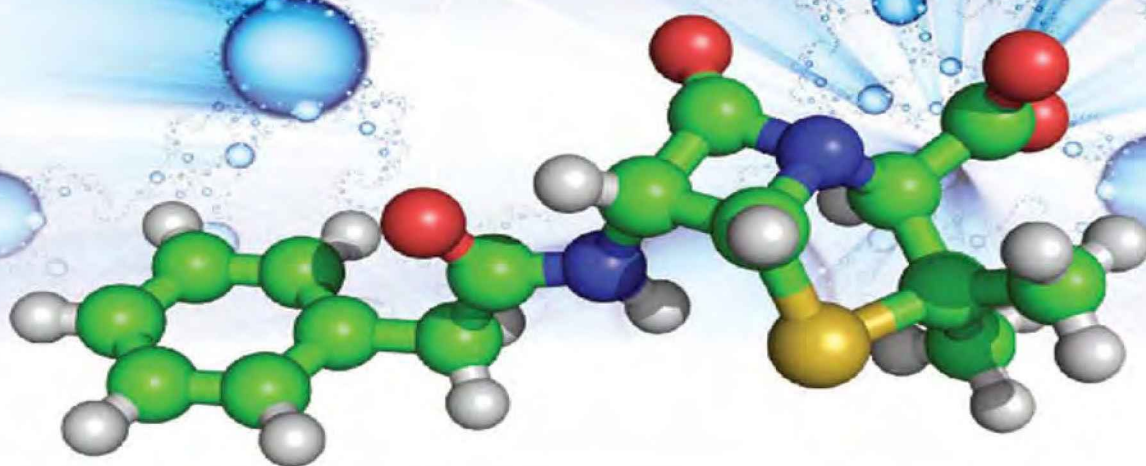


Goyal's

IIT Foundation Course Chemistry

For Class 10



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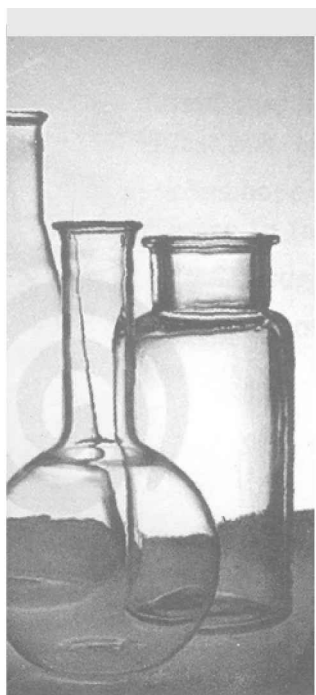
CHEMISTRY

CLASS 10

By

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New Delhi

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Preface

In today's competitive world, students need to tackle competitive exams in order to ensure a successful career. This can be achieved only by having a thorough knowledge of the subject which will help them to strengthen the application of the fundamental concepts and enhance their problem solving skills.

The “**IIT Foundation Series—Chemistry**” books for classes 6 to 10 are designed to provide a solid base to the students who aspire to undertake the IIT and other competitive exams for entrance to engineering institutions after Class 12. It will also ensure their excellent performance in all other similar competitive exams with ease.

The distinction features of this series are :

- 1 The syllabus goes beyond the usual school syllabus to cover a wider aspect of the subject.
- 1 **Textbook and Practice Material** are present in a single book.
- 1 **A concise description** of each topic with **important concepts, definition and words.**
- 1 **Important points** at the end of each chapter giving brief summary of the concepts learned in the chapter.
- 1 **Objective and subjective** Questions in each chapter based on the latest examination pattern.
- 1 **Challenging questions/problems solved** for encouraging the students to come up with solutions of more tough questions/problems on their own.
- 1 **Challenging questions/problems solved** for encouraging the students to come up with solutions of more tough questions/problems on their own.
- 1 Exercises for practice with **Simple Problems, Conceptual Problems, Multiple Choice Questions, Numerical Problems, Paragraph Questions, Assertion and Reasoning Questions**, etc. as asked in the IIT entrance exams.

The series hope to serve as a self-learning kit to the students which will give them the confidence to take up any entrance exam as a challenge.

Any queries/suggestions regarding the subject matter can be sent to the publisher.

We will strive our best to solve these queries and incorporate and suggestions given to us.

— Author

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12. Chemistry and Industry
13. Nuclear Chemistry
14. Analytical Chemistry

1

Atomic Structure

'If, in some cataclysm, all of scientific knowledge were to be destroyed, and only one sentence passed on to the next generation of creatures, what statement would contain the most information in the fewest words? I believe it is the atomic hypothesis that all things are made of atoms—little particles that move around in perpetual motion, attracting each other when they are a little distance apart, but repelling upon being squeezed into one another. In that one sentence, you will see, there is an enormous amount of information about the world, if just a little imagination and thinking are applied.'

Richard Feynman

1.0 INTRODUCTION

Dalton proposed in 1808 that atom was indivisible. This proposal was proved wrong due to the findings of the discharge experiments.

Dalton's proposal about atoms of the same element being similar in all respects was also proved wrong when *isotopes* were discovered.

Yet another proposal of Dalton about atoms of different elements being different in all respects was proved wrong when *isobars* (atoms of different elements with same mass number) were discovered.

Dalton was also proved wrong about atoms combining in small ratios when macromolecules like cellulose were discovered. [Cellulose is $(C_6H_{10}O_5)_n$, where n is a large number]

Dalton's main achievement was that he studied matter at the micro level and gave proposals that became the basis of further research on the atom.

In the previous classes we have learnt some important facts about the atom.

Atomic Number of an element is the number of protons in the atom. It is equal to the number of electrons in the *neutral* atom.

Mass Number of an element is the number of protons and neutrons in the nucleus of the atom.

Isotopes are atoms of an element that have same atomic number but different mass number.

Isobars are atoms of different elements that have different atomic number but same mass number.

The e/m ratio of cathode ray particles is a constant. This shows that these particles are present in all atoms.

The e/m ratio of canal ray particles is not a constant for all gases. However, e/m ratio is found to have the largest value when hydrogen gas is used. This leads to the conclusion that the positively charged particle in H-atom is the smallest positively charged particle (unit positive charge).

1.1 ATOMIC MODELS

It was clear by the end of the 19th century that

- (a) the atom was divisible, and
- (b) the atom was made up of smaller particles.

The next big question that scientists tried to answer was to find out how the particles are 'arranged' inside the atom.

An atomic model gives the arrangement of the sub atomic particles inside the atom.

1.2 RUTHERFORD'S ATOMIC MODEL, 1911

Rutherford, relying on the observations and conclusions of his alpha scattering experiments, gave the following postulates :

An atom is a hollow spherical body in which :

- (a) The atom has a small central region called the nucleus.
- (b) The entire positive charge is in the nucleus.
- (c) The mass of the atom is almost entirely due to this nucleus.
- (d) The electrons revolve at high velocity round the nucleus in circular path and have negligible mass.

To explain the stability of the atom in his model, Rutherford further postulated that, two types of forces operate in the atom. These forces were equal and opposite to each other.

- (i) A *centripetal force* that pulls the electrons towards the nucleus due to electrostatic force of attraction, and
- (ii) A *centrifugal force* that pulls the electrons away from the nucleus due to high speed of their revolution around the nucleus.

Due to these two equal and opposing forces, Rutherford said that, the atom is stable. The electrons continue to revolve around the nucleus indefinitely.

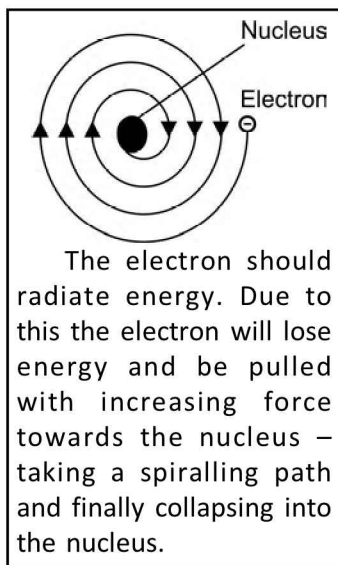
Defects of Rutherford's atomic model

The drawbacks of Rutherford's model were that he could not explain the stability of atoms with reference to the classical theory of electrodynamics and the line spectra of atoms.

- (a) Laws of Electrodynamics state that when a charged particle (like an electron) moves in a circular path at such high speed *it will radiate energy*. Hence the electrons should radiate energy continuously. Due to this continuous emission of energy the electrons would lose energy. As they lose energy they must be pulled with greater force towards the nucleus finally taking a path that spirals into the nucleus. The atom will collapse if this happens.

James Clerk Maxwell

- (b) Secondly, if an electron radiates energy continuously, the atomic spectrum should be a *continuous spectrum*. But all individual atoms form *line spectra*. If the electron is releasing energy, then the spectrum formed would be a *series of lines whose wavelength is decreasing*. But in reality it is found that every atom releases a *single line spectrum that is specific to that element*. For example sodium atom shows a single line spectrum in the yellow region of the visible spectrum.



James Clerk Maxwell

We will study atomic spectra after the next section.

1.3 MAXWELL'S WAVE THEORY

Consider that you are standing at a small distance away from a furnace. How does the heat reach you?

When you switch on a light bulb in a dark room you are able to see the objects in the room. How does the light reach the objects?

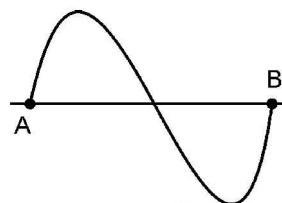
How does the heat and light radiation from the sun reach the earth?

According to Maxwell's wave theory :

All radiations (both visible and invisible) are propagated as waves.

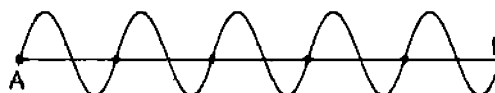
A wave has the following properties.

- (1) **Wave cycle** – A wave cycle is shown in the illustration below.



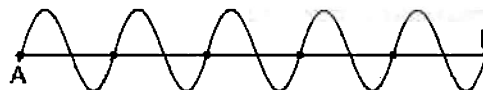
As the wave travels from point A to point B it is said to have completed one cycle.

- (2) **Wavelength** – The distance between two consecutive crests is called wavelength. Wavelength is denoted by the symbol – λ .
- (3) **Frequency** – The number of cycles a wave completes in one second is called its frequency. Frequency is denoted by the symbol – ν .



If the wave takes 1 second to travel from point A to point B and completes five wave cycles, then frequency of the wave is 5 cycles / second.

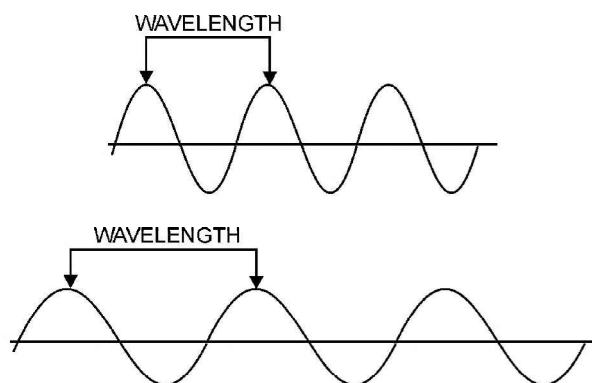
- (4) **Velocity** – The linear distance travelled by a wave in unit time is called the velocity of a wave.



If the linear distance AB = 10cm, and the wave takes 2 seconds to travel from A to B, the velocity of the wave is 5 cm / sec.

- (5) **Relationship between wavelength and frequency when velocity is same** – If two waves have the same velocity, the wave that has a

smaller wavelength will have a higher frequency.



- (6) **Relationship between velocity, frequency and wavelength of a wave** – The relationship between velocity (c), frequency (ν) and wavelength (λ) is given by the expression $c = \nu\lambda$

Examples

(1) If the velocity of light is 3×10^{10} cm/s, what is the frequency of violet light having wavelength $3800 \text{ \AA}$ ($1 \text{ \AA} = 10^{-8}$ cm).

Ans: As, $c = \nu\lambda$

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

$$= \frac{3 \times 10^{10}}{3800 \times 10^{-8}} \simeq 7.9 \times 10^{14} \text{ cycles/second}$$

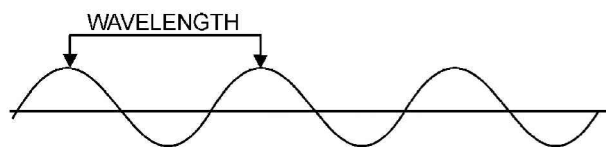
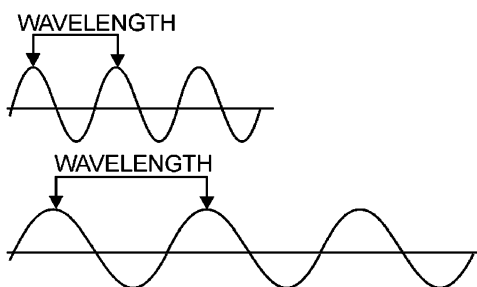
(2) If the velocity of light is 3×10^{10} cm/s, what is the frequency of red light having wavelength $6200 \text{ \AA}$?

Ans: As, $c = \nu\lambda$

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

$$= \frac{3 \times 10^{10}}{6200 \times 10^{-8}} \simeq 4.8 \times 10^{14} \text{ cycles/second}$$

- (7) **Energy of a wave** – The energy of a wave depends on its frequency (and hence its wavelength). If two waves have the same velocity, the wave with longer wavelength will have lesser energy.



A wave with short wavelength will have high frequency and more energy and vice-versa.

Comparison of the wavelengths, frequency and energy

Wave length	Frequency	Energy
short	more	high
medium	less	less
longer	least	least

1.4 PLANCK'S QUANTUM THEORY (1900)

According to Max Planck :

- Energy is propagated in the form of waves.
- The propagation is not as a continuous wave but in small packets of energy called *quanta*.
- The energy of the radiation is directly proportional to its frequency.



Max Planck

$$E \propto \nu$$

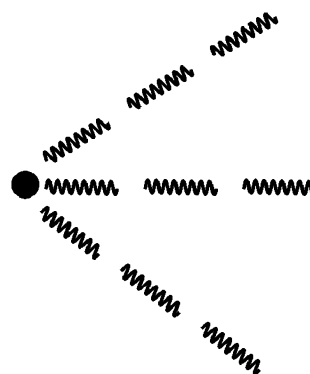
$E = h\nu$, where h is called Planck's constant and ν = frequency.

The value of Planck's constant,

$$h = 6.625 \times 10^{-27} \text{ erg.sec.}$$

Illustration

The radiant energy is not propagated continuously in the form of waves but is associated with small packets of energy travelling at the speed of light.



Source of energy – Energy is propagated as packets of energy

Example

- (1) Compare the energies of the different colours in the visible spectrum, given that their wavelengths are as follows: violet – 3800 Å, blue – 4500 Å, green – 5000 Å, yellow – 5700 Å, orange – 6000 Å, red – 6200 Å and the velocity of light is 3×10^{10} cm/s.

Ans: From wave properties we have

$$c = \nu\lambda$$

$$\text{or } \nu = \frac{c}{\lambda} \quad \dots (1)$$

$$E = h\nu \quad \dots (2)$$

Substituting equation (1) in equation (2)

$$\text{we get, } E = h \times \frac{c}{\lambda}$$

$$\begin{aligned} \therefore E_{\text{violet}} &= 6.625 \times 10^{-27} \times \frac{3 \times 10^{10}}{3800 \times 10^{-8}} \\ &= 5.23 \times 10^{-12} \text{ erg} \end{aligned}$$

Similarly,

$$\begin{aligned} E_{\text{blue}} &= 6.625 \times 10^{-27} \times \frac{3 \times 10^{10}}{4500 \times 10^{-8}} \\ &= 4.42 \times 10^{-12} \text{ erg} \end{aligned}$$

$$\begin{aligned} E_{\text{green}} &= 6.625 \times 10^{-27} \times \frac{3 \times 10^{10}}{5000 \times 10^{-8}} \\ &= 4.00 \times 10^{-12} \text{ erg} \end{aligned}$$

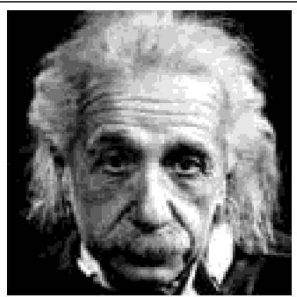
$$\begin{aligned} E_{\text{yellow}} &= 6.625 \times 10^{-27} \times \frac{3 \times 10^{10}}{5700 \times 10^{-8}} \\ &= 3.49 \times 10^{-12} \text{ erg} \end{aligned}$$

$$\begin{aligned} E_{\text{orange}} &= 6.625 \times 10^{-27} \times \frac{3 \times 10^{10}}{6000 \times 10^{-8}} \\ &= 3.31 \times 10^{-12} \text{ erg} \end{aligned}$$

$$\begin{aligned} E_{\text{red}} &= 6.625 \times 10^{-27} \times \frac{3 \times 10^{10}}{6200 \times 10^{-8}} \\ &= 3.21 \times 10^{-12} \text{ erg} \end{aligned}$$

$$\text{Thus, } E_{\text{violet}} > E_{\text{blue}} > E_{\text{green}} > E_{\text{yellow}} > E_{\text{orange}} > E_{\text{red}}$$

Einstein in 1905 extended Planck's quantum theory to all types of electromagnetic radiations. Both emission and propagation of energy, *according to him*, take place in the form of packets of energy called photon or quanta.



Albert Einstein

Wavelengths of visible light	
Colour	Wavelength (in Å)
Violet	3800–4500
Blue	4500–4950
Green	4950–5700
Yellow	5700–5900
Orange	5900–6200
Red	6200–7500

All radiant energy travel with the velocity of light.

Energy is released in the form of photons and they continue to exist as photons till another body absorbs them.

When a body absorbs light energy in form of photons it is excited from a lower energy state (E_1) to a higher energy state (E_2).

Conversely, the transition of a particle from an excited state (E_2) to the ground state (E_1) is accompanied by the emission of light energy.

Photoelectric effect: It had been observed that when light of certain colours falls on the surface of some metals like cesium, electrons are emitted. This is known as *Photoelectric Effect* and the electrons are called *photoelectrons*.

Explanation of photoelectric effect

Einstein explained *Photoelectric Effect* (ejection of electrons from certain metal surfaces when exposed to light) as follows :

- It is observed that violet part of the visible spectrum is able to eject electrons from the surface of cesium metal but red light has no effect.
- According to Einstein, electron is ejected from a metal, when it is struck by a photon, which has sufficient energy.
- If the photon has insufficient energy, it cannot eject electron from the metal atom. Photons of violet light have higher energy than that of red light. When the 'violet' photon strikes the metal, the electron in the metal atom absorbs the energy of the photon, causing the photon to disappear.
- A part of the photon energy is used to free the electron from the attractive forces in the metal

and the remaining energy is transformed into the kinetic energy of the released electron.

Black Body radiation: When a black hollow metal sphere with a small hole on it is heated to very high temperatures (2000°C), it emits coloured radiations through the hole. The colour of radiations changes from red to yellow to white as the temperature of the black body increases. Also when the heating is stopped and the temperature falls, the colour of the radiation emitted is in the reverse order.

