one of the products of the reaction. Equilibria that contain different numbers of gaseous reactant and product molecules are sensitive to changes in volume or pressure; higher pressures favour the side with fewer gaseous molecules. Removing heat from an exothermic reaction favours the formation of products, whereas removing heat from an endothermic reaction favours the formation of reactants.

The effect of catalyst on equilibrium

The addition of a catalyst to a reaction increases the rate by providng a new, lower-energy alternative pathway for the conversion of reactants to products. Because the forward and reverse reactions pass through the same transition state, a catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. If a reaction mixture is at equilibrium in the absence of a catalyst (that is, the forward and reverse rates are equal), it will still be at equilibrium after a catalyst is added because the forward and reverse rates, though faster, remain equal. If a reaction mixture is not at equilibrium, a catalyst accelerates the rate at which equilibrium is reached, but it does not affect the composition of the equilibrium mixture. Because a catalyst has no effect on the equilibrium concentrations, it does not appear in the balanced chemical equation or in the equilibrium constant expression (As the catalyst is not consumed in the reaction they are not considered in the overall rate equation and therefore do not affect the equilibrium of the reaction but only the rate). Even though a catalyst doesn't change the position of equilibrium it can nevertheless significantly influence the choice of optimum conditions for a reaction.



(a) (b)

Figure 2.14 Comparison of the reaction profile with and without a catalyst. The addition of a catalyst to a reaction increases the rate by providng a new, lower-energy alternative pathway as shown in (a). Also the reaction may find the similar path with multi steps and proceed via an intermediate as shown in (b).

For example, in the Haber synthesis of ammonia, because the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is exothermic, its equilibrium constant decreases with increasing temperature, and optimum yields of $NH_3(g)$ are obtained at low temperatures. At those low temperatures, however, the rate at which equilibrium is reached is too slow for the reaction to be practical. Thus, low temperatures give good yields but slow rates, whereas high temperatures give satisfactory rates but poor yields. The answer to the dilemma is to find a catalyst. A catalyst consisting of iron mixed with certain metal oxides causes the reaction to occur at a satisfactory rate at temperatures where the equilibrium concentration of $NH_3(g)$ is reasonably favourable. The yield of $NH_3(g)$ can be improved further by running the reaction at high pressures. Typical reaction conditions for the industrial synthesis of ammonia are 400 – 500 °C and 130 – 300 atm.

Following table summarizes the shifts in equilibrium in response to stresses imposed on an equilibrium system.

Table 2.1 Response of equilibrium system to the stresses applied

Stress	Response of the system	Effect on equilibrium constant
Increase in concentration at constant temperature	System shifts to decrease the reactant or the product added	Does not change. The concentrations of all reactants and products change to keep the ratio constant
Decrease in concentration at constant temperature	System shifts to increase the reactant or the product removed	Does not change. The concentrations of all reactants and products change to keep the ratio constant
Increase in volume (Decrease in pressure) at constant temperature	System shifts to the side with more gaseous species. (when the number of gaseous species are the same on both sides, consider the exo/endo-thermic nature)	Does not change. The concentrations of all reactants and products change to keep the ratio constant
Decrease in volume (Increase in pressure) at constant temperature	System shifts to the side with least gaseous species. (when the number of gaseous species are the same on both sides, consider the exo/endo-thermic nature)	Does not change. The concentrations of all reactants and products change to keep the ratio constant
Increase in temperature	Favours the endothermic reaction by using the added heat	Equilibrium constant changes because the equilibrium position shifts
Decrease in temperature	Favours the exothermic reaction by releasing more heat	Equilibrium constant changes because the equilibrium position shifts
Addition of a catalyst	No change in the system because the catalyst increases the rates of forward and backward reactions by the same extent. Only thing happens is that the system reaches the equilibrium faster	Does not change
Addition of an inert gas	No change in the system because it does not participate in the reaction	Does not change

2.2 Ionic equilibrium in aqueous solutions

A solution can be defined as a homogeneous mixture of two or more substances. The solute is the substance present in a smaller amount or the substance that has being dissolved, and the solvent is the substance present in a larger amount. A solution may be gaseous (such as air), solid (such as an alloy), or liquid (seawater, for example). In this section we will discuss only *aqueous solutions***,** in which the solute initially is a liquid or a solid and the solvent is water and once the solution is formed we consider the ionic form of the substances which are in equilibrium in aqueous phase.

For example, under the effect of change of concentration on the direction of equilibrium, we have earlier considered the following equilibrium which involves ions:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$$

There are numerous equilibria that involve ions only. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called *electrolytes* while the other does not and are thus, referred to as *nonelectrolytes*. Faraday further classified electrolytes into *strong* and *weak* electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is entirely composed of sodium ions and chloride ions, i.e.

$$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

Acids and bases are also electrolytes. Some acids, like hydrochloric acid (HCl) and nitric acid (HNO_3), are strong electrolytes. These acids ionize completely in water; for example, when hydrogen chloride gas dissolves in water, it forms hydrated H^+ and Cl^- ions:

$$HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$$

or we write the reaction as:

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

However, that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and protons. i.e.

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^{-}(aq) + H^{+}(aq)$$

or we write the reaction as:

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

We can see that the → (single arrow) is used in the case of dissociation of HCl to show the complete or almost 100% ionization. Also we can understand that a solution of HCl does not have any free HCl(aq) molecules as they are completely dissociated to $H_3O^+(aq)$ and $Cl^-(aq)$ ions. In the case of acetic acid, a ⇌ (double arrow) is used to show the partial or less than 5% ionization in water and the reaction is reversible. Initially, a number of CH_3COOH molecules break up into $CH_3COO^-(aq)$ and $H^+(aq)$ ions. As time goes on, some of the $CH_3COO^-(aq)$ and $H^+(aq)$ ions recombine into CH_3COOH molecules. Eventually, a state is reached in which the acid molecules ionize as fast as the ions recombine reaching a state of *chemical equilibrium.* It is very important to show the physical state of each species in the system where **(aq)** is used to show that the species are in aqueous phase. Further, as the amount of water (solvent) is in large excess, a bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give *trigonal pyramidal* hydrated proton called the *hydronium ion,* $H_3O^+(aq)$. It has to be noted that the use of $H^+(aq)$ and $H_3O^+(aq)$ means the same i.e., a proton or a hydrated proton.

With the above simple explanations we can note that in weak electrolytes, equilibrium is established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

2.2.1 Acids, bases (and salts)

Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids. As most of the acids taste sour, the word "acid" has been derived from a latin word "*acidusî* meaning sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen (H_2) on reacting with metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give *salts*. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced.

Arrhenius concept of acids and bases

According to Arrhenius theory, *acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$ and bases are substances that produce hydroxyl ions $OH^-(aq)$.* The ionization of an acid HX (aq) can be represented by the following equations:

$HX\ (aq) \rightarrow H^+(aq) + X^-\ (aq)$

or

$HX\ (aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-\ (aq)$

Similarly, a base molecule like MOH(aq) ionizes in aqueous solution according to the equation:

$MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$

The hydroxyl ion also exists in the hydrated form in the aqueous solution (eg. $H_3O_2^-(aq)$). Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.

The Brönsted -Lowry definition of acids and bases

The Danish chemist, Johannes Brönsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brönsted-Lowry theory, *acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+*. In short, *acids are proton donors* and *bases are proton acceptors*. For example;

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

Here we can see that the HCl(aq) molecule donates a proton to water forming $Cl^-(aq)$ and $H_3O^+(aq)$ ions. i.e. Therefore, HCl(aq) is classified as a Brønsted acid because it can donate a H^+ ion. (We can also see that the $H_2O(l)$ molecule accepts that proton acting as a base; further insights of this nature will be explained in a latters section dealing with *conjugate acid-base pairs*).

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

Here we can see that the $NH_3(aq)$ molecule accepts a proton from water forming $NH_4^+(aq)$ and $OH^-(aq)$ ions. i.e. Therefore, $NH_3(aq)$ is classified as a Brønsted base because it can accept a H^+ ion.

Lewis acids and bases

G.N. Lewis in 1923 defined an *acid as a species which accepts an electron pair and a base as a species which donates an electron pair*. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides

a lone pair in both the cases. However, in Lewis concept many acids do not have protons. A typical example is reaction of electron deficient species BF_3 with NH_3. BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,

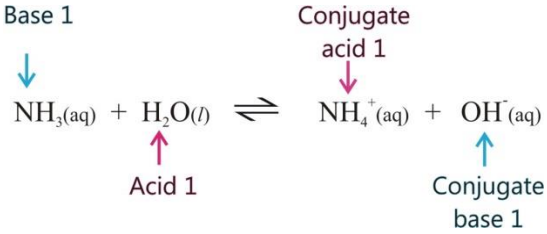
$$BF_3 + :NH_3 \rightarrow BF_3:NH_3$$

Electron deficient species like $AlCl_3$, Co^{3+}, Mg^{2+}, etc. can act as Lewis acids while species like H_2O, NH_3, OH^- etc. which can donate a pair of electrons, can act as Lewis bases.

2.2.2 Conjugate acid – base pairs

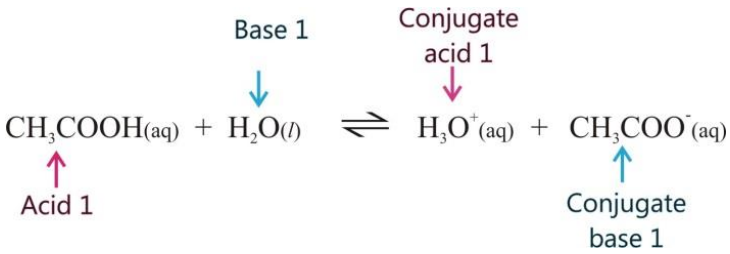
Brønsted definition of acids and bases can further be extended to the concept of the ***conjugate acid-base pair,*** which can be defined as *an acid and its conjugate base* or *a base and its conjugate acid.* The conjugate base of a Brønsted acid is the species that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Brønsted base.

Consider the partial dissolution of $NH_3(aq)$ in water.



A basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brönsted acid and base, respectively. In the reverse reaction, H^+ is transferred from $NH_4^+(aq)$ to $OH^-(aq)$. In this case, $NH_4^+(aq)$ acts as a Bronsted acid while OH^- acted as a Brönsted base. The acid-base pair that differs only by one proton is called a ***conjugate acid-base pair***. Therefore, $OH^-(aq)$ is called the conjugate base of an acid H_2O and $NH_4^+(aq)$ is called conjugate acid of the base $NH_3(aq)$. If Brönsted acid is a strong acid, its conjugate base is a weak base and ***vice versa.*** It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of acetic acid $CH_3COOH(aq)$ in water. $CH_3COOH(aq)$ acts as an acid by donating a proton to H_2O molecule which acts as a base.



It can be seen in the above equation, that water acts as a base because it accepts the proton. The species $H_3O^+(aq)$ is produced when water accepts a proton from $CH_3COOH(aq)$. Therefore, $CH_3COO^-(aq)$ is a conjugate base of $CH_3COOH(aq)$ acid and $CH_3COOH(aq)$ is the conjugate acid of base $CH_3COO^-(aq)$. Similarly, H_2O is a conjugate base of the acid $H_3O^+(aq)$ and $H_3O^+(aq)$ is the conjugate acid of base H_2O.

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with CH_3COOH acid, water acts as a base while in case of ammonia it acts as an acid by donating a proton.

Example 2.12

(i) What will be the conjugate bases for the following Brönsted acids: HF, H_2SO_4 and HCO_3^-

Answer

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F^-, HSO_4^- and CO_3^{2-} respectively.

(ii) Write the conjugate acids for the following Brönsted bases: NH_2^-, NH_3 and $HCOO^-$.

Answer

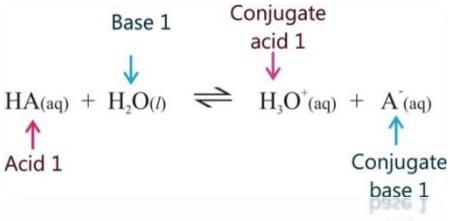
The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3, NH_4^+ and HCOOH respectively.

2.2.3 Ionization of acids and bases

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hyrdoiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $Ba(OH)_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH–. According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H_3O^+ and OH^- ions respectively in the medium.

Alternatively, the strength of an acid or base may also be gauged in terms of Brönsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and

a strong base implies a good proton acceptor. Consider, the acid-base dissociation equilibrium of a weak acid HA,



As we saw earlier, acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and H_3O^+(aq) present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is the stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed the stronger acid and the equilibrium will shift in the direction of the weaker acid. Say, if $HA_{(aq)}$ is a stronger acid than $H_3O^+_{(aq)}$, and then $HA_{(aq)}$ will donate protons and not H_3O^+(aq), and the solution will mainly contain $A^-_{(aq)}$ and $H_3O^+_{(aq)}$ ions. The equilibrium moves in the direction of formation of weaker acid and weaker base because *the stronger acid donates a proton to the stronger base.*

It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., *strong acids have very weak conjugate bases.* Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4^-, Cl^-, Br^-, I^-, NO_3^- and HSO_4^- , which are much weaker bases than H_2O. Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the *weak acids have very strong conjugate bases*. For example, NH_2^-, O^{2-} and H^- are very good proton acceptors and thus, much stronger bases than H_2O.

Therefore we can summarize the following on conjugate acid-base pairs.

- If an acid is strong, its conjugate base has no measurable strength. Thus the Cl^- ion, which is the conjugate base of the strong acid HCl, is an extremely weak base.
- H_3O^+ is the strongest acid that can exist in aqueous solution. Acids stronger than H_3O^+ react with water to produce H_3O^+ and their conjugate bases. Thus HCl, which is a stronger acid than H_3O^+, reacts with water completely to form H_3O^+ and Cl^-:

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

Acids weaker than H_3O^+ react with water to a much smaller extent, producing H_3O^+ and their conjugate bases. For example, the following equilibrium lies primarily to the left:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

- The OH^- ion is the strongest base that can exist in aqueous solution. Bases stronger than OH^- react with water to produce OH^- and their conjugate acids. For example, the oxide ion (O^{2-}) is a stronger base than OH^-, so it reacts with water completely as follows:

$$O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$$

For this reason the oxide ion does not exist in aqueous solutions.

2.2.4 The ionization constant of water and its ionic product

Water and some substances are unique in their ability of acting both as an acid and a base. We have seen this in case of water in the section above. In the presence of an acid HA, it accepts a proton and acts as the base while in the presence of a base, B^- it acts as an acid by donating a proton. In pure water, one H_2O molecule donates a proton and acts as an acid and another water molecule accepts a proton and acts as a base at the same time. The following equilibrium exists:

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

The dissociation constant for the reaction is represented by,

$$K = \frac{[H_3O^+(aq)][OH^-(aq)]}{[H_2O(l)]^2}$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant (Concentration of water in 1.00 dm^3 of solution is 10^3 g dm^{-3}/18 g mol^{-1} = 55.55 mol dm^{-3} is a constant) . Therefore, incorporation of $[H_2O(l)]$ into the equilibrium constant to give a new constant, K_w, which is called the ***ionic product of water***.

i.e, $K[H_2O(l)]^2 = K_w = [H_3O^+(aq)][OH^-(aq)]$

The concentrations of $H_3O^+(aq)$ and $OH^-(aq)$ have been found out experimentally as 1.0×10^{-7} mol dm^{-3} at 298 K. As dissociation of water produces equal number of $H_3O^+(aq)$ and $OH^-(aq)$ ions, the value of K_w at 298K is,

$$K_w = [H_3O^+(aq)][[OH^-(aq)]] = (1 \times 10^{-7} \text{ mol dm}^{-3})^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

It has to be noted that the K_w is temperature dependent and is an equilibrium constant. When $[H_3O^+(aq)] = [OH^-(aq)]$, the aqueous solution is said to be neutral. In an acidic solution there is an excess of hydronium ions and $[H_3O^+(aq)] > [OH^-(aq)]$. In a basic solution there is an excess of hydroxide ions, so $[H_3O^+(aq)] < [OH^-(aq)]$.

2.2.5 The pH scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the **pH scale**. The pH of a solution is defined as the negative logarithm to base 10 of the activity ($a_{H_3O^+(aq)}$) or ($a_{H^+(aq)}$) of the hydronium or hydrogen ion. In dilute solutions (< 0.01 mol dm^{-3}), activity of hydrogen ion is equal in magnitude to molarity represented by $[H_3O^+(aq)]$. It should be noted that activity has no units and is defined as:

$$(a_{H_3O^+(aq)}) \text{ or } (a_{H^+(aq)}) = [H_3O^+(aq)]/\ 1 \text{ mol dm}^{-3}$$

Therefore, from the definition of pH is

$$\text{pH} = -\log (a_{H_3O^+(aq)}) = -\log \{[H_3O^+(aq)]/\ 1\text{mol dm}^{-3}\}$$

As the $[H_3O^+(aq)]$ has units mol dm^{-3},

pH = – log {$[H_3O^+(aq)]$ mol dm^{-3}/ mol dm^{-3}}

pH = – log {$[H_3O^+(aq)]$ }

That is, pH value has no units.

Thus, an acidic solution of HCl (10^{-2} mol dm^{-3}) will have a pH = 2. Similarly, a basic solution of NaOH having $[OH^-] = 10^{-4}$ mol dm^{-3} and $[H_3O^+] = 10^{-10}$ mol dm^{-3} will have a pH = 10. At 25 °C, pure water has a concentration of hydronium or hydrogen ions, $[H_3O^+]$ or $[H^+] = 10^{-7}$ mol dm^{-3}. Hence, the pH of pure water is given as:

$$\text{pH} = -\log(10^{-7} \text{ mol dm}^{-3}/ \text{ mol dm}^{-3}) = 7$$

Acidic solutions possess a concentration of hydrogen ions, $[H^+] > 10^{-7}$ mol dm^{-3}, while basic solutions possess a concentration of hydrogen ions, $[H^+] < 10^{-7}$ mol dm^{-3}. Thus, we can summarisethat

Acidic solution has pH < 7

Basic solution has pH > 7

Neutral solution has pH = 7

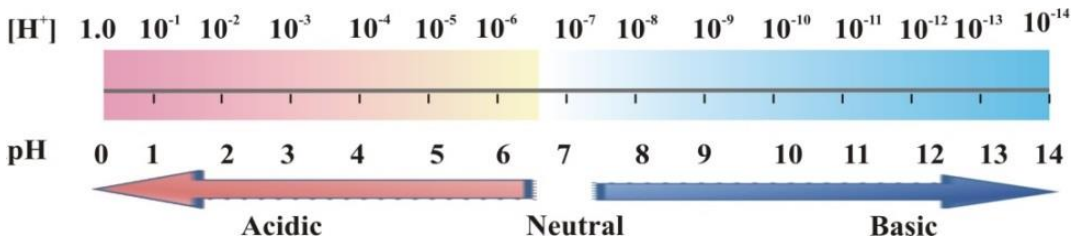


Figure 2.15 Simple visualization of the pH scale. At pH 7.0 solutions are said to be neutral. Proceeding to the lower pH values increases the acidity while the otherway increases the basisity of solutions.

$$K_w = [H_3O^+(aq)][OH^-(aq)]$$

Taking negative logarithm on both sides of equation, we obtain

$$-\log K_w = -\log\{[H_3O^+(aq)][OH^-(aq)]\}$$
$$pK_w = -\log[H_3O^+(aq)] - \log[OH^-(aq)]$$
$$pK_w = pH + pOH$$

or

$$pH + pOH = 14$$

Note that although K_w may change with temperature, the variations in pH with temperature are so small that we often ignore it. pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in $[H^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[H^+]$ changes by a factor of 100, the value of pH changes by 2 units. Now you can realize why the change in pH with temperature is often ignored.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that gives different colours in solutions of different pH. The *p*H in the range of 1-14 can be determined with an accuracy of ~0.5 using a pH paper. In the laboratory, the pH of a solution is also measured with a pH meter.

Let's consider following examples involving calculations based on pH.

Example 2.13
Calculate pH of a 1.0×10^{-4} mol dm^{-3} solution of HCl.

Answer
*p*H = –log(10^{-4} mol dm^{-3}/ mol dm^{-3}) = 4

Example 2.14
In a NaOH solution $[OH^-]$ is 1.0×10^{-4} mol dm^{-3}. Calculate the pH of the solution.

Answer
$[OH^-] = 1.0 \times 10^{-4}$ mol dm^{-3}
pOH = –log(10^{-4} mol dm^{-3}/ mol dm^{-3}) = 4Therefore, pH = 14 -4 = 10
or
$[OH^-] = 1.0 \times 10^{-4}$ mol dm^{-3} gives $[H^+] = 1.0 \times 10^{-10}$ mol dm^{-3}
pH = –log(10^{-10} mol dm^{-3}/ mol dm^{-3}) = 10

Example 2.15
Calculate pH of a 1.0×10^{-8} mol dm^{-3} solution of HCl.

Answer
In this calculation some may make a wrong approach by taking pH as
pH = –log(10^{-8} mol dm^{-3}/ mol dm^{-3}) = 8

One should note that here the $[H^+]$ from HCl is less than that coming from the self-ionization of water (i.e. 1.0×10^{-7} mol dm^{-3}). Therefore, we should consider the $[H^+]$ generated from both HCl and water. That is, $[H^+]$ from the given HCl solution is 1.0×10^{-8} mol dm^{-3} and take that from water as x.
Therefore, $[OH^-] = x$ and $[H_3O^+] = 10^{-8} + x$
$K_w = [H_3O^+(aq)][OH^-(aq)] = 10^{-14} = (10^{-8} + x)\, x$
$x^2 + 10^{-8}x - 10^{-14} = 0$

Solving the above quadratic equation, we get
$[OH^-] = 9.5 \times 10^{-8}$ mol dm^{-3} and hence pOH = 7.02
Therefore, pH = 6.98

In the above calculations in examples, it was easy to decide the concentration of $[H^+]$ and $[OH^-]$ as we know that HCl and NaOH are a strong acid and a base, respectively, giving rise to complete ionization. However, when we have aqueous solutions of weak acids or bases, it needs some more information on the system as they undergo partial dissociation. In the next section we consider dissociation of weak acids and bases with the emphasis on their equlibria.

2.2.6 Weak acids and their ionization (dissociation) constant

Consider a weak monoprotic acid, HA. Its ionization in water is represented by

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

The equilibrium expression for this ionization is

$$K = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)][H_2O(l)]}$$

We can write,

$$K[H_2O(l)] = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

Taking $K[H_2O(l)] = K_a$, as a constant, because $[H_2O(l)]$ is a constant, we can write

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

K_a is called the ***dissociation or ionization constant*** of the weak acid which is the *equilibrium constant for the ionization of the acid.* At a given temperature, the strength of the acid HA is measured quantitatively by the magnitude of K_a . Large K_a , indicates that the acid is stronger, which means a greater the concentration of $[H_3O^+(aq)]$ or $[H^+(aq)]$ ions at equilibrium due to its ionization in aqueous solution. Only weak acids have K_a values associated with them.

The above definition of the acid ionization constant can also be treated as follows considering the partial ionization of HA in aqueous solution. Assuming that the initial concentration of the undissociated acid is ***c*** and its extent of ionization (or degree of ionization) is α, we can express the equilibrium as,

	$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$		
Initial concentration/ mol dm^{-3}	c	0	0
Concentration change/ mol dm^{-3}	$-c\alpha$	$+c\alpha$	$+c\alpha$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$\therefore K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]} = \frac{c\alpha.c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

$$\therefore K_a = \frac{c\,\alpha^2}{(1-\alpha)}$$

As the ionization of a weak acid is very small, we can assume that α **is very small or** $(1-\alpha) \sim 1$. **Hence,** $\therefore K_a = c\alpha^2$

This is called Ostwald's law of dilution.

Note: *This is valid for weak bases in aqueous solutions too.*

The values of the ionization constants of some weak acids at 298 K are given in the following table.

Table 2.2 The ionization constants of some selected weak acids (at 298K)

Acid	K_a
Hydrofluoric Acid (HF)	3.5×10^{-4}
Nitrous Acid (HNO_2)	4.5×10^{-4}
Acetic Acid (CH_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.50×10^{-5}
Hypochlorous Acid (HCIO)	3.00×10^{-8}
Hydrocyanic Acid (HCN)	4.90×10^{-10}
Phenol (C_6H_5OH)	1.30×10^{-10}

Note: *K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1 mol dm^{-3}. That is all the concentration terms appearing in the equilibrium constant expression is divided by 1 mol dm^{-3}. Otherwise we indicate the units as relevant to the equilibrium constant expression.*

The pH scale for the hydrogen ion concentration has been so useful that besides pK_w (-log K_w), it has been extended to other species and quantities. Thus, we have:

$$\mathbf{p}K_a = -\log (K_a)$$

Knowing the ionization constant, K_a of an acid and its initial concentration ***c***, it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of a weak electrolyte as follows:

Step 1. The species present before dissociation are identified as Brönsted-Lowry acids/ bases.

Step 2. Balanced equations for all possible reactions i.e., with a species acting both as acids as well as bases are written.

Step 3. The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.

Step 4. Enlist in a tabular form the following values for each of the species in the primary reaction.

(a) Initial concentration, ***c***

(b) Change in concentration on proceeding to equilibrium in terms of α, degree of ionization

(c) Equilibrium concentration

Step 5. Substitute equilibrium concentrations into equilibrium constant equation for the principal reaction and solve for α.

Step 6. Calculate the concentration of species in the principal reaction.

Step 7. Calculate pH = – log[H_3O^+] or calculate [H_3O^+] once pH is known using **[H_3O^+]= 10^{-pH}**

The following example(s) illustrate(s) the above mentioned approach in calculating pH.

Example 2.16

The ionization constant of HF is 3.2×10^{-4} at 298 K. Calculate the degree of dissociation of HF in its 0.20 mol dm^{-3} solution. Calculate the concentration of all species present (H_3O^+, F^- and HF) in the solution and its pH.

Answer

Procedure I:

The following proton transfer reactions are possible:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \text{ ---------- (1)}$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \text{ ---------- (2)}$$

As K_a (3.2×10^{-4}) >> K_w (1.0×10^{-14}), we can understand that reaction (1) is the major reaction.

	$HF(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$F^-(aq)$
Initial concentration/ mol dm^{-3}	0.2			0		0
Concentration hacnge/ mol dm^{-3}	-0.2α			$+0.2\alpha$		$+0.2\alpha$
∴ Equilibrium concentration/ mol dm^{-3}	$0.2(1-\alpha)$			$+0.2\alpha$		$+0.2\alpha$

Substituting equilibrium concentrations in the equilibrium reaction for the principal reaction gives:

$$\therefore K_a = \frac{\mathbf{0.2\alpha} \times \mathbf{0.2\alpha}}{\mathbf{0.2(1-\alpha)}} = \frac{\mathbf{(0.2\alpha)^2}}{\mathbf{0.2(1-\alpha)}}$$

As the acid considered is weak, we can assume that the ionization is small compared to the initial concentration of the acid $\therefore \mathbf{(1-\alpha) \sim 1}$ **or** $\mathbf{0.2(1-\alpha) \sim 0.2}$

Substituting in $K_a = \frac{\mathbf{0.2\alpha} \times \mathbf{0.2\alpha}}{\mathbf{0.2(1-\alpha)}} \sim \frac{\mathbf{(0.2\alpha)^2}}{\mathbf{0.2}} = 3.2 \times 10^{-4}$

$$\alpha^2 = 1.6 \times 10^{-3}$$

$$\alpha = 4.0 \times 10^{-2}$$

$[H_3O^+] = [F^-] = c\alpha = 0.2 \text{ mol } dm^{-3} \times 0.04 = 8.0 \times 10^{-3} \text{ mol } dm^{-3}$

$[HF] = c\,(1 - \alpha) = 0.2 \text{ mol } dm^{-3}\,(1 - 0.04) = 19.2 \times 10^{-2} \text{ mol } dm^{-3}$

Hence, pH = – log[H_3O^+] = –log(8.0×10^{-3}) = 2.10

Validity of the approximation we made can be checked by calculating the percent value of the ionization with respect to the initial concentration of the acid. When the percent value is less than 5% we usually accepts the approximation and otherwise it is necessary to solve the quadratic equation to obtain the value of α.

From the above estimated value 0.04 we get,

$$\frac{0.04}{0.20} \times 100\% = 2.0\ \%$$

Thus the approximation used can be accepted.

We can further confirm/clarify the above approximation by obtaining the value of α after solving the quadratic equation and taking the relative percent deviation of it.

For the above example: $K_a = \frac{0.2\alpha \times 0.2\alpha}{0.2(1-\alpha)} = 3.2 \times 10^{-4}$

We obtain the following quadratic equation:

$\alpha^2 + 1.6 \times 10^{-3}\alpha - 1.6 \times 10^{-3} = 0$

Note: *The values for x of the quadratic equation, $ax^2 + bx + c = 0$ are given by*

$$x = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a}$$

The quadratic equation with α can be solved and the two values of α are:

$\alpha = + 3.92 \times 10^{-2}$ and $- 4.08 \times 10^{-2}$

The negative value is not acceptable and hence

$$\alpha = 3.92 \times 10^{-2}$$

Now we can calculate the relative percent deviation as

$$\frac{0.04 - 3.92 \times 10^{-2}}{0.04} \times 100\% = 2.0\ \%$$

We can see that the close similarity in the above two methods and therefore usually we make the said approximation for this type of calculations.

Note: *The above approximation can be applied in the cases when the initial concentration of the acid/base is much larger (at least 3 orders of magnitude) than the acid ionization constant K_a of the acid.*

In the above example: initial concentration is 0.2 mol dm^{-3} and $K_a = 3.2 \times 10^{-4}$, so the ratio is

$$\frac{2.0 \times 10^{-1}}{3.2 \times 10^{-4}} \sim 10^3$$

Therefore, we can make the approximation.

Procedure II:

The example above can also be treated as follows. We know that the major reaction in system is,

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

Now taking the dissociated concentration or change in concentration as x, we can write,

	$HF(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$F^-(aq)$
Initial concentration/ mol dm^{-3}	0.2			0		0
Concentration change (mol dm^{-3})	$-x$			$+x$		$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$0.2 - x$			$+x$		$+x$

Substituting equilibrium concentrations in the equilibrium reaction gives:

$$\therefore K_a = \frac{x \times x}{(0.2 - x)} = \frac{(x)^2}{(0.2 - x)}$$

As the acid considered is weak, we can assume that the ionization is small compared to the initial concentration of the acid $\mathbf{0.2 - x \sim 0.2}$

Substituting in $K_a \sim \frac{(x)^2}{0.2} = 3.2 \times 10^{-4}$

$$x^2 = 6.4 \times 10^{-5}$$

$$x = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

And we have

$[H_3O^+] = [F^-] = x = 8.0 \times 10^{-3}$ mol dm^{-3}

$[HF] = 0.20 - x = 0.2 - 0.008 = 19.2 \times 10^{-2}$ mol dm^{-3}

Hence, $pH = -\log[H_3O^+] = -\log(8.0 \times 10^{-3}) = 2.10$

Note that the procedure II gives us the values of equilibrium concentrations directly.

Example 2.17

The pH of 0.10 mol dm^{-3} monobasic acid HA(aq) is 4.50. Calculate the concentration of species $H^+(aq)$, $A^-(aq)$ and HA(aq) at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Answer

pH = – log $[H_3O^+]$

Therefore, $[H_3O^+] = 10^{-pH} = 10^{-4.50} = 3.16 \times 10^{-5}$

$[H_3O^+] = [A^-] = 3.16 \times 10^{-5}$ mol dm^{-3}

$[HA]_{eqlbm} = 0.1 - (3.16 \times 10^{-5}) \sim 0.1$ mol dm^{-3}

We can summarize these as follows

	$HA(aq)$ + $H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$A^-(aq)$
Initial concentration/ mol dm^{-3}	0.1	0	0
Concentration change/ mol dm^{-3}	-3.16×10^{-5}	3.16×10^{-5}	3.16×10^{-5}
∴ Equilibrium concentration/ mol dm^{-3}	$(0.10 - 3.16 \times 10^{-5})$	3.16×10^{-5}	3.16×10^{-5}
∴ Equilibrium concentration/ mol dm^{-3}	0.10	3.16×10^{-5}	3.16×10^{-5}

Thus, $\boldsymbol{K_a} = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$

$\therefore K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8}$ mol dm^{-3}

$pK_a = -\log(10^{-8}) = 8$

2.2.7 Weak bases and base ionization constant

The ionization of base MOH can be represented by equation:

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

We can write this reaction as,

$$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

In a weak base there is partial ionization of $MOH_{(aq)}$ into $M^+_{(aq)}$ and $OH^-_{(aq)}$, is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by $\boldsymbol{K_b}$. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$$K = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)][H_2O(l)]}$$

Similar to treatment in weak acids,

$$K[H_2O(l)] = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

$$K_b = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

or for the reaction, $BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$

$$K_b = \frac{[B^+(aq)][OH^-(aq)]}{[BOH(aq)]}$$

Alternatively, if c = initial concentration of base and α = degree of ionization of base, when equilibrium is reached, the equilibrium constant can be written as:

$$\therefore K_b = \frac{c\alpha^2}{(1-\alpha)}$$

The production of hydroxide ions in this *base ionization reaction* means that $[OH^-(aq)] > [H^+(aq)]$ and therefore pH > 7.

The values of the ionization constants of some weak bases at 298 K are given in the following table.

Table 2.3 The ionization constants of some selected weak bases (at 298K)

Base	K_b
Dimethylamine, $(CH_3)_2NH$	5.40×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Pyridine, C_5H_5N)	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $CO(NH_2)_2$	1.30×10^{-14}

In solving problems involving weak bases, we follow the same procedure we used for weak acids. The main difference is that we calculate $[OH^-(aq)]$ first rather than $[H^+(aq)]$ and the following example shows this approach.

Example 2.18

Calculate the pH of a 0.40 mol dm^{-3} ammonia solution. $K_b = 1.80 \times 10^{-5}$

Answer

The following equilibrium reaction exists and let x be the equilibrium concentration of $NH_4^+(aq)$ and $OH^-(aq)$ ions in mold m^{-3}, we summarize:

	$NH_3(aq) + H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq) +$	$OH^-(aq)$
Initial concentration/ mol dm^{-3}	0.4		0	0
Concentration change/ mol dm^{-3}	$-x$		$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$(0.4-x)$		$+x$	$+x$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]} = 1.80 \times 10^{-5}$$

$$\frac{(x)(x)}{(0.4-x)} = 1.80 \times 10^{-5}$$

Applying the approximation $0.40 - x \sim 0.40$, we obtain

$$\frac{(x^2)}{0.4} = 1.80 \times 10^{-5}$$

$x = [OH^-(aq)] = 2.7 \times 10^{-3}$ mol dm^{-3}

Note: *To test the approximation, {[2.7 × 10^{-3}]/0.4 }× 100% = 0.68 %, i.e. the assumption is valid.*

$\therefore$ pOH = -log (2.7 × 10^{-3}) = 2.57

Applying the relationship pH + pOH = 14.00, we get

pH = 14.00 – 2.57 = 11.43

(or $[OH^-(aq)] = (2.7 \times 10^{-3})$, $\therefore [H^+(aq)] = 10^{-14}/2.7 \times 10^{-3} = 3.7 \times 10^{-12}$ $\therefore$ pH = 11.43)

2.2.8 Relation between K_a and K_b

K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Consider the example:

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

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

The conjugate base, $CH_3COO^-(aq)$, reacts with water according to the equation

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

The base ionization constant for the reaction,

$$K_b = \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

Consider the product of these two ionization constants.

$$K_a \times K_b = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} \times \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

$$K_a \times K_b = [H_3O^+(aq)][OH^-(aq)]$$

i.e. $\boldsymbol{K_a \times K_b = K_w}$

When the two reactions are added we see that it is simply the autoionization of water.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \quad \text{-----} \quad K_a$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq) \quad \text{-----} \quad K_b$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad \text{-----} \quad K_w$$

This follows the general rule in chemical equilibrium as we have discussed earlier,

Note: *If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.*

Note that the relation $\boldsymbol{K_a K_b = K_w}$ can also be obtained by considering the ionization of a weak base too.

From this we have $K_a \times K_b = K_w$ and thus,

$$K_a = \frac{K_w}{K_b} \text{ and } K_b = \frac{K_w}{K_a}$$

From this we can see that the stronger the acid (the larger K_a), the weaker is the conjugate base (the smaller K_b), and vice versa.

2.2.9 Hydrolysis of salts and the pH of their solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions formed on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending on the nature of salts. The process of interaction between water and cations/anions or both of salts is called ***hydrolysis***. The pH of the solution gets affected by this interaction. The cations (e.g.: Na^+, K^+, Ca^{2+}, Ba^{2+}, etc.) of strong bases and anions (e.g.: Cl^-, Br–, NO_3^-, ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. For example;

$$NaNO_3(s) \rightarrow Na^+(aq) + NO_3^-(aq)$$

However, the other categories of salts do undergo hydrolysis.
We now consider the hydrolysis of the salts of the following types:

(i) salts of a weak acid and a strong base, e.g.: CH_3COONa.
(ii) salts of a strong acid and a weak base, e.g.: NH_4Cl.
(iii) salts of a weak acid and a weak base, e.g.: CH_3COONH_4.

In the first case, CH_3COONa being a salt of the weak acid CH_3COOH and the strong base NaOH, gets completely ionised in aqueous solution.

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH^- ions

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

Acetic acid being a weak acid ($K_a = 1.8 \times 10^{-5}$) remains mainly unionized/undissociated in solution. This results in increase of OH^- ion concentration in the solution making it basic. The pH of such a solution is more than 7.

Example 2.19

Calculate the pH of a 0.10 mol dm^{-3} solution of sodium acetate (CH_3COONa). $K_{b(CH_3COO^-)} = 5.6 \times 10^{-10}$

Answer

As CH_3COONa completely ionizes into $CH_3COO^-(aq)$ and $Na^+(aq)$ in solution, $CH_3COO^-(aq)$ ion undergoes hydrolysis.

	$CH_3COO^-(aq) + H_2O(l)$	$\rightleftharpoons$ $CH_3COOH(aq)$	$+ OH^-(aq)$
Initial concentration/ mol dm^{-3}	0.10	0	0
Concentration change/ mol dm^{-3}	$-x$	$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$0.10 - x$	$+x$	$+x$

Now we can write the equilibrium constant for the hydrolysis or the base ionization constant as.

$$K_b = \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

Substituting above values at equilibrium,

$$K_b = \frac{x^2}{(0.10 - x)} = 5.6 \times 10^{-10}$$

Since K_b is very small and the initial concentration of the base is large, we can apply the approximation $0.10 - x \sim 0.10$

$$\frac{x^2}{0.10} \sim 5.6 \times 10^{-10}$$

$$x^2 = 5.6 \times 10^{-11}$$

$$x = [OH^-(aq)] = 7.5 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\therefore pOH = 5.13$$

$$pH = 14.00 - 5.13 = 8.87$$

Similarly, NH_4Cl formed from the weak base, NH_4OH and the strong acid, HCl, dissociates completely in water.

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

Ammonium ions undergo hydrolysis with water to form $NH_4OH(aq)$ and $H^+(aq)$ ions

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH\,(aq) + H^+(aq)$$

Ammonium hydroxide is a weak base ($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionised in solution. This results in increase of H^+ ion concentration in solution making the solution acidic. Thus, the pH of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of CH_3COONH_4 salt formed from a weak acid and a weak base. The ions formed undergo hydrolysis as follow:

$$CH_3COO^-(aq) + NH_4^+(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NH_4OH(aq)$$

CH_3COOH and NH_4OH, also remain in partially dissociated form:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$
$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

However, whether a solution containing such a salt is acidic, basic, or neutral depends on the relative strengths of the weak acid and the weak base. We can make qualitative predictions about these solutions as follows.

- ***$K_b > K_a$ ($pK_b < pK_a$); i.e if K_b for the anion is greater than K_a for the cation, then the solution must be basic because the anion will hydrolyze to a greater extent than the cation. At equilibrium, there will be more OH^- ions than H^+ ions.***
- ***$K_b < K_a$ ($pK_b > pK_a$); i.e, if K_b for the anion is smaller than K_a for the cation, the solution will be acidic because cation hydrolysis will be more extensive than anion hydrolysis.***
- ***$K_a \sim K_b$ ($pK_b \sim pK_a$); If K_a is approximately equal to K_b, the solution will be nearly neutral.***

2.2.10 Aqueous solutions containing a common ion

In previous sections in acid-base ionization and salt hydrolysis we have discussed the properties of solutions containing a single solute. In the solutions of two dissolved solutes containing the same ion or a *common ion*, properties will be different. A common ion suppresses the ionization of a weak acid or a weak base.

For example, when both sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and ionize to produce CH_3COO^- ions as shown in the following equations where $CH_3COONa(aq)$ dissociates completely while $CH_3COOH(aq)$ undergoes partial dissociation.

$$CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

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

According to Le Chatelier's principle, the addition of CH_3COO^- ions from CH_3COONa to a solution of CH_3COOH will suppress the ionization of CH_3COOH by shifting the equilibrium from right to left causing decrease in the hydrogen ion concentration. Therefore a solution containing both CH_3COOH and CH_3COONa will be *less* acidic than a solution containing only CH_3COOH at the same concentration. The shift in equilibrium of the ionization of acetic acid is caused by the acetate ions from the salt. CH_3COO^- is the common ion because it is supplied by both CH_3COOH and CH_3COONa.

> The ***common ion effect*** is *the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substances.*

The common ion effect plays an important role in determining the pH of a solution and the solubility of a slightly soluble salt.

Let us consider the pH of a solution containing a weak acid, HA, and a soluble salt of the weak acid, such as NaA.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

We can write,

$$[H_3O^+(aq)] = K_a \frac{[HA(aq)]}{[A^-(aq)]}$$

Taking -log on both sides,

$$-\log [H_3O^+(aq)] = -\log K_a - \log \frac{[HA(aq)]}{[A^-(aq)]}$$

$$-\log \left[H_3O^+(aq)\right] = -\log K_a + \log \frac{[A^-(aq)]}{[HA(aq)]}$$

We can write,

$$pH = pK_a + \log \frac{[A^-(aq)]}{[HA(aq)]}$$

or

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

The above expression is called ***Henderson-Hasselbalch*** *equation.*

If we know $\boldsymbol{K_a}$ and the concentrations of the acid and the salt of the acid, we can calculate the pH of the solution.

In problems that involve the common ion effect, we are usually given the starting concentrations of a weak acid HA and its salt, such as NaA. As long as the concentrations of these species are reasonably high (0.10 mol dm^{-3}), we can neglect the ionization of the acid and the hydrolysis of the salt. This is a valid approximation because HA is a weak acid and the extent of the hydrolysis of the $A^-(aq)$ ion is generally very small. Moreover, the presence of common ion $A^-(aq)$ from the salt NaA further suppresses the ionization of HA and the presence of unionized HA further suppresses the hydrolysis of $A^-(aq)$. Thus we can use the starting concentrations as the equilibrium concentrations in the Henderson-Hasselbalch equation.

Example 2.20

(i) Calculate the pH of a solution containing 0.20 mol dm^{-3} CH_3COOH and 0.40 mol dm^{-3} CH_3COONa.

(ii) What would be the pH of a 0.20 mol dm^{-3} CH_3COOH solution if no salt was present? $K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$

Answer

(i) $CH_3COONa(s)$ is a strong electrolyte and hence it dissociates completely giving $[CH_3COO^-(aq)]$ as 0.40 mol dm^{-3} and we can neglect the $[CH_3COO^-(aq)]$ from the CH_3COOH acid as its dissociation is suppressed. Therefore, we can take $[CH_3COO^-(aq)]$ as 0.40 mol dm^{-3} and $[CH_3COOH(aq)]$ as 0.20 mol dm^{-3}.

$$CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

$$\underset{0.20 \text{ mol dm}^{-3}}{CH_3COOH(aq)} + H_2O(l) \rightleftharpoons \underset{0.40 \text{ mol dm}^{-3}}{CH_3COO^-(aq)} + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 1.8 \times 10^{-5}$$

$$[H_3O^+(aq)] = \frac{(0.20)}{(0.40)} \times 1.8 \times 10^{-5} = 9.0 \times 10^{-6} \text{ mol dm}^{-3}$$

$$pH = -\log[H_3O^+(aq)] = 5.04$$

or we can use

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$pH = -\log(K_a) + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$pH = 4.74 + \log \frac{0.40}{0.20}$$

$$pH = 4.74 + \log 2$$

$$pH = 5.04$$

(ii) without common ion we have only the equilibrium of

	$CH_3COOH(aq) + H_2O(l)$	$\rightleftharpoons$	$CH_3COO^-(aq)$	+	$H_3O^+(aq)$
Initial concentration/ mol dm^{-3}	0.20		0		0
Concentration change/ mol dm^{-3}	$-x$		$+x$		$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$0.20 - x$		$+x$		$+x$

Substituting with the assumption $0.20 - x \sim 0.20$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 1.8 \times 10^{-5}$$

$$\frac{(x)^2}{0.20} = 1.8 \times 10^{-5}$$

$$x = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\therefore [H_3O^+(aq)] = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = 2.70$$

This shows clearly that the presence of the common ion CH_3COO^- suppresses the ionization of the acid CH_3COOH.

Following example shows an important situation, when the concentration of the acid and salt are the same.

Example 2.21

Calculate the pH of a 1.0 dm^3 solution made by adding 0.10 mol of acetic acid and 0.10 mol of sodium acetate.

Answer

In this case the $[CH_3COO^-(aq)]$ is the concentration of CH_3COONa because it ionizes completely and therefore we can write:

	$CH_3COOH(aq) + H_2O(l)$	$\rightleftharpoons$	$CH_3COO^-(aq)$	+	$H_3O^+(aq)$
Initial concentration/ mol dm^{-3}	0.10		0		0.10
Change in concentration/ mol dm^{-3}	$-x$		$+x$		$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$0.10 - x$		$+x$		$0.10 + x$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 1.8 \times 10^{-5}$$

$$\frac{x\,(0.10 + x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

As x is small, we can write,

$$\frac{x\,(0.10)}{(0.10)} = 1.8 \times 10^{-5}$$

$$x = [H_3O^+(aq)] = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = 4.74$$

$$\textbf{i.e. pH} = \textbf{pK}_\textbf{a}$$

The common ion effect also operates in a solution containing a weak base, such as NH_3, and a salt of the base, say NH_4Cl. At equilibrium

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

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

Here, $NH_4^+(aq)$ is predominant over $NH_3(aq)$ as it comes from the complete ionization of NH_4Cl and hence the equilibrium $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ is suppressed. Therefore, in this solution, pH is mainly controlled by the equilibrium

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

We can write,

$$K_a = \frac{[H_3O^+(aq)]\,[NH_3(aq)]}{[NH_4^+(aq)]}$$

$$[H_3O^+(aq)] = \frac{K_a\,[NH_4^+(aq)]}{[NH_3(aq)]}$$

$$-\log [H_3O^+(aq)] = -\log K_a - \log \frac{[NH_4^+(aq)]}{[NH_3(aq)]}$$

$$-\log [H_3O^+(aq)] = -\log K_a + \log \frac{[NH_3(aq)]}{[NH_4^+(aq)]}$$

We can write

$$\text{pH} = \text{pK}_a + \log \frac{[NH_3(aq)]}{[NH_4^+(aq)]}$$

$$\text{pH} = -\log(K_a) + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

A solution containing both NH_3 and its salt NH_4Cl is less basic than a solution containing only NH_3 at the same concentration. The common ion NH_4^+ suppresses the ionization of NH_3 in the solution containing both the base and the salt.

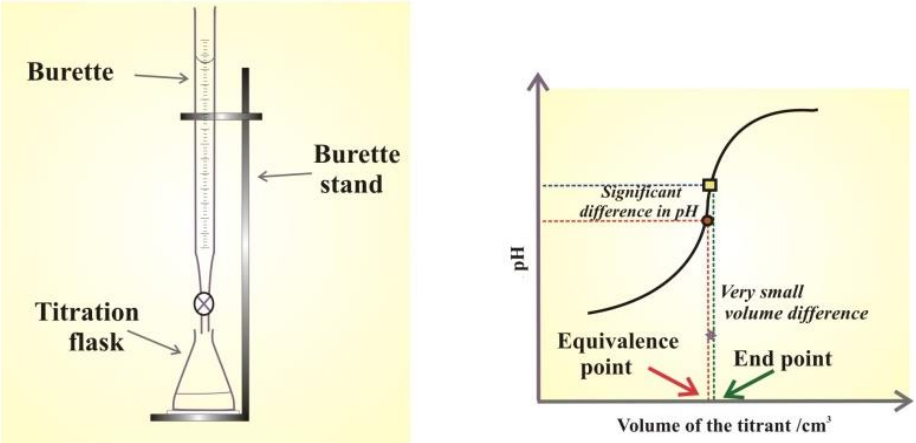
2.2.11 Volumetric titrations

Titration is a procedure for determining the concentration of a solution using another solution of known concentration, called the standard solution. In this usually we perform the volume measurements and find the required volume of the one necessary to react completely with the other. The determination of the volume depends on the way we find the completion of the reaction.

Equivalence points and end points

For a titration to be accurate we must add a stoichiometrically equivalent amount of the titrant (a solution with known concentration in a burette) to a solution containing the analyte (a solution with unknown concentration in a titration flask). We call the volume of the titrant required to reach this stoichiometric mixture the **equivalence point, V_{eq}.**

Knowing the stoichiometry of the titration reaction(s), we can calculate the amount of moles of the analyte. Unfortunately, in most titrations we usually have no obvious indication that the equivalence point has been reached. Instead, we stop adding titrant when we reach an **end point** of our choosing. Often this end point is indicated by a change in the color of a substance added to the solution containing the analyte. Such substances are known as **indicators.** Usually**,** indicators change their colour along with the change in pH of the solution, so that the volume of the titrant needed to reach the end point is little in excess compared to the equivalence point volume (1 drop of the titrant or 0.05 cm^3). The difference between the end point and the equivalence point is called the **titration error.** Though the difference in volume is very small, we can see that this causes a significant change in pH. Hence the pH values at the end point and equivalence point are not comparable. In the case when we know the concentrations of both the titrant and the analyte, we can construct the pattern of change in a measured property (for example pH) with the volume of the titrant and by this way the equivalence point is clearly defined. Following figures show the set-up of the titration and the comparison between equivalence and end points.



(a) (b)

Figure 2.16 **(a)** A sketch of a titration set up: A solution with unknown concentration is placed in a titration flask and the solution is titrated against the tirant in the burette by adding it slowly. **(b)** shows the difference in end point and equivalence point where end point is determined by using an indicator in which we need some excess of the titrant (~ 0.05 cm^3) to observe the colour change in the indicator. In the case of equivalnce point it is the point at which stoichiometric amounts are exacatly reacted. Therefore, equivalence point volume is always less than that of end point volume. This small difference in volumes, however, causes very large difference in pH.

Acid-base titrations

Under this section, we will consider four types of titrations involving:

(i) a strong acid and a strong base,
(ii) a weak acid and a strong base,
(iii) a strong acid and a weak base, and
(iv) a weak acid and a weak base .

Titrations involving a weak acid and a weak base are complicated by the hydrolysis of both the cation and the anion of the salt formed.

In the following section, we will consider the above types of titrations with the understanding of their respective equivalence points and the variation and calculation of pH along the titration (along the volume of the titrant). It has to be noted that it is simply an understanding of pH variation theoretically by considering the titration between the analyte of known concentration and the titrant with a known concentration. With these considerations, we can construct the **titration curves (volume *vs* pH)** theoretically. i.e. A **titration curve** provides us with a visual picture of how a property, such as pH, changes as we add the titrant.

- **Strong acid – strong base titrations**

Consider the titration of 25.00 cm^3 of 0.100 mol dm^{-3} HCl with 0.100 mol dm^{-3} NaOH.

***(Note:** The volumes are measured with burette and pipette with the accuracy of 0.00 cm^3.)*

Reaction taking place is,

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

As HCl(aq), NaOH(aq) and NaCl(aq) are strong electrolytes, we can write the above reaction as,

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

We can see that the pH of the solution depends on the relative concentrations of $H^+(aq)$ and $OH^-(aq)$ ions present at each stage of the volume of NaOH added and therefore it is possible to consider the situations like pH at the equivalence point, pH before the equivalence point, and pH after the equivalence point.

Let us first calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point,

moles HCl = amount of moles NaOH (as the stoichiometry between HCl and NaOH is 1 : 1)

Applying the simple formula $C_aV_a = C_bV_b$
where the subscript 'a' indicates the acid, HCl, and the subscript 'b' indicates the base, NaOH:

(i) The volume of NaOH needed to reach the equivalence point, therefore, is

$$0.100 \times 25.00 = 0.100 \times V_b$$
$$\therefore V_b = 25.00 \text{ cm}^3$$

(ii) Initially the solution is 0.100 mol dm^{-3} in HCl. Since HCl is a strong acid, means that the pH is

$$pH = -\log[H_3O^+] = -\log[HCl] = -\log(0.100) = 1.00$$

(iii) Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of excess HCl. After adding 10.00 cm^3 of NaOH, i.e. stoichiometrically lesser amount of NaOH compared to the amount of HCl present, the concentration of excess (or remaining) HCl has to be estimated.

Initial amount of HCl (in moles) $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$
$= 2.50 \times 10^{-3}\ \text{mol}$

Amount of NaOH added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 10.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$
$= 1.0 \times 10^{-3}\ \text{mol}$

∴ Amount of HCl reacted $= 1.0 \times 10^{-3}\ \text{mol}$

∴ Amount of HCl remaining $= (2.50 \times 10^{-3} - 1.00 \times 10^{-3})\ \text{mol}$
$= 1.50 \times 10^{-3}\ \text{mol}$

∴ Concentration of HCl (H_3O^+) remaining $= \frac{1.5 \times 10^{-3}\ \text{mol}}{35.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$
$= 0.043\ \text{mol dm}^{-3}$

∴ pH = -log (0.043) = 1.37

(iv) At the equivalence point (after addition of 25.00 cm^3 of NaOH) all the H^+ and OH^- ions are consumed. Also the salt NaCl present as Na^+ and Cl^- does not undergo hydrolysis. Therefore, for the reaction of a strong base with a strong acid at the equivalence point the only equilibrium reaction (net reaction) of importance is,

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

At the equivalence point, $[H^+(aq)]=[OH^-(aq)]$ *and the* pH *of the solution is 7.00.*

(v) After adding 35.00 cm^3 of NaOH, i.e. stoichiometrically higher amount of NaOH compared to the amount of HCl present, the concentration of excess (or remaining) NaOH has to be estimated.

Initial amount of HCl (in moles) $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$
$= 2.50 \times 10^{-3}\ \text{mol}$

Amount of NaOH added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 35.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$
$= 3.50 \times 10^{-3}\ \text{mol}$

∴ Amount of HCl reacted $= 2.5 \times 10^{-3}\ \text{mol}$

∴ Amount of NaOH remaining $= (3.50 \times 10^{-3} - 2.50 \times 10^{-3})\ \text{mol}$
$= 1.0 \times 10^{-3}\ \text{mol}$

∴ Concentration of NaOH (OH^-) remaining $= \frac{1.0 \times 10^{-3}\ \text{mol}}{60.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$
$= 0.017\ \text{mol dm}^{-3}$

∴ pOH = -log (0.017) = 1.77

∴ pH = 14.00 - 1.77 = 12.23

Important: *Now we can see that the* pH *curve has some deflection around* pH=*7. Let's see the changes in* pH *in the vicinity of the equivalence point.*

Addition of 24.90 cm^3 of NaOH:

After adding 24.90 cm^3 of NaOH, i.e. stoichiometrically lesser amount of NaOH compared to the amount of HCl present, the concentration of excess (or remaining) HCl has to be estimated.

Initial amount of HCl (in moles) $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 2.50 \times 10^{-3}\ \text{mol}$

Amount of NaOH added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 24.90\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 2.49 \times 10^{-3}\ \text{mol}$

$\therefore$ Amount of HCl reacted $= 2.49 \times 10^{-3}\ \text{mol}$

$\therefore$ Amount of HCl remaining $= (2.50 \times 10^{-3} - 2.49 \times 10^{-3})\ \text{mol}$

$= 1.00 \times 10^{-5}\ \text{mol}$

$\therefore$ Concentration of HCl (H_3O^+) remaining $= \frac{1.00 \times 10^{-5}\ \text{mol}}{49.90\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$

$= 2.00 \times 10^{-4}\ \text{mol dm}^{-3}$

$\therefore$ pH = -log (2.00×10^{-4}) = 3.7

Addition of 25.10 cm^3 of NaOH:

Initial amount of HCl (in moles) $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 2.50 \times 10^{-3}\ \text{mol}$

Amount of NaOH added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.10\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 2.51 \times 10^{-3}\ \text{mol}$

$\therefore$ Amount of HCl reacted $= 2.50 \times 10^{-3}\ \text{mol}$

$\therefore$ Amount of NaOH remaining $= (2.51 \times 10^{-3} - 2.50 \times 10^{-3})\ \text{mol}$

$= 1.0 \times 10^{-5}\ \text{mol}$

$\therefore$ Concentration of NaOH (OH^-) remaining $= \frac{1.0 \times 10^{-5}\ \text{mol}}{50.10\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$

$= 2.00 \times 10^{-4}\ \text{mol dm}^{-3}$

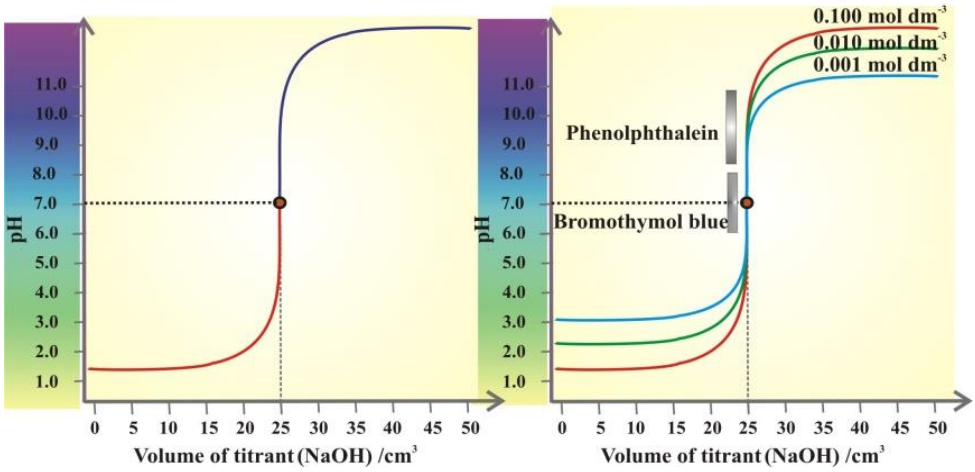
$\therefore$ pOH = -log (2.00×10^{-4}) = 3.7

$\therefore$ pH = 14.00 - 3.70 = 10.30

After addition of NaOH volumes higher than 25.00 cm^3, i.e. stoichiometrically higher amount of NaOH compared to the amount of HCl present, the concentration of excess (or remaining) NaOH has to be estimated.

In this strong acid *vs* strong base titration we can see that there is a drastic change in pH in the vicinity of the equivalence point (6.6 pH unit change within the 0.020 cm^3 volume interval). By plotting the calculated pH values against different volumes of NaOH added,

we can obtain the pH curve in Figure 2.17(a) and 2.17(b) shows the behaviour of pH curves with the variation of initial concentration of the acid and base.



(a) (b)

Figure 2.17 **(a)** Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} HCl with 0.100 mol dm^{-3} NaOH. A steep change in pH occurs in the vicinity of equivalence point at which pH = 7.0 with 25.00 cm^3 of NaOH. **(b)** Shows the variation in pH curves with the initial concentrations of HCl and NaOH. When the initial concentration decreases the spread of the pH curve decreases. Role of indicators phenolphthalein and bromothymol blue will be discussed in a separate section.

- **Weak acid – strong base titrations**

Consider the reaction between acetic acid (a weak acid) and sodium hydroxide (a strong base):

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

As NaOH is a strong base we can rewrite the reaction as,

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

As we have discussed earlier, the CH_3COO^- (aq) undergoes hydrolysis and the reaction will determine the pH at the equivalence point of the titration.

The acetate ion undergoes hydrolysis as follows:

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

Therefore, at the equivalence point, where we have only sodium acetate, the pH will be greater than 7 as a result of the excess OH^-(aq) ions formed due to the hydrolysis of acetate ions. Let's try to understand the titration curve of this type of a titration where a weak acid is titrated with a strong base.

Consider the titration of 25.00 cm^3 of 0.100 mol dm^{-3} $CH_3COOH(aq)$ with 0.100 mol dm^{-3} NaOH. K_a $(CH_3COOH) = 1.80 \times 10^{-5}$

We can see that the pH of the solution depends on the relative concentrations of the undissociated $CH_3COOH(aq)$ acid and $CH_3COO^-(aq)$ ions (formed as $CH_3COONa(aq)$) present) at each stage of the volume of NaOH added. Similar to the titration between a strong acid and a strong base, it is possible to consider the situations like pH at the equivalence point, pH before the equivalence point, and pH after the equivalence point.

Let us first calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point ,

Amount of moles CH_3COOH = Amount of moles NaOH (as the stoichiometry between CH_3COOH and NaOH is 1 : 1)

Applying simple formula $C_aV_a = C_bV_b$
where the subscript 'a' indicates the acid, CH_3COOH, and the subscript 'b' indicates the base, NaOH.

(i) The volume of NaOH needed to reach the equivalence point, therefore, is

$$0.100 \times 25.00 = 0.100 \times V_b$$
$$\therefore V_b = 25.00 \text{ cm}^3$$

(ii) Initially the solution is 0.100 mol dm^{-3} in CH_3COOH. Since CH_3COOH is a weak acid, $[H_3O^+]$ will be determined by its partial ionization, i.e

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

$[H_3O^+]$ is calculated from $\boldsymbol{K_a}$ as,

	$CH_3COOH(aq)$ + $H_2O(l)$ ⇌	$CH_3COO^-(aq)$ +	$H_3O^+(aq)$
Initial concentration/ mol dm^{-3}	0.1	0	0
Change in concentration/ mol dm^{-3}	x	$+x$	$+x$
∴ Equilibrium concentration/ mol dm^{-3}	$(0.10 - x)$	$+x$	$+x$
∴ Equilibrium concentration/ mol dm^{-3} (with the assumption $(0.10 - x) \sim 0.1$)	0.10	$+x$	$+x$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = \frac{x^2}{(0.1)} = 1.80 \times 10^{-5}$$
$$x^2 = 1.80 \times 10^{-6}$$
$$x = 1.34 \times 10^{-3}$$

$$pH = -\log[H_3O^+] = -\log[1.34 \times 10^{-3}] = 2.87$$

Or

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

$$K_a = \frac{\left[H_3O^+(aq)\right]^2}{C_0},$$

where initail concentration of the acid is C_0

$$\left[H_3O^+(aq)\right] = (K_a\, C_0)^{1/2}$$

$$-\log\left[H_3O^+(aq)\right] = -\log(K_a)^{\frac{1}{2}} - \log(C_0)^{\frac{1}{2}}$$

$$-\log\left[H_3O^+(aq)\right] = -\frac{1}{2}\log(K_a) \quad -\frac{1}{2}\log(C_0)$$

$$\mathbf{pH} = -\frac{1}{2}\mathbf{pK_a} - \frac{1}{2}\log(C_0)$$

(iii) Before the equivalence point, the added amount of NaOH is stoichiometrically lesser than the amount of CH_3COOH acid present in the solution. Therefore, the solution contains undissociated CH_3COOH acid and the salt CH_3COONa. In other words, now we have a mixture of a weak acid and its salt (conjugate base), i.e. a buffer solution. To calculate pH, we can use the **Henderson-Hasselbalch** equation with our knowledge of buffer solutions.

Let's consider the reaction after the addition of 10.00 cm^3 of 0.100 mol dm^{-3} NaOH.

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Initial amount of CH_3COOH $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$
$= 2.50 \times 10^{-3}\ \text{mol}$

Amount of NaOH added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 10.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$
$= 1.0 \times 10^{-3}\ \text{mol}$

$\therefore$ Amount of CH_3COOH reacted $= 1.0 \times 10^{-3}\ \text{mol}$

$\therefore$ Amount of CH_3COOH remaining $= (2.50 \times 10^{-3} - 1.00 \times 10^{-3})\ \text{mol}$
$= 1.50 \times 10^{-3}\ \text{mol}$

$\therefore$ Concentration of CH_3COOH remaining $= \frac{1.5\times10^{-3}\ \text{mol}}{35.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$
$= 0.043\ \text{mol dm}^{-3}$

Amount of CH_3COONa formed = Amount of NaOH added $= 1.0 \times 10^{-3}\ \text{mol}$

Concentration of CH_3COONa formed $= \frac{1.0\times10^{-3}\ \text{mol}}{35.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$
$= 0.029\ \text{mol dm}^{-3}$

Substituting these values in,

$$\text{pH} = \text{pK}_a + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = 4.74 + \log\frac{(0.029)}{(0.043)}$$

$$\text{pH} = 4.57$$

(iv) At the equivalence point (after addition of 25.00 cm^3 of NaOH) all the CH_3COOH and NaOH are consumed. The salt CH_3COONa present undergoes hydrolysis as,

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

According to the reaction, $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$
The amount of CH_3COONa ($CH_3COO^-(aq)$) formed $= 2.50 \times 10^{-3}$ mol

$\therefore$ The concentration of the salt $= \frac{2.5\times10^{-3}\ \text{mol}}{50.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$
$= 0.05\ \text{mol dm}^{-3}$

	$CH_3COO^-(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$CH_3COOH(aq)$ +	$OH^-(aq)$
Initial concentration/ mol dm^{-3}	0.05	0	0
Change in concentration/ mol dm^{-3}	$-x$	$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$(0.05 - x)$	$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}) (with the assumption $(0.05 - x) \sim 0.05$)	0.05	$+x$	$+x$

For the above hydrolysis reaction we can write the expression for K_b as,

$$K_b = \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]} = \frac{x^2}{(0.05)} = \frac{K_w}{K_a} = 5.6 \times 10^{-10}$$

$$x = [OH^-(aq)] = 5.3 \times 10^{-6}\ \text{mol dm}^{-3}$$

$$\therefore pOH = 5.28$$

$$\therefore pH = 14.00 - 5.28$$

$$\therefore pH = 8.72$$

Or,

$$K_b = \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

$$K_b = \frac{[OH^-(aq)]^2}{S},$$

where S is the concentration of the salt

$$[OH^-(aq)] = (K_b\ S)^{1/2}$$

$$-\log[OH^-(aq)] = -\log(K_b)^{\frac{1}{2}} - \log(S)^{\frac{1}{2}}$$

$$-\log[OH^-(aq)] = -\frac{1}{2}\log(K_b) - \frac{1}{2}\log S$$

$$pOH = -\frac{1}{2}pK_b - \frac{1}{2}\log S$$

Substituting, $pH + pOH = pK_w$ *and* $pK_a + pK_b = pK_w$

$$pK_w - pH = -\frac{1}{2}(pK_w - pK_a) - \frac{1}{2}\log S$$

$$\therefore pH = \frac{1}{2}pK_a + \frac{1}{2}pK_w + \frac{1}{2}\log S$$

(v) After the equivalence point the total amount of CH_3COOH initially present gets converted to the salt CH_3COONa and excess NaOH will present as OH^-. Therefore, the pH of the mixture is determined by the excess concentration of $[OH^-(aq)]$.

After adding 35.00 cm^3 of NaOH, i.e. stoichiometrically higher amount of NaOH compared to the amount of CH_3COOH present, the concentration of excess (or remaining) NaOH has to be estimated.