Explanation of Black Body radiation:

- (i) The electrons revolve in different orbits of the atom with different energy. These orbits are called *energy levels*.
- (ii) In the first orbit, the electron requires lesser energy to revolve around the nucleus when compared to the energy required to revolve in the second orbit which is larger and so on.
- (iii) When the black body is heated, the electrons absorb energy and move into higher energy (i.e., larger) orbits.
- (iv) The radiant light that is emitted by the black body will therefore not have the wavelengths of light that have been absorbed by the electrons. As temperature increases due to heating, certain wavelengths are absorbed. The light radiated shows the resulting colour.
- (v) When the heating is stopped and the black body is allowed to cool, the 'excited' electrons release energy as they jump or return back to the 'ground state' or the original orbits. The difference in energy is now emitted by the black body. The radiation will therefore contain only these wavelengths of light that have been released by the electrons. The light radiated shows the resulting colour.

1.6 ATOMIC SPECTRA

We have seen that one failure of Rutherford's Atomic Model was that he could not explain the atomic spectra of the atoms. Let us now study atomic spectra in more detail.

We know that when white light is made to pass through a prism, it disperses and splits into seven colours. It is found that violet light suffers the maximum dispersion and red light the least. By observing the actual dispersion suffered by the seven colours it can be concluded that smaller wavelengths suffer more dispersion than larger wavelengths.

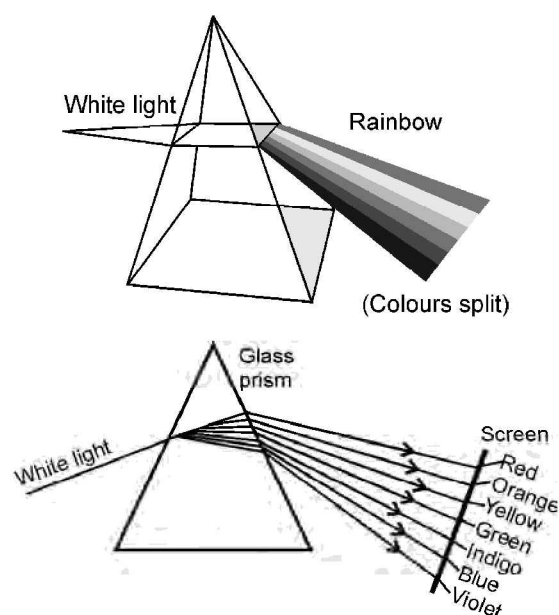
Wavelength Frequency Energy Dispersion

- | | Wavelength | Frequency | Energy | Dispersion |
|-----|------------|-----------|--------|------------|
| (1) | Low | high | high | more |
| (2) | High | low | low | less |

Thus, the extent of dispersion of a wave when it passes through a prism is directly proportional to its energy or frequency. On passing through a prism, if the dispersion of a wave is more, the energy in the wave and its frequency is also high.

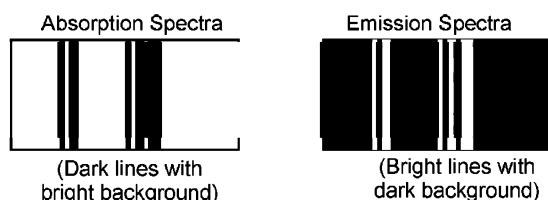
This observation is used to analyse the spectra generated in experiments using the discharge tube.

Illustration



- When the radiation coming out of the discharge tube is passed through a prism, the rays get dispersed. *The longer wavelength rays are dispersed less as they have smaller frequency when compared to shorter wavelength rays.*
- When the dispersed rays are made to fall on a photographic plate, they show specific lines called **atomic spectra**.
- In the discharge tube the electrons absorb energy when jumping to higher energy orbits in the atoms. ***The emerging rays will therefore not contain these wavelengths.*** The spectra will have dark lines corresponding to the wavelengths that have been absorbed. The spectrum obtained is called **absorption spectrum**.
- The electrons release energy when jumping back to lower energy orbits in the atoms. ***The emerging rays will therefore contain only these wavelengths.*** The spectra will have

bright lines corresponding to the wavelengths that have been released. The spectrum obtained is called **emission spectrum**.



→ Each element gives a unique spectrum. For example, sodium will always give a spectral line in the yellow region of the spectrum.

1.6 BOHR'S ATOMIC MODEL

Neil Bohr (1885-1962) was one of the greatest scientists of the 20th century. He won the 1922 Nobel Prize in physics for his study of the structure and radiation of atoms.

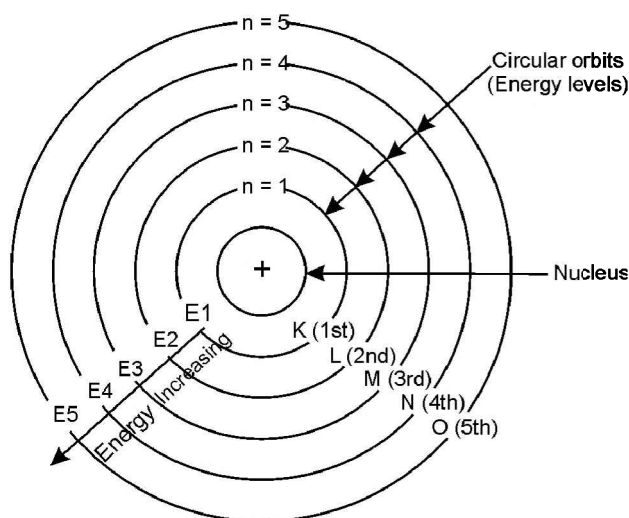


Neil Bohr

Bohr tried to overcome the defects in the Rutherford's Atomic Model.

According to his atomic model:

- (a) Electrons revolve around the nucleus with definite velocities in concentric circular orbits called **stationary orbits**. The orbits are numbered outwards. The orbit closest to the nucleus is numbered $n = 1$, the next $n = 2$ and so on.



- (b) The electrons in the orbit closer to the nucleus have lesser energy. Electrons in $n = 1$ will have the least energy in the atom when com-

pared to $n = 2$. Electrons in $n = 2$ will have lesser energy than the electrons in $n = 3$ and so on. In other words $E_1 < E_2 < E_3 \dots$

- (c) As long as the electron revolves in the same circular orbit it neither radiates nor absorbs energy.
- (d) The angular momentum of the electron is

quantized and is an integral multiple of $\frac{h}{2\pi}$.

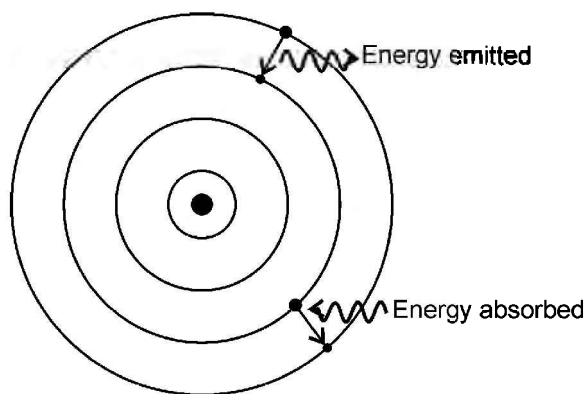
Mathematically, $mvr = nh/2\pi$, where n is the number of the orbit.

The value of ' n ' is always a non-zero positive integer: $n = 1, 2, 3, 4, \dots$

- (e) Energy of the electron changes only when it moves from one orbit to another orbit. Energy is absorbed when an electron jumps from an inner orbit to an outer orbit and vice-versa.

Illustration

When an electron jumps from a lower energy orbit to a higher orbit, energy is absorbed. For example when an electron transits from $n = 3$ to $n = 4$ energy is absorbed. The energy absorbed is calculated as follows. $E_{\text{absorbed}} = E_4 - E_3$



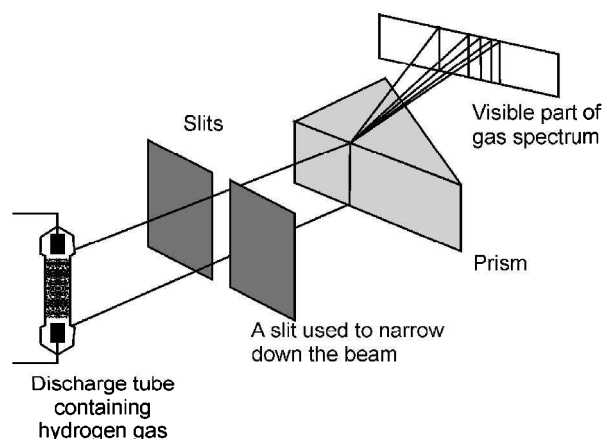
The electron absorbs energy when jumping from a lower orbit to a higher orbit and emits energy when coming back from higher energy orbit to lower orbit.

When an electron transits from $n = 3$ to $n = 4$, energy is absorbed. The energy absorbed is calculated as follows. $\text{Energy absorbed} = E_4 - E_3$

1.7 BOHR'S EXPLANATION OF HYDROGEN SPECTRUM

When hydrogen gas is kept in the discharge tube at a very low pressure and an electric discharge is sent through the gas it emits radiation. The radiation when sent through a prism gives different spectral lines. Bohr explained this spectrum as follows.

- (i) When the electric discharge hits the molecules of hydrogen they split into atoms of hydrogen.
- (ii) The electrons in the atoms of hydrogen further absorb energy and get into a high energy or *excited state*.
- (iii) Different atoms absorb different amounts of energy and are *excited* to different higher energy levels.
- (iv) A bright light is emitted from the discharge tube.
- (v) When this is passed through a prism it gets dispersed.
- (vi) When the dispersed beam of light emerging from the prism is made to fall on a photographic plate, the atomic spectrum of hydrogen is obtained. It contains a number of *groups of lines*.



The prism disperses the beam into different wavelengths which is as a spectrum.

As different electrons absorb different energies they jump to different energy levels depending on the energy absorbed. The atomic spectrum will give black lines over bright background as the emerging radiation will **not** contain wavelengths that are absorbed – hence a black line.

Possible electron transitions in hydrogen atom

While absorbing energy depending on the amount absorbed, the electron may jump to any higher energy orbit starting from $n = 2$. The electron in the excited state tends to emit energy and come back to the lower energy level or *ground state*. ***This may happen in a single step or in multiple steps.***

Illustration

Energy absorbed Electron transition from ground state to excited state

$$n = 1 \rightarrow n = 2$$

$$n = 1 \rightarrow n = 3$$

$$n = 1 \rightarrow n = 4$$

$$n = 1 \rightarrow n = 5 \text{ and so on.}$$

Energy released Electron transition from excited state to ground state

$$n = 2 \rightarrow n = 1$$

$$n = 3 \rightarrow n = 2 \rightarrow n = 1$$

$$\text{or } n = 3 \rightarrow n = 1$$

$$n = 4 \rightarrow n = 3 \rightarrow n = 2 \rightarrow n = 1$$

$$\text{or } n = 4 \rightarrow n = 1$$

$$n = 5 \rightarrow n = 4 \rightarrow n = 3 \rightarrow n = 2 \rightarrow n = 1$$

$$\text{or } n = 5 \rightarrow n = 1$$

These transitions result in the *formation of separate or discrete lines in the infrared region, visible region and ultraviolet region.*

Depending on the type and number of transitions, the electron in the excited state may give a number of lines and a number of series in the atomic spectrum.

Failings of Bohr's atomic model

The failings of this theory are:

- (a) The theory has limited application to only one-electron systems (atoms / ions). Bohr's Theory could only explain the spectrum of hydrogen and other one-electron species like He^+ , Li^{2+} , Be^{3+} .
- (b) The theory fails to satisfactorily explain the spectra of multi-electron species.
- (c) The theory fails to explain splitting of atomic spectral lines when the radiation in the discharge tube is subjected to a magnetic field or electric field. The lines split further into finer lines under the influence of a magnetic field (Zeeman Effect) and electric field (Stark Effect).
- (d) The theory assumes that electrons revolve around the nucleus in fixed orbits. This gives the possibility of finding the position and velocity of the electron simultaneously. This has been proved not to be possible.
- (e) Bohr's Theory could not explain chemical bonding between atoms.

1.8 CONCEPT OF QUANTUM NUMBERS

Based on the observed data coming from various discharge tube experiments it was found that to locate an electron in an atom a set of four identification numbers called **Quantum Numbers** are required. The term '**Quantum**' is used to signify that all the energy levels are governed by the Laws of Quantum Mechanics. Each electron in the atom is identified by a set of 4 quantum numbers. For example to locate the 6th electron in sodium atom that has 11 electrons in all, a set 4 quantum numbers would be required.

The four quantum numbers are

- (i) Principal Quantum Number (n)
- (ii) Azimuthal Quantum Number (l)
- (iii) Magnetic Quantum Number (m)
- (iv) Spin Quantum Number (s)

I. Principal Quantum Number, n (proposed by Bohr)

The Principal Quantum Number (PQN) has the following features.

- (1) PQN is a non-zero positive whole number denoted by the symbol ' n '.
- (2) PQN can have values from 1 to infinity.
- (3) PQN gives information of the orbit number in which the electron is located.
- (4) A large n value indicates that the size of the orbit and energy of the electron is large.
- (5) The value of n is used to find the maximum number of electrons in the orbit. The maximum number of electrons in a given orbit is given by $2n^2$.

K-shell ($n = 1$) can have a maximum of 2 electrons,

L-shell ($n = 2$) can have a maximum of 8 electrons and

M-shell ($n = 3$) can have a maximum 18 electrons and so on.

Example: Consider two electrons, one in $n = 1$ and another in $n = 2$ in an atom.

This tells us that :

- (i) the electron with $n = 1$ is in the first orbit of the atom and the electron with $n = 2$ is in the second orbit
- (ii) the electron in $n = 1$ will have less energy than the electron in $n = 2$

Other developments

Further developments that took place in the fascinating evolution of the knowledge of the structure of the atom are given below briefly.

Sommerfield's Atomic Model: After Bohr's atomic model failed to explain the splitting of atomic spectra into very fine lines in a magnetic or electric field, Sommerfield proposed his atomic model based on elliptical orbits to explain the radiations and spectral lines of the atoms.

Heisenberg's Uncertainty Principle: To locate an electron moving with high velocity it should be illuminated with a beam of light having the wavelength less than the dimensions of the electron. Radiations having shorter wavelengths than the size of electron consist of high-energy photons. During the collision with such a high-energy photon, the electron gets deflected as it absorbs considerable amount of energy. This results in increase in momentum of the electron. The changes in momentum automatically change the position of the electron. Thus as we try to observe the position or the electron's speed its direction changes. Hence it is impossible to determine the exact position and velocity of the electron accurately both at the same time. If the position is certain, velocity is uncertain and vice versa. This is called Heisenberg's Uncertainty Principle.

According to Bohr, an electron revolves in certain fixed orbits with definite velocity. This indicates that the position and velocity of the electron are known exactly. This is in contradiction to Heisenberg's Uncertainty Principle.

Schrodinger's Wave Equation: This was one of the most satisfactory models of the atom. It assumed that the electron not only has particle nature but also wave nature. Using his wave equation, Schrodinger could explain the wave nature of the electron. He could largely explain the atomic structure even of higher elements.

(iii) also the electron with $n = 1$ will be closer to the nucleus

(iv) the maximum number of electrons in $n = 1$ is 2 and in $n = 2$ is 8.

II. Azimuthal Quantum Number, l (proposed by Sommerfield)

Azimuthal Quantum Number gives the number of sub levels that are present in each Principal Quantum Number, n . It is denoted by l .

Consider an electron transition from $n = 2$ (excited) to $n = 1$ (ground state).

This transition is from a higher energy orbit to a lower energy orbit. The difference in energy will be emitted as radiation. The emitted radiation when observed using an ordinary spectroscope will give one single bright line in the spectrum.

But, when the same radiation is observed using a powerful spectroscope it is seen that *the single line is in reality two lines very close together*. The lines pertain to two waves whose wavelengths are very marginally different.

Illustration

Electron transition from $n = 2$ to $n = 1$ – emission spectrum

When seen with an ordinary spectroscope a single spectral line is seen.

When seen with a powerful spectroscope the single line seen above is actually two very thin lines separated by a very small distance.

This shows that there are two sub-energy levels for $n = 2$. Some of the electrons after absorbing energy may have jumped from $n = 1$ to 2(a) (first sub energy level) and some others from $n = 1$ to 2(b) (second sub energy level).

Thus while jumping back to the ground state the electron transition from $n = 2 \rightarrow 1$, is actually a transition from two sub-levels: either $n = 2(a) \rightarrow 1$ or $n = 2(b) \rightarrow 1$.

- In the former case, the electron jumps back from $n = 2(a)$ to 1 and emits the difference of energy as radiation of wavelength say λ .
- In the latter case the electron jumps from 2(b) to 1 and emits the energy as radiation of wavelength $\lambda + \delta\lambda$, where $\delta\lambda$ is a very small difference which can be noticed only by a powerful spectroscope.

From a study of the H-spectrum and other studies, it has been shown that the following sub levels exist for various n values.

For $n = 1$, one sub-level is present – s-orbital

$n = 2$, two sub-levels are present – s-orbital and p-orbital

$n = 3$, three sub-levels are present – s-orbital, p-orbital and d-orbital

$n = 4$, four sub-levels are present – s-orbital, p-orbital, d-orbital and f-orbital and so on.

These sub-levels are denoted by Azimuthal Quantum Number, l as follows.

For all s-orbitals $l = 0$

For all p-orbitals $l = 1$,

For all d-orbitals $l = 2$

For all f-orbitals $l = 3$

And thus, for a given PQN, n , l can have values from 0 to $(n - 1)$

III. Magnetic Quantum Number, m , (proposed by Lande)

Concept of Atomic Orbital

The electron revolves around the nucleus of the atom. Let us for a moment imagine that it is possible to take a photograph of the electron at a given instant while it is revolving around the nucleus. If many such photographs are taken continuously and all these photographs are superimposed then a cloud like figure can be imagined having high density at a certain place. (See figure).



An atomic orbital

The electrons revolve at such high speed around the nucleus that the movement creates a dense cloud called orbital.

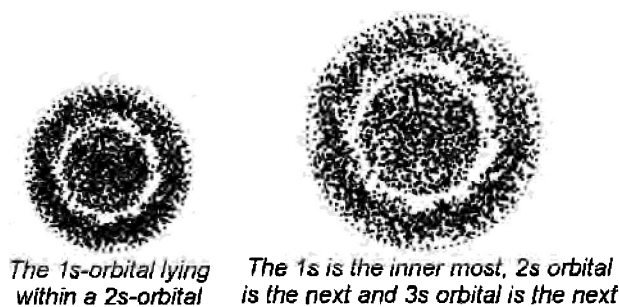
Atomic Orbital is the 3-D space around the nucleus where the probability of finding the electron is highest. (In the superimposed photograph it is the region that is darkest)

The probability of finding an electron in the orbital is 95%. Probability of finding an electron in the nucleus is zero.

Shapes of the orbitals

s-orbital – The s-orbital is spherical. The electrons in s-orbital revolve in a spherical space around the nucleus of the atom.

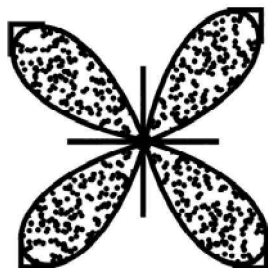
p-orbital – The p-orbital is dumb-bell shaped.



The electrons in p-orbital revolve in a dumb-bell shaped region as shown.



d-orbital – The d-orbital is double dumb-bell shaped. The electrons in d-orbital revolve in the double dumb bell shaped region as shown.



Zeeman and Starke Effect: When the radiation of the hydrogen spectrum was subjected to a magnetic field in the discharge tube and the radiation was then observed using a powerful spectroscopy, it was seen that the fine lines of the H-spectrum were actually a bunch of *still finer lines*. This is called Zeeman Effect.

Note: The splitting of spectral lines under the influence of electric field is called Starke Effect.

It was subsequently proved that *the transition to the p-orbital from another energy level could be to three orientations in three-dimensional space – p_x , p_y and p_z (along the three axes).*

To illustrate, consider a hypothetical case in which the electron transits from $n = 1$ to $n = 2$ in three H-atoms in the discharge tube. The following are possible:

- $n = 1 \rightarrow 2p_x$ where the electron after jumping to the excited state will revolve around x – axis
- $n = 1 \rightarrow 2p_y$ where the electron after jumping to the excited state will revolve around y – axis
- $n = 1 \rightarrow 2p_z$ where the electron after jumping to the excited state will revolve around z – axis.

Hence when the electron jumps back from $n = 2 \rightarrow 1$ it can do so in three possible ways :
 $n = 2p_x \rightarrow 1$. This jump would give a particular line

$n = 2p_y \rightarrow 1$. This jump would give another line close to the previous line

$n = 2p_z \rightarrow 1$. This jump would give yet another line close to the previous lines.

Illustration

Spectral line	Electron transition from $n = 2$ to $n = 1$ – emission spectrum <i>When seen with an ordinary spectroscopy a single spectral line is seen.</i>
$2 \rightarrow 1$	<i>When seen with a powerful spectroscopy it will be seen that the single line seen above is actually two very thin lines separated by a</i> 1st line – $2s \rightarrow 1s$ very small distance. 2nd line – $2p \rightarrow 1s$
1st line – $2s \rightarrow 1s$ 2nd line – $2p_x \rightarrow 1s$ 3rd line – $2p_y \rightarrow 1s$ 4th line – $2p_z \rightarrow 1s$	<i>When the radiation is passed through a magnetic field before it is dispersed through a prism and then seen with a powerful spectroscopy it will be seen that the double line seen above are actually four lines, three of these lines being very close together.</i>

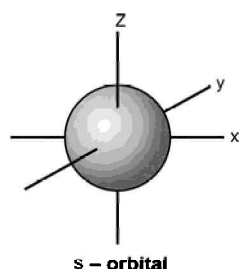
Illustration

However, the wavelength difference would not be visible to the naked eye. If the rays are subjected to a magnetic field, the three lines corresponding to the transition from p_x , p_y and p_z can be seen as three fine lines separated by a very small distance.

Importance of MQN: The MQN gives the possible number of orientations of the orbital to which the electron is transiting.

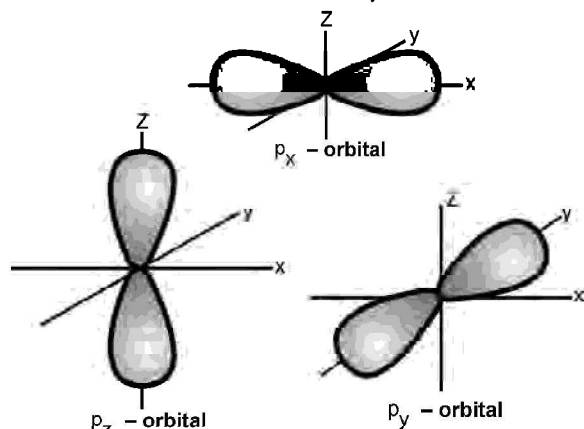
Possible 'm' values: Number of orientations for a particular l value is given by $(2l + 1)$

s-orbital orientations: For s-orbital, $l = 0$, and only one orientation is possible. This is obvious as the s-orbital is spherical.



s - orbital

p-orbital orientations: For p-orbital, $l = 1$, three orientations are possible – p_x , p_y and p_z .



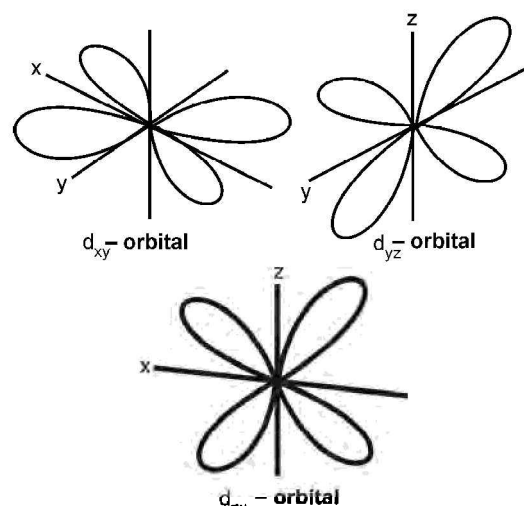
p_z - orbital

p_y - orbital

d-orbital orientations: For d-orbital, $l = 2$, five orientations are possible – d_{xy} , d_{zx} , d_{yz} , $d_{x^2-y^2}$, d_{z^2} .

The d-orbital orientations can be divided into two sets:

1st set: The d-orbitals in which the two dumbbells do not touch the axes viz.

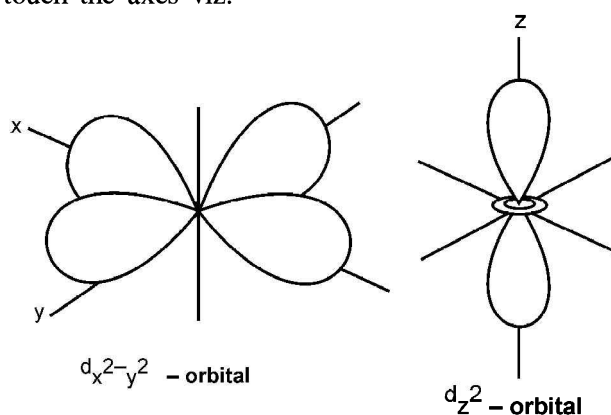


d_{xy} - orbital

d_{yz} - orbital

d_{zx} - orbital

2nd set: The d-orbitals in which the dumb bell touch the axes viz.



$d_{x^2-y^2}$ - orbital

d_{z^2} - orbital

f-orbital orientations: For f-orbital, $l = 3$, seven orientations are possible.

Specific 'm' value for each orientation taken separately

Each orientation is assigned MQN values on the integer scale.

Orbital AQN value	Maximum number of electrons	Possible orientations $(2l + 1)$	Orbital names	Specific m value of each orientation	Maximum number of electrons in each orientation
s-orbital – $l = 0$	2	1	s	$m = 0$	2
p-orbital – $l = 1$	6	3	p_x	$m = -1$	2
			p_y	$m = 0$	2
			p_z	$m = +1$	2
d-orbital – $l = 2$	10	5	d_{xy}	$m = -2$	2
			d_{yz}	$m = -1$	2
			d_{xz}	$m = 0$	2
			$d_{x^2-y^2}$	$m = +1$	2
			$d_{y^2-z^2}$	$m = +2$	2

IV. Spin Quantum Number, s (proposed by Uhlenbeck and Goudsmidt)

Further studies have shown that an electron while revolving around the nucleus also spins on its own axis *either in a clockwise or anti-clockwise direction*. This is similar to the earth rotating on its axis while revolving around the sun. The maximum number of electrons in any given orbital is 2.

For stability, both electrons in an orbital cannot spin in same direction as they will set up like magnetic fields that will repel making the atom unstable. The values of s are $s = +\frac{1}{2}$ and $s = -\frac{1}{2}$ for clockwise and anti-clockwise spins respectively.

Degenerate orbitals

From the table on the previous page, it can be seen that for a given value of AQN, l , there will be 'm' number of sub-levels or orbitals. The electrons in each of these orbitals will have the same energy.

Such orbitals, in which the electrons require same energy to revolve, are called degenerate orbitals. Degenerate orbitals will thus have the same value for n and l .

To illustrate, for L-shell ($n = 2$), there are two sub-levels: s- and p-orbitals.

The s-orbital has only one orientation ($m = 1$). But, p-orbital can have three orientations – p_x , p_y and p_z – the electron requires the same energy to revolve in any one of these 2p-orbitals. The three 2p orbitals ($2p_x$, $2p_y$ and $2p_z$ orbitals) are called *degenerate orbitals*.

1.9 RULES OF ELECTRONIC CONFIGURATION

Electrons occupy the orbitals in atoms according to a set of rules.

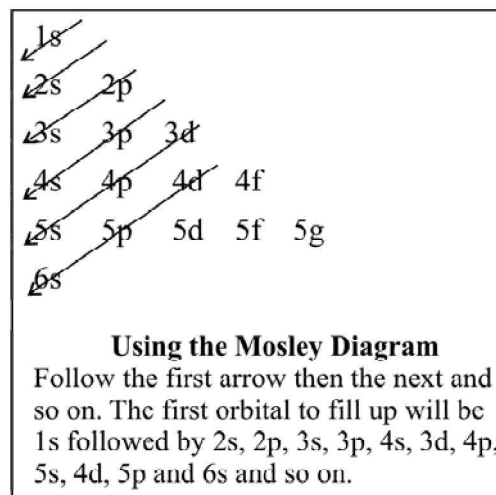
- The maximum number of electrons in a given principal quantum level, n is $2n^2$.
- Aufbau principle** states that the orbitals are successively filled in increasing order of energy levels.

Filling electron follows energy ranking. Among the available orbitals, the orbital of lowest energy is filled first.

$(n + l)$ rule: The energy value of an orbital increases as $(n + l)$ value increases. If two orbitals

have same value for $(n + l)$, the orbital having lower n value is filled first.

The increasing order of filling of orbitals can be found by either using the Mosley diagram or by using the $(n + l)$ rule.



Orbital	n	l	$n + l$
1s	1	0	1
2s	2	0	2
2p	2	1	3
3s	3	0	3
3p	3	1	4
3d	3	2	5

- Hund's rule** states that degenerate orbitals of same kind should be half filled before electron pairing can take place. Unpaired electrons have parallel spin.
- Half filled and completely filled degenerate orbitals give greater stability to the atoms.
- Pauli's exclusion principle** states that no two electrons in an atom can have the same set of four Quantum Numbers.

Pauli's exclusion principle implies that :

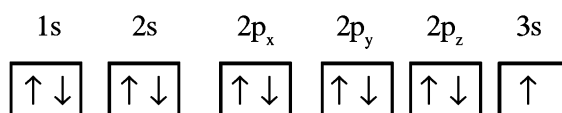
- the maximum number of electrons for a given orbital cannot be more than two.
- as two electrons in a given orbital have the same values of n , l and m they will necessarily differ in their spin quantum number. The two electrons must spin in opposite directions.

Quantum Numbers of each electron in sodium atom :

(Atomic Number 11 – Electronic configuration: $1s^2 2s^2 2p^6 3s^1$)

	Orbital	n	l	m	s
1st electron	1s	1	0	0	$+\frac{1}{2}$
2nd electron	1s	1	0	0	$-\frac{1}{2}$
3rd electron	2s	2	0	0	$+\frac{1}{2}$
4th electron	2s	2	0	0	$-\frac{1}{2}$
5th electron	2p	2	1	-1	$+\frac{1}{2}$
6th electron	2p	2	1	0	$-\frac{1}{2}$
7th electron	2p	2	1	+1	$+\frac{1}{2}$
8th electron	2p	2	1	-1	$-\frac{1}{2}$
9th electron	2p	2	1	0	$+\frac{1}{2}$
10th electron	2p	2	1	+1	$-\frac{1}{2}$
11th electron	3s	3	0	0	$+\frac{1}{2}$

Short form representation of the electronic configuration of sodium atom:



Writing the electronic configuration of the elements

Element	At No.	Shell configuration	Electronic configuration
H	1	1	1s ¹
He	2	2	1s ²
Li	3	2, 1	[He] 2s ¹
Be	4	2, 2	[He] 2s ²
B	5	2, 3	[He] 2s ² 2p ¹
C	6	2, 4	[He] 2s ² 2p ²
N	7	2, 5	[He] 2s ² 2p ³
O	8	2, 6	[He] 2s ² 2p ⁴
F	9	2, 7	[He] 2s ² 2p ⁵
Ne	10	2, 8	[He] 2s ² 2p ⁶
Na	11	2, 8, 1	[Ne] 3s ¹
Mg	12	2, 8, 2	[Ne] 3s ²
Al	13	2, 8, 3	[Ne] 3s ² 3p ¹
Si	14	2, 8, 4	[Ne] 3s ² 3p ²
P	15	2, 8, 5	[Ne] 3s ² 3p ³
S	16	2, 8, 6	[Ne] 3s ² 3p ⁴
Cl	17	2, 8, 7	[Ne] 3s ² 3p ⁵
Ar	18	2, 8, 8	[Ne] 3s ² 3p ⁶
K	19	2, 8, 8, 1	[Ar] 4s ¹

Ca	20	2, 8, 8, 2	[Ar] 4s ²
Sc	21	2, 8, 9, 2	[Ar] 4s ² 3d ¹
Ti	22	2, 8, 10, 2	[Ar] 4s ² 3d ²
V	23	2, 8, 11, 2	[Ar] 4s ² 3d ³
Cr	24	2, 8, 13, 1	[Ar] 4s ¹ 3d ⁵ (Anomalous configuration)
Mn	25	2, 8, 13, 2	[Ar] 4s ² 3d ⁵
Fe	26	2, 8, 14, 2	[Ar] 4s ² 3d ⁶
Co	27	2, 8, 15, 2	[Ar] 4s ² 3d ⁷
Ni	28	2, 8, 16, 2	[Ar] 4s ² 3d ⁸
Cu	29	2, 8, 18, 1	[Ar] 4s ¹ 3d ¹⁰ (Anomalous configuration)
Zn	30	2, 8, 18, 2	[Ar] 4s ² 3d ¹⁰
Ga	31	2, 8, 18, 3	[Ar] 4s ² 3d ¹⁰ 4p ¹
Ge	32	2, 8, 18, 4	[Ar] 4s ² 3d ¹⁰ 4p ²
As	33	2, 8, 18, 5	[Ar] 4s ² 3d ¹⁰ 4p ³
Se	34	2, 8, 18, 6	[Ar] 4s ² 3d ¹⁰ 4p ⁴
Br	35	2, 8, 18, 7	[Ar] 4s ² 3d ¹⁰ 4p ⁵
Kr	36	2, 8, 18, 8	[Ar] 4s ² 3d ¹⁰ 4p ⁶
Rb	37	2, 8, 18, 8, 1	[Kr] 5s ¹ and so on.....

[He] implies configuration of the element Helium.

[Ne] implies configuration of Neon.

[Kr] implies configuration of the element Krypton and so on.

Anomalous configuration

Chromium has the valence configuration 4s¹ 3d⁵ instead of 4s² 3d⁴. This is because of the extra stability of a half filled d-orbital. This is achieved by taking an electron from 4s-orbital. In the case of Cu the valence configuration is 4s¹ 3d¹⁰ instead of 4s² 3d⁹. This is because of the extra stability of a fully filled d-orbital. This is achieved by taking an electron from 4s-orbital.

1.10 PROPERTIES OF THE ATOM

- Atomic radius** is the distance from the centre of the nucleus to the outermost orbital. It is measured in Angstrom units.
- Ionisation energy (potential)** is the *energy required* (i.e. absorbed) to pull out an electron

from the outermost orbit of a *neutral gaseous* atom in its ground state. It is thus an endothermic process. It is measured in electron volts (eV) or kJoules / mole

- (c) **Electron affinity** is the *energy released* when an electron is added to the outermost orbit of the *neutral gaseous* atom in its ground state. It is thus an exothermic process. It is measured in electron volts (eV).
- (d) **Electronegativity** is tendency of a *bonded* atom to pull a shared pair of electron towards itself.

We will study these properties in the next chapter.

Paramagnetic and diamagnetic atoms

Atoms having unpaired electrons in the valence orbitals exhibit **para-magnetism**. When they are placed in an external magnetic field, they are attracted into the magnetic field.

Atoms having completely paired electrons in the valence orbitals are repelled by the external magnetic field and are called **diamagnetic**.

1.11 RADIUS OF ORBITS OF HYDROGEN ATOM

Since the electrostatic force of attraction between the electron and the proton in the nucleus is balanced by the centrifugal force of the revolving electron we can equate the two to find the radius of the orbits.

$$-\frac{e^2}{r^2} = -\frac{mv^2}{r}$$

$$\text{or } \frac{e^2}{r^2} = \frac{mv^2}{r} \quad \text{---Equation 1}$$

Also using Bohr's postulates:

$$mvr = \frac{nh}{2\pi} \quad \text{i.e. } v = \frac{nh}{2\pi mr}$$

$$\text{Hence, } v^2 = \frac{n^2 h^2}{4\pi^2 m^2 r^2} \quad \text{---Equation 2}$$

Substituting equation 2 in 1 and generalising this formula for nth orbit:

$$r_n = \frac{n^2 h^2}{4\pi^2 m e^2}$$

Also, it can be seen that in the formula 'n' can have only positive integral values. Thus the radii are finite and the electron can occupy these orbits only.

Some important calculations.

(a) Radius of 1st orbit of H-atom

By substituting the values in CGS system,

$n = 1$ and h (in terms of erg.sec),

m (in terms of g),

e (charge in terms of esu)

Radius of 1st orbit of H-atom

$$r_1 = \frac{n^2 h^2}{4\pi^2 m e^2} = 0.529.$$

(b) Ratio of the sizes of the orbits

The ratio of the size of 2nd and 5th orbits of

$$\text{hydrogen atom} = \frac{r_2}{r_5} = \frac{n_2^2}{n_5^2} = \frac{2^2}{5^2} = 4:25$$

- (c) If r_1 is radius of the first atom, the radius of the nth orbit is given by the expression $r_n = r_1 n^2$

1.12 ENERGY OF THE ORBITS OF HYDROGEN ATOM

The energy of an electron in an atom can be calculated as follows.

Total energy of electron,

$E_n = \text{Kinetic Energy} + \text{Potential Energy}$

Since, $\text{KE} = \frac{1}{2} mv^2$ and $\text{PE} = -\frac{e^2}{r}$

$$E_n = \frac{1}{2} mv^2 - \frac{e^2}{r}$$

From equation 1, we get, $E_n = -\frac{e^2}{2r}$ —Equation 3

Substituting expression for r_n we now get

$$E_n = -\frac{2\pi^2 m e^4}{h^2} \times \frac{1}{n^2}$$

The negative sign of the energy indicates that the energy of electron increases with increase in 'n'.

Some important calculations

(a) Ratio of energies of orbits

The ratio of energy of 1st and 3rd orbits

$$= \frac{E_1}{E_3} = \frac{n_3^2}{n_1^2} = \frac{3^2}{1^2} = 9:1$$

By substituting the values of $n = 1$, h (in terms of erg. sec), m (in terms of g), e (charge in terms of esu) the energy of electron in 1st orbit of H-atom can be calculated as -21.72×10^{-12} erg or -13.6 eV (conversion units: $1 \text{ eV} = 1.602 \times 10^{-12}$ ergs)

Also, $E_n = \frac{E_1}{n^2}$

(b) Difference in energies between two orbits

The difference in energy between two orbits n_1

and $n_2 = E_{n_2} - E_{n_1} = -\frac{2\pi^2 me^4}{h^2} \times \frac{1}{n_1^2} - \frac{1}{n_2^2}$

Applying Bohr's postulate, $E_{n_2} - E_{n_1} = h\nu$ and rearranging,

Since wave number, $\frac{1}{\lambda} = \frac{\nu}{c}$

$$= \frac{2\pi^2 me^4}{ch^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

In this expression λ , m , e , c , h are constants and whole expression can be reduced to

$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$, where R is called Rydberg

constant, and $R = 1,09,677 \text{ cm}^{-1}$.