Initial amount of CH_3COOH $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 2.50 \times 10^{-3}\ \text{mol}$

Amount of NaOH added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 35.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 3.50 \times 10^{-3}\ \text{mol}$

$\therefore$ Amount of CH_3COOH reacted $= 2.5 \times 10^{-3}\ \text{mol}$

$\therefore$ Amount of NaOH remaining $= (3.50 \times 10^{-3} - 2.50 \times 10^{-3})\ \text{mol}$

$= 1.0 \times 10^{-3}\ \text{mol}$

$\therefore$ Concentration of NaOH (OH^-) remaining $= \frac{1.0 \times 10^{-3}\ \text{mol}}{60.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$

$= 0.017\ \text{mol dm}^{-3}$

$\therefore$ pOH = -log (0.017) = 1.77

$\therefore$ pH = 14.00 - 1.77 = 12.23

Or, After the equivalence point, $[H_3O^+(aq)] = \frac{K_w}{[OH^-(aq)]}$

$[OH^-(aq)]$ ***is the excess concentration of the strong base***

And taking excess $[OH^-(aq)] = B'$

$$[H_3O^+(aq)] = \frac{K_w}{B'}$$

$$-\log[H_3O^+(aq)] = -\log(K_w) - (-\log B')$$

$$\mathbf{pH} = \mathbf{p}K_w + \log(B')$$

At the half-equivalence point:

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Concentrations of the acid and the conjugate base are equal.

$$\therefore \mathbf{pH} = \mathbf{p}K_a$$

We can summarize the above in the following pH curve in **Figure 2.18**.

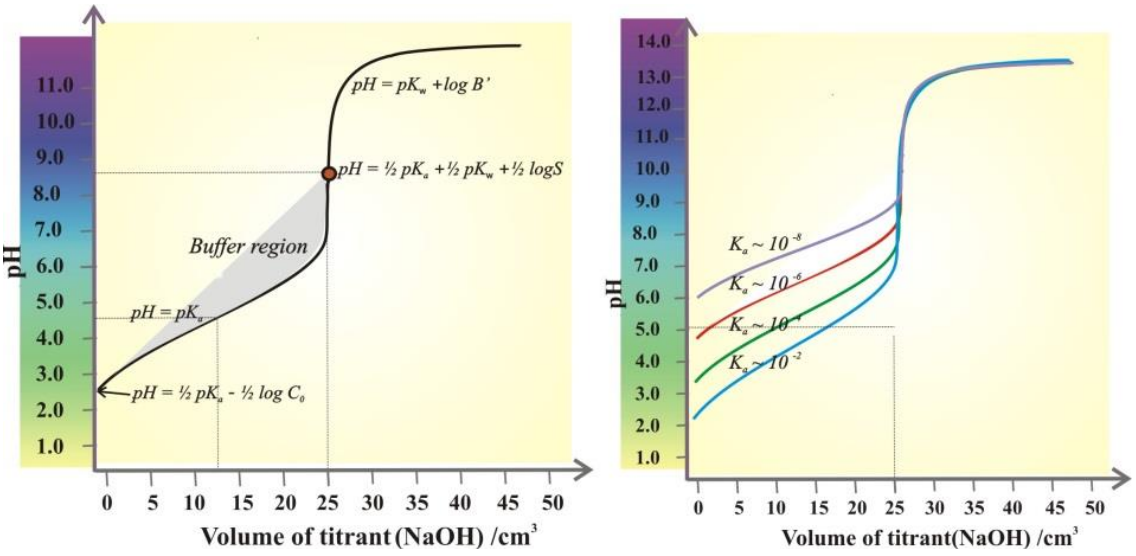


Figure 2.18 **(a)** Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} CH_3COOH with 0.100 mol dm^{-3} NaOH. Equivalnvce point occurs in basic region with pH of 8.72. In these titrations a buffer solution is formed below the equivalence point (will be explained in a separate section 12.3). Charateristics points with the pH functions are also marked. In **(b)** variations of pH curves with the strength of the weak acid are compared. Weaker the acid, the equivalence point shifts more to the basic side.

- **Strong acid – weak base titrations**

Let us consider the titration between NH_3, a weak base and HCl, a strong acid: the reaction taking place is;

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

or simply

$$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$$

We can see that the pH at the equivalence point is *less than 7* due to the hydrolysis of the $NH_4^+(aq)$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

Because of the volatility of an aqueous ammonia solution, it is more convenient to add HCl acid from a burette to the ammonia solution.

Example:

Let 25.00 cm^3 of 0.10 mol dm^{-3} NH_3, a weak base be titrated with 0.10 mol dm^{-3} HCl, a strong acid.

We can see that the pH of the solution depends on the relative concentrations of the undissociated NH_4Cl and NH_3 at each stage of the volume of HCl added. Therefore, like the case considered for the weak acid-strong base titration, it is possible to consider pH at the equivalence point, pH before the equivalence point, and pH after the equivalence point.

Let us first calculate the volume of HCl needed to reach the equivalence point. At the equivalence point,

Amount of moles of NH_3 = Amount of moles of HCl (as the stoichiometry between NH_3 and HCl is 1 : 1)

Applying the formula $C_aV_a = C_bV_b$

(i) The volume of HCl needed to reach the equivalence point, therefore, is

$$0.100 \times 25.00 = 0.100 \times V_b$$

$$\therefore V_b = 25.00 \text{ cm}^3$$

(ii) Initially the solution is 0.100 mol dm^{-3} in NH_3. Since NH_3 is a weak base, $[OH^-]$ will be determined considering its partial ionization, i.e

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

$[OH^-]$ is calculated from K_b as,

	$NH_3(aq) + H_2O(l)$ ⇌	$NH_4^+(aq)$ +	$OH^-(aq)$
Initial concentration/ mol dm^{-3}	0.1	0	0
Change in concentration/ mol dm^{-3}	$-x$	$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$(0.10 - x)$	$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3} (with the assumption $(0.10 - x) \sim 0.1$)	0.10	$+x$	$+x$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]} = \frac{x^2}{(0.1)} = 1.80 \times 10^{-5}$$

$$x^2 = 1.80 \times 10^{-6}$$

$$x = 1.34 \times 10^{-3}$$

$$pOH = -\log[OH^-(aq)] = -\log[1.34 \times 10^{-3}] = 2.87$$

$$\therefore pH = 14.00 - 2.87 = 11.13$$

(iii) Before the equivalence point, the added amount of HCl is stoichiometrically lesser than the amount of NH_3 present in the solution. Therefore, the solution contains undissociated NH_3 and the salt NH_4Cl. In other words, now we have a mixture of a

weak base and its salt (conjugate acid), i.e. a buffer solution. To calculate pH, we can use our knowledge of buffer solutions.

Let's consider the reaction after the addition of 10.00 cm^3 of 0.100 mol dm^{-3} HCl.

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

Initial amount of NH_3 $= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3}$
$= 2.50 \times 10^{-3}$ mol

Amount of HCl added $= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 10.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3}$
$= 1.0 \times 10^{-3}$ mol

$\therefore$ Amount of NH_3 reacted $= 1.0 \times 10^{-3}$ mol

$\therefore$ Amount of NH_3 remaining $= (2.50 \times 10^{-3} - 1.00 \times 10^{-3})$ mol
$= 1.50 \times 10^{-3}$ mol

$\therefore$ Concentration of NH_3 remaining $= \frac{1.5 \times 10^{-3} \text{ mol}}{35.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3}$
$= 0.043 \text{ mol dm}^{-3}$

Amount of NH_4Cl formed = Amount of HCl added $= 1.0 \times 10^{-3}$ mol

Concentration of NH_4Cl formed $= \frac{1.0 \times 10^{-3} \text{ mol}}{35.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} = 0.029 \text{ mol dm}^{-3}$

Substituting these values in,

$$pOH = pK_b + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$pOH = 4.74 + \log \frac{(0.029)}{(0.043)}$$

$$pOH = 4.57$$

$\therefore$ pH = 14.00 – 4.57 = 9.43

(iv) At the equivalence point (after addition of 25.00 cm^3 of HCl) all the NH_3 and HCl are consumed. The salt NH_4Cl present undergoes hydrolysis as,

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

According to the reaction, $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$
The amount of NH_4Cl (NH_4^+ (aq)) formed = 2.50×10^{-3} mol

$\therefore$ The concentration of the salt = $\frac{2.5 \times 10^{-3} \text{ mol}}{50.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} = 0.05 \text{ mol dm}^{-3}$

	$NH_4^+(aq) + H_2O(l)$	$\rightleftharpoons$ $NH_3(aq)$	$+ H_3O^+(aq)$
Initial concentration/ mol dm^{-3}	0.05	0	0
Change in concentration/ mol dm^{-3}	$-x$	$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$(0.05 - x)$	$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3} (with the assumption $(0.05 - x) \sim 0.05$)	0.05	$+x$	$+x$

For the above hydrolysis reaction we can write the expression for K_b as,

$$K_b = \frac{[NH_3(aq)][H_3O^+(aq)]}{[NH_4{}^+(aq)]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.05} \quad \text{(with the assumption)}$$

$$x^2 = 28 \times 10^{-12}$$

$$x = [H_3O^+(aq)] = 5.3 \times 10^{-6}$$

$$\therefore pH = 5.28$$

(v) After the equivalence point the total amount of NH_3 initially present gets converted to the salt NH_4Cl and excess HCl will be present as H_3O^+. Therefore, the pH of the mixture is determined by the excess concentration of $[H_3O^+(aq)]$.

In order to calculate pH after adding 35.00 cm^3 of HCl, i.e. stoichiometrically a higher amount of HCl compared to the amount of NH_3 present, the concentration of excess (or remaining) HCl has to be estimated.

Initial amount of NH_3 $= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3}$

$= 2.50 \times 10^{-3}$ mol

Amount of HCl added $= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 35.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3}$

$= 3.50 \times 10^{-3}$ mol

$\therefore$ Amount of NH_3 reacted $= 2.5 \times 10^{-3}$ mol

$\therefore$ Amount of HCl remaining $= (3.50 \times 10^{-3} - 2.50 \times 10^{-3})$ mol

$= 1.0 \times 10^{-3}$ mol

$\therefore$ Concentration of HCl ($H_3O^+(aq)$) remaining $= \frac{1.0 \times 10^{-3} \text{ mol}}{60.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3}$

$= 0.017 \text{ mol dm}^{-3}$

$\therefore$ *pH* = -log (0.017) = 1.77

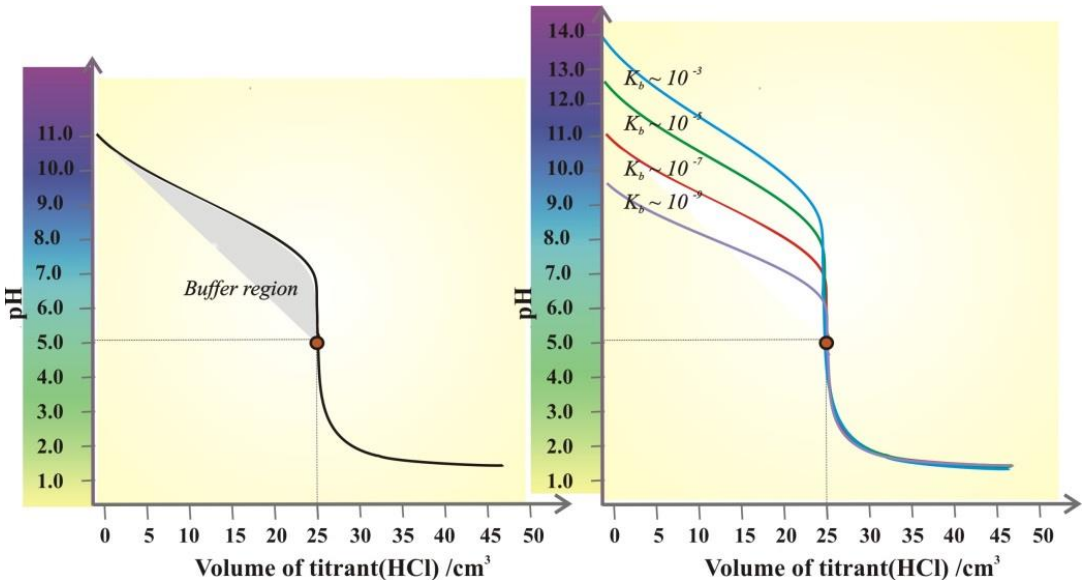


Figure 2.19 (a) Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} NH_3 with 0.100 mol dm^{-3} HCl. Equivalnvce point occurs in acidic region with pH of 5.28. In these titrations a buffer solution is formed too below the equivalence point. In (b) variations of pH curves with the strength of the weak base are compared. Weaker the base, the equivalence point shifts more to acidic side.

- **Weak acid- weak base titration**

When acetic acid, which is a weak acid, reacts with ammonia, the reaction taking place is,

$$CH_3COOH(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$$

Now we can see that the products contain the base CH_3COO^- and the acid NH_4^+. Therefore, the pH at the equivalence point id determined by the strength of the hydrolysis of these. We can write,

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \quad : \boldsymbol{K_a}$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \quad : \boldsymbol{K_b}$$

From these reactions, we see that H_3O^+ and OH^- ions are formed and they undergo neutralization. Though neutralization occurs, still we may not have equal amount of H_3O^+ and OH^- and hence pH ≠ 7 at the equivalence point. It depends on the relative strengths of $\boldsymbol{K_a}$ and $\boldsymbol{K_b}$: ***if*** $\boldsymbol{K_a} > \boldsymbol{K_b}$, ***the solution is acidic and if*** $\boldsymbol{K_a} < \boldsymbol{K_b}$, ***the solution is basic*** .

Another important feature in this kind of a titration is that there is no steep pH changing region in the pH curve and it mainly shows a deflecting point, resulting in difficulty to use an indicator to locate the equivalence point. Therefore, the titrations between a weak acid and a weak base are hardly carried out. Figure 2.20 shows the variation of pH in this type of a titration.

Note: *It has to be noted that the* pH *of such solutions is determined by using* p*K values of the acid and the base using the mathematical formula,*

$$pH = 7 + ½ (pK_a - pK_b)$$

The pH *of the solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.*

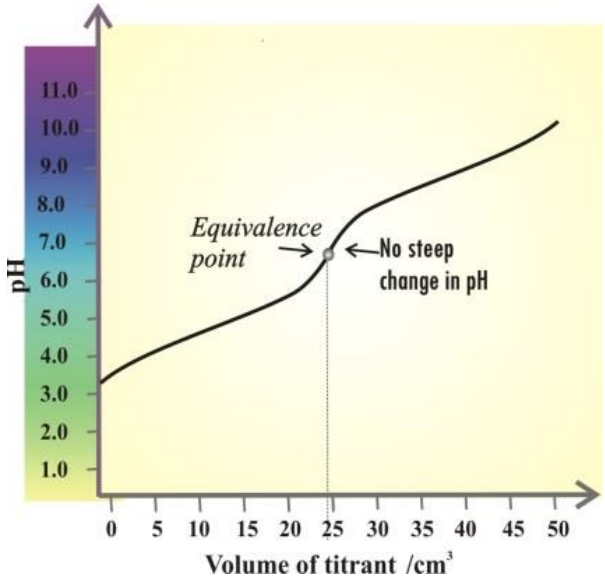


Figure 2.20 Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} CH_3COOH with 0.100 mol dm^{-3} NH_3. It is difficult to judge to location of the equivalence point as it depends on the relative strengths of the acid and the base. There is no steep change in pH in these types of systems.

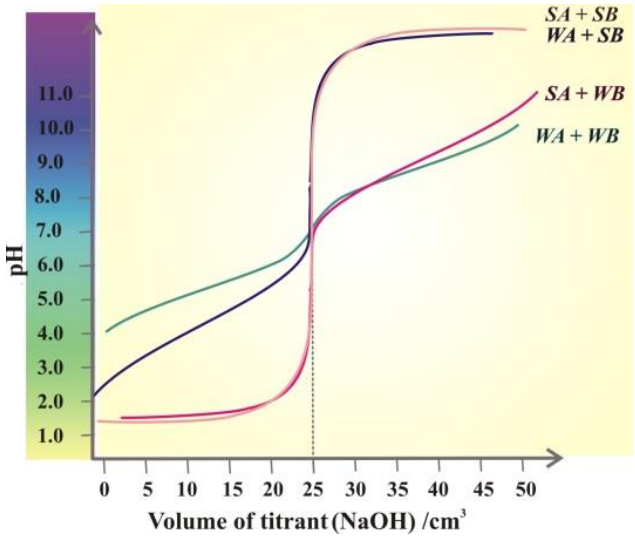


Figure 2.21 Summary of the four types of titrations with 0.100 mol dm^{-3} acid (mono basic) and 0.100 mol dm^{-3} base (mono acidic) discussed above. (SA-strong acid, SB-strong base, WA-Weak acid and WB-Weak base)

2.2.12 Di- and polybasic acids and di- and polyacidic bases

Some of the acids like oxalic acid ($H_2C_2O_4$), sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids. The ionization reactions of a *dibasic acid* H_2A are represented by the equations:

$$H_2A(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HA^-(aq)$$
$$HA^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^{2-}(aq)$$

And the corresponding equilibrium constants (*acid ionization constants*) are given below:

$$K_{a_1} = \frac{[H_3O^+(aq)][HA^-(aq)]}{[H_2A(aq)]}$$

$$K_{a_2} = \frac{[H_3O^+(aq)][A^{2-}(aq)]}{[HA^-(aq)]}$$

Likewise, the ionization reactions of a *diacidic base* B_2^- are represented by the equations:

$$B^{2-}(aq) + H_2O(l) \rightleftharpoons HB^-(aq) + OH^-(aq)$$
$$HB^-(aq) + H_2O(l) \rightleftharpoons H_2B(aq) + OH^-(aq)$$

And the corresponding equilibrium constants (*base ionization constants*) are given below:

$$K_{b_1} = \frac{[HB^-(aq)][OH^-(aq)]}{[B^{2-}(aq)]}$$
$$K_{b_2} = \frac{[H_2B(aq)][OH^-(aq)]}{[HB^-(aq)]}$$

Polyacidic base titrations

The pH curve for the titration of hydrochloric acid with sodium hydroxide has only one equivalence (end) point (Figure 2.17), but the pH curve for the addition of HCl(aq) (titrant) to Na_2CO_3(aq) (Figure 2.22) displays two equivalence points, i.e. two rapid change in pH. Here, for example, two successive reactions occur. The two end points in Figure 2.22 can be explained by two different proton transfer equations.

Sodium carbonate is a strong electrolyte and so fully dissociates into $Na^+(aq)$ and $CO_3^{2-}(aq)$ ions.

$$Na_2CO_3(aq) \rightarrow Na^+(aq) + CO_3^{2-}(aq)$$

Therefore, the major entities in the mixture are $Na^+(aq)$, $CO_3^{2-}(aq)$ and $H_2O(l)$. At the beginning of the titration, $H^+(aq)$ ions from HCl(aq) react with $CO_3^{2-}(aq)$ ions since carbonate ions are the strongest bases present in the initial mixture.

$$H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$$

Then, in a second reaction, protons from HCl(aq) react with the hydrogen carbonate ions formed in the first reaction.

$$H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$$

It is clear that at the first equivalence point, following equilibrium exists in the mixture and therefore the pH is determined by the hydrolysis of $HCO_3^-(aq)$ ions.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

At the second equivalence point following equilibrium exists in the mixture and therefore the pH is determined by the hydrolysis (first ionization) of H_2CO_3 (aq) acid.

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

By looking at the above two reactions one may note that; at the first equivalence point mixture is basic while it becomes acidic at the second equivalence point.

Example:

Let's consider a titration of 25.00 cm^3 of 0.10 mol dm^{-3} Na_2CO_3(aq) solution with 0.10 mol dm^{-3} HCl(aq) acid. Acid dissociation constants for the carbonic acid, H_2CO_3 are $K_{a_1} = 4.3 \times 10^{-7}$ mol dm^{-3} and $K_{a_2} = 4.7 \times 10^{-11}$ mol dm^{-3}.

From the molarities of the solutions, one can note that the first equivalence point occurs at 25.00 cm^3 and the second equivalence point occurs at the 50.00 cm^3 of HCl.

When we consider the dissociation of H_2CO_3 acid:

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) : K_{a_1}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) : K_{a_2}$$

Therefore,

$$K_{a_1} = \frac{[H_3O^+(aq)][HCO_3^-(aq)]}{[H_2CO_3(aq)]} = 4.3 \times 10^{-7} \text{ mol dm}^{-3}$$

$$K_{a_2} = \frac{[H_3O^+(aq)][CO_3^{2-}(aq)]}{[HCO_3^-(aq)]} = 4.7 \times 10^{-11} \text{ mol dm}^{-3}$$

Initial pH (at 0.00 cm^3 of HCl):

At this point as no acid has been added, and only 0.10 mol dm^{-3} Na_2CO_3(aq) sodium carbonate solution is present. The pH is determined by the extent of carbonate ion reaction with water to give $HCO_3^-(aq)$ and $OH^-(aq)$.

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq)$$

Here water acts as an acid, providing a proton to carbonate ion, the base. The equilibrium constant for this reaction can be written as;

$$K' = \frac{[HCO_3^-(aq)][OH^-(aq)]}{[CO_3^{2-}(aq)]}$$

Consider; $\frac{K_w}{K_{a_2}} = \frac{[H_3O^+(aq)][OH^-(aq)]}{\frac{[H_3O^+(aq)][CO_3^{2-}(aq)]}{[HCO_3^-(aq)]}} = \frac{[HCO_3^-(aq)][OH^-(aq)]}{[CO_3^{2-}(aq)]} = K' = K_{b_1}$

$$\therefore K_{b_1} = \frac{1.0 \times 10^{-14}\ mol^2\ dm^{-6}}{4.7 \times 10^{-11}\ mol\ dm^{-3}} = 2.13 \times 10^{-4}\ mol\ dm^{-3}$$

$$\therefore K_{b_1} = \frac{[OH^-(aq)]^2}{[CO_3^{2-}(aq)]} \text{ (as } [HCO_3^-(aq)] = [OH^-(aq)])$$

$$[OH^-(aq)]^2 = K_{b_1}[CO_3^{2-}(aq)] = 2.13 \times 10^{-4}\ mol\ dm^{-3} \times 0.10\ mol\ dm^{-3}$$

$$= 2.13 \times 10^{-5}\ mol\ dm^{-3}$$

$$\therefore [OH^-(aq)] = 4.61 \times 10^{-3}\ mol\ dm^{-3}$$

$$[H_3O^+(aq)] = 2.2 \times 10^{-12}\ mol\ dm^{-3}$$

$$\therefore pH = 11.71$$

First equivalence point S (at 25.00 cm^3 of HCl):
As previously explained, at the first equivalence point equilibrium existing is;

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \quad \ldots\ldots\ldots (1)$$

For the above equilibrium we can write,

$$K = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]}$$

This K has a direct relationship with the K_{a_1} of carbonic acid as,

$$K = \frac{K_w}{K_{a_1}} = \frac{[H_3O^+(aq)][OH^-(aq)]}{\frac{[H_3O^+(aq)][HCO_3^-(aq)]}{[H_2CO_3(aq)]}} = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]} = K_{b_2}$$

K_{b_2} is the second ionization constant of $CO_3^{2-}(aq)$ as we can write,

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) : K_{b_1}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) : K_{b_2}$$

$$\therefore K_{b_2} = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]} = \frac{1.0 \times 10^{-14}\ mol^2\ dm^{-6}}{4.3 \times 10^{-7}\ mol\ dm^{-3}} = 2.33 \times 10^{-8}\ mol\ dm^{-3}$$

For the reaction (1),

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

$$K_{b_2} = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]}$$

At equilibrium:

$$K_{b_2} = \frac{[OH^-(aq)]^2}{[HCO_3^-(aq)]} \quad (\text{as } [H_2CO_3(aq)] = [OH^-(aq)])$$

As the first equivalence point occurs at 25.00 cm^3 of HCl;

$$[HCO_3^-(aq)] = \frac{0.10\ mol\ dm^{-3} \times 25.00 \times 10^{-3}\ dm^3}{50.00 \times 10^{-3}\ dm^3} = 0.05\ mol\ dm^{-3}$$

$$\therefore [OH^-(aq)]^2 = K_{b_2}[HCO_3^-(aq)] = 2.33 \times 10^{-8}\ mol\ dm^{-3} \times 0.05\ mol\ dm^{-3}$$

$$\therefore [OH^-(aq)] = 3.4 \times 10^{-5}\ mol\ dm^{-3}$$

$$[H_3O^+(aq)] = 2.9 \times 10^{-10}\ mol\ dm^{-3}$$

$$\therefore \mathbf{pH = 9.47}$$

Second equivalence point (at 50.00 cm^3 of HCl):

As previously explained, at the second equivalence point equilibrium exist is;

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad \ldots\ldots\ldots\ldots (2)$$

For the above equilibrium we can write;

$$K' = \frac{[HCO_3^-(aq)][H_3O^+(aq)]}{[H_2CO_3(aq)]} = K_{a_1} = \frac{[H_3O^+(aq)]^2}{[H_2CO_3(aq)]}$$

$$(\text{as } [H_2CO_3(aq)] = [H_3O^+(aq)])$$

To reach the second equivalence point after the first equivalence point another 25.00 cm^3 of HCl is needed. Therefore, $[H_2CO_3(aq)]$ at the second equivalence point can be calculated as follows.

$$[H_2CO_3(aq)] = \frac{0.10\ mol\ dm^{-3} \times 25.00 \times 10^{-3}\ dm^3}{75.00 \times 10^{-3}\ dm^3} = 0.03\ mol\ dm^{-3}$$

$$[H_3O^+(aq)]^2 = K_{a_1}[H_2CO_3(aq)]$$

$$[H_3O^+(aq)]^2 = 4.3 \times 10^{-7}\ mol\ dm^{-3} \times 0.03\ mol\ dm^{-3} = 1.3 \times 10^{-8} mol^2\ dm^{-6}$$

$$[H_3O^+(aq)] = 1.14 \times 10^{-4} mol\ dm^{-3}$$

$$\therefore \mathbf{pH = 3.94}$$

According to above findings the pH at the first equivalence point is 9.4 and that at the second equivalence point it is ~ 4.0. Therefore, it is clear that in an experiment, the first equivalence point can be detected by phenolphthalein indictor while methyl orange is suitable to detect the second equivalence point. Figure 2.22 shows the variation of pH during the titration.

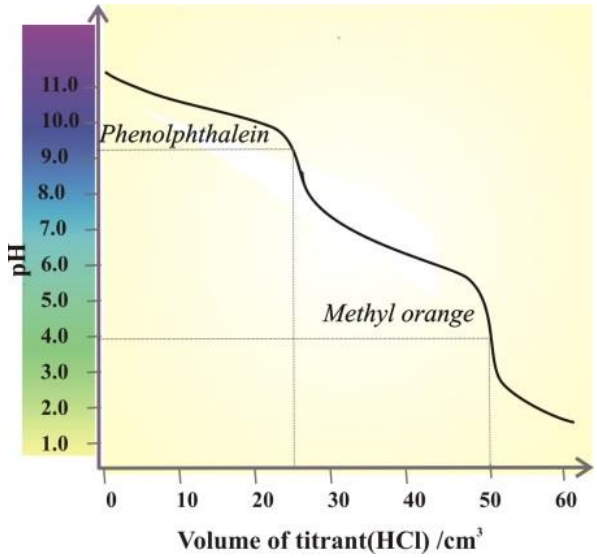


Figure 2.22 Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} Na_2CO_3 with 0.100 mol dm^{-3} HCl. There are two equivalence points: first is due to the reaction of CO_3^{2-} with HCl to form HCO_3^- and the second one is due to the conversion of HCO_3^- to H_2CO_3.

2.2.13 Acid-base indicators

In the previous section, we discussed the equivalence point of a titration of an acid and a base, as the point at which the number of moles of OH^- ions added to a solution is equal to the number of moles of H^+ ions originally present. To determine the equivalence point in a titration, then, we must know exactly what volume of a solution of a base has to be added from a burette to an acid in a flask. One way to achieve this goal is to add a few drops of a foreign substance called an acid-base indicator to the acid solution at the start of the titration.

Finding the end point with an indicator

One interesting group of these indicators is weak acids and bases which are derivatives of organic dyes. Because such compounds have at least one conjugate acid–base species that is highly coloured, their use in a titration results in a change in colour with the change in pH. This change in colour can serve as a useful means for determining the ***end point*** of a titration, provided that it occurs at the titration's equivalence point. Indicator has distinctly different colours in its non-ionized and ionized forms. These two forms are related to the pH of the solution in which the indicator is dissolved. The pH at which an

acid–base indicator changes colour is determined by its acid dissociation constant. For an indicator that is a monoprotic weak acid, HIn, the following dissociation reaction occurs.

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

for which the equilibrium constant is,

$$K_{In} = \frac{[H_3O^+(aq)][In^-(aq)]}{[HIn(aq)]}$$

Taking the negative log of each side of equation and rearranging to solve for pH gives a familiar equation.

$$-\log[H_3O^+(aq)] = -\log K_{In} + \log\frac{[In^-(aq)]}{[HIn(aq)]}$$

$$pH = pK_{In} + \log\frac{[In^-(aq)]}{[HIn(aq)]}$$

The two forms of the indicator, HIn and In^-, have different colours. The colour of a solution containing an indicator, therefore, continuously changes as the concentration of HIn decreases and the concentration of In^- increases. If we assume that both HIn and In^- can be detected with equal ease, then the transition between the two colours reaches its midpoint when their concentrations are identical or when the **pH** is equal to the indicator's **pK_{In}**. The equivalence point and the end point coincide, therefore, if an indicator is selected whose **pK_{In}** is equal to the pH at the equivalence point, and the titration is continued until the indicator's colour is exactly halfway between that for HIn and In^-.

Unfortunately, the exact pH at the equivalence point is rarely known. In addition, detecting the point where the concentrations of HIn and In^- are equal may be difficult if the change in colour is subtle. We can establish a range of **pH**s within which we can observe a change in colour of the indicator if we assume that a solution of the indicator is the colour of HIn whenever its concentration is ten times more than that of In^-, and the colour of In^- whenever the concentration of HIn is ten times less than that of In^-.

i.e. If the indicator is in a sufficiently acidic medium, the equilibrium, according to Le Chatelier's principle, shifts to the left and the predominant colour of the indicator is that of the nonionized form (HIn). On the other hand, in a basic medium the equilibrium shifts to the right and the colour of the solution will be due mainly to that of the conjugate base (In^-). Therefore, we can use the following concentration ratios to predict the perceived colour of the indicator:

When,

$$\frac{[HIn(aq)]}{[In^-(aq)]} \geq 10$$

$$\text{pH} = \text{p}K_{\text{In}} + \log\frac{1}{10}$$
$$\text{pH} = \text{p}K_{\text{In}} - 1$$

$\therefore$ color of *HIn* acid predominates

When,

$$\frac{[\text{In}^-(\text{aq})]}{[\text{HIn}(\text{aq})]} \geq 10$$
$$\text{pH} = \text{p}K_{\text{In}} + \log\frac{10}{1}$$
$$\text{pH} = \text{p}K_{\text{In}} + 1$$

color of In^- conjugate base predominates

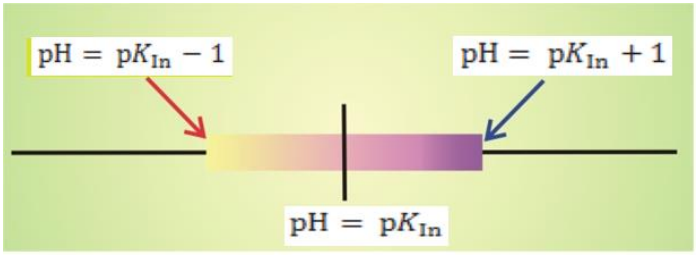


Figure 2.23 Behaviour of an indicator: $HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$

The end point of an indicator does not occur at a specific pH; rather, there is a range of pH within which the end point will occur. In practice, we choose an indicator whose end point lies on the steep part of the titration curve. Because the equivalence point also lies on the steep part of the curve, this choice ensures that the pH at the equivalence point will fall within the range over which the indicator changes colour. For example, phenolphthalein is a suitable indicator for the titration of NaOH and HCl. Phenolphthalein is colourless in acidic and neutral solutions, but reddish pink in basic solutions. Measurements show that at pH = 8.3 the indicator is colourless but that it begins to turn reddish pink when the pH exceeds 8.3. As shown in Figure 2.22, the steepness of the pH curve near the equivalence point means that the addition of a very small quantity of NaOH (~ 0.05 cm^3) brings about a large rise in the pH of the solution. What is important, however, is the fact that the steep portion of the pH profile includes the range over which phenolphthalein changes from colourless to reddish pink. Whenever such a correspondence occurs, the indicator can be used to locate the equivalence point of the titration.

Table 2.4 Some common acid-base indicators

Indicator	Colour in acid	Colour in base	pH range	pK_{In}
Thymol blue	Red	Yellow	1.2–2.8	1.7
Bromophenol blue	Yellow	Purple	3.0–4.6	4.1
Methyl orange	Orange	Yellow	3.1–4.4	3.7
Methyl red	Red	Yellow	4.2– 6.3	5.0
Chlorophenol red	Yellow	Red	5.2– 6.8	6.0
Bromothymol blue	Yellow	Blue	6.0 –7.6	7.1
Cresol red	Yellow	Red	7.2– 8.8	8.2
Phenolphthalein	Colorless	Reddish pink	8.3–10.0	9.6

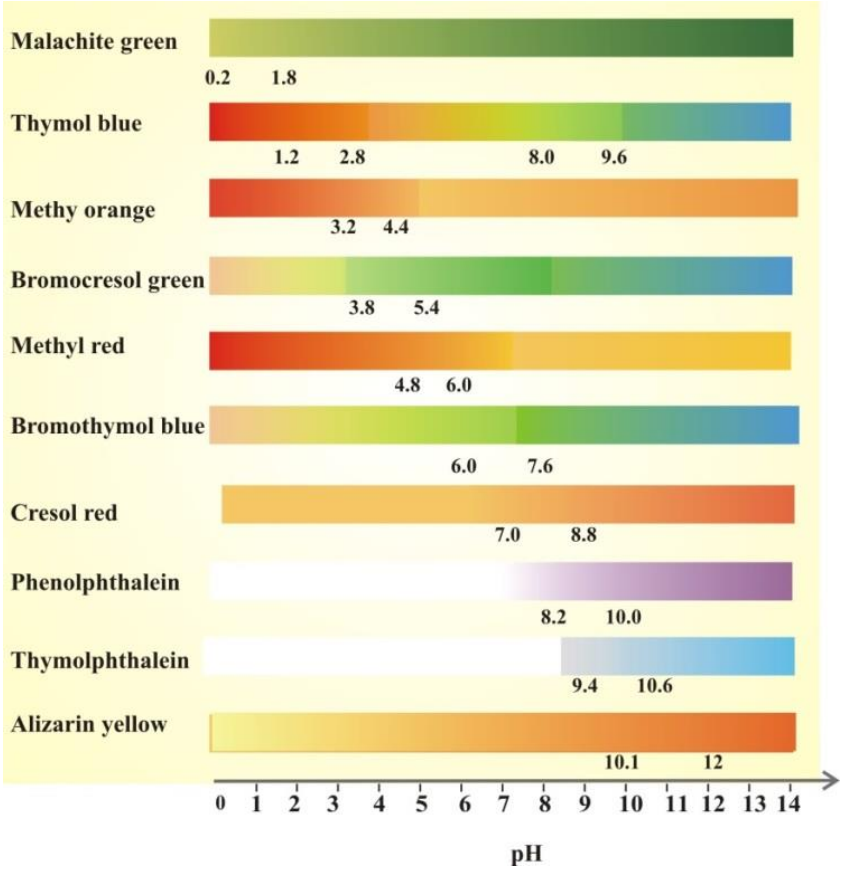


Figure 2.24 Colour changing pH ranges for some indicators

Selection of an indicator for a titration

The relatively broad range of pHs over which any indicator changes colour places additional limitations on the feasibility of a titration. To minimize a titration error or to conduct the titration with acceptable high accuracy, an indicator's entire colour transition must lie within the sharp transition in pH occurring near the equivalence point. Thus, in Figure 2.25 (a) we see that phenolphthalein is an appropriate indicator for the titration of 0.1 mol dm^{-3} acetic acid with 0.1 mol dm^{-3} NaOH. Methyl red, on the other hand, is an

inappropriate indicator since its change in colour begins before the initial sharp rise in pH and, as a result, spans a relatively large range of volumes. The early change in color increases the probability of obtaining inaccurate results, and the range of possible end point volumes increases the probability of obtaining imprecise results. Figure 2.25 (b) shows that for a titration of 0.1 mol dm^{-3} HCl acid with 0.1 mol dm^{-3} NaOH i.e. strong acid vs strong base titration, both phenolphthalein and methyl red can be used as the indicator.

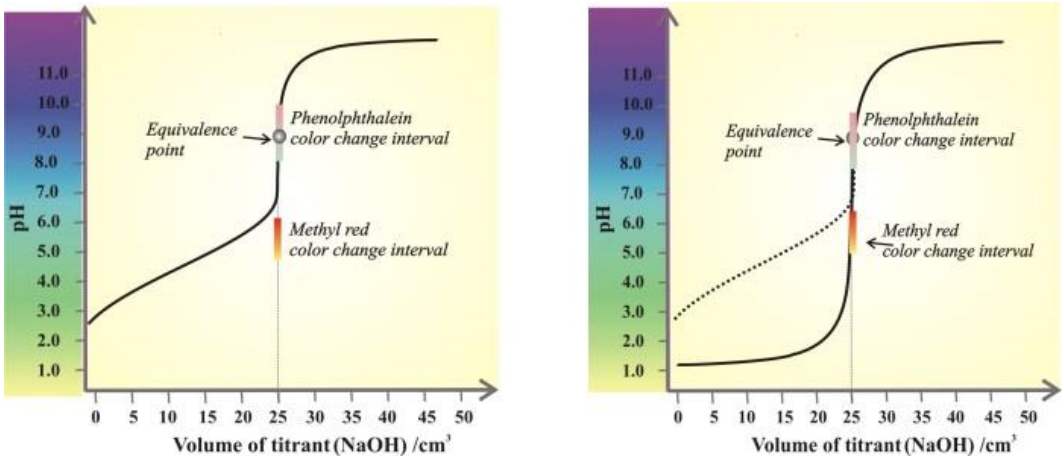


Figure 2.25 Selection of an appropriate indicator for a given titration. In the case of weak acid-strong base titration phenolphthalein is a sutable indicator. Methyl orange indicator has no colour changing pH range in the equivalence point pH changing range as shown in **(a)**. As shown in **(b)** both the indicators can be used for the titration between a strong acid and a strong base.

2.3 Buffer solutions

From a simple experiment we can observe that adding as little as 0.10 cm^3 of concentrated HCl to a 1.0 dm^3 of H_2O shifts the pH from 7.0 to 3.0. Also the addition of about 0.10 cm^3 of concentrated NaOH to a 1.0 dm^3 of H_2O shifts the pH from 7.0 to 11.0. However, the same addition of either HCl or NaOH to a solution that is 0.10 mol dm^{-3} in both a weak acid and its conjugate weak base, results in only a negligible change in pH. Such solutions are called **buffers,** and their buffering action is a consequence of the relationship between pH and the relative concentrations of the conjugate weak acid/weak base pair.

i.e. *A **buffer solution*** is *a solution of a weak acid or a weak base and its salt. The solution has the ability to resist changes in* pH *upon the addition of small amounts of either acid or base.*

Or

A buffer solution is a solution containing a conjugate weak acid/weak base pair that is resistant to a change in pH *when small volumes of a strong acid or a strong base are added.*

According to above definition, a buffer solution must contain a relatively large concentration of acid to react with any OH^- ions that are added to it, and it must contain a similar concentration of base to react with any added H^+ ions. The acid and the base components of the buffer must not consume each other in a neutralization reaction. These requirements are satisfied by an acid-base conjugate pair, for example, a weak acid and its conjugate base (supplied by a salt) or a weak base and its conjugate acid (supplied by a salt). Buffer solutions of known pH can be prepared from the knowledge of $\mathbf{p}K_\mathbf{a}$ of the acid or $\mathbf{p}K_\mathbf{b}$ of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide act as a buffer around pH 9.25. Let us consider a buffer solution prepared by adding comparable amounts of acetic acid (CH_3COOH) and its salt sodium acetate (CH_3COONa) to water. The equilibrium concentrations of both the acid and the conjugate base (from CH_3COONa) are assumed to be the same as the starting concentrations as the presence of a common ion suppresses the dissociation of a weak acid/base. A solution containing these two substances has the ability to neutralize either added acid or added base. In the solution CH_3COONa, a strong electrolyte, dissociates completely in water:

$$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

If an acid is added, the H^+ ions will be consumed by the conjugate base in the buffer, CH_3COO^-, according to the equation:

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$$

If a base is added to the buffer system, the OH^- ions will be neutralized by the acid in the buffer:

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

Similarly let us consider a buffer solution prepared by adding comparable amounts of ammonia (NH_3) and its salt ammonium chloride (NH_4Cl) to water. The equilibrium concentrations of both the base and the conjugate acid (from NH_4Cl) are assumed to be the same as the starting concentrations as the presence of a common ion suppresses the dissociation of a weak base NH_3. A solution containing these two substances has the ability to neutralize either added acid or added base. In the solution NH_4Cl, a strong electrolyte, dissociates completely in water:

$$NH_4Cl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$$

If an acid is added, the H^+ ions will be consumed by the base in the buffer, NH_3, according to the equation:

$$NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$

If a base is added, the OH^- ions will be consumed by the conjugate acid in the buffer, NH_4^+, according to the equation:

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

Common expression for the pH *of buffer solutions*

A general buffer equation can be derived by considering the following reactions for a weak acid, HA, and the salt of its conjugate weak base, NaA in an aqueous solution. Following reactions are the reactions involved with the species present in a solution.

$$NaA(aq) \rightarrow Na^+(aq) + A^-(aq)$$

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Here we can take $[A^-(aq)]$ as the concentration of $A^-(aq)$ from NaA and assume that the dissociation of HA is suppressed due to the presence of $A^-(aq)$ as the common ion. Substituting these terms in the K_a expression of a weak acid we have,

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

We can also neglect the concentrations of H_3O^+ and OH^- from water as these values are much smaller compared to the initial concentrations of HA and NaA. Hence,

$$[H_3O^+(aq)] = K_a \frac{[HA(aq)]}{[A^-(aq)]}$$

and finally we get the equation,

$$pH = pK_a + \log \frac{[A^-(aq)]}{[HA(aq)]}$$

or

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}.$$

i.e. the ***Henderson-Hasselbalch*** *equation.*

This Henderson–Hasselbalch equation provides a simple way to calculate the pH of a buffer and to determine the change in pH upon adding a strong acid or strong base.

Example 2.22

How many moles of NH_4Cl are necessary to be added to1.0 dm^3 of 0.10 mol dm^{-3} NH_3 solution to prepare a buffer solution with pH 9.0. K_b (NH_3) = 1.8 × 10^{-5}.

Answer

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

First, we need to estimate the $[NH_4^+(aq)]$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]} = 1.8 \times 10^{-5}$$

As we know the pH of the solution, $[OH^-(aq)]$ can be calculated.

pOH = 14 – pH = 5.0 and hence $[OH^-(aq)] = 1.0 \times 10^{-5}$ mol dm^{-3}

$$[NH_4^+(aq)] = K_b \frac{[NH_3(aq)]}{[OH^-(aq)]}$$

$$= 1.8 \times 10^{-5} \text{ mol dm}^{-3} \times \frac{0.10 \text{ mol dm}^{-3}}{1.0 \times 10^{-5} \text{ mol dm}^{-3}}$$

$$= 0.18 \text{ mol dm}^{-3}$$

∴Number of moles of NH_4^+ = 0.18 mol dm^{-3} × 1.0 dm^3

= 0.18 mol

Example 2.23

Calculate the pH of a buffer system containing 1.0 mol dm^{-3} CH_3COOH and 2.0 mol dm^{-3} CH_3COONa. What is the pH of the buffer system after the addition of 0.10 mole of HCl to 1.0 dm^3 of the solution? Assume that the volume of the solution does not change when the HCl is added.

$K_a(CH_3COOH) = 1.8 \times 10^{-5}$ mol dm^{-3}

Answer

Due to the presence of common ion of CH_3COO^- from $CH_3COONa(aq)$, we can neglect the ionization of CH_3COOH and hydrolysis of the CH_3COO^- ion. Therefore,

$[CH_3COOH(aq)] = 1.0$ mol dm^{-3} and $[CH_3COO^-(aq)] = 2.0$ mol dm^{-3}

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 1.8 \times 10^{-5}$$

$$[H_3O^+(aq)] = \frac{[1.0]}{[2.0]} \times 1.8 \times 10^{-5}$$

$$[H_3O^+(aq)] = 9.0 \times 10^{-6}$$

$$pH = 5.05$$

After the addition of 0.2 mol of HCl to 1.0 dm^3 of the buffer solution (i.e. $[H^+(aq)] = 0.10$ mol dm^{-3}), complete ionization of HCl acid occurs:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

0.10 0.10 0.10 mol dm^{-3}

Then the H^+ from HCl is neutralized by the 2.0 mol dm^{-3} CH_3COONa as

$$H^+(aq) + CH_3COO^-(aq) \rightleftharpoons CH_3COOH(aq)$$

0.10 0.10 0.10 mol dm^{-3}

(Equilibrium constant for the reaction is very large and therefore we can assume that the reaction goes to completion giving 0.10 mol dm^{-3} of CH_3COOH)

∴ The number of moles of acetic acid and the number of moles of acetate ions present in 1.0 dm^3 solution are,

$CH_3COOH(aq) = 1.10$ mol or $[CH_3COOH(aq)] = 1.10$ moldm^{-3}

$CH_3COO^-(aq) = 1.90$ mol or $[CH_3COO^-(aq)] = 1.90$ moldm^{-3}

Substituting these values in K_a expression,

$$[H_3O^+(aq)] = \frac{1.1}{1.9} \times 1.8 \times 10^{-5}$$

$$[H_3O^+(aq)] = 1.04 \times 10^{-5} \text{ mol } dm^{-3}$$

$$pH = 4.98$$

Note: *if the initial concentrations of the acid and the salt in the buffer solution are the same, for example, 1. 0 mol dm^{-3}, without adding any acid or base, we get*

$$[H_3O^+(aq)] = \frac{1.0}{1.0} \times 1.8 \times 10^{-5}$$
$$[H_3O^+(aq)] = 1.8 \times 10^{-5}$$
$$pH = 4.74$$

i.e. pH = pK_a

This can be easily understood by, applying the equation,

$$pH = pK_a + \log\frac{[A^-(aq)]}{[HA(aq)]}$$
$$pH = pK_a + \log\frac{1.0}{1.0}$$
$$\therefore pH = pK_a$$

Example 2.24

Calculate the pH of a buffer that is 0.020 mol dm^{-3} in NH_3 and 0.030 mol dm^{-3} in NH_4Cl. What is the *p*H after adding 1.00 cm^3 of 0.10 mol dm^{-3} NaOH to 0.10 dm^3 of this buffer? The acid dissociation constant for NH_4^+ is 5.70×10^{-10} mol dm^{-3}

Answer

We can directly use,

$$pH = pK_a + \log\frac{[NH_3(aq)]}{[NH_4^+(aq)]}$$
$$pH = 9.24 + \log\frac{(0.02)}{(0.03)}$$
$$pH = 9.06$$

Adding NaOH converts a portion of the NH_4^+ to NH_3 due to the following reaction

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

Since the equilibrium constant for this reaction is large, we may treat the reaction as if it went to completion. The new concentrations of NH_4^+ and NH_3 are therefore

$$[NH_4^+(aq)] = \frac{\text{moles of initial } NH_4^+ - \text{moles of } OH^- \text{ added}}{\text{total volume}}$$

$[NH_4^+(aq)] = \frac{(0.03)\times(0.1) - (0.1)\times(1.0\times10^{-3})}{(0.101)} = 0.029 \text{ mol dm}^{-3}$

and

$[NH_3\,(aq)] = \frac{\text{moles of initial } NH_3 + \text{ moles of } OH^- \text{ added}}{\text{total volume}}$

$[NH_3\,(aq)] = \frac{(0.02)\times(0.1)+(0.1)\times(1.0\times10^{-3})}{(0.101)} = 0.021 \text{ mol dm}^{-3}$

Substituting these in the equation, we get

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[NH_3(aq)]}{[NH_4^+(aq)]}$$

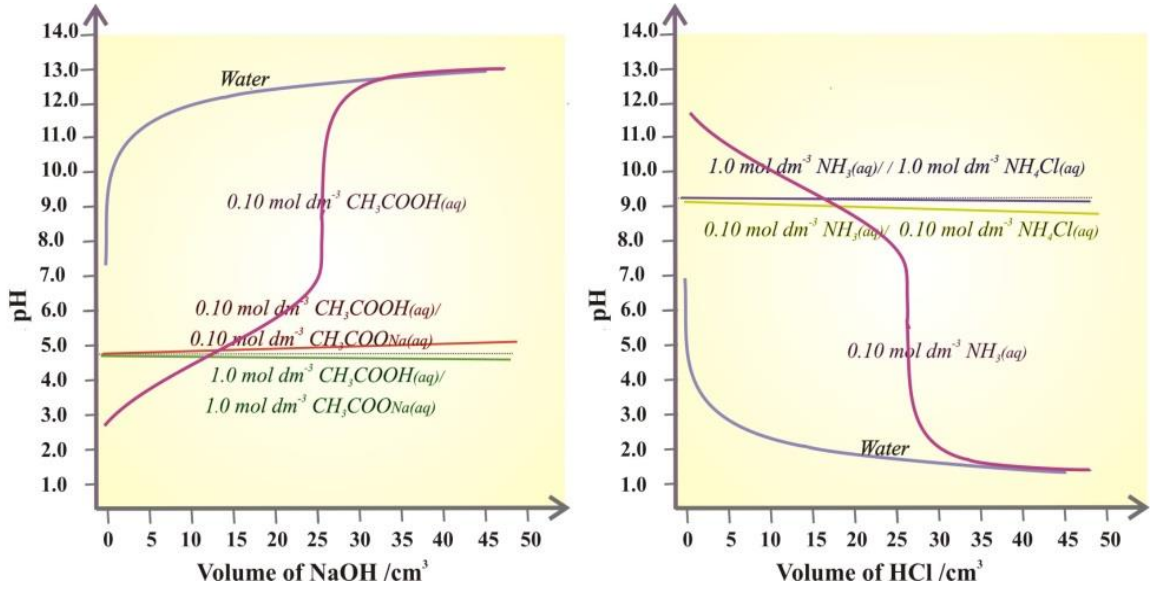
$$\text{pH} = 9.24 + \log\frac{(0.021)}{(0.029)}$$

$$\text{pH} = 9.10$$

From the above examples we can see that the addition of a little amount of acid or base does not afftect the pH of the buffer solutions significantly. This nature is explained in Figure 2.26 in which the addition of either an acid or a base to the buffer solutions are compared with the addition of an acid or a base to water and buffer solutions with different concentrations of acid-base pairs. Figure 2.27 also explains the events happening in buffer solutions when an acid or a base is added. Finally, the following can be considered the basic charateristics of buffer solutions.

(i) Contain relatively large concentrations of a weak acid (base) and its conjugate base (acid).
(ii) When acid is added, it reacts with the conjugate base.
(iii) When base is added, it reacts with the conjugate acid.
(iv) pH is determined by the ratio of the base and acid.

These characteristics are depicted in Figure 2.26 and Figure 2.27.



(a) (b)

Figure 2.26 Comparison of buffer action for acidic- and basic- buffers is given in **(a)** and **(b)** sides respectively. When the strength of the acid and salt (conjugate base) of the buffer is high the variation in pH with the addition of either an acid or a base is minimal. The varaiation in pH upon the addition of either an acid or a base to water and acid alone (or base alone) are also shown for comparison.

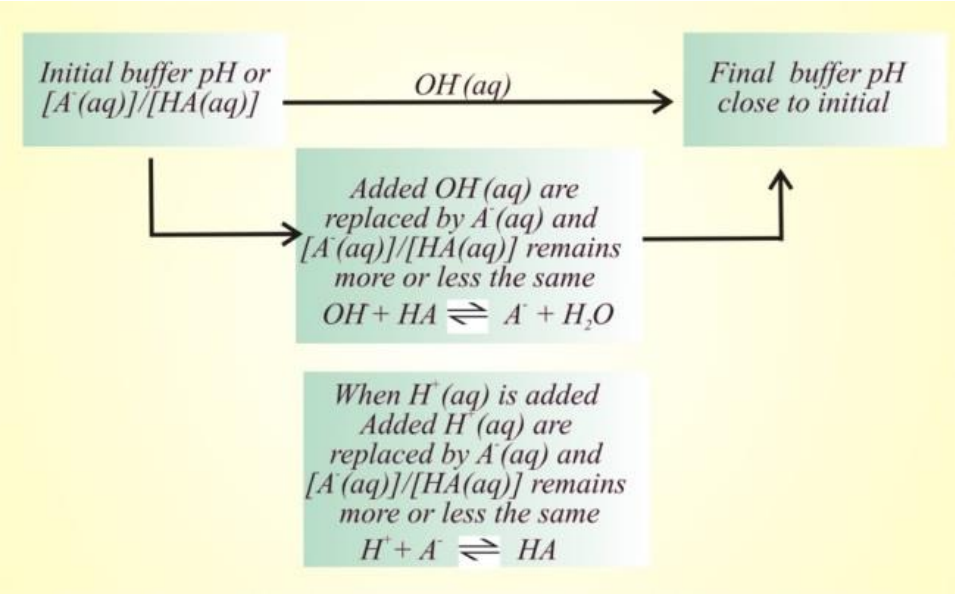


Figure 2.27 Summary of buffer action

For convenience, we will assume that an acid–base buffer exists when the concentration ratio of weak base to weak acid is between 0.1 and 10. Applying the Henderson–Hasselbalch equation:

$$\text{pH} = \text{p}K_\text{a} + \log\frac{1}{10} = \text{p}K_\text{a} - 1$$

and

$$\text{pH} = \text{p}K_\text{a} + \log\frac{10}{1} = \text{p}K_\text{a} + 1$$

Thus it is seen that acid–base buffer exists within the range of $\mathbf{pH = pK_a \pm 1}$

2.4 Solubility equilibria

Solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride, sodium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from the atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly termed insoluble. The solubility depends on a number of factors important amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution. For a salt to dissolve in a solvent, the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions. The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e. energy is released in the process of solvation. The amount of solvation enthalpy depends on the nature of the solvent. In case of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent. As a general rule, for a salt to be able to dissolve in a particular solvent, its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by the former. With this fact we can start to understand the term solubility in the following way: First see the solubility of ionic salts and then understand the solubility of molecular compounds/ covalent compounds and then see the difference with sparingly soluble salts in a saturated solution.

2.4.1 Ionic and covalent solutions

Solutions are made up of two components, the solute and the solvent. There are many examples for different types of solutions such as solid-solid (metal alloys), solid-liquid (salt-water), liquid-liquid (alcohol-water), liquid-gas (soft drinks like soda water) and gas- gas (air) in which we see that he two components are distributed homogeneously to making the system appear to be in one phase. In this section we mainly deal with the solid-liquid systems where the solvent is water or in other words we deal with "*ionic equilibria*".

We know that an ionic or covalent solution is a *homogeneous mixture* consisting of one phase when the concentration of the solute is small or the solution is very dilute. In an ionic solution like the salt solution, NaCl is dissolved (or dissociated) in water to produce ions of $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ while in a covalent solution, a covalent substance like sugar is

dissolved in water. That is, ionic compounds dissolve by separating into respective ions and covalent substances dissolve as the entire molecule. Therefore, we can simply distinguish these two compounds by the following equations.

Ionic compounds: $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

Covalent compounds: $C_6H_{12}O_6(s) \rightarrow : C_6H_{12}O_6(aq)$

This in turn helps us to understand that ionic solutions as electrolytes which show conductivity while covalent or molecular solutions are non-electrolytes which do not show conductivity.

When we consider ionic salts, each salt has its characteristic solubility which depends on the temperature. It is possible to classify salts on the basis of their solubility in the following three categories.

Category I : Soluble - Solubility > 0.10 mol dm^{-3}
Category II : Slightly soluble - 0.01 mol dm^{-3} $<$ Solubility $<$ 0.10 mol dm^{-3}
Category III : Sparingly soluble - Solubility < 0.01 mol dm^{-3}

Usually we know that when 0.10 mol of solid NaCl is dissolved in 1.00 dm^3 of water, i.e. the concentration of solution is 0.10 mol dm^{-3}, it produces 0.10 mol dm^{-3} $Na^+(aq)$ and 0.10 mol dm^{-3} $Cl^-(aq)$ ions showing complete dissociation.

$$NaCl(s) + Water \rightarrow NaCl(aq) \rightarrow Na^+(aq) + Cl^-(aq)$$
$$0.10 \qquad 0.10 \quad 0.10 \quad \text{mol } dm^{-3}$$

A set of conditions need to be considered to understand the solubility. First, a *saturated* solution is needed in which the maximum amount of solute is dissolved and in the case of sparingly soluble salts some amount of the solid has to remain still.

Under this condition, we can understand that there is a heterogeneous equilibrium in the system as the rate of dissolution equals the rate of precipitation or crystallization - or in other words the system is in dynamic equilibrium. Simply, the following equation explains this situation.

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

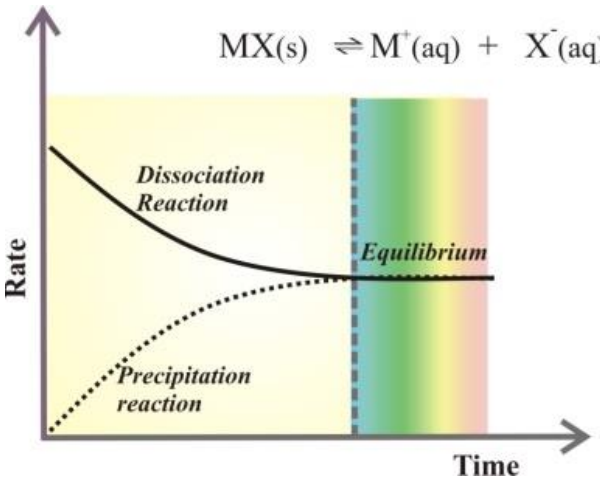


Figure 2.28 In saturated solutions dynamic equilibrium exists between undissolved solids and ionic species in the solution. Hence solid continues to dissolve and ion-pairs continue to form the solid and the rate of dissolution is equal to the rate of precipitation.

Solubility of a substance: ***Equilibrium concentration*** *of a substance in a* ***saturated*** *solution at a given temperature or solubility is a measure of how much of a solute (maximum amount)can dissolve in a solvent at a given temperature*. Therefore it is a quantitative value and is expressed mainly as molar solubility (mol dm^{-3}). Other units used to express solubility are g dm^{-3}, g cm^{-3} etc. i.e to find solubility experimentally, it is necessary to find the amount (mass) of solute required to make a known volume of a saturated solution.

Note: *There are two ways by which a saturated aqueous solution of a salt MX can be made.*

(i) *Direct method: Add solid MX salt to water with vigorous stirring until excess MX salt remains on the bottom of the beaker.*

(ii) *Indirect method: Mix two solutions together, one containing M^+ and the other containing X^- and at a certain point a saturated solution of MX will be formed.*

Example 2.25
1.00 dm^3 of a saturated AgCl solution was prepared by dissolving 1.8×10^{-3} g of AgCl completely. What is the molar solubility of AgCl? (AgCl : 143.4 g mol^{-1})

Answer
Amount of moles of AgCl = 1.8×10^{-3} g / 143.4 g mol^{-1} = 1.26×10^{-5} mol
Since molar solubility is expressed in units of mol dm^{-3}:
Molar solubility = 1.26×10^{-5} mol/ 1.00 dm^3 = 1.26×10^{-5} mol dm^{-3}
We can express solubility in other units as 1.8×10^{-3} g dm^{-3}

2.4.2 Solubility product (solubility product constant)

Let us now consider a solid MX in contact with its **saturated** aqueous solution. The equilibrium between the undissolved solid and the ions in a saturated solution is represented by the equation:

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

The equilibrium constant K is given by the equation:

$$K = \frac{[M^+(aq)][X^-(aq)]}{[MX(s)]}$$

For a pure solid substance the concentration remains constant and we can write;

$$K\,[MX(s)] = [M^+(aq)][X^-(aq)]$$
$$\therefore K_{sp} = [M^+(aq)][X^-(aq)]$$

In general, if we have an equilibrium;

$$M_mX_n(s) \rightleftharpoons mM^{n+}(aq) + nX^{m-}(aq)$$

Solubility product,

$$K_{sp} = [M^{n+}(aq)]^m[X^{m-}(aq)]^n$$

K_{sp} is called as the *solubility product constant* or simply the *solubility product* and its expression does not have a denominator because the reactant is a solid. It has to be noted that the solubility product is defined only for saturated solutions. Large values for K_{sp} indicate that the products are favored; therefore, the *larger the value of K_{sp}, the greater the number of ions and hence the greater the solubility of the compound.* Usually, it has no units as we described in equilibrium constant when the concentrations are measured with respect to standard concentration of 1.0 mol dm^{-3}. Unless a mention is made about the standard conditions, we include the respective units for the concentrations appearing in

the solubility product expression. The units for solubility products differ depending on the solubility product expression.

In general, if we have an equilibrium;

$$M_mX_n(s) \rightleftharpoons mM^{n+}(aq) + nX^{m-}(aq)$$

Solubility product,

$$K_{sp} = [M^{n+}(aq)]^m[X^{m-}(aq)]^n$$

Units:

$$(mol^m dm^{-3m})\ (mol^n dm^{-3n})$$

$$\mathbf{mol^{(m+n)}\ dm^{-3(m+n)}}$$

Simply for the equilibrium: $MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$

$$K_{sp} = [M^+(aq)][X^-(aq)]\ mol^2\ dm^{-6}$$

2.4.3 Solubility and solubility product calculations

Calculations involving K_{sp} are simpler than for previous equilibrium calculations because the reactant is a solid and therefore omitted from the equilibrium expression. There are only two types of problems that need to be solved:

(a) Calculating K_{sp} from solubility data or

(b) Calculating solubility from K_{sp}.

Consider the example,

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) : K_{sp} = [Ag^+(aq)][Cl^-(aq)]$$

$$\text{At } 298\ K, \quad K_{sp} = 1.60 \times 10^{-10}\ mol^2\ dm^{-6}$$

When we consider the above equilibrium, concentrations of the two ions will be equal to the molar solubility of silver chloride. If molar solubility is $\boldsymbol{s}$, then

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

At the equilibrium: $\quad s \quad s \quad mol\ m^{-3}$

$$\text{At } 298\ K, \quad K_{sp} = 1.60 \times 10^{-10}\ mol^2\ dm^{-6} = \boldsymbol{s} \times \boldsymbol{s} = \boldsymbol{s^2}$$

$$\therefore \boldsymbol{s} = 1.26 \times 10^{-5}\ mol\ dm^{-3}$$

Thus, at 298 K, molar solubility of silver chloride will be equal to $1.26 \times 10^{-5}\ mol\ dm^{-3}$.

A solid salt of the general formula

$$M_mX_n(s) \rightleftharpoons mM^{n+}(aq) + nX^{m-}(aq)$$

Molar solubility S in equilibrium $\quad m\,\boldsymbol{s} \quad n\,\boldsymbol{s}$

$$K_{sp} = [M^{n+}(aq)]^m[X^{m-}(aq)]^n$$

$K_{sp} = (m\ s)^m(n\ s)^n = m^m\ n^n\ s^{(m+n)}$

$$S^{(m+n)} = \frac{K_{sp}}{m^m\ n^n}$$

$$S = \left[\frac{K_{sp}}{m^m\ n^n}\right]^{1/(m+n)}$$

Example 2.26

Derive an expression for the solubility (s) of aqueous saturated solution $Zr_3(PO_4)_4(s)$ at 298 K.

Answer

$$Zr_3(PO_4)_4\ (s) \rightleftharpoons 3Zr^{4+}(aq)\ +\ 4PO_4^{3-}(aq)$$

At equilibrium: $3s$ $4s$

$K_{sp} = [Zr^{4+}(aq)]^3[PO_4^{3-}(aq)]^4 = (3s)^3(4s)^4 = 6912\ (s)^7$

$$\therefore s = \left[\frac{K_{sp}}{6912}\right]^{1/7}$$

In this example we can notice that $K_{sp} = [Zr^{4+}(aq)]^3[PO_4^{3-}(aq)]^4$ has units $(moldm^{-3})^7$. And the units of s is $[(mol\ dm^{-3})^7]^{\frac{1}{7}} = mol\ dm^{-3}$

That is the units of molar solubility.

Example 2.27

At 298 K, 100.00 cm^3 of a saturated PbI_2 solution was prepared by dissolving 5.60×10^{-2} g $PbI_2(s)$. Calculate K_{sp}.

Answer

First we need the molar solubility of PbI_2:

Moles of PbI_2 $= 5.60 \times 10^{-2}$ g /461 g $mol^{-1} = 1.21 \times 10^{-4}$ mol

Molar solubility of PbI_2 $= 1.21 \times 10^{-4}$ mol/ 0.100 dm^3

$= 1.21 \times 10^{-3}$ mol dm^{-3}

Next calculate the concentration of the ions and substitute in the *Ksp* expression:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

At equilibrium : $[Pb^{2+}(aq)] = 1.21 \times 10^{-3}$ mol dm^{-3} and

$[I^-(aq)] = 2 \times 1.21 \times 10^{-3}$ mol dm^{-3} $= 2.42 \times 10^{-3}$ mol dm^{-3}

$K_{sp} = [Pb^{2+}(aq)]\ [I^-(aq)]^2$

$K_{sp} = (1.21 \times 10^{-3}$ mol $dm^{-3}) \times (2.42 \times 10^{-3}$ mol $dm^{-3})^2$

$K_{sp} = 7.1 \times 10^{-9}$ mol^3 dm^{-9}

Example 2.28

At 298 K, the values of K_{sp} of two sparingly soluble compounds $Ni(OH)_2$ and AgCN are 2.0×10^{-15} mol^3 dm^{-9} and 6×10^{-17} mol^2 dm^{-6} respectively. Which salt is more soluble?

Answer

Consider the equilibrium,

$$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$$

If the solubility is x,

At equilibrium : x $2x$

$K_{sp} = [Ni^{2+}(aq)][OH^-(aq)]^2 = 4x^3$

$4x^3 = 2.0 \times 10^{-15}$ mol^3 dm^{-9}

$x = 7.94 \times 10^{-5}$ mol dm^{-3}

Similarly,

$$AgCN(s) \rightleftharpoons Ag^+(aq) + CN^-(aq)$$

If the solubility is y,

At equilibrium : y y

$K_{sp} = [Ag^+(aq)][CN^-(aq)] = y^2$

$y^2 = 6 \times 10^{-17}$ mol^2 dm^{-6}

$y = 7.8 \times 10^{-9}$ mol dm^{-3}

we can notice that; $x > y$

Therefore, $Ni(OH)_2(s)$ is more soluble than AgCN(s).

(It is also possible to predict this comparing K_{sp} values; Since K_{sp} ($Ni(OH)_2(s)$) > K_{sp} (AgCN(s)), solubility of $Ni(OH)_2(s)$ is higher than that of AgCN(s)).

Calculating ion concentrations from K_{sp}

Example 2.29

Estimate the $[Ag^+(aq)]$ in a saturated solution of Ag_2CO_3 at 298 K.

K_{sp} $(Ag_2CO_3) = 8.1 \times 10^{-12}$ mol^3 dm^{-9}

Answer

First, consider the equilibrium, and if ***x*** is the molar solubility, we can write

$$Ag_2CO_3(s) \rightleftharpoons 2\ Ag^+(aq) + CO_3^{2-}(aq)$$

At equilibrium: $2x$ x mol dm^{-3}

$K_{sp} = [Ag^+(aq)]^2 [CO_3^{2-}(aq)]$

$= (2x)^2(x) = 4x^3$

$\therefore 4x^3 = 8.1 \times 10^{-12}$ mol^3 dm^{-9}

We get

$x = (8.1 \times 10^{-12}$ mol^3 dm$^{-9})^{1/3}$

$x = 1.26 \times 10^{-4}$ mol dm^{-3}

$\therefore [Ag^+(aq)] = 2x = 2 \times 1.26 \times 10^{-4}$ mol dm^{-3} $= 2.53 \times 10^{-4}$ mol dm^{-3}

Example 2.30

Which of the saturated solutions AgCl and Ag_2CO_3 will have a higher $[Ag^+(aq)]$ at 298 K? $K_{sp}(AgCl) = 1.8 \times 10^{-10}$ mol^2 dm^{-6} and $K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12}$ mol^3 dm^{-9}

Answer

One can note that this problem is similar to the Example 12.29. However, we were asked to estimate $[Ag^+(aq)]$. Also one has to note that we cannot compare the values of K_{sp} as the two constants have different units. Therefore, it is necessary to estimate the $Ag^+(aq)$ concentrations in cases.