This expression can be used to calculate the frequency of any radiation if the transition orbit numbers are known.

This expression can also be used to calculate frequency of radiation emitted.

We can also calculate from Planck's Equation energy of the radiation emitted when an electron transits from higher energy n_2 to lower energy n_1 orbit.

1.13 IMPORTANT POINTS TO REMEMBER

- Electrons, protons and neutrons are called sub-atomic particles.
- Protons and neutrons are present in the nucleus and electrons revolve around it.
- J.J. Thomson's atomic model placed the electron inside the nucleus. This could not explain the atomic spectra.
- Rutherford proposed 'planetary model' for atoms based on his alpha ray scattering experiments.
- According to Rutherford's model, electrons are subjected to two types of forces viz., the force of attraction between electrons and nucleus and the centrifugal force. These two forces are equal and opposite.
- Max Planck proposed quantum theory of radiation.

- Energy, E is given by $E = h\nu$
- Bohr proposed his atomic model based on Planck's quantum theory.
- According to Bohr's model, electrons are revolving in specified paths called 'stationary orbits or stationary shells'. The energy of these shells is constant.
- The stationary states are designated by K, L, M, N, O ...
- When an electron jumps from a higher orbit (higher energy) to lower orbit (lower energy), energy is liberated.
- The angular momentum of electron is equal to integral multiples of $h/2\pi$.
- Bohr calculated the radii and energies of various orbits of hydrogen atom.
- Bohr's model is applicable for species containing one electron only (ex. H, He^+ , Li^{2+} , etc.)
- Bohr's theory could not give the validity of quantization of angular momentum. It could not explain the splitting of spectral lines in the presence of magnetic field. (Zeeman Effect)
- Sommerfeld proposed the elliptical orbits.
- Each stationary state is divided into sub-stationary states or sub-levels.
- Stationary state is indicated by principal quantum number ' n ' and sub-stationary states by Azimuthal quantum number, l .
- The number of sub-stationary states in a given stationary state is dependent on the value of ' n '.
 $n = 1$ (K – shell) has one, $n = 2$ (L-shell) has two, $n = 3$ (M – shell) has three sub-stationary states.
- In the presence of magnetic field, the sub-stationary states split into groups or states.
- The principal quantum number n can take values 1, 2, 3, 4, ...
- Principal quantum number gives the size and energy of stationary orbits.
- Azimuthal quantum number (l) gives the shape of sub-shell or orbital.
- The maximum value of l is $(n - 1)$.
- Magnetic quantum number is proposed by Lande and designated as m .
- For a given ' l ' value, the number of m values is $(2l + 1)$. It ranges from $-1 \dots 0 \dots +1$

- The value of m gives information regarding the orientation of orbital in the presence of magnetic field.
- Spin quantum number (s), can take only $+1/2$ or $-1/2$ values.
- The region in space where there is finite probability of finding an electron is called 'atomic orbital'.
- s orbital is spherically symmetric.
- p orbital is dumb-bell shaped and d orbital is double dumb-bell shaped.
- p orbitals are present from L shell onwards, d from M onwards and f from N onwards.
- Aufbau principle states that electron occupies the orbital having the least energy.
- An electron occupies an orbital whose $(n + l)$ value is minimum. If $(n + l)$ value is same for two orbitals, it occupies the orbital having the lesser ' n ' value.
- Orbitals having same energy are called 'degenerate' orbitals.
- Hund's rule states that pairing of electrons takes place when all the available degenerate orbitals are occupied by one electron each.
- Pauli's exclusion principle states that no two electrons will have all four quantum numbers same.
- The physical quantities of atom are (i) atomic radius, (ii) ionization potential, (iii) electron affinity, (iv) electronegativity, (v) oxidising and reducing properties.
- Atomic radius is the distance between the nucleus and outermost orbital. It is expressed in $\text{\AA}$ (Angstrom) units. $1 \text{\AA} = 10^{-8} \text{ cm}$.
- Ionization potential (I.P) is the minimum energy required to remove an electron from the outermost orbital in the gaseous state.
- Units of ionisation potential are eV or kJ mol^{-1} or kcal mol^{-1} .
- Ionisation potential is dependent on (i) nuclear charge (ii) size of the atom and (iii) charge on the ion.
- Electron affinity (EA) is the energy released when an electron is added to a neutral gaseous atom in the ground state. Units of EA are eV or kJ mol^{-1} .

EXERCISE

I. Choose the correct answer

- The electromagnetic radiation that has maximum wavelength is
 - ultraviolet
 - radio waves
 - x-rays
 - infrared
- As an electron is brought from an infinite distance close to nucleus of an atom, the energy of the electron
 - increases to greater +ve value
 - decreases to a smaller +ve value
 - increases to a smaller -ve value
 - decreases to a greater -ve value
- The ratio of energy of photon of $2000 \text{ \AA}$ wavelength to that of $4000 \text{ \AA}$ wavelength is
 - $1 : 4$
 - $4 : 1$
 - $1 : 2$
 - $2 : 1$
- The spectrum of the He^+ ion is not expected to be similar to that of the
 - H atom
 - H^+ ion
 - Li^{2+} ion
 - Be^{3+} ion
- In the Bohr hydrogen atom, the electronic transition emitting light of longest wavelength is
 - $n = 2$ to $n = 3$
 - $n = 4$ to $n = 3$
 - $n = 3$ to $n = 2$
 - $n = 2$ to $n = 1$
- With increasing principal quantum number, the energy difference between adjacent energy levels in hydrogen atom
 - decreases
 - increases
 - remains constant
 - may increase or decrease
- In an atom when an electron jumps from K- shell to M-shell
 - energy is absorbed
 - energy is emitted
 - energy is neither absorbed nor emitted
 - sometimes energy is absorbed and sometimes emitted
- As an electron moves away from the nucleus its potential energy _____ and kinetic energy _____
 - Decreases, increases
 - Increases, increases
 - Decreases, decreases
 - Increases, decreases

- (9) The ratio of the radii of the first three orbits in an atom of hydrogen is
 (a) 1 : 4 : 9 (b) 9 : 4 : 1
 (c) 1 : 2 : 3 (d) 3 : 2 : 1
- (10) The energy of the electron when it is at an infinite distance from the nucleus is
 (a) infinity (b) zero
 (c) minimum (d) cannot be predicted
- (11) When there are two electrons in the same orbital they have _____ spins.
 (a) + (b) -
 (c) + and - (d) Zero
- (12) The maximum number of electrons that can be filled into all the orbitals corresponding to the Azimuthal quantum number, $l = 3$ is
 (a) 2 (b) 6
 (c) 10 (d) 14
- (13) The impossible set of quantum numbers is
 (a) $n = 2, l = 0, m = 0, s = +1/2$
 (b) $n = 2, l = 1, m = 0, s = +1/2$
 (c) $n = 2, l = 0, m = 1, s = -1/2$
 (d) $n = 3, l = 1, m = -1, s = -1/2$
- (14) The correct set of quantum numbers for the unpaired electron of chlorine atom is
- | | n | l | m |
|-----|-----|-----|-----|
| (a) | 2 | 1 | 0 |
| (b) | 2 | 1 | 1 |
| (c) | 3 | 1 | 0 |
| (d) | 3 | 1 | 1 |
- (15) The impossible set of quantum numbers is
- | | n | l | m | s |
|-----|-----|-----|-----|--------|
| (a) | 3 | 2 | -2 | $+1/2$ |
| (b) | 4 | 0 | 0 | $+1/2$ |
| (c) | 3 | 3 | 2 | $+1/2$ |
| (d) | 5 | 3 | 0 | $-1/2$ |
- (16) The two electrons occupying an orbital are distinguished by
 (a) Principal quantum number
 (b) Azimuthal quantum number
 (c) Magnetic quantum number
 (d) Spin quantum number
- (17) The maximum number of electrons that can be present in an orbital with $s = +1/2$ and $l = 2$
 (a) 1 (b) 3
 (c) 5 (d) 7
- (18) The quantum number which is equal for all the d-electrons in an atom is
 (a) l (b) m
 (c) s (d) none
- (19) Which of the following is impossible?
 (a) 4f (b) 5g
 (c) 2d (d) 6p
- (20) The $(n + l)$ value for 4f - orbital is
 (a) 4 (b) 5
 (c) 6 (d) 7
- (21) Which one of the following set of quantum numbers is not possible for a 4p electron?
 (a) $n = 4, l = 1, m = +1, m_s = +1/2$
 (b) $n = 4, l = 1, m = 0, m_s = -1/2$
 (c) $n = 4, l = 1, m = +2, m_s = +1/2$
 (d) $n = 4, l = 1, m = -1, m_s = -1/2$
- (22) Which of the following configuration is not possible?
 (a) $2p^2$ (b) $3f^7$
 (c) $3d^5$ (d) $4p^6$
- (23) If r is the radius of the first orbit, the radius of n th orbit of the hydrogen atom will be
 (a) $r n^2$ (b) $r n$
 (c) r / n (d) $r^2 n^2$
- (24) The maximum probability of finding an electron of a particular energy in an orbital is about
 (a) 80% (b) 85%
 (c) 95% (d) 99%
- (25) The total number of 'p' electrons present in phosphorous ($Z = 15$) atom is
 (a) 9 (b) 2
 (c) 8 (d) 3
- (26) Which atom has as many s-electrons as p-electrons?
 (a) H (b) N
 (c) Na (d) Mg
- (27) An atom differs from its ion in
 (a) nuclear charge (b) mass number
 (c) number of electrons (d) number of neutrons
- (28) Only paired electrons are found in
 (a) atom with atomic number 22
 (b) nitride ion
 (c) atom with valence configuration $3s^2 3p^4$
 (d) none
- (29) Identify the incorrect match for Zn ($Z = 30$)
- | Values of quantum numbers | Number of electrons with the given quantum numbers |
|--------------------------------------|--|
| (1) $l = 0$ | (a) 8 |
| (2) $l = 1, m = 1$ | (b) 4 |
| (3) $n = 3, l = 1$ and $2, s = +1/2$ | (c) 8 |
| (4) $m = 0$ | (d) 16 |

(30) Identify the incorrect match.

List - 1

- | | |
|---|--------|
| (1) Total number of orbitals with $(n + l)$ value = 5 | (a) 9 |
| (2) No. of vacant orbitals present in an atom with $Z = 14$ | (b) 6 |
| (3) No. of orbitals completely filled with electrons in an atom with $Z = 24$ | (c) 15 |
| (4) No. of degenerate orbitals present in d-sub shell | (d) 5 |

(31) In which of the following Aufbau principle is violated?

	2s		2p	
(a)	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow$	$\uparrow$
(b)	$\uparrow$	$\uparrow \downarrow$	$\uparrow$	$\uparrow$
(c)	$\uparrow \downarrow$	$\uparrow$	$\uparrow$	$\uparrow$
(d)	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow \downarrow$	$\uparrow$

(32) The configuration of $1s^2 2s^2 2p^5 3s^1$ shows

- (a) ground state of fluorine atom
 (b) excited state of fluorine atom
 (c) excited state of neon atom
 (d) excited state of oxygen atom

(33) The set of quantum numbers denoting highest energy

- (a) 3, 2, 1, $-\frac{1}{2}$ (b) 4, 2, -1, $-\frac{1}{2}$
 (c) 4, 1, 0, $-\frac{1}{2}$ (d) 5, 0, 0, $-\frac{1}{2}$

(34) Which of the following ions is not isoelectronic with O^{2-}

- (a) N^{3-} (b) F^-
 (c) Ti^+ (d) Na^+

II. Give one word answers

- (i) The energy required to add an electron to the valence orbit of a neutral gaseous atom in its ground state.
 (ii) The splitting of spectral lines in a magnetic field.
 (iii) The state of hydrogen atom when the only electron in the atom transits to $n = 2$.

III. Match the following.

- | | |
|---|------------------------|
| (1) Column A | Column B |
| (i) K-shell $\rightarrow$ M-shell electron transition | (a) $\frac{2h}{2\pi}$ |
| (ii) angular momentum in $n = 2$ | (b) absorption spectra |

(iii) maximum number of electrons in d-orbital that can have same spin (c) emission spectra

(iv) maximum number of electrons in p-orbital that can have $m = 0$ d) 2
 (e) 5

(f) $\frac{h}{2\pi}$

(2) Set I

- (i) Zeeman effect
 (ii) degenerate orbitals

(iii) Stark effect
 (iv) $l = 1$

Set II

- (a) all 3d orbitals
 (b) splitting of atomic spectral lines in electric field
 (c) all p-orbitals
 (d) splitting of atomic spectral lines in magnetic field

(3) Set A

- (i) PQN values
 (ii) MQN values
 (iii) AQN values
 (iv) SQN values

B

- (a) $\pm \frac{1}{2}$
 (b) 0 to infinity
 (c) 0 to $(n - 1)$
 (d) $(2l + 1)$
 (e) 1 to $(n - 1)$
 (f) 1 to infinity

(4) The electronic configuration of zinc atom in its ground state is $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$. In the dipositive ion the correct match is (more than one match is possible)

Set I

- (i) the number of shells occupied
 (ii) electrons with same spin
 (iii) completely filled orbitals
 (iv) unpaired electrons

Set II

- (a) 15
 (b) 0
 (c) 6
 (d) 3
 (e) 4
 (f) 14

IV. State whether the following statements are True or False

- (i) The correct electronic configuration of an atom is $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ but not $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$.
 (ii) When 5p orbitals are filled completely, the next electron enters into 5d.
 (iii) The number of orbitals in $l = 3$ is 5.

V. Choose the correct word that fills the blank.

- (1) Cathode rays have _____ mass and _____ charge.
 (negligible / unit, positive / negative)

- (2) The ratio of the specific charges of a proton and α -particle is _____. (2:1 / 1:2)
- (3) The mass of a neutron is of the order of _____. (10^{-24}kg / 10^{-27}kg)
- (4) Rutherford's α -particle scattering experiment showed for the first time that the atom has _____. (neutrons / nucleus)
- (5) A beam of light falling on an atom of cesium causes electron emission. This is called _____. (photoelectric effect / electron transition)
- (6) The spectrum of Be^{3+} , Li^{2+} , He^{+} is expected to be similar to that of _____. (visible light / hydrogen atom)
- (7) As value of n increases, energy difference between the adjacent levels in an atom _____ (increases / decreases).
- (8) The orientation of the orbital in space is governed by _____ Quantum Number (Magnetic / Azimuthal).
- (9) Spin quantum number has _____ value (fractional / integral).
- (10) The magnetic quantum number for the valence electron of sodium atom is _____ (+1 / 0).

VI. Find the odd one out

- (i) $3p_x$, $3d_{xy}$, $3d_{yz}$, $3d_{xz}$, $3d_{x^2-y^2}$,
- (ii) neutrons, protons, electrons, mesons
- (iii) $1s^1$, $[\text{Ar}] 4s^1 3d^5$, $[\text{Ne}] 3s^2 3p^5$, $1s^2$, $[\text{He}] 2s^2 2p^6$

VII. Fill in the blanks

- (1) The d-orbital with the orientation along x and y-axes is _____.
- (2) If an electron has Spin Quantum Number of $+\frac{1}{2}$ and Magnetic Quantum Number of -1 , then it cannot be present in _____.
- (3) Energy of atomic orbitals in the n^{th} shell is of the order _____.
- (4) For a particular principal quantum level, the energy will be maximum for _____.
- (5) A species M^{2+} has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$. The atomic number of M is _____.
- (6) The total number of electrons associated with quantum number n is _____.
- (7) For a particular value of Azimuthal Quantum Number, l , the number of possible values for Magnetic Quantum Number is given by $m =$ _____.
- (8) An electron with the quantum numbers $n = 4$, $l = 3$, $m = 0$ and $s = -\frac{1}{2}$ is in _____.
- (9) The permissible values of l for $n = 3$ are _____.
- (10) An atom has the following electronic configuration: K(2), L(8), M(11), N(2). The total number of electrons with $l = 2$ will be _____.

VIII. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, Statement R is true; Statement R is correct explanation for statement A

Choose B if Statement A is true, statement R is true; Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D if Statement A is false, statement R is true

- (1) **Statement A:** Bohr's orbits are called stationary orbits.

Statement R: Electrons remain stationary in these orbits for some time.

- (2) **Statement A:** Hydrogen has only one electron in the orbit but produces several spectral lines.

Statement R: There are many excited energy levels available in a sample of Hydrogen gas.

- (3) **Statement A:** The p-orbital has dumb-bell shape.

Statement R: Electron present in the p-orbital can have any one of the three values of magnetic quantum numbers (0, +1, -1)

- (4) **Statement A:** For $n = 3$, l may be 1, 2 and ' m ' may be 0: (2, 1 and 0)

Statement R: For each value of n there are 0 to $(n - 1)$ possible values of l . For each value of l ' m ' values are $-1 \dots 0 \dots +1$

- (5) **Statement A:** A spectral line will be seen for $2p_x$, to $2p_y$ transition.

Statement R: Energy is released in the form of wave of light when electron drops from $2p_x$ to $2p_y$ orbital.

- (6) **Statement A:** The energy of electron is largely determined by its principal quantum number.

Statement R: The principal quantum number is a measure of the most probable distance of finding the electron around the nucleus

- (7) **Statement A:** The electronic configuration of nitrogen atom is represented as $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ but not as $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^0$

Statement R: The electronic configuration of ground state of an atom is the one with greatest multiplicity.

- (8) **Statement A:** The pairing of electrons in the orbitals of a sub-shell does not occur until all the orbitals are singly occupied.

Statement R: Singly occupied orbitals must have the electrons with parallel spins.

- (9) **Statement A:** The electronic configuration of boron cannot be $1s^2 2s^3$.

Statement R: No two electrons can have the same set of all the four quantum numbers.

- (10) **Statement A:** The ground state configuration of Cr is $3d^5 4s^1$.

Statement R: A set of half filled orbitals with their spin parallel provide extra stability to the system.

IX. Answer the following questions.

- What is the maximum number of electrons possible in the last and 5th shell of an atom?
- Write the electronic configuration of the following atoms / ions : ${}_{18}\text{Ar}^{40}$, Na^+ , H^+ .
- How is energy transmitted?
- Explain photoelectric effect?
- Explain black body radiation?
- What is the extent of dispersion of different wavelengths?
- What are atomic spectra?
- What are absorption spectra and what are its characteristics?
- What are emission spectra and what are its characteristics?

- (10) Why is Bohr's Atomic Model applicable only to single electron species like H-atom and not to multi-electron species like say Na^+ ?

- (11) Given that the 'diameter' of the atom is of the order of 10^{-8}cm and that of the nucleus is 10^{-13}cm find the ratio of their volumes. How many times is the atom bigger than the nucleus?

- (12) Using the formula, density = mass / volume, find the density of the nucleus of H-atom given that the mass of a proton is $1.66 \times 10^{-24}\text{gm}$ and the diameter of its nucleus is 10^{-13}cm . Do you agree that the densest substance on earth is the nucleus of an atom? Can you think of anything denser?

- (13) Differentiate between orbit and orbital.

- (14) A neutral atom has a nucleus with a nuclear charge 13 times and mass 27 times that of hydrogen nucleus. How many electrons would be present in the stable positively charged ion. [Hint: $Z = 13$]

- (15) State and explain the principle, which restricts the number of electrons in an orbital to two.

- (16) Why is Bohr's atomic model superior to Rutherford's atomic model?