	AgCl	Ag_2CO_3
From previous examples:		
$[Ag^+(aq)]$	1.34×10^{-5} mol dm^{-3}	2.53×10^{-4} mol dm^{-3}

Now we can see that the saturated Ag_2CO_3 solution has higher $[Ag^+(aq)]$ though the $K_{sp}(Ag_2CO_3) < K_{sp}(AgCl)$.

2.4.4 Predicting the formation of a precipitate

Whenever two solutions containing ions are mixed, there is a possibility that a precipitate may form. If the concentrations of the ions is 0.10 mol dm^{-3} or higher any compound having low solubility will precipitate. However, if the concentrations of the ions is less than 0.10 mol dm^{-3}, a calculation must be performed to predict the formation of the precipitate.

For example, if we mix equal volumes of 0.20 mol dm^{-3} $AgNO_3$ and NaCl solutions, a precipitate of AgCl(s) will form with NO_3^- and Na^+ ions as spectators. In this case as $AgNO_3$ and NaCl are strong electrolytes there is a precipitate of AgCl formed with 0.10 mol dm^{-3} cocentrations.

However, the situation with very dilute solutions (concentrations < 0.10 mol dm^{-3}) is different: When two soluble salt solutions are mixed, a cation from one solution is introduced to an anion from another solution, and *vise versa*.

> *One or both of the new ion combinations (cation and anion) could have low solubility. If this is the case, and there are too many of the low solubility ions present (more than what is necessary for a saturated solution), a precipitate will result.*
>
> *If there is not enough of the low solubility ions present to reach the saturation concentration, a precipitate will not form and the ions will stay dissolved in solution.*

In such situations **Ion-product *(IP)*** calculation is required to predict the formation of a precipitate.

Ion-product can be calculated for these mixtures to deduce whether a precipitate will form or not when the two solutions are mixed and the following conditions are defined.

> *If the **Ion-product** is larger than the actual K_{sp}, the concentration of low solubility ions is greater than saturation, so a precipitate will form.*
>
> *If the **Ion-product** is smaller than the actual K_{sp}, the concentrations of low solubility ions have not yet reached saturation, a precipitate will not form.*

We can summarize the above as;

***IP* > K_{sp}** then **precipitate forms**
***IP* = K_{sp}** then solution is saturated, **no precipitate**
***IP* < K_{sp}** then solution is not saturated, **no precipitate**

Example 2.31

Will a precipitate form if the solutions 50.00 cm^3 of 5.0×10^{-3} mol dm^{-3} $Mg(NO_3)_2$ and 50.00 cm^3 of 1.0×10^{-2} mol dm^{-3} K_2CO_3 are mixed?

$K_{sp(MgCO_3)} = 3.5 \times 10^{-8}$ mol^2 dm^{-6}

Answer

First write the reaction between $Mg(NO_3)_2$ and K_2CO_3

$$Mg(NO_3)_2(aq) + K_2CO_3(aq) \rightarrow 2KNO_3(aq) + MgCO_3(s)$$

As two solutions are being mixed, dilution occurs.

Therefore the concentrations of the solutions are different when mixed.

$[Mg(NO_3)_2(aq)] = (5.0 \times 10^{-3}$ mol $dm^{-3} \times 50 \times 10^{-3}$ $dm^3) / 100 \times 10^{-3}$ dm^3

$= 2.5 \times 10^{-3}$ mol dm^{-3}

$[K_2CO_3(aq)] = (1.0 \times 10^{-2}$ mol $dm^{-3} \times 50 \times 10^{-3}$ $dm^3) / 100 \times 10^{-3}$ dm^3

$= 5.0 \times 10^{-3}$ mol dm^{-3}

As $Mg(NO_3)_2(aq)$ and $K_2CO_3(aq)$ dissociate completely, we can write:

$Mg(NO_3)_2(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq)$

2.5×10^{-3} 2.5×10^{-3} mol dm^{-3}

$K_2CO_3(aq) \rightarrow 2K^+(aq) + CO_3^{2-}(aq)$

5.0×10^{-3} 5.0×10^{-3} mol dm^{-3}

As the precipitate formed is $MgCO_3$:

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$

$K_{sp} = [Mg^{2+}(aq)][CO_3^{2-}(aq)]$

Ion Product $= [Mg^{2+}(aq)][CO_3^{2-}(aq)] = (2.5 \times 10^{-3})(5.0 \times 10^{-3})$ $mol^2 dm^{-6}$

$= 12.5 \times 10^{-6}$ mol^2 dm^{-6}

IP $(12.5 \times 10^{-6}$ mol^2 $dm^{-6}) > K_{sp(MgCO_3)}$ $(3.5 \times 10^{-8}$ mol^2 $dm^{-6})$

Therefore a precipitate of $MgCO_3$ will form.

Example 2.32

Will a precipitate form if 50.00 cm^3 of 1.0×10^{-3} mol dm^{-3} $CaCl_2$ solution is added to 50.00 cm^3 of 1.0×10^{-2} mol dm^{-3} Na_2SO_4 solution? $K_{sp}(CaSO_4) = 2.4 \times 10^{-5}$ mol^2 dm^{-6}

Answer

First write the reaction between $Mg(NO_3)_2$ and K_2CO_3.

$$CaCl_2(aq) + Na_2SO_4(aq) \rightarrow 2NaCl(aq) + CaSO_4(s)$$

As two solutions are mixed, dilution occurrs

Therefore the concentrations of the solutions are different when mixed.

$[CaCl_2(aq)] = (1.0 \times 10^{-3}$ mol $dm^{-3} \times 50 \times 10^{-3}$ $dm^3) / 100 \times 10^{-3}$ dm^3

$= 5.0 \times 10^{-4}$ mol dm^{-3}

$[Na_2SO_4(aq)] = (1.0 \times 10^{-2}$ mol $dm^{-3} \times 50 \times 10^{-3}$ $dm^3) / 100 \times 10^{-3}$ dm^3

$= 5.0 \times 10^{-3}$ mol dm^{-3}

$CaCl_2(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$

5.0×10^{-4} 5.0×10^{-4} mol dm^{-3}

$Na_2SO_4(aq) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$

5.0×10^{-3} 5.0×10^{-3} mol dm^{-3}

As the precipitate formed is $CaSO_4$:

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

$K_{sp} = [Ca^{2+}(aq)][SO_4^{2-}(aq)]$

Ion Product $= [Ca^{2+}(aq)][SO_4^{2-}(aq)] = (5.0 \times 10^{-4})(5.0 \times 10^{-3})$ mol^2 dm^{-6}

$= 2.5 \times 10^{-6}$ mol^2 dm^{-6}

IP $(2.5 \times 10^{-6}$ mol^2 $dm^{-6}) < K_{sp}(CaSO_4) = 2.4 \times 10^{-5}$ mol^2 dm^{-6}

Therefore a precipitate of $CaSO_4$ will not be formed.

Example 2.33

What is the maximum $[Sr^{2+}(aq)]$ that can exist in a 0.020 mol dm^{-3} solution of K_2SO_4 without forming a precipitate of $SrSO_4$? $K_{sp(SrSO_4)} = 3.2 \times 10^{-7}$ mol^2 dm^{-6}

Answer

$$K_2SO_4(aq) \rightarrow 2K^+(aq) + SO_4^{2-}(aq)$$
$$2.0 \times 10^{-2} \qquad 2.0 \times 10^{-2} \quad mol\ dm^{-3}$$

$SrSO_4(s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp} = [Sr^{2+}(aq)][SO_4^{2-}(aq)]$

$\therefore 3.2 \times 10^{-7}\ mol^2\ dm^{-6} = [Sr^{2+}(aq)](2.0 \times 10^{-2}\ mol\ dm^{-3})$

$[Sr^{2+}(aq)] = 1.6 \times 10^{-5} mol\ dm^{-3}$

Example 2.34

XA(s) and YA(s) are two sparingly water soluble salts.

At 298 K, $K_{sp}(XA) = 1.80 \times 10^{-10}$ mol^2 dm^{-6} and $K_{sp}(YA) = 1.80 \times 10^{-7}$ mol^2 dm^{-6}. A completely water soluble salt of NaA is added slowly to a 1.00 dm^3 solution containing 0.100 moles of $X^+(aq)$ and $Y^+(aq)$.

(i) Predict which of the salts precipitates first.

(ii) Calculate also the cation concentration that remains in the solution of the salt that precipitates first when the second salt begins to precipitate.

Answer

(i) For XA

$K_{sp} = [X^+(aq)]\,[A^-(aq)]$

$[A^-(aq)] = K_{sp} / [X^+(aq)] = (1.80 \times 10^{-10} / 0.100)\ mol\ dm^{-3} = 1.80 \times 10^{-9}\ mol\ dm^{-3}$

For YA

$K_{sp} = [Y^+(aq)]\,[A(aq)]$

$[A^-(aq)] = K_{sp}[Y^+(aq)] = (1.80 \times 10^{-7} / 0.100)\ mol\ dm^{-3} = 1.80 \times 10^{-6}\ mol\ dm^{-3}$

$[A^-(aq)]$ necessary to precipitate XA is less than that needed to precipitate YA.

$\therefore$ XA precipitates first.

(ii) $K_{sp(XA)} = [X^+(aq)]\,[A^-(aq)]$

at this stage $[A^-(aq)]$ is the $[A^-(aq)]$ needed to start precipitation of YA.

$[X^+(aq)]$ left in the solution $= (1.80 \times 10^{-10} / 1.80 \times 10^{-6})\ mol\ dm^{-3}$

$= 1.0 \times 10^{-4}\ mol\ dm^{-3}$

Example 2.35

Consider a solution of 0.10 mol dm^{-3} $A^{2+}(aq)$ and 0.20 mol dm^{-3} $B^{3+}(aq)$.

$K_{sp}(AI_2) = 9.0\times10^{-9}$ and $K_{sp}(BI_3) = 1.6\times10^{-18}$

(i) What are the minimum concentration of $I^-(aq)$ needed to start precipitation of the $A^{2+}(aq)$ and $B^{3+}(aq)$?

(ii) What range of concentrations of $I^-(aq)$ can be used to precipitate only $B^{3+}(aq)$?

Answer

(i) For AI_2

$K_{sp} = [A^{2+}(aq)]\,[I^-(aq)]^2$

$$[I^-(aq)] = \sqrt[2]{\frac{K_{sp}}{[A^{2+}(aq)]}}$$

$$= \sqrt[2]{\frac{9.0\times10^{-9}}{0.10}}$$

$= 3.0 \times 10^{-4}$ mol dm^{-3}

For BI_3

$K_{sp} = [B^{3+}(aq)]\,[I^-(aq)]^3$

$$[I^-(aq)] = \sqrt[3]{\frac{K_{sp}}{[B^{3+}(aq)]}}$$

$$= \sqrt[3]{\frac{1.6\times10^{-18}}{0.20}}$$

$= 2.0 \times 10^{-6}$ mol dm^{-3}

(ii) 2.0×10^{-6} mol $dm^{-3} < [I^-(aq)] < 3.0 \times 10^{-4}$ mol dm^{-3}

2.4.5 Factors affecting solubility

Common-ion effect

Consider the following equilibrium in a saturated solution of AgCl at 298 K.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

If $[Ag^+(aq)]$ is increased, according to Le Chatelier principle the equilibrium will shift to left to keep the value of equilibrium constant, i. e. K_{sp} constant. This increase of $[Ag^+(aq)]$ can be achieved by adding a soluble salt like $AgNO_3$ to the initial equilibrium. Because of this shift, more AgCl(s) is produced and hence the solubility of AgCl is decreased. This is called the "***common-ion effect***" because an ion that is already a part of the equilibrium (common to the equilibrium) is being added.

This can be stated as follows too.

> *If we cause the equilibrium to* ***shift to the left*** *then the rate of crystallization is increased more than the rate of dissolving. More Ag^+ ions and Cl^- ions will combine to form solid AgCl and its* ***solubility decreases.***

According to Le Chatelier's principle, the opposite is also true: if we can cause the equilibrium to shift to the right, then the rate of dissolution is increased more than the rate of crystallization and more solid AgCl will dissolve and its solubility increases.

Example 2.36

Calculate the molar solubility of $Ni(OH)_2$ in 0.10 mol dm^{-3} NaOH.
$K_{sp}(Ni(OH)_2) = 2.0\times10^{-15}$ mol^3 dm^{-9}

Answer

Let the solubility of $Ni(OH)_2$ as ***s***.

$$Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$$

At equilibrium : s $2s + 0.10$

$K_{sp} = [Ni^{2+}(aq)][OH^-(aq)]^2$

$= s\,(2s + 0.10)^2$

As K_{sp} is small, $(2\boldsymbol{s} << 0.10)$

$\therefore (2\boldsymbol{s} + 0.10) \approx 0.10$

2.0×10^{-15} mol^3 $dm^{-9} = \boldsymbol{s}\,(0.10)^2$

$s = 2.0 \times 10^{-13}$ mol dm^{-3}

If we do not have a common ion solubility is 7.94×10^{-6} mol dm^{-3}.

Example 2.37

Calculate the molar solubility of $BaCrO_4$ in (i) 0.100 mol dm^{-3} and (ii)1.00×10^{-3} mol dm^{-3} $BaCl_2$ solutions at 298 K. $K_{sp}(BaCrO_4) = 1.2 \times 10^{-10}$ mol^2 dm^{-6}.

Answer

(i) $$BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq)$$

At equilibrium : $s + 0.100$ s

$K_{sp} = [Ba^{2+}(aq)][CrO_4^{2-}(aq)] = (s + 0.10)\,s$

As K_{sp} is small, $(\boldsymbol{s} << 0.100)$

$\therefore (s + 0.100) \approx 0.100$

1.2×10^{-10} mol^2 $dm^{-6} = s\,(0.100)$

$\boldsymbol{s = 1.2 \times 10^{-9}}$ **mol dm^{-3}**

(ii) $$BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq)$$

At equilibrium : $s + 0.001$ s

$K_{sp} = [Ba^{2+}(aq)][CrO_4^{2-}(aq)] = (s + 0.001)\,s$

As K_{sp} is small, $(\boldsymbol{s} << 0.001)$

$\therefore (s + 0.001) \approx 0.001$

1.2×10^{-10} mol^2 $dm^{-6} = s\,(0.001)$

$\boldsymbol{s = 1.2 \times 10^{-7}}$ **mol dm^{-3}**

These results indicate that the solubility of $BaCrO_4(s)$ is comparatively high in dilute solutions of $BaCl_2$.

As we know that according to Le Chatelier's principle, if we can cause the equilibrium to shift to the right then the rate of dissolution is increased more than the rate of crystallization.

Consider the following equilibrium:

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

The solubility of the $PbCl_2(s)$ can be increased by decreasing either $[Pb^{2+}(aq)]$ or $[Cl^-(aq)]$.
The $[Pb^{2+}(aq)]$ can be decreased by adding some ion which precipitates the Pb^{2+}. Any of the following ions: Br^-, I^-, SO_4^{2-}, S^{2-}, OH^-, PO_4^{3-}, CO_3^{2-}, SO_3^{2-}, will precipitate Pb^{2+}. Even though there is a possibility to add any of the above anions, all of them may not decrease the $[Pb^{2+}(aq)]$.

A new precipitate formed must have a lower solubility than that of the $PbCl_2$. Therefore, for example, we can choose a soluble salt containing I^- ions like KI because K_{sp} of PbI_2 is 1.4×10^{-8} mol^3 dm^{-9} while K_{sp} of $PbCl_2$ is 1.8×10^{-5} mol^3 dm^{-9}. Similarly, $AgNO_3$ can be added to decrease the $[Cl^-(aq)]$ which precipitates as AgCl.

Example 2.38
Compare the relative solubility of $CaC_2O_4(s)$ in 0.10 mol dm^{-3}solutions of (i)NaOH, (ii)KCl and (iii) $Ca(NO_3)_2$

Answer
As $CaC_2O_4(s)$ is a spairingly soluble salt we can write,

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

(i) In NaOH(aq) : $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$
$OH^-(aq)$ will precipitate $Ca^{2+}(aq)$ as $Ca(OH)_2(s)$
Thus, $[Ca^{2+}(aq)]$ decreases, causing a shift to right, so the solubility of $CaC_2O_4(s)$ increases.

(ii) In KCl(aq): $KCl(aq) \rightarrow K^+(aq) + Cl^-(aq)$
$K^+(aq)$ and $Cl^-(aq)$ will not affect the equilibrium.

(iii)In $Ca(NO_3)_2$ (aq): $Ca(NO_3)_2(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^-(aq)$
$Ca^{2+}(aq)$ is a common ion, so $[Ca^{2+}(aq)]$ increases, causing a shift to left, forming more $CaC_2O_4(s)$. Therefore the solubility of CaC_2O_4 decreases.

2.4.6 pH effect

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. For example consider the effect of pH on the solubility of a salt, MA where A^- is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:

$$MA(s) \rightleftharpoons M^+(aq) + A^-(aq) \quad : \quad K_{sp} = [M^+(aq)][A^-(aq)] \ldots\ldots\ldots (1)$$

The anion can also react with water in a hydrolysis reaction:

$$A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq) \ldots\ldots\ldots (2)$$

Because of the reaction described above, solubility of salt MA increases as the $A^-(aq)$ produced in (1) is removed by reaction (2). For example predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-}, PO_4^{3-}, or CO_3^{2-} is increased. If instead a strong acid is added to the solution, the added H^+ will react almost completely with A^- to form HA. This reaction decreases $[A^-(aq)]$, which decreases the magnitude of the ionic product ($IP = [M^+(aq)][A^-(aq)]$). According to Le Chatelier's principle, more MA will dissolve until $IP = K_{sp}$. Hence *an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid*.

Consider the following equilibrium:

$$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$$

If HNO_3 is added, the following reaction occurs:

$$H_3O^+(aq) + PO_4^{3-}(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$$

This reaction reduces PO_4^{3-} in solution, causing more solid Ag_3PO_4 to dissolve (NO^{3-} ions remain in the solution as spectators without participating in any events).

Consider the following equilibrium:

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

- Increasing the pH means increasing $[OH^-]$ and equilibrium will shift to the left, causing some of $Cu(OH)_2$ to precipitate out or decrease the solubility.
- If the pH is lowered, $[OH^-]$ decreases and equilibrium shifts to the right, causing solid $Cu(OH)_2$ to dissolve or increase the solubility.
- The solubility of compounds of the type $M(OH)_n$ decreases as pH is increased, and increases as pH is decreased.

Thus, insoluble basic salts tend to dissolve in acidic solutions. Similarly, insoluble acidic solutions tend to dissolve in basic solutions.

Example 2.39

Calculate the $Cu^{2+}(aq)$ concentration in a saturated solution of $Cu(OH)_2$ at 298 K, (i) when pH =10.0 and (ii) when pH = 5.0. $K_{sp(Cu(OH)_2)} = 2.2 \times 10^{-20}\ mol^3dm^{-9}$.

Answer

(i) when pH = 10.00

$[H^+(aq)] = 1.0\times10^{-10}$ and $[OH^-(aq)] = 1.0\times10^{-4}\ mol\ dm^{-3}$

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

At equilibrium: x $1.0\times10^{-4}\ mol\ dm^{-3}$

$K_{sp} = [Cu^{2+}(aq)][OH^-(aq)]^2 = 2.2 \times 10^{-20}\ mol^3dm^{-9}$

$x\ (1.0\times10^{-4}\ mol\ dm^{-3})^2 = 2.2 \times 10^{-20}$

$\therefore x = [Cu^{2+}(aq)] = \mathbf{2.2 \times 10^{-12}\ mol\ dm^{-3}}$

(ii) when pH = 5.00

$[H^+(aq)] = 1.0\times10^{-5}$ and $[OH^-(aq)] = 1.0\times10^{-9}\ mol\ dm^{-3}$

$$Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2OH^-(aq)$$

At equilibrium : x 1.0×10^{-9}

$K_{sp} = [Cu^{2+}(aq)][OH^-(aq)]^2 = 2.2 \times 10^{-20}$

$x\ (1.0\times10^{-9}\ mol\ dm^{-3})^2 = 2.2 \times 10^{-20}\ mol^3dm^{-9}$

$\therefore x = [Cu^{2+}(aq)] = \mathbf{2.2 \times 10^{-2}\ mol\ dm^{-3}}$

We can note that decreasing pH increases the solubility of such metal hydroxides.

In the above example, the anion $OH^-(aq)$ is derived from water and thus we could consider the effect of $H^+(aq)$ in the medium. Such pH-dependent solubility is not restricted to salts that contain anions derived from water (metal hydroxides). For example, CaF_2 is a sparingly soluble salt containing a basic anion: consider the equilibrium below at 298 K.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)\ ; \quad K_{sp} = 3.45 \times 10^{-11}$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs.

$$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq)$$

Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system and the net reaction of CaF_2 with strong acid is thus

$$CaF_2(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2HF(aq)$$

In another case of metal carbonates: $MCO_3(s)$

$$MCO_3(s) \rightleftharpoons M^{2+}(aq) + CO_3^{2-}(aq)$$

$$H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq)$$

The overall reaction is thus,

$$MCO_3(s) + H^+(aq) \rightarrow M^{2+}(aq) + HCO_3^-(aq)$$

i.e. More $MCO_3(s)$ dissolves to relieve the stress on the system which means that the increase in pH decreases the solubility while decrease in pH increases the solubility.

From the above, we can note that sparingly soluble salts derived from weak acids such as fluorides, oxalates, carbonates, phosphates, etc. tend to be more soluble in an acidic solution.

Consider the following example.
PbC_2O_4, PbI_2 and $PbSO_4$ are sparingly soluble salts with K_{sp} values of 4.8×10^{-10} mol^2dm^{-6}, 9.8×10^{-9} mol^3dm^{-9} and 2.5×10^{-5} $mol^2\,dm^{-6}$, respectively at 298 K. Compare their relative solubilities when a strong acid is added to saturated solutions of them.

We can write:

$$PbC_2O_4(s) \rightleftharpoons Pb^{2+}(aq) + C_2O_4^{2-}(aq)\,;\ K_{sp} = 4.8 \times 10^{-10}\ mol^2\,dm^{-6}$$

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)\,;\ K_{sp} = 9.8 \times 10^{-9}\ mol^3\,dm^{-9}$$

$$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)\,;\ K_{sp} = 2.5 \times 10^{-5}\ mol^2\,dm^{-6}$$

The anions $C_2O_4^{2-}$, I^-, and SO_4^{2-} formed in the above equilibria are all conjugate bases of acids $H_2C_2O_4$, HI, and H_2SO_4. Because the strongest conjugate base will be most affected by the addition of a strong acid, we can then relate the relative solubilities to their relative basicities.

Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form $H^+(aq)$ and the corresponding anion.

$C_2O_4^{2-}(aq)$ has high affinity for one proton and low affinity for a second proton. Therefore, addition of a strong acid to a saturated solution of $PbC_2O_4(s)$ will result in the following reactions:

$$C_2O_4^{2-}(aq) + H^+(aq) \rightleftharpoons HC_2O_4^-(aq)$$

and

$$HC_2O_4^-(aq) + H^+(aq) \rightleftharpoons H_2C_2O_4(aq)$$

These reactions will decrease [$C_2O_4^{2-}$(aq)], causing more lead oxalate to dissolve to relieve the stress on the system.

Adding a strong acid to a saturated solution of $PbSO_4$ will result in the following reaction.

$$SO_4^{2-}(aq) + H^+(aq) \rightleftharpoons HSO_4^-(aq)$$

The pK_a of HSO_4^-(aq) (1.99) << pK_{a2} of oxalic acid, so the reverse reaction in the above equilibrium is largely favored. In other words, basicity of oxalic acid >>> basicity of sulfuric acid. Therefore, the effect of the strong acid added is significantly less on the solubility of $PbSO_4$ than on PbC_2O_4.

From this example we can also note that the solubilities of salts containing anions (such as Cl^-, Br^-, I^-) that do not hydrolyze are unaffected by pH.

Example 2.40
A sample has 3.0×10^{-6} mol dm^{-3} of M^{3+}(aq) in an acidic solution. To what pH must the solution be adjusted to begin precipitation of M^{3+} as $M(OH)_3$?
Ksp = 2.4×10^{-20} mol^4 dm^{-12}

Answer
K_{sp} = [M^{3+}(aq)] [OH^-(aq)]^3= 2.4×10^{-20} mol^4 dm^{-12}

$$[OH^-(aq)] = \sqrt[3]{\frac{2.4 \times 10^{-20}}{3.0 \times 10^{-6}}} = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$$

$\therefore$ pOH = **4.7**
pH = **9.3**

Thus, the solution will not begin to precipitate until enough base is added to adjust the pH to 9.3.

2.4.7 Application of solubility product in qualitative (cation) analysis

It is useful to know how to detect the presence of specific ions in an aqueous solution and the procedure used here comes under *qualitative analysis*, which addresses the question "What is in a sample?" The basis of qualitative analysis is the fact that ions will undergo specific chemical reactions with certain reagents to yield observable products. For example, silver ion can be precipitated with hydrochloric acid to yield insoluble solid silver chloride. Because many cations will not react with hydrochloric acid in this way, this simple reaction can be used to separate ions that form insoluble chlorides from those that do not. In fact, the qualitative detection of ions in a mixture is commonly accomplished by a systematic analysis in which precipitation reactions play a major role.

The various salts of the cations have varying solubilities in water. The differences in solubilities of these salts can be exploited in such a way as to allow for separation of the ions. For example, the addition of an appropriate chemical reagent to an aqueous mixture of cations can selectively cause one or more of the cations to form a precipitate while one or more of the cations will remain dissolved in water.

We know that cations can be separated into five major groups according to the solubilities of their compounds:

Group I (Ag^+, Pb^{2+}, Hg_2^{2+}) cations produce insoluble chlorides so they can be precipitated with dilute HCl, while all other cations remain in solution.

Group II (Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}, As^{3+}, Sb^{3+}, Sn^{4+}/ Sn^{2+}) cations produce very insoluble sulfides (K_{sp} values less than 10^{-25}) so they can be precipitated by low amounts of sulfide ion; this can be achieved by adding H_2S to an acidic solution of metal ions.

Group III (Al^{3+}, Cr^{3+}, Fe^{2+}, Fe^{3+}) cations produce very insoluble hydroxides and they can be precipitated by adding relatively low amount of hydroxyl ions.

Group IV(Zn^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}) cations produce slightly soluble sulfides (K_{sp} values more than 10^{-20}) so they can be precipitated by relatively high amounts of sulfide ion; this can be achieved by adding H_2S to a basic solution of metal ions.

Group V (Ca^{2+}, Sr^{2+}, Ba^{2+}) cations, as well as all of the above groups, produce insoluble carbonates so they can be precipitated by the addition of carbonate once the ions of the first four groups have been removed.

(Mg^{2+}, Na^+, K^+, NH_4^+) cations do not precipitate with any of the above reagents.

The chemistry of the precipitation of the Group I cations

The precipitating reagent of Group I is a dilute solution of hydrochloric acid (6 M), and the ions precipitated are those of silver, Ag^+, mercury (I), Hg_2^{2+}, and lead (II), Pb^{2+}. The net ionic equations are:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$
$$Hg_2^{2+}(aq) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s)$$
$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$$

A slight excess of chloride ion is used to reduce the solubility of the precipitates in accordance with the common ion effect. Even so the solubility of lead chloride is sufficiently high for an appreciable concentration of lead ion to remain in solution. Most of this is precipitated with the Group II reagent.

The chemistry of the precipitation of the Group II cations

The ions of Group II (and Group IV) are separated by precipitation as their insoluble sulfides. The sulfide ion is furnished by the weak electrolyte of gaseous hydrogen sulfide, which is only sparingly soluble in water. At 25 °C and 1 atmosphere pressure, a saturated aqueous solution contains about 0.1 mol in a litre). The dissolved molecular hydrogen sulfide dissociates into hydrogen ions, hydrogen sulfide ions, $HS^-(aq)$, and sulfide ions, $S^{2-}(aq)$ and we can consider the following equilibria.

Three equilibria are involved:

$$H_2S(g) \rightleftharpoons H_2S(aq)$$

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq); \quad K_1 = \frac{[H^+(aq)]\,[HS^-(aq)]}{[H_2S(aq)]} = 9.1 \times 10^{-8}\ \text{mol dm}^{-3}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq); \quad K_2 = \frac{[H^+(aq)]\,[S^{2-}(aq)]}{[HS^-(aq)]} = 1.0 \times 10^{-19}\ \text{mol dm}^{-3}$$

The low value of K_2 suggests that there is very little free S^{2-} in aqueous solutions unless they are extremely basic. Therefore, the precipitation of metal sulfides is best written as:

$$M^{2+}(aq) + H_2S(aq) \rightleftharpoons MS(s) + 2H^+(aq)$$

As with any equilibrium, the extent of reaction depends on the relative concentrations of products and reactants. In this case, making the solution acidic will tend to prevent precipitation of metal sulfides. Adding an acid shifts the above equilibrium to left. As The K_{sp} values of group II metal ions is very low. Therefore sulfides of the metal ions with very low solubility will precipitate from acidic hydrogen sulfide solutions, while sulfides of greater solubility (Group IV) will remain in solution. Controlling the concentration of $H^+(aq)$, therefore, can be used to separate ions on this basis of differences in the solubility of their sulfides. Group II is often called the acid hydrogen sulfide group in which the hydrogen ion concentration is maintained in the range of 0.1 mol dm^{-3} - 0.3 mol dm^{-3} (pH = 0.5 - 1.0). By this the concentration of sulfide ions is so adjusted that only ionic products of the sulphides of group II exceed their solubility products and, therefore, get precipitated, but not the ions of group IV of which the sulfides are more soluble. These conditions can be achieved by passing $H_2S(g)$ into the filtrate from group I separation.

The reactions involved in the precipitation of Group II cations are as follows.

$$Cu^{2+}(aq) + H_2S(aq) \rightarrow CuS(s) + 2H^+(aq)$$
$$Cd^{2+}(aq) + H_2S(aq) \rightarrow CdS(s) + 2H^+(aq)$$
$$Hg^{2+}(aq) + H_2S(aq) \rightarrow HgS(s) + 2H^+(aq)$$
$$2Bi^{3+}(aq) + 3H_2S(aq) \rightarrow Bi_2S_3(s) + 6H^+(aq)$$
$$2As^{3+}(aq) + 3H_2S(aq) \rightarrow As_2S_3(s) + 6H^+(aq)$$

$$2Sb^{3+}(aq) + 3H_2S(aq) \rightarrow Sb_2S_3(s) + 6H^+(aq)$$
$$Sn^{4+}(aq) + 2H_2S(aq) \rightarrow SnS_2(s) + 4H^+(aq)$$

The chemistry of the precipitation of the Group III cations

K_{sp} values of the hydroxides of group III cations are very low and hence they can be precipitated as hydroxide by controlling the concentration of hydroxide ions very low. In this separation care must be taken not to have the solution of hydrogen sulfide too basic. If the concentration of hydroxide ion is sufficiently high, unwanted precipitation of magnesium hydroxide will take place. To achieve a hydroxide ion concentration of the necessary concentration (about 1×10^{-5} mol dm^{-3}) an ammonia-ammonium chloride (NH_3 / NH_4Cl) buffer is used. In the ammonia solution the following ionization equilibrium prevails:

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

$$NH_4Cl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

If 0.10 mol dm^{-3} NH_3 solution is used, the hydroxide ion concentration will be 1.3×10^{-3} mol dm^{-3} which is sufficiently high to precipitate magnesium hydroxide. The presence of the added ammonium ion concentration from the ammonium chloride displaces the ammonia equilibrium to the left (common ion effect) reducing the hydroxide ion concentration. A $[OH^-(aq)]$ of about 1×10^{-5} mol dm^{-3} is sufficient to precipitate the slightly soluble aluminum and chromium hydroxides but not the more soluble magnesium hydroxide. We can understand this by comparing their K_{sp} values : $K_{sp(Al(OH)_3)} = 1.8 \times 10^{-33}$ $mol^4\,dm^{-12}$, $K_{sp(Cr(OH)_3)} = 3.0 \times 10^{-29}$ $mol^4\,dm^{-12}$, $K_{sp(Fe(OH)_3)} = 1.4 \times 10^{-28}$ $mol^4 dm^{-12}$ and $K_{sp(Mg(OH)_2)} = 1.8 \times 10^{-11}$ $mol^3 dm^{-9}$.

The equations for the precipitation of the ions of Group III are:

$$Al^{3+}(aq) + 3H_2O(aq) + 3NH_3(aq) \rightarrow Al(OH)_3(s) + 3NH_4^+(aq)$$
$$Cr^{3+}(aq) + 3H_2O(aq) + 3NH_3(aq) \rightarrow Cr(OH)_3(s) + 3NH_4^+(aq)$$
$$Fe^{3+}(aq) + 3H_2O(aq) + 3NH_3(aq) \rightarrow Fe(OH)_3(s) + 3NH_4^+(aq)$$

At this stage, if the $[OH^-_{(aq)}]$ is high enough to precipitate $Mg(OH)_2$

$$Mg^{2+}(aq) + OH^-(aq) \rightarrow Mg(OH)_2(s)$$

Therefore, control of OH^- concentration is a must in the separation of Al^{3+}, Cr^{3+} and Fe^{3+} without the precipitation of Mg^{2+} ions.

The chemistry of the precipitation of the Group IV cations

The ions of Group IV are precipitated as their sulfides, from a basic solution of hydrogen sulfide. In a basic solution, more of the ionization of H_2S occurs and, thus, concentration of S^{2-} ions increases. It becomes so high that ionic products of the sulphides of group IV exceed their solubility products and they get precipitated.

$H_2S(g) \rightleftharpoons H_2S(aq)$

$H_2S(aq) \rightleftharpoons 2\,H^+(aq) + S^{2-}(aq)$

In the presence of $OH^-(aq)$ ions, the $H^+(aq)$ ions are neutralized and therefore the solution contains fairly high concentration of $S^{2-}(aq)$ ions enough to precipitate group IV cations as their sulfides.The sulfides of the ions of group IV are not sufficiently insoluble to be precipitated in the acidic solution of hydrogen sulfide of Group II but will be precipitated by basic solutions of hydrogen sulfide. The equations for the precipitation of the ions of Group IV are:

$Zn^{2+}(aq) + H_2S(aq) \rightarrow ZnS(s) + 2H^+(aq)$

$Ni^{2+}(aq) + H_2S(aq) \rightarrow NiS(s) + 2H^+(aq)$

$Co^{2+}(aq) + H_2S(aq) \rightarrow CoS(s) + 2H^+(aq)$

$Mn^{2+}(aq) + H_2S(aq) \rightarrow MnS(s) + 2H^+(aq)$

The chemistry of the precipitation of the Group V cations

The ions of Group V are precipitated as their carbonates in basic solution. This condition is achieved by removing $H_2S_{(aq)}$ in filtrate from group IV by boiling and adding NH_4Cl/ NH_4OH in excess. Adding $(NH_4)_2CO_3$ solution will enable the precipitation of group V cations. The equations for the precipitation of the ions of Group V are:

$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$

$Sr^{2+}(aq) + CO_3^{2-}(aq) \rightarrow SrCO_3(s)$

$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$

The chemistry of the precipitation of the Group VI cations

Magnesium : If only Mg^{2+} ions present in a solution it is easy to identify by simple tests. However, in a mixture of cations, it is difficult to identify and therefore, a specific test with 8-hydroxyquinoline is carried out to identify Mg^{2+} by precipitation which forms a yellow-green precipitate or complex.

Na^+, K^+, NH_4^+ cations do not precipitate with any of the above reagents and usually identified by the flame test by the observation of their characteristic colors in the flame.

The following example explains the importance of pH in selective precipitation.

Example 2.41

A solution contains 0.1 mol dm^{-3} Zn^{2+} and 0.1 mol dm^{-3} Fe^{2+} ions. What should be the *p*H of the solution, if they are to be separated by passing H_2S gas through the solution?

Given that K_{sp} for ZnS = 1.6×10^{-24} mol^2 dm^{-6} and K_{sp} for FeS= 6.3×10^{-18} $mol^2 dm^{-6}$. In a solution $H_2S(aq)$ has a concentration of 0.10 mol dm^{-3}.

Answer

When $H_2S(g)$ is passed through a solution following equilibria exist.

$$H_2S(g) \rightleftharpoons H_2S(aq)$$

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq); \quad K_{a_1} = \frac{[H_3O^+(aq)]\,[HS^-(aq)]}{[H_2S(aq)]}$$

$$= 9.1 \times 10^{-8} \text{ mol dm}^{-3}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq); \quad K_{a_2} = \frac{[H_3O^+(aq)]\,[S^{2-}(aq)]}{[HS^-(aq)]}$$

$$= 1.0 \times 10^{-19} \text{ mol dm}^{-3}$$

From these two equations we can write

$$K_{a_1} K_{a_2} [H_2S(aq)] = [H_3O^+(aq)]^2 [S^{2-}(aq)]$$

Substituting the given, we get,

$$[H_3O^+(aq)]^2 [S^{2-}(aq)] = (9.1 \times 10^{-8})(1.0 \times 10^{-19})(0.1) \text{ mol}^3 \text{ dm}^{-9}$$

$$= 9.1 \times 10^{-28} \text{ mol}^3 \text{ dm}^{-9}$$

From the given data, we have,

$K_{sp}(ZnS) = [Zn^{2+}(aq)][S^{2-}(aq)] = 1.6 \times 10^{-24}$ mol^2 dm^{-6} and

$K_{sp}(FeS) = [Fe^{2+}(aq)][S^{2-}(aq)] = 6.3 \times 10^{-18}$ mol^2 dm^{-6}

In case when $[Zn^{2+}(aq)] = 0.1$ mol dm^{-3}, minimum $[S^{2-}(aq)]$ required for precipitating ZnS can be calculated as,

$$[S^{2-}(aq)] = \frac{1.6 \times 10^{-24}}{0.1} = 1.6 \times 10^{-23} \text{ mol dm}^{-3}$$

Corresponding to this minimum concentration of S^{2-} ions we can calculate the maximum H_3O^+ concentration by using the following equation

$$[H_3O^+(aq)]^2 [S^{2-}(aq)] = 9.1 \times 10^{-28} \text{ mol}^3 \text{ dm}^{-9}$$

$$\therefore [H_3O^+(aq)]^2 = \frac{9.1 \times 10^{-28}}{1.6 \times 10^{-23}} = 5.7 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$

$$\therefore [H_3O^+(aq)] = 7.6 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log[H_3O^+(aq)] = 2.1$$

$\therefore$ The minimum pH required for precipitation of ZnS= 2.1

Likewise in case when $[Fe^{2+}(aq)]$ = 0.1 mol dm^{-3}
Minimum $[S^{2-}(aq)]$ required for precipitating FeS is,

$$[S^{2-}(aq)] = \frac{6.3 \times 10^{-18}}{0.1} = 6.3 \times 10^{-17} \text{ mol dm}^{-3}$$

And the maximum $[H_3O^+(aq)]$ required is given by,

$$\therefore [H_3O^+(aq)]^2 = \frac{9.1 \times 10^{-28}}{6.3 \times 10^{-17}} = 1.4 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$$

$$\therefore [H_3O^+(aq)] = 3.7 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log[H_3O^+(aq)] = 5.4$$

Therefore, the minimum pH at which FeS precipitates = 5.4
It is seen that if the H_3O^+ ion concentration is higher than $10^{-5.4}$ mol dm^{-3} (3.7×10^{-6} mol dm^{-3}), Fe^{2+} will not be precipitated whereas Zn^{2+} will get precipitated.

The pH of the solution to separate the two ions should be between 2.1 and 5.4.

2.5 Equilibria in different phases

As we already have an idea that the matter exists in three phases solid, liquid and gas and when the matter undergoes phase changes (transformations) from one phase to another macroscopic properties of the system remain unchanged while microscopic properties change. Usually, phase changes occur when the temperature or pressure of the system is changed and the phase changes are physical changes characterized by changes in molecular order; molecules in the solid phase have the greatest order, and those in the gas phase have the greatest randomness. In this section, we deal with systems having liquid – vapour equilibrium.

Liquid- vapour equilibrium

Molecules in a liquid are not arranged tidily as those in a solid and therefore they have lesser freedom than those of gaseous molecules, though they are in constant motion. Because liquids have higher intermolecular attractions than gases, the collision rate among molecules is much higher in the liquid phase than in the gas phase. The *average* energy of the particles in a liquid is governed by the temperature as shown in Figure 2.29. When the molecules in a liquid have sufficient energy to escape from the surface a phase change occurs. ***Evaporation,*** or ***vapourization,*** is *the process in which a liquid is transformed into a gas.*

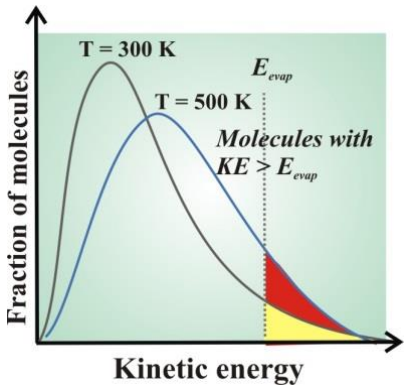


Figure 2.29 The distribution of the kinetic energies of the molecules of a liquid at two temperatures of 300 K and 400 K. Increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_{evap} can escape from the liquid to enter the vapour phase, and the proportion of molecules with $KE > E_{evap}$ is greater at the higher temperature.

For example, when we consider a liquid (water or alcohol) in an open container, at any given instant a small fraction of the molecules in the liquid phase will be moving quite fast. If one of these is close to the surface and is travelling upward, it can escape from the attraction with its fellow molecules entirely and pass into the gas phase. As the higher energy molecules depart, the average energy of the molecules in the liquid decreases and the temperature of the liquid falls due to the absorption of energy in the form of heat by the surroundings, an effect which you can feel if you let water or alcohol to evaporate from your skin. Absorption of heat maintains the average molecular speed in the liquid, so that, given enough time, all the liquid can evaporate. *The heat absorbed during the entire process corresponds to the enthalpy of vapourization.* The evaporation only takes place on the surface of the liquid. If we look at water which is just evaporating in the sun, we don't see any bubbles. Water molecules are simply breaking away from the surface layer and the process is different from boiling where we observe bubbling.This is illustrated in Figure 2.30.

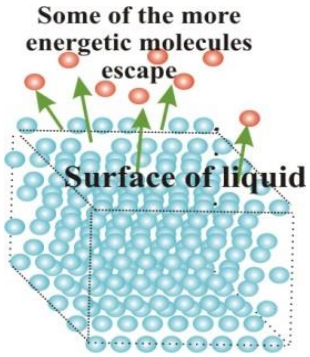


Figure 2.30 Patter of evaporation of a liquid in an open container at a given temperature. Most of the molecules with high energy that escape into the vapour phase will not collide with the surface of the liquid again and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container.

2.5.1 Evaporation of a liquid in a closed container

If the liquid is in a closed container, at the first look it doesn't seem to evaporate and also it doesn't disappear over time. But there is constant evaporation from the surface. Particles continue to break away from the surface of the liquid but this time they are trapped in the space above the liquid.

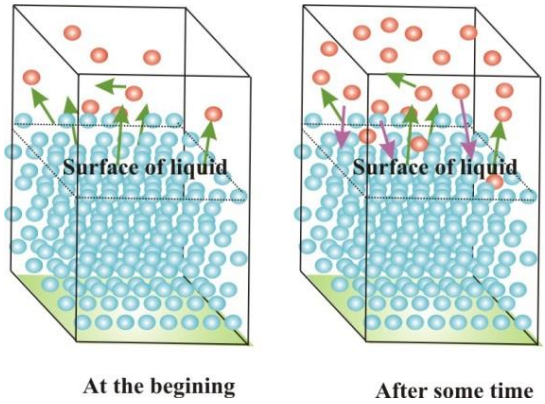


Figure 2.31 Macroscopic view of the molecular interpretation of vapour pressure. When a liquid is placed in a closed container at a given temperature, few molecules start to evaporate at the beginning and none of them can come back and re-enter into the liquid. After some time the density of the molecules in the vapour phase becomes high and some of the molecules start to condense.

On the microscopic level, though molecules are still escaping from the liquid surface into the vapour above, the vapour remains inside the container. Molecules of the vapour behave like any other gas: they bounce around colliding with each other and the walls of the container and hence producing a pressure above the liquid surface. In this case one of these "walls" is the surface of the liquid. Once a molecule collides with the liquid surface there is a tendency that the molecule will re-enter into the liquid.

When the liquid is first introduced into the container, there are very few molecules of vapour and the rate of recapture/ condensation will be quite low, but as more and more molecules evaporate, the chances of a recapture will become proportionately larger. Eventually the vapour pressure will be attained, and the rate of recapture will exactly balance the rate of escape. There will then be no net evaporation of liquid or condensation of gas. i.e. the amount of vapour remains the same only because molecules are reentering the liquid just as fast as they are escaping from it.

Once the vapour-liquid system has attained this state, the macroscopic properties such as the amount, the volume, the pressure, the temperature, the density, etc., of both liquid and gas will all remain constant with time and therefore the system has attained an *equilibrium*. As there is no change in the macroscopic level of the system, the two opposing microscopic processes of *vaporization* and *condensation* occur with equal rates.

Since both microscopic processes are still in operation, the system is in ***dynamic equilibrium*.** When these particles hit the walls of the container, they exert a pressure. *The pressure exerted by a vapour in dynamic equilibrium with a liquid is defined as the* ***equilibrium vapor pressure*** *of the liquid (sometimes called the* ***saturated vapour pressure*** *of the liquid).* This process is shown in Figure 2.32 where we have to note that the evaporation rate is constant over the time and the rate of condensation increases with time and reaches the equilibrium.

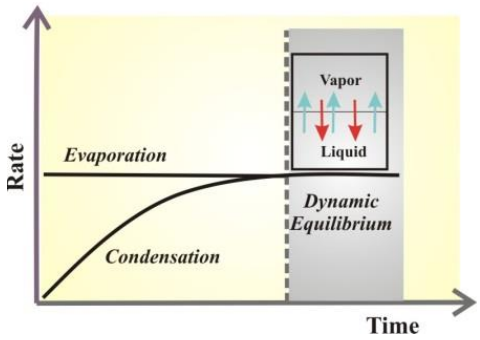


Figure 2.32 Variation of the rates of evaporation and condensation over the time for a liquid in a closed container at a given temperature. Rate of evaporations remains a constant while the rate of condensataion increases as the number of molecules in the vapour phase increases till the two rates become equal. At this point the system reaches a state of dynamic equilibrium having the equilibrium vapour pressure of the liquid at a constant temperature.

The magnitude of the vapour pressure of a liquid depends mainly on two factors: the strength of the forces holding the molecules together and the temperature. It is easy to see that if the intermolecular forces are weak, the vapour pressure will be high and vice versa. Weak intermolecular forces will permit molecules to escape relatively easily from the liquid. The rate at which molecules escape will thus be high. Quite a large concentration of molecules will have to build up in the gas phase before the rate of re-entry can balance the escape rate. Consequently the vapour pressure will be large.

2.5.2 Measuring the equilibrium (saturated) vapour pressure

The equilibrium vapour pressure can be measurd with a simple mercury - barometer as described below. At the atmosphere pressure the height of the mercury column will be 760 mm. [100 kPa = 760 mmHg ("millimetres of mercury")]. This is illustrated in Figure 2.33 (a). When a few drops of liquid is added into the tube, it will rise to form a thin layer floating on top of the mercury. Some of the liquid will vapourize and the equilibrium is attained. At this point some liquid will remain on top of the mercury. The vapour pressure of the liquid forces the mercury level down a bit. The drop in the mecury level gives a value for the saturated vapour pressure of the liquid at this temperature.

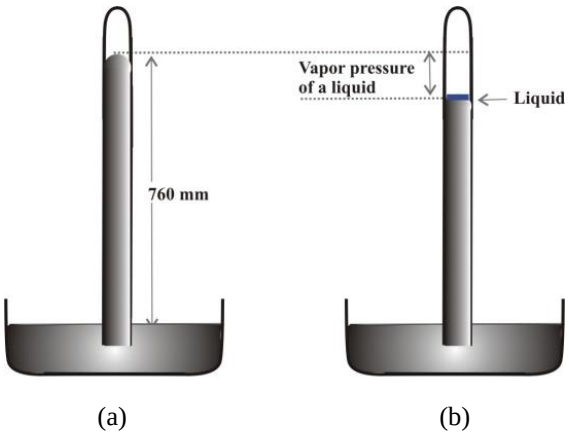


Figure 2.33 Measuring the saturated vapour pressure. **(a)** when a mecury barometer is just in air, the reading is 760 mmHg. **(b)** when a liquid is introduced into the tube, it goes on to the top of the mecury in a barometer and the level of Hg falls down. The difference is the saturated vapour pressure of the liquid.

2.5.3 The variation of saturated vapour pressure with temperature

Increase in the temperature increases the average energy of the molecules present. That means, more of them are likely to have enough energy to escape from the surface of the liquid. That will tend to increase the saturated vapour pressure.

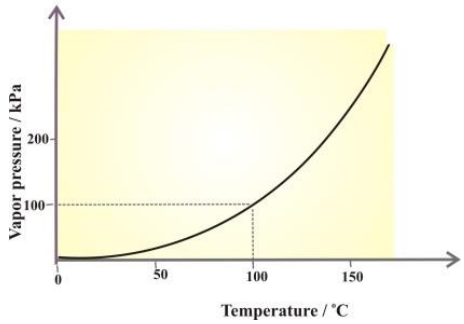


Figure 2.34 Variation of the saturated vapour pressure of water with temperature.

For example, any size sample of water held at 25 °C will produce a vapour pressure of 23.8 mmHg (3.168 kPa) in any closed container, provided all the water does not evaporate.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapour phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and the equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it "disappears". The speed with which this occurs depends on the vapour pressure of the liquid and the temperature. Volatile liquids have relatively high vapour pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and

evaporate slowly. As a general guideline, we consider that substances with vapour pressures greater than that of water (3.168 kPa*)* are relatively volatile, whereas those with vapour pressures less than that of water are relatively nonvolatile. Thus diethyl ether, acetone, and gasoline are volatile, but mercury, ethylene glycol, etc. are non-volatile. The equilibrium vapour pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapour pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 2.35. Molecules that can have hydrogen bonds, such as ethylene glycol, have a much lower equilibrium vapour pressure than those that cannot make hydrogen bonds, such as octane. The non-linear increase in vapour pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. This is mainly due to the dependence of vapour pressure on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid phase, and this fraction increases exponentially with temperature.

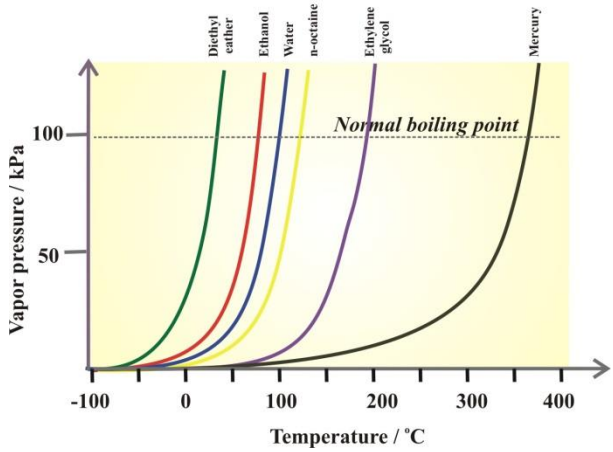


Figure 2.35 The vapour pressures of several liquids as a function of temperature. The point at which the vapour pressure curve crosses the P = 100 kPa line (dotted) is the normal boiling point of the liquid.

2.5.4 Boiling point

As the temperature of a liquid increases, the vapour pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapour begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 100 kPa (1atm) pressure is the ***normal boiling point*** of the liquid. For water, the normal boiling point is exactly 100 °C at the sea level. The normal boiling points of the other liquids in Figure 2.35 are represented by the points at which the vapour pressure curves cross the line corresponding to a pressure of 1 atm.

Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 100 kPa (1 atm), water boils at a temperature greater than 100 °C because the increased pressure forces vapour molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 100 kPa (1 atm), water boils below 100 °C. Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. At an elevation of Mount Everest, for example, the boiling point of water is about 70 °C. However, in the case of pressure cookers, which have a seal that allows the pressure inside them to exceed 100 kPa (upto around 200 kPa /2 atm), are used to cook food more rapidly by raising the boiling point of water to around 120 °C and thus the temperature at which the food is being cooked.

As pressure increases, the boiling point of a liquid increases and vice versa. Volatile substances have low boiling points and relatively weak intermolecular interactions; non-volatile substances have high boiling points and relatively strong intermolecular interactions.

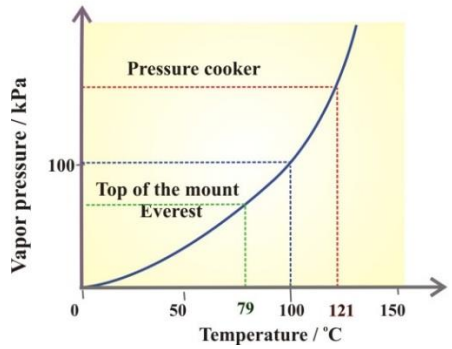
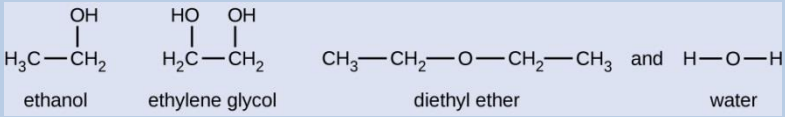


Figure 2.36 Change in boiling point of water with the pressure: water boils at normal boling point of 100 °C at atmospheric pressure of 100 kPa, boiling of water occurs at around 79 °C at mountain top and the boiling temperature increses to around 121 °C when it boils inside a pressure cooker.

Example 2.42
Compare the variation in relative vapour pressures of ethanol, ethelene glycol, diethyl eather and water at 100 kPa pressure and room temperature.

Answer
First, we have to know the structures of these compounds and we have,



Diethyl ether: is the largest, however, it has a very small dipole and its intermolecular attractions are London forces. As a result, its molecules most readily escape from the liquid. It also has the highest vapour pressure.

Ethanol: Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. It has a capability to form hydrogen bonds. Therefore it exhibits stronger overall intermolecular forces, which means that fewer molecules escape from the liquid at any given temperature, so ethanol has a lower vapour pressure than diethyl ether.

Water: is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapour pressure than in either diethyl ether or ethanol.

Ethylene glycol: has two −OH groups like water and therefore, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall intermolecular forces are the largest of these four substances, which means its vapourization rate will be the slowest and, consequently, its vapour pressure being the lowest.

Therefore, the variation in vapour pressure is in the order,
diethyl eather > ethanol > water > ethelene glycol

Example 2.43
At 20 °C, the vapour pressures of methanol, ethanol, propanol and butanol are 12.0 kPa, 6.0 kPa, 2.7 kPa and 0.60 kPa, respectively. Explain this variation.

Answer
All of these are alcohols and exhibit hydrogen bonding. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed.

$P_{methanol} > P_{ethanol} > P_{propanol} > P_{butanol}$

2.5.5 Enthalpy of vapourization

Vapourization is an endothermic process. This can be understood with a simple phenomenon of our own. When water on the skin evaporates, it removes heat from the body and causes to feel cold. The energy change associated with the vapourization process is the enthalpy of vapourization, ΔH_{vap}. For example, the vapourization of water at standard temperature is represented by:

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H_{vap} = 44.01 \text{ kJ mol}^{-1}$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$H_2O(g) \rightarrow H_2O(l) \qquad \Delta H_{con} = -44.01 \text{ kJ mol}^{-1}$$

Example 2.44
At normal body temperature, how much heat is required when 1.5 dm^3 of water (as sweat) is evaporated from the body? ΔH_{vap} = 43.46 kJ mol^{-1} at 37 °C.

Answer
Weight of 1.5 $dm^3$of water = 1.5 $dm^3 \times$ 1000 g dm^{-3} = 1.5 $\times 10^3$ g
$\therefore$ Amount of moles of water evaporated = 1.5 $\times 10^3$ g/ (18 g mol^{-1}) = 83.333 mol
$\therefore$ Heat required = 43.46 kJ $mol^{-1} \times$ 83.333 mol = 3621 kJ

In the sequel other phase changes of a single component system are also described as they are essential in understanding the behaviour of them in the light of getting knowledge of energy/ enthalpy changes during such events in chemical processes.

Melting and Freezing

When a crystalline solid is heatd, the average energy of its atoms is increased and molecules or ions and the solid get some kinetic energy. At some point, when the added energy/ heat becomes large enough to partially overcome the forces holding the molecules or ions together, the solid starts the process of transition to the liquid state, or melting. At this point, despite the continuous heating the temperature remains constant until the entire solid is melted. After all of the solid has melted the temperature of the liquid then increases if the heating is continued.

For example, if we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container, the solid and liquid phases remain in equilibrium. This can be observed experimentally when a mixture of ice and water is kept in a thermos flask and we can observe that the mixture of solid ice and liquid water remains for hours. At this point the mixture of solid and liquid is at equilibrium and the reciprocal processes of melting of ice and freezing of water occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the *melting point of the solid or the freezing point of the liquid*. This equilibrium is expressed as:

$$\textbf{Solid} \underset{\text{freezing}}{\overset{\text{melting}}{\rightleftharpoons}} \textbf{Liquid}$$

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the *enthalpy of fusion*, ΔH_{fus} of the substance. The enthalpy of fusion (melting) of ice is 6.0 kJ mol^{-1} at 0 °C and is an endothermic process:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta H_{fus} = 6.0 \text{ kJ mol}^{-1}$$

The opposite process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ mol^{-1} at 0 °C:

$$H_2O(l) \rightarrow H_2O(s) \quad \Delta H_{fus} = -6.0 \text{ kJ mol}^{-1}$$

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the repeating units present in the crystal. Molecules with weak attractive forces form crystals with low melting points while crystals consisting of particles with stronger attractive forces melt at higher temperatures.

Sublimation and deposition

Some solids can undergo transition directly into the gaseous state, bypassing the liquid state, via a process known as *sublimation*. For example, at room temperature and standard pressure, a piece of dry ice (solid CO_2) use in fire extingushers sublimes (disappear) without ever forming any liquid. Snow and ice sublime at temperatures below the melting

point of water. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms. The reverse of sublimation is called *deposition*, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.

Like vapourization, the sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub}, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$CO_2(s) \rightarrow CO_2(g) \qquad \Delta H_{sub} = 26.1 \text{ kJ mol}^{-1}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$CO_2(g) \rightarrow CO_2(s) \qquad \Delta H_{sub} = -26.1 \text{ kJ mol}^{-1}$$

Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vapourization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vapourization for which Hess Law can be applied.

$$\text{solid} \rightarrow \text{liquid:} \quad \Delta H_{fus} \quad \text{and} \quad \text{liquid} \rightarrow \text{gas:} \quad \Delta H_{vap}$$

Therefore by applying Hess's law we can write,

$$\text{solid} \rightarrow \text{gas:} \quad \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

Viewed in this manner, the enthalpy of sublimation for a substance may be approximated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 2.37.

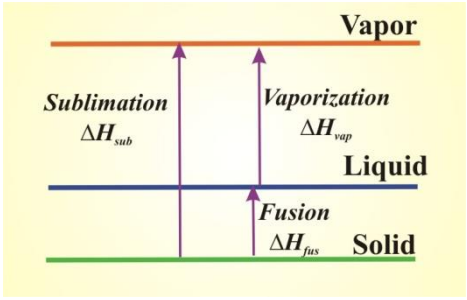


Figure 2.37 For a given substance, the sum of its enthalpy of fusion and enthalpy of vapourization is approximately equal to its enthalpy of sublimation.

The processes of phase transiations described above can be experimentally observed by constructing either heating or cooling curves. When a substance for example ice ($H_2O(s)$)

being heated or cooled reaches a temperature corresponding to one of its phase transitions (melting/fusion) and further heating results in vapourization. The heating curve of this process is depicted in the Figure 2.38.

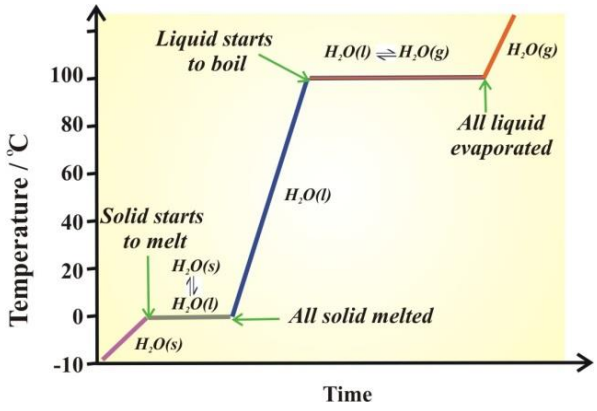


Figure 2.38 A typical heating curve for water depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the water undergoes phase transitions. Longer plateau for the equilibrium of $H_2O(l) \rightleftharpoons H_2O(g)$ compared to that of $H_2O(s) \rightleftharpoons H_2O(l)$ is due to $\Delta H_{fus} < \Delta H_{vap}$.

Example 2.45

How much heat is required to convert 180 g of ice at −15 °C into liquid water at 0 °C?

Answer

First, 180 g (10 moles) of ice at −15 °C has to be converted into ice at 0 °C. The heat required for this can be calculated by using $q_1 = ms(\Delta t)$, where, s is the specific heat capacity of ice: 2.09 J g^{-1} °C^{-1}

$\therefore q_1 = ms(\Delta t) = 180\ g \times 2.09\ J\ g^{-1}\ °C^{-1} \times 15\ °C = 5643\ J = 5.6\ kJ$

Then, the heat needed to induce a phase change of ice to liquid water is a given $q_2 = n \times \Delta H_{fus}$.

$\therefore q_2 = 10\ mol \times 6.0\ kJ\ mol^{-1} = 60\ kJ$

$\therefore$ Total heat required = $q_1 + q_2 = 65.6$ kJ

2.5.6 Phase diagrams of pure substances

As we know, a phase is simply a physical state of a substance present under given conditions such as at a given temperature and pressure. That is, a phase is another meaning for solid, liquid or gas. If we consider some ice floating in water, there are two phases of a solid present and a liquid. If there is air above the mixture, then that is another phase.

We can further understand this by considering the system where oil floats on water. This consists two phases of liquids, oil and water. If the oil and water are contained in a beaker, then beaker is yet another phase. From this we can recognise the presence of the different phases and they are separated by a boundary between them.

Phase diagrams

A phase diagram depicts exactly what phases are present at any given temperature and pressure and they are separated by lines which are called boundaries between them. The line between two phases gives the temperature and pressure at which two phase are in equilibrium. For simplicity of understanding first we will consider phase diagrams of pure substances or we define these as phase diagrams of one-component systems. For example, Figure 2.39 shows a skeptual phase diagram of a one component system.

In the diagram we can see that there are three lines, three areas marked "solid", "liquid" and "vapour", and two special points marked "C" and "T". This indicates that we have a pure substance at three different sets of conditions of ranges of temperature and pressure corresponding to solid, liquid and vapour phases.

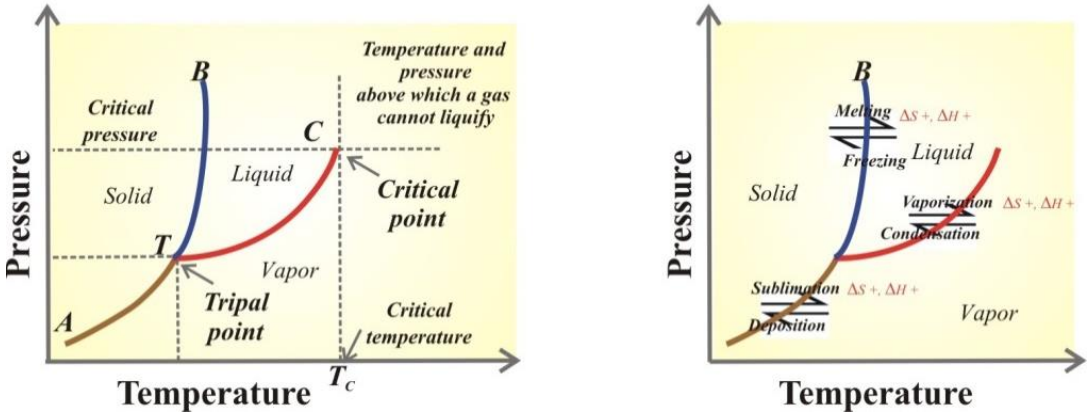


Figure 2.39 Phase diagrams of one component system. In **(a)** curve TB represents the equilibrium that can exist between the molecules of a given solid and those of the same compound in its liquid state. This situation is only found at the melting point of the compound concerned. Line TB is therefore represents the melting point at various pressures. The line TC represents the equilibrium that exists between molecules in the vapour phase and those in the liquid state, i.e. the equilibrium that is found at the boiling point of the compound concerned. The line TC then shows the variation of boiling point with pressure. AT represents the sublimation curve showing the relationship that exists between the sublimation temperature and the pressure – an equilibrium which is only possible if the external pressure is below that at T, the triple point of the compound. **(b)** shows the equilibria existing in those regions and the signs of ΔS and ΔH.

Point T: The triple point

In the phase diagram shown in Figure 2.39, the three curves representing solid-vapour equilibrium (curve AT), solid-liquid equilibrium (curve TB) and liquid-vapour equilibrium (curve TC) meet at the point T.

Where all three curves meet, there is a *unique combination of temperature and pressure* where all three phases are in equilibrium together and that point is called the *triple* point. If the conditions of temperature and pressure are controlled in order to reach this point, there would be an equilibrium which involves the solid melting and subliming, and the boiling liquid in contact with its vapour.

Point C : Critical point

In the phase digram illustrated in Figure 2.39**,** the liquid-vapour equilibrium curve (TC) has a top limit labelled **C**. This is known as the **critical point**. The temperature and pressure corresponding to this are known as the **critical temperature (T_C)** and **critical pressure**.

If the pressure of a gas is increased at a temperature lower than the critical temperature, the system will cross the liquid-vapour equilibrium line and the vapour will condense to give a liquid. However, when the temperature is *above* the critical temperature, thre is no any line to cross. That is because, above the critical temperature, it is impossible to condense/liquify a gas into a liquid just by increasing the pressure. What we get only is a highly compressed gas.

For example, if the gaseous molecules are compressed together by a high external pressure, but with a temperature high enough not to allow condensation to occur, we will have properties pertaining to both the liquid as well as the gaseous states. The density will be that of a liquid but in this state called the **super critical fluid state**, the compound behaves like a gas also.

The critical temperature obviously varies from substance to substance and depends on the strength of the attractions among molecules. "*The stronger the intermolecular attractions, the higher the critical temperature."*

Understanding of the bevaviour of the substance undergoing phase changes can be interpreted as follows with the help of Figure 2.40.

Point P: Solid phase

In the Figure 2.40 (a), we can see that at the point **I** with temperature (T_1) and pressure (P_1) water exists as a solid. Assume that the temperature of the system is slowly increased to (T_2) while keeping the pressure constant (P_1), *i.e. temperature moves along the line PQ*. It crosses the curve TB at the point X at which there is equilibrium between solid and

liquid (*Anywhere on this line, there is an equilibrium between solid and liquid.*) and then turn to a pure liquid at the temperature T_2 (point Q) or in other words, it melts.

If we repeate this at a higher fixed pressure (P_2), the melting temperature is higher ($T`_2$). See the point **I`** as illustrated in Figure 2.40 (a). From this we can understand that the curve TB which separate solid and liquid phases simply illustrates the *effect of pressure on melting point of a solid*.

Further understanding of this behaviour of change in melting point can be treated as follows: As now you have knowledge on Le Chatelier's principle, increase in the pressure leads the equilibrium to move in such a way as to counter the change. As we are having solid ⇌ liquid equilibrium, increasing the pressure on the equilibrium mixture of solid and liquid at its original melting point will convert the mixture back into the solid again. In other words, it will no longer melt at this temperature. Therefore, to make it melt at this higher pressure (P_2), increase in the temperature is needed. Thus, raising the pressure raises the melting point of most solids.