- (17) If the radius of the first Bohr orbit of H-atom is 0.53 find the radius of the third orbit of H-atom.

- (18) Calculate the wavelength of radiation emitted when an electron transits from third to first orbit of H-atom. ($R = 109737 \text{ cm}^{-1}$)

- (19) Find frequency of spectral line obtained in the transition $n = 5 \rightarrow 2$ in H-atom. ($R=109737 \text{ cm}^{-1}$).

KEY TO EXERCISE

- I.** (1) b (2) d (3) d (4) b (5) b (6) a (7) a (8) d (9) a
 (10) b (11) c (12) d (13) c (14) c (15) c (16) d 17) c (18) a
 (19) c (20) d (21) c (22) b (23) a (24) c 25) a (26) d (27) c
 (28) b (29) b (30) c (31) b (32) c (33) b (34) c

- II.** i. electron affinity ii. Zeeman Effect iii. excited state

- III.** (1) i-b ii. a iii. e iv d (2) i. d ii. c iii. b iv. c
 (3) i. f ii. d iii. c iv. a (4) i. e ii. a iii. a iv. b

- IV.** i. true ii. false iii. false

- V.** 1-negligible, unit negative 2. 1:2 3. 10^{-27}kg 4. nucleus 5. photoelectric effect
 6. hydrogen atom 7. decreases 8. Magnetic 9. fractional 10. 0

- VI.** i. $3p_x$ ii. mesons iii. $[\text{Ar}] 4s^1 3d^5$ (Anomalous configuration)

- VII.** 1. d_{x-y} 2. s-orbital 3. $s < p < d < f \dots$ 4. orbital with $l = (n - 1)$
 5. 29 6. $2n^2$ 7. $(2l + 1)$ 8. 4f orbital 9. $l = 0, 1, 2$ 10. 3

- VIII.** (1) C (2) A (3) B (4) A (5) D (6) C (7) A (8) B (9) B (10) A

2

Periodic Table

2.0 INTRODUCTION

A scientific study of the more than 110 elements known would be a very difficult task. The scientific study of all these elements will be easy if they are classified based on some characteristic features. In the previous class we have seen that the earlier classification had some defects. The Modern Periodic Table is currently accepted as the best method of classification of elements. We will now study the Modern Periodic Table in more detail particularly with respect to periodicity and periodic properties.

2.1 IMPORTANCE OF CLASSIFYING ELEMENTS

Classification of elements has the following advantages.

- Classification of elements helps us to study them better.
- Classification of elements helps in correlating properties of the elements.
- Classification of elements helps to establish relationships between them.

2.2 EARLIER ATTEMPTS AT CLASSIFICATION

Many attempts were made to classify the elements on the basis of some scientific factors. Each of these early attempts at classification had their merits

and demerits. As the elements were slowly discovered, their properties were studied scientifically.

All the initial attempts at classification were based on a simple observation. It appeared that all elements had a unique atomic weight. Hence many of the earlier classifications made the atomic weights of the elements as the basis of classification.

It was later realized that atomic number of an element is a better basis for classification. The Modern Periodic Table classifies elements based on atomic number.

* Some of the important earlier attempts at classifications of elements are listed below.

- Dobereiner's Triads, 1817
- Newland's Law of Octaves, 1869
- Meyer's Periodic Law, 1869
- Mendeleev's Periodic Law, 1869
- Modern Periodic Table

I. Dobereiner's Triads, 1817

Dobereiner classified elements into groups of three (*triad*) where

'The atomic weight of the middle element was the average of the other two elements.'

Examples: Three examples of Dobereiner Triad are given below. The atomic weights are given in brackets following the symbols of the elements.

	First element	Middle element	Third element	Average calculation
(1)	Ca(40),	Sr (88),	Ba (137)	$\frac{40+137}{2} = \frac{177}{2} = 88$
(2)	Li (7),	Na (23),	K (39)	$\frac{7+39}{2} = \frac{46}{2} = 23$
(3)	Cl (35.5),	Br (80)	I (127)	$\frac{35.5+127}{2} = \frac{162.5}{2} = 80$

Merits - The main achievement of this classification is that it recognised a relationship between properties of elements and their atomic weights.

Drawbacks of this classification – The drawbacks of this classification are as follows.

- Some elements which are dissimilar were

being grouped into a triad.

(ii) There are many elements that cannot be grouped into triads as proposed by Dobereiner.

II. Newland's Law of Octaves, 1863

Newland arranged the known elements in increasing order of their atomic weights and found that

'The properties of the elements recurred after every seven elements.'

Example:

An octave is formed by the elements

H, Li, Be, B, C, N, O

followed by the second octave

F, Na, Mg, Al, Si, P, S.

Here, hydrogen (H) and fluorine (F) are similar in some properties. Similarly, lithium (Li) and sodium (Na) are similar in some properties.

Merits - The main achievement of this classification was that it improved upon the earlier attempt by Dobereiner using atomic weight as a basis of classification. Further it recognised the repetition of certain properties periodically.

Drawbacks of this classification – The drawbacks of this classification are as follows :

(i) This classification did not include elements beyond atomic weight 40 (calcium).

(ii) This classification could not classify or place the transition elements.

III. Lothar Meyer's classification, 1869

Meyer found that the properties of elements are directly dependent on atomic volume.

He stated that *'atomic volume is the periodic function of atomic weight.'*

However the credit for classifying elements on the basis of atomic weights in a new way does not go to Meyer but to Mendeleev as he published his works a few months later.

IV. Dimitri Mendeleev's classification, 1869

Mendeleev's classification is based on the principle that

'The physical and chemical properties of the elements are a periodic function of their atomic weights'.

A modified version of Mendeleev's Periodic Table based on atomic weights giving due importance to similarity of chemical properties was in use for quite some time.

Drawbacks of this classification

There are several drawbacks of this classification.

- (i) Anomalous pairs: $_{18}\text{Ar}$ was placed before $_{19}\text{K}$ although their respective atomic weights were 40 and 39.
- (ii) Position of hydrogen: Hydrogen was placed in both groups IA and VIIA.
- (iii) Position of rare earths was not clear. They were placed in Group IIIA.
- (iv) Positioning of the isotopes (atoms of the same elements with different mass numbers) was not clear.
- (v) Transition elements were placed without reasonable justification into Group VIII.
- (vi) Some elements with hardly any similarities were placed together. For example alkali metals and Cu, Ag, Au were kept in Group I.
- (vii) The classification does not give importance to electronic configuration of the elements which is a very important factor in deciding chemical property.

2.3 MODERN PERIODIC TABLE

The Modern Periodic table is also known as the Long Form of the Periodic Table. The classification is based on the principle that **'The physical and chemical properties of the elements are a periodic function of their atomic numbers'.**

In the Modern Periodic table elements are arranged in increasing order of their atomic numbers.

Advantage of using atomic number instead of atomic weight

Atomic number gives the number of protons in the atom of the element. Atomic number is a positive whole number. Atomic weight can be a fraction. For example the atomic weight of chlorine is 35.5. The advantages of arranging elements in increasing order of atomic number rather than atomic weight are as follows :

- (i) Since atomic number is a whole number we can arrange the elements in successive serial order.
- (ii) If elements are arranged in increasing order of atomic weight, new elements as and when discovered will necessitate a rearrangement.
- (iii) In the Modern Periodic Table a place is kept blank for that atomic number for which new elements have not yet been discovered.

Characteristics of the Modern Periodic Table

- In the Modern periodic table, the elements are arranged in increasing order of their atomic numbers.
- The vertical columns are called **GROUPS**
- The horizontal columns are called **PERIODS**.
- There are 18 groups and 7 periods.
- From left to right the **atomic number increases by 1** for each successive element.
- The number of elements in each period is as follows:

Period:	1	2	3	4	5	6	7
Number of elements:	2	8	8	18	18	32	20
							* (incomplete period)

- The first period contains only 2 elements.
- The second and third period contains 8 elements.
- The 4th, 5th, 6th periods contain the **transition elements** - each series containing 10 transition elements.
- The 6th period is the longest and contains the first set of **inner-transition elements—the Lanthanides**—14 elements.
- The 7th period is an incomplete period and contains the second set of **inner-transition elements—the Actinides**—14 elements.
- The two sets of inner transition elements are placed separately at the bottom of the table.

The Modern Periodic Table

1 ← Modern Group No. 1A ← Old Group No.																		18 0	
1	2											13	14	15	16	17	18		
1 H Hydrogen 1.00794	2 He Helium 4.002602											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00644	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797		
3	4											11	12	13	14	15	16	17	18
1 Li Lithium 6.941	2 Be Beryllium 9.012282											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00644	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797		
11	12											13	14	15	16	17	18		
1 Na Sodium 22.989768	2 Mg Magnesium 24.3050											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00644	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797		
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36		
1 K Potassium 39.0983	2 Ca Calcium 40.078	3 Sc Scandium 44.955910	4 Ti Titanium 47.88	5 V Vanadium 50.9415	6 Cr Chromium 51.9961	7 Mn Manganese 54.938045	8 Fe Iron 55.847	9 Co Cobalt 58.933195	10 Ni Nickel 58.69	11 Cu Copper 63.546	12 Zn Zinc 65.38	13 Ga Gallium 69.723	14 Ge Germanium 72.61	15 As Arsenic 74.921595	16 Se Selenium 78.96	17 Br Bromine 79.904	18 Kr Krypton 83.80		
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54		
1 Rb Rubidium 85.4678	2 Sr Strontium 87.62	3 Y Yttrium 88.90584	4 Zr Zirconium 91.224	5 Nb Niobium 92.90638	6 Mo Molybdenum 95.94	7 Tc Technetium (98)	8 Ru Ruthenium 101.07	9 Rh Rhodium 102.90550	10 Pd Palladium 106.42	11 Ag Silver 107.8682	12 Cd Cadmium 112.411	13 In Indium 114.818	14 Sn Tin 118.710	15 Sb Antimony 121.757	16 Te Tellurium 127.60	17 I Iodine 126.90447	18 Xe Xenon 131.29		
55	56	57	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86		
1 Cs Cesium 132.90545	2 Ba Barium 137.327	3 La Lanthanum 138.90547	4 Hf Hafnium 178.49	5 Ta Tantalum 180.94788	6 W Tungsten 183.84	7 Re Rhenium 186.207	8 Os Osmium 190.23	9 Ir Iridium 192.222	10 Pt Platinum 195.078	11 Au Gold 196.966569	12 Hg Mercury 200.59	13 Tl Thallium 204.3833	14 Pb Lead 207.2	15 Bi Bismuth 208.98039	16 Po Polonium 209	17 At Astatine (210)	18 Rn Radon (222)		
87	88	89	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118		
1 Fr Francium (223)	2 Ra Radium (226)	3 Ac Actinium (227)	4 Rf Rutherfordium (261)	5 Db Dubnium (262)	6 Sg Seaborgium (266)	7 Bh Bohrium (264)	8 Hs Hassium (277)	9 Mt Meitnerium (268)	10 Ds Darmstadtium (271)	11 Rg Roentgenium (272)	12 Uu Ununbium (285)	13 Uut Ununtrium (284)	14 Uuq Ununquadium (289)	15 Uup Ununpentium (288)	16 Uuh Ununhexium (289)	17 Uus Ununseptium (286)	18 Uuo Ununoctium (289)		

Thick line shown as a stepwise ladder separates the metals from non-metalloids.

f-Block Inner-Transition Elements

58 Ce Cerium 140.116	59 Pr Praseodymium 140.90768	60 Nd Neodymium 144.242	61 Pm Promethium (145)	62 Sm Samarium 150.127	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.92534	66 Dy Dysprosium 162.500	67 Ho Holmium 164.93032	68 Er Erbium 167.259	69 Tm Thulium 168.93421	70 Yb Ytterbium 173.04	71 Lu Lutetium 174.967
90 Th Thorium 232.0377	91 Pa Protactinium 231.03688	92 U Uranium 238.02891	93 Np Neptunium (237)	94 Pu Plutonium (244)	95 Am Americium (243)	96 Cm Curium (247)	97 Bk Berkelium (247)	98 Cf Californium (251)	99 Es Einsteinium (252)	100 Fm Fermium (257)	101 Md Mendelevium (258)	102 No Nobelium (259)	103 Lr Lawrencium (262)

2.4 CONCEPT OF DIFFERENTIATING ELECTRON

Differentiating Electron is the last electron in the atom as the shells are progressively filled up.

For example the eleventh electron in M-shell of sodium atom is the differentiating electron that differentiates it from the preceding element:

$_{10}\text{Ne}$ (2, 8) and $_{11}\text{Na}$ (2, 8, 1)

2.5 SIGNIFICANCE OF SUFFIXES IN GROUP NUMBERS

Significance of suffix A in Group number

When the differentiating electron is in *the last shell*, the group number gives the number of valence electrons with the suffix A.

Example: In all the elements of Group IA

(i) the differentiating electron is in *the last shell*

(ii) the number of valence electron is 1.

In all the elements of Group IIA

(i) the differentiating electron is in *the last shell*

(ii) the number of valence electrons is 2.

In all the elements of Group IIIA

(i) the differentiating electron is in *the last shell*

(ii) the number of valence electrons is 3.

In all the elements of Group IVA

(i) the differentiating electron is in *the last shell*

(ii) the number of valence electrons is 4.

In all the elements of Group VA

(i) the differentiating electron is in *the last shell*

(ii) the number of valence electrons is 5.

In all the elements of Group VIA

(i) the differentiating electron is in *the last shell*

(ii) the number of valence electrons is 6.

In all the elements of Group VIIA

(i) the differentiating electron is in *the last shell*

(ii) the number of valence electrons is 7.

Significance of suffix B in Group number

When the differentiating electron is in *the second last or third last shell*, the group number gives the number of electrons available for bonding with other elements with the suffix B.

Example: In all the elements of Group IB

(i) the differentiating electron is in *the second last shell*

(ii) the number of electrons available for bonding with other elements is 1.

In all the elements of Group IIB

(i) the differentiating electron is in *the second last shell*

(ii) the number of valence electrons is 2.

In all the elements of Group IIIB

(i) the differentiating electron is in *the second last or third last shell*

(ii) the number of valence electrons is 3.

In all the elements of Group IVB

(i) the differentiating electron is in *the second last shell*

(ii) the number of valence electrons is 4.

In all the elements of Group VB

(i) the differentiating electron is in *the second last shell*

(ii) the number of valence electrons is 5.

In all the elements of Group VIB

(i) the differentiating electron is in *the second last shell*

(ii) the number of valence electrons is 6.

In all the elements of Group VIIB

(i) the differentiating electron is in *the second last shell*

(ii) the number of valence electrons is 7.

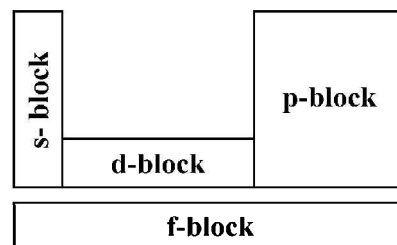
2.6 BLOCKS IN THE MODERN PERIODIC TABLE

In the Modern periodic table, the elements are divided into distinct blocks based on the orbital of the differentiating electron. (see valence configurations)

s-Block elements: When the differentiating electron enters the s-orbital the elements are called s-block elements. In Group IA and IIA (two in all) the differentiating electron enters the s-orbital and hence these elements are also called s-block elements. The valence configuration is ns^1 or ns^2 .

p-Block elements: When the differentiating electron enters the p-orbital the elements are called p-block elements. In Group IIIA, IVA, VA, VIA, VIIA and 0 (six in all) the differentiating electron enters the p-orbital and hence these elements are called p-block elements. The valence configuration is np^1 , np^2 , np^3 , np^4 , np^5 or np^6 . (i.e. np^1 to 6)

d-Block elements: When the differentiating electron enters the d-orbital the elements are called d-block elements. In Group IB to VIIB and Group VIII comprising three vertical columns (ten groups in all) the differentiating electron enters the d-orbital and hence these elements are also called d-block elements. The valence configuration is ns^1 or $2(n-1)d^1$ to 10 .



f-Block elements: When the differentiating electron enters the f-orbital the elements are called f-block elements. In Group IIIB the differentiating electron enters the f-orbital and hence these

elements are also called f-block elements. It is to be noted that f-block elements fall into only one group (Group IIIB). The valence configuration is $ns^2(n-1)d^0 \text{ or } 1(n-2)f^{2-14}$

The general valence configuration of the s, p, d and f-block elements is tabulated below.

Block	s-block	p-block	d-block	f-block
General valence configuration	$ns^{1 \text{ or } 2}$	$ns^2np^{1 \text{ to } 6}$	$ns^{1 \text{ to } 2}(n-1)d^{1 \text{ to } 10}$	$ns^2(n-1)d^0 \text{ or } 1(n-2)f^{2 \text{ to } 14}$
Level being filled	1	1	2	3
Placement in PT	Left	Right	Middle	Bottom

2.7 REPRESENTATIVE ELEMENTS OR NORMAL ELEMENTS

The representative elements are the elements in which the differentiating electron enters the last shell in the atom.

In other words, the last shell of these elements is incomplete. All the elements of the *s-block* placed to the left and *p-block* placed to the right in the table are Representative Elements. They exclude the zero group of elements at the extreme right.

Characteristics of representative elements

- The differentiating electron enters the valence shell.
- The outer shell is incomplete.
- The representative elements are either s-block or p-block elements.
- The valence configuration is $ns^{1-2} np^{0 \text{ to } 5}$
- The representative elements comprise of a few metals, all non-metals and all the metalloids.

2.8 TRANSITION ELEMENTS

The transition elements are the elements in which the differentiating electron enters the second last shell of the atom.

In other words, the second last shell or penultimate shell of these elements is incomplete. All the elements of the *d-block* placed in the middle of the table are transition elements.

Characteristics of transition elements

- The differentiating electron enters the penultimate or second last shell.
- The second last shell is incomplete.
- Transition elements comprise all the *d-block* elements.

- The valence configuration is $ns^{1 \text{ to } 2}(n-1)d^{1 \text{ to } 10}$.
- All transition elements are hard and dense metals.
- They are good catalysts.
- They form coloured compounds as the electrons in the second last shell (d-electrons) can be excited by absorption of a portion of white light.
- They readily form alloys with other metals. For example bronze is an alloy of copper and zinc.

2.9 INNER TRANSITION ELEMENTS

The inner transition elements are elements in which the differentiating electron enters the third last shell of the atom.

In other words the third last shell or anti-penultimate shell of these elements is incomplete. All the elements of the *f-block* placed at the bottom of the table are inner transition elements.

Characteristics of inner transition elements

- The differentiating electron enters the anti-penultimate or third last shell.
- The third last shell is incomplete.
- Inner transition elements are comprised of all the *f-block* elements.
- The valence configuration is $ns^2(n-1)d^0 \text{ or } 1(n-2)f^{2 \text{ to } 14}$.
- They show similar properties because of the similar electronic configuration of the last two shells.
- All inner transition elements belong to Group III-B.

2.10 INERT GAS ELEMENTS

The inert gas elements are elements which have

a valence configuration of ns^2 or $ns^2 np^6$.

In other words the last shell of these elements has either 2 or 8 electrons.

Characteristics of inert gas elements

- (i) The differentiating electron is either the second or eighth electron in the last shell.
- (ii) The last shell is *complete*.
- (iii) Inert gas elements are all gaseous elements.
- (iv) The valence configuration is ns^2 or $ns^2 np^6$.
- (v) All inert gases show similar properties as the electronic configuration is similar.
- (vi) All inert gas elements belong to Group 0 (zero).

2.11 SPECIAL NAMES OF THE GROUPS

A brief look at the different Groups and the special names given to them is given below :

Alkali Metals—Group IA elements are called Alkali Metals as they form oxides and hydroxides with a strong alkaline nature.

Alkaline Earth Metals—Group IIA elements are called Alkaline Earth Metals as their oxides were known earlier than the metals, their oxides are alkaline and exist in the earth's crust.

Picogens—Group VA elements (N, P, As, Sb and Bi) are called Picogens (Greek for 'suffocation') as the hydrides of this group (NH_3 , PH_3 , and AsH_3) have pungent odour and cause suffocation.

Chalcogens—Group VIA are called Chalcogens (Greek for ore-forming). Oxygen and sulphur are two important elements of this group associated with ores of many metals.

Halogens—Group VIIA elements are known as Halogens (Greek for salt producer) as the elements of this group form salts.

Inert Gas Elements—Group 0 elements are known as Inert / Noble Gas Elements as they are found in very small quantities and are non-reactive.

Coinage Metals—Group IB (Cu, Ag, and Au) are called coinage metals as they are / were used in the manufacture of currency coins.

Ferrous metals and Platinum metals—Group VIII (Fe, Co, Ni / Ru, Rh, Pd / Os, Ir, Pt). This group consists of 3 triads. The first is called ferrous metals. The second and third metals are called Platinum metals.

2.12 PERIODIC PROPERTIES AND PERIODICITY

Periodic properties are those properties that show a **graded variation** in the same group or period.

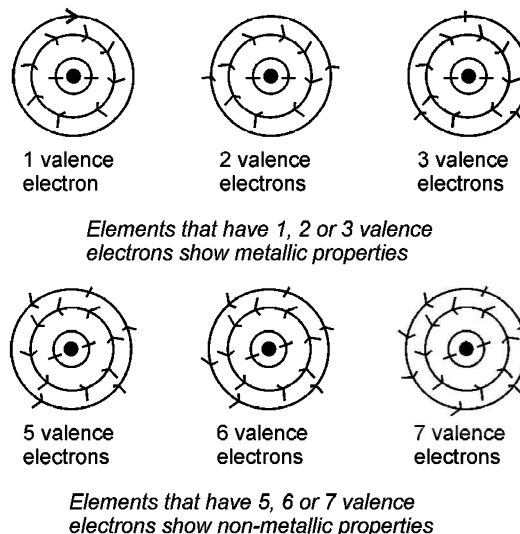
Example: In the third period as we go left from sodium to chlorine the valence electrons increase from 1 to 8.

Periodicity of properties is the **repetition** of properties of the elements after specific intervals of 2, 8, 8, 18, 18 and 32 elements. These numbers are called *magic numbers*.

Example: The element lithium occurs in the same group as hydrogen and has properties similar to hydrogen.

Factors that affect properties of elements

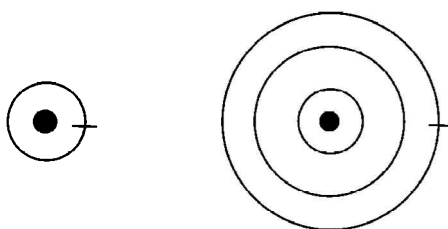
The properties of an element depend on its electronic configuration. The number of valence electrons play a major role in deciding the properties of an element. For example elements with 1, 2 or 3 valence electrons have metallic properties while elements with 5, 6 or 7 valence electrons have non-metallic properties.



The properties of an element show a graded variation as we move from left to right in a given period and repetition as we move down a group. The properties of elements depend on the following factors.

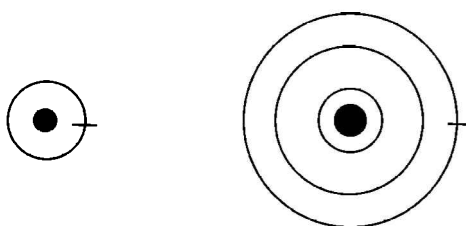
- (i) *size of the atom*
- (ii) *nuclear charge*
- (iii) *screening effect*.

(i) **Size of atom** – As the size of the atom increases the valence electrons are held with weaker force of attraction by the nucleus of the atom.



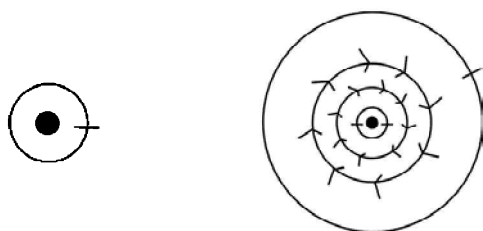
As the number of shells increase, the distance of the valence electron from the nucleus increases. The force of attraction between the nucleus and the electron decreases.

(ii) **Nuclear charge** – As the number of protons in the nucleus (nuclear charge) increases the pull of the nucleus on the valence electron increases.



As the positive charge in the nucleus increases the pull of the nucleus on the valence electrons increases.

(iii) **Screening Effect** – A valence shell electron experiences attractive force due to the nucleus and repulsive force due to the inner transition electrons. The resultant force is thus weakened. This is called screening or shielding effect. As the inner electrons increase in number, the screening effect increases. Due to this effect the Effective Nuclear Charge denoted by Z^* will be less than the actual nuclear charge.



As the number of shells increase, the electrons in the inner shells repel the valence electron with more force. This repulsive force counters the attractive pull of the nucleus as the direction of force is opposite.

2.13 ATOMIC PROPERTIES

Atoms of elements exhibit the following properties.

(1) Atomic radius

Atomic radius is the distance from the centre of the nucleus to the valence orbital.

As atomic radius is a very small quantity it is measured in Angstrom units – $1\text{Å} = 10^{-8}\text{cm}$.

For example the radius of hydrogen atom is 0.53Å or $5.3 \times 10^{-9}\text{cm}$.

(2) Ionisation potential

Ionisation potential is the energy required to pull out an electron from the outermost orbit of a neutral gaseous atom in its ground state.

As the electron absorbs energy before it can be removed from the atom, the process is endothermic. Ionisation potential is measured in electron volts (eV) or kJoules / mole.

(1 eV / mole = 96.5 kJoules / mole)

For example the ionization energy of hydrogen atom is 13.6 eV or 1312.4 kJoules / mole. This means to remove the valence electron from one mole of gaseous hydrogen atoms in the ground state, 13.6 eV of energy is to be supplied.

(3) Electron affinity

Electron Affinity is the energy released when an electron is added to the outermost orbit of a neutral gaseous atom in its ground state.

As energy is released when an electron is added to the valence shell of the atom the process is exothermic. Electron affinity is measured in electron volts (eV) or kJoules / mole.

For example the electron affinity of hydrogen atom is -0.75 eV or $-72.4\text{ kJoules / mole}$.

This means when an electron is added to the valence shell of one mole of gaseous hydrogen atoms in the ground state, 0.75 eV or $72.4\text{ kJoules / mole}$ of energy is released.

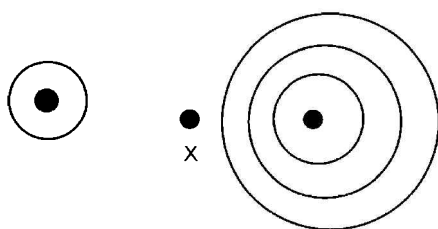
(4) Electronegativity

Electronegativity is tendency of a bonded atom to pull a shared pair of electron towards itself.

Electronegativity is only a measure of the tendency of an atom to pull the shared pair of electrons in a bond. So electronegativity is a relational property. Electronegativity is measured on the Pauling scale and has values from 0 to 4.

For example the electronegativity of hydrogen atom is 2.1.

This means that hydrogen atom tends to pull the electron pair more than the other element in the bond if the other element has lower electronegativity.



Electronegativity of hydrogen atom is 2.1, while that of chlorine atom is 3.0. When hydrogen atom and chlorine atom form a bond by sharing two electrons, the shared pair will be closer to chlorine atom as chlorine atom is more electronegative than hydrogen.

(5) Metallic nature and Non-metallic nature

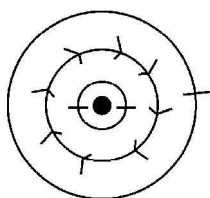
A metal atom loses electrons more easily than a non-metal atom. Conversely a non-metal atom gains electrons more easily than a metal atom.

The ease with which an element loses or gains electrons determines its metallic or non-metallic nature.

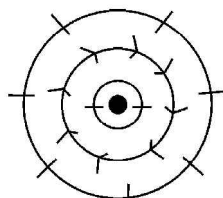
For example sodium atom loses electrons more easily than a chlorine atom. Conversely chlorine atom gains electrons more easily than a sodium atom. Sodium is metallic, chlorine is non-metallic in nature.

(6) Oxidising property and Reducing property

In chemical reactions when an atom loses electrons it transfers it to another atom. The atom that loses electrons is said to be oxidised and the atom which gains the electrons is said to be reduced.



Sodium atom has one valence electron. It has a tendency to lose this electron easily.



Chlorine atom has 7 valence electrons. It has a tendency to gain one electron easily.

When the two atoms come close together sodium atom transfers the valence electron to chlorine.

Sodium is oxidised. Chlorine is reduced. Sodium acts as a good reducing agent as it facilitates the reduction of chlorine by transferring the electron. *The reducing property of sodium is high*

Chlorine acts as a good oxidising agent as it facilitates the oxidation of sodium by accepting the transferred electron. *The oxidising property of chlorine is high.*

(7) Basic and acidic nature of oxides

When an element combines with oxygen it forms an oxide. When metals combine with oxygen they form metallic oxides. When non-metals combine with oxygen they form non-metallic oxides. Most metallic oxides are basic in nature while most non-metallic oxides are acidic nature.

For example sodium metal combines with oxygen to form sodium oxide. Sodium oxide is basic in nature as it reacts with acids forming salt and water.

Sulphur is a non-metal that combines with oxygen to form sulphur dioxide. Sulphur dioxide is acidic in nature as it reacts with bases forming salt and water.

2.14 VARIATION OF ATOMIC RADIUS

Variation of atomic radius in a period

Atomic radius shows a graded decrease across a period such that it decreases up to the halogen element in the period. The largest atomic radius in a period is of the alkali metal while the smallest is of the halogen element.

Example – The elements of the third period show graded variation as given below.

3rd period	Na	Mg	Al	Si	P	S	Cl	Ar	
Atomic-									
radius	⁰ Å	1.86	1.36	1.25	1.17	1.10	1.04	0.99	1.54

Observation – The atomic radius decreases from sodium up to chlorine and then increases with argon.

But the increase is such that the first element in the period sodium is the largest and the halogen element in the period is the smallest.

Similar variation is found to be true for other periods also.

Reason – As we move across a period, the nuclear charge increases successively by one. At the same time an electron is added to the same valence shell. The valence electrons are pulled with more force by the nucleus as they get added to the same shell. This results in shrinking of the atom.

Variation of atomic radius in a group

Atomic radius increases down a group with every successive element.

Example – The elements of Group IA show graded variation as given below.

Group IA	Configuration	Atomic Radius
H	1	0.59 Å
Li	2, 1	1.52 Å
Na	2, 8, 1	1.86 Å
K	2, 8, 8, 1	2.31 Å
Rb	2, 8, 18, 8, 1	2.44 Å
Cs	2, 8, 18, 18, 8, 1	2.62 Å
Fr	2, 8, 18, 32, 18, 8, 1	2.70 Å

Observation – The atomic radius increases from hydrogen to francium.

Similar variation is found to be true for other groups also.

Reason – As we move down a group, shells are added and hence the atomic radius increases.

The size decreases with the increase in nuclear positive charge, due to increase in attractive force.

Ion (10 electrons each)	C ⁴⁺	N ³⁺	O ²⁺	F ⁻	Na ⁺	Mg ²⁺	Al ³⁺	Si ⁴⁺
Number of protons	6	7	8	9	11	12	13	14
Ionic radius (Å)	2.60	1.71	1.40	1.36	0.95	0.65	0.50	0.41

2.15 VARIATION OF IONISATION POTENTIAL

Ionisation potential depends on :

- (1) Atomic radius – Larger the atom, more easy is it to pull out an electron and lesser the ionisation potential value. So smaller atoms have more ionisation potential.
- (2) Nuclear charge – Larger the atom, more the nuclear charge, more the attractive force on the valence electrons, more the energy re-

Ionic Radius:

The cation is smaller than the parent neutral atom as fewer electrons share the attractive force of the positively charged nucleus and so there is a contraction of the ionic size.

Example – The atomic size of Na is 1.86Å, but Na⁺ is 1.02Å.

Similarly, atomic size of Fe is 1.17Å, but, Fe²⁺ is 0.76Å and Fe³⁺ is 0.64 Å.

The anion is larger than the neutral atom as more electrons share the attractive force of the nucleus and so the ion increases in size.

Example – The size of chlorine atom is 0.99, but Cl⁻ is 1.81.

Variation of radius in an isoelectronic series

An isoelectronic series is made up of atoms or ions having the same number of electrons.

quired to pull out an electron, higher the ionisation potential value.

Variation of ionisation potential in a period

Across a period, ionisation potential increases reaching the maximum value with the inert gas element. The increase is not even and sudden increase is seen sometimes. The alkali metal in a period has the lowest and the inert gas element has the maximum ionisation potential value.

Example – The elements of the third period show graded variation as given below :

3rd period	Na	Mg	Al	Si	P	S	Cl	Ar
Valence configuration	3s ¹	3s ²	3s ² 3p ¹	3s ² 3p ²	3s ² 3p ³	3s ² 3p ⁴	3s ² 3p ⁵	3s ² 3p ⁶
Ionisation potential	5.1 eV	7.6 eV	6.0 eV	8.1 eV	11.0 eV	10.4 eV	13.0 eV	15.8 eV
Observations	Minimum							Maximum
	Sharp increase			Sharp increase	Slight decrease			

Observation–Sharp increase is seen between the ionization energy of magnesium and sodium and also between silicon and phosphorous.

There is a small decrease in ionization energy between phosphorous and sulphur. Sodium has minimum and argon has maximum ionization energy.

Similar variation is found to be true for other periods also.

- Reason –
- (i) It is more difficult to remove the electron from the fully filled valence s-orbital of magnesium than from sodium.
 - (ii) It is more difficult to remove an electron from the half filled valence p-orbital in phosphorous than from silicon.
 - (iii) It is more difficult to remove an electron from the half filled valence p-orbital in phosphorous than from sulphur.
 - (iv) It is more difficult to remove the electron from the fully filled valence p-orbital of argon.

Variation of ionization potential in a group

Ionization energy decreases down a group with every successive element.

Example – The elements of Group IA show graded variation as given below :

Group IA	Atomic radius (Å)	Ionisation potential
H	0.59	13.6 eV
Li	1.52	5.4 eV
Na	1.86	5.1 eV
K	2.31	4.3 eV
Rb	2.44	4.2 eV
Cs	2.62	3.9 eV

Observation – The ionization potential decreases from hydrogen to cesium.

Similar variation is found to be true for other groups also.

Reason – As we move down a group atomic radius increases. Due to the increase in atomic radius and the shielding effect of the inner electrons, the pull of the nucleus on the valence electron decreases. Hence ionization potential decreases.

Important points to note

- (i) Ionisation potential is sometimes referred to as ionisation energy.
- (ii) In a given shell the increasing order of energy levels is $s > p > d > f$. The ionisation potential of the orbitals also has the same increasing order. In a given shell, the order of ionisation

potential is $s\text{-electrons} > p\text{-electrons} > d\text{-electrons} > f\text{-electrons}$.

- (iii) In general ionisation potential increases across a period and decreases down a group.
- (iv) First ionisation potential, I_1 , is the minimum energy required for removing an electron from the outermost orbit of the neutral gaseous atom of an element.
- (v) Second ionisation potential, I_2 , is the minimum energy required for removing an electron from the outermost orbit of the uni-positive gaseous ion of the element.
- (vi) For a given atom, $I_2 > I_1$ as the same number of protons attract a lesser number of electrons in the uni-positive ion.
- (vii) Ionisation potential is inversely proportional to the atomic radius.
- (viii) In general, there is a large jump in the ionisation potential value between the first and second element in a period due to filled s-orbital.
- (ix) In a given period, ionisation potential is the highest for inert gas element and least for alkali element.
- (x) Atoms having half-filled or fully filled orbitals are more stable and need more energy for ionisation. (Nitrogen has greater ionisation potential than oxygen due to half-filled p-orbitals in nitrogen atom).

2.16 VARIATION OF ELECTRON AFFINITY

Electron affinity depends on :

- (1) Atomic radius – Larger the atom, more the repulsion and shielding effect of inner electrons, less the tendency to attract incoming electrons, lesser the electron affinity. So, smaller atoms have higher electron affinity values.
- (2) Nuclear charge – Larger the atom, more the nuclear charge, more the tendency to attract electrons.

Variation of electron affinity in a period

Across a period, electron affinity increases reaching the maximum value with the halogen element. The alkali metal in a period has the lowest and the halogen has the highest electron affinity value. Inert gas elements have zero electron affinity values as electron cannot be added to the valence shell.

Example – The elements of the third period show graded variation as given below :

3rd period	Na	Mg	Al	Si	P	S	Cl	Ar
Electron affinity	-0.82eV	0 eV	-0.52 eV	-1.9 eV	-0.8 eV	-2 eV	-3.8 eV	0 e

Observation – Electron affinity values are negative. Electron affinity is zero for magnesium and argon. Electron affinity value is the highest for chlorine.

Similar variation is found to be true for other periods also.

Reason – Electron affinity is highest for chlorine as chlorine requires just one more electron to get 8 electrons in the valence shell.

Electron affinity is zero for magnesium because of filled s-orbital as no more electrons can be added.

Electron affinity is zero for argon because of filled s-orbital and p-orbital.

Variation of electron affinity in a group

Electron affinity decreases down a group with every successive element.

Example – The elements of the Group IA show graded variation as given below :

Group IA	Ionisation potential
H	- 0.75 eV
Li	- 0.61 eV
Na	- 0.82 eV
K	- 0.69 eV

Observation– The electron affinity decreases from hydrogen to cesium.

Electron affinity values of very few elements are known.

Similar variation is found to be true for other groups also.

Reason – As we move down a group there is an increase in the number of shells. The incoming electron is shielded from the nucleus and repelled by inner electrons making it difficult to add electrons. Hence electron affinity decreases.

Important points to note

- Electron affinity values of very few elements are known.
- In general, the second element in a group has a higher electron affinity value than the first after which it decreases. Example, E.A of Cl > F > Br > I.

(iii) Energy is released only when the first electron is added.

(iv) Energy is absorbed when the second electron is added as the incoming second electron has to overcome the repulsion of the uni-negative ion.

(v) In general, electron affinity increases across a period and decreases down a group.

(vi) In a given period, the halogen element has the highest electron affinity value.

(vii) Electron affinity values of very few elements are known as most elements are metals. Metals have a tendency to lose not gain electrons.

2.17 VARIATION OF ELECTRONEGATIVITY

Electronegativity depends on

- Atomic radius – Larger the atom, more the shielding of the nucleus from the shared pair of electrons in a bond, lesser the tendency to attract the electron pair and lesser the electronegativity. So, smaller atoms have higher electronegativity values.
- Nuclear charge – Larger the atom, more the nuclear charge, more the tendency to attract the pair of electrons in a bond.