Point Q

If we continue heating at the same pressure (P_1), along line PR, the liquid will meet the TC curve at point Y at which there is equilibrium between liquid and vapour and then turns into a pure vapour at the temperature T_3 (point R). In other words, it vapourizes. i.e., the liquid will change into a vapour through boiling when it crosses the boundary line between the two phases (TC curve) shown in Figure 2.40 (b). *Therefore by varying the temperature at a constant pressure the boiling temperature can easily be read at that pressure from the phase diagram*. As we know, anywhere along this line, there will be an equilibrium between the liquid and the vapour.

Further, if the pressure of the system is decreased by keeping the temperature constant at T_2, (downward arrow from "point Q"), we meet the TC curve and further decrease in pressure to **P_2`** will turn the liquid into vapour. Therefore, the curve TC illustrates the *effect of pressure on the boiling point of the liquid*. As the pressure increases, the boiling point increases and vice versa.

Point S: Moving from solid to vapour

Consider the point **S** labelled in the phase diagram in Figure 2.40 (c). Solid phase exists at that given temperature (T_4) and pressure (P_4). The curve AT represents the boundary between solid and vapour phases on which solid-vapour equilibrium exists. As we have discussed the points P and Q, the curve AT can be crossed by either increasing the temperature of the solid, or decreasing the pressure.

The arrow in the diagram shows the effect of increasing the temperature of a solid phase at a (probably very low) constant pressure. The pressure obviously has to be low enough that a liquid can't form - in other words, it has to happen below the point labelled **T**. Once

the line meets the curve AT, solid starts to sublime attaining equilibrium between solid and vapour phases. When the selected temperatures and pressures are below the temperature and pressure of the point **T** we can see that only the solid or vapour phase can exists in the system. Once the point T is passed, it can be seen that the vapour at a constant temperature can be converted into a liquid by increasing the pressure, where the phenomenon of liquifaction of gasses can be understood.

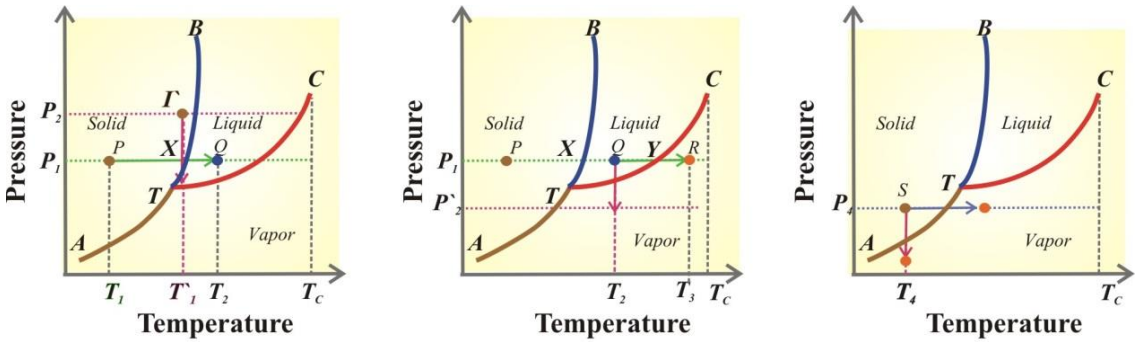


Figure 2.40 Behaviour of substance undergoing phase changes

Normal melting and boiling points

As the normal melting and boiling points are the temperatures when the pressure is 100 kPa, these can be found from the phase diagram by drawing a line across 100 kPa pressure.

Deatailed phase diagram of water

Notice that the triple point for water occurs at a very low pressure of 611 Pa and at the temperature of 0.01 °C. Melting and boiling points are at 0.00 °C and 100 °C, respectively, where the pressure is 100 kPa. The critical temperature is 374 °C and the critical pressure is 201 kPa. The complete phase diagram of water is thus depicted in the Figure 2.41 with the inclusion of above information.

Note: *In the case of water, "the melting point gets lower at higher pressures".*

For the melting, we have the equilibrium of;

$$\text{Ice} \rightleftharpoons \text{Water}$$

Ice is less dense than water; therefore, water formed by melting of ice occupies a smaller volume. When the pressure is increased, according to Le Chatelier's Principle the equilibrium will move to reduce the pressure again. That means it will move to the side with the smaller volume. Liquid water is produced. Therefore, to make the liquid water freeze again at this higher pressure, temperature has to be reduced and hence higher pressures bring about lower melting (freezing) points. Thus, the slope of the line/curve for the equilibrium between solid and liquid phases of water has a negative gradient.

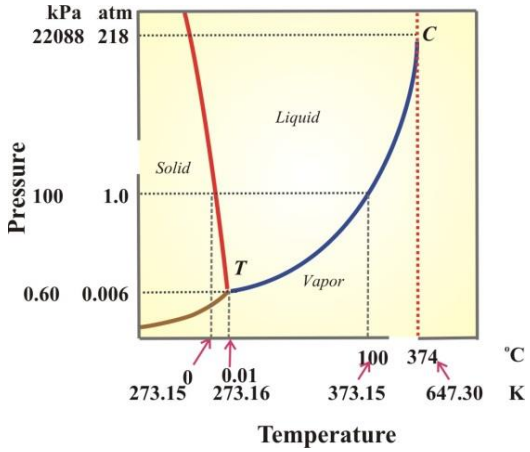


Figure 2.41 Phase diagram of water

When the different phases of water are considered there is a marked difference in the density near ambient conditions and at critical conditions. For example:

At 100 kPa (1 atm) and 0 ° C:

Density of liquid water = 1 g cm^{-3} = 55.6 mol dm^{-3}

Density of gaseous water = 2.7×10^{-4} mol dm^{-3}

At 218 atm and 374 ° C:

Density of gaseous water = Density of liquid water = 4.1 mol dm^{-3}

Phase diagram of CO_2 is shown in the Figure 2.42.

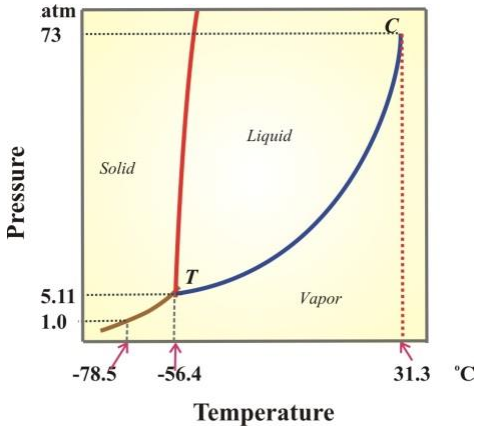


Figure 2.42 Phase diagram of CO_2

Compared to the phase diagram of water, the only thing special about the the phase diagram of CO_2 is the position of the triple point which is well above atmospheric pressure. Therefore, it is impossible to get any liquid carbon dioxide at pressures less than 5.11 atm. That is CO_2 does not display normal melting and boiling points. That means at 1 atm pressure, carbon dioxide can only sublime at a temperature of -78 °C. This is the reason why solid carbon dioxide is often known as "dry ice". You can't get liquid carbon dioxide under normal conditions - only the solid or the vapour.

2.6 Liquid - vapour equilibrium in binary liquid systems

In this section, characteristics of the mixtures of two volatile liquids will be discussed wth the help of therotical concepts first. In the first part the discussion is made on the cases where the two liquids are entirely miscible in all proportions to give a single liquid. To understand the behaviour of these solutions, a concpt of an ideal mixture will be introduced and the characteristics of phase diagrams of such ideal mixtures. Are dealt with. Later on, a comparison between ideal and non-ideal mixtures will be made.

2.6.1 Characteristics of ideal mixtures

When a completly miscible liquid mixture is formed by mixing two very closely similar liquids, we assume that they get fairly close to being ideal. Some examples are *hexane and heptane, benzene and toluene, water and ethanol etc.*

Intermolecular forces

As we have discuused under the vapour pressure, in a pure liquid, some of the more energetic molecules have a tendency to escape from the liquid surface to form the vapour and in substances having smaller intermolecular forces, more molecules will be able to escape at any given temperature. For another liquid the same thing is true and this is illustrated in Figure 2.43.

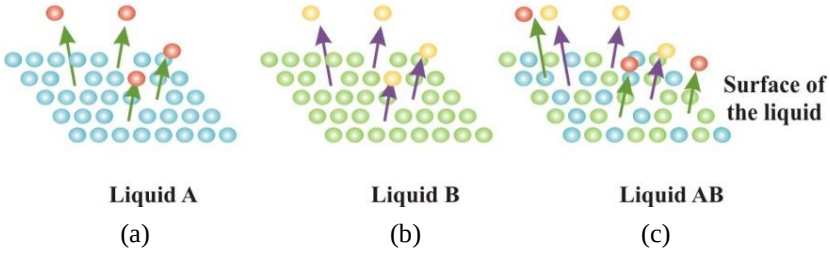


Figure 2.43 Formation of 1:1 ideal liquid mixture AB with the pure components of A and B

Once these two liquids are mixed assuming a complete miscibility the resultant mixture is said to be an ideal (*subjected to obey some rules*), and the tendency of the two different molecules of the liquids to escape is unchanged as described in Figure 2.43(c).

In the Figure 2.43(c) you can see that when the mixture is 1:1 of the two liquids and the proportion of each type of molecule escaping is the same. In other words, the number of molecules escape from each component of the mixture is the same.

If A and B molecules still have the same tendency to escape as before (when tthey exist alone), we can understand that the intermolecular forces between two A molecules must be exactly the same as the intermolecular forces between a A and a B molecule (If the forces were any different, the tendency to escape would change).

With this characteristic we can understand that the intermolecular interactions between A and B molecules also be exactly the same as the interactions between A-A and B-B molecules.

Enthalpy change of mixing

When a mixture of liquids is made, breaking of the existing intermolecular attractions and the remaking of new attarctions occur. Energy is needed to break the interactions while energy is released during the formation of new attarctions. If all these attractions are the same, there won't be any heat either evolved or absorbed. That means an ideal mixture of two liquids will have zero enthalpy change of mixing.

> *At a given temperature, when a binary completely miscible liquid mixture is formed by mixing liquid A and liquid B, with the intermolecular interactions between $f_{A\text{-}A}$, $f_{B\text{-}B}$ and $f_{A\text{-}B}$ are equal ($f_{A\text{-}A} = f_{B\text{-}B} = f_{A\text{-}B}$) and with no enthalpy change, such a solution is called an ideal solution.*

A mixture of hexane and heptane gets close to ideal behaviour because they are similar in size and so have equal van der Waals attractions between them.

Roult law

Consider and ideal binary liquid solution (mixture) made by mixing of liquids **A** and **B** in a closed container with a vaccum above at a given temperature. As we know, the molecules of **A** and **B** with sufficient energy will escape into the space above the surface of liquid and build up a pressure. Once the system reaches the dynamic equilibrium, rates of evaporation and condensation of **A** and **B** become equal. The dynamic equilibrium at this pont can be testified with the consistency of the ***total vapour pressure*** and the ***composition of the vapour phase*** at a constant temperature. According to Dolton law, *total pressure is the sum of partial pressures of components in the system.* Composition of the vapour phase depends on the relative volatilities (boiling points) of **A** and **B** and the relative concentrations of **A** and **B** in the solution.

The component with high volatility (low boiling point) and higher concentration in solution tends to buid up the higher partial pressure. That is, concentration of a component in the vapour phase is proportional to its partial pressure ($[A(g)] \alpha p_A$) and in a mixture the concentration of a component is proportional to its mole fraction ($[A_{(l)}] \alpha x_A$).

Consider the vapor – liquid equilibrium of an ideal solution with components **A** and **B** described above. As the rate of evaporation equals the rate of condensation, we can write:

$$\mathrm{A(l)} \underset{r_c}{\overset{r_v}{\rightleftharpoons}} \mathrm{A(g)} \quad \ldots\ldots(1) \qquad\qquad \mathrm{B(l)} \underset{r_c'}{\overset{r_v'}{\rightleftharpoons}} \mathrm{B(g)} \quad \ldots\ldots\ldots(2)$$

r_v *and* r_c are the rates of vapourization and condensation, respectively of the component A.
r_v' and r_c' are the rates of vapourization and condensation, respectively of the component B.

Considering (1), we can write;

$$r_v = k\,[\mathrm{A(l)}] \;=\; k_1\,x_\mathrm{A}$$

X_A is the mole fraction of A in solution.

Likewise,

$$r_v' \;=\; k\,'[\mathrm{A(g)}] \;=\; k_2\,p_\mathrm{A}$$

P_A is the partial pressure of A in vapour phase.

At equilibrium,

$$r_v = r_v'$$
$$k_2\,p_\mathrm{A} \;=\; k_1\,x_\mathrm{A}$$
$$\therefore\; p_\mathrm{A} \;=\; \frac{k_1}{k_2}x_\mathrm{A} \text{ or } \;\therefore\; p_\mathrm{A} \;=\; k\,x_\mathrm{A}$$
$$when\ x_\mathrm{A} = 1,\ p_\mathrm{A} = \; p_\mathrm{A}^0 = saturated\ vapor\ pressure\ of\ A$$
$$\therefore\; k = p_\mathrm{A}^0$$
$$\therefore \quad p_\mathrm{A} = p_\mathrm{A}^0\,x_\mathrm{A}$$
$$\text{and} \quad p_\mathrm{B} = \; p_\mathrm{B}^0\,x_\mathrm{B}$$

Thus;

> *In an ideal solution, the partial pressure of a given component is equal to the product of its saturated vapour pressure and the mole fraction of it in the liquid phase at a constant temperature.* This relationship is called ***Roult law.***

It is clear that $\therefore \quad p_\mathrm{A} < p_\mathrm{A}^0$ and $p_\mathrm{B} < p_\mathrm{B}^0$
Therefore, decrease or lowering in the vapor pressure of A
$= \; p_\mathrm{A}^0 - p_\mathrm{A} = p_\mathrm{A}^0 - p_\mathrm{A}^0 x_\mathrm{A} = \; p_\mathrm{A}^0(1 - x_\mathrm{A})$
$= \; p_\mathrm{A}^0\,x_\mathrm{B}$

$$\therefore\; \frac{p_\mathrm{A}^0 - p_\mathrm{A}}{p_\mathrm{A}^0} = x_\mathrm{B} \text{ and } \frac{p_\mathrm{B}^0 - p_\mathrm{B}}{p_\mathrm{B}^0} = x_\mathrm{A}$$

The above is an alternative form of Roult law.

Relative lowering of vapour pressure of a given component in the vapour phase is equal to the mole fraction of the other component in the solution.

Combining the Roult law with Dolton law of partial pressures, it is possible to determine the composition in the vapour phase. If ***p*** is the total vapour pressure and y_A and y_B are the mole fractions of A and B in the vapor phase, respectively, from Dolton law:

$p_A = py_A = (p_A + p_B)y_A$

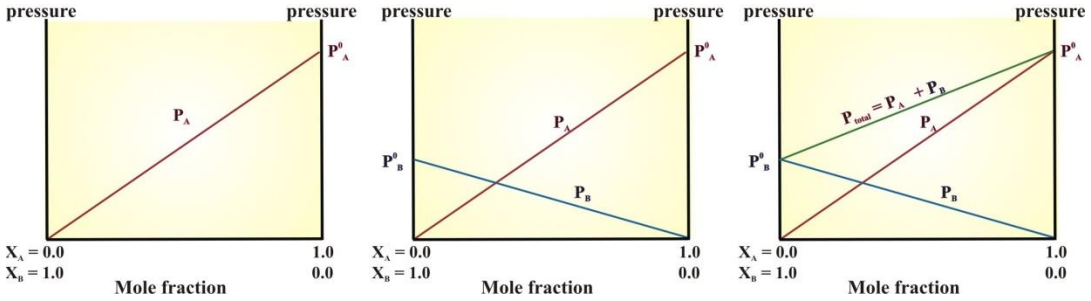
$$p_A^0 x_A = (p_A^0 x_A + p_B^0 x_B)y_A$$

$$\therefore Y_A = \frac{p_A^0 x_A}{(p_A^0 x_A + p_B^0 x_B)} \text{ and } y_B = \frac{p_B^0 x_B}{(p_A^0 x_A + p_B^0 x_B)}$$

Roult law is only applied for ideal mixtures or ideal mixtures follow Roult law.

Vapour pressure/ composition diagrams

In an ideal mixture of two liquids A and B, each of A and B is making its own contribution to the overall vapour pressure of the mixture at a constant temperature.When we consider the component A alone we have $p_A = p_A^0 x_A$; p_A^0 being a constant, results a straight line for the dependence of p_A on x_A as shown in Figure 2.44 (a). (*if x = 0, p_A = 0. p_A increases proportionately with the increase in x_A: if you double the x_A, P_A will be doubled. Therefore, the straight line goes through the (0,0) point in the graph).* Similar behaviour will be followed by the component B. If we assume that $p_A^0 > p_B^0$, i.e A is more volatile than B, Figure 2.44 (b) shows the line of variation of vapor pressure of B with its composition (x_B). The total vapour pressure of the mixture at each composition is therefore the sum of the vapour pressures of A and B at the point concerned. The complete graph of the ideal liquid mixture formed by mixing liquids A and B at a constant temperature is shown in Figure 2.44 (c). The line p_T (p_{AB}) shows the variation of total vapour pressure of the system with the composition of A and B.



(a) (b) (c)

Figure 2.44 Vapour pressure – composition diagrams for an ideal mixture AB which obeys the Roult law at constant temperature. **(a)** Variation of vapour pressure of component A; **(b)** variation of vapour pressure of component B included and **(c)** variation in total vapour pressure of the mixture.

Temperature (Boliling point) - composition diagrams

As we have discussed before, if the molecules are escaping easily from the liquid surface at a constant pressure it means that the intermolecular forces are relatively weak and the liquid needs little energy to boil and vapourize.

> *Therefore, the liquid with the higher vapour pressure at a particular temperature has the lower boiling point.*

Or we can understand the relation between vapour pressure and boiling point (temperature) as follows too.

Liquids boil when their vapour pressures become equal to the external atmospheric pressure. If a liquid has a high vapour pressure at a given temperature, little increase in the temperature is enough to bring the vapour pressure equal to the level of the external atmospheric pressure. On the other hand if the vapour pressure is low, more heat/energy is needed to reach the external pressure.

> *Therefore, the liquid with the higher vapour pressure at a given temperature has the lower boiling point.*

When an ideal mixture is formed by two liquids at the same temperature;

> *the one with the higher vapour pressure is the one with the lower boiling point*.

Constructing a temperature (boiling point) - composition diagram

First what we have to perform is the conversion of vapour pressure – composition diagram to a temperature (boiling point) – composition diagram at constant (external) pressure. Some may think that the task is an easy one with the thaught of it as simply a reciprocal of the vapour pressure – composition diagram. Though it looks like a correct argument still we have to consider some facts as follows.

In the ideal mixture aforesaid with $p_{\mathrm{A}}^{0} > p_{\mathrm{B}}^{0}$ at constant pressure $T_{\mathrm{b(A)}} < T_{\mathrm{b(B)}}$where T_b is the boiling point (A has a lower boiling point).

For mixtures of A and B, perhaps you might have expected that their boiling points would form a straight line joining the two points. However, it is a curve. You may recall that the vapour pressure of a liquid has an exponential variation with the temperature as discussed in the section 2.5.3 (see the Figure 12.34).

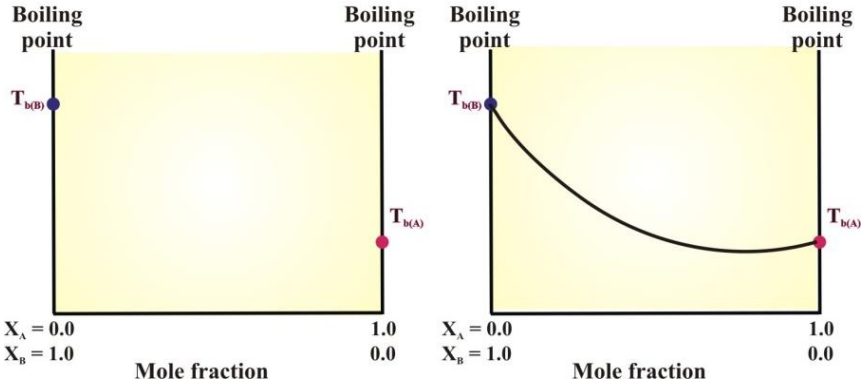


Figure 2.45 Boiling point (temperature) – composition diagrams for an ideal mixture AB at constant pressure. **(a)** Boiling points of components A and B; **(b)** variation of boiling point of the mixture.

First we can mark the boiling points on the respective axes with $T_{b(A)} < T_{b(B)}$ as shown in Figure 2.45 (a) and with the idea on the variation of the vapour pressure of the mixture with the composition of the liquid, the two points can be connected as shown in Figure 2.45 (b).

Now we need to know how the vapour pressure changes with the composition of the vapour. When a liquid mixture is boiled at constant pressure, the more volatile substance escapes to form the vapour more easily than the less volatile one. That means, in the present system higher proportion of A (the more volatile component) will be in the vapour than in the liquid. The composition of the vapour at this point can be estimated /determined by condensing the vapour first and analyzing it. Consider the point (P) marked on the diagram as shown in Figure 2.46 (a). The liquid at point P boils at temperature T_p and the composition of the vapour corresponding to T_p can be obtained by drawing a horizontal line through P and T_p. That the point in vapour is marked as Q.

Repeating this exercise with liquid mixtures with different compositions of the liquid, the second curve for the variation of the vapour pressure of the vapour with the composition can be plotted as shown in Figure 2.46 (b). We can see that the area inside the two lines consists of an equilibrium between the liquid and the vapour.

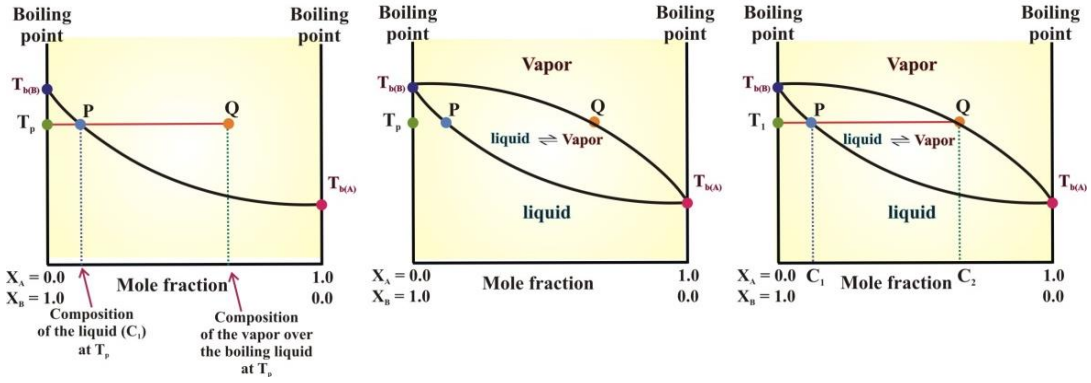


Figure 2.46 Boiling point (temperature) – composition diagrams for an ideal mixture AB at constant pressure. (a) Variation of boiling point of the mixture with the selected liquid composition C_1 which boils at T_p. Extrapolation of the line T_pP gives the composition of vapour at point P. (b) Variation of the boiling point in the vapor and inside envelop where the equilibrium liquid ⇌ vapor exists. (c) Finds the composition of the liquid corresponds to the point Q as C_2.

As described in Figure 2.46 (b), by boiling a liquid mixture we can find the temperature at which it boils, and the composition of the vapour over the boiling liquid. For example, in the Figure 2.46 (c), a liquid mixture of composition C_1 boils at a temperature T_1 and the vapour over the top of the boiling liquid will have the composition C_2. Likewise we can repeat this for other compositions and from the liquid composition curve the boling point can be determind. Then the composition of the vapour in equilibrium with the liquid of that composition could be estimated. This behaviour is very helpful in separating liquids from mixtures through distillation/ fractional distillation and the details on this will be discussed in a later section. Before going to discus that application it is worth seeing the characteristics of systems of liquid mixtures showing some devistions from the Roult law.

Non-ideal mixtures of liquids

A liquid mixture which does not obey Roult law is called a non-ideal liquid mixture. Such a mixture is formed by the components A and B among which the intermolecular interactions are not equal. These systems differ in behavior from ideal mixtures. In a non-idael mixture with components A and B, $f_{A\text{-}A} \neq f_{B\text{-}B} \neq f_{A\text{-}B}$, so there is a change in enthalpy during mixing. Therefore, the tendency for the molecules to escape is not the same in the mixture and in the pure liquids.

Vapour pressure - composition diagrams for non-ideal mixtures

As we know, the ideal mixtures obey the Roult law and dependence of vapour pressure on the composition of the liquid phase at a constant temperature results in a straight line as shown in Figure 2.44 (a), where A is the more volatile one and hence $p_A^0 > p_B^0$.

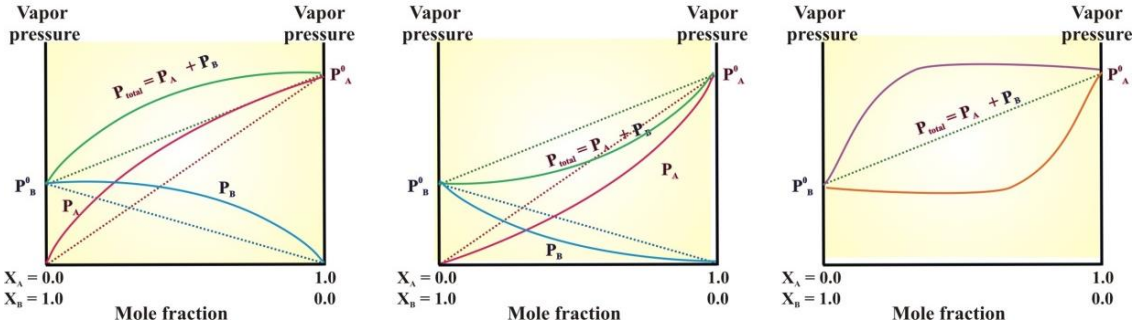


Figure 2.47 Vapour pressure – composition diagrams for non-ideal mixture AB at constant temperature. (a) Positive deviation from Roult law and (b) negative deviation from Roult law. (c) Shows mixtures having large positive and negative deviations from Roult law.

Positive deviations from Raoult law

Some mixtures are formed at constant temperature by components A and B where $f_{A\text{-}B} < f_{A\text{-}A}$ and $f_{B\text{-}B}$, i.e. the intermolecular forces between molecules of A and B are less than those in pure liquids. Therefore, the tendency for the molecules to escape into the vapour phase is higher than that in the case of an ideal mixture.

Therefore, $p_A > p^0_A x_A$ and $p_B > p^0_B x_B$: this results;

$$p_{AB} > (p^0_A x_A + p^0_B x_B)$$

This means that the total vapor pressure of the mixture is higher than that of an ideal mixture;

$$p_{AB} > p_{(AB)_{ideal}}$$

These type of mixtures/solutions are said to exhibit ***positive deviations*** from Roult law. In mixtures showing a positive deviation from Raoult's Law, the vapour pressure of the mixture is always higher than that expected from an ideal mixture. Thus, the curve in the vapour pressure – composition diagram loops upwards from the ideal line as shown in Figure 2.47 (a). In these mixtures, the vapour pressure which is higher than that of ideal mixtures implies that molecules are breaking away more easily than they do in the pure liquids. As the intermolecular forces between molecules of A and B are less than they are in the pure liquids, less heat is evolved than the heat absorbed to break the original attractions between molecules A-A and B-B when the liquids are mixed. Heat will therefore be absorbed when these liquids are mixed. Thus, the enthalpy change of mixing is positive (endothermic). We can see that along this curve the highest vapour pressure anywhere is still the vapour pressure of pure A as $p^0_A > p^0_B$. Cases like this, where the deviation is small, behave just like ideal mixtures as far as distillation is concerned. But some liquid mixtures have very large positive deviations from Raoult law and in these cases, the curve becomes distorted as shown in Figure 2.47 (c). For example a mixture of

this kind is ethanol and water that produces a highly distorted curve with a maximum vapour pressure for a mixture containing 95.6% of ethanol by mass.

Negative deviations from Raoult's law

In some mixtures formed at constant temperature by components A and B with $f_{A\text{-}B} > f_{A\text{-}A}$ and $f_{B\text{-}B}$, the tendency for the molecules to escape into the vapour phase is less than that in the case of an ideal mixture. That is the molecules break away from the mixture less easily than they do from the pure liquids. Thus stronger forces must exist in the mixture than in the original liquids.

Therefore, $p_A < p_A^0 x_A$ and $p_B < p_B^0 x_B$: this results;

$$p_{AB} < (p_A^0 x_A + p_B^0 x_B)$$

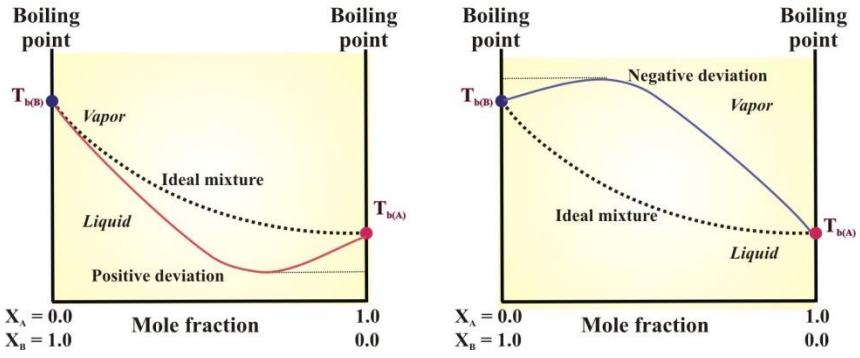
This means that the total vapor pressure of the mixture is lower than that of an ideal mixture;

$$p_{AB} < p_{(AB)_{ideal}}$$

These type of mixtures/solutions are said to exhibit ***negative deviations*** from Roult law. In mixtures showing a negative deviation from Raoult's Law, the vapor pressure of the mixture is always lower than that expected from an ideal mixture. Thus, the curve in the vapour pressure – composition diagram loops downwards from the ideal line as shown in Figure 2.47 (b). We can see a minimum and along this curve the highest vapour pressure anywhere is still the vapour pressure of pure A as $p_A^0 > p_B^0$. On mixing the liquids to form this type of a mixture, heat is evolved because the new bonds formed are stronger than the original weaker ones which are broken. For example when water and nitric acid is mixd, more heat is evolved because of the formation of ionic species NO_3^- and H_3O^+ (Figure 2.47 (c)).

Boiling point - composition diagrams for non-ideal mixtures

A mixture with positive deviation from Roult law has a high vapour pressure which means that it has a low boiling point. The molecules escape easily and it is not necessary to heat the mixture much to overcome the intermolecular attractions completely. Therefore, the boiling point - composition curve will have a minimum value lower than the boiling points of either A or B as shown in Figure 2.48 (a). For example, in the mixture of ethanol and water, this minimum occurs with 95.6% of ethanol by mass in the mixture. The boiling point of this mixture is 78.2 °C where as the boiling point of pure ethanol is 78.5 °C, and the boiling point of water is 100 °C.



(a) (b)

Figure 2.48 Boiling point – composition diagrams for non-ideal mixture AB at constant temperature. **(a)** Positive deviation from Roult law and **(b)** negative deviation from Roult law.

In the case of the mixtures with negative deviation from Roult law, molecules break away to form the vapour with much more difficulty than in either of the pure liquids. Therefore, such mixtures can have boiling points higher than either of the pure liquids because it needs extra heat to break the stronger forces in the mixture. Therefore, the variation of boiling point with the composition goes through a maximum value compared to boiling points of pure A and B and is shown in Figure 2.48 (b). For example, in a mixture of nitric acid and water, there is a maximum boiling point of 120.5 °C when the mixture contains 68% by mass of nitric acid. That can be compared with the boiling point of pure nitric acid (86 °C), and water (100 °C). It is easy to understand that this large difference in boiling points is due to the presence of the new ionic interactions as described earlier.

Fractional distillation

Consider Figure 2.44 (c) and assume that the vapour relavent to the liquid composition C_1 is collected and condensed to get a new liquid mixture with the composition C_2 which is reboiled. This liquid will boil at a new temperature T_2, and the vapour over the top of it would have a composition C_3 as shown in Figure 2.49. We can see that the vapour with composition C_3 is very close to pure A. Therefore, by repeating this process of condensing the vapour and reboiling the resultant liquid will eventually end up with pure A. This process is the basis of the technique called ***fractional distillation*** which is very useful in separating liquid mixtures to their pure components

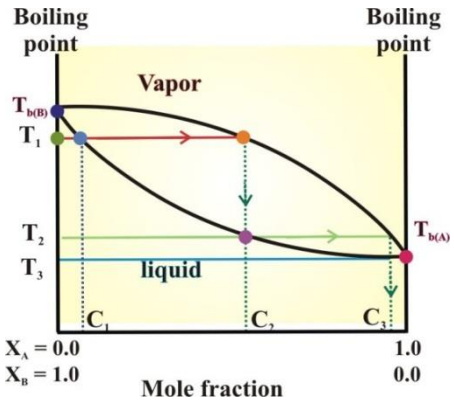


Figure 2.49 Concept of fractional distillation

If we continue the process of ocondensing and reboiling described in Figure 2.49, reboiling liquid C_3 will give a vapour still richer in the more volatile component A and we will be able to collect a liquid which is virtually pure B. Therefore, we can notice that *the more volatile component from a mixture of liquids can be separated by successive boiling-condensing-reboiling operations.* However, the repeating of this process is really time consuming and it needs some high efficiency in the view of industrial applications. Also it is not quite clear how a component with high boiling point is obtained. Fractionating columns are used to overcome this barrier by automating this condensing and reboiling process. Figure 2.50 shows a sketch of a complete set up used for fractional distillation with a fractionating column.

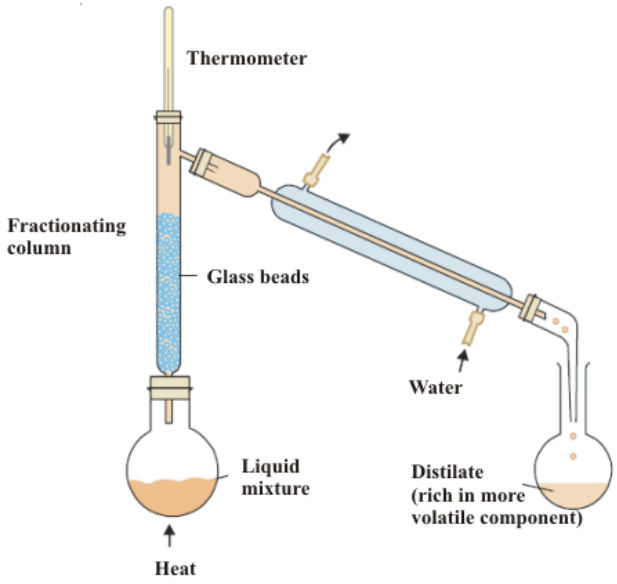


Figure 2.50 A sketch of the complete set up use for the fractional distillation with fractionating column

The fractionating column is packed with glass beads or spikes attached to the walls of a column to facilitate the vapour to condense. These glass beads or spikes make a lot of surface area inside the column allowing the maximum possible contact between the liquid falling down and the hot vapour rising leading to efficient boiling – condensation cycles. A thermometer bulb is placed exactly at the outlet of the fractionating column and the column is connected to a water-cooled condenser.

Consider boiling of a mixture with composition C_1.

Analysing the vapor;

As we know, the vapour over the top of the boiling liquid is richer in the more volatile component with low boiling point, and will have the composition C_2 (Figure 2.49). The vapour produced on top of the liquid now starts to travel up along the fractionating column and eventually it will reach a height at which the temperature is low enough to condense it giving a liquid on/in glass beads or spikes. The composition of that liquid is still C_2. Once the vapour is condensed, it will start to fall down along the column and will meet new hot vapour rising. Now as the falling liquid mixes up with the hot vapour that will cause it to reboil.

Assume now the composition of the vapour as C_3. As described above, this new vapour will again move further up the fractionating column until it gets to a temperature where it can condense. Then the whole process repeats itself. We can see that each time the vapour condenses to a liquid, the liquid will start to fall down the column through the glass beads. It will be reboiled by the up-coming hot vapour producing a vapour rich in the more volatile component A. If the boling points of the two liquids are very close, we need longer fractionating columns.

Analysing the liquid

As the vapour is richer in the more volatile component A, the liquid remaining in the flask will be getting richer in the other component B. During this repeating process of boilng and condensastions and as the condensed liquid falling down the column constantly reboiled by the up-coming vapour, each reboiling makes it rich in the less volatile component.

Therefore, over the time, component A passes out from the top of the column into the condenser and the liquid in the flask will become richer in B. By controlling the temperature carefully, a binary mixture is separated in which the component A (with lower boling point) passes into the collecting flask and B will remain in the original flask.

2.6.2 Immiscible liquid – liquid systems

Immiscible liquids are those which do not mix to give a mixture with a single phase at a given temperature and pressure. Oil and water are examples of immiscible liquids, where oil floats on top of water. Therefore, we can understand that when immiscible liquids are mixed together, they separate out into different layers with the denser liquid settling to

the bottom and the other floating on top of that. In such a case, if the liquids are in a closed container with static condition and there are no interactions between molecules of two liquids, the vapour pressure of the system will simply be the vapour pressure of the one which is floating on top because there is no way for the liquid in the bottom to travel up.

Let us assume that the mixture is stirred or the static situation is perturbed and the two liquids are broken up into drops. Therefore, the top layer of liquid does not alter the bottom layer - molecules to evaporate, though it may slow it down from reaching its equilibrium. Now, at any time there will be drops of both liquids on the surface giving indication that both of them contribute to the overall vapour pressure of the mixture. As such it is desirable to assume that the molecules of both liquids are in equilibrium with their respective molecules in the gas phase and both of those contribute to the total vapour pressure of the system. Therefore, the total vapour pressure of the system would be the sum of partial pressures of the components; assuming that the component liquids are A and B,

$$p_T = p^\circ_A + p^\circ_B$$

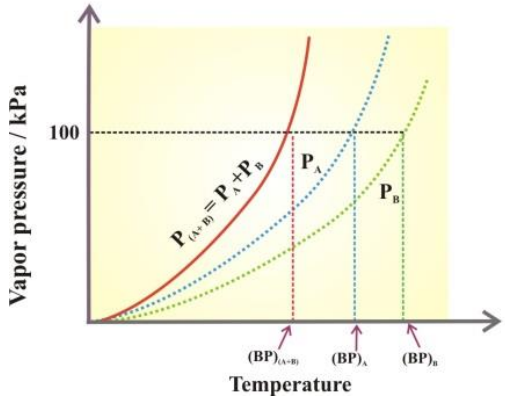


Figure 2.51 Variation of vapor pressure of totally immiscible liquid – liquid system

As the two liquids are immiscible, the variation in their vapor pressures with temperature is independent of each other as depicted in Figure 2.51. Once we sum-up these partial pressure values, the total vapour pressure curve intersects the 100 kPa line at a point which has a lower boiling point compared to pure A and B. Therefore, in these types of mixtures of immiscible liquids, it is very important to note that the boiling point of the mixture will be lower than the boling points of the pure components.

This principle is very useful in purification of temperature sensitive compounds, particularly those that decompose at their boiling points. As the mixture boils at a lower temperature than those of the components, it is easy to extract high-boling compounds by the application of steam distillation. For example, phenylamine $C_6H_5NH_2$ oxidizes rapidly at its normal boiling temperature (184 °C). However, a mixture of phenylamine

and water will boil at a temperature lower than 100 °C. With the understanding of the Figure 2.51, we can treat this mixture as follows.

At 98 °C, the saturated vapour pressures of the two pure liquids are:

phenylamine	7.07 kPa
water	94.30 kPa

The total vapor pressure of the mixture would than be the sum of these which is 101.37 kPa and this is slightly higher than the normal external pressure. Therefore, the mixture would boil at a temperature just less than 98 °C which is little lower than the boiling point of pure water (100 °C) and much lower than the boiling point of phenylamine (184 °C).

Thus, the isolation of this compound from a mixture can easily be carried out by steam distillation. In this procedure, steam is continuously passed through the heated mixture and the vapour is condensed by a water-cooled condenser. Then the condensed vapour of pure components is collected in a container. It is necessary to keep in mind that the steam distillation technique is useful to separate/purify a substance when the substance is immiscible with water or insoluble in water, has a high molecular mass, has high vapour pressure at around 100 °C and the impurities present are non volatile under the conditions used.

2.7 Partition/ Distribution coefficient

When two immiscible solvents **A** and **B** are placed in a beaker, they will not mix and instead form separate layers. At a constant temperature, when a solute **X** which is soluble in both solvents in the same molecular–form and non-reactive is added, and the system is shook vigorously, the solute X gets dissolved in both solvents depeding on its solubility in each solvent. This can further be explained as the solute is ***distributed*** or ***partitioned*** between the two solvents. After allowing the system to settle, layers of the solvents will separate and **X** molecules of the solute pass through the boundary between two solvents back and forth. Finally a dynamic equilibrium will be reached with the constant concentrations of X in each layer.

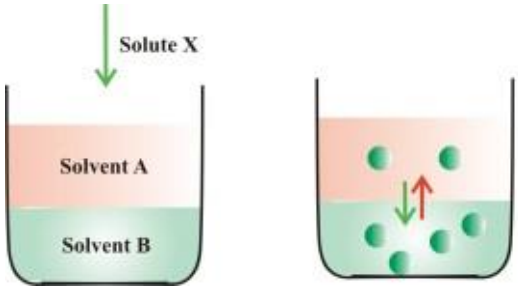


Figure 2.52 Skeptual diagram for the distribution of solute X in A and B solvents

At the same temperature, if more of the solute X is added to the system, *the solute will distribute itself between the layers keeping the same ratio of the solute concentrations at constant temperature*. Therefore, at a constant temperature, the equilibrium constant for the system can be written as:

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = \text{constant}$$

i.e.

When a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents,

$$\frac{[\,X_A\,]}{[\,X_B]} = K_D$$

The constant $\boldsymbol{K_D}$ is called the Distribution coefficient or the partition coefficient or the distribution ratio.

When a solute is shaken with two immiscible solvents at a constant temperature, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, we can write the distribution law as

$$\frac{[\,X_A\,]}{[\,X_B]} = \frac{S(X)_A}{S(X)_B} = K_D$$

$S(X)_A$ and $S(X)_B$ are the solubilities of the solute in the two solvents. Hence knowing the value of the Distribution coefficient $\boldsymbol{K_D}$ and the solubility of solute in one of the solvents, the solubility of solute in the second solvent can be calculated.

Example 2.46

A solid X is added to a mixture of benzene and water at 25 °C. After shaking well and allowing to settle, 20.00 cm^3 of the benzene layer was found to contain 0.20 g of X and 100.00 cm^3 of water layer cantained 0.40 g of X. X has its normal molecular weight in both solvents. Calculate the $\boldsymbol{K_D}$.

Answer

Concentration of X in benzene, $C_b = \frac{0.20\text{ g}}{20.00\text{ cm}^3} = 1.0 \times 10^{-2}\text{ g cm}^{-3}$

Concentration of X in water, $C_w = \frac{0.40\text{ g}}{100.00\text{ cm}^3} = 4.0 \times 10^{-3}\text{g cm}^{-3}$

$$\therefore K_D = \frac{C_b}{C_w} = \frac{1.0 \times 10^{-2}\text{ g cm}^{-3}}{4.0 \times 10^{-3}\text{g cm}^{-3}} = 2.5$$

Note: *It is not necessary to find the concentration in mol dm^{-3} always. As K_D is a dimentionless quantity, units are cancelling out. It is important to remember that the units of both concentrations should be the same.*

Example 2.47

At 25 ºC an aqueous solution of iodine containing 0.05 g dm^{-3} is in equilibrium with a carbon tetrachloride (CCl_4) solution containing 4.00 g dm^{-3}. The solubility of iodine in water at 25 ºC is 0.40 g dm^{-3}. Find the solubility of iodine in carbon tetrachloride.

Answer

$$K_D = \frac{C_{CCl_4}}{C_{H_2O}} = \frac{4.00\ \text{g dm}^{-3}}{0.05\ \text{g dm}^{-3}} = 80$$

$$\therefore \frac{(Solubility)_{CCl_4}}{(Solubility)_{H_2O}} = \frac{(Solubility)_{CCl_4}}{0.40\ \text{g dm}^{-3}} = 80$$

$$\therefore (Solubility)_{CCl_4} = 32.00\ \text{g dm}^{-3}$$

Understanding K_D *as a constant at constant temperature*

As we are considering a system in dynamic equilibrium with the distribution of solute X, the rate (r_1) at which molecules of X pass from solvent A to B is proportional to its concentration (C_1) in A. The rate (r_2) at which molecules of X pass from solvent B to A is proportional to its concentration (C_2) in B. At equilibrium, the rate of migration of solute from one solvent to the other is equal at a constant temperature.

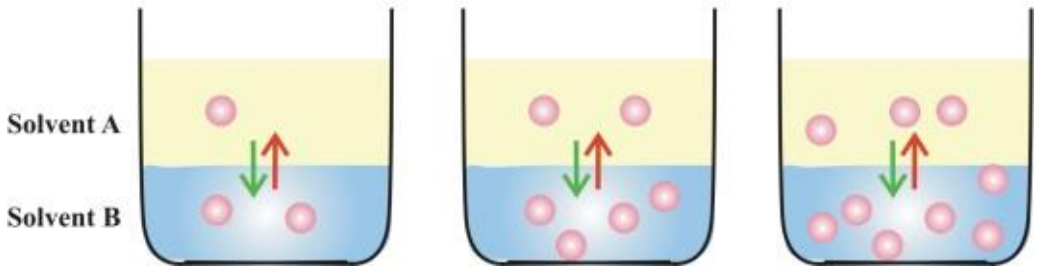


Figure 2.53 Distribution of X solute increases to keep the K_D constant at constant temperature

Thus we have,

$r_1 \propto C_1$ and $r_2 \propto C_2$

$\therefore r_1 = k_1 C_1$ and $r_2 = k_2 C_2$

k_1 *and* k_2 are rate constants.

At equilibrium,

$r_1 = r_2$ *therefore,* $k_1 C_1 = k_2 C_2$

$$\frac{C_1}{C_2} = \frac{k_2}{k_1} = K_D$$

Usually following conditions are necessary to apply this distribution law.

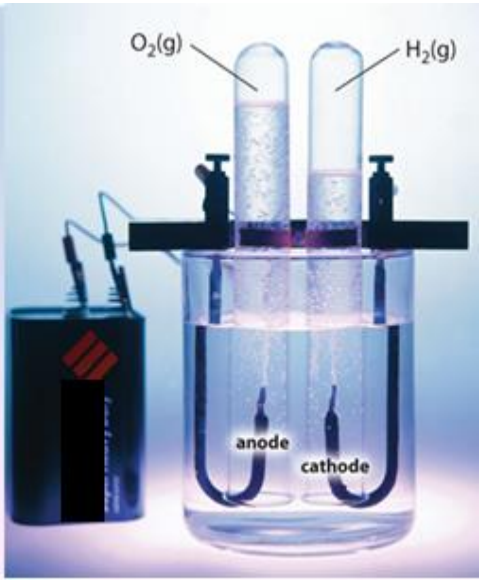
(i) Constant temperature: The temperature should be constant throughout the experiment.

(ii) Same molecular state: The molecular state of the solute should be the same in the two solvents.

(iii) Equilibrium concentrations: The concentrations of the solute are measured or estimated after the equilibrium has been established.

(iv) Dilute solutions: The concentrations of the solute in the two solvents should be low. The law does not hold when the concentrations are high.

(v) Solvents should be immiscibile.



3. Electrochemistry

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Introduction

Electrochemistry, the study of the exchange between electrical and chemical energy, dealing with chemical reactions that produce electricity in which the energy released by a spontaneous reaction is converted to electricity and/ or electrical energy is used to cause a nonspontaneous reaction to occur. In these specific systems the reactions involve electron transfer, and so they are mainly a pair of reactions named oxidation-reduction (redox) reactions. An oxidation involves the loss of one or more electrons from a chemical species while a reduction involves the gain of one or more electrons by a chemical species. When an oxidation and a reduction are paired together in a redox reaction, electrons can flow from the oxidized species (the reducing agent or reductant) to the reduced species (the oxidizing agent or oxidant). That electron flow can either be spontaneously produced by the reaction and converted into electricity, as in a galvanic cell, or it can be imposed by an outside source to make a non-spontaneous reaction proceed, as in an electrolytic cell. The following descriptions on electrochemistry involve basics in redox reactions, galvanic cells, electrolytic cells, and the applications with electrolysis.

3.1 Conductivity

We encounter different materials in our day to day life such as paper, wood, glass, plastics, rubber, metals, and composite materials (i.e. mix of two different kind of materials). These materials have different properties thus differ in applications. One such important property is ability of a material to flow electricity through it. It is necessary to define a few terms before we consider the subject of conductance of electricity through electrolytic solutions. The electrical resistance is represented by the symbol *'R'* and it is measured in ohm (Ω) which in terms of SI base units is equal to (kg m^2). It can be measured with the help of a Wheatstone bridge. The electrical resistance of any object is directly proportional to its length, *l*, and inversely proportional to its area of cross section, *A*. That is,

$$R \propto l \quad \text{and} \quad R \propto \frac{1}{A}$$

$$\text{Therefore,} \quad R \propto \frac{l}{A}$$

$$R = \rho \frac{l}{A}$$

The constant of proportionality, **ρ** (rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (Ω m) and quite often, ohm centimetre (Ω cm) is also used. That is, physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2. It can be seen that: 1 Ω m = 100 Ω cm.

The inverse of resistance, R, is called **conductance**, G, and we have the relation,

$$\textbf{Conductance } (\boldsymbol{G}) = \frac{\mathbf{1}}{\boldsymbol{R}}.$$

The SI unit of conductance is siemens, represented by the symbol 'S' and is equal to ohm^{-1} (also known as mho) or Ω^{-1}.

Further we can write,

$$\textbf{Conductance } (G) = \frac{1}{R} = \frac{A}{\rho\, l} = \kappa \frac{A}{l}$$

The inverse of resistivity, $\frac{1}{\rho} = \kappa$, called **conductivity** (specific conductance) is represented by the symbol, κ (Greek, kappa). The SI units of conductivity are S m^{-1} but quite often, κ is expressed in S cm^{-1}. Conductivity of a material in S m^{-1} is its conductance when it is 1 m long and its area of cross section is 1 m^2. It may be noted that 1 S cm^{-1} = 100 S m^{-1}. These definitions can be depicted by Figure 3.1 as given below.

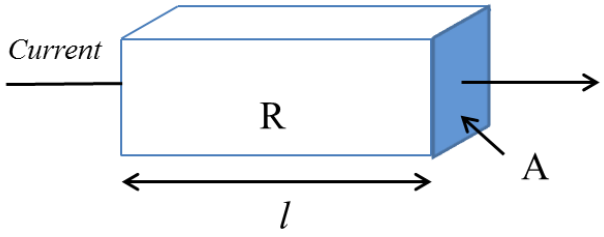


Figure 3.1 Resistance and resistivity

Conductivity and resistivity are constant for a particular substance (metal or an ionic solution with known concentration). However, it is important to provide the temperature at which conductivity or resistivity was measured as it varies with the temperature. In general, about 2% change in conductivity per one degree Celsius is observed for solutions.

Electricity can be conducted through materials (such as metals) as a flow of electrons in the metal. Such materials are known as **electrical conductors**. Electricity can also be conducted as a flow of ions in a solution or molten ionic compound. These are called **ionic conductors**. So, to conduct electricity through materials, it is essential to present electrons (or holes) which can move or ions in solid or liquid state when an electric field is applied.

Solutions can be categorized as **strong electrolytes, weak electrolytes and non-electrolytes (insulators)**. If a particular substance is fully ionized in solution, such as ionic solids and strong acids/ bases, it is called a **strong electrolyte**. Such solutions have concentration of ions proportional to the concentration of strong electrolytes used. Examples for strong electrolytes are aqueous solutions of NaCl, KNO_3, HCl. In the case where electrolytes added are partially ionized in aqueous solution, these are called **weak electrolytes**. Weak aqueous Bronsted acids and bases such as CH_3COOH, NH_3, H_2O are examples for weak electrolytes. The other extreme of electrolytes are the substances

which do not produce ions in aqueous media. These are called ***non-electrolytes*** or insulators and these do not conduct electricity. Non polar organic compounds such as Benzene (C_6H_6) and Kerosene are examples for such non-electrolytes.

The conductivity and resistivity of an electrolyte solution can be measured using two oppositely charged metal electrodes placed in an imaginary cuboid shaped portion of a solution with dimensions, length (*l*) and area of cross section(A) as shown in Figure 3.2.

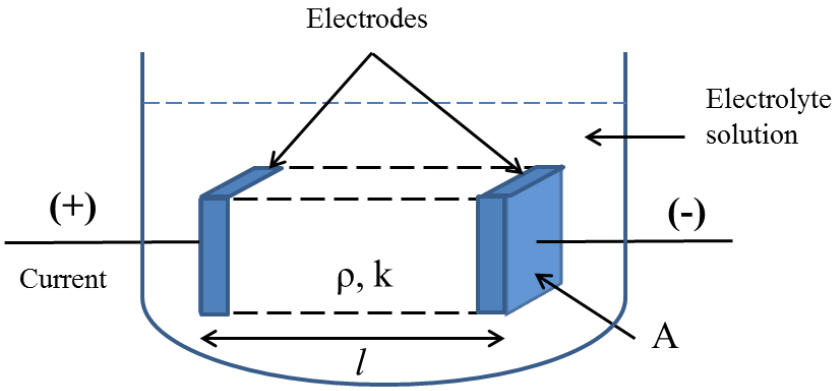


Figure 3.2 Conductivity and resistivity through a solution of electrolytes

3.1.1 Factors affecting conductivity of a solution

There are several factors which affect the conductivity of a solution. These are: **nature of the solute, concentration of the solute, and the temperature of the solution**. All of these factors affect conductivity because mobility of charge carriers is dependent on the above factors and as a result conductivity is dependent on the mobility of charge carriers.

The nature of the species plays important role as it determines presence of ions or mobile charge carriers. Aqueous solutions of strong electrolytes (e.g.: KCl, NaCl) can conduct electricity as these species produce ions due to complete dissociation. However, in the solid state these strong electrolytes do not conduct electricity due to absence of ions. If such a solid electrolyte is brought to the molten state, such as NaCl(l) then ions gain mobility thus conduct electricity. On the other hand, weak acids and bases are also able to conduct electricity as these will react with water to produce ionic species through partial dissociation.

Example 3.1
Which of the following substances once dissolved in water will conduct electricity?
(a) table salt (b) glucose (c) vinegar

Answer
(a) Chemical formula of table salt is NaCl. It is an electrolyte which fully dissolves in water to produce Na^+ and Cl^- ions. Since table salt is a substance that produces ions in water, it is capable of conducting electricity.
(b) Glucose is an organic compound with formula $C_6H_{12}O_6$. When glucose is dissolved in water it will not produce any ionic species. Therefore, a glucose solution cannot conduct electricity.
(c) Vinegar is mostly consists of acetic acid, CH_3COOH. Acetic acid is a weak acid which partially dissociates in water to produce H_3O^+ and CH_3COO^- ions. As a result vinegar solution is able to conduct electricity due to presence of ions.

Another important factor that affects the conductivity of a solution is concentration. When the concentration of dilute aqueous solution is decreased, the conductivity is also decreased. This is due to decreased amount and interactions of ions upon dilution. The Table 3.1 illustrates the effect of concentration on conductivity.

Table 3.1 Conductivities of various water samples and solutions at 298 K

Sample	Conductivity / μS cm^{-1}
Distilled water	1 – 2
0.01 mol dm^{-3} KCl solution	1,480
0.10 mol dm^{-3} KCl solution	12,400
1.0 mol dm^{-3} KCl solution	110,000
Well water	100 – 200
Pipe borne water	50 – 150
Sea water	40,000

μS: micro seimans

The temperature of the solution has a considerable influence on the conductivity values measured. When the temperature is increased, conductivity of the solution is also increased at a given concentration due to enhanced speed of ions. This effect is clearly demonstrated in the Table 3.2 below.

Table 3.2 Conductivities of KCl(aq) and solutions at different temperatures

Concentration / mol dm^{-3}	Conductivity / μS cm^{-1}		
	0 °C	**13 °C**	**25 °C**
1.00 KCl solution	6.5×10^4	9.8×10^4	1.1×10^5
0.10 KCl solution	7.2×10^3	1.1×10^4	1.3×10^4
0.01 KCl solution	7.8×10^2	1.2×10^3	1.4×10^3

Current carried by an ion at a given temperature and an electric field depends on the concentration of ions and their speed. The speed of an ion depends on it's charge, size, and potential gradient of the applied electric field. According to Table 3.3, H^+ and OH^- ions have the highest speeds due to relatively small size. Thus, these ions are major contributors for the conductance of an aqueous solution.

Table 3.3 Speeds of ions in an aqueous solution under the potential gradient 1 V cm^{-1} at 298 K

Ion	Speed/ mm min^{-1}	Ion	Speed/ mm min^{-1}
H^+	2.05	NO_3^-	0.40
OH^-	1.12	Cl^-	0.42
Na^+	0.29	SO_4^{2-}	0.88
K^+	0.42	Ca^{2+}	0.67

Conductivity of a solution plays an important role when analyzing ionic content of a water sample. In practice, conductivity meters are used to measure the conductivity of a solution. Such measurements can be used in evaluating salinity, calculating solubility products, and in many other applications.

3.2 Electrodes in equilibrium

3.2.1 Metal – metal ion electrode

Before discussing details about this *electrode equilibrium* it may be worth understanding the behaviour of reactivity of metals in solutions as that would be the basic concept of building up an electrode.

As we know, when metals react, they give away electrons and form positive ions. For example, $Mg^{2+}(aq)$, $Zn^{2+}(aq)$ or $Cu^{2+}(aq)$ ions are formed when the respective metals react in aqueous solutions of their ions and form positive and negative charges as shown by the following reaction.

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e$$

This occurs as follows; once a piece of solid magnesium is dipped in a beaker of Mg^{2+} solution there will be some tendency for the magnesium atoms to remove electrons and

go into solution as $Mg^{2+}(aq)$ ions. The electrons will be left behind on the magnesium as depicted in the Figure 3.3.

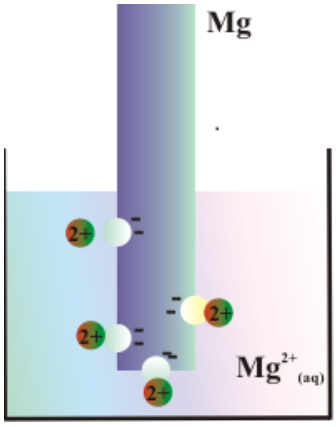


Figure 3.3 Behaviour of Mg metal in an aqueous solution of $Mg^{2+}(aq)$ ions

Once the Mg rod is dipped in Mg^{2+} solution, there will be a quick build-up of electrons on the magnesium, and it will be surrounded in the solution by a layer of positive Mg^{2+} ions. These will tend to stay close because they are attracted to the negative charge on the piece of metal. Some of them will be attracted enough that they will reclaim their electrons and stick back on to the piece of metal. A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again. At that point there will be a constant negative charge on the magnesium rod and a constant number of $Mg^{2+}(aq)$ ions surround the rode. This dynamic equilibrium is shown in Figure 3.4 in which the negative charge on the Mg rod is balanced by the positive charges surrounded by it in the solution. Once this situation is achieved, we consider and define such a system as an electrode.

A system where a metal is in dynamic equilibrium with its ions can be defined as an ***electrode****.*

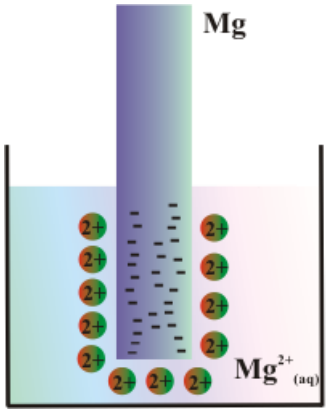


Figure 3.4 Behaviour of Mg metal in an aqueous solution at dynamic equilibrium

As with the above descriptions it is notable that the equilibrium exists in two ways; in one direction Mg solid is converted to $Mg^{2+}(aq)$ ions while in the other direction $Mg^{2+}(aq)$ ions in the solution are converted to Mg metal. In other words, Mg oxidizes in one direction and $Mg^{2+}(aq)$ reduces in the other direction indicating that the overall system exhibits an oxidation-reduction couple.

Accordingly, we can get the idea that a charge separation occurs at the interface between metal and the solution/water. The tendency of this charge separation depends on the activity of metal. For example if we use a rod of Cu metal, the charge separation will be less compared to that of Mg. This relates the activity of metals described in electrochemistry (detailed discussion of this will appear in a later section).

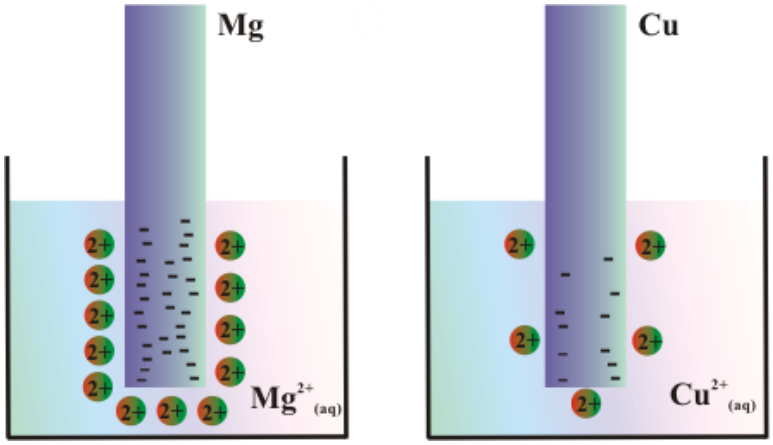


Figure 3.5 Behaviour of Mg and Cu metals in an aqueous solutions at dynamic equilibrium. As Cu is less reactive than Mg, Cu forms its Cu^{2+} ions less readily.

In general any ions which do break away are more likely to reclaim their electrons and stick back on to the metal again. The equilibrium position can still reachable, but there will be less charge on the metal, and fewer metal ions in solution as compared in Figure 3.5.

Once systems are in dynamic equilibrium, two reactions can be written as given below and it will also be possible to compare the positions of equilibrium of the two systems.

$$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s) \quad \ldots\ldots\ldots\ldots (1)$$

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s) \quad \ldots\ldots\ldots\ldots\ldots (2)$$

According to Figure 3.5, the position of the equilibrium (1) is further to the left than that of the equilibrium (2).

It has to be noted the way that the two equilibria are written. By convention, all these equilibria are usually written with the electrons on the left-hand side of the equation that is as a reduction reaction.

As the position of equilibrium is different in the above two cases, the ability to reach the equilibrium may be expressed by introducing some numbers and that can be directly related to the term **electrode potential** which is simply an attempt to attach some numbers to these differing positions of equilibria. In principle, that is quite easy to do. In the case of magnesium, there is a large difference between the negativeness of the metal and the positiveness of the solution around it. In the copper case, the difference is much less and this can be used to understand the potential which arises due to the charge separation at the interface of the particular electrode.

This **potential difference** can be recorded as a voltage meaning that the bigger the difference between the positiveness and the negativeness, the bigger the voltage. Unfortunately, that voltage is impossible to measure by connecting a device to the above mentioned systems.

Even though, it would be easy to connect a voltmeter to the piece of metal, the problem is how a connection is made to the solution. If any probe is put into the solution a similar sort of equilibrium would happen around it. Therefore, the best measure would be some sort of combination of the effects at the probe and the piece of metal of interest.

That means, it is not required to measure the absolute voltage between the metal and the solution. It is enough to compare the voltage with a standardized system called a **reference electrode** and the system used is called a *standard hydrogen electrode (SHE)* which is shown in Figure 3.6.

As we know from the unit 12 (Equilibrium), the position of any equilibrium can be changed by changing conditions. That means the conditions must be standardized so that you can make fair comparisons.

In the standard hydrogen electrode the following conditions are used: 101325 Pa ~100 kPa, 1 atm pressure of hydrogen gas, the temperature of 298 K (25 °C) and 1.0 mol dm^{-3} concentration of the hydrogen ions in the solution.

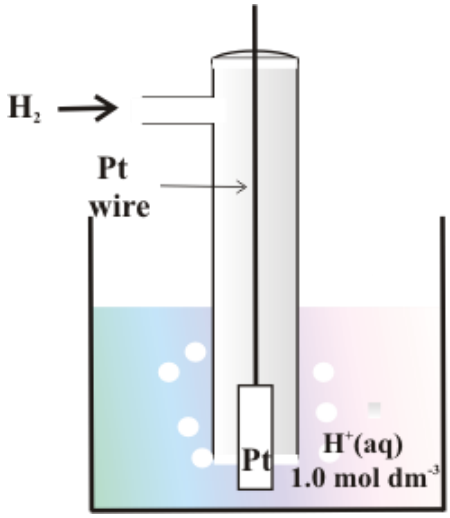


Figure 3.6 The standard hydrogen electrode

In this electrode, as the hydrogen gas flows over the porous platinum, an equilibrium is established between hydrogen molecules and hydrogen ions in solution which is catalyzed by platinum.

$$2H^+(aq) + 2e \rightleftharpoons H_2(g)$$

Now let us see how we would measure the potential of a given electrode. In this measurement, the standard hydrogen electrode is attached to the electrode system for example, a piece of magnesium in a solution containing magnesium ions as considered earlier; a conducting Pt wire is introduced to connect the voltmeter and a salt bridge is introduced as shown in Figure 3.7.

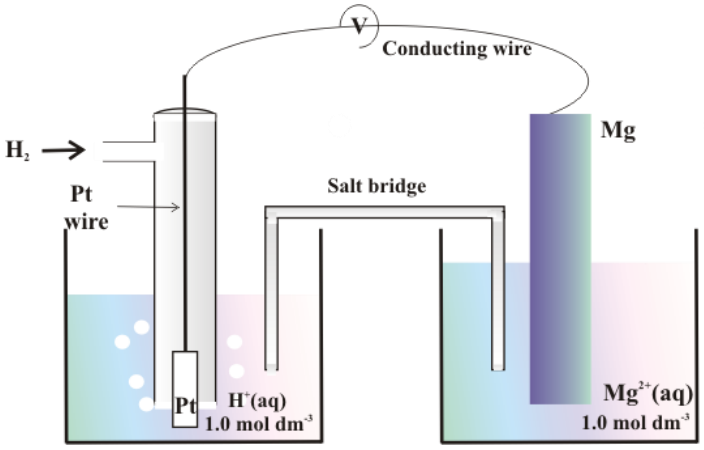


Figure 3.7 Measurement of electrode potential using the standard hydrogen electrode

The salt bridge is introduced to complete the electrical circuit making a liquid junction. It is just a glass tube filled with a solution of an electrolyte like potassium nitrate. The ends are "stoppered" by bits of cotton wool or sometimes with agar gel to prevent mixing of the contents in the salt bridge with the contents of the two beakers. Each electrode on one side is defined as a *half-cell*.

It has to be noted that the electrolyte in the salt bridge is chosen so that it doesn't react with the contents of either beaker.

Once the two electrodes are connected two equilibria are set up on the two electrodes as follows.

$$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$$

$$2H^{+}(aq) + 2e \rightleftharpoons H_2(g)$$

Magnesium has a much higher ability to form its ions than hydrogen does. Therefore, position of the Mg/Mg^{2+} equilibrium will be more to the left than that of the H_2/H^+ equilibrium. This means that there is a much greater build-up of electrons on the piece of magnesium than on platinum. Therefore, there is a major difference between the charges on the two electrodes and hence a potential difference which can be measured with a voltmeter.

The value of potential mentioned above for $Mg^{2+}(aq)$ / Mg(s) is actually the standard electrode potential of the $Mg^{2+}(aq)$ / Mg(s) system.