Variation of electronegativity in a period

Across a period, electronegativity increases reaching the maximum value with the halogen element. The alkali metal in a period has the lowest and the halogen has the highest electronegativity value. Inert gas elements have zero electronegativity as they do not generally participate in bond formation with other elements.

Example – The elements of the third period show graded variation as given below :

3rd period	Na	Mg	Al	Si	P	S	Cl
Electronegativity	0.9	1.2	1.5	1.8	2.1	2.5	3.0

Observation – Electronegativity increases steadily across the period.

Electronegativity of chlorine is the highest in the period.

Electronegativity of sodium is the least in the period.

Similar variation is found to be true for other periods also.

Reason – As we move across a period the metallic character decreases and non-metallic character increases.

Variation of electronegativity in a group

Electronegativity decreases down a group with every successive element.

Example – The elements of Group IA show graded variation as given below :

Group IA	Electronegativity
H	2.1
Li	1.0
Na	0.9
K	0.8
Rb	0.8
Cs	0.7
Fr	0.7

Observation – The electronegativity decreases from hydrogen to francium.

Similar variation is found to be true for other groups also.

Reason –As we move down a group there is an increase in the number of shells. The shared pair of electrons in the bond is shielded from the nucleus and repelled by inner electrons. Hence electronegativity decreases.

Important points to note

- (i) Fluorine is the most electronegative element.
- (ii) Alkali metals in a given period have the least electronegative values.

2.18 SYNOPSIS OF ATOMIC PROPERTIES

The *general trends* in atomic properties in a group and period is tabulated below. You can write short notes in the comments column.

Atomic Property	In a group T → B	In a period L → R	Comments
1. Atomic Radius	↑	↓	
2. Ionisation Potential	↓	↑	
3. Electron Affinity	↓	↑	
4. Electronegativity	↓	↑	
5. Electropositivity	↑	↓	
6. Metallic Character	↑	↓	
7. Non-metallic Character	↓	↑	
8. Acidic nature of Oxides	↓	↑	
9. Basic Nature of Oxides	↑	↓	

2.19 LANTHANIDE CONTRACTION

In the lanthanide elements the differentiating electron enters the 4f orbital. Since these electrons do not effectively screen the valence electrons from the increased nuclear charge due to poor shielding effect and dispersed nature of f-orbitals, the size gradually decreases. Due to this contraction, the atomic size of 5-d transition elements is almost the same as 4-d transition elements. Due to Lanthanide Contraction, 5-d and 4-d transition elements have similar properties. The increase in size that should be there due to the addition of a shell is almost compensated by the lanthanide contraction.

2.20 SOME SPECIAL ATOMS

Isotopes

Atoms of the *same element* having same Atomic Number but different Mass Numbers are called *isotopes*. They have the same number of electrons and protons but differ in the number of neutrons. Example: Chlorine has two isotopic forms: ${}_{17}\text{Cl}^{37}$, ${}_{17}\text{Cl}^{35}$

Isobars

Atoms of *different elements* having different Atomic Numbers but same Mass Number are called *isobars*. They differ in the number of protons and neutrons in the nucleus, but their sum is same.

Example – Argon and calcium are isobars: $_{18}\text{Ar}^{40}$ and $_{20}\text{Ca}^{40}$.

Isotones

Atoms of *different elements* having different Atomic Numbers and Mass Numbers but the same number of neutrons are called *isotones*.

Example: Potassium and calcium are isotones: $_{19}\text{K}^{39}$, $_{20}\text{Ca}^{40}$

Isodiaphers

Atoms of *different elements* having different Atomic Numbers and Mass Numbers but having the same isotopic number are called *isodiaphers*. {Isotopic number is $(n - p)$ or $(A - 2Z)$ }.

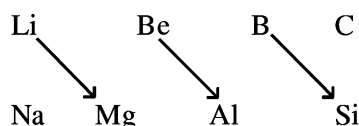
Example – Fluorine and sodium are isodiaphers: $_{9}\text{F}^{19}$, $_{11}\text{Na}^{23}$

Isosters

Isosters are molecules having *same number of atoms and electrons*.

Example: Nitrous oxide and carbon dioxide are isosters: N_2O and CO_2 . Similarly, carbon monoxide and nitrogen are isosters: CO and N_2

Bridge elements: The lighter elements of short periods show similarity of properties when viewed diagonally in the periodic table.



Li and Mg are diagonal neighbours in the periodic table. The two elements form a diagonal bridge between the two adjacent periods. So, they are also called **bridge elements**.

2.21 IMPORTANT POINTS TO REMEMBER

- * The first attempt of classification of elements was made by Dobernien.
- * In Dobernien triad, the atomic weight of the middle element is nearly the arithmetic mean of the first and third elements.
- * Mendeleev and Lothar Meyer used atomic property i.e., atomic weight, for classification of elements.
- * Mendeleev's periodic law states that the properties of elements are in periodic dependence on their atomic weights.
- * Modern periodic law states that the properties of the elements are periodic functions of their

atomic number or electronic configuration.

- * Modern periodic table is divided into 7 periods and 16 groups.

Some interesting facts from the periodic table

- The non-metal having highest melting point is *Diamond*–3727 °C. For metals, it is *Tungsten (W)* 3380°C
- The metal with poorest conductivity is *Lead* and the non-metal with poorest conductivity is *Sulphur*.
- The most abundant elements in the earth's crust are *Oxygen, Silicon, and Aluminium* in that order.
- The compound with highest ionic character is *CsF*. (EN of Cs is 0.7 eV and of F is 4.0 eV).
- The strongest acid is *per chloric acid*. (HClO_4) and strongest alkali is *CsOH*.
- The element that is stored under water is *P* and under kerosene are *K* and *Na*.
- The element that forms maximum number of compounds is *Hydrogen*.
- Non-metals having shine like metals (lustre) are *Graphite* and *Iodine*.
- The best conductor amongst non-metals is *Graphite (allotrope of C)*
- The lightest element and most abundant element in universe is *Hydrogen*.
- The most electropositive and least electronegative element is *Cs*.
- The least electropositive and most electronegative element is *F*.
- *Cesium, Francium and Gallium* have low melting points.
- *Copper, Silver, and Gold* are known as *Coinage metals*.
- The liquid non-metal is *Bromine* and the liquid metal is *Hg*.
- The most rare element on the earth is *Astatine* (a halogen).
- The heaviest naturally occurring element is *Uranium*.
- The best conductor of heat and electricity is *Silver*.
- The most reactive *gaseous* element is *Fluorines*.
- The element that sublimates on heating is *Iodine*.
- Gold and platinum are known as *Noble metal*.
- The most abundant transition element is *Iron*.

- *Osmium* and *Iridium* are the densest metals.
- The most reactive *liquid element* is *Cesium*.
- The most reactive *solid element* is *Lithium*.
- The most *poisonous element* is *Plutonium*.
- *Chlorine* has the highest electron affinity.
- The artificial element is *Technetium (Tc)*.
- The most abundant *metal* is *Aluminium*.
- *He* has the highest *Ionisation potential*.
- The most abundant gas is *Nitrogen*.
- The lightest metal is *Lithium*.
- * The first period has only two elements
- * The second and third periods have 8 elements each.
- * Fourth and fifth periods have 18 elements each.
- * Sixth period has 32 elements.
- * Seventh period is incomplete.
- * Lanthanides and actinides are placed at the bottom of the periodic table in separate blocks.
- * Based on electronic configuration, the elements are classified into four types. They are inert gases, representative elements, transition elements and inner transition elements.
- * Atomic radius is the distance between the centre of the nucleus and outermost orbital
- * Atomic radius is expressed in units of Angstrom.
- * In a period, atomic radius decreases from left to right and in a group it increases from top to bottom.
- * Ionization energy (IE) is the energy required to remove an electron from the outermost orbital in the gaseous state.
- * I E is expressed in eV or k cal mol⁻¹ or k J mol⁻¹
- * In a group ionization energy decreases from top to bottom and in a period ionization energy varies irregularly.
- * Electron affinity (EA) is the energy released when an electron is added to the outermost orbit of a neutral gaseous atom in its ground state.
- * EA is measured in electron volts (eV) or k Joules/mole.
- * EA decreases down a group and increases across a period.
- * Electronegativity (EN) is the ability of the bonded atom to attract the electron density of the shared electrons.
- * EN is expressed in Pauling's scale.
- * In a period EN values increase from left to right of the periodic table and in a group the values decrease from top to bottom.



EXERCISE



I. Choose the correct answer

- (1) The period that contains only gaseous elements is
 - (a) 1
 - (b) 2
 - (c) 3
 - (d) 4
- (2) The longest and shortest periods are
 - (a) 1 and 6
 - (b) 2 and 6
 - (c) 6 and 1
 - (d) 1 and 7
- (3) In the periodic table, the elements are arranged in the periods following the
 - (a) Hund's rule of maximum multiplicity
 - (b) Pauli's exclusion principle
 - (c) Aufbau principle
 - (d) Both (a) and (b)
- (4) The number of elements present in 2nd, 3rd, 4th and 5th periods of modern periodic table respectively are
 - (a) 2, 8, 8 and 18
 - (b) 8, 8, 18 and 32
 - (c) 8, 8, 18 and 18
 - (d) 8, 18, 18 and 32
- (5) The pair of elements with the following atomic

numbers have the same chemical properties

- (a) 13 and 22
 - (b) 3 and 11
 - (c) 4 and 24
 - (d) 2 and 1
- (6) Element with atomic number 15 and mass number 31 is present in
 - (a) Group 5 and period 4
 - (b) Group 5 and period 3
 - (c) Group 15 and period 3
 - (d) Group 15 and period 4
- (7) The total number of gaseous elements are
 - (a) 8
 - (b) 9
 - (c) 10
 - (d) 11
- (8) The atomic number of the element next to be discovered below Radon would be
 - (a) 101
 - (b) 118
 - (c) 173
 - (d) 222
- (9) The artificially created (man-made) element is
 - (a) Ce
 - (b) Lu
 - (c) Tc
 - (d) Pb

- (10) The element with atomic number 117 if discovered, could be placed in _____ family of periodic table.
 (a) carbon (b) nitrogen
 (c) oxygen (d) fluorine
- (11) The atomic number of an element is always equal to
 (a) number of neutrons in nucleus
 (b) half of the atomic weight
 (c) electrical charge of the nucleus
 (d) weight of the nucleus
- (12) The period that includes all types of elements is
 (a) 1 (b) 2
 (c) 6 (d) 7
- (13) Element with electronic arrangement $[\text{Ar}]3d^2 4s^2$ belongs to
 (a) s – block (b) p – block
 (c) d – block (d) f – block
- (14) The general electronic configuration of d – block elements is
 (a) $ns^{1-2}(n-1)d^{1-10}$
 (b) $ns^2(n-1)d^1(n-2)f^{1-10}$
 (c) $ns^{1-2}(n-1)d^{1-9}$
 (d) $ns^{1-2}np^6(n-1)d^{1-10}$
- (15) The general electronic configuration of f – block elements is
 (a) $ns^2np^6(n-1)d^{0-1}(n-2)f^{1-14}$
 (b) $ns^2(n-1)d^{0-1}(n-2)f^{1-14}$
 (c) $ns^2nd^{0-1}nf^{1-14}$
 (d) $ns^2(n-1)d^{0-1}(n-1)f^{1-14}$
- (16) The representative elements get the nearest inert gas configuration
 (a) By losing electrons
 (b) By gaining electrons
 (c) By sharing electrons
 (d) By losing or gaining or sharing electrons
- (17) In transition elements, the shells that are incompletely filled are
 (a) ultimate shell only
 (b) penultimate shell only
 (c) both ultimate and penultimate shells
 (d) outermost three shells
- (18) The period in which only single block elements are present is
 (a) 6 (b) 2
 (c) 3 (d) 1
- (19) Which of the following process refers to ionization potential?
 (a) $X_{(s)} \rightarrow X_{(g)}^+ + e^-$ (b) $X_{(g)} + aq \rightarrow X_{(aq)}^+ + e^-$
 (c) $X_{(g)} \rightarrow X_{(g)}^+ + e^-$ (d) $X_{(g)} + e^- \rightarrow X_{(g)}^-$
- (20) Which of the following processes requires largest amount of energy?
 (a) $\text{Al}_{(g)} \rightarrow \text{Al}_{(g)}^+ + e^-$ (b) $\text{Al}_{(g)}^{2+} \rightarrow \text{Al}_{(g)}^{3+} + e^-$
 (c) $\text{Al}_{(g)}^+ \rightarrow \text{Al}_{(g)}^{2+} + e^-$
 (d) All the processes require same amount of energy
- (21) A sudden jump between the values of second and third ionization energies of an element would be associated with the electronic configuration
 (a) $1s^2 2s^2 2p^6 3s^2 3p^2$ (b) $1s^2 2s^2 2p^6 3s^2$
 (c) $1s^2 2s^2 2p^6 3s^2 3p^1$ (d) $1s^2 2s^2 2p^6 3s^1$
- (22) The ionisation energy of nitrogen is more than that of oxygen because
 (a) of extra stability of half filled p orbitals in nitrogen
 (b) of the small size of nitrogen
 (c) the former contains less no. of electrons
 (d) the former is less electronegative
- (23) When the screening effect increases, ionization energy
 (a) decreases (b) increases
 (c) first increases and then decreases
 (d) remains constant
- (24) Atoms of the following group possess the highest ionization energies
 (a) IA (b) IIA
 (c) VA (d) Zero
- (25) Atoms of the following group possess the lowest ionization energies
 (a) IA (b) IIA
 (c) VA (d) Zero
- (26) First four ionization energy values of an element are 191, 578, 872 and 5972 kcal / mole. The number of valence electrons in the element is
 (a) 4 (b) 3
 (c) 1 (d) 2
- (27) IP_1 value of chlorine is 12eV and electron affinity of chlorine is 3.6eV. Number of chlorine atoms in the gaseous state that can be ionised by utilizing the energy that is liberated in the process $\text{Cl}_{(g)} + e^- \rightarrow \text{Cl}_{(g)}^-$ involving one mole of chlorine atoms is
 (a) 1.8×10^{23} (b) 3
 (c) 3×10^{23} (d) 1.8×10^{22}
- (28) The incorrect statement among the following is
 (a) The first ionization potential of Al is less than the first ionization potential of Mg
 (b) The second ionization potential of Mg is greater than the second ionization potential of Na

- (c) The first ionization potential of Na is less than the first ionization potential of Mg
(d) The third ionization potential of Mg is greater than the third ionization potential of Al
- (29) Elements with high electron affinity values are
(a) good oxidants (b) good reductants
(c) high melting solids
(d) chemically inactive gases
- (30) Elements with high electronegativity are generally
(a) good reductants (b) hard solids
(c) good oxidants (d) soft solids
- (31) Which of the following is the most electronegative element?
(a) O (b) Cl
(c) F (d) N
- (32) In the isoelectronic species the ionic radii ($\text{\AA}$) of N^{3-} , O^{2-} , F^- are respectively given by
(a) 1.36, 1.71, 1.40 (b) 1.36, 1.40, 1.71
(c) 1.71, 1.36, 1.40 (d) 1.71, 1.40, 1.36
- (33) Atomic radii of fluorine and neon in $\text{\AA}$ are
(a) 0.762, 1.60 (b) 1.60, 1.60
(c) 0.72, 0.72 (d) 1.60, 0.72
- (34) The atomic radius decreases in a period due to
(a) increase in nuclear attraction
(b) decreases in nuclear attraction
(c) increases in number of electrons
(d) decrease in number of electrons
- (35) The outermost electronic configuration of the most electropositive element is
(a) ns^1 (b) $ns^2 np^2$
(c) $ns^2 np^3$ (d) $ns^2 np^5$
- (36) Generally non-metal oxides are _____ in nature.
(a) basic (b) acidic
(c) amphoteric (d) neutral
- (37) Acidic nature of the oxides in a group _____ from top to bottom.
(a) increases (b) decreases
(c) remains constant
(d) first increases and then decreases
- (38) Which of the following is not a periodic property?
(a) valency (b) specific heat
(c) ionisation potential (d) atomic size
- (39) Aluminium is diagonally related to
(a) Li (b) Be
(c) C (d) B
- 40) The following are some statements about the modern periodic table.
(i) It is based on the electronic configuration
(ii) It contains 7 periods and 18 groups
(iii) Each period need not begin with group IA element
(a) All are correct
(b) only i and ii are correct
(c) only i is correct
(d) only ii and iii are correct
- (41) Following are the statements about modern periodic table.
(i) It consists of s, p, d and f blocks
(ii) The energy levels filling order in 6th period is 6s, 4f, 5d and 6p
(iii) Group IIIB contains maximum number of elements
(a) only (i) and (ii) are correct
(b) only (i) is correct
(c) only (ii) and (iii) are correct
(d) none are correct
- (42) The following are some statements about noble gases.
(i) They are between halogens and IA group
(ii) Except Rn all the remaining are present in air
(iii) These elements belongs to 17th group in IUPAC system
(a) only (i) and (ii) are correct
(b) only (i) is correct
(c) only (ii) and (iii) are correct
(d) all are correct
- (43) The following are some statements about transition elements.
(i) Transition elements belong to Group IIB.
(ii) In these elements last two shells ns, $(n-1)d$ are partially filled
(iii) Show variable valencies
(a) all are correct
(b) only (iii) is correct
(c) (ii), (iii) are correct
(d) only (i) and (ii) are correct
- II. Give one or two word answers to represent the statements given below.
(i) The repetition of properties after specific intervals (numbers) of elements in the periodic table.
(ii) The gradual variation in properties in the periodic table.
(iii) The energy consideration to add an electron to the valence shell of a neutral gaseous atom.
(iv) The energy consideration to remove an electron from the valence shell of a neutral gaseous atom.
(v) The tendency of an atom to attract the shared pair of electrons in a bond.

III. Match the following.

- (1) Match the general valence configurations in Set I with blocks in the periodic table in Set II

Set I	Set II
(a) $ns^2(n-1)d^{0-1}(n-2)f^{2-14}$	(i) s block
(b) ns^{1-2}	(ii) f block
(c) $ns^2 np^{1-6}$	(iii) d block
(d) $ns^{1-2}(n-1)d^{1-10}$	(iv) p block

- (2) Match the elements in Column I with their Group in Column II

Column I	Column II
(a) O, S, Se, Te, Po	(i) IB
(b) Fe, Co, Ni / Ru, Rh, Pd / Os, Ir, Pt	(ii) VA
(c) N, P, As, Sb, Bi	(iii) VIA
(d) Cu, Ag, Au	(iv) VIII

- (3) Match the elements in Column I with the properties in Column II. More than one match is possible.

Column I	Column II
(a) Inert Gas Elements	(i) low IE
(b) Alkaline Earth Metals	(ii) high IE
(c) Halogens	(iii) radioactive elements
(d) f block elements	(iv) acidic nature

- (4) Match the following

List A	List B
(A) s – block	(1) rare earths
(B) d – block	(2) Noble gases
(C) f – block	(3) strong reducing agents
(D) p – block	(4) $(n-1)s^2p^6d^{10}$
	(5) Complex compounds

Correct matching is

	A	B	C	D
(a)	2	1	4	3
(b)	5	3	1	2
(c)	3	5	1	2
(d)	4	1	2	3

- (5) Match the following in view of highest values

List – 1	List – 2
(A) Ionisation potential	(1) Chlorine
(B) Electronegativity	(2) Cesium
(C) Electron affinity	(3) Helium
(D) Oxidation state	(4) Fluorine
	(5) Osmium

The correct match is

	A	B	C	D
(a)	4	3	2	1
(b)	3	4	1	5
(c)	1	2	3	4
(d)	2	1	4	5

- (6) Match the following in view of periodic number and the orbitals being filled.