The potential difference measured when a metal / metal ion electrode is coupled to a hydrogen electrode under standard conditions is known as the standard electrode potential of that metal / metal ion combination. This means that each $E°$ value shows whether the position of the equilibrium lies to the left or right of the hydrogen equilibrium. The difference in the positions of equilibrium causes the number of electrons built up on the metal electrode and the platinum of the hydrogen electrode to be different. Here, as a convention the number of electrons produced on the Pt surface is considered to be negligible. The standard cell potential $E^{\mathbf{0}}$ of the standard hydrogen electrode is taken as 0.00 V at room temperature. The potential difference produced is measured as a voltage having units of volts (V).

As we know that magnesium has the greater amount of negativeness, the voltage measured would be 2.37 V and the voltmeter would show magnesium as the negative electrode and the hydrogen electrode as positive. Therefore, the standard electrode potential of the $Mg^{2+}(aq)$/ Mg(s) electrode is recorded as E^0 = -2.37 V.

In the case when a similar measurement is done with the $Cu^{2+}(aq)/ Cu(s)$ electrode, copper forms its ions less readily than hydrogen does.

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$$

$$2H^{+}(aq) + 2e \rightleftharpoons H_2(g)$$

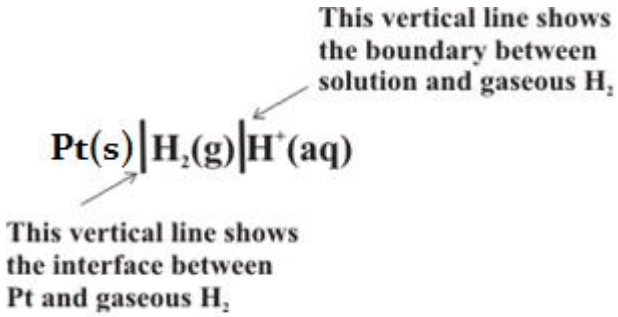
Therefore, the equilibrium in the hydrogen electrode lies further to the left. As a result there will be less build-up of electrons on copper than that is on the platinum of the hydrogen electrode. Therefore, there is less difference between the electrical charges on the two electrodes, so the voltage measured will be less (only +0.34 volts).

The other major change is that this time the copper is the more positive (less negative) electrode. The voltmeter will show the hydrogen electrode as the negative electrode and the copper electrode as the positive electrode and hence the electrode potential is recorded as + 0.34 V.

(If any current flows, the voltage measured drops. In order to make proper comparisons, it is important to measure the maximum possible voltage in any situation. This is called the ***electromotive force*** *or* ***e.m.f****. Details of this will be discussed in coming sections).*

Electrode notations

The hydrogen electrode is represented as below.



From the above descriptions we know that the standard electrode potential of a metal / metal ion combination is the potential difference measured when that metal / metal ion electrode is coupled to a hydrogen electrode under the standard conditions.

The measurement of electrode potentials allows us to determine the position of the metal/ metal ion equilibrium with respect to the equilibrium involving hydrogen.

A few typical standard electrode potentials are shown in the table below.

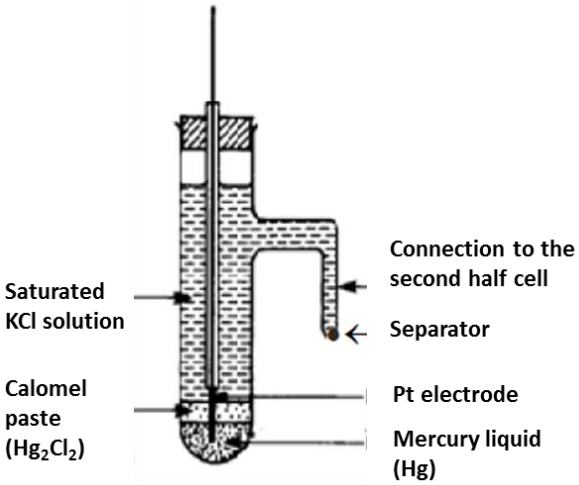
Metal / metal ion combination	$E°$/ V
$Mg^{2+}(aq)/ Mg(s)$	-2.37
$Zn^{2+}(aq)/ Zn(s)$	-0.76
$Cu^{2+}(aq)/ Cu(s)$	+0.34
$Ag^{+}(aq)/ Ag(s)$	+0.80

Comparing these with the $E°$ values, it can be seen that the ones whose positions of equilibrium lie furthest to the left have the most negative $E°$ values. That is because they form ions more readily leaving more electrons behind on the metal. Those which don't release electrons readily have positions of equilibrium further to the right. Their $E°$ values get progressively more positive.

In addition to these metal-metal ion electrodes, there are other types of electrodes as discussed below.

3.2.2 Metal – insoluble salt electrode

In order to define an electrode it is necessary to have oxidized and reduced species of the same element to be present. Accordingly, if a metal is in contact with the solid salt of the same metal, such electrodes are called **metal – insoluble salt type**. Examples for such electrodes are calomel electrode and silver-silver chloride electrode. Figure 3.8 shows details of the calomel electrode. A Pt wire is used to establish the electrical connection with an external circuit. A saturated solution of KCl is used for the electrical conductance.

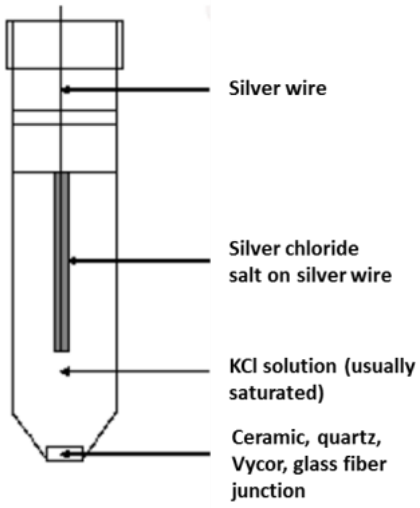


$$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$$

Figure 3.8 Calomel electrode

Silver – silver chloride is another example for metal-insoluble salt type of an electrode. The essential components of this electrode comprise a silver wire coated with AgCl which

is in contact with the KCl electrolyte. An important part of silver – silver chloride electrode is the tip (ceramic, quartz, vycor tip, glass fibre) that connects electrode with the external solution. Figure 3.9 illustrates silver-silver chloride electrode.



$$AgCl(s) + e \longrightarrow Ag(s) + Cl^-(aq)$$

Figure 3.9 Silver – silver chloride electrode

In general, calomel electrode and silver – silver chloride electrode are also known as **reference electrodes** as potential of these electrodes remains almost constant during experiment time.

3.2.3 Gas electrodes

Hydrogen electrode

Standard Hydrogen Electrode is an example for a gas electrode. The standard conditions used here are 1.0 mol dm^{-3} H^+ ion concentration, 1 atm pressure for H_2 gas, and temperature of the system is at 298 K. This hydrogen electrode is called the **standard electrode** as the potential of this electrode is defined as 0.00 V as described earlier.

$$2H^+_{(aq)} + 2e \rightleftharpoons H_2(g)$$

Chlorine electrode

Chlorine is well known as an oxidizing agent. Since the electrochemical series is about ranking substances according to their oxidizing or reducing ability, it makes some insights to the electrode reactions with gases like chlorine. Again, as has been done above, we can measure the position of this equilibrium relative to the hydrogen equilibrium.

$$Cl_2(g) + 2e \rightleftharpoons 2Cl^-(aq)$$

Note that as usual, the equilibrium is still written with the electrons on the left-hand side of the equation. That's why the chlorine gas has to appear on the left-hand side rather than on the right indicating the reduction during the reaction. For this chlorine electrode, a half-cell can be built as similar to the hydrogen electrode by bubbling chlorine gas over a platinum electrode, which is immersed in a solution containing chloride ions with a concentration of 1.0 mol dm^{-3}.
The notation of writing the cell looks like this.

$$Pt(s)|Cl_2(g) \mid Cl^-(aq)$$

It can be noted that the chloride ions are losing electrons and hence the cell has a positive potential difference.

3.2.4 Redox electrodes

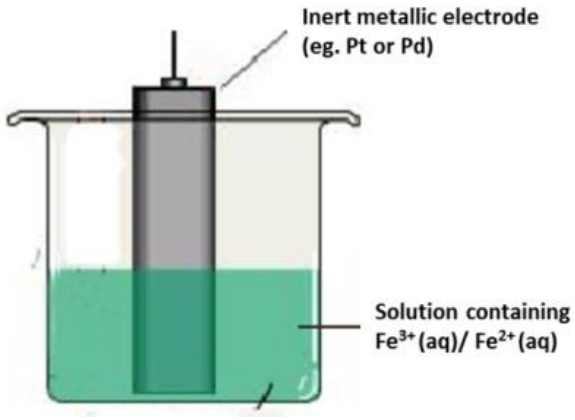
These types of electrodes are frequently observed in redox reactions. Both oxidized and the reduced species must be present in the solution when defining a particular redox electrode. A Pt wire can be used to establish the electrical connection with the external circuit. Such a redox type of electrode is given in Figure 3.10.

Fe^{2+}/ Fe^{3+} redox electrode system

Iron(II) ions can easily be oxidized to iron(III) ions, and iron(III) ions are fairly easily reduced to iron(II) ions. The equilibrium for this can be written as follows.

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

To measure the redox potential of this, a platinum electrode can be inserted into a beaker containing a solution of both iron(II) and iron(III) ions (1.0 mol dm^{-3} with respect to each), and couple this to a hydrogen electrode.



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

Figure 3.10 The Fe^{2+}/ Fe^{3+} redox electrode system

- When writing electrode in standard notation, phase boundaries are separated by a vertical line "|"

  E,g. Gas electrodes: $Pt(s)|O_2(g)|OH^-(aq)$

- Physical states must be included next to each chemical species and conditions should be included where possible.

  E.g. Redox electrodes: $Pt(s)|Fe^{2+}(aq,1\ mol/dm^3), Fe^{3+}(aq,1\ mol/dm^3)$

The following table summarizes the types of different electrodes with some examples.

Table 3.4 Summary of different types of electrodes

Type of electrode	Standard notation	Redox couple	Reduction half reaction
Metal – metal ion	**$M(s)|M^{n+}(aq)$**	**$M(s)/M^{n+}(aq)$**	**$M^{n+}(aq) + ne \rightarrow M(s)$**
	$Zn(s)|Zn^{2+}(aq)$	$Zn(s)/Zn^{2+}(aq)$	$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$
Metal – insoluble salt	**$M(s)|MX_n(s)|X^-(aq)$**	**$M(s)/MX_n(s)$**	**$MX(s) + ne \rightarrow nM(s) + X^-(aq)$**
	$Ag(s)|AgCl(s)|Cl^-(aq)$	$Ag(s)/Ag^+(aq)$	$AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$
	$Pt(s)|Hg(l)|Hg_2Cl_2(s)|Cl^-(aq)$	$Hg(l)/Hg_2Cl_2(s)$	$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$
Gas	**$Pt(s)|X_2(g)|X^+(aq)$**	**$X_2(g)/X^+(aq)$**	**$X^+(aq) + e \rightarrow ½X_2(g)$**
	$Pt(s)\ |X_2(g)\ |X^-(aq)$	$X^-(aq)/X_2(g)$	$½X_2(g) + e \rightarrow X^-(aq)$
	$Pt(s)|H_2(g)|H^+(aq)$	$H_2(g)/H^+(aq)$	$H^+(aq) + e \rightarrow ½H_2(g)$
	$Pt(s)|O_2(g)|OH^-(aq)$	$OH^-(aq)/O_2(g)|$	$2O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^-(aq)$
Redox	**$Pt(s)|M^+(aq),M^{2+}(aq)$**	**$M^+(aq)/M^{2+}(aq)$**	**$M^{2+}(aq) + e \rightarrow M^+(aq)$**
	$Pt(s)|Sn^{2+}(aq),Sn^{4+}(aq)$	$Sn^{2+}(aq)/Sn^{4+}(aq)$	$Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq)$

Note: *When writing any electrode reaction, a single arrow is used when there is a current passing through (not in equilibrium) and an equilibrium arrow is used when the electrode is isolated. Also, it is compulsory to mention the physical state of the chemical species whenever electrode reactions are written.*

As indicated in above examples it is necessary to note that the electrode potentials of half-cells are given as redox potentials (the potential of the redox reaction).

Therefore, by arranging various redox equilibria in the order of their standard electrode potentials (redox potentials) we can build up the **electrochemical series**. The most negative $E°$ values are placed at the top of the electrochemical series, and the most positive at the bottom as summarized in Table 3.5.

Table 3.5 Standard reduction potentials of selected electrodes at 298K

Reduction half reaction	**Standard reduction potential (E^{Θ} / V)**
$Li^{+}(aq) + e \rightarrow Li(s)$	-3.05
$K^{+}(aq) + e \rightarrow K(s)$	-2.93
$Ca^{2+}(aq) + 2e \rightarrow Ca(s)$	-2.87
$Na^{+}(aq) + e \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$	-2.36
$Al^{3+}(aq) + 3e \rightarrow Al(s)$	-1.66
$Mn^{2+}(aq) + 2e \rightarrow Mn(s)$	-1.18
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^{-}(aq)$	-0.83
$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$	-0.76
$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	-0.44
$Ni^{2+}(aq) + 2e \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$	-0.13
$H^{+}(aq) + e \rightarrow 1/2H_2(g)$	**0.0**
$Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq)$	+0.15
$AgCl(s) + e \rightarrow Ag(s) + Cl^{-}(aq)$	+0.22
$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^{-}(aq)$	+0.27
$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	+0.34
$O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^{-}(aq)$	+0.40
$I_2(s) + 2e \rightarrow 2I^{-}(aq)$	+0.54
$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$	+0.77
$Ag^{+}(aq) + e \rightarrow Ag(s)$	+0.80
$Br_2(l) + 2e \rightarrow 2Br^{-}(aq)$	+1.09
$O_2(g) + 4H^{+}(aq) + 4e \rightarrow 2H_2O(l)$	+1.23
$Cl_2(g) + 2e \rightarrow 2Cl^{-}(aq)$	+1.36
$Au^{3+}(aq) + 3e \rightarrow Au(s)$	+1.40
$S_2O_8^{2-}(aq) + 2e \rightarrow 2SO_4^{2-}(aq)$	+2.05
$F_2(g) + 2e \rightarrow 2F^{-}(aq)$	+2.87

Reducing agents and oxidizing agents

As we know, a **reducing agent** reduces some other chemical species. That means that a **reducing agent** gives electrons to another chemical species. Conversely, an **oxidizing agent** oxidizes something else by accepting electrons.

According to the above electrochemical series, magnesium is good at giving away electrons to form its ions. Hence Magnesium is a good reducing agent. On the other hand, copper doesn't form its ions very readily, and its ions easily pick up electrons to convert to metallic copper. Hence, copper(II) ions must be a good as an oxidizing agent.

It is with this idea we notice that the metals at the top of the series (with negative standard electrode potential) are good at giving away electrons hence act as good reducing agents. The reducing ability of the metal increases going up the series.

Metal ions at the bottom of the series are good at picking up electrons. These are good oxidizing agents. The oxidizing ability of the metal ions increases down the series.

In other words, the more negative the $E°$ value, the position of the equilibrium to the left and the tendency of the metal to lose electrons. Therefore, the more negative the value, a particular species is stronger reducing agent. The situation is opposite for the species at the bottom of the electrochemical series as these are good oxidizing agents. Therefore, metals such as Na, Mg, Zn, etc. with negative reduction potential prefer to be in ionic state rather elemental state and shows higher reactivity. The opposite is true for the species listed below the potential of standard hydrogen electrode. When two metals are in contact, metals with higher negative standard potential prefer to be in ionic state, thus can be used to reduce ions of the other metal in contact.

3.3 Electrochemical cells

3.3.1 Construction of an electrochemical cell

So far we have considered combinations of a hydrogen electrode with the different electrodes as we measure standard reduction potential. It is interesting to consider what happens if a zinc half-cell is combined with a copper half-cell through a voltmeter and the solutions are connected via a salt bridge as shown in Figure 3.11.

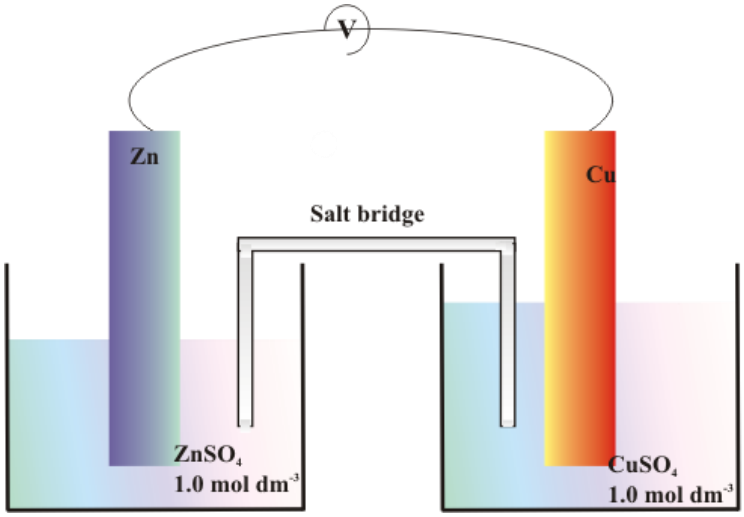


Figure 3.11 An electrochemical cell prepared by connecting two half-cells of Zn and Cu

This type of set up is defined as an **electrochemical cell** which **consists of two electrodes in contact with an electrolyte**. In an electrochemical cell, there can be a common electrolyte or may be in different electrolytes. In the latter case, electrodes in two different electrolytes are connected via a salt bridge. The potential generated due to presence of two different electrolytes in the electrode compartments is called "liquid junction potential". However, this potential can be minimized if two electrolytes are joined using a salt bridge. A salt bridge is essentially a medium consisting of an electrolyte such as KCl or KNO_3 which is jellified with agar in an inverted "U" shaped tube. The two ends of liquid junction are dipped in respective electrode units. This liquid junction can also be made by a permeable membrane/ diaphragm/ porous partitioning which allows ions to pass through it.

The two equilibria which are set up in the above half cells are as follows.

$$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s) \qquad E^0 = -0.76\ V$$

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s) \qquad E^0 = +0.34\ V$$

The negative sign of the $E°$ value for zinc shows that it releases electrons more readily than hydrogen does. The positive sign of the copper $E°$ for copper shows that it releases electrons less readily than hydrogen.

This allows us to compare the two electrode equilibria directly. The position of the zinc equilibrium lies further to the left than the copper equilibrium. Therefore, the voltmeter will show that the zinc as the negative electrode and copper is the (relatively) positive one. It will indicate a voltage showing the difference between them.

Usually the high resistivity voltmeter is used stop any current flow in the circuit. If the circuit is constructed without a voltmeter but two half-cells still connected, then electrons will flow from where there are lot of them (on zinc) to where there are fewer (on copper). The movement of the electrons is thus an electrical current. At this situation the equilibrium is disturbed, hence we may apply Le Chatelier's Principle to understand the changes in the system due to current flow. Here following two opposing effects are noticed.

On one side, electrons are flowing away from the zinc equilibrium, according to Le Chatelier's principle; the position of equilibrium will move to replace the lost electrons.

On the other side of copper, electrons are added onto the piece of copper in the copper equilibrium. According to Le Chatelier's Principle, the position of equilibrium will move to remove these extra electrons. As a result, the changes occur as shown in the following sketch and can be illustrated by Figure 3.12.

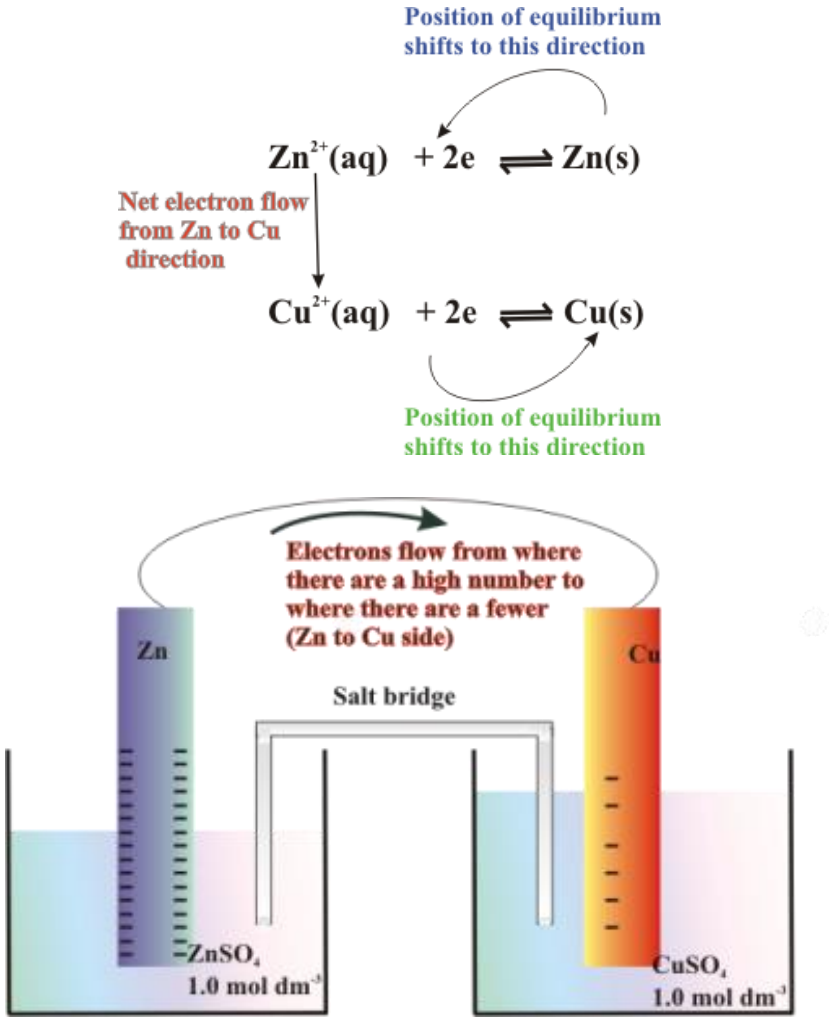


Figure 3.12 A Galvanic cell prepared by combining two half-cells of Zn and Cu without a voltmeter

In the above system, if electrons continue to flow from Zn side to Cu side, the positions of equilibrium keeps on shifting. Therefore, the two equilibria essentially turn into two one-direction (side) reactions. The zinc continues to ionize, and the copper(II) ions keep on collecting up electrons and the two reactions can be written as follows.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$$

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$

Therefore, on the whole we can see that there is a **net chemical reaction going on** in which zinc is going into solution as zinc ions, and is giving electrons to copper(II) ions to turn them into metallic copper. The overall reaction can be obtained by adding the above two reactions which are called half-cell reactions.

In the above, it is seen that the current is produced in the cell due to the occurrence of a spontaneous chemical reaction. Therefore, it is possible to categorize electrochemical cells into two types. If the cell is able to produce electricity through a spontaneous reaction, then it is called a **galvanic cell** or a **voltaic cell**. If the reaction is not spontaneous then an external source of current is required to operate the cell. Such a cell is called an **electrolytic cell.**

In a galvanic cell, oxidation and reduction reactions are responsible for the operation of the cell. When the cell is in operation, electrons released at one electrode due to oxidation travels to the other electrode resulting in reduction of the chemical species in that compartment. The electrode at which *oxidation* takes place is called the **anode** and the electrode at which *reduction* takes place is called the **cathode**. The overall cell reaction is obtained as combination of reduction and oxidation half reactions. Therefore, for the galvanic cell consisting of Zn and Cu electrodes which is named as Daniel cell, the overall reaction is given by the sum of the two half reactions.

Cathode (reduction half reaction): $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ (Right hand side electrode, RHE)

Anode (oxidation half reaction) : $\underline{Zn(s) \rightarrow Zn^{2+}(aq) + 2e}$ (Left hand side electrode, LHE)

Cell reaction : $\mathbf{Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)}$

It has to be noted that, if an external opposite potential is applied to the galvanic cell described above and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V at which the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction ($\mathbf{Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)}$).

It now functions as an **electrolytic cell**, a device which uses electrical energy to carry non-spontaneous chemical reactions. Here, it is important to pay attention to the voltage of 1.1 V stated above and how it arises for the presently considered Daniel cell. This can be understood as follows.

The oxidation and reduction half reactions occur in two different parts of the Daniell cell. The reduction half reaction occurs at the copper electrode while the oxidation half reaction occurs at the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples** as mentioned earlier. The copper electrode may be called the reduction half-cell and the zinc electrode, the oxidation half-cell.

In a galvanic cell, the half-cell in which oxidation takes place (**anode)** has a **negative potential** with respect to the solution. The other half-cell in which reduction taking place (**cathode)** has a **positive potential** with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of the electron flow. The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. The ***cell potential*** is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the *cell* **electromotive force (emf)** of the cell *when no current is drawn through the cell*. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing a galvanic cell. If there is an electrochemical cell where two electrodes are in two different electrolyte solution, there is an additional potential difference arise across the boundary. This is termed as "***liquid junction potential***". The contribution of liquid junction potential can be minimized using a salt bridge to join two electrolyte solutions.

A Galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Following points are important in writing the **cell notation.**

- *Electrode corresponding to the oxidation half reaction in a cell is always written on the left hand side and electrode where reduction half reaction take place is written on the right hand side.*
- *Phase boundaries are represented by a vertical bar "|"*
- *If there is a liquid junction potential present then a " ⋮ " is used between two electrodes*
- *If there is a salt bridge (i.e. no liquid junction potential), two electrodes are separated by a double vertical bars "||"*
- *Indication of the physical state is compulsory for all species and indication of conditions such as concentration, pressure, temperature must be in cooperated if known.*

According to the cell notation, the Daniel cell above can be written as,

$$Zn(s)|Zn^{2+}(aq, 1.0 \text{ mol dm}^{-3}))||Cu^{2+}(aq, 1.0 \text{ mol dm}^{-3})|Cu(s)$$

Other examples are:

$$Mg(s)|\ Mg^{2+}(aq, 1.0 \text{ mol dm}^{-3})\ ||\ H^{+}(aq, 1.0 \text{ mol dm}^{-3})\ |\ H_2(g)\ |Pt(s)$$

$$Pt(s)|H_2(g)\ |H^{+}(aq)\ ||\ Cl^{-}(aq)\ |Cl_2(g)\ |Pt(s)$$

When a common electrolyte HCl is used for both electrodes,

$$Pt(s)|H_2(g)\ |H^{+}(aq),\ Cl^{-}(aq)\ |AgCl(s)\ |Ag(s)$$

Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side i.e.,

$$E_{cell} = E_{right} - E_{left}$$

or

$$E_{cell} = E_{cathode} - E_{anode}$$

Thus, for the cell that we are considering,

$$E_{cell} = E_{Cu^{2+}(aq)/Cu(s)} - E_{Zn^{2+}(aq)/Zn(s)}$$

$$E_{cell} = 0.34 \text{ V} - (-0.76 \text{ V})$$

$$E_{cell} = +1.10 \text{ V}$$

This can further be understood by the following example.

Consider the cell reaction:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

Half-cell reactions:

Cathode (*reduction*): $2Ag^{+}(aq) + 2e \rightarrow 2Ag(s)$

Anode (*oxidation*): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e$

It can be seen that the sum of half reactions leads to the overall reaction in the cell and that silver electrode acts as the cathode and copper electrode acts as the anode. The cell can be represented as:

$$Cu(s)|Cu^{2+(}aq)||Ag^{+}(aq)|Ag(s)$$

and we have ,

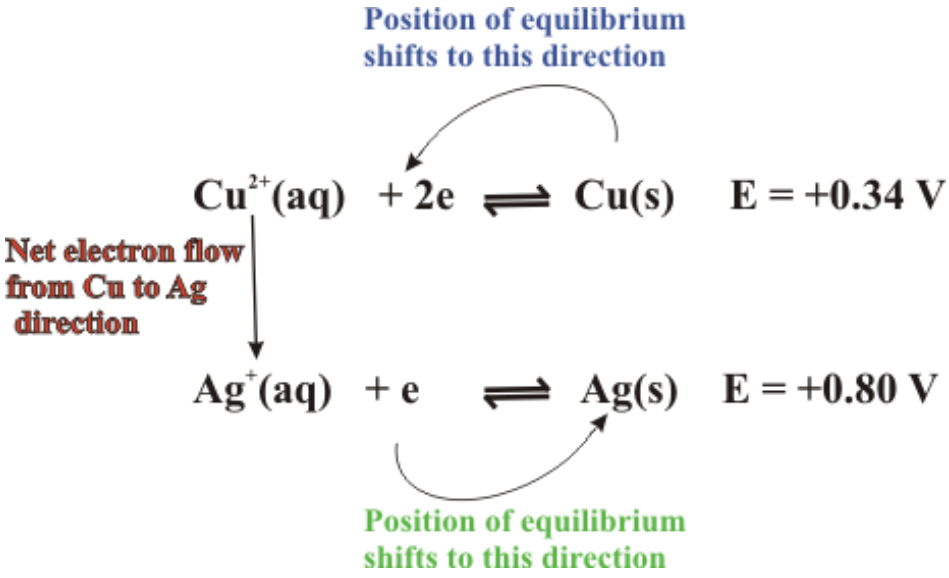
$$E_{cell} = E_{right} - E_{left} = E_{Ag^{+}/Ag} - E_{Cu^{2+}/Cu}$$

Therefore, by substituting corresponding reduction potentials of the half-cells the value of the emf of the cell can be estimated.

$$E_{cell} = +0.80 \text{ V} - (0.34 \text{ V}) = +0.46 \text{ V}$$

This reaction can also be treated like below.
Both of these $E°$ values are positive. $E_{Ag^+/Ag} = +0.80$ V and $E_{Cu^{2+}/Cu} = +0.34$ V indicating that neither copper nor silver produces ions and releases electrons as easily as hydrogen does.

However, of the two, copper releases electrons more readily as it has a less positive E^0 value. In a cell, copper would have the greater buildup of electrons, and is the negative electrode. If copper and silver are connected by a bit of a wire, electrons would flow from the copper to silver as described below.

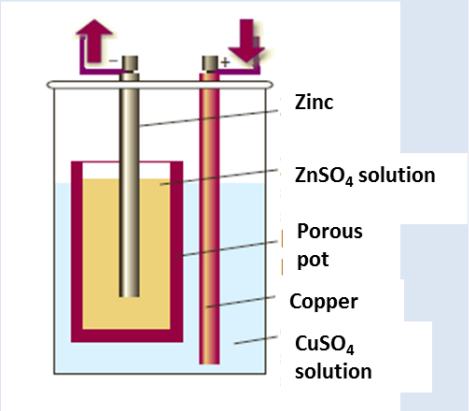


Therefore, it can be confirmed that the given cell reaction is feasible.

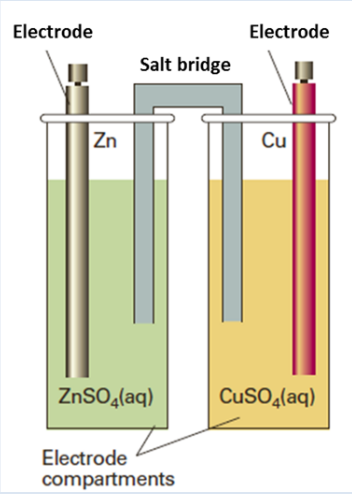
Example 3.2

Following diagrams indicate different versions of Daniel cells. Write the cell in standard notation.

(a)



(b)



Answer

(a) In this diagram, there is a liquid junction between the two different electrolytes. Therefore, cell notation is $Zn(s)|Zn^{2+}(aq)\vdots Cu^{2+}(aq)|Cu(s)$.

(b) In this diagram, the presence of liquid junction potential is minimized using a salt bridge. Therefore, cell notation is $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$.

3.3.2 Factors affecting the electrode potential

The potential of an electrode depends on several factors as listed below.

- temperature
- concentration of the electrolyte
- nature of the electrolyte
- pressure of the gas
- type of electrolyte

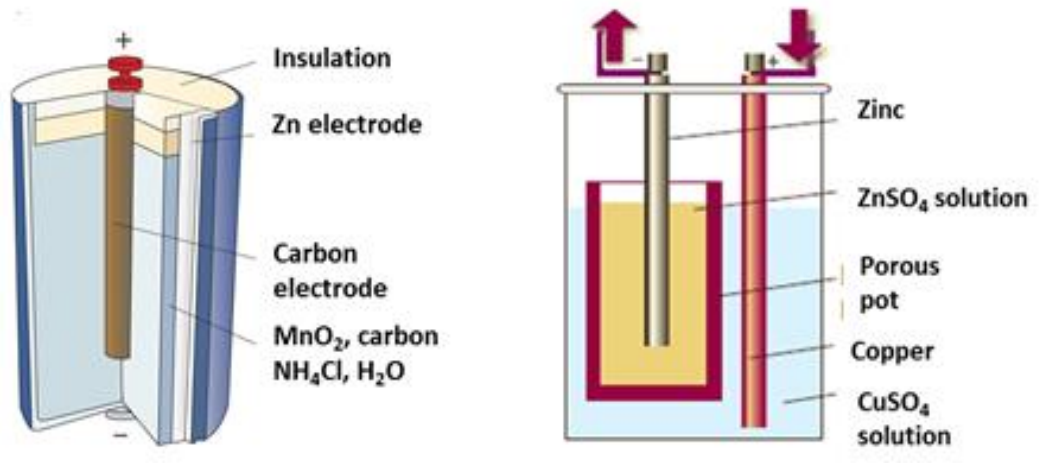
For an electrochemical reaction to take place, metal ions must collide with the electrode surface with proper orientation and energy. Therefore, temperature and concentration of the electrolyte are important when determining the electrode potential. The nature of the electrolyte is also important when considering charge transport during the operation of the cell. This is discussed under section 3.1.1. When gas electrodes are used, it is very

important to mention the pressure of the gas as it can be used to define number of molecules in a unit volume.

The electrode potential of silver-silver chloride measured with respect to SHE is 0.220 V. However, if the concentration of KCl electrolyte used is 0.10 mol dm^{-3}, then the electrode potential is changed to 0.288 V and in the case of 1.00 mol dm^{-3} KCl it is further changed to 0.235 V.

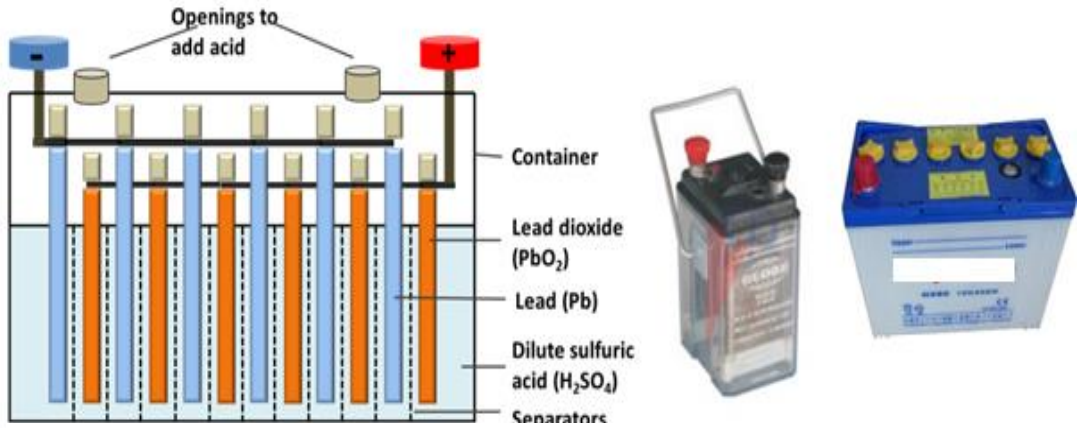
3.3.3 Different types of electrochemical cells

Electrochemical cells are used to convert chemical energy to electrical energy. Therefore, such electrochemical cells are employed in many aspects of daily life where electrical items are operated with 'batteries'. In these cells chemical reactions occur when two electrodes are connected externally using a conductor to generate the current. When the cell reaction cannot be reversed by providing electrical energy, such electrochemical cells are called "**primary cells**" (i.e. non rechargeable). Normal Leclanche cell in Figure 3.11(a) and Daniel cell in Figure 3.11 (b) are examples for primary cells.



(a) (b)

Figure 3.11 (a) Normal Leclanche cell (b) Daniel cell



(a) (b) (c)

Figure 3.12 (a) Schematic diagram of a lead accumulator (b) Lead accumulator (c) Commercial lead accumulator (car battery)

Another type of cell that is used in daily life is the lead accumulator. This is more commonly known as the "car battery". These cells can be recharged by reversing the cell reaction (rechargeable), so these cells are referred as "**secondary cells**". Figure 3.12 illustrates a lead accumulator.

Table 3.6 Summary on different types of electrochemical cells

Electrochemical cell	Normal Leclanche cell (primary cell)	Daniel cell (primary cell)	Lead accumulator (secondary cell)
Electrolyte	NH_4Cl / $ZnCl_2$	$ZnSO_4$ (aq)/ $CuSO_4$(aq)	Dil. H_2SO_4
(+) pole	C/ MnO_2	Cu	PbO_2
(-) pole	Zn	Zn	Pb
Reaction at (+) pole (Cathode reaction)	$2NH_4^+(aq) + 2MnO_2(s) + 2e \rightarrow Mn_2O_3(s) + H_2O(l) + 2NH_3(g)$	$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	(During discharging) $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \rightarrow PbSO_4(s) + 2H_2O(l)$
Reaction at (-) pole (Anode reaction)	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$	(During discharging) $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(aq) + 2e$
Cell reaction	$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l) + 2NH_3(g)$	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	(During discharging) $PbO_2(s) + 4H^+(aq) + Pb(s) \rightarrow 2\ PbSO_4(s) + 2H_2O(l)$

3.4 Electrolysis

In Galvanic cells, a spontaneous chemical reaction can convert chemical energy to electrical energy. However, in daily life we come across situations where non-spontaneous redox reactions must be carried out to produce useful items. Examples are electroplating where precious metals like silver (Ag) can be coated on a less expensive metal to get a more appealing cover or can be used to coat a protective metal layer. In such a situation, the corresponding non-spontaneous chemical reaction can be driven forward giving electrical energy from outside. Conducting a non-spontaneous chemical reaction using electrical energy from outside is known as **electrolysis**. A direct current is passed through a molten substance or substance dissolved in a suitable solvent when conducting electrolysis. Chemical reactions at electrodes will result in the desired product.

When conducting electrolysis, the electrode connected to the positive terminal of the external source of electricity (battery) is the **positive electrode (anode)**. The electrode connected to the negative terminal is the **negative electrode (cathode).** When conducting electrolysis, positive ions in the solution are attracted towards the negative electrode (cathode) and undergo reduction. The opposite happens at the anode where negatively charged ions in the solution are oxidized.

3.4.1 Electrolysis of water

Water is a very stable chemical substance. Therefore, electrolysis of water to produce hydrogen gas and oxygen gas is not a spontaneous chemical reactions under atmospheric conditions (1 atm, 25 °C, $\Delta G^{\ominus}$ is 474.4 kJ mol^{-1}). In order electrolyse water, external electrical energy must be supplied to carry out the redox reaction.

Electrolysis of water can be performed using the setup given in the Figure 3.14.

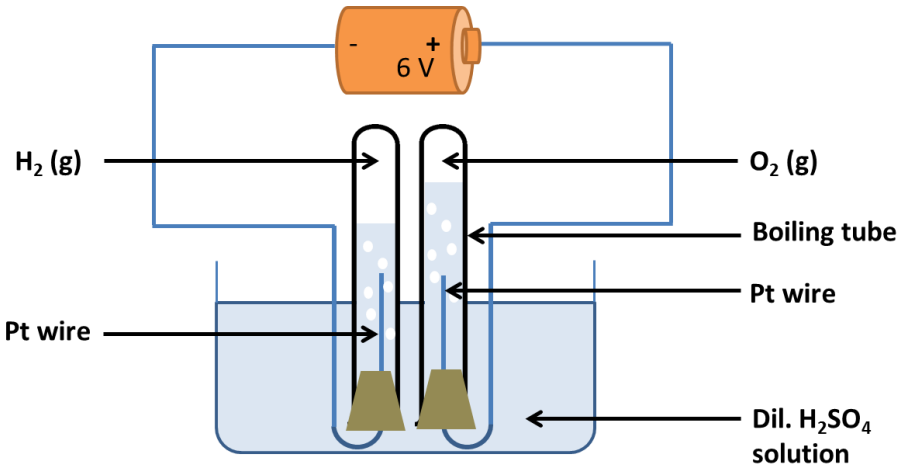


Figure 3.14 Experimental set up for electrolysis of water

The main ionic species in pure water are $H^+(aq)$ ion and $OH^-(aq)$ ions each having a concentration of 1×10^{-7} mol dm^{-3}. Therefore, dilute H_2SO_4 (0.10 mol dm^{-3}) is added to

water to enrich $H^+(aq)$ ions in solution. This facilitates conducting electricity due to the presence of sufficient number of ionic species than in pure water.

The overall reaction is given by

Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode (reduction): $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$

Overall: $\mathbf{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$

It is clear from the overall reaction of electrolysis that H_2SO_4 concentration has no effect on the electrolysis.

Example 3.3
Using standard electrode potentials listed in Table 3.5, calculate the minimum voltage required for the electrolysis of water.

Answer
Standard electrode potentials for the electrolysis of water is given below.

Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ ($E^\ominus = 1.23$ V)

Cathode (reduction): $4H^+(aq) + 4e^- \rightarrow 2H_2(g)$ ($E^\ominus = 0.00$ V)

Overall: $\mathbf{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$

$E^\ominus cell = E^\ominus cathode - E^\ominus anode = 0\ V - (1.23\ V) = \mathbf{-1.23\ V}$

Since $E^\ominus cell$ is negative, $\Delta G^\ominus$ is positive. Therefore, reaction is not spontaneous. In order to conduct this reactions external electrical supply must give a minimum voltage of 1.23 V.

3.4.2 Electrolysis of $CuSO_4(aq)$ using copper electrodes

Electrolysis of $CuSO_4$ (aq) solution using Cu electrodes is a method practiced commercially to purify copper. In general raw copper is extracted from the ore using carbon. However, copper produced in this way comprises many impurities. Therefore, pure Cu can be obtained when $CuSO_4$ (aq) solution is electrolysed with a positive electrode (anode) made of impure Cu and a negative electrode (cathode) of pure Cu. When the system is connected to an electrical source (e.g. 9V battery), impure Cu rod (anode) will dissolve providing Cu^{2+} ions to the solution while more Cu will deposit on the pure Cu rod (cathode) growing it's size.

Anode (oxidation): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

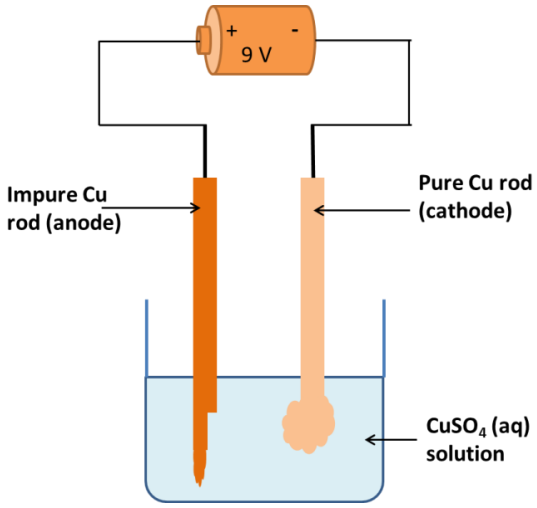


Figure 3.15 Experimental set up for electrolysis of $CuSO_4(aq)$

3.4.3 Electrolysis of $CuSO_4(aq)$ using inert electrodes

A scenario different from above is observed when electrolysis of $CuSO_4$ solution is conducted using inert electrodes such as Pt or graphite. In this case, at the anode O_2 gas is released and deposition of Cu is observed at the cathode. The experimental set up used here is much similar to Figure 3.15. The only change is the use of inert electrodes.

Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Overall reaction: $\mathbf{2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq)}$

In this experiment if ions that are present near the cathode (negative electrode) are considered, reduction of Cu^{2+} ions to Cu metal (+0.34 V) is easier compared to reduction f H^+ ions to H_2 gas (0.00 V) according to the values of standard reduction potentials listed in **Table 13.5.** Similarly, when anode (positive electrode) is concerned, SO_4^{2-} and OH^- ions are attracted. Among these ions, oxidation of water (+1.23V) is more feasible than the oxidation of $SO_4^{2-}(aq)$ ion (+2.05 V). Therefore, at the anode, O_2 gas is released by oxidation of water.

3.4.4 Electrolysis of NaCl(aq) using inert electrodes

When considering electrolysis of NaCl(aq) solution, it is important to analyze oxidation and reduction reactions that can happen at the corresponding electrodes first. Then comparison of standard reduction potentials of competing reactions can be used to predict final products. Following are competing reduction reactions taking place near the cathode.

$2H^+(aq) + 2e \rightarrow H_2(g)$ $\quad E^\ominus = 0.00$ V (1)

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ $\quad E^\ominus = -0.83$ V (2)

$Na^+(aq) + e \rightarrow Na(s)$ $\quad E^\ominus = -2.71$ V (3)

When considering standard reduction potentials, the most probable reduction is reaction (1). However, this reaction requires standard conditions and also, [H^+(aq)] in water is too low (10^{-7} mol dm^{-3}). Hence it is not possible under ordinary laboratory conditions. The reaction (3) which involves reduction of Na^+(aq) ion cannot happen due to large negative potential. Therefore, when electrolysis of NaCl(aq) solution is considered, the most possible reduction reaction that can happen at the cathode is (2) which involves reduction of water to produce H_2(g) and OH^-(aq) ions.

In order to determine the most possible oxidation reactions that happen at the anode, first it is important to list all oxidation reactions.

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e \qquad (4)$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e \qquad (5)$$

Then we can write the standard reduction potentials for the reduction of above reactions before predicting the most possible reaction.

$$Cl_2(g) + 2e \rightarrow 2Cl^-(aq) \qquad E^\ominus = +1.36\ V \qquad (4')$$

$$O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l) \qquad E^\ominus = +1.23\ V \qquad (5')$$

According to above data, reduction reaction of (*4'*) is more feasible than (*5'*) i.e. oxidation of (5) is more feasible than (4). Therefore, according to standard reduction potentials, most favourable oxidation reaction is (5). However, when this experiment is conducted the gas evolved is Cl_2 and NOT O_2! That is because the actual potential that needs to be supplied for the reaction to take place is sometimes greater than the standard reduction potential. This extra potential is termed **over potential** (Detailed discussion of over potential is beyond the scope of G. C. E. (A/L) Chemistry syllabus). In other words, standard reduction potentials can be used to obtain minimum voltage values that can be supplied to drive the reaction of interest; however, actual voltage may be higher due to presence of over potentials. Therefore, Cl_2 (g) is observed, because over potential for reaction (5) (release of O_2(g)) could be much greater than for the reaction (4). Thus reaction (4) requires less potential to be supplied than for reaction (5).

Finally, the reactions taking place at the cathode and anode when electrolyzing NaCl(aq) solution using inert electrodes can be written as follows.

Anode (oxidation): $2Cl^-(aq) \rightarrow Cl_2(g) + 2e$

Cathode (reduction): $2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

Overall reaction: $\mathbf{2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)}$

3.4.5 Electrolysis of NaCl(l) (molten NaCl) using inert electrodes

NaCl exits in solid form at room temperature, thus does not conduct electricity due to absence of mobile ionic species. However, if the temperature is raised to more than the melting point of NaCl(s) (i.e. > 801 °C), molten NaCl(l) consists of mobile Na^+ ions and

Cl^- ions. Therefore, electrolysis of molten NaCl will result in reduction of Na^+ ion to produce Na metal and Cl_2 gas as the oxidation product.

Anode (oxidation): $2Cl^-(l) \rightarrow Cl_2(g) + 2e$

Cathode (reduction): $\underline{Na^+(l) + e \rightarrow Na(l)}$

Overall reaction: $\mathbf{2Cl^-(l) + 2Na^+(l) \rightarrow Cl_2(g) + 2Na(l)}$

According to the standard reduction potentials listed in Table 3.5, the minimum voltage that should be supplied for the overall reaction to take place is 4.07 V. However, in practice, much higher voltage is required to drive the reaction due to the presence of a large over potential associated with the reaction. Industrially Na metal is extracted by this method by electrolyzing molten NaCl solution. The industrial set up is known as the **Downs cell**.

Example 3.4

Predict the gases evolved at the cathode and anode when Na_2SO_4 (aq) solution is electrolyzed using inert electrodes.

Answer

Step 1: Identify possible oxidation reactions that can happen near the anode (Hint: Anions are likely to be oxidized at the anode) and write standard reduction potentials using **Table 13.5**.

$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e$ (Standard reduction potential = +2.05 V) …..(1)

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ (Standard reduction potential = +1.23 V) …..(2)

When over potential is not considered, the lower the standard reduction potential easier is to oxidize when the direction of oxidation is concerned.

At the anode O_2 gas will be evolved.

Step 2: Identify possible reduction reactions that can happen near the cathode (Hint: cations are likely to be reduced at the cathode) and write standard reduction potentials using **Table 3.5**.

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ (Standard reduction potential = -0.83 V) ……(3)

$Na^+(aq) + e \rightarrow Na(s)$ (Standard reduction potential = -2.71 V) ……(4)

The higher the negative value of standard reduction potential of a species, it is more likely to be in the oxidized form. Reduction of Na^+ has a higher negative value compared to reduction of water as listed above. Therefore, Na^+ tends to stay in the Na^+ state while H_2O will be reduced at the **cathode to produce H_2 gas.**

Both half reactions involve oxidation and reduction of water instead of OH^- ions and H^+ ions. That it is because Na_2SO_4 is a neutral salt which keeps the solution at a pH of approximately 7. Therefore, H_2O oxidize and reduce itself due to the absence of high concentrations of OH^- and H^+ ions.

Step 3: Write the overall reaction combining cathode and anode reactions.

Anode (oxidation): $2\ H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$

Cathode (reduction): $4\ H_2O(l) + 4e \rightarrow 2H_2(g) + 4OH^-(aq)$

Overall reaction: $\mathbf{2\ H_2O(l) \rightarrow O_2(g) + 2H_2\ (g)}$

3.4.6 Quantitative aspects of electrolysis

Michael Faraday was the first scientist who described the quantitative aspects of electrolysis. Faraday's laws stem from what has been discussed earlier.

Faraday's laws of electrolysis

The following well known Faraday's two laws of electrolysis is mainly used for quantitative analysis in electrolysis.

(i) First Law: *The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).*

(ii) Second Law: *The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal / Number of electrons required to reduce the cation).*

The quantity of electricity *Q*, passed is given by

$$\boldsymbol{Q = It}$$

Q is in coloumbs when *I* is in ampere and *t* is in second. That is **1 C = 1 A × 1 s**

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:

$$Ag^+(aq) + e \rightarrow Ag(s)$$

one mole of electrons is required for the reduction of one mole of silver ions. We know that charge on one electron is equal to 1.6021×10^{-19}C.

Therefore, the charge on one mole of electrons is equal to:

$N_A \times 1.6021 \times 10^{-19}\ C = 6.02 \times 10^{23}\ mol^{-1} \times 1.6021 \times 10^{-19}\ C = 96487\ C\ mol^{-1}$

This quantity of electricity is called **Faraday (constant)** and is represented by the symbol **F**.
For approximate calculations we use 1F ≃ 96500 C mol^{-1}.
For the electrode reactions:

$$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$$

$$Al^{3+}(aq) + 3e \rightarrow Al(s)$$

it is obvious that one mole of Mg^{2+} and Al^{3+} require 2 moles of electrons (2F) and 3 moles of electrons (3F) respectively.

Application of Faraday constant to electrochemical calculations
When electrolysis experiments are conducted, it is important to know quantitatively the yield of the products at the cathode and the anode. The yield is associated with the current passed through the cell for a known period of time. For example, consider following reduction reactions.

$$Na^{+}(aq) + e \rightarrow Na(s)$$

$$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^{-}(aq)$$

In order to produce 1 mole of Na(s) metal, 1 mole of electrons must be used to reduce Na^{+}. Similarly, to produce 1 mole of H_2 gas, 2 moles of electrons are required.

The charge in coulombs for a one mole of electrons is given by the **Faraday constant** which is **96485 C mol^{-1}**. Therefore, if the charge in coulombs passed through the cell is known, then the amount product of consumption of reactants can be calculated. In general, the current passed though the electrolytic cell for given period of time is known. Then the following relationship can be used to calculate the charge associated during that period of time when the current passed through is given in amperes (A) and time in seconds (s).

Current(A) × time(s) → coulombs(C) → moles of electrons → moles of product or reactant

Example 3.5

Calculate the volumes of gases evolved at the cathode and anode when dil. H_2SO_4(aq) solution is electrolyzed using inert electrodes for a period of 5 h passing a current of 1.5 A under 25 °C and 1 atm pressure.

Answer

Step 1: Identify possible oxidation reactions that can happen near the anode (Hint: anions are likely to be oxidized at the anode) and write standard reduction potentials using **Table 13.5**.

$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e$ (Standard reduction potential = +2.05 V) …..(1)

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ (Standard reduction potential = +1.23 V) …..(2)

As illustrated in **Example 3.4**, the reaction at the cathode is (2). Therefore, **at the anode O_2 gas is evolved**.

Step 2: Identify possible reduction reactions that can happen near the cathode (Hint: Cations are likely to be reduced at the cathode) and write standard reduction potentials using **Table 3.5**.

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ (Standard reduction potential = -0.83 V) …..(3)

$H^+(aq) + e \rightarrow H_2(g)$ (Standard reduction potential = 0.00 V) …..(4)

Since it is a dilute H_2SO_4 solution, there is sufficient H^+ concentration present for reaction (4) to take place preferably at the cathode. Therefore, **the gas evolved at the cathode is H_2 gas**.

Step 3: Write the overall reaction combining cathode and anode reactions.

Anode (oxidation): $2\ H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$

Cathode (reduction): $4H^+(aq) + 4e \rightarrow 2H_2(g)$

Overall reaction: **$2\ H_2O(l) \rightarrow O_2(g) + 2H_2(g)$**

Step 4: Calculate the amount of charge passed through during electrolysis period.

Charge = current (A) × time (s) =1.5A × (5 ×60 ×60) s = **27000 C**

Amount of moles of electrons = 27000 C × (1/96485 C mol^{-1})

= **0.28 moles of electrons**

Step 5: Calculate volume of O_2 gas evolved at the anode
According to the oxidation half reaction,

4 moles of electrons → 1 mole of $O_2(g)$

Amount of moles of O_2 (g) produced

$$= 0.28 \text{ moles of electrons} \times \frac{1 \text{ mole of } O_2(g)}{4 \text{ moles of electrons}}$$

= 0.07 moles of O_2 (g)

Apply ideal gas equation to calculate volumes of O_2 (g) produce, V = nRT/P

Volume of $O_2(g)$ = (0.07 mol × 8.314 J K^{-1} mol^{-1}×298 K) / 1×10^5 Pa

= 173.4 × 10^{-5} m^3 =**1.734 dm^3**

Step 5: Calculate the volume of H_2 gas evolved at the cathode.
According to the reduction half reaction,

2 moles of electrons → 1 moles of $H_2(g)$

Amount of moles of H_2 (g) produced

$$= 0.28 \text{ moles of electrons} \times \frac{1 \text{ mole of } H_2 \text{ (g)}}{2 \text{ moles of electrons}}$$

= 0.14moles of H_2 (g)

Apply ideal gas equation to calculate volumes of H_2 (g) produce, V = nRT/P

Volume of $H_2(g)$ = (0.14 mol × 8.314 J K^{-1} mol^{-1}×298 K) / 1×10^5 Pa

= 346.8 × 10^{-5} m^3 = **3.47 dm^3**

3.4.7 Comparison of galvanic cells and electrolytic cells

The main difference between the two types of cells is the spontaneous nature of the cell reaction. In Galvanic cells, the cell reaction is spontaneous and chemical energy is converted to electrical energy. Therefore, electricity is produced in galvanic cells. The anode in a Galvanic cell is negatively charged due to electrons left behind during oxidation. The cathode is positively charged due to taking up of electrons for the reduction half reaction.

The opposite is taking place during electrolysis or in electrolytic cells. The overall cell reaction is not spontaneous. Therefore, it is necessary to pump electrons from an external source to proceeds the reaction. Therefore, a battery is used in electrolysis to supply electricity for the chemical reaction to take place. Here, the anode is connected to the positive terminal of the battery. The oxidation reaction taking place at the anode will generate electrons that are attracted towards the positive terminal of the battery. Therefore, the anode is positively charged. The opposite is true for the cathode and it is connected to the negative terminal of the battery. So the cathode in electrolytic cell is negatively charged.

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G. C. E. (Advanced Level)

CHEMISTRY

Grade 13

Unit 14 - Industrial Chemistry and Environmental Pollution

Department of Science
Faculty of Science and Technology
National Institute of Education
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Chemistry

Resource Book

Grade 13

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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.

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1.Industrial Chemistry and Enviornmental Pollution

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1.1 Industrial Chemistry

1.1.1 Chemical industries

Colossal changes occurred in the mode of production and the force of production during the periods identified as the first industrial revolution (1750-1850) and the second industrial revolution (1870-1914 or 1850-1940) in modern civilization. Along with the diversified market concepts (consumerism) based on the basic requirements of human, world scale productions and services speeds up making profits. Various types of technological tools and methods of productions were created for this. With industrialization, environmental and social problems tended to emerge. Hence more attention had to be paid to reduce the risk of environmental problems and disasters, optimize efficiency and increase productivity. Alongside the gaming of a special place by chemical industries in the process of industrial production, a field of study of which came to be known as Chemical Engineering emerged. Today it has become a well-established discipline.

Iron, ammonia, sulphuric acid, nitric acid, caustic soda and petroleum can be given as some of the main chemical products in the world. Specially medicines, monomers, polymers, lubricants and organic dyes are examples for the products manufactured using organic compounds obtained from the petroleum industry. Plastic and rubber goods, cosmetics, soap, detergents, adhesives, paper, glass, salt, sugar, used in day-to-day life are some more examples for the products of chemical industries. Production of salt using sea water is one of the chemical industries in our country.

Production of soap using major chemicals produced in the world, production of various materials and goods using natural rubber latex and production of cement, paint and glass are some of the chemical industries carried out in our country at present.

Chemical industries spread out and establish in global scale area diverse. They can be classified as chemical industries producing organic chemicals and inorganic chemicals. In addition, they can also be classified as industries which produce agrochemicals, medicine, lubricants, dyes, metals and other substances.

Only few industries are discussed as examples which are based on modern knowledge and technology. Paying attention on the enviornmental, health and social issues at present worldwide, the industries suitable to our country are considered. Management of the knowledge on such is an entrance to 'Industrial Chemistry' discussed here.

1.1.2 Requirements to be considered in establishing chemical industries

There are requirements that should be considered when establishing a chemical industry. Some of them are given below.

- Capital
- Supply of raw materials
- Labour
- Technology

- Assurance of the production process
- Assurance of continuity
- Waste products and methods of waste management.
- Strategies for preventing the addition of environmental pollutants by the industry.
- Site of installation
- Nature of power supply (fossil, solar energy, nucleic energy, bio mass) and cost
- Transport facilities and market
- Nature of probable accidents and strategies that can be adopted to prevent accidents
- Government rules, regulations and policies.

Safety of the production process and prevention of accidents are very important in chemical industry. For this some of the disasters occurred in relation to chemical industries should be investigated. On 21 September 1921, 500-600 people died at an explosion occurred in Oppau on of Germany. The explosion was caused by 4500 tons of a mixture of ammonium nitrate and ammonium sulphate meant to be used as fertilizers. Similarly, the accident at the Chernobil nuclear power station in Ukrane (26 April, 1986) claimed nearly 4000 human lives at once. Because of the Bhopal incident in India (27 December, 1984), about 8000 men and women had to lay down their lives within a period of one week. The reason for this was found to be the leakage of the highly poisonous gas methyl isocyanide. Therefore, it is very important to understand properly the real need of a chemical industry and the political, social, economic and environmental changes associated with it. Moreover, the understanding about the maintenance of the production process safely, efficiently and effectively is also great importance.

1.1.3 Use of raw materials of chemical industry

Raw materials are the substances that are supplied from outside for a chemical industry and which take part in the production process. Production of compounds such as $NaHCO_3$, H_2SO_4 can be given as examples for this. In some chemical industries, chemical components contained in raw materials exist in the product as they were. That is chemical changes do not occur; but physical changes do occur. Paint production is an example for this.

Various raw materials are used for chemical industries. Different sources are used for this. For example, nitrogen gas is used as one of the raw materials to produce ammonia. Atmospheric air is the source from which this nitrogen is obtained. Atmospheric air is first liquefied; then N_2 gas is separated by fractional distillation and used for ammonia production. But in the production of nitric acid, instead of pure oxygen gas, atmospheric air is directly used to obtain NO_2 gas by oxidizing ammonia. In ammonia production (Haber process) though atmospheric air is the source for N_2 gas, which is an essential raw material for it is obtained, in the manufacturing of nitric acid, atmospheric air itself

is used as a raw material. Thus, facts such as the way the entire production process is planned, expenditure and what level of purity should be maintained are useful to decide in which form the raw materials should be used.

When using a natural resource as a raw material, it is useful to take the following into consideration.

- Occuring in large deposits for long term usage
- Easy to reach
- Purity

Specially, crude oil is the source for the production of many basic organic compounds. Hydrogen gas obtained by cracking of hydrocarbons is used as an essential raw material for the production of ammonia. Coke is a non-renewable raw material used for the production of iron.

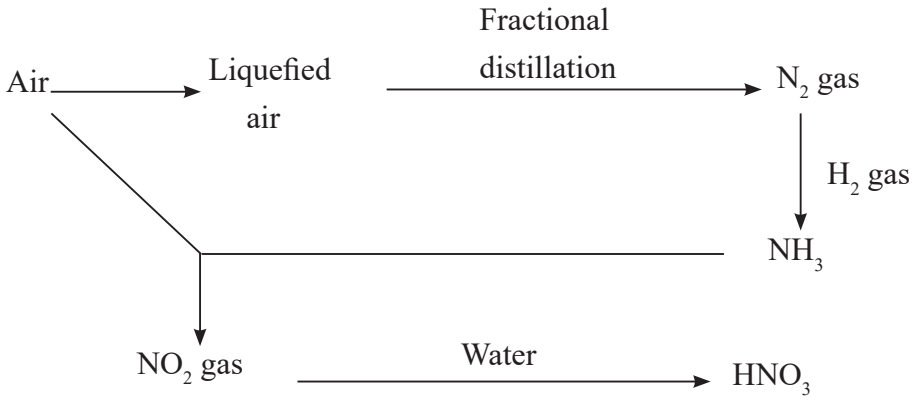
A brief account on the raw materials used for some products is given below.

Air

a) Oxygen is needed as an active component in iron extraction, production of nitric acid and sulphuric acid. Atmospheric air is used as a raw material in these productions.

b) Atmospheric air is used as a natural source of nitrogen. Nitrogen gas obtained by liquefaction of air followed by fractional distillation is used as a raw material in manufacturing ammonia. In the process of separating nitrogen gas from atmospher, atmospheric air is used as a raw material.

When using atmospheric air for chemical industries, it could be identified as a source of nitrogen or oxygen gas



Water

Water is used for the production of sodium hydroxide and, nitric acid, sulphuric acid and calcium hydroxide. Sea water is not used as a source of water in these industries. The

reason for this is that various salts presents in sea water interfere with the production process and also get into the product as impurities. Hence it is very important to take care about the standards of the raw materials.

NaCl

NaCl is obtained using sea water as a raw material or from the ores of rock salt. Caustic soda is produced using NaCl as a raw material. It is also used as raw material in the extraction of Na metal. Sea water can be counted as a source for the production of NaCl. But sea water cannot be used as a raw material for the production of caustic soda.

Minerals

Minerals are non-renewable resources. For the extraction of metals such as iron, copper, nickel, aluminum and titanium, minerals containing those metals are used as raw materials. Also minerals containing phosphates are used for the production of phosphate fertilizers. As minerals are non-renewable resources, there could be a recycling process after using the products from minerals. Further, it is also important to use those products to produce useful substances that are long-lasting.

Coal

Coal is a non-renewable resource. It is mainly used as a fuel. In extraction of iron, it is used as a fuel, a direct reductant as well as a raw material essential to generate CO which is a major reducing agent.

Crude oil

Crude oil is a non-renewable resource. It is used as the main source of fuels such as petrol and diesel. Crude oil is the main source from which raw materials for the production of monomers for polymers, medicine and basic organic compounds are obtained. As this is a non-renewable resource, continuation of the productions based on it becomes a problem with its consumption. Another crisis is the increase in global warming caused by the carbon dioxide produced during the burning of fuel obtained from crude oil.

Plants

Plants are very important resources for the production of various oils, latex (rubber latex), resins and medicine. Plant materials are known as biomass and used as fuel for industries and also as raw materials for the production of various orgnic compounds. As Plants is a renewable resource, it is a source that can be managed without disturbing the natural cycles in the environment. Industries which used petroleum oil to generate power have started to use biomass as an alternative source of energy. Industries in our country too are inclined towards this.

1.2 Extraction of Mg – Dow process

Raw materials essential for extracting Mg by Dow process.

Minerals containing magnesium is abundant in the earth crust. But, extraction of Mg from sea water is more profitable.

Other than Na^+, Mg^{2+} is the most abundance cation in sea water. In sea water, about 0.13% by weight is magnesium. The solution discarded at the last stage of producing salt from sea water is called bittern. As bittern contains significant amounts of magnesium ions, it is more suitable to use bittern to extract magnesium. Either sea water or disposable brine obtained after the reverse -osmosis of sea water is suitable for this. The main steps of this process can be briefly presented as follows.

Step 1

The main aim of this step is the production of CaO, which is obtained by the thermal decomposition of limestone. Dolomite also can be used for this purpose.

$$CaCO_3(s) \rightleftharpoons^{\Delta} CaO(s) + CO_2(g)$$

$$CaCO_3\,MgCO_3(s) \rightleftharpoons^{\Delta} CaO(s) + MgO(s) + 2CO_2(g)$$

As this reaction is reversible, by designing the thermal decompostion process, carbon dioxide gas is efficiently removed. Contamination of calcium oxide with calcium carbonate is a disadvantage.

Step 2

The object of this step is to produce $Mg(OH)_2$ from the solution containing Mg^{2+} ions. The oxides produced in the first step (CaO or CaO and MgO) are reacted with bittern solution. Here, CaO reacts with water forming calcium hydroxide. $Ca(OH)_2$ dissolves slightly in water giving Ca^{2+} and OH^- ions. Since the solubility product of $Mg(OH)_2$ is lower than that of $Ca(OH)_2$, Mg^{2+} ions in the solution are precipitated as $Mg(OH)_2$ by OH^- ions supplied by $Ca(OH)_2$ with this, more and more $Ca(OH)_2$ goes into solution releasing OH^- ions without remaining $Ca(OH)_2$ as precipitate, it dissolves. The amount of CaO required to precipitate the Mg^{2+} ions in the solution is added. Prcipitaion of $Ca(OH)_2$ with $Mg(OH)_2$ is a disadvantage.

$$CaO(s) + H_2O(l) \longrightarrow Ca(OH)_2(s) \quad \text{-------} \quad (1)$$

$$Ca(OH)_2(s) \rightleftharpoons^{\Delta} Ca^{2+}(aq) + 2OH^-(aq) \quad \text{-------} \quad (2)$$

$$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s) \quad \text{-------} \quad (3)$$

Step 3

$Mg(OH)_2$ formed is filterd and removed and reacted with concentrated HCl to get $MgCl_2$

$$Mg(OH)_2(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + 2H_2O(l)$$

If burnt dolomite (MgO.CaO) was used, CaO in it, reacts with the Mg^{2+} ions in the solution as above. But as MgO is insoluble in water, MgO is mixed with $Mg(OH)_2$ precipitaed.

Step 4

The solution is heated strongly to vaporize water. Then it is dried so that the amount of water of crystallization becomes considerably low. The dried salt contains about 16% (w/w) water.

$$MgCl_2.6H_2O(s) \longrightarrow MgCl_2.4H_2O(s) + 2H_2O(l)$$

$$MgCl_2.4H_2O(s) \longrightarrow MgCl_2.2H_2O(s) + 2H_2O(l)$$

First the solid formed is fused in the steel chambers where electrolysis is done and then it is electrolized. During heating for fusion, all the water in the salt gets completely removed by vaporization. The temperature in the cell is maintained within the range 700-800 ^{0}C. Since the melting points of $MgCl_2$ and magnesium metal are 714 ^{0}C and 650 ^{0}C respectively, the temperature of the fused salt should be maintained above those melting temperatures. As Mg metal formed during the electrolysis of the fused salt exists in the molten state, its withdrawal from the cell is easier. The density of molten Mg at its melting point is 1.584 g cm^{-3} while the density of fused $MgCl_2$ (at the melting point) is 1.68 g cm^{-3}. Thus, fused Mg metal floats on fused $MgCl_2$

Reaction at the anode (graphite) :

$$2Cl^-(l) \longrightarrow Cl_2(g) + 2e$$

Cl_2 gas liberated is used to produce HCl. HCl is reacted again with $Mg(OH)_2$ to produce $MgCl_2$

Reaction at the cathode (steel) :

$$Mg^{2+}(l) + 2e \longrightarrow Mg(l)$$

Liquid magnesium formed is taken out from the cell. From this about 99.8% yield of Mg can be obtained. As the melting point of magnesium is about 650 ^{0}C, it exists as a liquid at 700 ^{0}C.

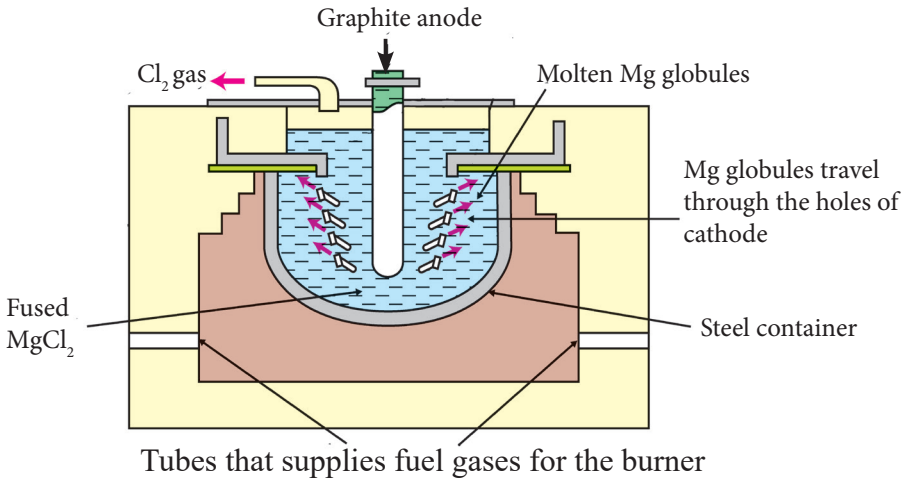


Figure 1.1 The cross sectional structure of the electro chemical cell producing magnesium

Strong and light weight metals are required for aircrafts and vehicles. Magnesium metal is very important for the production of alloys to have this kind of properties.

In this production, release of CO_2 to the atmosphere is a disadvantage. CO_2 is added to the atmosphere during the burning of limestone or dolomite and combustion of petroleum fuels to obtain a higher temperature associated with the electrolysing cell.

1.3 Production of caustic soda (NaOH)

A pure concentrated solution of sodium chloride is called brine. NaOH is produced by electrolyzing a brine solution. As the by-products hydrogen gas and chloride gas are released at the cathode and the anode respectively.

$$NaCl\,(s) + H_2O(l) \longrightarrow NaCl(aq)$$

$$2NaCl(s) + 2H_2O(l) \xrightarrow{\text{electrolysis}} 2NaOH(aq) + Cl_2(g) + H_2(g)$$

When 2.25 metric tons are produced from a solution containing 50% (w/w%) caustic soda, nearly I metric ton of chlorine gas and 30 kg hydrogen gas are produced. Though there is a consequence difference by mass like this, when the amounts of moles are considered, the amount of moles of chlorine and the amount of moles of hydrogen are approximately equal. In spite of the amounts of moles of chlorine and hydrogen formed are equal theoritically, the amounts of moles of chlorine and hydrogen that can be collected as gases are not equal. Since chlorine gas can slightly dissolve in the aqueous reaction medium, the amount of chlorine gas that can be collected in gaseous form is somewhat less than the amount of hydrogen.

The cells used to produce caustic soda by electrolysis are refered to as chlor-alkali cells. There are three types of cells.

a) Mercury cells

b) Diaphragm cells

c) Membrane cells

Earlier, production of NaOH was based on the mercury cell method. However, possibility of releasing mercury to the environment and contamination of NaOH with minute quantities of mercury are its main disadvantages. The basis of membrane cell and the diaphragm cell are almost identical. The major difference is that in the membrane cell, instead of a diaphragm, a membrane, permeable to Na^+ ions is used to separate the anode and the cathode. Compared to the membrane cell, in the diaphragm cell, the liquid level in the anode chamber is above the liquid level in the cathod chamber. Therefore, a hydrostatic pressure is exerted from the anode chamber solution to the cathode chamber solution across the asbestos diaphragm. This hydrostatic pressure affects the migration of Na^+ ions from the anode chamber to the cathode chamber. It also prevents the movement of OH^- ions from the cathodic solution to the anode chamber solution. But in the membrane cell, the anode is separated from the cathode by a membrane that permits only the movement of positive ions. Higher purity of NaOH produced, lesser consumption of electricity and minimal impact on the environment are the advantages of the employment of membrane cells.

In this electrolytic process, electric potential used for electrolysis and the charge released from a unit area of the electrode surface in a unit time (current density) are important factors. This information is given in the following table.

Table 1.1 The factors included in associated with the cells are used for caustic soda production

	Mercury cell	Diaphragm cell	Membrane cell
Apply cell potential / V	4.4	3.45	2.95
Current density/ A cm^{-2}	1	0.2	0.4
NaOH composition (w/w%)	50	12	35

Membrane cell method

The brine that is used in the membrane cell method should be very pure. Presence of Mg^{2+}, Ca^{2+} and SO_4^{-2} ions in brine hinders the production process. Precipitations of these cations when the solution becomes basic disturbs the cell action. Lowering of the purity of

caustic soda because of the addition of these ions to the sodium hydroxide solution is also a disadvantage. Therefore, the concentration of these ionic impurities in brine that is used for the production should be at a very low level. Salt (NaCl) extracted from sea water contains Mg^{2+}, Ca^{2+} and SO_4^{2-} ions. Hence, chemical treatment to remove impurity ions in brine prepared by this salt is a very important step. Sulfate ions can be precipitated and removed as $BaSO_4$ by adding barium chloride in adequate quantities. Mg^{2+} and Ca^{2+} ions can be precipitated as $Mg(OH)_2$ and $CaCO_3$ by adding NaOH and Na_2CO_3 adequately.

$$Mg^{2+}(aq) + 2OH^-(aq) \longrightarrow Mg(OH)_2(s) \downarrow$$

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s) \downarrow$$

$$Ba^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow BaSO_4(s) \downarrow$$

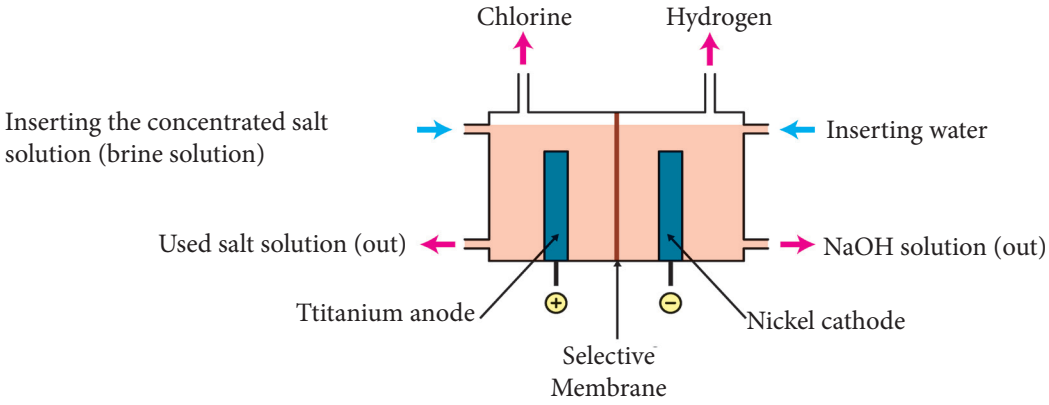


Figure 1.2 Membrane cell

At the beginning the solution in the anode chamber mainly contains Na^+ and Cl^- ions and very small amounts of H^+ and OH^- ions formed by the dissociation of water. The standard electrode potential required to oxidize OH^- ions at the anode to give O_2 is 0.4 V whereas the standard electrode potential for oxidizing Cl^- ions at the anode to liberate Cl_2 gas is 1.36 V. Hence, there is a possibility of liberating O_2 in addition to Cl_2. Several precautions have been taken to minimize releasing oxygen.

$$4OH^-(aq) \longrightarrow O_2(g) + 2H_2O(l) + 4e$$

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$$

NaCl concentration in the brine used to produce caustic soda is relatively high. In a situation where the OH^- concentration is very low and the Cl^- concentration is very high, the probability of forming an oxygen molecule and two water molecules by combining four OH^- ions on the electrode is relatively low. Since there is a relatively higher concentration

of Cl^- ions in the anode chamber solution, the ability of forming Cl_2 gas by the oxidation of Cl^- ions is relatively greater.

With the electrolysis when the Cl^- ion concentration decreases, there is a chance for the oxidation of OH^- ions liberating O_2. Because of this, a concentrated salt solution is continuously pumped into the anodic chamber and anodic chamber solution is continuously removed. Though the Cl^- ion concentration in the system decreases, Na^+ ion concentration does not decrease. When the entire cell is considered, maintenance of electric neutrality in the system is a fundamental feature, so, when Cl^- ions are given off from the anodic chamber as Cl_2 gas, either another negative ion should come into the anodic chamber solution or Na^+ ions should migrate into the cathodic chamber solution. Reduction takes place in the cathodic chamber. H^+ ion is more easily reduced than the aqueous Na^+ ion. At the beginning the medium in the cathodic chamber has no sodium chloride, so its main component is water. Since H^+ ions resulted by the dissociation of water molecules are continuously reduced, the equilibrium maintained by the reversible dissociation of water molecules drops. Since water molecules continuously dissociate with the removal of H^+ ions formed by the dissociation of water as H_2 molecules, OH^- ion concentration in the cathodic chamber increases. When electrolysis is carried out continuously, OH^- ion concentration in the cathodic chamber rises with time.

The equilibrium brought about by the dissociation of water molecules can be shown by equation (1)

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq) \text{ --------- (1)}$$

The situation where the equilibrium is lost due to reduction of H^+ ions to H_2 molecules is represented by equation (2)

$$H_2O(l) \longrightarrow H^+(aq) + OH^-(aq) \text{ --------- (2)}$$

In the cathodic chamber H^+ ions get reduced to H_2 molecules at a rate equal to the rate of oxidation of Cl^- ions to Cl_2 molecules in the anodic chamber. Because of this, the rate in which, water in the cathodic chamber continuously dissociates generating OH^- ions is equal to the rate of decreasing of Cl^- ions in the anodic chamber solution. Thus, the entire system is electrically neutral.

Along with the electrolysis, in a membrane cell, though the concentration of Cl^- ions in the anode chamber decreases, Na^+ ion concentration does not decrease. Meanwhile, in the cathodic chamber OH^- ion concentration increases because of the reduction of H^+ ions formed by the dissociation of water. This develops a potential difference across

the membrane. If OH^- ions in the cathodic chamber pass into the anode chamber, they react with chlorine in it. But, in the case of a membrane cell, OH^- ions are not capable to migrate across the membrane, so this reation does not occur in the cathodic chamber solution.

In the membrane cell, the anodic and cathodic compartments are separated by a membrane permeable to positive ions (Na^+). This membrane has very tiny pores and negative ions are bound to the borders of these pores. The negative electric fields in the space around the pores attract positive ions towards the pores and repel negative ions. While water is continuously added to the cathodic chamber by an inlet tube while the solution containing NaOH is removed by an outlet.

Anode is made of titanium and cathode is made of nickel. Possibility to carry out the NaOH production process continuously is a special feature. Brine with concentration 26% is continuously pumped into the anodic chamber and as shown of the flow chart the concentration in the solution removed from the anodic solution has dropped up to 24%. In the anodic chamber, when the generation of Cl_2 by the oxidization of Cl^- ions, H_2 are formed by the reduction of H^+ ions in the cathodic chamber. Comparing to the increasing of the OH^- ion concentration in the cathodic chamber, Na^+ ions existing in the anodic chamber move to the cathodic chamber. Therefore, a concentration of sodium hydroxide builds up in the cathodic chamber. With the movement of Na^+ ions, an electrical neutrality is brought about in each chamber. These process continuously occur during electrolysis.

The Cl^- ions in the anodic chamber do not move into the cathodic chamber through the membrane. Hence, NaCl does not get mixed up as an impurity with NaOH.

Anodic reaction (Positive terminal)

$$2Cl^-(aq) \longrightarrow Cl_2(g) + 2e$$

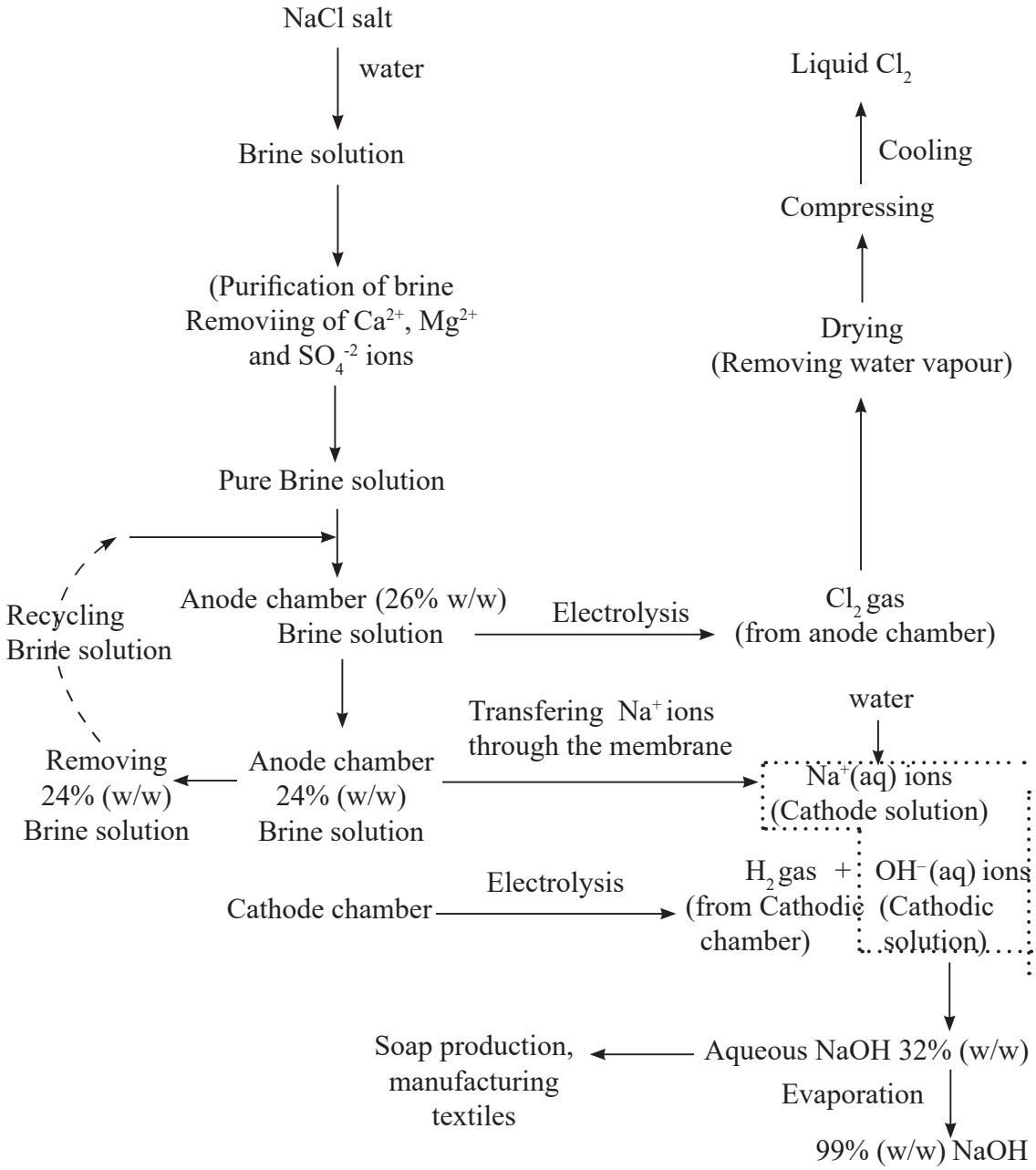
Cathodic reaction (Negative terminal)

$$2H_2O(l) + 2e \longrightarrow 2OH^-(aq) + H_2(g)$$

Overall reaction

$$2NaCl(aq) + 2H_2O(l) \longrightarrow 2NaOH(aq) + Cl_2(g) + H_2(g)$$

The flow chart for the production of NaOH by the membrane cell method.



Uses of NaOH and by-products

Uses of NaOH

1. Production of soap
2. Production of paper, artificial silk and dyes
3. Using as a strong base
4. Precipitation of heavy metal as their hydroxides in waste water treatment.

Uses of chlorine

1. Bleaching textiles, woods and paper pulp
2. Purifying the drinking water
3. Production of HC1
4. Production of chlorinated rubber, insecticides, dyes and medicine
5. Production of vinyl chloride required to produce polymers like PVC

Uses of hydrogen

1. Manufacture of HCl
2. Production of NH_3
3. Production of margarine by hydrogenation of vegetable oil
4. Using as a fuel

1.4 Production of soap

During the manufacting of soap chemically, triglycerides are subject to a hydrolysis reaction with caustic soda (saponification) forming glycerol and sodium salts of long chain carboxylic acids. These salts are known as soap. A soap molecule comprises a hydrophobic tail made of carbon and hydrogen atoms and a site with a hydrophilic head, The hydrophilic head contains Na^+ or K^+ ion and the $–COO^-$ ionic group.
Animal fat or plant oil is a one raw meterial for the production of soap. The other raw meterial is NaOH or KOH.

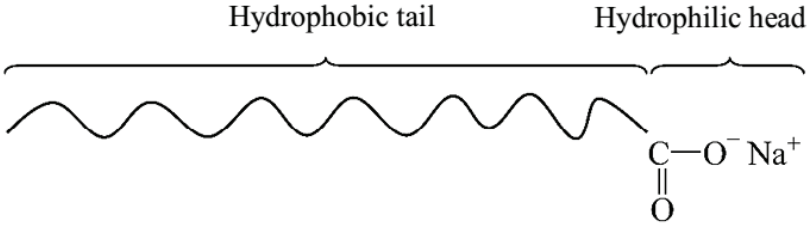


Figure 1.3 Hydrophobic tail and hydrophilic head in a soap molecule

Soap is manufactured by two processes, hot process and the cold process. In the cold process, soap and glycerol are not separated. Glycerol is deposited in soap. Here only the hot porcess and its main 4 steps are considered

1. Saponification
2. Removal of the by-product, glycerin
3. Purification
4. Finishing

The number of carbon atoms in a soap molecule varies as 12, 14, 16 and 18. In coconut oil, lauric acid, myristic acid, stearic acid and oleic acid are bound by ester bonds in the triglycerides. The amount of long chain carboxylic acids (fatty acids) present in the form of triglycerides is indicated as a percentage. In addition to this, a small amount of fatty acids occurs as free fatty acids without forming ester bonds. In coconut oil 44 – 52% of Lauric acid prercent. The number of carbon atoms in it is 12. 11 atoms out of them are in the hydrophobic tail. The percentage of myristic acid in coconut oil is 14% and it contains 14 carbon atoms. The percentages of parmitic acid (16 carbon atoms) and stearic acid (18 carbon atoms) in it are 8% and 3% respectively. Oleic acid has 18 carbon atoms and a double bond and its percentage in coconut oil is in the range of 5-8%. Soap produced using coconut oil is a mixture of sodium salts of these acids.

To remove the pigments and impurities in oil, it is sent over a special type of clay referred to as activated fuller earth. It's temperature is maintained at about 90 ^{0}C. After removing the clay particles in oil, it is used to make soap. Soap production can be conducted either as a continuous process or a Batch Process.

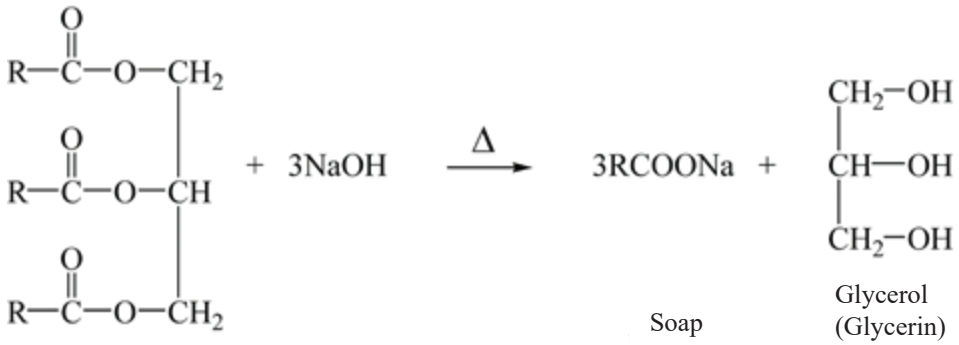
Batch Process is the traditional method. In it all the amounts of raw materials are added together to the reaction chamber and allowed to react. Afterwards the products are separated. In the continuous process, reactants are continuously supplied to the reaction chamber and products are continuously removed.

1. Saponification

Here, purified vegetable oil (coconut oil) is mixed with a solution of aqueous NaOH and heated. The purified vegetable oil (e.g. coconut oil) and the caustic soda (NaOH) solution or the caustic potash (KOH) solution are pumped into the reaction chamber. Dissolving of caustic soda in water is exothermic. Therefore dissolving of caustic soda in water is done as a separated process.

Oil and aqueous sodium hydroxide are two immiscible phases. Glycerin and soap are formed as a result of the saponification reaction taking place at the interface of these two layers. Since NaOH is neutralized here, heat is produced. The temperature of the reaction mixture is maintained at 70 ^{0}C and the mixture is mixed well. Oil divides into tiny droplets and increases the surface area. Therefore the reaction occurs uniformly throughout the entire volume of reaction mixture.

The saponification reaction can be written as follows.



$R = C_{17}H_{35} / C_{15}H_{31} / C_{11}H_{23} / C_{13}H_{27}$

2. Removal of glycerin

In the aqueous phase obtained after saponification, basicity has dropped. Glycerin and a certain amount of soap have dissolved in the aqueous phase. Soap molecules dissolved in the aqueous phase are ionized and maintain an equilibrium as follows. To decrease the solubility of soap in the aqueous phase NaCl (brine) is added. As the Na^+ ion concentration is high, the above equilibrium shifts to the left and the soap molecules separate from the aqueous phase. Glycerin dissolves in the salt solution. Density of the aqueous phase increases due to the addition of NaCl. After separating impure soap from the aqueous phase, the aqueous phase containing glycerin is pumped out.

$$\text{Water} + RCOO^-Na^+(s) \rightleftharpoons RCOO^-(aq) + Na^+(aq)$$

When increasing Na^+ ion concentration

Pumping of crude soap is easy because the temperature is 70 ^{0}C and crude soap contains a considerable amount of wetness (water). The aqueous salt solution removed from the reaction chamber contains glycerin. Thus, it is a good source to obtain glycerin. Adequate sodium chloride is added again to the solution obtained after removing glycerin and recycled. This salt solution is used to remove glycerin in impure soap. In this salt

solution, though glycerin dissolves, soap does not dissolve. Here, mixing soap well with the salt solution is very important. By this crude soap can be purified to a certain extent by removing glycerin remaining it. Then, the salt solution containing glycerin and soap partially purified and separated.

3. Purification

Water and NaCl salt are present in the soap which is purified upto a certain extent by removing glycerine. Wet soap with salt is centrifuged. Then the aqueous salt solution separates from soap. The NaCl content in soap decreases to 0.5% (w/w).

Presence of caustic soda in soap is harmful to the user. Soap with high caustic soda content can severely damage the skin and tender tissues in eyes. Therefore citric acid, phosphoric acid or free fatty acids associated with coconut oil are added to neutralize sodium hydroxide which may be present even in minute quantities in soap.

4. Finishing

It is essential to remove water in soap after removing salts. To reduce the water content in soap to 12% (w/w) soap heated to about 120 ^{0}C is sprayed into a low pressure zone in the form of small droplets. As heat is abosorbed for the vaporization of water, the temperature of the droplets decreases. While water vapour is removed, soap settles down in the low pressure vessel. Dry soap is then separated. Finished soap is made by mixing fillers, colouring and perfumes and moulded into required shapes.

TFM value of soap

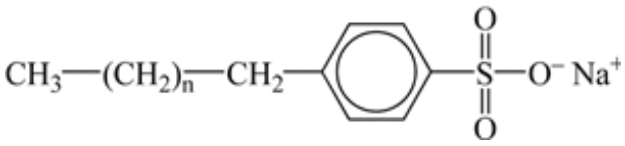
TFM (Total Fatty Matter) means the total fatty matter presents in soap. It is the percentage of RCOONa (soap) present in a cake of soap. The TFM value of a cake of washing soap is about 54-56% and the rest is fillers, colouring and substances which promote the cleaning action and colouring.

A disadvantage of soap is not dissolving and not lathering in hard water. Reason for this is, reaction of soap molecules with cations caused for the hardness and get precipitated.

$$RCOO^- Na^+ + M^{2+} \longrightarrow (RCOO)_2M + 2Na^+$$

$M = Ca^{2+}, Mg^{2+}, Fe^{2+}$ etc.

Detergents do not precipitate in hard water. The main ingredients of artificial detergents is sodium alkylbenzenesulphonate.



Cleaning action of soap

Dirt is a mixture of dust particles and organic compounds gathered around on a layer of oil. As the surface tension of water is high dirt doesn't remove only with water. Soap lowers the surface tension of water and improves its cleaning action.

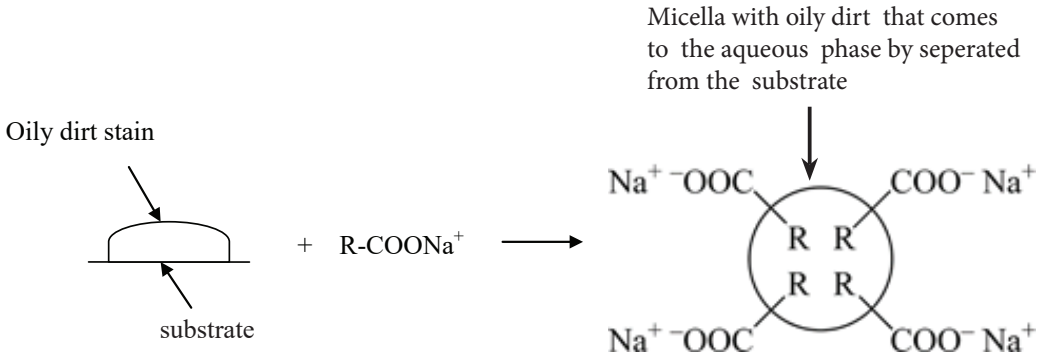


Figure 1.4 Cleaning action of soap

Since soap molecules form micella with oily droplets as shown above, dirt gets removed.

1.5 Production of Na_2CO_3 (Solvey process/ Ammonia – soda process)

Sodium carbonate is a raw material required for a number of chemical industries. Therefore Na_2CO_3 production is a major chemical industry in the world. Presently about 20 million metric tons of Na_2CO_3 are annually produced in the world.

The main chemical reactions involved in the production of Na_2CO_3 are given below.

$$NH_3 + H_2O \rightleftharpoons NH_4OH$$

$$NH_4OH + CO_2 \longrightarrow NH_4HCO_3$$

$$NaCl + NH_4HCO_3 \longrightarrow NaHCO_3 + NH_4Cl$$

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

NH_3 essential for the production of Na_2CO_3 is obtained by the Haber process. CO_2 is produced by the thermal decomposition of limestone. The other main raw material is purified concentrated NaCl solution by removing Ca^{2+}, Mg^{2+} and SO_4^{2-} ions. This is refered to as brine.

$$CaCO_3 \xrightleftharpoons{\Delta} CaO + CO_2$$

The basic steps of the process occur in specially setup towers for the production of Na_2CO_3, can be briefly stated as follows.

Step 1 – Ammonification

First the brine solution is introduced from the top of the tower and ammonia gas is introduced from the bottom of the tower. Mixing reactants efficiently by sending the reactants in opposite directions is referred to as the countercurrent principle. Ammonification of brine is an exothermic process. Hence, if the temperature of brine increases, efficiency of dissolving ammonia decreases. It is important to maintain a low temperature in the tower by removing the heat in the tower through heat exchange.

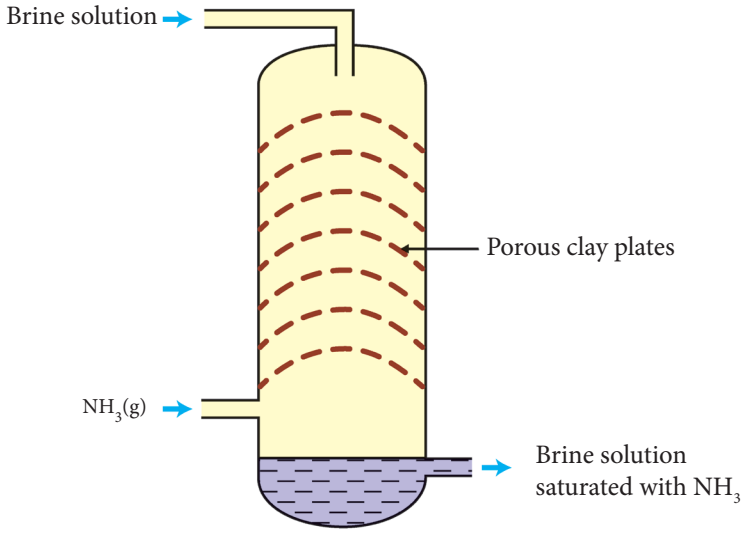


Figure 1.5 Ammonification tower

Step 2 – Carbonation

The brine solution saturated with ammonia is introduced from the top of the second tower while CO_2 is introduced from the bottom. Here, the reactants efficiently mix under the counter current method. Ammonified brine is a basic medium. CO_2 is an acidic gas. Dissolving it in water is exothermic. Hence formation of NH_4HCO_3 by reacting aqueous CO_2 with NH_4OH is also exothermic. For this also keeping the second tower cool is very important.

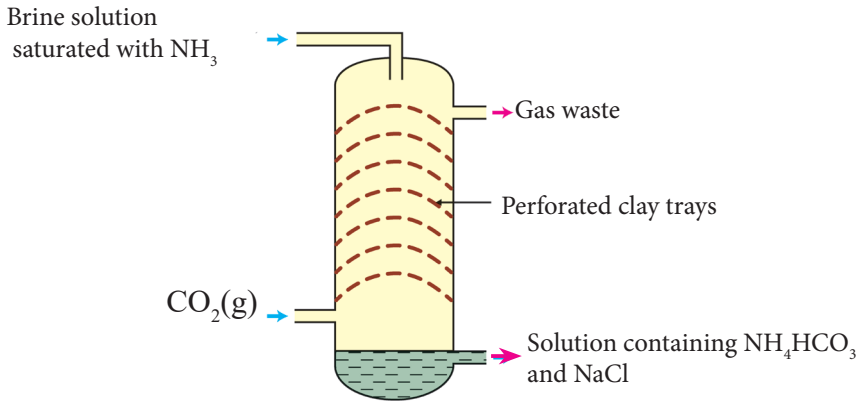


Figure 1.6 Carbonation tower

NH_3 is readily soluble in water but the solubility of CO_2 gas in water is relatively low. The concentration of HCO^-_3 ions formed by the dissolution of carbon dioxide in water is also very low. As ammonification proceedes carbonation, CO_2 gas is absorbed well into the basic $NH_3(aq)$ solution. This produces a high concentration of HCO^-_3 ions.

Step 3 – Seperation of $NaHCO_3$

As ammonification brine solution is carbonated, the concentration of NH_4HCO_3, in the solution is increased. Since this brine has a high concentration of Na^+ ions, $NaHCO_3$ Crystallizes and separates out from the solution when the concentrations of Na^+ and HCO^-_3 ions exceed the saturation limit of $NaHCO_3$. The overall reaction can be indicated as,

$$Na^+(aq) + HCO_3^-(aq) \longrightarrow NaHCO_3(s)$$

The solid $NaHCO_3$ that forms is removed from the solution.

The overall reaction of forming $NaHCO_3$ can be written as follows.

Accordingly the raw materials essential for the production of $NaHCO_3$ in theoritical point through Solvey process are NH_3, CO_2, NaCl and H_2O.

$$NH_3(g) + CO_2(g) + NaCl(aq) + H_2O(l) \longrightarrow NaHCO_3(s) + NH_4Cl(aq)$$

Step 4 – Obtaining Na_2CO_3 by heating $NaHCO_3$

Anhydrous Na_2CO_3 is obtained by heating $NaHCO_3$ which is separated. CO_2 gas formed is sent back to the carbonation tower.

$$2NaHCO_3(s) \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

NH_4Cl which is a by-product of this process is used to regenerate NH_3 as follows. For this NH_4Cl solution is reacted with CaO oxide obtained by the decomposition of limestone.

$$CaO(s) + 2NH_4Cl(aq) \longrightarrow 2NH_3(g) + CaCl_2(aq) + H_2O(l)$$

NH_3 formed is passed to the ammonifying tower. Accordingly the overall theroitical reaction for the entire process is as follows. However by mixing solid $CaCO_3$ and aqueous NaCl, Na_2CO_3 cannot be prepared.

$$CaCO_3(s) + 2NaCl(aq) \longrightarrow CaCl_2(aq) + Na_2CO_3(s)$$

The final by-product of this process is $CaCl_2$. It can also be used for other industries.

Due to following reasons Solvey process is economical profitable.

1) NaCl and $CaCO_3$ can be obtained easily and with low cost.
2) NH_3 is not consumed and can be used again and again by re-cycling.
3) A part of CO_2 can be re-used.

Solubility of $KHCO_3$ is higher than the solubility of $NaHCO_3$. So $KHCO_3$ is not precipitated in the tower. Therefore above method cannot be used to make $KHCO_3$.

Uses of Na_2CO_3

1) Removal of hardness of water
2) Addition to improve cleaning action when producing soap and detergents.
3) Using as washing soda
4) Mixing to the wood pulp in paper industry
5) Production of glass

1.6 Production of ammonia (Haber-Bosch process)

In modern context, manufacture of ammonia is mainly needed for the production of artificial fertilizers. At present the world population is nearly 7.3 billion and it has been estimated that it will increase to about 9 billion by 2050. With the increasing of the population, production of food is a necessity. Production of fertilizer is considered as an important field of chemical manufacture in this regard.

Of the total ammonia production 83% is used to produce fertilizer. Specially 80% of the total ammonia production is used to manufacture urea.
The chemical reaction related to the production of ammonia is given below.

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) + \text{heat}$$
$$1 \quad : \quad 3 \qquad\qquad 2$$

Raw materials required to produce ammonia

N_2 gas and H_2 gas are the main raw materials. N_2 gas is separated by fractional distillation of liquefied atmospheric air. Therefore N_2 gas has a production cost.

Hydrogen gas is obtained by cracking hydrocarbons (naphtha) or using methane, which is the main component of natural gas.

Extra knowledge

Natural gas is used as a fossil fuel to generate power. Natural gas occurs in large quantities as underground ores in the Earth. Production of H_2 from natural gas is known as Steam-Methane-Reforming (SMR). A small quantities of H_2S is present in natural gas; H_2S disturbs Nickel catalytic process. Furthermore H_2 is formed by a catalytic reaction after removing H_2S in the natural gas.

The reaction related with removals of H_2S

$$H_2S\,(g) + ZnO\,(s) \rightleftharpoons ZnS\,(s) + H_2O\,(g)$$

The first step of the SMR process is reacting methane and water vapour at 700 ^{0}C - 800 ^{0}C to produce CO and H_2. This is an endothermic reaction.

$$CH_4(g) + H_2O\,(g) \longrightarrow CO(g) + 3H_2\,(g) \quad +206\ kJ\ mol^{-1} \quad \text{-------} \quad (1)$$

During the second step this gaseous mixture is further reacted with water vapour. Here, CO is converted to CO_2. This is an exothermic reaction.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad -41\ kJ\ mol^{-1} \quad \text{-------} \quad (2)$$

In addition to this, there is a possibility for the following reaction to occur.

$$CH_4(g) + 2H_2O(g) \longrightarrow 4H_2(g) + CO_2(g) \quad \text{-------} \quad (3)$$

The yield of H_2 can be increased by maintaining more water vapuour and shifting the total reaction to the right.

To have some understanding of the thermodynamic nature of the SMR, the relationship $\Delta G = \Delta H - T\Delta S$ can be used.

According to the above thermodynamic relationship the exothermic second reaction is spontaneous even at low temperature. Since the number of gaseous molecules does not change, pressure has no effect. Further the effect of $T\Delta S$ on ΔG is almost nil.

First and third endothermic reactions occur relatively at higher temperatures. The entropy increases because the number of gaseous molecules increases to the forward

direction. So, with increase in temperature, the positive value of TΔS increases. Therefore according to ΔG = ΔH - TΔS, in reactions 1 and 3 ΔG becomes more negative at higher temperatures. Reaction 1 is alllowed to occur at a high temperature (1000 – 1800 °C). There even reaction 3 may occur. In order to reduce the CO concentration and increase the yield of H_2, the second reaction is allowed to occur at relatively at low temperatures (200 – 400 ^{0}C). By adding water vapour to the hot gaseous mixture of CO and H_2 its temperature can be lowered (200 – 400 ^{0}C). As the second reaction is exothermic, the heat generated by the second reaction is used to obtain the higher temperature suitable for the first reaction.

In United States, about 60% of natural gas production is used for the production of ammonia gas. Hydrogen gas can also be obtained by cracking naphtha (C_6H_{14}). It also release CO_2 to the atmosphere. The relevant reactions that occur are as follows.

$$C_6H_{14}(g) + 6H_2O(g) \longrightarrow 6CO(g) + 13H_2(g)$$

$$CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g)$$

Production of NH_3 from hydrogen and nitrogen gases is an exothermic reaction and it is reversible. But, under normal temperature and pressure this reaction hardly happens. The reason is the activation energy is relatively high.

Producing NH_3 by H_2 and N_2

Industrially, ammonia is manufacture by the Haber-Bosh process. The optimum industrial conditions employed for the process are a temperature in the range 450-500 ^{0}C, a pressure of 250-300 atm, iron catalyst and K_2O and Al_2O_3 as catalystic promoters.

$$N_2(g) + 3H_2(g) \underset{450 - 500\ °C}{\overset{250 - 300\ atm}{\rightleftharpoons}} 2NH_3(g) + heat$$

The compressed mixture of reactant gases pass over the surface of the catalyst and gets converted to NH_3. Since the reaction is reversible the gaseous mixture passing the catalyst surface contains unreacted $H_2$and N_2 gas in addition to NH_3. Therefore NH_3 gas should be seperated from this mixture. When the mixture is cooled upto - 33.34 ^{0}C, NH_3 gas liquefies. The boiling points of nitrogen and hydrogen gases are – 195.8 ^{0}C and – 252.9 ^{0}C respectively. So by cooling this mixture only ammonia can be liquefied and the mixture of H_2 and N_2 can be separated from the reaction mixture. The gaseous mixture containing H_2, N_2 and NH_3 under high pressure can be cooled by decreasing the pressure suddenly in another chamber. Then NH_3 liquefies. Remaining H_2 and N_2 gases are then pumped back into the reaction chamber. Equal amounts of H_2 and N_2 that have been used to make NH_3 are then freshly added.

This process can be depicted by Figure 1.7 in a simplified way.

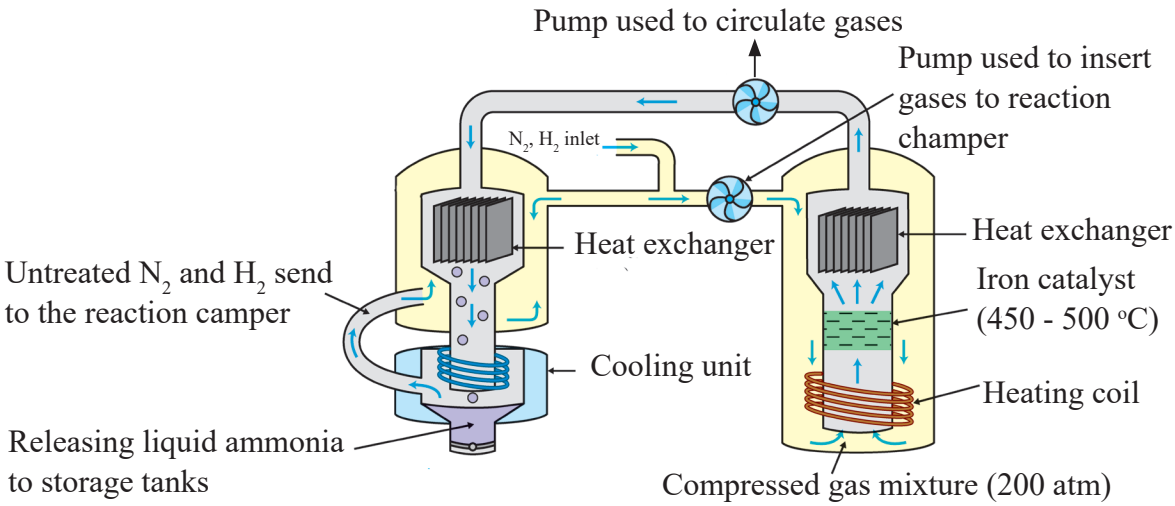


Figure 1.7 Process of ammonia production

After the removal of liquid ammonia, the gaseous mixture containing unreacted and newly added N_2 and H_2 gases (under a temperature of around -33.34 ^{0}C) is heated to 450 – 500 ^{0}C. The heat energy required to have this temperature can be supplied by the combustion of fuel also. This releases CO_2 to the atmosphere. In the Haber process CO_2 is produced at the step in which hydrogen is produced and also during the burning of fuel to gain high temperature. Due to the overall process, CO_2 which is a green house gas releases to atmosphere. Globally, when 1 tonne of ammonia is produced by overall process, about 2.9 tonnes of CO_2 is released to the atmosphere. Compared to the releasing of CO_2 to atmosphere by other processes, approximately 1.4% of it, is by ammonia production.

In ammonia production N_2 and H_2 are mixed according to their stoichiometric ratio (1:3). Since some cost has to be borne to produce nitrogen gas and hydrogen gas they are not mixed beyond their stoichiometric ratio and this prevents wastage of raw materials. Further if one gas is used in excess it would be adsorbed by the surface of the catalyst covering the surface completely. Coverage of catalyst surface by one gas reduces the chances for the reaction to occur. Both the gases need to be absorbed to the catalyst surface. Use of the catalyst decreases the time to reach the equilibrium. Based on all the factors, N_2 and H_2 gases are mixed in the optimal ratio of 1:3.

The reaction is exothermic, so it's ΔH is negative. When the reaction proceeds, entropy decreases because the number of molecules decreases. Hence ΔS of the reaction is negative. Thus $T\Delta S$ is negative and $-T\Delta S$ is positive. Therefore with the increase in temperature ΔG changes from negative to positive. The fact that high temperatures do not favour the forward reaction can also be explained by Le Chatelier's principle.

On increasing the temperature the spontaneous nature of the reaction decreases. Thermodynamically, when the spontaneity decreases, the yield decreases. To increase the yield, the temperature should be decreased. But when the temperature is decreased the rate of the reaction decreases and the efficiency of the entire process declines. A temperature of 450-500 ^{0}C is used to maintain an optimum efficiency. The NH_3 yield obtained under these conditions is relatively low. Yet, the production process has been designed so that the unreacted H_2 and N_2 gases are brought into the catalytic cycles again and again. Despite the fact that the amount of NH_3 yield by a single step is small, the process as a whole gains a high yield because it has been designed to carry out via number of catalytic cycles. According to Le Chatelier's principle, higher pressures favour the forward reaction. But the maintenance cost of the plants withstanding high pressures is high. Therefore at present, a pressure of 250-300 atm is used. Maintenance of reactant concentration at a high level and product concentration at a low level results in a higher yield of NH_3. This can be explained by the Le Chatelier's Principle. This requirement is fulfilled by introducing N_2 and H_2 into the reaction chamber from time and removal of NH_3 by cooling the gaseous mixture containing NH_3 and liquefying the gas.

Uses of ammonia

1. Production of nitric acid, fertilizers and nylon
2. Petroleum industry utilizes ammonia in neutralizing the acid constituents of crude oil
3. Used in water and waste water treatment, such as pH control, in solution form to regenerate weak anion exchange resins
4. Used as a refrigerant
5. Used in the rubber industry for the stabilization of natural and synthetic latex to prevent premature coagulation

1.7 Production of nitric acid (Ostwald method)

For this, ammonia gas, atmospheric air and water are used as raw materials. Nitrogen dioxide gas obtained by the reaction between ammonia and oxygen gas is reacted with water to produce nitric acid. The reaction involved are;

$$4NH_3(g) + 5O_2(g) \xrightarrow{\Delta} 4NO(g) + 6H_2O(l) \quad (-907 \text{ kJ mol}^{-1})$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g) \quad (-114 \text{ kJ mol}^{-1})$$

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

$$4NO_2(g) + 2H_2O(g) + O_2(g) \longrightarrow 4HNO_3(aq)$$

Figure 1.8 simply illustrates this process.

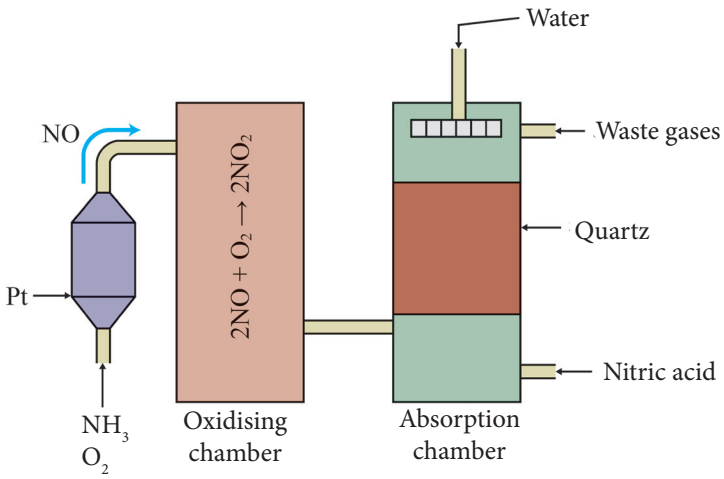


Figure 1.8 Production of nitric acid

In the first chamber ammonia is oxidized in the presence of the catalyst. In the second chamber nitrogen monoxide gas (nitric oxide) is oxidized. Nitrogen dioxide gas is reacted with water in the third chamber.

Ammonia is oxidized using atmospheric air from which dust and water vapour have been removed. Ordinary air contains 78% nitrogen gas and 21% oxygen gas by volume. A volume of atmospheric air which contains the required amount of oxygen is pumped into the reaction chamber. For a unit volume of ammonia, 9-12 units of atmospheric air by volume are required. A high temperature range (800-850 ^{0}C) is maintained. Under these conditions around 97% of NO gas can be obtained. If the ammonia concentration is high explosions may occur. Therefore maintaining the volumes of ammonia and atmospheric air in the correct proportion is important. When this gas mixture is passed through the Pt/Rh catalyst under pressure it is converted to NO gas. This NO gas is cooled to 150^{0}C. When the temperature is 150 ^{0}C, further oxidation of NO to NO_2 occurs in the oxidation chamber. In the absorption chamber NO_2 gas is allowed to react with water conforming to the counter-current principle. The gaseous mixture containing oxygen and NO_2 is pumped into the absorption chamber under a pressure of 5-10 atm. As the absorption chamber is packed with chemically inactive substances greater chance is offered for the reaction between water and NO_2. Finally a yield of around 96% is obtained.

Uses of nitric acid

1. Making fertilizer and explosives
2. Making nitrates essential for industries

   KNO_3 – to produce gun power

   $AgNO_3$ – photography

3. Making aqua regia
4. Cleaning surfaces when welding metals

1.8 Production of sulfuric acid (Contact process)

Raw materials required to produce sulphuric acid

Sulphur or ores containing shlphur and water are used in this manufacture. When extracting the metals Pb, Cu and Zn from ores containing PbS, CuS and ZnS, sulphur dioxide is obtained as a by – product. This can also be used to produce H_2SO_4. Shlphur obtained as a by – product during petroleum refining or sulphur extracted from earth can also be used for this.

In the production of sulphuric acid, sulphur dioxide is made by burning sulphur or metal sulphides. Second step is the preparing of sulphur trioxide by reacting sulphur dioxide with atmospheric oxygen. Sulphuric acid is obtained by hydrolyzing pyrosulphuric acid ($H_2S_2O_7$, oleum) made by reacting sulphur trioxide with concentrated sulphuric acid.

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

$$2SO_2(g) + O_2(g) \underset{V_2O_5(s)\text{ catalyst}}{\overset{1\text{ atm, }450\ ^0C}{\rightleftharpoons}} 2SO_3(g) + \text{heat}$$

$$SO_3(g) + H_2SO_4(aq) \longrightarrow H_2S_2O_7(aq)$$

$$H_2S_2O_7(aq) + H_2O(l) \longrightarrow 2H_2SO_4(aq)$$

Production of sulphur dioxide by burning elemental sulphur is a separate process. In the school laboratory sulpher dioxide can easily be prepared by burning a piece of sulphur with the bunsen burner. But production of sulphur dioxide industrially is not that easy. First sulphur is heated to 140 ^{0}C and melted. Liquid sulphur is filtered to remove various solid impurities in it.

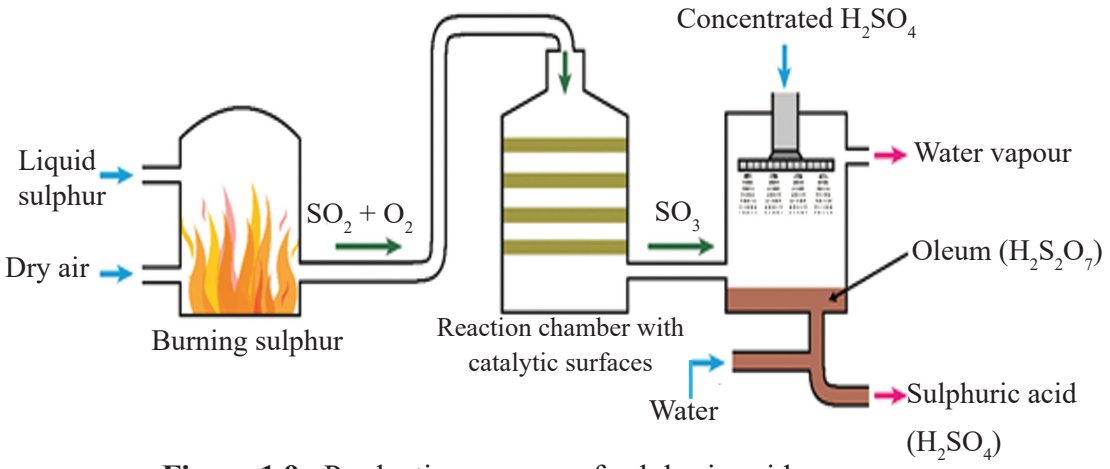
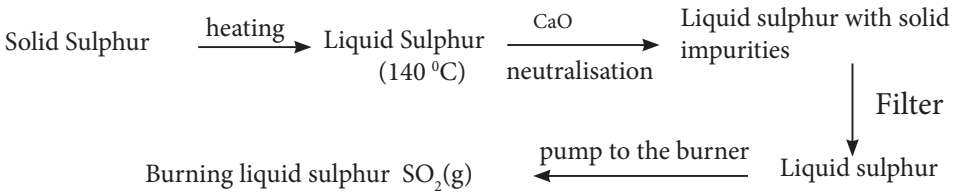


Figure 1.9 Production process of sulphuric acid



Liquid sulphur and atmospheric air should be pumped into the furnace. Liquid sulphur is pumped in the form of very small droplets which burn easily. Combution of sulphur is exothermic. In the gaseous mixture obtained after burning, the composition of sulphur dioxide is maintained between 8-9%.

The temperature around the burner is about 830 ^{0}C. In the gasous mixture of sulphur dioxide, oxygen and nitrogen in the combusion chamber, various solid particles (ash) may be present. Removal of them is crucial because the particles of dust and ash setting on the surface of V_2O_5 catalyst retards the catalytic action. Therefore, first the gaseous mixture containing SO_2 is purified. The reaction producing sulphur trioxide is reversible and exothermic. The molar ratio (or ratio by volume) between oxygen and sulphur dioxide is maintained at 1:1.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + \text{heat}$$

For efficient progression of the reaction, an optimum temperature of 400 – 500 ^{0}C is maintained. The reaction itself generates heat. Thus, if the production plan was designed to react the whole amount of SO_2 with O_2 at once, a huge amount of heat would be liberated. This favours the backward reaction and reduces the yield. Hence the entire amount of SO_2 is converted to SO_3 in four steps. In every step the gaseous mixture is passed through the catalyst bed.

In order to increase the SO_3 yield by shifting the above reversible reaction to the right, oxygen concentration can be increased by supplying atmospheric air. As atmospheric air is a cheap raw material, this does not increase the production cost. According to the stoichiometry the ratio of SO_2: O_2 is 2:1. The amount of oxygen required for one mole of SO_2, is 0.5. But during the production the molar ratio maintained as 1:1. So 0.5 moles of O_2 is in excess for 1 mole of SO_2. Though atmospheric air is cheap, maintaining a higher oxygen concentration above the required concentration, decreases the efficiency of the process. This is because of higher the oxygen concentration, more O_2 molecules get adsorbed to the catalyst surface. This reduces the capacity of the catalyst to adsorb SO_2 molecules there by decreasing the probability for the reaction to occur.

This reaction is exothermic. Therefore increase in the yield on cooling can be predicted from Le Chaterier's Principle. But the decrease in the rate of the reaction at low temperatures brings down the efficiency of the production process. Hence, it has been decided that the optimum temperature is 400-450 ^{0}C.

Le Chaterier's Principle predicts that with increasing pressure the reversible reaction tends to move in favour of the direction in which the number of molecules in the gas phase decreases. In this reaction, increase in pressure favours the forward reaction increasing the productivity of SO_3. But in this particular reaction the yield is as higher as 99% even under 1 atm pressure. Therefore applying high pressures is unnecessary.

As this reaction is highly exothermic the production process is conducted in four steps managing heat exchange. This is illustrated in the following flow chart (Figure 1.10)

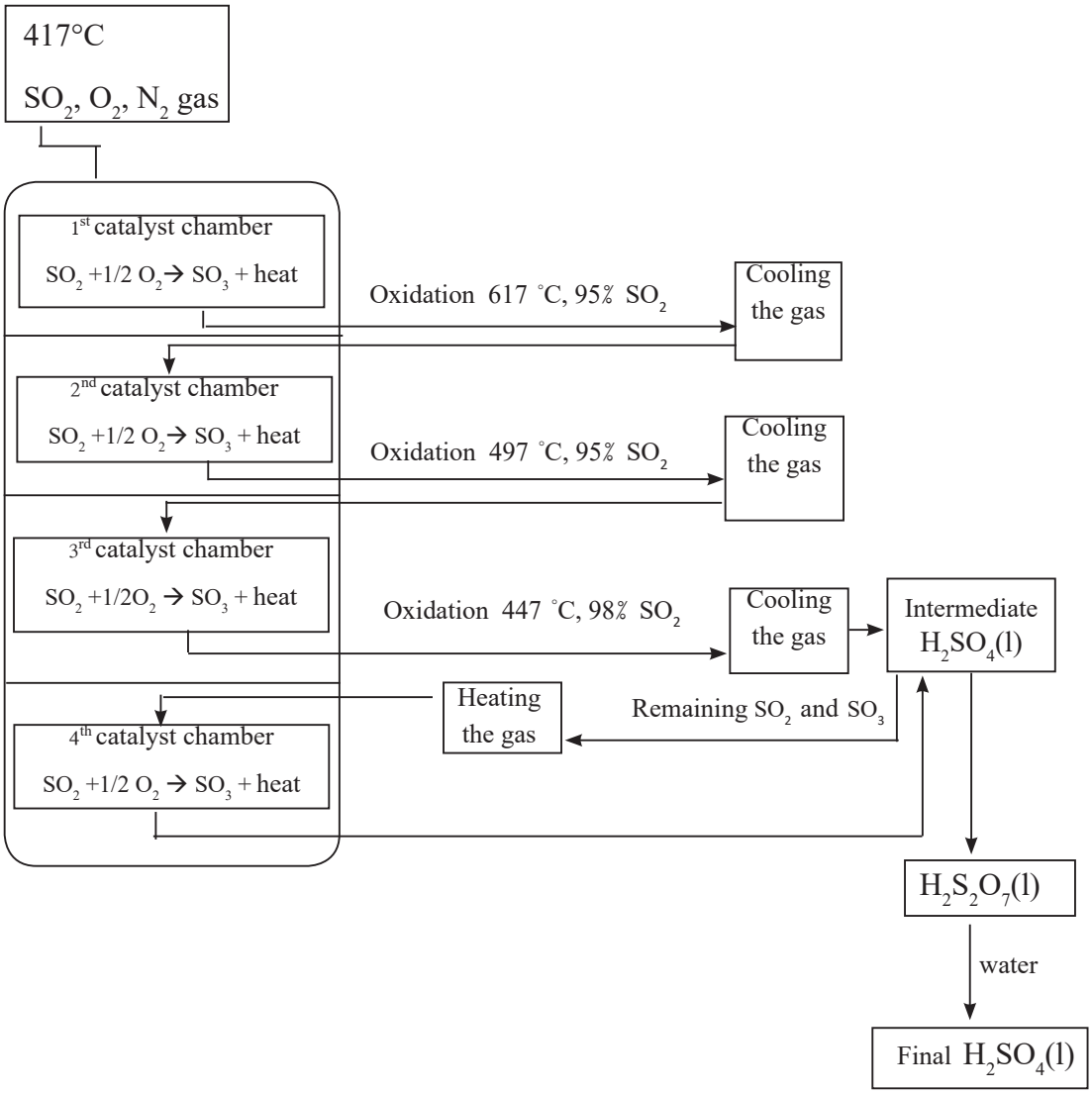


Figure 1.10 Main heat exchange steps in the production of sulfuric acid

The temperature of the gases entering the first chamber is around 690 K (417 ^{0}C). When passing through the catalyst, the temperature rises to 890 K (617 ^{0}C) and about 70% of SO_2 gets oxidized. The gases cooled to about 700 K (427 ^{0}C) is passed through the second bed of catalyst. At this stage the amount of SO_2 present is relatively low. For this reason the amount of SO_3 formed is less than that formed in the first step and the amount of heat generated is also relatively low. The second heat exchanger cools the gaseous mixture whose temperature has risen to 770 K (497 ^{0}C) to 720 K (447 ^{0}C). By that time, a considerable amount of SO_2 from its initial amount has reacted. After passing through catalyst bed in the third chamber 98% of SO_2 of its initial amount turns into SO_3.

Sulphuric acid is made by the SO_3 obtained from the third step. Here also, 100% of SO_3 is not converted to H_2SO_4. The gaseous mixture containing the remaining SO_3 and the SO_2 left due to reversibility is heated again and passed through the catalyst in the fourth chamber which converts it to SO_3. This SO_3 is also converted to H_2SO_4 again.

The reaction between SO_3 and water is violent and highly exothermic. Therefore water vaporizes and a mist of sulphuric acid fumes is made. To avoid this SO_3 gas is converted to H_2SO_4 via the steps described above. The absorption of SO_3 is maximum in concentrated (98%) sulphuric acid at 70 ^{0}C. Therefore under those conditions SO_3 is absorbed into concentrated sulphuric acid and H_2SO_4 is made by adding water to it.

Sulphur trioxide and concentrated sulphuric acid are reacted according to the counter current principle. This happens in absorption towers which are packed with ceramic materials. Because of the packing, sulphuric acid slowly trickles down the chamber from top to bottom and the surface area of liquid H_2SO_4 is increased. Sulphur trioxide moves up the chamber. Increased surface area of the acid coupled with its slow flow and the upward movement of SO_3 gas make the absorption efficient. Here, SO_3 reacts with H_2SO_4 giving oleum ($H_2S_2O_7$). Concentrated sulphuric acid is made by adding water to oleum carefully.

Uses of sulphuric acid

1. Production of phosphate fertilizers
2. Production of ammonium sulphate fertilizer
3. Production of artificial fibers including rayon and plastics
4. Production of detergents containing alkyl and aryl sulphonates
5. Production of dyes, explosives and medicines
6. Production of battery acid
7. Drying gases (e.g. Cl_2)

1.9 Production of titanium dioxide from rutile

Ilmenite and rutile are main minerals which contain titanium. The mineral in which titanium is present in abundance in the form of TiO_2 is rutile. Ilmenite is a mixture of the two oxides TiO_2 and FeO. When producing TiO_2 using Ilmenite, first FeO in it is removed. This increases its TiO_2 percentage. Removal of FeO from ilmenite is called sulphate process.

High purity TiO_2 is produced from ilmenite in which the percentage of TiO_2 is brought above 70% by removing FeO. High purity TiO_2 can be produced starting from ilmenite purified until its TiO_2 percentage is above 70% or by using rutile. The production process is referred to as the chloride process.

Chemistry of the production of titanium dioxide from rutile (Chloride process)

The aim of this process is to remove various inorganic impurities in rutile and produce high purity TiO_2. It comprises two steps.

1. Chlorination
2. Oxidation

Chlorination

Drying to remove moisture in rutile and coke is indispensable. For this they are dried well by heating to 200-300 ^{0}C.

For chlorination the mixture of rutile and coke is heated to about 950 ^{0}C and stream of chlorine is passed over it. In the presence of coke, titanium dioxide reacts with chlorine giving titanium tetrachloride gas as the product. This reaction is exothermic. The main reason for this is the oxidation of coke giving carbon dioxide. The relevant reactions are,

$$TiO_2(s) + C(s) \longrightarrow Ti(s) + CO_2(g)$$

$$Ti(s) + 2Cl_2(g) \longrightarrow TiCl_4(g)$$

The overall reaction is

$$TiO_2(s) + C(s) + 2Cl_2(g) \xrightarrow{950\,^0C} TiCl_4(g) + CO_2(g)$$

The boiling point of $TiCl_4$ is 134 ^{0}C. Therefore the exit gas mixture coming out from the reaction chamber mainly contained $TiCl_4$ and CO_2. In addition dust particles and as

a result of side reactions hydrogen chloride and carbon monoxide gases may also occur. Here inorganic impurities present in TiO_2 are removed. After the removal of dust particles liquid $TiCl_4$ is separated by cooling the gaseous mixture. After further purification of separated liquid $TiCl_4$, it is oxidized.

Oxidation

Here, $TiCl_4$ produced in the first step is reacted with oxygen and TiO_2 is regenerated. This process is important for producing pure TiO_2 free of inorganic impurities present in rutile. Resulting chlorine gas is used again for chlorination. Therefore chlorine gas is re-cycled.

$$TiCl_4(g) + O_2(g) \xrightarrow{1000\ ^0C} TiO_2(s) + 2Cl_2(g)$$

$$TiO_2(s) + C(s) + 2Cl_2(g) \longrightarrow TiCl_4(g) + CO_2(g)$$

$O_2(g)$ (1000 °C)

recycling

$Cl_2(g) + TiO_2(s)$

During this process coke is oxidized and carbon dioxide is added to the atmosphere. Hence chloride process contributes to global warming. In 2006, the total amount of CO_2 released to the atmosphere by this industry was 3.6 million metric tons. Half of this was due to the burning of fuel to raise the temperature and the other half was produced by the production process.

Uses of titanium dioxide

1. TiO_2 is white in colour. Therefore it is used as a pigment to obtain bright white colour in paint, plastic goods and paper. The high refractive index if TiO_2 is also a reason for using it as a pigment.
2. TiO_2 is chemically inert. Therefore it is used as a pigment to give white colour to medicine and toothpaste.
3. TiO_2 is also used to produce substances applied to prevent sunburns in the skin due to UV radiations in solar rays. TiO_2 prevents the reach of UV rays to the skin.
4. It is used to make some solar cells.

1.10 Extraction of iron

We have an ancient history of production of iron. Archeological studies have revealed that the ancestors of this country were aware of iron extraction thousands of years ago. They have extracted iron using natural wind power and wood charcoal. Gill Juleff, an archeologist of the university of Exeter, England has confirmed the technology of iron extraction prevailed in this country by recreating an old iron extraction furnace at the wind gap of Balangoda. Her findings have been published in the periodical 'nature' under the title 'An ancient wind-power iron smelting technology'.

Raw materials essential for iron extraction

- Iron ore
- Limestone
- Coke (coal)
- Air

The furnace used to extract iron using the above raw materials is called the 'blast furnace'. Inside of the blast furnace is lined by a special type of bricks withstanding higher temperatures. The mixture of iron ore, limestone and coke is fed into the blast furnace from the inlet at the top while air is introduced near the bottom. Molten iron is tapped out from the bottom end of the furnace. The slag is removed a little above the level at which molten iron is tapped off. In the blast furnace a mass flow occurs from the top to the bottom under gravity. Simultaneously compressed air passes from the bottom to the top. Since substances flow in opposite directions (from the bottom to the top and from the top to the bottom), possibility for the reactions to occur between the solid phase and the gas phase increases. This also creates a temperature gradient.

Some facts to which attention should be drawn in the process of iron production are given below.

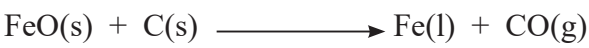
1. Ratio among the components of the mixture of ore, coke and limestone
2. Particle size
3. Rate at which the mixture is added to the blast furnace from the top
4. Rate of flow of the air current and its pressure

Here, the role of coke is as follows.

1. Acts as a fuel

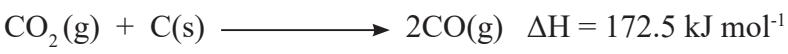
$$C(s) + O_2(g) \longrightarrow CO_2(g) + \text{heat} \qquad \Delta H = -393.5 \text{ kJ mol}^{-1}$$

2. Acts as a direct reducing agent at high temperatures.



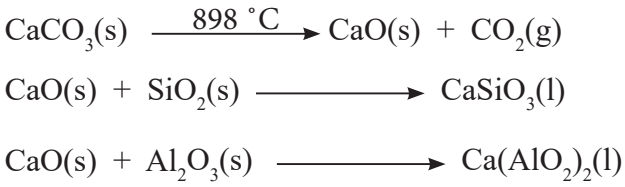
$$FeO(s) + C(s) \longrightarrow Fe(l) + CO(g)$$

3. Generates carbon monoxide which is the main reductant.



$$CO_2(g) + C(s) \longrightarrow 2CO(g) \quad \Delta H = 172.5 \text{ kJ mol}^{-1}$$

Deposition of silicates and aluminates in the ore, should be prevented as impurities in iron. Calcium oxide obtained from the thermal decomposing of calcium carbonate is useful in this regard.



$$CaCO_3(s) \xrightarrow{898\ ^\circ C} CaO(s) + CO_2(g)$$

$$CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(l)$$

$$CaO(s) + Al_2O_3(s) \longrightarrow Ca(AlO_2)_2(l)$$

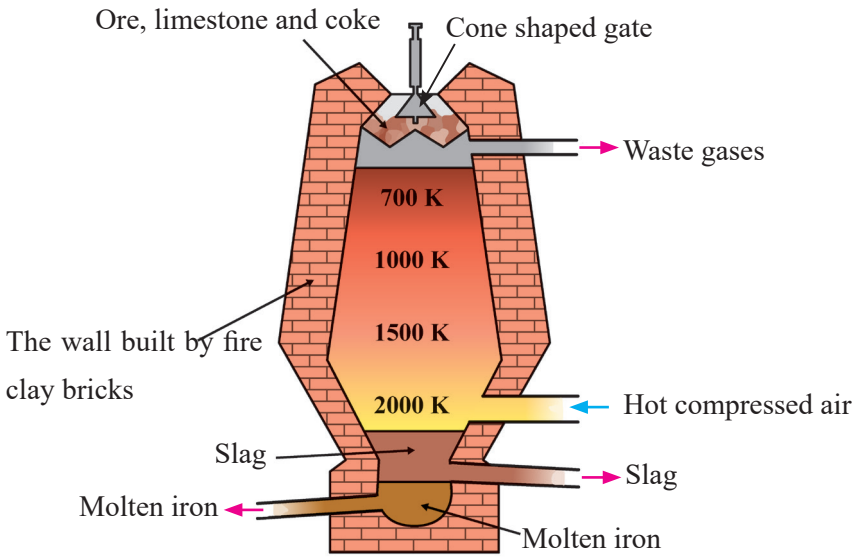


Figure 1.11 The blast furnace

Calcium silicate ($CaSiO_3$) and calcium aluminate ($Ca(AlO_2)_2$) formed are called the slag. The density of the slag is lower than that of molten iron. Therefore liquid slag layer floats on molten iron. As the slag covers the surface of molten iron, the chances for molten iron to react with oxygen are less.

From the lower part of the blast furnace hot, compressed air is injected into the furnace. Coke burns and with admission of air burning reaction is speeded up. The rate of the burning reaction is decided by the temperature of hot air, pressure and the size of coke particles.

As the combustion reaction is fast and the combustion of coke is highly exothermic large amount of heat is evolved in a short period of time. Therefore the temperature of the basal part of the furnace rises at once to about 1700 ^{0}C. The rate of the combustion reaction and the amount of coke burnt are important factors in maintaining the temperature of the basal part stable. It is important to mainain the rate of air flowing upward and the rate of mixture containing coke flowing down to maintain at optimum.

Hot carbon dioxide gas formed during combustion passes upwards through the ore. At high temperatures carbon dioxide reacts reversibly with coke forming carbon monoxide.

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g)$$

Number of gaseous molecules increases. Therefore entrophy increases.

ΔS is positive for this reaction (176.5 J). When the temperature increases, magnitude of the numerical value of $T\Delta S$ increases. At high temperatures and in the presence of coke (C), there is a tendency for reduction of carbon dioxide to carbon monoxide. Under such conditions CO gas is relatively stable thermodynamically. When the temperature is around 1000 ^{0}C nearly 100% of CO_2 is converted to CO. Figure 1.12 given below shows this variation.

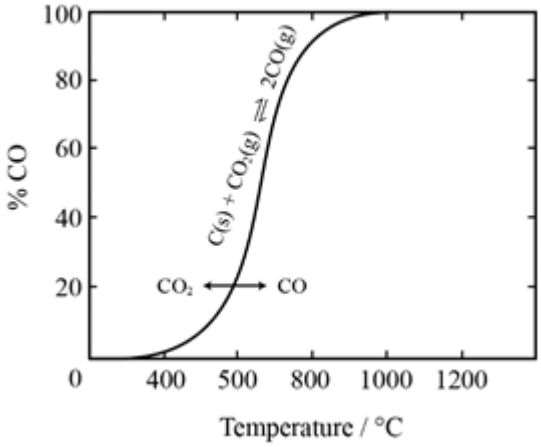


Figure 1.12 Variation of the amount of carbon monoxide against temperature

$$O_2(g) + C(s) \longrightarrow CO_2(g) + \text{heat} \text{ ---------- (1)}$$

Number of gaseous molecules does not change

No considerable change in entropy. Exothermic

$O_2(g) + 2C(s) \longrightarrow 2CO(g) + \text{heat}$ ---------- (2)

Number of gaseous molecules increases

$\longrightarrow$

Entropy increases. Exothermic

$\Delta G = \Delta H - T\Delta S$

Because both reactions are exothermic ΔH is negative. When the temperature increases reaction (2) has a conspicuous increase in the value of $T\Delta S$. With temperature a marked increase in the negative nature of ΔG is expected for reaction (2). When the temperature drops thermodynamic stability of CO decreases; thermodynamic stability of CO_2 increases.

Since the temperature of the bottom area is as high as 1700 ^{0}C, CO gas is formed liberating heat when CO_2 the gas interacts with red hot coke in the mixture.

When CO gas formed in the hot lower region of the furnace moves up through the mixture containing the ore, the stability of CO decreases because the temperature decreases. Hence the tendency of CO becoming CO_2 increases. As oxygen gas is not available in the region above at where coke is burnt in the furnace, CO oxidized to CO_2 by reducing Fe_2O_3. As a result of this Fe_2O_3 is gradually reduced. Going upward the furnace along with the decreasing temperature, so reduction of Fe_2O_3 in the ore continues. At temperatures below 1000 ^{0}C, reduction of Fe_2O_3 can be indicated stepwise as follows.

$$3Fe_2O_3(s) + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g)$$

Fe_3O_4 (ferrosoferric oxide) is a mixture of FeO and Fe_2O_3 .About 33% of the iron in +3 oxidation state in Fe_2O_3 has reduced to the +2 state.

$$2Fe_3O_4(s) + 2CO(g) \longrightarrow 6FeO(s) + 2CO_2(g)$$

$$\text{or } [Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g)]$$

$$FeO(s) + CO(g) \longrightarrow Fe(l) + CO_2(g)$$

Fe_2O_3 partially reduces to Fe_3O_4 and this mixture goes down the furnance. There, it further reacts with CO gas and its Fe atoms of +3 state reduce to +2 oxidation state. FeO, which is formed as its result, reacts further with CO gas and reduces up to free iron (Fe).

Further, decomposition of $CaCO_3$ occurs at a temperature below 1000 ^{0}C (i.e. 898 ^{0}C). Carbon dioxide gas generated by it also has the ability to react with coke to produce CO.

Even this produced CO, when going upward the furnace, by reacting with Fe_2O_3 in the ore, possible to become CO_2.

Above 1000 ^{0}C, that is somewhat in the lower part of the blast furnace following reactions occur. In this region coke directly reduces FeO.

$$2FeO(g) + C(s) \longrightarrow 2Fe(s) + CO_2(g)$$

$$CO_2(g) + C(s) \longrightarrow 2CO(g)$$

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g) \qquad \Delta H = -566 \text{ kJ}$$

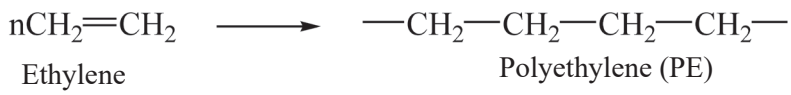
In the blast furnace a part of the total amount of coke participate for the combustion reaction. Another part reacts with CO_2 to produce CO. Another part reduces FeO. Air acting as an oxidant and generates heat and CO_2 by the combustion reaction. If excess air is supplied thermodynamically it is likely that in addition to the reaction with Fe_2O_3, carbon monoxide would react with oxygen to give carbon dioxide. This is a disadvantage. Therefore in the extraction of iron, it is very important to maintain the volumetric flow rate of air and the flow rate of the solid mixture containing the ore at an optimum level. In the lower part of the furnace the amount of O_2 decreases at once but, producing a proportionate amount of CO_2. For this reason there is a sudden increase in the concentration of CO_2 and production of intense heat. This CO_2 in the high temperature zone tends to move up through the solid mixture falling down. Therefore the reaction of CO_2 with the coke in the solid mixture occurs in the lower part of the furnace where the temperature is high. Because of this when the CO_2 concentration gradually decreases, CO concentration increases. Even CO generated in the lower region passes upwards through the solid mixture. Ascending the furnace the temperature decreases, so the thermodynamic stability of CO gas decreases while the tendency for the conversion to CO_2 increases. As O_2 is absent CO gas gets oxidized to CO_2 gas abstracting oxygen in Fe_2O_3. Therefore going upward the furnace, CO concentration decreases and CO_2 concentration increases again.

Because of the use of coke CO_2 is released from the furnace and this causes global warming. Thus, seeking renewable alternatives for coke is environmentally important. Avoiding unnecessary use of iron is also important.

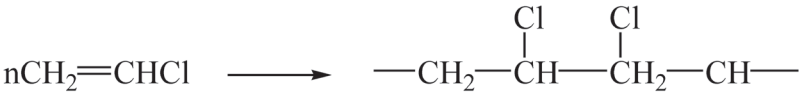
1.11 Polymers

Polymers are formed by the chemical bonding of a very large number of relatively small molecules referred to as monomers.

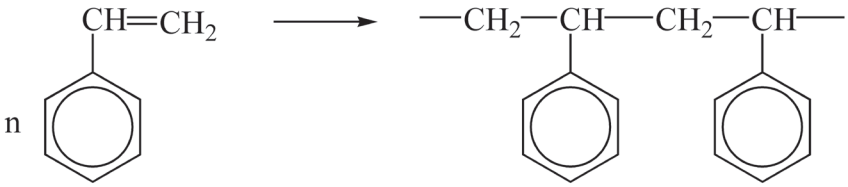
Examples :



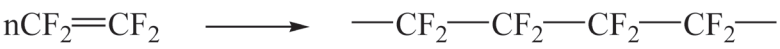
Ethylene — Polyethylene (PE)



Vynil chloride — Polyvynil chloride (PVC)



Styrene — Polystyrene (PS)



Tetrafluoro ethylene — Polytetrafluoro ethylene (PTFE)

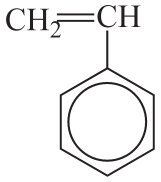
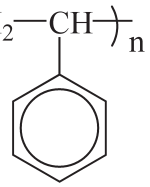
Due to the joining of a large number of monomers like this, the carbon skeleton of the monomer is repeatedly placed in the polymer. Therefore it is called the repeating unit.



Ethylene — Polyethylene (Polythene)

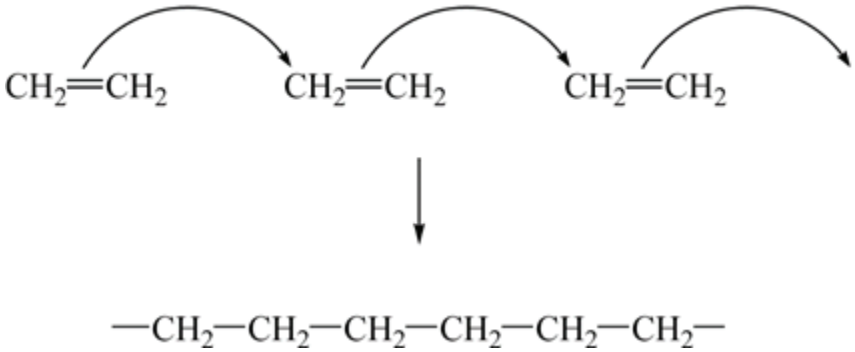
The repeating unit of polythene (polyethylene or polythene) is $–CH_2$- CH_2-. As there is a large number of repeating units in a polymer molecule. The polymer is symbolized by writing ‘n’. Some examples are given in Table 1.2.

Table 1.2 Repeating units of polymers formed by some monomers

Monomer	Polymer related to the repeating unit
$CH_2{=}CH_2$	$-\left(CH_2{-}CH_2\right)_n-$
$CH_2{=}CH(Cl)$	$-\left(CH_2{-}CH(Cl)\right)_n-$
	
$CF_2{=}CF_2$	$-\left(CF_2{-}CF_2\right)_n-$

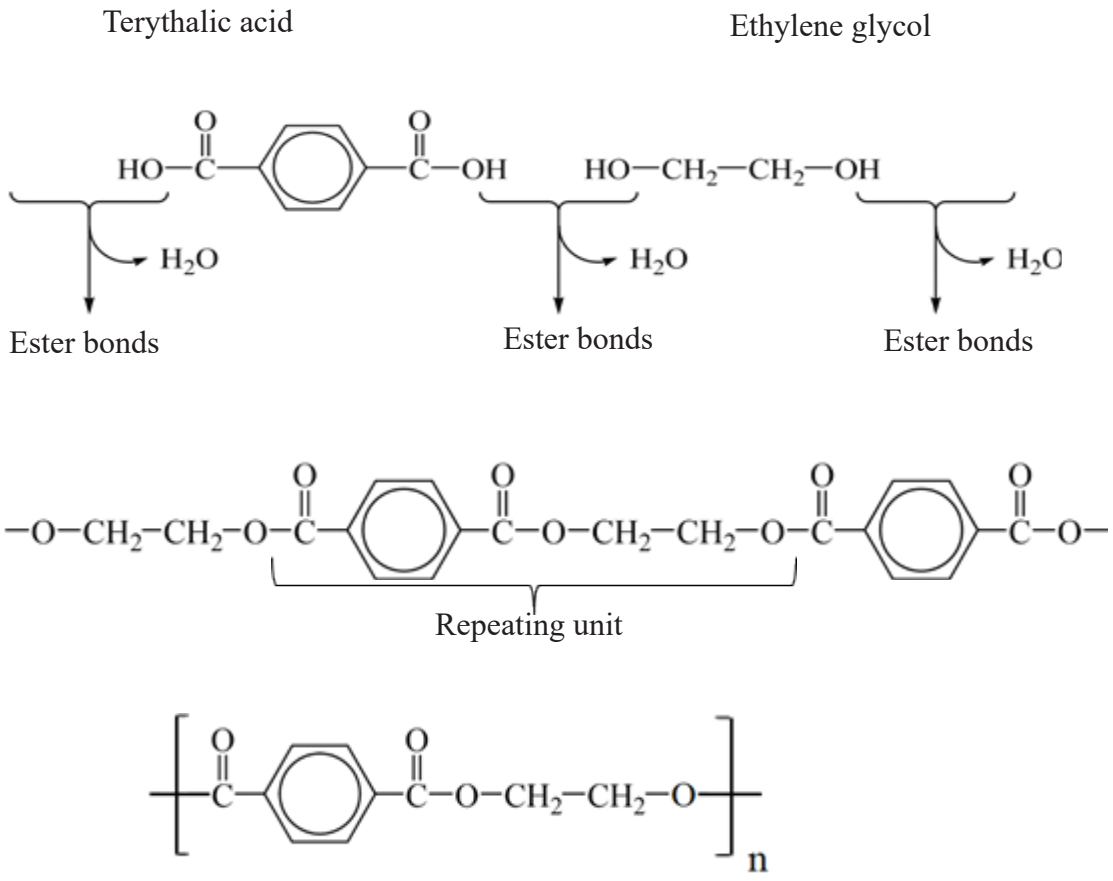
Production of polymers from monomers is called polymerization. According to the reaction occurring in polymerization polymers can be classified into two classes, addition polymers and condensation polymers.

If a polymer is formed by the bonding of monomers by an addition reaction, such a polymer is known as an addition polymer. The unsaturated bonds in the monomer are important in this regard. The molar mass of the monomer is equal to the molar mass of the repeating unit of the polymer. However the three dimensional structure and the hybridization state of the carbon atom of the monomer and the repeating unit change.



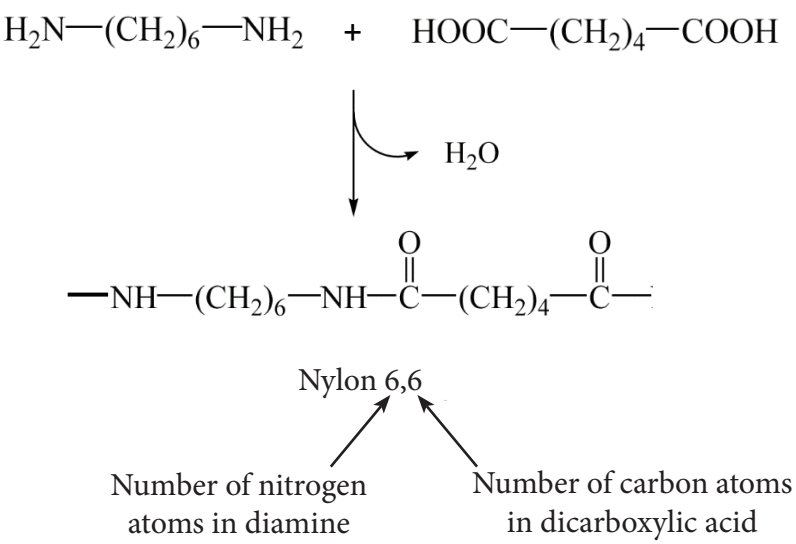
During the formation of condensation polymers a condensation reaction occurs. Therefore, in addition to the polymer, small molecules of low mass are produced. For example when an ester bond is formed by the reaction between a –COOH group and a –OH group. H_2O molecule is formed. Hence in the production of polyester a condensation reaction takes place. A number of water molecules equal to the number of ester bonds formed are

released. If the volume of water produced to be measured correctly, the number of ester bonds formed could be calculated using the density and molar mass of water.

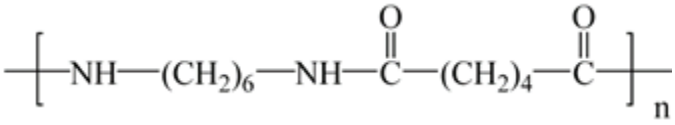


In terms of the repeating unit the structure of polyethylene terephthalate (PET) can be shown as above.

Polyamides are obtained by the polymerization reaction between a dicarboxylic acid and diamine. Nylon is such a polyamide. Production of nylon is also a condensation reaction.



The structure of nylon 6, 6 can be indicated as follows using the repeating unit. The first number here represents the number of carbon atoms of the diamine while the second number presents the number of carbon atoms in the dicaboxylic acid.



From the examples used thus to describe the structure of polymers, it is clear that the polymer molecule is created as a single chain. For this reason such polymers are referred to as 'linear polymers'.

Sometimes the polymers are formed as three dimensional networks. The reason for this is that the monomers have more than two reactive sites. If we consider phenol as an example, the number of sites in the benzene nucleus at which substitution can take place is three. A three dimensional network polymer is formed by the reaction between phenol and formaldehyde. The polymer is known as bakelite and the reaction is a condensation reaction.

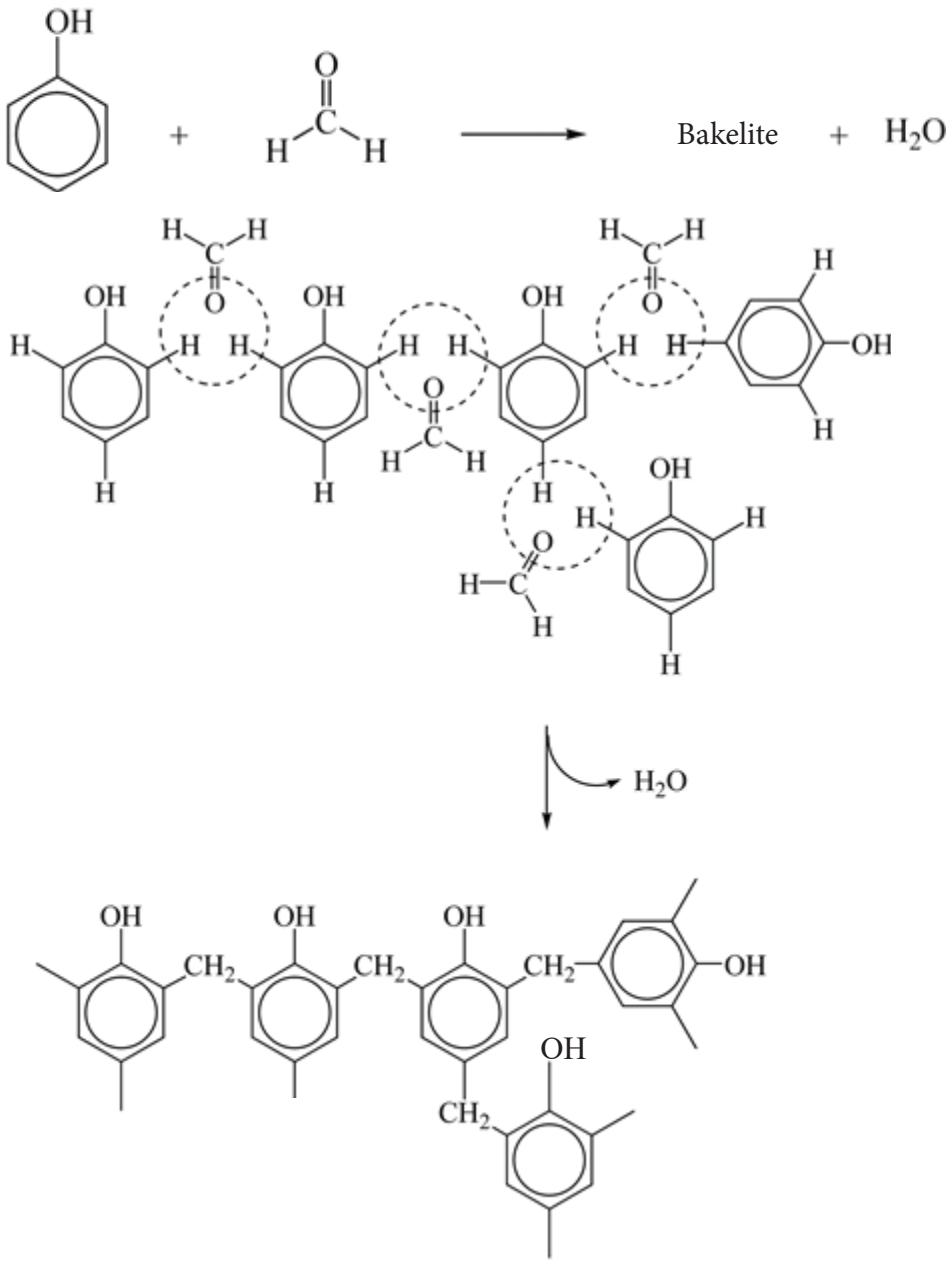


Figure 1.13 Formation of bakelite by the reaction between phenol and formaldehyde

In such instances a specific repeating unit cannot be identified.

According to the nature of the structure polymers can be classified as linear, branched and network. PS, PVC, PTFE and PET polymer molecules have a linear structure.

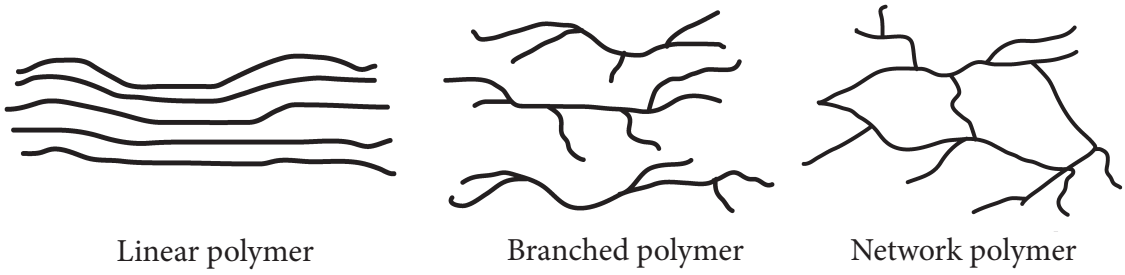


Figure 1.14 Structure of the polymers

Linear and branched polymers are packed in various ways as separate molecules. Sometimes in some regions the molecules are closely packed and orderly arranged. Such regions are called crystalline areas. In some other regions the molecules may be twisted and entwined with one another. Such regions are called amorphous regions. Some polymeric substances are totally amorphous. But some polymers have a certain amount of crystalline regions. Such substances are known as semicrystalline polymers. Polythene is an example for semicrystalline polymers. Light does not penetrate well through the membranes of semi crystalline polymers. Crystalline regions in them scatter light and reduce transparency. Light does not scatter through semicrystalline layers. Therefore they are transparent.

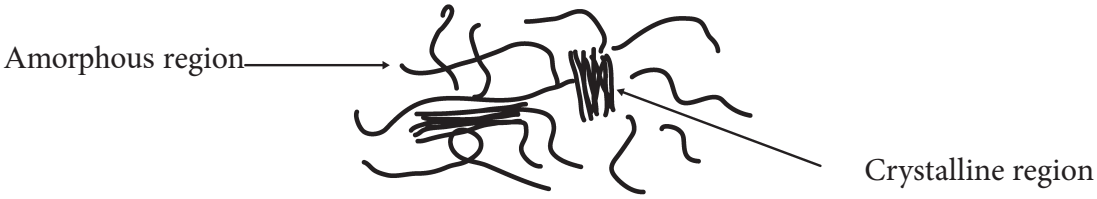


Figure 1.15 How linear and branched polymers are packed

Polyethene can be synthesized so that a branched structure is obtained. Linear polythene molecules pack closely with each other and have more high density areas. Such polyethelene are named High Density Polythene (HDPE).When branched the molecules do not pack that closely. Their density is low and have more amorphous regions. This type of polythene is referred to as Low Density Polythene (LDPE).

1.11.1 Rubber and plastic

Rubber is considered as the polymeric material which possess very high elastic properties reversibly. The elastic properties of rubber can be controlled. Starting from monomers, the polymer called rubber can be synthesized. Those are known as artificial rubber (e.g.: nitryl rubber). Highly elastic polymer can be obtained from the latex of the rubber tree too. Those are known as natural rubber (NR).

Polymers with limited elastic properties can be considered as plastics. For example; polymeric substances such as PVC, PET, PP and PE are considered as plastics. When stretched beyond the elastic limit its shape changes irreversibly. Plastic can be classified further as thermoset and thermoplastics. Thermoplastics are composed of linear polymer molecules or branched polymer molecules. Thermoset plastic have a molecular structure arranged as a network. Thermoplastic can be softened by heating. Therefore they can easily be moulded to the required shape by heating. The shape can be made permanent by cooling. PVC, PE, and PS are examples for this. Thermoset polymers cannot be softened like that. Phenol-formaldehyde (bakelite) is an example for this.

1.11.2 Natural rubber

Natural rubber (NR) is the substance with high elastic properties obtained by coagulating latex of the rubber tree (*Hevea braziliensis*). Rubber latex is collected by the systematic removal of the bark of the rubber tree. Rubber latex contains 60-65% water and 30-35% rubber. In rubber latex rubber occurs as a colloidal solution in which very small rubber particles are dispersed. Simple sugars and salts are also dissolved in this colloidal solution.

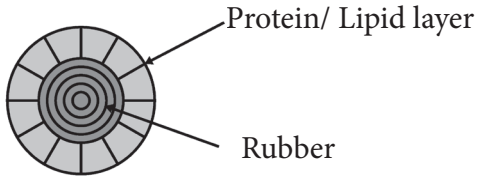


Figure 1.16 A rubber particle

There is a lipid and protein layer around a rubber particle. Inner to it lie rubber molecules. Since $-COO^-$ groups associate the outer layers of a rubber partical its outer surface is negatively charged. As electrostatic repulsion forces operate among these negatively charged particles, they are spreaded throughout the solution.

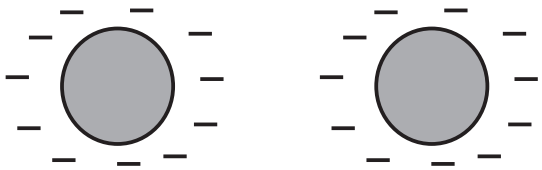


Figure 1.17 Location of negative charges on the outer surface of rubber particles

Because of the repulsive forces among the negatively charged surfaces, the particles do not combine together. In addition of acids H^+ ions neutralize the $-COO^-$ groups and the surface of the particles become electrically neutral. Then the particles combine together and settle down as a mass. This is known as 'coagulation of latex'.

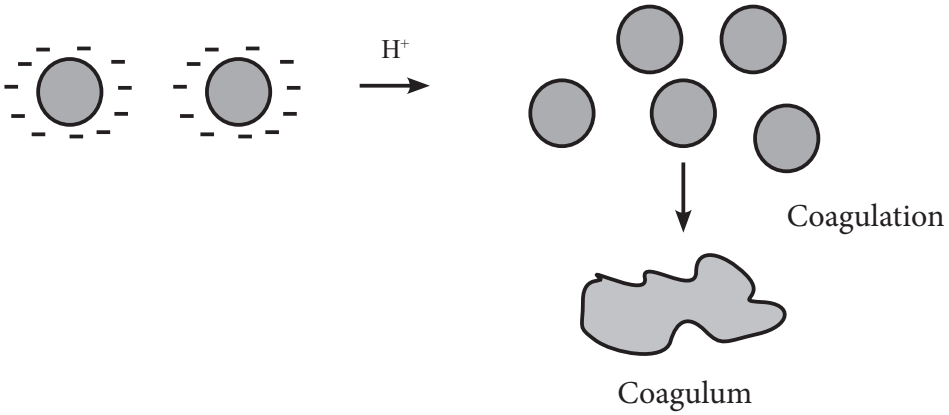
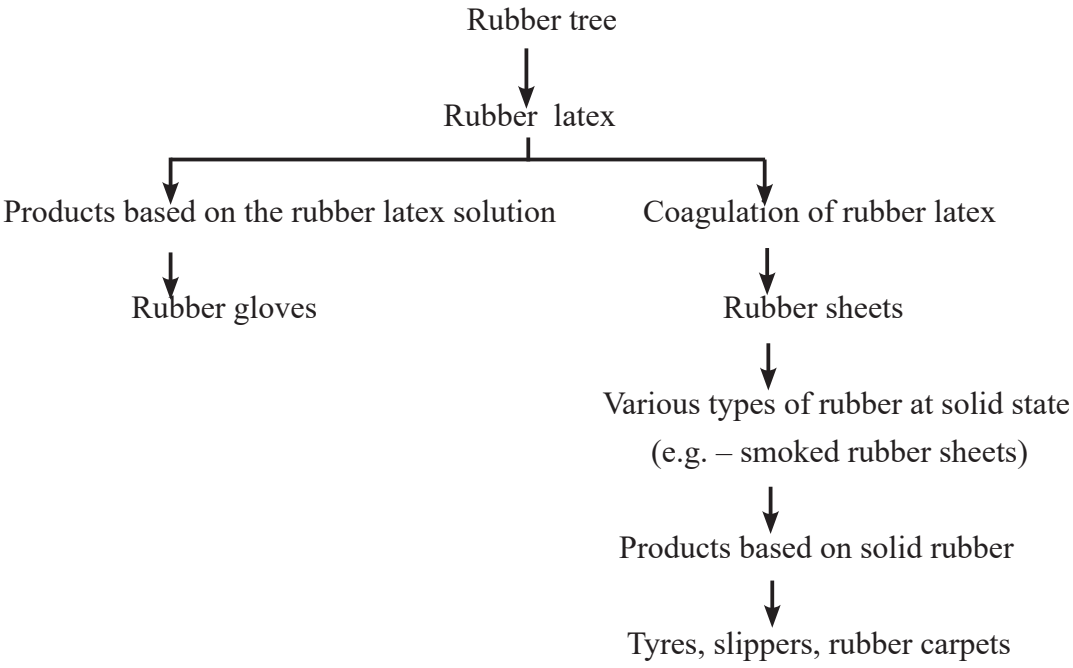
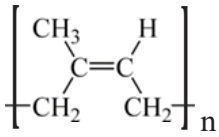


Figure 1.18 Coagulation of latex

Since the rubber latex contains salts, sugar, amino acids etc. It is a suitable medium for microbial action. Because of the acids released by the action of micro-organisms latex coagulates. Therefore, after the collection of rubber latex its coagulation can be prevented by stopping the microbial activity till it is subjected to the production process. The coagulation can be prevented by basifying the latex by adding an ammonia solution. Ammonia prevents the medium becomes acidic and stabilizes the negative charges around the rubber particles. Under these basic conditions the microbial action is suppressed.

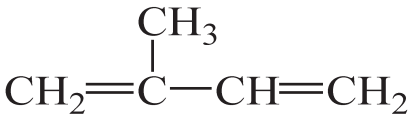


In the natural rubber molecule there are two $-CH_2$ groups and one $-CH_3$ groups joined to the doubly bonded carbon atoms in a repeating unit. It is named as cis-1,4 polyisoprene. Gutta percha has a trans structure. This natural polymer is known as trans-1,4-polyisoprene. It does not show elastic properties. There is a maximum distance between the adjacent two $-CH_2$ groups in the trans structure.



cis -1,4-polyisoprene

Polyisoprene can be made synthetically by polymerizing the monomer, isoprene. It belongs to the category of synthetic rubber. They are termed Isoprene Rubber (IR).



Isoprene

In synthetic rubber the monomer is isoprene but we can't say that it is the monomer of natural rubber. In the rubber tree rubber molecules are produced by very complex biochemical reactions.

1.11.3 Vulcanizing of natural rubber

Existence of cis-polyisoprene chains is the reason for the elasticity of natural rubber. But to change the elastic property of rubber as required industrially and strengthen it, it is heated with 1-3% sulphur. This is called vulcanization of rubber. During vulcanization cross links are formed among the poly isoprene chains by sulphur atoms which decrease its elastic property but increase the resilience or the ability to regain its original dimensions. Ebonite is obtained when rubber is heated with 25-35% sulphur by weight. Ebonite doesn't show elastic properties. This is due to the fact that activity associated with the double bonds in rubber molecules form large number of crosslinks with sulphur atoms. Rubber vulcanized with an optimal amount of sulphur is not sticky and possess an optimum elasticity and high mechanical qualities. Figure 1.19 illustrates how rubber molecules are crosslinked by sulphur atoms.

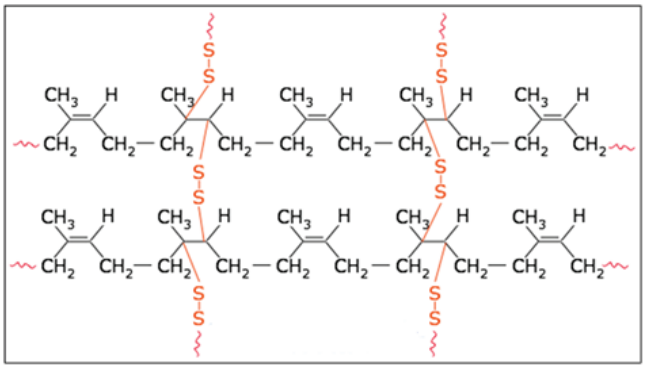


Figure 1.19 How sulphur crosslinks bind rubber molocules

1.11.4 Additives used for the polymer related products

The substances used to improve the qualities of the end product and reduce its production cost in the production of polymers are referred to as additives. Specially by using fillers, the volume required for the end product is obtained. In the production of tyres carbon black is used as the filler. Carbon back improves its physical and mechanical qualities. For example it reduces wear and increases strength. But release of these carbon black particles to the enviornment cause environmental problems. To make vulcanizing efficient various organic catalysts and catalyst promoters such as zinc oxide (ZnO) are used. Most of these organic catalysts are toxic. Various fillers are used for plastics as well. Calcium carbonate is one of them. In the production of plastics, compounds called 'plasticizers' are added to increase their flexibility. For example, PVC pipes used to supply water are hard and rigid but the outer covering of the domestic electric cables made of same material is flexible. This is because PVC of the latter is mixed with plasticizers. Therefore it gets flexibility. In addition to these, additives are added to reduce inflammability and prevent the damage caused by ultraviolet rays. Additives are added in small amounts. Most of the additives added to plastics are phthalates. It has been discovered that many additives distrupt the action of the endocrine systems. Hence much attention should be paid when plastics are used as packaging materials in food storage. Production of plastic goods using PVC is a process where additives are simply used. The reason for this is that in PVC, chlorine atoms are bonded to secondary carbon atoms. Various additives are used to prevent the breaking of C-Cl bonds easily. Because of the temperature used in the production process or when those goods are exposed to ultraviolet rays HCl (hydrogen chloride) gets removed from PVC molecules.

1.12 Chemical products related to plant sources

1.12.1 production of vinegar

Acetic acid is the active ingredients in vinegar. When toddy is subject to continued microbial activity it is oxidized to acetic acid. During this, the amount of acetic acid increases to about 48%. The vinegar so prepared is called natural vinegar. Artificial vinegar is produced by diluting appropriately, the acetic acid obtained by the oxidation of ethanol produced from raw materials turned out by petroleum industry. Natural vinegar contains salts, simple sugars, esters and alcohols in minute quantities.

1.12.2 Production of ethanol

Ethanol is used as a solvent for perfumes and scents. It is also used a medium for chemical reactions. The use of ethanol as an environmental-friendly renewable fuel is on increase. Ethanol produced from biomasses by microbial activity is referred to as bioethanol.

Industrially ethanol is produced by hydration of ethylene or fermentation of sugar or starch in the presence of yeast. Alcohol contained in alcoholic beverages is generated by various plant sources.

E.g. Grapes - vine
Barley - Beer

Various cereals, fruit juices, molasses which is a by-product of the sugar industry etc. are used to produce alcohol industrially. As yeast cannot live in a concentrated solution of ethanol, the percentage of ethanol in fermented solution is around 12%.

Products with higher alcohol content are produced by distilling the aqueous solution obtained by fermentation.

E.g. Brandy (about 40%) - by distilling vine
Arrack (about 40%) - by distilling coconut toddy

The maximum concentration of ethanol obtainable by the fractional distillation of aqueous ethanol is 96.5%. This is called rectified spirit.

As regards the current use of narcotics and drugs in the world medical specialists state that arrack is one of the most dangerous alcoholic beverage. Let's see what is arrack available in the market. Its main constitutent is ethanol. In the world today there are many methods to produce ethnol. In Sri Lanka too ethanol is produced by some of them. Legally ethanol is produced from fermented coconut toddy and molasses which is a by-product in the production of sugar form sugar cane.

Coconut toddy is produced by fermentation of sweet toddy, a sugar solution obtained by tapping the tender inflorescence of the coconut tree. The spores of yeast floating in air get deposited in the sweet toddy. During fermentation these grow in the solution using sugar as a substrate. The enzymes produced by the yeast cells gradually convert sugar into ethanol and carbon dioxide.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11} + H_2O} \xrightarrow{\text{sucrase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

(monosacaride sugars)

$$C_6H_{12}O_6 \xrightarrow{\text{yeast}} \underset{\text{ethanol}}{2C_2H_5OH} + 2CO_2$$

Within a period of about two days sweet toddy turns into fermented toddy and during this process the sugar concentration gradually decreases.

If fermented toddy is left to stay further, bacteria oxidize alcohol in the toddy converting it to acetic acid. Therefore the alcohol percentage decreases and the acid percentage increases.

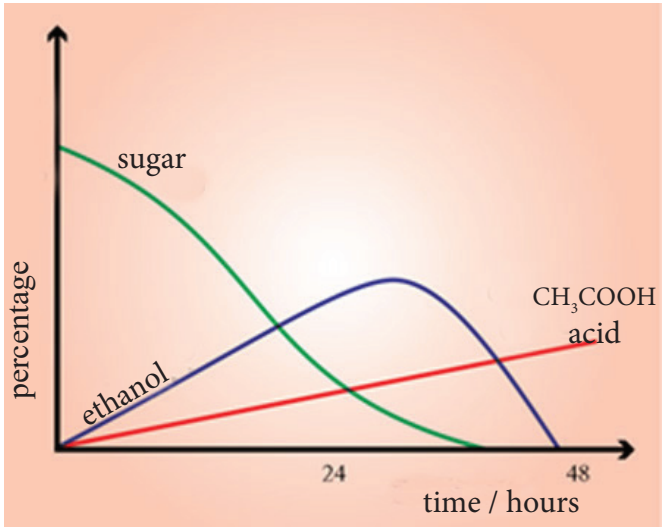


Figure 1.20 Variation of the composition of sweet toddy during fermentation

Fractional distillation

The distillation technique used to separate components which are miscible and have different boiling points from a mixture of them is called fractional distillation.

Table 1.3 Boiling point of some components

Compound	Melting point/ °C
methanol	64.6
ethanol	785
propan -1-ol	971
propan -2-ol	824
butanal	747
butanone	795
ethyl ethanoate	772

Except from coconut toddy ethanol is produced from other plant materials also containing starch Beet, potato, fruits, rice are examples. During the fermentation of these plant sources compounds like esters, aldehydes and ketones are also produced. These too add on to the aqueous mixture. If their boiling points fall within the boiling range of ethanol, they also vaporize with ethanol and pass into the distillate containing ethanol.

In this process the first distillate mainly contains methanol. This is toxic and is used as vine spirit. The second fraction of the distillation mainly contains ethanol. The third fraction obtained at higher temperatures contains higher alcohols and it is called ‘fusel oil’.

1.12.3 Essential oils

Water - insoluble volatile liquids extracted from plant materials are known as essential oils. Various essential oils have a characteristic smell of their own. They add fragrance to food and increases appetite. Essential oils are also used to make perfumes. In the commercial field of the world today, there is a huge demand for perfumes and flavours. History says that even the kings in the past used fragrances.

Essential oils are obtained from plants such as cinnamon, clove, citronella, cardamom, wintergreen. In plants there are special body parts which contain essential oils.

Table 1.4 Examples for plant parts containing essential oils.

Part that contain essential oil	Example
Root	Cinnamon, Khus-Khus (Savandara)
Stem	Sandle wood
Bark	Cinnamon
Leaf	Citroriella, lemon grass, eucaliptus, cinnamon
Bud	Clove
Flower	Jasmine, rose
Fruit	Orange, lemon
Seed	Cardomom, nutmeg

Methods of extracting essential oils

1. Steam distillation
2. Solvent extraction
3. Pressing

Stem distillation

Many essential oils are likely to decompose or polymerize under the influence of heat. Therefore heating them to high temperatures is not suitable. So, they are subjected to steam distillation and extracted under low temperatures. This phenomenon can be explained by the law of partial pressures. When the systems containing water and plant parts with essential oils are heated, those tissues are damaged and essential oils liberate. The gaseous phase of the system contains water vapour and volatile compounds. At the temperature at which the system boils the sum of the pressures exerted by water vapour and the essential oil vapour is equal to the outer atmospheric pressure. Hence at that temperature if,

Partial pressure of water vapour (saturated vapour pressure) = P_{H2O}
Partial pressure of essential oil (saturated vapour pressure) = P_A
Total pressure of the immiscible system = P
According to Dalton law of partial pressures $P = P_{H2O} + P_A$

When the total pressure (P) becomes equal to the atmospheric pressure, the mixture boils. The boiling point of this mixture is lower than the boiling point of pure water and the boiling point of the essential oil. Therefore essential oil can be distilled at a temperature below 100 ^{0}C and the boiling point of the essential oil.

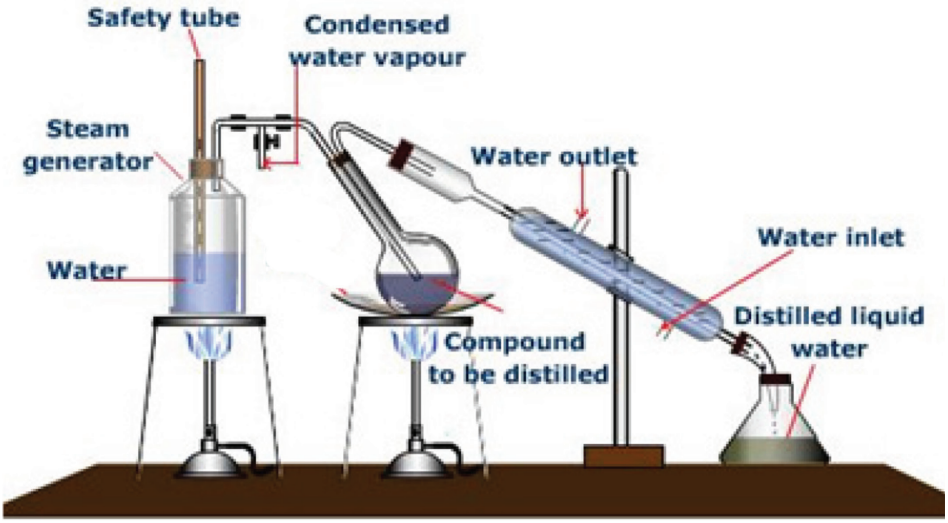


Figure 1.21 Extraction of essential oil in the laboratory by steam distillation

Steam produced by the steam generator is passed into the vessel which has plant material containing the essential oil. As steam is sent separately or from a steam generator its volumetric flow can be controlled. It is an advantage. When steam enters into the vessel containing plant parts, as plant cells destroy due to the heat of the steam, volatile compounds release. While vapour is condensed, certain amount of water vapour is accumulated in it. Water vapour and essential oil vapour exsist above the liquid water by the continuous flow of water vapour. Then the essential oil in the plant material comes into the vapour phase along with water. However, as water vapour flows continuously, the vapour coming out of the vessel contains essential oil vapour as well as water vapour. When the vapour is passed through a condenser and cooled, the distillate is obtained as two layers of water and essential oil. It can be separated easily.

Example: Main components of cinnamon oil which is obtained by the steam distillation of various parts of the cinnamon tree.

Leaf – eugenol

Bark – cinnamaldehyde

Root – camphor

Main constitution of citronella oil – geraniol

Solvent extraction

The principle of this is the dissolving of the essential oil in a solvent in which it is more soluble. The solubility of essential oils in water is very low. Nevertheless they are very soluble in organic solvents (e.g. petroleum ether, chloroform, toluene, ethanol). Plant materials are shaken with such a solvent majority of the essential oils pass into the solvent. The solvent is removed by vaporizations or by some other means thereby separating the essential oil.

Pressing

By applying a suitable pressure on plant materials, the volatile oils in them could be obtained. If pressing is done with another adsorbent, the essential oil is adsorbed into it. For example when a plant material is pressed between two glass slides coated with wax, essential oil in it is adsorbed into wax. Essential oil can then be extracted form wax using another solvent (ether) . Pressing method is rarely used because;

1. The yield is poor
2. Oil gets mixed up with other organic substances

In the extraction of oil from cardamom seeds, pressing method is also used.

Extraction of cinnamon oil is mainly done in areas like Ambalangoda, Hikkaduwa and Baddegama. First Cinnamon leaves are dried in air for 2-3 days in a shady place. Extraction of oil is easier from dried leaves than from fresh leaves. During distillation, essential oil can easily be removed when cuticles of the leaves are broken. It has been found that leaves of the middle age are most suitable than the tender or more mature leaves for oil extraction.

Earlier copper boilers were used for distillation but copper reacts with eugenol in the oil giving a dark colour to the oil. Therefore at present stainless steel or aluminum is used instead of copper.

Generally citronella is grown in Hamabantota district. There are 3 main varieties of citronella.

1. Heen pengiri (*Cymbopogon nadus*)
2. Maha pengiri (*Cumbopogon winterianus*)
3. Lenabatu pengiri

Of these the first two types are endemic to Sri Lanka. *Cymbopogon winterianus* has been introduced by Philippine. The value of citronella oil depends on the occurrence of the compound geraniol. Gereniol is an unsaturated, aliphatic alcohol. *Cymbopogon winterianus* has a greater demand because it's gereniol content is high.

1.12.4 Biodiesel

With the production of engines which can use petroleum fuels efficiently, a rapid development in the field of transport occurred. In modern civilization, the main source of power is petroleum fuel. Easy usage and ability to use safely are their special features. Therefore extraction of petroleum widened rapidly.

Petroleum fuel is a non-renewable source of energy. Therefore in the near future all the petroleum resources in the world will be exhausted. Moreover, in the burning of petroleum fuels carbon occurred as fossils is converted to carbon dioxide. It increases the amount of carbon dioxide in the atmosphere and engenders severe environmental problems such as global warming. For this reason attention is being drawn towards the production of energy using renewable resources. Biodiesel is such a renewable fuel.

Biodiesel is produced from non-volatile plant oils. Plant oil is a renewable resource. Therefore combustion of them does not cause increase in the carbon dioxide content in the atmosphere.

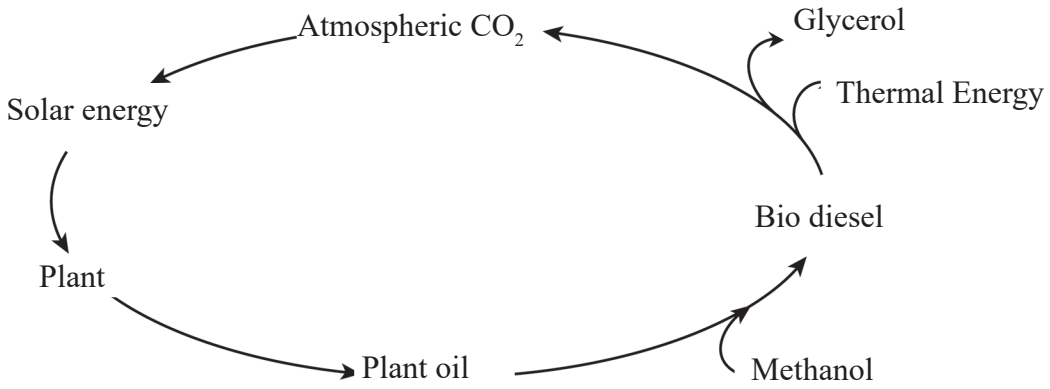


Figure 1.22 Production of biodiesel

Methanol is essential to produce biodiesel. Methanol is obtained from the products of the petroleum industry. Therefore when biodiesel is obtained using methanol is not a biodiesel product produced from 100% renewable resources. Hence attention is being focused on the production of methanol using carbohydrates and other biomasses employing micro-organisms. Methanol so produced is called bio-methanol. Biodiesel produced using bio-methanol is biodiesel 100% based on renewable raw materials.

Biodiesel is produced form the triglycerides present in plant oils. The reaction that converts the fatty acid of these triglycerides into methyl ester (FAME – Fatty acid methyl ester) is refered to as a transesterification reaction. Here, one ester is converted to another ester. A sodium hydroxide solution is used as the catalyst. Biodiesel and glycerol formed

are immiscible and separate out into two layers. The main by-product of this production is glycerol. Hence biodiesel is a mixture of several methyl esters of fatty acids. Biodiesel that has low density floats on the glycerol layer.

If plant oils contain free fatty acid of the type RCOOH they may react with sodium hydroxide to give soap (RCOONa). If soap is formed, foam is also formed which inhibits the catalytic action. Thus in plant oils used for this purpose free fatty acid content should be less than 2% (w/w) and the acid value should be 0.1 mg (KOH) g^{-1}.

Production of biodiesel involves several steps.

Step 1 - Treating the plant oil taken as the raw material

Step 2 - Preparation of the catalyst mixture

Step 3 - Reacting triglycerides with methanol

Step 4 - Separating the products

Step 5 - Further purification of crude biodiesel

Step 1

Free fatty acids and non- saponifiable compounds in the plant oils are removed. This enables to have high yield by the transesterification reaction and maintain a high level of purity of the biodiesel obtained.

Step 2

Sodium hydroxide catalyst is dissolved in methanol. Afterwards the solution is mixed with triglycerides (plant oil). It is very important that the alcohol does not contain water. The amount of methanol used is also very important. Although the methanol - tryglyceride ratio is 1 : 3, methanol is added in little excess. As the reaction is reversible this makes the reaction more efficient. However methanol is not added in large excess because removal of methanol from biodiesel is difficult. In addition to sodium hydroxide compounds such as potassium hydroxide and sodium methoxide ($NaOCH_3$) are used as homogenous catalysts. Compounds like magnesium oxide and zinc oxide can be used as heterogeneous catalysts.

Step 3

Since the alcohol and plant oil are immiscible, they are mixed with continuous stirring while the temperature is maintained between 50-60 ^{0}C.

The trans esterification reaction occurring here produces biodiesel and glycerol.

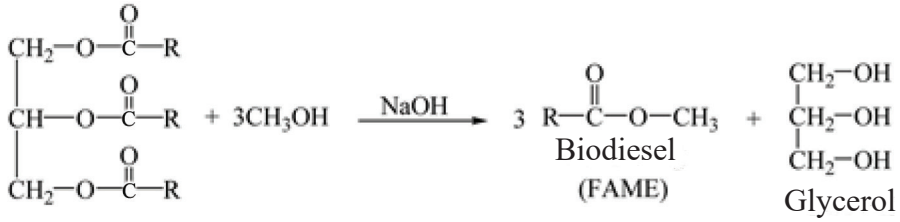
Step 4

The main products exist as two phases because they do not mix. The upper layer consists of biodiesel, unreacted triglycerides and diglycerides, and glycerol and methanol in small amounts. Lower layer contains glycerol with excess methanol and the catalyst. After the separation of the phases these layers are separated.

Step 5

When the biodiesel phase is washed with water glycerol, methanol and the catalysts dissolved in it can be removed. Finally it is possible to remove water.

Remaining methanol may occur in both the layers of biodiesel and glycerol as an impurity. By separating and heating the layers, methanol contained in them can be removed. This methanol can be re-used. Water is bubbled through biodiesel to purify it by removing sodium hydroxide and glycerol which are present in it as impurities. Then, water (moisture) sticking to biodiesel is removed.



In order to prepare a sample of biodiesel, a solution prepared by dissolving 0.75 g of sodium hydroxide in 26 g of methanol and 250 g of soya oil can be used.

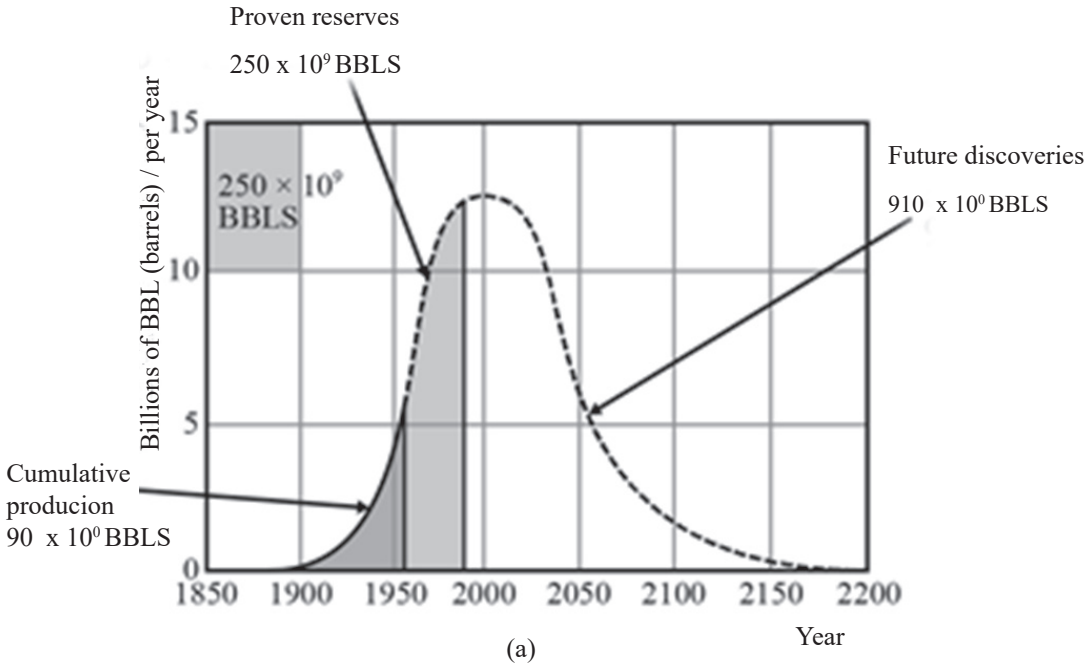
Petroleum fuel is a non-renewable source of energy. Petroleum which is a limited natural resource is not uniformity distributed throughout the world geographically. Therefore crude oil has become a very strong and crucial factor in international relations and international politics.As crude oil is used to produce petroleum fuel and the organic compounds obtained from the by-products are used to produce medicine and monomers required to make plastics and artificial rubber, petroleum industry has become the motive force of the modern human civilization. With the combustion of petroleum fuels obtained from the underground crude oil, the carbon dioxide content in the atmosphere rises. Increasing the global warming due to this is a booming threat for the modern human civilization.

Extra knowledge

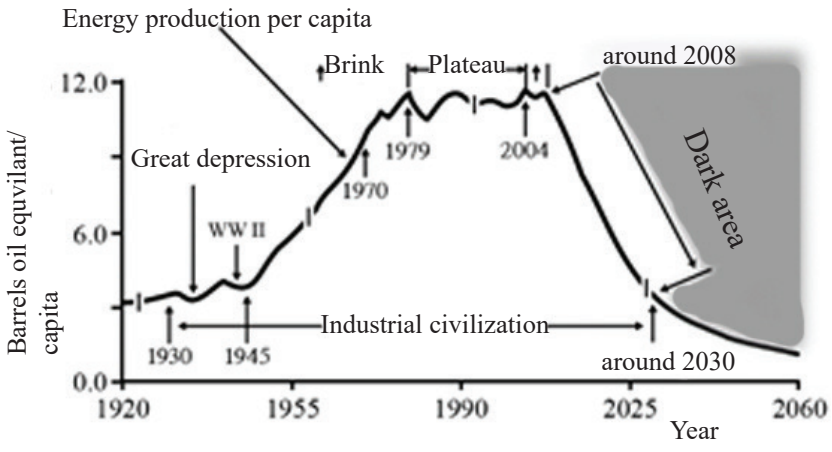
Dr. M.K. Hubbert is a geophysicist who described the nature of exhaustion of petroleum, a non renewable resource as against the pattern of human consumption. According to the theory put forward by him (Hubbert peak theory), in a geographical area concerned, the rate of production of petroleum oil varies with time according to a bell-shaped pattern. With the increase in the demand for petroleum with the increasing population and fuel consumption, crude oil production (number of barrels of crude oil production per year) has to be increased. Yet, as the amount of crude oil in the oil wells is limited, there comes a state beyond which the rate of production cannot be increased further. Hence, the amount of barrels of crude oil produced per year comes to a maximum. Meanwhile, the rate of production cannot be maintained at a high constant level because the crude oil resources become more and more limited in

spite of the demand. So, the number of barrels that can be produced yearly gradually decreases causing a decline in the production rate. In 1965, Hubbert, showed that by 1965-70 the amount of barrels of crude oil produced by United States of America reaches a peak. The validity of this prognosis was confirmed when we went past 1970. As per this theory the global production of crude oil reaches the maximum by 2000. Afterwards the yearly production of crude oil would decrease.

Despite the rate of production of crude oil after 1995 was somewhat different from the pattern predicted this theory, today we are basically passing the zone of consumption. Specially, global political factors, alternative sources of power and invention of high efficiency energies etc. have changed this rate of depletion a little. Figure 1.23 (a) depicts the curve suggested by Hubbert with regard to the production of crude oil.



(a)



(b)

Figure 1.23 Alternative sources of power and fuel efficiency

Presented in Figure 1.23 (b) is a graph based on the Oldvai theory on the spread of annual power production. In this theory, on the production of power in 1930 and prospective production 100 years afterwards (i.e. in 2030) are almost equal. For this reason attention has been focused on the global scale on the production of power using renewable raw materials and synthesizing various organic compounds using them.

1.13 Chemistry of air pollution caused by industrial emissions

1.13.1 Acid rain

Rain is one component of the water cycle. From the vapourization of water from various sources of water in the Earth's surface water enters the atmosphere. The condensation of this gaseous water due to various factors in the atmosphere and returning back to the surface of the Earth is called precipitation. There are several forms of precipitation. Rain is return as liquid water. Return in solid form occurs as snow and hails. In addition restoration also occurs by condensation into tiny droplets (aerosol) resulting in mist and fogs. Whatever is the way of return, the water coming back to the Earth from the atmosphere is the purest part of the hydrologic cycle. Except the solid particles in the atmosphere and some dissolved gases like nitrogen, oxygen and carbon dioxide there is no other substance in atmospheric water. Of the gases dissolved carbon dioxide has drawn much attention. That is because when atmospheric carbon dioxide dissolves in water, it combines with water to form a weak acid named carbonic acid.

$$CO_2(g) + H_2O(l) \longrightarrow H_2CO_3(aq)$$

Carbonic acid dissociates weakly and add H^+ ions to water.

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$$

Therefore pH of rain water is little less than the pH of neutral water.

Based on the present carbon dioxide composition in the air, 400 mg dm^{-3} or ppm (0.04%), the minimum pH value of rain water is 5.6. That is, rain water is slightly acidic even in the absence of any other factor affecting it. This mild acidity is not harmful to aquatic organisms, man or any other water related activity. This is the ordinary situation.

But due to various natural and human activities more acidic gases are added to the atmosphere. These are gaseous acidic oxides of nitrogen (NO_X) and gaseous acidic oxides of sulphur (SO_X). Nitric oxide (NO) and nitrogen dioxide (NO_2) can be considered as the gaseous acidic oxides of nitrogen. Sulphur dioxide (SO_2) and sulphur trioxide (SO_3) are the gaseous acidic oxides of sulphur.

Ways of gaseous acidic oxides of nitrogen enter the atmosphere

Natural process

During lightning where the temperature is high, atmospheric nitrogen reacts with atmospheric oxygen forming nitric oxide (NO) and nitrogen dioxide (NO_2).

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

NO and NO_2 are also produced by volcanic eruptions and nitrifying bacteria living in the environment. Gaseous acidic compounds of nitrogen are also produced by the oxidation of ammonia (NH_3) in the atmosphere which is produced by the microbial decomposition of nitrogenous compounds under anaerobic conditions. The amount of acidic gaseous compounds released to the atmosphere by all these natural process is very small. Thus the composition of naturally produced acidic gases of nitrogen in the atmosphere is very small and has no significant effect on making rain water acidic.

Human activities

The main anthropogenic (human) activity that emits gaseous acidic compounds of nitrogen to the atmosphere is the burning of fuel in motor vehicles. Internal combustion engines produce energy by combusting liquid fuel in air under a very high pressure and high temperature. Atmospheric nitrogen which is inert under normal condition reacts with oxygen under these conditions of high pressure and temperature mainly producing nitric oxide. Nitric oxide gets oxidized further in the atmosphere giving nitrogen dioxide.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

$$2NO\,(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Acidic NO_X produced by human activities makes rain water acidic.

Ways of adding oxides of sulfur to the atmosphere

Natural ways

In the volcanic eruption, ash and gases containing huge amounts of sulphur dioxide are freed and these directly enter the atmosphere. As a result of microbial activities taking place under anaerobic conditions in the sediments on the bottom of the ocean and water resources hydrogen sulphide gas is produced. Oxidation of this gas in the atmosphere gives sulphur dioxide. However the sulphur dioxide concentration in the atmosphere remains at a very low level because sulphur dioxide produced as above spread across a

very large area of the atmosphere. Sulphur dioxide gas entering the atmosphere due to natural ways hardly contributes to make the rain water acidic. (Acid rains restricted to the relevant areas have been reported after volcanic eruptions.)

Human activities

Compounds of sulphur includes as impurities in less volatile fuels such as diesel and furnace oil produced during the refining of crude oil. These compounds containing sulphur turn into sulphur dioxide on combustion and enter the atmosphere.

Further, elemental sulphur and sulphur compounds (e.g. FeS) presents as impurities in coal get oxidized during the combustion of coal and enter the atmosphere as sulphur dioxide. Sulphur dioxide produced by human activities like this largely adds on to the atmosphere at certain specific regions. For this reason there could be a very high concentration of sulpher dioxide in the areas around such sites (e.g; coal power stations). Acidic oxide of sulphur (SO_x) generated by such human activities cause acidity of rain water.

How pH is lowered in rain water by acidic gases

NO is produced during the combustion in engines.

$$N_2(g) + O_2(g) \longrightarrow 2NO(g)$$

NO in vehicular emissions gets oxidezed in the atmosphere giving NO_2.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

In the presence of air NO_2 reacts with water and produces nitric acid, a strong acid.

$$4NO_2(g) + 2H_2O(l) + O_2(g) \longrightarrow 4HNO_3(aq)$$

SO_2 gas entering the air is further oxidized to SO_3 gas.

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$$

SO_3 reacts with water vapour to form sulphuric acid. In the presence of air SO_2 gas also reacts with water vapour giving sulphuric acid.

$$SO_3(g) + H_2O(1) \longrightarrow H_2SO_4(aq)$$

$$2SO_2(g) + O_2(g) + 2H_2O(l) \longrightarrow 2H_2SO_4(aq)$$

The compounds HNO_3 and H_2SO_4 formed above are strong acids. They completely ionize in water adding H_3O^+ ions to water in large amounts.

$$HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$$

$$H_2SO_4(aq) + 2H_2O(l) \longrightarrow 2H_3O^+(aq) + SO_4^{2-}(aq)$$

Because of the H_3O^+ ions added to water by the strong acids, the pH value of water decreases below the pH caused by carbonic acid formed by dissolving CO_2 gas.

Lowering of pH in rain water below 5.6 by adding strong acids to the rain is called acidification of air or formation of acid rain. High acidity of water leads to many problems.

Effects of the acidification of water

Aquatic organisms are very sensitive to the change of pH in water. Therefore even a small drop in pH in water is harmful to them. This causes changes in behavioural patterns, retardation of organogeny and destruction of eggs and immature organisms of fish and other aquatic organisms etc. This is detrimental to biodiversity.



Figure 1.24 Distroying of aquatic organisms



Figure 1.25 Destroying of forests

Death of coral polyps responsible for the formation of coral reefs stops their formation and bleaches the reefs.

Continuous fall of acid rains in forested areas leads to degradation of chlorophyll in plant leaves which causes gradual death of the plants. Death of plants from their top to bottom is a sign of their ruin brought about by acid rains.

Acid rains make soil acidic. Owing to the acidity, poisonous metal ions (Al^{3+}, Cd^{2+}, Cr^{2+}, Hg^{2+}) and other toxic ions strongly bound to the insoluble soil structure get detached and dissolve in water. Increased concentration of these ions is harmful to aquatic organisms and not suitable for human consumption.

Examples :

High concentration of Al^{3+}, Fe^{3+} and heavy metal ions such as is very harmful to aquatic organisms.

High acidity rain water brings about speedy dissolving of micronutrient metal ions in the soil such as Fe^{3+}, Zn^{2+} and Cu^{2+} in water which are then leached out easily. This makes soil infertile.

Acid water dissolves rocks and minerals in soil containing calcium, magnesium and aluminum. Excessive ions of these in water raises the hardness of water.

Acidity increases the rate of corrosion of metal structures in constructions. This weakens their mechanical strength and reduces the life time.

Acid rains damage statues and other artistic creations made of calcium carbonate minerals such as marble. This obliterates their fine carvings denigrating their historic value.

It decreases the mechanical strength of houses and other constructions made by mortar and cement which contain lime stone. Acid rains and acidic gases convert the less soluble corbonates in mortar and cement into more soluble sulphates and nitrates.

$$2CaCO_3 + 2SO_2 + O_2 + 2H_2O \longrightarrow 2CaSO_4.2H_2O + 2CO_2$$

Measures that could be taken to reduce acid rains and acidification of water

1. Using coal and diesel with low sulphur content in coal and diesel power plants.

2. Adopting methods to remove acidic gases like sulphur dioxide like acidic gases emitted by power plants.

   (i) Burning coal with substances ($CaCO_3$) that can react with sulphur dioxide (Fluidized bed combustion)

   $$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

   $$CaO(s) + SO_2(g) \longrightarrow CaSO_3(s)$$

   (ii) Converting sulphur dioxide in power plant waste gases into solid substances. (reacting with calcium hydroxide (Lime slurry process))

   $$Ca(OH)_2(aq) + SO_2(g) \longrightarrow CaSO_3(s) + H_2O\ (l)$$

3. Employing environmental-friendly fuels or alternative energy sources such as solar energy, wind power, tidal energy, geothermal energy and nuclear power in place of coal and diesel.

1.13.2 Global warming

For all natural process and dynamic activities carried out by man on the Earth, energy is provided by the sun. There is an empty space between the sun and all the other plants including the Earth. Because of this reason solar energy travels to the Earth as radiations. This radiant energy comes to the Earth mainly as visible, infrared and ultraviolet radiations. Radiation energy of the Sun reaching the Earth like this are subjected to various transformation in the Earth. Finally leaves the Earth. That is to say, there is an energy equilibrium in the Earth.

Because of the transformations undergone by the radiant energy reaching the Earth, heat is generated in the Earth. As a result the earth gets heated up and reaches a certain temperature. Because of the transformation of solar energy, its return and establishment

of an equilibrium, the extent to which the earth is heated remains constant. Therefore on the whole the average temperature of the Earth is assumed to be a constant value. This is about 15 ^{0}C. However due to Earth's 23.5^0 inclination to its axis's situation of latitude intensity of solar energy received by various regions is different. Because of this seasonal changes the temperature in different parts of the world in various time intervals is different.

For example, in equatorial regions the temperature is high and it is uniform throughout the year. From the equator to polar regions seasonality becomes acute and temperature within the year varies with in wide limits. The summer is extremely hot while the winter is intensely cold. In polar regions an extremely cold weather prevails throughout the year.

The average temperature of the Earth, that is 15 ^{0}C is a favorable condition for the existance of life. The reason for the prevalence of the favourabe temperature is the green house effect existing on the Earth. The potency of the green house effect on the earth helps to maintain an optimum temperature favourable for life.

Greenhouse effect

Before studying the greenhouse effect let us understand what a greenhouse is. As we all know, to grow an agricultural crop a certain optimum temperature is essential throughout the life of the crop. When we go from the equator of the Earth to mid latitude regions, the annual period of time with this optimum temperature gradually decreases. On reaching the polar regions, the time with optimal temperature necessary for plant growth becomes so short that plants do not grow in those regions. If plants grow at all, they are plants with a very short life span (e.g. The life span of plants growing in Tundra regions is about 2-3 weeks). In mountain regions a low temperature prevails year-long (e.g. Nuwara Eliya, Bandarawela etc.).

Hence, life in a particular region, if the time interval during which the optimum temperature necessary for a certain crop is less than its life span, growing that crop in the relevant, region is difficult. A greenhouse lengthens this period of optimal temperature without an external heat supply in a safe house located in that particular region. The temperature in a greenhouse is higher by 2 ^{0}C to 6 ^{0}C than the temperature outside. For this reason, even outer temperature is lower than the optimal temperature, it can be maintained that optimum temperature inside the greenhouse. In a greenhouse the time period with optimal temperature can be extended by 2-3 weeks longer than that in the normal environment. Now let's inquire into how this happens.

Action of a greenhouse

A greenhouse is an almost completely safe kept house. Its roof and walls are made of transparent material so that solar rays can penetrate them. Through these transparent materials visible and ultraviolet radiations coming from the sun, passes into the greenhouse.



Figure 1.26 A Greenhouse

Inside the greenhouse, these radiations are absorbed by the soil and other substances in it. A part of the radiant energy absorb is re-emitted as low energy ultraviolet and visible radiations while another part is re-radiated as infrared radiations. The roofing materials and materials for the walls of the greenhouse are selected in such a way that they are transparent for the visible and UV radiations but reflect IR radiations. When IR rays are reflected inside the greenhouse for a longer period of time they are absorbed by carbon dioxide and water vapour and are converted to heat. This increases the temperature inside the greenhouse. This is the process takes place inside a green house. The atmosphere of the Earth too exhibits a process somewhat equal to the action of greenhouse. This is known as the greenhouse effect of the earth.

Greenhouse effect of the earth

Solar radiations falling on the Earth are mainly belong to the ultraviolet and visible zones. Of these most of the radiations belonging to the ultraviolet zone are absorbed by the upper atmosphere and very little reaches the Earth's surface. It is UV radiations of very low energy that come like this. Visible ray and low energy UV rays reaching the Earth surface are absorbed by the Earth's surface (soil) and re-radiated as low energy radiations like in a greenhouse. In this re-radiation energy is emitted as low energy visible rays and IR rays. The emitted visible rays return to space without undergoing any significant change. But the IR radiations emitted could be absorbed by certain gases in the air. Fortunately the main gases in the air – N_2 (78%), O_2 (21%), Ar (1%), cannot absorb these IR radiations. If these gases occupying more than 99% of the Earth's atmosphere had absorbed IR radiations, the temperature of the earth could have been very high.

Greenhouse gases

The gases which can absorb infrared radiations exist stably in the atmosphere for a long period of time are referred to as greenhouse gases.

Any gas having two or more atoms can absorb IR radiations. Also a hetero diatomic gases (e.g CO) can absorb IR radiations. Homo diatomic gases (N_2, O_2) and monatomic gases (e.g. Ar) cannot absorb IR rays. Hence any gas which is not monatomic and homo diatomic can absorb IR rays. Nevertheless, if a gas is to act as a greenhouse gas in the Earth's atmosphere, it should have following characteristics.

1. Ability to absorb infrared rays
2. Ability to stay stably in the atmosphere for a long period of time.

The gases in the atmosphere which are though capable of absorbing IR rays, unstable

or short-lived are not considered greenhouse gases. As per the foregoing facts the main greenhouse gases present in the atmosphere are,

1. Water vapour (H_2O)
2. Carbon dioxide (CO_2)
3. Methane (CH_4)
4. Nitrous oxide (N_2O)
5. Volatile halogenated hydrocarbons (CFC, HFC, HCFC)

Although would be present in certain amounts in the atmosphere and they are capable of absorbing IR rays, the gases such as SO_2, NO_2, NO and CO are not reckoned as greenhouse gases. This is because their life span in the atmosphere is very short. Of the above greenhouse gases, all the gases except halogenated hydrocarbons exist in nature.

The greenhouse gases aforementioned absorb IR rays emitted from the Earth and retain them long in the Earth. Therefore the Earth gets heated. The result of this heating is the maintenance of the normal temperature of the earth at around 15 ^{0}C. Thus greenhouse effect is favourable factor essential for the perpetuation of life.

Extra knowledge

The hottest planet in our solar system is not Mercury which is closest to the Sun but the second from it, Venus. Venus receives about 25% of the solar energy received by Mercury. The reason for this is the strong greenhouse effect existing in Venus. Around 95% of the atmosphere of Venus comprises carbon dioxide gas. For this reason, the atmosphere of Venus largely absorbs infrared rays and creates a strong greenhouse effect. Hence, though situated second from the sun, Venus holds the record of being the hottest planet of the solar system.

The percentages of greenhouse gases in the Earth are given in Table 1.5.

Table 1.5 Amounts of greenhouse gases in the Earth

Greenhouse gas	Quantity
Water vapor (%)	0.001 – 0.5
Carbon dioxide (ppm)	415
Methane (ppb)	1745
Nitrous oxide (ppb)	315
Volatile halogenated hydrocarbons (CFC, HFC, HCFC) (ppt)	53.3

What would happen if the percentage of greenhouse gases in the Earth increases? The

outcome is production of more heat in the Earth due to absorption of more IR radiations by the increased amount of greenhouse gases. The heat so produced circulated longer in the Earth causing an increase in Earth's temperature. Along with the industrial ventures initiated by man with the industrial development the proportion of greenhouse gases is gradually increasing. It increased rapidly with the industrial awakening got under way after the second world war started with the industrial revolution.

Table 1.6 Changes in the composition of greenhouse gases before the industrial revolution and at present.

Gas	Composition in 1750 (Volume percentage)	Present composition (Volume percentage)
CO_2	0.028	0.041
CH_4	0.00007	0.00018
N_2O	0.000027	0.0000314
Halogenated hydrocarbons	0	0.00000000533

From Table 1.6 it is clear that the amount of all greenhouse gases has drastically increased. Though the amount of water vapour in the earth atmosphere changes with geographical factors and some weather factors on short-term, the total amount of water vapour in the Earth remains unchanged on long-term. Because of this, although water vapour is a greenhouse gas it does not contribute to global warming. Owing to the increase in greenhouse gases the temperature of the Earth has risen by about 0.95 ^{0}C from 1750. This increase is 0.65 ^{0}C from 1950. This shows that global warming has rapidly increased during the few decades in the recent past.



Figure 1.27 Impact of the increase in the temperature of the Earth

Human activities leading to the increase in greenhouse gas concentration

Carbon dioxide (CO_2)

To meet the energy requirement of man, coal and petroleum are being burnt in excessive amounts. The carbon reserves which occurred inertly inside the Earth for millions of years were burnt in a very short time adding the resulting CO_2 to the atmosphere. When the rate of addition of CO_2 to the atmosphere exceed the rate of the mechanisms which remove CO_2 from it, CO_2 gas accumulates in the atmosphere.

Because of excessive deforestation, trees are felled indiscriminately. The debris contain carbon reserves collected over hundred of years. When these are decomposed by the microbial activity CO_2 is added to the atmosphere. This causes the carbon dioxide content in the atmosphere to rise.

Methane

When the indiscriminately disposed organic wastes decay in the environment they are acted upon by anaerobic bacteria. When those bacteria decompose organic substances methane is produced. Disposal of urban wastes as heaps of garbage is also a reason for the production of methane in large amounts. Agricultural practices (paddy cultivation) undertaken in marshy and water-logged areas favour anaerobic decomposition of organic substances producing methane.

Methane is also produced in the guts of the ruminants like cattle, sheep and goats due to bacterial decomposition of plant material under anaerobic conditions. Therefore rearing such animals in commercial scale is a reason to release methane in large amounts to atmosphere. Crude oil mining too increases the methane content in the atmosphere. During the mining process methane gas occurring as natural gas in crude oil deposits is freed to the atmosphere.

Nitrous oxide

Oxides of nitrogen are mainly added to the atmosphere by the bacterial action on nitrogenous compounds. Action of denitrifying bacteria on the nitrogen compounds added to the soil as fertilizers in agriculture produces nitrous oxide (N_2O).

Gaseous halogenated hydrocarbons

Halogenated hydrocarbons are very powerful greenhouse gases. These are ten thousand times as strong as carbon dioxide. For this reason, presence of these gases in the atmosphere even in small quantities contributes significantly to global warming.

Halogenated hydrocarbons are scare in nature. Halogenated hydrocarbons responsible for increasing the global warming are,

1. Chlorofluorocarbon (CFC)
2. Hydrochlorofluorocarbon (HCFC)
3. Hydrofluorocarbon (HFC)

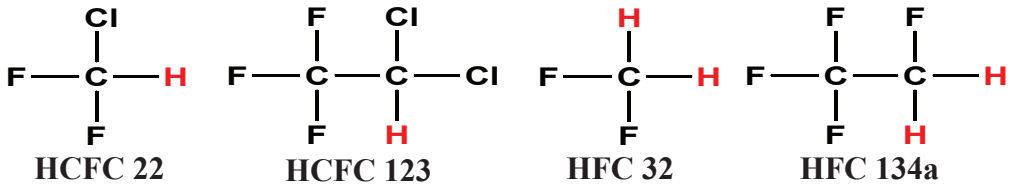


Figure 1.28 Some halogenated hydrocarbon molecules

All these three types are compounds synthesized by man and are used as cooling gases in air conditioners and refrigerators. They are also used as a blowing agent in the production of perforated plastics and in aerosols, for example in deodorant sprays and pesticides. In repair and disposal of the above equipment these compounds enter the atmosphere. The atmospheric lifetime of these are hundreds of years.

Adverse effects of global warming

- With the global warming polar ice caps and glaciers in high mountains areas tend to melt while the oceanic waters expand. This entails in inundation of costal lowlands. (e.g. Ganges river in Bangladesh, the delta of river Brahmaputra, Mekong delta in Vietnam). Loss of settlements, destruction of costal ecosystems, infertility of soil caused by the sea water swamping inland and devastation of crops are the other outcomes of this. Moreover it may obliterate Maldives and many other small island states in the pacific ocean completely from the world map.



Figure 1.29 Melting of ice caps in polar regions

- Because of the high temperature epidemics (e.g; dengue, Ebola) spread fast.
- Increase in the number of hot days and decrease in the number of cold days per year, occurrence of strong heat waves more frequently and lasting for a longer period of time (rapid increase in the temperature in regions within a small time interval).
- Frequent emergence of hurricanes, tornadoes etc. of greater violence.
- Rapid spread if invasive plants and animals. Such plants and animals may encroach new areas (cold blooded animals like snakes and other reptiles would migrate to cooler areas).
- Excessive drying of some regions (South Asia, Central Africa) while some other regions (e.g. Europe) receive heavy rainfall.
- Frequent long-standing droughts and flash floods due to heavy rainfall in a short period of time.

Global climatic changes

Many human activities in the world are connected with the climate of the relevant region. For examples, agriculture, animal husbandry, tourism and pottery are strongly linked to climatic patterns. These climatic patterns are created by the differences in solar energy received by various parts of the world. The shift of energy circulation caused by global warming brings about changes in the climatic patterns.

Not receiving rain on time, untimely rains, droughts and occurrence of whirl winds and tornadoes in regions where they have not been experienced before are examples. Prolonged droughts causing desertification in some regions forcing people to leave those areas. Climatic changes may indirectly engender political crises among nations and even battles.

For example, when the citizens of a certain country are displaced they migrate to neighbouring countries and a need arises to provide political asylum for them. Political crisis and wars may erupts for sharing water in rivers common to several countries (e.g. Nile, Brahmaputra, Mekong) specially when water goes scarce.

Global warming and climatic changes caused by it, is a problem common to the entire world. The most affected by this are the underdeveloped and developing countries which contribute least to global warming. So, in order to control global warming all the countries in the world should get together and have to adopt measures that minimize the emission gases which cause it.

The following solutions could be suggested in this regard.

- Limited the burning of fossil fuels and inclining to use alternative fuels. The best option is sloar energy. In addition nuclear power and wind power be used. Updating the machinery of current use and increasing their fuel efficiency could also be done.
- Instead of fossil fuels it is suitable to use renewable sources of energy such as ethanol and biodiesel. The amount of pure carbon added to the atmosphere by the combustion of bio-fuels is nil.
- By getting used to a simple lifestyle, high energy demand essential for a luxurious life can be minimized.
- Minimizing deforestation. To make furniture and paper and obtain firewood, fast-growing plants can be used without destroying forests.
- Avoiding indiscriminate waste disposal and adopting systematic method of waste disposal with proper management of waste. This minimize the emission of methane to the atmosphere.
- Refraining from the consumption of meat as much as possible getting used to vegetarian diet. By this rearing of animals such as cattle, goats and sheep for meat can be minimized.

- Use of compost in place of chemical fertilizers. This helps minimize the emission of nitrous oxide (N_2O) to the atmosphere.
- Restricting the use of refrigerators and air conditioners and using in such machines with less powerful gases such as hydrofluroolefines (HFO), isobutene (R600a) and coolant gas like ammonia in place of more stronger greenhouse gases like CFC and HCFC.

1.13.3 Depletion of the ozone layer

Energy for all the process taking place in our planet Earth is provided by the sun. Energy is transmitted from one place to another by three methods, conduction, convention and radiation. Of these, conduction and convention need a medium for the transmission of energy. Radiation does not require a medium for energy transmission. In our planetary system an empty space (vacuum) occurs between the sun and the planets. Therefore there is no possibility at all to transmit energy from the Sun to the Earth by conduction and convention. Hence the solar energy reaches the Earth by radiation which does not need a medium. The radiation that carry energy from the Sun to the Earth are known as electromagnetic radiations.

Electromagnetic radiations are classified according to the energy in them. That is as X-rays, ultraviolet rays, visible rays, infrared rays, micro waves and radio waves. Table 1.7 indicates the properties of various electromagnetic waves.

Table 1.7 Properties of electromagnetic waves

Electromagnetic waves	Mean wave length	Mean frequency/ s^{-1}	Mean energy/ kJ mol^{-1}
Radio waves	1 cm	3×10^{10}	1.2×10^{-2}
Micro waves	1 mm	3×10^{11}	1.2×10^{-1}
Infared waves	10 μm	3×10^{13}	12
Visible waves	500 nm	6×10^{14}	240
Ultraviolet waves	250 nm	1.2×10^{15}	479
X ray	1 nm	6×10^{17}	1.2×10^{5}

Of these X-rays and ultraviolet rays are highly energetic. Therefore when exposed to them they cause chemical changes in the bio-molecules in our body. The structural changes in the active bio-molecules in our body namely DNA, RNA and proteins (enzymes) obstruct their functions causing various complication in our bodies. We discuss these complications at length under the sections to come.

Energy is transmitted from the Sun to our planet Earth mainly in the form of ultraviolet rays, visible rays and infrared rays. Of these visual rays and infrared rays are low in energy and we are not harmed by the exposure to them. In the electromagnetic spectrum the only ray type sensitive to our eyes are visible rays and they help to give us the sense

of vision. We become sensitive to infrared by sensing heat.

Figure 1.30 illustrates the nature of the solar rays reaching the Earth and their intensity. From it we see that a considerable portion of the solar energy reaching the upper limit of the Earth's atmosphere are lost before reaching the earth's surface. Further examination of the figure, reveals that most of the UV rays have been eliminate before they reach the Earth's surface. Why does it happen so? It is because the absorption of those rays by the gas molecules in the upper strata of the atmosphere while the solar rays travel to the Earth's surface across the atmosphere.

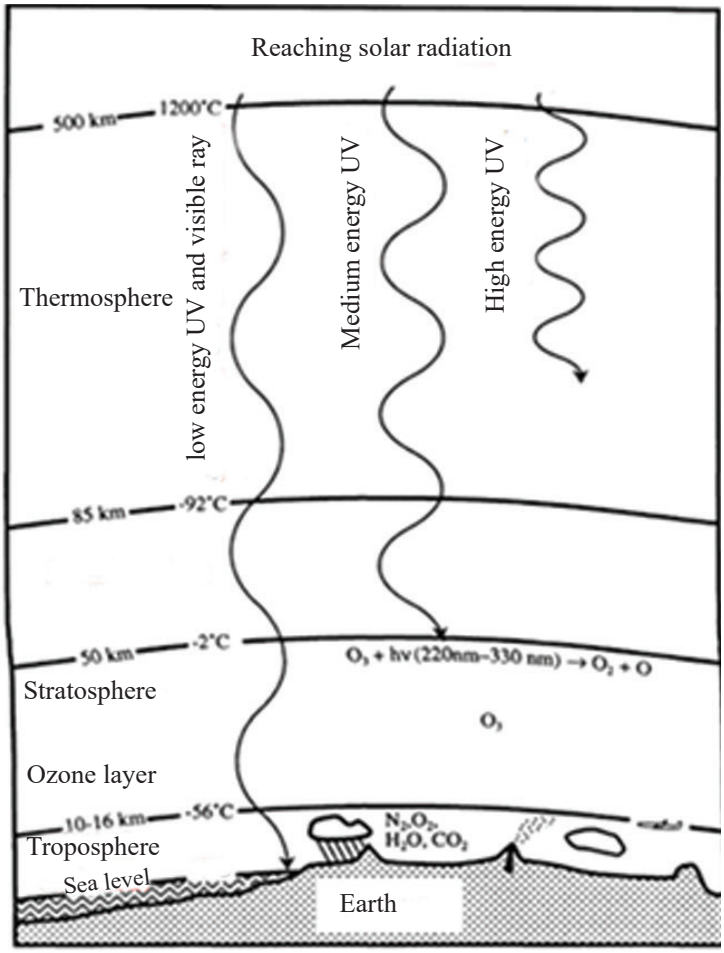


Figure 1.30 Stratification of Earth's atmosphere and penetration of strata by solar radiations

Stratification of the atmosphere

For the convenience of studying the atmosphere is divided into several layers. This stratification is based on the variation of temperature and the density of the gases in respective regions.

Troposphere This stretches from the Earths surface to about 15 km upwards. A greater percent (about 99%) of the atmospheric gases is found in this region.

Ascending from the Earth's surface, the temperature decreases.

Stratosphere — The region from 15 km to 50 km from the Earth's surface is stratosphere. The percentage of gases here is very low and ascending the layer, the temperature increases.

Thermosphere — It is the region above 50 km from the Earth's surface. Amount of gases in this region is extremely small and the temperature is very high.

Ozone layer — A sub-zone in the stratosphere is referred to as the ozone layer. This extends from 20 km to about 35 km from the Earth's surface. This is called ozone layer because most of the naturally occurring ozone gas in the Earth (around 95%) is found in this region. However it should be remembered that this is not composed only of ozone.

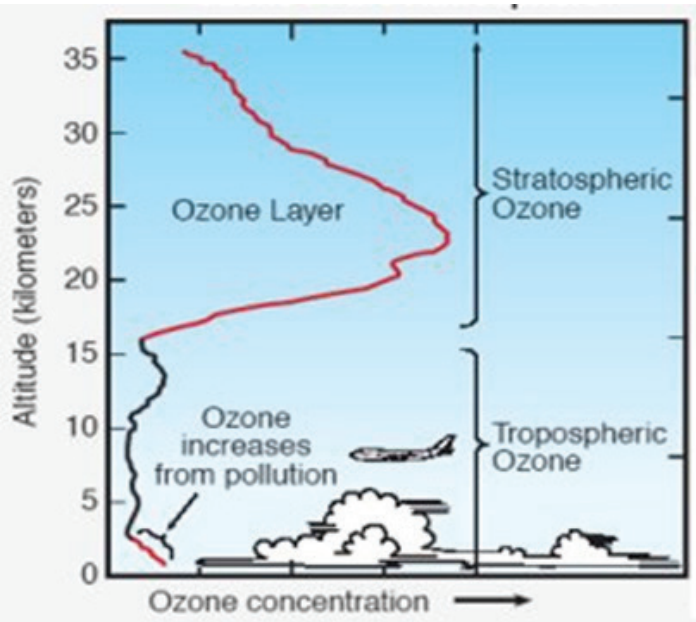


Figure 1.31 Ozone layer and the stratification of Earth's atmosphere

A greater part of the UV rays received from the Sun is spent to maintain the ozone gas in the ozone layer in the stratosphere. Therefore most of the harmful UV radiations coming from the Sun does not reach the Earth's surface. In other words, the ozone layer protects us from being exposed to higher energy UV rays by acting as a filter to them. This phenomenon is vital for the survival of life on the Earth. It is important for the maintenance of the life as much as the existence of water and an optimum temperature.

Functioning of the ozone layer

When higher energy UV rays coming from the Sun reach the stratosphere, they decompose oxygen gas and produce atomic oxygen.

$$O_2(g) \xrightarrow{h\nu} O(g) + O(g) \quad \Delta H > 0 \quad \text{----------} (1)$$

As this atomic oxygen is very reactive it reacts with another oxygen molecule forming ozone.

$$O_2(g) + O(g) \longrightarrow O_3(g) \quad \Delta H < 0 \quad \text{----------} (2)$$

Ozone is an unstable gas. In the presence of UV rays it decomposes giving oxygen.

$$O_3(g) \xrightarrow{h\nu} O_2(g) + O(g) \quad \Delta H > 0 \quad \text{----------} (3)$$

$$O_3(g) + O(g) \longrightarrow 2O_2(g) \quad \Delta H < 0 \quad \text{----------} (4)$$

(1) + (2)×2 , $3O_2(g) \longrightarrow 2O_3(g)$; O_3 formation

(3) + (4) , $2O_3(g) \longrightarrow 3O_2(g)$; breaking of O_3

In the ozone layer when the rates of breaking and making of ozone like this become a dynamic equilibrium sets in maintaining a fixed amount of ozone in this region. i.e. the following equilibrium exists in the ozone layer.

$$2O_3(g) \rightleftharpoons 3O_2(g)$$

As UV rays coming from the Sun are absorbed in maintaining this equilibrium, the entry of those harmful rays to the Earth's surface is prevented.

Depletion of the ozone layer

The ozone level in the ozone layer was continuously measured from 1950 with the aid of weather balloons. During making this measurement an amount of the ozone level in the ozone layer was observed decreasing annually from mid-seventies.

Generally the ozone level in the ozone layer does not remain constant every day. It changes to some extent with the temperature of the environment, seasonal changes and geographical factors. But annually it drops gradually. This continuous decrease in the ozone level in the ozone layer is, called ozone layer depletion. Depletion of ozone layer is a serious environmental problem.

The ozone layer prevents the entry of harmful UV rays to the Earths' surface. Because of the depletion of ozone layer in upper levels more harmful UV rays reach the Earth's surface. Exposure of the Earth's inhabitants more to the harmful UV rays causes various complications in them.

Causes for ozone layer depletion

Both natural factors and human activities cause ozone layer depletion. Of these the natural causes are temporary and the damage made is recovered in a short period of time. Sulphur containg compounds added to the upper atmosphere during powerful volcanic eruptions

is one natural factor damaging the ozone layer.

The most severe and non-reversible damages to the ozone layer are brought by the human. This is caused by the volatile compounds released to the atmosphere by man.

Examples are,

1. Chlorofluorocarbon

   In addition to this, volatile organic compounds containing bromine (bromofluorocarbon) indirectly contribute to ozone layer depletion.

2. Nitric oxide (NO) gas emitted by the aircrafts flying close to the upper atmosphere also depletes the ozone layer.

The main class of compounds which contributes to ozone layer depletion is chlorofluorocarbons. These are derivatives of hydrocarbons with one or two carbon atoms. Of these, all the hydrogen atoms are replaced by chlorine or fluorine.

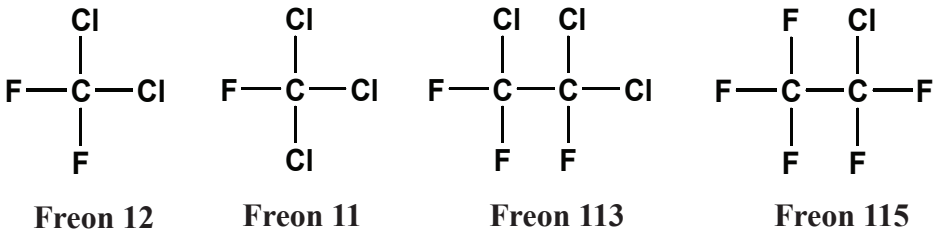


Figure 1.32 Some CFC molecules and their industrial names

All CFCs are synthetic compounds and not found in nature. Mainly they have the following industrial applications.

1. Used as the coolant gas in air conditioners and refrigerators
2. Used as an aerosol spray under high pressure in perfumes
3. Used as a blowing agent in the production of foam plastic (e.g.: polystyrene, cushions, mattresses, thermal insulating porous walls) to give porosity to them
4. Bromofluorocarbons are used in fumigation and in fire extinguishers.

How CFCs and other compounds damage the ozone layer

We should remember that none of the above compounds react directly with ozone. The CFCs describe above are very stable compounds. They are not thermally decomposed and are resistant to bio-degradation. For this reason these compounds can stay long in the atmosphere. However, these compounds are very volatile. Hence, they can evaporate rapidly and reach the stratosphere which accommodates the ozone layer where they are exposed to high energy UV rays in upper atmosphere which do not found in lower atmosphere. Under the influence of these C-Cl bonds undergo fission producing $\dot{C}l$ free

radicals. These free radicals react with ozone. They catalyze the breakdown reaction of ozone speeding it up and adding another process of breakdown other than to the natrual breakdown of ozone. Because of this the ozone-breaking process outstrips the ozone making process and the ozone layer is subjected to degradation. This can be illustrated by the following equations.

$\dot{C}l$ free radicals react with ozone

$$\dot{C}l(g) + O_3(g) \longrightarrow O_2(g) + \dot{O}Cl(g) \quad \text{---------- (1)}$$

$\dot{O}C1$ free radicals formed react with oxygen atoms formed by the natural breakdown of ozone and regenerates free radical.

$$O_3(g) \longrightarrow O_2(g) + \dot{O}(g) \quad \text{---------- (2)}$$

$$\dot{O}C1(g) + \dot{O}(g) \longrightarrow O_2(g) + \dot{C}l(g) \quad \text{---------- (3)}$$

(1) + (2) + (3),

$$2O_3(g) \longrightarrow 3O_2(g)$$

This shows that after the decomposition of an O_3 molecule by a $\dot{C}1$ free radical the $\dot{C}1$ free radical is regenerated without being destroyed. That means, until getting destroyed by another reaction a $\dot{C}1$ free radical can decompose a large number of O_3 molecules. Hence $\dot{C}1$ free radicals have acted as a catalyst in the breakdown of O_3 molecules.

Adverse effects of ozone layer depletion

The main adverse effect of ozone layer depletion is the entrance of high energy, harmful UV rays in high intensity to the Earth's surface. A grater amount of such UV rays gains admission to the Earth's surface after the degradation of the ozone layer than that reached to the Earth's surface before its degradation. Then Earth's creatures expose more to the harmful, high enegy UV rays and become victims to their injurious effects.

Listed below are such unfavourable effects.

1. Skin cancer

   Due to high energy in UV rays, exposure to them brings about structural changes in the molecules like DNA in the skin cells. In the presence of UV radiations, hydrogen bonds in these large molecules break and rearrange in another way. These molecular deforemations give birth to cancer cells which spread fast in the skin ultimately causing cancer.

2. Cataract in eyes

   DNA molecules as well as proteins maintain their structure through hydrogen bonds. Under the influence of the UV rays these bonds break and rearrange changing the

structure of proteins. The eye lens which is essential for vision is made up of a transparent, semi-solid protein. Owing to UV rays, the structure of the proteins in the eye lens changes and its transparency gradually decreases. This is called cataract (e.g.:when transparent egg white is heated it becomes white. This is because the structure of the protein albumin in egg white changes on heating). Cataract in the eye happens not only in humans but also in animals like cattle and goats which live mostly outdoor.

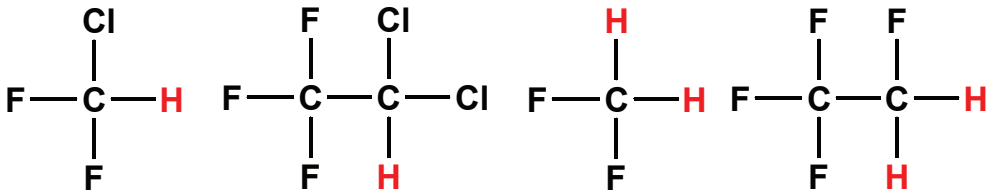
3. Mutations
   Plants with gene mutations would arise when they are excessively exposed to UV rays (e.g.: dwarf plants, plants with deformities in leaves)
4. Bleaching
   UV rays bleach pigments in cloths and degrade their quality.

Measures to be taken to protect the ozone layer

If the ozone layer goes on degrading at the rate it is happening at present, the Earth will become a place unsuitable for the perpetuation of life; or it would be a place where eye cataract and skin cancer patients are omnipresent.

Therefore immediate action should be taken to reduce the rate of ozone layer depletion. As CFC is the main destroyer of the ozone canopy its production and usage should be stopped. Action has already been taken in this regard and the Montreal Convention ended the production of CFCs from about 1996. At present alternative gases are being used for the industrial applications for which CFCs were used.

HCFC (Hydrochlorofluorocarbon) was the first alternative gas used for CFCs. This molecule is very much similar to CFC and the only difference was presence of a hydrogen atom in addition to chlorine and fluorine atoms.



HCFC 22 (a) HCFC 123 (b) HFC 32 (c) HFC 134 a (d)

Figure 1.33 (a) and (b) some HCFC molecules and (c) and (d) some HFC molecules

The C-H bond is this molecules is disassociated by solar rays carrying relatively lower energy than the energy in the lower atmosphere. For this reason a considerable part of this compound is decomposed before it reaches the ozone layer. But due to high volatility this gas also can reach the stratosphere. If it reaches the ozone layer like this it has the potential to damage the of ozone layer by cleavage of the C-Cl bond under the influence of high energy UV rays and formation of $\dot{C}l$ free radicals. The other alternative used to protect the ozone layer is the use of hydrofluorocarbon (HFC) gas as the coolant in refrigerators. HFCs lack chloride atoms and have only fluorine and hydrogen atoms. Their stability is also low due to the existence of hydrogen atoms (as in HCFC) but they do not form $\dot{C}l$ free radicals in the upper atmosphere for they do not contain chlorine atoms. Therefore they do not damage the ozone layer. Hence the coolant use in the airconditions and refrigerators in the world today is HFC (HFC 134a).

Note : Though HFC gas does not harm the ozone layer HFC, CFC and HCFC all are very powerful greenhouse gases. The global warming potential (GWP) of these gases is thousand times the GWP of carbon dioxide.

Table 1.8 Greenhouse gases and their GWP values

Gas	GWP value
CO_2	1
CH_4	22
N_2O	310
HFC 23	11700
HFC 134a	1300
CFC 12	10600
HCFC 22	1700

Despite the fact that the above gases occur in the atmosphere in very small concentrations (ppt), they can contribute considerably to increase global warming because of their very high GWP values. HFC is a good alternative for the ozone layer depletion. But its use is questionable because it contribute to another global environmental issue, the global warming. This has prompted the global community to use cooling gases that do not damage the ozone layer and contribute little to global warming.

Use of volatile hydrocarbons (e.g. R600a) and unsaturated hydrofluorocarbon compounds (Hydrofluoroolefin) (e.g. HFO-1234a) which are less stable in the atmosphere has been already started as alternatives. Isobutene (industrially labeled R600a) is being used as a volatile hydrocarbon. Usage of hydrofluoroolefin (HFO) have been prescribed as an

unsaturated hydrofluorocarbon. HFO is structurally similar to HFC and has a double bond. As compounds with double bonds are more reactive, HFO compounds decompose faster in the lower atmosphere and get removed. Thus their contribution to global warming is very low.

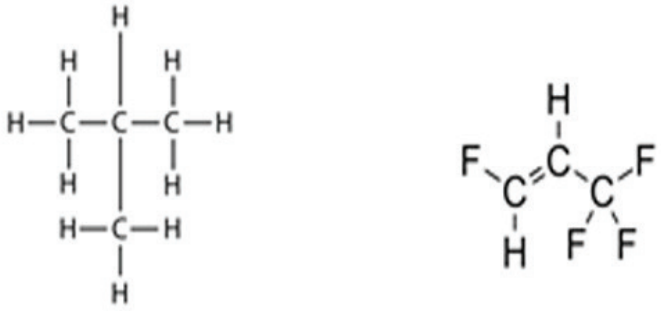


Figure 1.34 (a) Isobutene (R600a) (b) hydrofluoroolefin (HFO - 1234a)

1.13.4 Photochemical smog

Are you a person living in a town congested traffic jams? If so, have a look over the town form a fairly tall building in an afternoon. You will able to see a less transparent, brown coloured mist above the relevant buildings. On less windy days with a clear sky this could be seen in areas close to towns like Pettah, Borella, Kaduwelan and Kandy. Though somewhat rare in Sri Lanka this is a dreadful common in towns like New Dilhi, Mumbai, Culcata, Shanhai, Bejing and Kuala Lumpur.

What is the reason that gives rise to this kind of a less transparent, browny haze in afternoons? The complex photochemical process leading to this phenomenon is called photochemical smog. Photochemical smog means the lowering of the transparency of the atmosphere due to scattering of solar rays by chemical substances formed by the interaction of several environmental pollutants, fine particles and droplets of water.

Chemical pollutants causing photochemical smog and their sources

Two types of chemical pollutants contribute to the photochemical smog. They are nitric oxide gas (NO) and volatile hydrocarbons (unburnt fuel). In addition to these sunlight and a temperature above 15 ^{0}C are requirements.

Chemical pollutants causing photochemical smog are **NO, $CH_3(CH_2)_nCH_3$ (n = 1- 4)**

Both these chemical substances are added to the air almost totally by the transportation by automobiles. Hydrocarbons are the main component of liquid petroleum fuels. The transportation of vehicles totally depends on liquid petroleum. These fuels filled into vehicles enter the environment as unburnt fuel in various ways. Because of the high volatility of gasoline fuel, they vaporize from the fuel tank of vehicles and the volatile hydrocarbons release to the enviornment. A considerable amount of hydrocarbons vaporizes from the carburetor as well. Yet, the largest amount of them enters the air

through the exhaust system of the vehicle. Although fuel is burnt in the engine of the vehicle under high temperature and pressure, all the fuel molecules entering the piston do not burn. Especially the hydrocarbon molecules lying closer to the outer wall of the piston do not burn. These unburnt fuel molecules are released to the atmosphere via the exhaust system.

Inside the engine, fuel is burnt by mixing fuel and air in an optimum ratio and igniting under high pressure. Due to the heat evolved by the combustion a high temperature and pressure are created in the engine. Under this high temperature and pressure nitrogen which is considered as an inert gas under normal conditions, reacts with oxygen to produce nitric oxide. This nitric oxide gas escapes into the air through the exhaust system of the vehicle. Accordingly both the pollutants causing the photochemical smog are added to the air by the transportaion of vehicles. This is the reason why the photochemical smog is intense in urban areas with lot of traffic jams.

Chemistry of the photochemical smog

The photochemical smog is a result of a series of complex chemical reactions happening in the lower atmosphere under the influence of sunlight. But to make the study facile, the reactions occurring in the photochemical smog can be simplified as follows.

Nitric oxide gas released from internal combustion engines is subjected to further oxidation in the atmosphere producing nitrogen dioxide. This NO_2 when exposed to solar rays, get decomposed forming atomic oxygen.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

$$NO_2(g) \xrightarrow{h\nu} NO(g) + O(g)$$

Atomic oxygen reacts again with molecular oxygen (O_2) forming ozone (O_3) which is a main pollutant in the photochemical smog.

$$O(g) + O_2(g) \longrightarrow O_3(g)$$

Formation of $^{\cdot}OH$ free radicals: $O(g) + H_2O(g) \longrightarrow {}^{\cdot}OH(g)$

In addition to these, $^{\cdot}OH$ free radicals and ozone which is formed by atomic oxygen react with volatile hydrocarbon forming alkyl and proxyalkyl free radicals. These alkyl ($R^{\cdot}$) and proxialkyl ($ROO^{\cdot}$) free radicals react with NO_2 and O_2 producing harmful volatile short chain aldehydes, preoxyactyle nitrate (PAN) and peroxybenzyl nitrate (PBN). Aldehydes produced are subjected to polymerization forming small particles suspended in air. Large particles are formed by these small particles by the deposition of dust, water vapour etc. on them. These particles scatter sunlight reducing the transparency and it appear like a mist in the lower atmospere. Photochemical smog is the only state of pollution visible to our naked eye.

Adverse effects of the photochemical smog

- Ozone is produced as a main product of the photochemical smog. Ozone is a toxic gas. When inhaled it causes respiratory complaints destruction of mucous membranes in the respiratory tract, cough etc.
- Ozone is an unstable and very reactive gas. Therefore when plants are exposed to ozone yellow spots appear especially in tender leaves due to destruction of chlorophyll. This cuts down food production resulting in retardation of growth and decrease in the yield of agricultural crops.
- Ozone spilts the double bonds in rubber molecules (ozonolysis). This shortens the chains of rubber molecules reducing the mechanical strength of rubber-based products. It also causes reduction in the elasticity of rubber and splits in rubber tyres.
- Many volatile aldehydes are produced by the photochemical smog. Inhalation of these compounds causes respiratory diseases and the people who are suffering from asthma, wheezing, bronchitis etc., their ailing conditions get worst and exacerbate. Inhalation of these compounds, also can cause allergic conditions.
- Peroxyacetyl compounds (PAN and PBN) produced by photochemical smogs are carcinogenic and cause gene mutations. They bring about chemical changes in active proteins and enzymes in the body and disrupt the action of enzymes.
- Ozone bleaches colourings. Therefore they deteriorate the quality of textiles.

1.14 Chemistry of the water pollution caused by industrial emissions

Water is one factor indispensable for the survival of life on the Earth. That is for the reason that water contributes to biochemical reactions and acts as the solvent for those reactions. Further, water also acts as the solvent for the natural environmental reactions. Water acts as the solvent for the bio-environmental reactions like this because of the exceptional properties of the water molecule. As regards the geometrical shape of water molecule is angular (Figure 1.35).

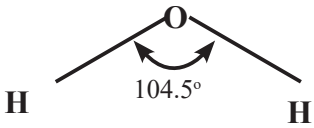


Figure 1.35 Geometrical shape of the water molecule

The value of its HOH angle is 104.5^0. Due to the difference in the electronegativities of the elements H and O of O-H bond in the water molecule, is polar. Since the two polar O-H bonds are angularly situated in space, the water molecule has a resultant polarity. This polarity is around 1.85 D (Debye). This has made the water molecule a strongly polar molecule. Because of this high polarity, strong hydrogen bonds form among the

water molecules. Therefore bulk water occurs as a liquid at room temperature. That is, water is a strongly polar liquid and because of this high polarity many polar compounds dissolve in water. Water is a good solvent for polar compounds. Many natural compounds as well as the compounds taking part in biochemical processes too are polar. For this reason water acts as a solvent for biochemical and environmental process. Hence water is named environmental polar solvent in environmental chemistry.

In the property of being a good solvent for polar compounds, there are demerits in water also. Many unwanted polar compounds readily dissolve in water and pollute it. Dissolving of various substances in water making it unsuitable for the relevant task, is called water pollution. Water pollution differs according to the task for which it is meant. For example there are occasions where water considered polluted for the drinking purpose, is reckoned unpolluted as far as agriculture is concerned. Water polluted by micro-organisms making it unsuitable for food processing is suitable to obtain steam.

Although the water is a strong polar solvent non-polar compounds also dissolve slightly in it. Some such non-polar compounds are highly toxic and even if dissolved in traces it would be at a harmful level. For example the solubility of benzene which is a very strong carcinogen, in water is about 1780 parts per million (1780 ppm). But for the drinking water parameters the maximum permissible value for benzene is 5 parts per billion (5 ppb). That is to say solubility of benzene in water is 350,000 times higher the permissible level. From this we can conclude that water is polluted by dissolving of polar as well as non-polar compounds in it. Oxygen is a completely non-polar molecule, yet oxygen is slightly soluble in water (8 ppm). This oxygen which is slightly soluble in water, is a vital factor for all the aquatic organism for their living processes. All the biological processes in the aquatic organisms occur because of this slightly dissolved oxygen in water.

1.14.1 Water cycle and water pollution

Figure 1.36 shows an environmental water (hydrological) cycle. This indicates the exchange of water among various sectors of the environment. Water is liable to get contaminated in every stage in this cycle. The least polluted water in the cycle is atmospheric water (clouds, water vapour, fog, frost and rain water). Water enters the atmosphere by evaporation of ground water. Since the boiling point of most of the polar compounds (salts etc.) dissolved in water is high, those compounds do not enter the atmosphere with the evaporation of water. For this reason water entering the atmosphere by evaporation is the purest and least polluted water in the environment. However, volatile polar compounds (H_2S, NH_3, NO_2) dissolve in water in the atmosphere. Besides, various chemical compounds produced by photochemical process (NO_2, SO_2, H_2SO_4, HNO_3, NH_4NO_3 etc.) in the atmosphere also dissolve in atmospheric water. Further, very small suspended particles (dust, pollen, bacteria etc.) found in the atmosphere blend with atmospheric water and pollute it.

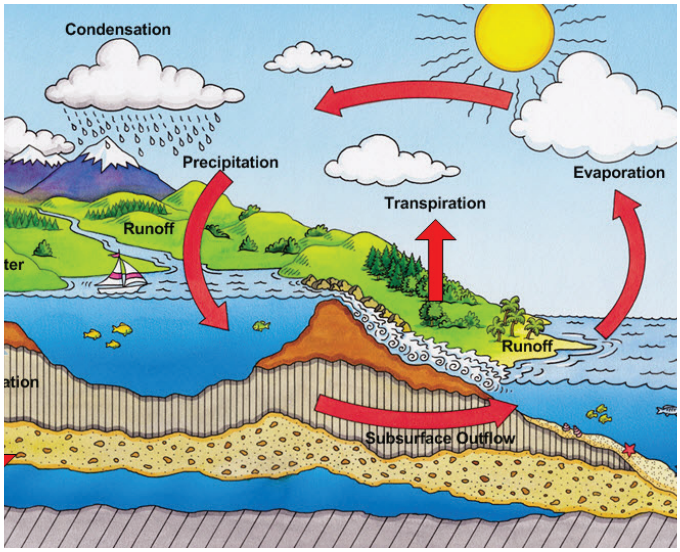


Figure 1.36 Water cycle

This atmospheric water reaches the Earth's surface by way of precipitation in the form of rain, snow, frost, fog and hales. Because of the runoff across the Earth's surface a portion of water reach the Earth's surface, is polluted further. It is also contaminated by the dissolving of salts formed by the weathering of minerals (heavy metal salts), various salts in the soil and various chemicals produced and added to the environment by man (fertilizers, industrial chemicals, agrochemicals). A part of water reaching the Earth's surface by rain percolates to the interior of the Earth (ground water) through the layers of rocks. When water passes through the layers of rocks and minerals, these layers decay. As a result, various mineral salts dissolve in water polluting the ground water as well.

1.14.2 Water quality parameters

As we have mentioned before, many polar as well as non-polar substances dissolve more or less in water. Since, though dissolve in large amounts, are not harmful (e.g. NaCl) Some are very toxic even when dissolved in minute quantities (e.g. heavy metal ions). For this reason it is essential to measure the suitability of water for the task in which it is used. For this, maximum and minimum thresholds or ranges with regard to the dissolved and undissolved substances have been stipulated. These pre-determined standards are called water quality parameters. Various countries and international institutions have published parameters for drinking water and parameters for releasing waste water. When the indicators fall outside the limits of these parameters, water is considered not suitable for the particular task.

Table 1.9 indicates the maximum level or the range of constituents published by the Sri Lanka Standards Institute for water suitable for domestic use.

Table 1.9 Domestic water quality parameters published by the Sri Lanka Standards Institute, Sri Lanka

Parameter	Unit	Maximum value or range
Colour	Hazen Units	15
Turbidity	NTU (Nephelometric Turbidity Unit)	2
pH	-	6.5 - 8.5
Chemical oxygen demand (COD)	mg L^{-1}	10
Total dissolved solids	mg L^{-1}	500
Hardness (as $CaCO_3$)	mg L^{-1}	250
Total phosphate (as PO_4^{3-})	mg L^{-1}	2.0
Arsenic (as As^{3+})	mg L^{-1}	0.01
Cadmium (as Cd^{2+})	mg L^{-1}	0.003
Lead (as Pb^{2+})	mg L^{-1}	0.01
Mercury (as Hg^0 and Hg^{2+})	mg L^{-1}	0.001

1.14.3 Waste Water quality parameters

Let us consider some waste water quality parameters very briefly.

pH value

Here, pH stands for the 'potential of hydrogen'. The pH scale means a scale that expresses the magnitude of acidity or alkalinity of a solution. pH value is the negative logarithm of the hydrogen ion concentration given in mol dm^{-3}.

There are several methods to determine the pH value of a solution.

1. By a titration or some other method: H^+ ion concentration of the solution is determined. By taking its negative logarithm, pH value can be found very accurately.
2. Using pH indicators (pH papers change colour according to the H^+ ion concentration in the solution): An approximate value for pH can be obtained by soaking a pH paper in the relevant solution and comparing the colour with a standard pH colour scale.
3. Using a pH meter: The potential of a special electrode (glass electrode) which changes with the H^+ ion concentration of the solution is measured relative to a standard electrode (Ag/AgCl electrode) and the pH value is read directly.

Figure 1.37 presents pH values of some common aqueous solution which we come across in our day to day life. It has been decided that the pH range of drinking water in Sri Lanka should be 6.5 – 8.5.



Figure 1.37 pH value of some aqueous solutions met in day to day life

Conductivity

The conductivity of an aqueous solution is a measure of the ability of the respective solution to conduct electricity. For this there must be free ions in water. The conductivity of pure water is very low. Pure water contains a very small amount of H^+ and OH^- ions formed by the self-ionization of water (1.0×10^{-7} mol dm^{-3}). The major cause for the conductivity of water is the amount of salts dissolved in water. When salts get dissolved in water they separate into cations and anions which occur as hydrated ions. As these ions are movable in water, they move towards the electrodes when a potential difference is applied, giving rise to conductivity. Water-soluble inorganic salts and organic compounds which can dissociate into ions (organic acids and bases) contribute to conductivity. The organic compounds like glucose and sucrose which dissolve in water but do not dissociate into ions, have very small contribution to the conductivity of water. The conductivity meter is used to measure the conductivity. The unit of measuring conductivity is siemens per centimeter (S cm^{-1}). But in many aqueous solutions which we often come across the conductivity expressed in S cm^{-1} takes a very small value, so microsiemens per centimeter ($\mu S\ cm^{-1}$) is used as the unit.

The conductivities of some aqueous solutions which we find in our day to day life are given in Table 1.10.

Table 1.10 Conductivities of some aqueous solutions which we find in our day to day

Solution	**Conductivity/** $\mu S\ cm^{-1}$
Deionized water	0.1- 5
Distilled water	1-10
Drinking water	50-1000
Milk	1000
0.01 M KCl solution (standard solution for conductivity measurements)	1410
Ground water	100-8000
Sea water	2000-60000
Apple juice	10000
Concentrated acids	60000-900000

Turbidity

Clean water is fully transparent; i,e, light passes through it without any obstruction. But due to addition of various foreign substances, water loses its transparency and appears cloudy. The loss of transparency in water like this is referred to as turbidity. The turbidity is caused by the presence of undissolved, suspended particles, that is fine particles which do not settle under the gravity in water. Because of these small particles light passing through water is scattered. Then, the sample of water appears cloudy or foggy. Presence of suspended particles is one visible instance in water pollution.

Existence of fine colloidal particles in water also leads to its turbidity. Fine clay particles, very small organic and inorganic particles, colonies of small unicellular organism and fine polymer particles are the suspended particles causing turbidity in water.

In order to gauge the turbidity in water, how much of a beam of light is scattered or transmitted by water is measured. The measurement is done by comparing the amount of light scattered by the solution concerned with the amount of light scattered by a solution of known turbidity. The unit of measuring turbidity is Nephlometric Turbidity Unit (NTU). Figure 1.38 shows the NTU values of some solutions with standard turbidity.

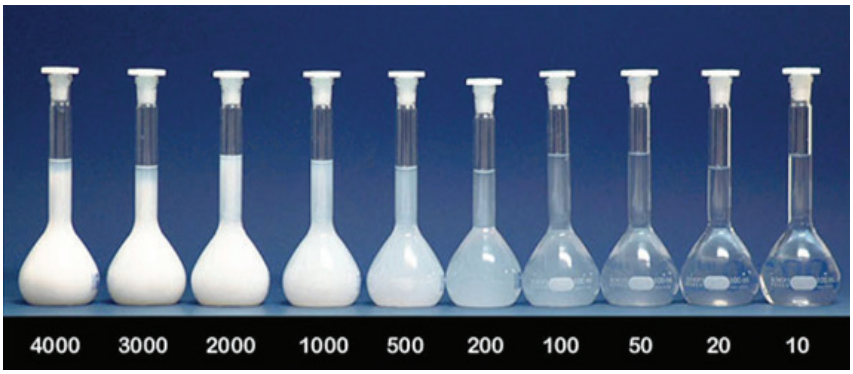


Figure 1.38 NTU values of a solution series with standard turbidity

Hardness of water

Are you living in the dry zone of Sri Lanka? Or have you ever drunk water drawn from a well or taken from any other source when you have visited such an area? Recall the taste of water you consumed. You would remember that the water is brackish in taste. Perhaps you would have observed that your hair becomes sticky and rough after bathing in that water. Why does it happen so? The brackish taste and roughness in hair were due to the high level of hardness in water.

The hardness of water is defined the capacity of water to precipitate soap. The chemical species causing the hardness in water are the polyvalent metal cations dissolved in water. It is the total concentration of Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+} and any other polyvalent metal cations. In natural water, the most abundant polyvalent metal cations are Ca^{2+} and Mg^{2+} ions. Therefore Mg^{2+} and Ca^{2+} are the two cations almost contribute to the hardness of natural water. But very rarely there are instances where ions like Mn^{2+}, Fe^{2+} and Al^{3+} also contribute to hardness. Soap is sodium or potassium salts of fatty acids. The carboxylate groups of these salts combine with polyvalent metal cations to form polyvalent metal cation slats of fatty acids. As these salts are less soluble in water they get precipitated. Since the density of this precipitate is less than that of water it floats on water as a soap scum. Hence soap does not function as a cleaning agent until all these polyvalent metal cations are removed. Also, these polyvalent metal cations neutralize the naturally occurring negative charges on the surface of hairs. Then, the hair which repelled one another due to the surface charges on them before come together making them sticky due to the loss of charges.

The permanent hardness in water has no relationship with the anions (e.g. Cl^-, SO_4^{2-}) present in water. The unit of expressing the hardness in water is parts per million calcium carbonate (ppm $CaCO_3$). The hardness level of water are classified approximately as follows (Table 1.11).

Table 1.11 The hardness level of water

Calcium carbonate/ mg L^{-1}	The quality of water
0 -50	Soft
50 -100	Moderately soft
100 - 200	Slightly hard
200 - 300	Moderately hard
300 - 450	Hard
450 +	Very hard

Temporary hardness

The presence of hydrogen carbonate (bicarbonate) ions and carbonate ions at a concentration above the total concentration of the polyvalent metal cations is temporary hardness. This is called temporary hardness because it can be removed by boiling of water. On boiling, the relevant metal cations are precipitated as their carbonates.

$$Ca^{2+} + 2HCO_3^- \xrightarrow{\Delta} CaCO_3 + CO_2 + H_2O$$

$$Mg^{2+} + 2HCO_3^- \xrightarrow{\Delta} MgCO_3 + CO_2 + H_2O$$

Permanent hardness

The presence of carbonate ions and hydrogen carbonate (bicarbonate) ions at a concentration very much below the total concentration of polyvalent metal cations is known as the permanent hardness.

This is termed permanent hardness because here, the metal ions existing in a concentration above the equivalent concentration of carbonate and bicarbonate ions cannot be precipitated by boiling. Permanent hardness can be removed by adding water-soluble carbonates (e.g. Na_2CO_3) from outside.

$$Ca^{2+} + 2Cl^- + Na_2CO_3 \longrightarrow CaCO_3 + 2Na^+ + 2Cl^-$$

Chemical oxygen demand (COD)

The chemical oxygen demand in water is the amount of oxygen required to oxidize the oxidizable substances dissolved in water. The most abundant oxydizable substances present in water are the various organic compounds. These occur in different oxidation states and can finally be oxidized to carbon dioxide or carbonates. Fatty acids, ammonia acids, sugars like glucose and fructose, starch and proteins are among these compounds.

Inorganic species like Fe^{2+} and Mn^{2+} ions also contribute to the chemical oxygen demand of water. COD of water is determined by a titration. The sample is distilled with a known amount of acidified potassium dichromate solution, a strong oxidant. The remaining

amount of dichromate ions is titrated with a standard Fe^{2+} solution and the value of COD value is determined.

Mostly the COD value is measured in the waste water discharged by industries. That is because when waster water with high COD is added to water bodies they get polluted.

Maximum COD values of waste water prescribed by the Central Environmental Authority of Sri Lanka for release into different water bodies are given in Table 1.12.

Table 1.12 Maximum COD values recommended by the Central Environmental Authority of Sri Lanka for release into different water bodies

Effluent	Maximum COD value/ mg L^{-1}
Industrial effluents to surface water	250
Industrial effluents to irrigation	400
Industrial effluents to marine water	250
Effluents from rubber factories	400
Effluents from textile factories	250

Disisolved oxygen level

The dissolved oxygen level (DO) is defined as the amount of molecular oxygen (O_2) dissolved in a unit volume of water. The dissolved oxygen comprised the oxygen gas directly dissolved from the 21% of oxygen present on the atmosphere and dissolving of oxygen gas produced by the photosynthetic aquatic plants and organisams (e.g.: algae, cyanobacteria) in the presence of sunlight. Because water molecule is polar and oxygen molecule is non-polar, solubility of oxygen in water is very low. For example at 21°C temperature and 1 atm atmospheric pressure at sea level the dissolved oxygen level in water is nearly 9 mg L^{-1} (9 ppm). Owing to various chemical and biological process occurring in water, the dissolved oxygen level in water decreases. When the dissolved oxygen level in water goes below 5 ppm, aquatic organisms are subjected to stress. In a situation like this, stress symptoms such as fish swimming to the water surface and keeping their mouths open to the atmosphere can be observed. When this value drops to 1-2 ppm fish start to die. Sometimes we have heard about sudden deaths of thousands of fish in reservoirs of different parts of the country. The main reason for such an incident is the slump of DO to a very low value.

When the DO decreases to a very low level (close to 0 ppm) anaerobic conditions set in water. This occurs in the bottom of deep lakes and tanks. There are several methods to determine the DO level in water.

1. Direct measurement using an oxygen meter/ probe sensitive to dissolved oxygen

2. By a titration (Winkler method) In this the DO level is determined by a back titration.

In this method, first dissolved oxygen is reacted with manganese ion Mn^{2+} in the basic media to form manganese dioxide.

$$2Mn(OH)_2 + \underset{\text{1 mol}}{O_2} \xrightarrow{\text{In water}} \underset{\text{2 mol}}{2MnO_2} + 2H_2O \qquad \text{---------- (1)}$$

The manganese oxide formed is reacted with iodide ions in an acid medium.

$$\underset{\text{1 mol}}{MnO_2} + 4H^+ + 2I^- \longrightarrow Mn^{2+} + \underset{\text{1 mol}}{I_2} + 3H_2O \qquad \text{---------- (2)}$$

The liberated iodine is then titrated with a standard thiosulphate solution.

$$\underset{\text{1 mol}}{I_2} + \underset{\text{2 mol}}{2S_2O_3^{2-}} \longrightarrow 2I^- + S_4O_6^{2-} \qquad \text{---------- (3)}$$

Four moles of thiosulphate are used up for one mole of oxygen. In the laboratory you can determine the DO level of various water samples by this method.

according to (1), (2), (3)

$$\underset{\text{1 mol}}{O_2} = \underset{\text{2 mol}}{MnO_2} = \underset{\text{2 mol}}{I_2} = \underset{\text{4 mol}}{S_2O^{2-}_3}$$

Eutrophication

The excessive growth of algae due to addition of nutrients to the water is defined as eutrophication.

When algae grow in abundance they form a thick blanket of their colonies on the water surface. This cuts down the penetration of sunlight to the lower layers of water bodies and prevents photosynthesis happening in them. This reduces the level of dissolved oxygen close to the bottom resulting in the death of aquatic plants and animals. When the dead bodies of these plants and animals are decomposed by aerobic bacteria, the DO level goes down further creating anaerobic conditions. Under anaerobic conditions gases like hydrogen sulphide are produced which make the area foul-smelling. Various nutrients are essential for algae growth but in many instances the limiting nutrient seems to be phosphate ions (PO_4^{3-}). Sometimes it could be nitrate ions (NO_3^-) as well. Because of these two ions becomes the limiting factor, the growth of algae in water bodies is controlled naturally. But by various human activities such as agriculture, disposal of industrial waste and addition of domestic detergents phosphate ions enter the water bodies. This eliminates the limiting conditions of the nutrient concerned ensuring rapid algae growth. This is eutrophication. If the algae growth has to be stopped, the phosphate level of the relevant water body should be maintained below 0.05 ppm. But in many urban wastes this phosphate level is high as 25 ppm.



Figure 1.39 Death of fish due to eutrophication

Occurrence of heavy metal ions in water

Absence of a strict definition for a heavy metal not with standing, the following denotations are in use.

1. In metallurgy a heavy metal is described as a metal whose density is greater than 5 g cm^{-3} or a metal whose relative density stands above 5.
2. In physics heavy metal defined as metal with the atomic number greater than 20.
3. In chemistry they are metals producing cations which give insoluble precipitates with sulphide ions (S^{2-}) and hydroxide ions (OH^-).

In some occasions these heavy metal ions are micronutrients (e.g. Zn^{2+}, Fe^{2+}). In many instances they are harmful and toxic (e.g. Hg^{2+}, Cd^{2+}, Pb^{2+}). Some are indispensable element at low concentrations but are harmful at high concentrations (e.g. Cu^{2+}). Some heavy metal ions do not contribute to any biological process. Heavy metals occur as sediments, deposits in soil, water and on the bottom of water bodies.

Heavy metals occurring as rocks, minerals and their debris in the Earth's crust enter the soil and water after the weathering of rocks. In natural water, heavy metals occur as hydrated ions and complex compounds. Table 1.13 lists the sources of few toxic heavy metals in water and their effects.

Table 1.13 Sources of a few toxic heavy metals in water and their effects

Heavy metal	Source to water	Effect
As (as As_2O_3)	Industrial waste water, waste of phosphate fertilizers, ground water, fungicides, ectronic items	Carcinogenic, arsenicosis
Cadmium (Cd^{2+})	Industrial emissions, mining waste, metal refining, rechargable batteries	Enzyme deactivation, high blood pressure, kidney damage
Lead (Pb^{2+})	Industrial emissions, mining waste, leaded gasoline, leaded paints, metal pipe welding materials	Kidney and reproductive disfunction, mental retardation of children, anaemia , inhibition of haemoglobin
Mercury (Hg, Hg^{2+})	Industrial waste, traces in many minerals, coal burning, equipment containing mercury (CFL bulbs, thermometers , vacuum apparatus)	Brain damage, insomnia, kidney damage, minamata disease



Arsenicosis



Minamata disease

Figure 1.40 Effects of toxic heavy metals

Dissoloved organic compounds

Dissolved organic compounds are compounds which are non – toxic but contribute to biochemical oxygen demand (BOD) or chemical oxygen demand (COD). Sugars, carbohydrates, lipids, fatty acids, amino acids, proteins, soluble hydrocarbons, primary and secondary metabolic products of plants and metabolic wastes products belong to this category. When these substances occur in water they are decomposed by bacteria. This increases the oxygen demand of water and decreases the dissolved oxygen level (DO). This impedes the biological processes in water.

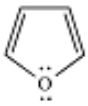
Toxic or hazardous organic compounds

Presence of these compound in water even in trace amount makes water unsuitable for use. Mostly persistent organic compounds belong to this class. Some pesticides, industrial chemicals, halogenated organic compounds, dioxin, furan, polychlorinated biphenyls (PCB), polyaromatic hydrocarbons (PAH) and disinfected by-products are examples for persistent organic compounds.

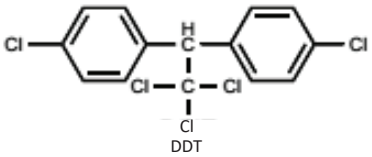
Given below are some organic compounds which are highly toxic or hazardous if present even in trace amounts in water.



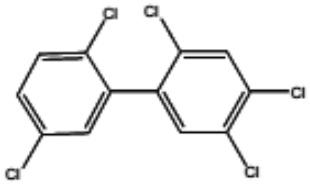
Benzo(a)pyrene(PAH)



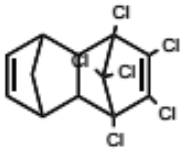
Furan



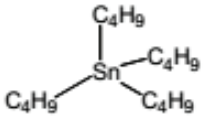
DDT



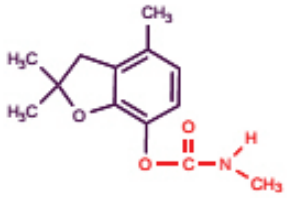
2,2',4,5,5' –pentachlorobiphenyl (PCB)



Aldrin

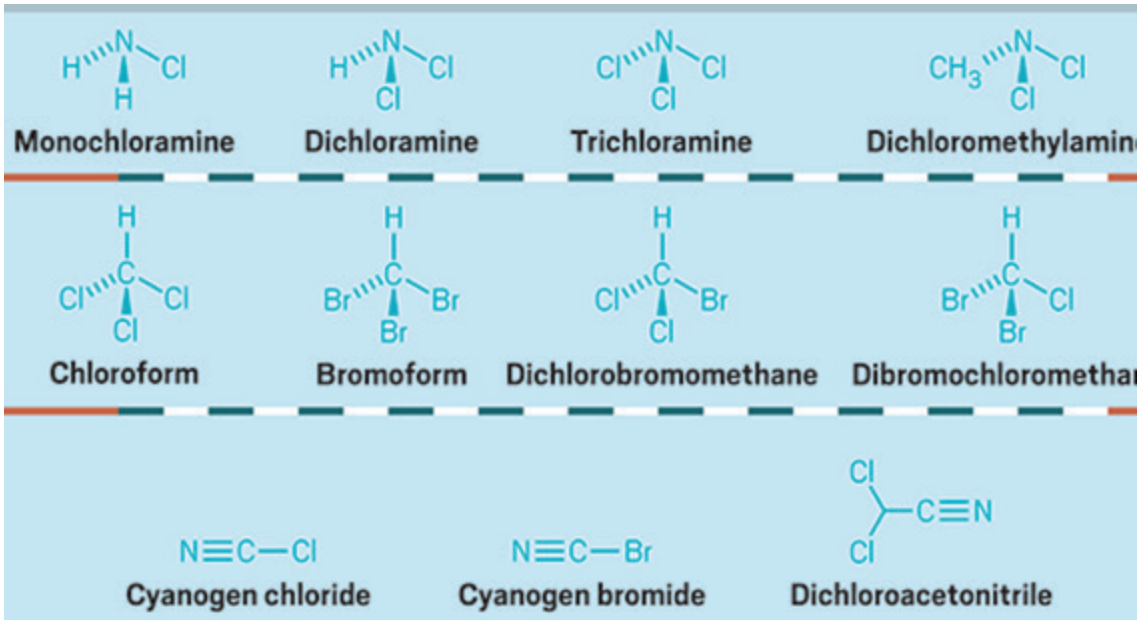


Tetra-n-butyltin



Carbofuran

Water disinfection by-product are the chlorine containing compounds formed by the reaction between hypochlorite ions (OCl^-) and some organic compounds dissolved in water. Hypochlorite ions are produced by chlorine (Cl_2) or hypochlorite salts (e.g. NaOCl, $Ca(OCl)_2$) added for disinfecting water. These compounds are poisonous. Some water disinfection by-products are given below.



Plastic additives

At present, virtually there is no consumer product devoid of plastic. Even if it is a food item, many plastic materials are connected with it. Few polymers are used to make all these consumer goods made of plastic. But do you know that many other additives are added when making plastic goods from these polymers? These additives are used to facilitate production, minimize cost, import various mechanical and workable properties and to get consumer attraction. These additives are ordinary chemical substances. During incorrect usage and when disposed to soil or water after use, there is a possibility of releasing these chemicals slowly from the plastic item. Some of these additives are hazardous. There are additives which cause cancer, affect the endocrine system and damage kidneys and various glands in the body. Escape of hazardous catalysts and monomers used in the synthesis of plastics from the finished product is also possible as traces. During the manufacture of plastic various additives are added to facilitate manipulation and mechanization. These also enter our bodies. Hazards additives also enter our bodies due to misuse of plastic items. A common example is the use of empty plastic water bottles to store liquids like coconut oil. Some additives in plastic bottels are insoluble in water but enter into non-polar liquids like coconut oil and enters our body.

Uses of some chemical substances commonly used as plastic additives and their effects are given in Table 1.14.

Table 1.14 Uses of some chemical substances commonly used as plastic additives and their effects

Additive	Uses	Effects
Pthalates Dioctyl phthalate Dimethyl phthalate Di (2-ethylhexyl) phthalate	Make plastics less rigid More flexible	Decrease the hormone secretion of endocrine system Carcinogen
Leaded pigments $PbCrO_4$(yellow) Pb_3O_4 (red) $PbCO_3$ (white)	To get vivid colours to plastic	Central nervous system damage, slow mental growth in children, kidney damage, delayed growth, likely carcinogen, decrease the hormone secretion of endocrine system
Brominated flame retardants Decabromodiphenyl ether Tetrabromobisphenol A	Used as a flame retardant in plastic covers, electrical cables, carpets and in plastic layers	Accumilate in the lipophilic and bio membranes and affect the nervous system. Decrease the endocrine hormone secretion of endocrine system
Bisphenol A	Used as a monomer in polycarbonate plastics item (school water bottles, baby feeding bottles) Used as an antioxdiant in the prduction of PVC. Polymers of bisphenol A is used as a protective coating for corrosion on the inner walls of metallic tin vessels.	Decrease the endocrine hormone secretion of endocrine system Mimics the action of estrogen hormone and disturbs its action Organ development issues in small children

Additive	Uses	Effects
Monomers and catalytic residues in plastic products Styrene, vinyl chloride, Bisphenol A as monomers Cr, Pb, Cd compounds as catalytic trace residues	Used to make polymers and accelerate polymer resin synthesis	Highly toxic, carcinogenic and mutagenic (monomer residues) Neurological damage and carcinogenic (catalytic residues)
Organotin compounds Dibutyl tin and tributyl tin compounds	Used as stabilizer in PVC and as a catalyst in Polyurethane production	Disturb the action of endocrine hormones in organisms Carcinogenic and mutagenic
Polyaromatic hydrocarbons Pyrene, benzopyrene	Fillers in plastics, processing oil in plastic manufacture	Some compounds are strongly carcinogenic

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