List – 1	List – 2
(A) 2	(1) s, f, d
(B) 4	(2) s, f, d, p
(C) 6	(3) s, p
(D) 7	(4) s
	(5) s, d, p

The correct match is

	A	B	C	D
(a)	4	1	3	5
(b)	2	3	4	5
(c)	3	5	2	1
(d)	1	2	4	3

IV. Read the paragraph and answer the questions that follow.

If the electronegativity difference between the two combining atoms is small or negligible, then the bond is purely covalent. However, if the difference between the combining atoms is not small then the bond formed is polar covalent bond. Polar covalent bonds have partial ionic character. But, if the electronegativity difference between the combining atoms is very large then such bonds will be purely ionic. Thus, electronegativity difference of the combining atoms decides the nature of the chemical bond.

- (1) Sodium chloride is an ionic compound. The electronegativity difference of sodium and chlorine atoms is

(a) small	(b) equal
(c) not significant	(d) large

- (2) Hydrogen chloride is a polar covalent molecule. The electronegativity difference of hydrogen and chlorine is

(a) very small	(b) equal
(c) significant	(d) large

- (3) The bond in a homonuclear diatomic molecule is

(a) ionic	(b) covalent
(c) metallic	(d) polar covalent

V. Tick the appropriate word from those given in brackets to fill the blank.

- (1) The property that increases left to right across a period is _____. (reducing property / acidic nature of oxides)
- (2) The element that has the smallest atomic radius is _____. (carbon / fluorine)
- (3) The property that does not reflect periodicity of the elements is _____. (ionisation potential / n : p ratio)
- (4) Across a period, atomic volume _____ (first increases and then decreases / first decreases and then increases).
- (5) All elements in a group have the same _____. (Atomic number / valence electrons).
- (6) All elements in a period have the same _____. (valency / number of shells).
- (7) Hydrogen resembles alkali metals in _____. (atomicity / valency)
- (8) Hydrogen differs from halogens in _____. (position in the table / valency).
- (9) The element having $Z = 37$, belongs to _____. (s-block / p-block)
- (10) In the Periodic Table all non-metals are concentrated in (p-block / d-block)
- (11) The energy indicated in the equation $\text{Cl}_{(g)} \rightarrow \text{Cl}_{(g)}^+ + e^- - 1254 \text{ kJ}$ is equal to _____.
- (12) When 5p orbitals are filled completely differentiating electron enters into _____.
- (13) Lithium is a strong reducing agent because of its _____.
- (14) To create inert conditions in chemical reactions nitrogen gas is used instead of inert gases due to _____.
- (15) The ionisation potential of nitrogen is _____ that of carbon and _____ that of oxygen.
- (16) The species X^{2+} has the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$. The atomic number of X is _____.

VI. Fill in the blanks

- (1) The first transition series starts in the _____ period and the first transition element is _____.
- (2) The number of unpaired electrons in the ground state of the element $Z = 24$ is _____.
- (3) The elements belonging to Group VIA group are called *chalcogens* because _____.
- (4) All artificially prepared elements have $Z >$ _____.
- (5) The chloride of an element A gives a neutral solution in water. The element A most probably belongs to Group _____.
- (6) The element with $Z = 36$ belongs to which period? _____.
- (7) The element with $Z = 50$ belongs to which group? _____.
- (8) Variable valency is the characteristic property of _____ elements.
- (9) Maximum numbers of elements are present in _____ Group.
- (10) Atomic numbers of next two inert gases if discovered will be _____ and _____.

VII. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, Statement R is true; Statement R is correct explanation for statement A.

Choose B if Statement A is true, statement R is true; Statement R is not correct explanation for statement A.

Choose C if Statement A is true, Statement R is false.

Choose D if Statement A is false, statement R is true.

- (1) **Statement – A:** Electron affinity of fluorine is less than that of chlorine.
Statement – R: Chlorine can accommodate an electron by utilizing its vacant 3d-orbital.
- (2) **Statement – A:** The negative ion is always larger than its atom.
Statement – R: As the number of electrons increases, the nuclear charge per electron is reduced.
- (3) **Statement – A:** The second ionization energy of O-atom is greater than that of N-atom.
Statement – R: The half filled p – orbitals cause greater stability for an atom.
- (4) **Statement – A:** The second electron affinity of oxygen is endothermic.
Statement – R: The oxygen is the second highest electronegative element.
- (5) **Statement – A:** Zinc is not a transition element.
Statement – R: Elements with incompletely filled d-orbital are called transition elements.
- (6) **Statement – A:** Ionisation potential of nitrogen is greater than oxygen.
Statement – R: Nitrogen has 5 unpaired electrons.

- (7) **Statement – A:** All inert gas elements are gases.
Statement – R: All inert gas elements have the lowest ionisation potential values in a given period.
- (8) **Statement – A:** Shielding effect increases as we go down the group.
Statement – R: With increase in the number of electrons in the penultimate shell, more is the shielding effect.
- (9) **Statement – A:** The order of ionisation potential across a period is $\text{Li} < \text{B} < \text{Be} < \text{C}$.
Statement – R: Ionisation potential decreases with decrease in atomic size.
- (10) **Statement – A:** F^- ion is larger in size compared to F.
Statement – R: Electron repulsion increases because of addition of electron which results in decrease in effective nuclear charge.

VIII. Answer the following questions.

- Give the benefits of classifying elements.
- Give some of the earlier basis for classification.
- List the demerits of earlier attempts at classification.
- Formation of $\text{F}_{(g)}^-$ from $\text{F}_{(g)}$ is an exothermic process

whereas formation of $\text{O}_{(g)}^{2-}$ from $\text{O}_{(g)}$ is endothermic. Why?

- For nitrogen, I_1 is greater than that of oxygen, whereas, it is opposite for I_2 . Explain.
- Fluorine has less electron affinity than chlorine but electronegativity of fluorine > electronegativity of chlorine. Explain.
- Electronegativity of nitrogen is considerable but it is used as inert gas.
- Across the period usually size of the atom decreases but size of inert gas in a period is greater than that of adjacent halogen in the same period.
- Electron affinity of nitrogen is zero while carbon and oxygen have substantial electron affinity values. Explain.
- Oxidising property of halogens decreases down the group. Explain.
- Differentiate between the following:
 - periodicity and periodic properties
 - orbit and orbital
 - valency and oxidation State
 - atom and molecule
 - oxidation and reduction
 - atomic weight and mass of 1 atom of an element

KEY TO EXERCISE

I. (1) a	(2) c	(3) c	(4) c	(5) b	(6) c	(7) d	(8) b	(9) c
(10) d	(11) c	(12) c	(13) c	(14) a	(15) b	(16) d	(17) c	(18) d
(19) c	(20) b	(21) b	(22) a	(23) a	(24) d	(25) a	(26) b	(27) a
(28) d	(29) a	(30) c	(31) c	(32) d	(33) a	(34) a	(35) a	(36) b
(37) b	(38) b	(39) b	(40) b	(41) b	(42) a	(43) b		
II.	i. periodicity	ii. periodic property	iii. electron affinity	iv. ionisation potential	v. electronegativity			
III. (1)	a. ii,	b. i, c iv,	d. iii	(2) a. iii,	b. iv,	c. ii,	d. i	(3) a. ii,
	b. i,	c. ii and iv.	d. iii	(4) c	(5) b	(6) c		
IV.	1. d	2. c	3. b					
V.	1. acidic nature of oxides	2. fluorine	3. n : p ratio	4. first decreases and then increases				
	5. valence electrons	6. number of shells	7. valency					
	8. position in the table	9. s-block	10. p-block					
VI. (1)	fourth, scandium							
(2)	six unpaired electrons $4s^1 3d^5$							
(3)	Chalcogen is Greek for ore-forming. Oxygen and Sulphur are two important elements of this group associated with ores of many metals. Hence these elements are called chalcogens.							
(4)	92	(5) Group IA or IIA	(6) fourth	(7) Group IVA or 14th Group				
(8)	Transition elements	(9) Group IIIB as they include the Inner Transition elements						
(10)	118 (= 86 + 32), 168 (= 118 + 50)	(11) Ionisation energy	(12) 6s	(13) low ionisation potential				
(14)	Half filled configuration of nitrogen atom	(15) greater than, greater than	(16) 29					
VII. (1)	C	(2) A	(3) A	(4) B	(5) A	(6) C	(6) C	(7) A
	(9) C	(10) A						

3

Chemical Bonding

3.0 INTRODUCTION

Most elements do not occur free in nature but as compounds. Only a very few elements occur free in nature. Elements that occur free are relatively non-reactive. *They do not react easily with other elements and so occur free.* Elements that do not occur free are relatively more reactive. *They react easily with other elements and so occur as compounds.* When elements react with other elements they form chemical bonds.

Isaac Newton in 1704, proposed that atoms attach to each other by some force. Berzelius, in 1819 proposed that elements combine due to their electronegative and electropositive character. By the mid 19th century, the theory of valency was well accepted. According to this theory, compounds form due to attraction between oppositely charged ions.

It was in 1916, G N Lewis developed a concept in which two atoms share one to six electrons, thus forming a bond. That same year, W Kossel put forward a theory similar to that of Lewis. He stated that bonds form by transfer of electrons between atoms. The bonds were due to attractive forces.

Today we know that it is the electrons in the combining atoms that are responsible for bond formation. We will now see why and how actually bonds form and also classify them to make our study easier.

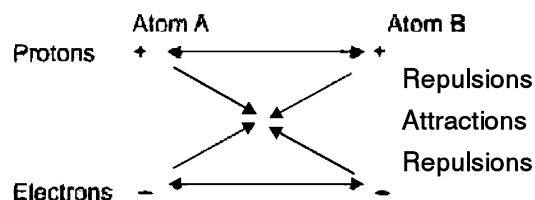
3.1 REASONS FOR FORMATION OF CHEMICAL BOND

A chemical bond is formed due to the attraction between atoms. Atoms combine with other atoms in definite proportion by weight to form molecules due to the following reasons.

- In terms of energy:* Atoms combine as the energy of the molecules is less than the sum of the energies of the individual atoms. So the combined atoms *having less energy are more stable.*
- In terms of electronic configuration:* Atoms combine to get duplet (ns^2) or octet (ns^2np^6)

configuration, which is *more stable as these configurations have less energy.*

- In terms of Quantum Theory and bonding :* When atoms are far apart, there are forces of attraction between electrons and protons in an atom. As two atoms, X and Y approach each other, two types of forces operate.
 - Attractive forces between electrons of one atom and protons of the other atom and vice-versa.
 - Repulsive forces between electrons of the two atoms as well as protons of the two atoms.



At certain internuclear distance between the atoms the attractive and repulsive forces balance each other and cancel out. At this distance the potential energy of the two atoms is the least and a chemical bond forms.

Kossel-Lewis Theory – Simple facts about bond formation bond

In 1916 Kossel and Lewis proposed Chemical Bond Theory based on the valence electrons and

Bond Bohr's atomic model

The postulates of their theory are summarized below.

- ⇒ Atoms do not combine randomly with any other atom.
- ⇒ Whether an atom combines with another atom depends on the electronegativity, electron affinity, ionization energy and other factors. These properties of atoms depend on their electronic configuration.
- ⇒ The number of electrons in the valence shell gives the valency of the atom.
- ⇒ Inert gases have either ns^2 or ns^2np^6 valence configuration. This is known as inert gas configuration. Inert gas elements do not

combine with other elements as they are very stable due to their valence configuration. *They are non-reactive.*

- ⇒ Elements that have less than 8 electrons in the valence shell are not stable. *They are reactive.*
- ⇒ Atoms try to get inert gas configuration in the valence shell by combining with other atoms.
- ⇒ When atoms combine chemically, *transfer or sharing of electrons takes place* such that after the transfer or sharing both the participating atoms get stable inert gas configuration – either duplet or octet.
- ⇒ When two atoms form a bond, there is a redistribution of electrons either by transfer or sharing of electrons between atoms.

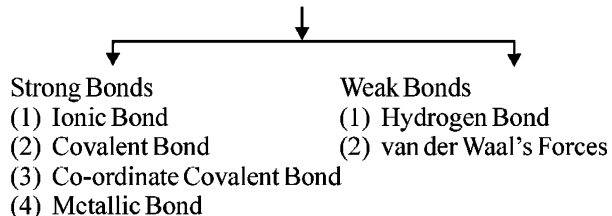
3.2 CLASSIFICATION OF CHEMICAL BONDS

Chemical bonds can be classified broadly into *Strong bonds and Weak bonds* as shown.

⇒ *Strong Bonds* are further classified into Ionic, Covalent and Co-ordinate Bonds.

⇒ *Weak Bonds* are further classified into Hydrogen Bond and van der Waal's Forces.

Classification of Chemical Bonds



We will study each of these bonds separately, excluding metallic bonds. Metallic bonds will be taken up in higher classes. Before we start the study, let us look, at a simple method of representing valence electrons. Lewis introduced a simple method to represent the valence electrons around the symbol of the element.

Lewis dot representation of valence electrons

The representation is tabulated below for the first 20 elements.

Element	Symbol	Electronic configuration	Number of valence electrons	Lewis dot representation of valence electrons
Hydrogen	H	1s ¹	1	H•
Lithium	Li	1s ² 2s ¹	1	Li•
Beryllium	Be	1s ² 2s ²	2	Be••
Boron	B	1s ² 2s ² 2p ¹	3	•B••
Carbon	C	1s ² 2s ² 2p ²	4	•C••
Nitrogen	N	1s ² 2s ² 2p ³	5	•N•••
Oxygen	O	1s ² 2s ² 2p ⁴	6	•O••••
Fluorine	F	1s ² 2s ² 2p ⁵	7	•F•••••
Sodium	Na	1s ² 2s ² 2p ⁶ 3s ¹	1	Na•
Magnesium	Mg	1s ² 2s ² 2p ⁶ 3s ²	2	Mg••
Aluminium	Al	1s ² 2s ² 2p ⁶ 3s ² 3p ¹	3	•Al••
Silicon	Si	1s ² 2s ² 2p ⁶ 3s ² 3p ²	4	•Si••
Phosphorous	P	1s ² 2s ² 2p ⁶ 3s ² 3p ³	5	•P•••
Sulphur	S	1s ² 2s ² 2p ⁶ 3s ² 3p ⁴	6	•S••••
Chlorine	Cl	1s ² 2s ² 2p ⁶ 3s ² 3p ⁵	7	•Cl•••••
Potassium	K	1s ² 2s ² 2p ⁶ 3s ² 3p ⁴ 4s ¹	1	K•
Calcium	Ca	1s ² 2s ² 2p ⁶ 3s ² 3p ⁴ 4s ²	2	Ca••

3.3 IONIC BOND

In 1916, Kossel proposed the theory of chemical bonding based on *transfer of valence electrons*.

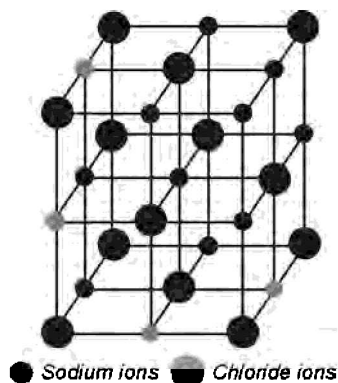
Ionic bond is a chemical bond formed between two atoms by the transfer of electrons from the valence shell of one atom to the valence shell of another atom. The transfer of electron takes place in

Examples :

		Cation formation	Anion formation	Ionic bond formation
1	Ion formation Configuration changes	$\text{Na} - 1e^- \rightarrow \text{Na}^+$ (2, 8, 1) $\rightarrow$ (2, 8) Neon	$\text{Cl} + 1e^- \rightarrow \text{Cl}^-$ (2, 8, 7) $\rightarrow$ (2, 8, 8) Argon	$\text{Na}^+ + \text{Cl}^- \rightarrow \text{NaCl}$
2	Ion formation Configuration changes	$\text{Mg} - 2e^- \rightarrow \text{Mg}^{2+}$ (2, 8, 2) $\rightarrow$ (2, 8) Neon	$\text{O} + 2e^- \rightarrow \text{O}^{2-}$ (2, 6) $\rightarrow$ (2, 8) Neon	$\text{Mg}^{2+} + \text{O}^{2-} \rightarrow \text{MgO}$
3	Ion formation Configuration changes	$2\text{Al} - 6e^- \rightarrow 2\text{Al}^{3+}$ (2, 8, 3) $\rightarrow$ (2, 8) Neon	$3\text{O} + 6e^- \rightarrow 3\text{O}^{2-}$ (2, 6) $\rightarrow$ (2, 8) Neon	$2\text{Al}^{3+} + 3\text{O}^{2-} \rightarrow \text{Al}_2\text{O}_3$
4	Ion formation Configuration changes	$\text{Ca} - 2e^- \rightarrow \text{Ca}^{2+}$ (2, 8, 8, 2) $\rightarrow$ (2, 8, 8) Argon	$2\text{Cl} + 2e^- \rightarrow 2\text{Cl}^-$ (2, 8, 7) $\rightarrow$ (2, 8, 8) Argon	$\text{Ca}^{2+} + 2\text{Cl}^- \rightarrow \text{CaCl}_2$

Nature of Ionic Bonds

Ionic bonds are *non-directional* in nature as they form between cations and anions due to electrostatic forces of attraction that operate in all directions. They form a crystal lattice network of oppositely charged ions in 3-dimensional space.



The distance between sodium and chlorine ions is 2.815 Å units. Each sodium ion is surrounded by 6 equally spaced chloride ions placed at the vertices of a cube. Each chloride ion is surrounded by 6 equally spaced sodium ions placed at the vertices of the cube as shown. Each sodium ion is surrounded and adjacent to 6 chloride ions and vice-versa. The co-ordination number of NaCl crystal is 6.

Crystal Lattice of sodium chloride

In sodium chloride, each Na^+ ion is attracted by

such a way that both the atoms attain inert gas configuration. The actual bond is formed due to electrostatic force of attraction between the resulting two oppositely charged ions.

Ionic bonds are formed due to electrostatic forces of attraction between the oppositely charged ions.

Cl^- ions and vice-versa. This gives a 3-dimensional network of ions called *crystal lattice*. Each sodium ion directly holds six chloride ions by electrostatic forces of attraction and each chloride ion directly holds six sodium ions by electrostatic forces of attraction.

Co-ordination Number is the number of oppositely charged ions adjacent to an ion in a crystal lattice. In NaCl crystal co-ordination number is 6.

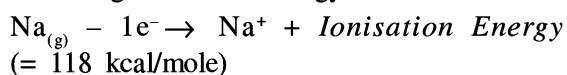
Unit Cell is the smallest unit in a crystal of an ionic compound. The unit cell of NaCl consists of 4 Na^+ and 4 Cl^- ions.

Lattice Energy

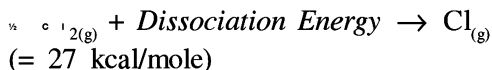
The formation of an ionic bond involves decrease in energy.

Consider the formation of sodium chloride. The energy changes which take place are as follows.

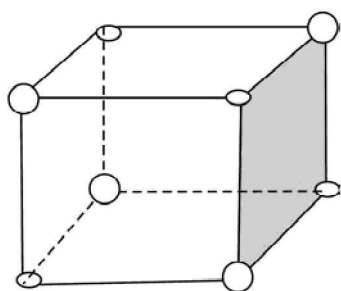
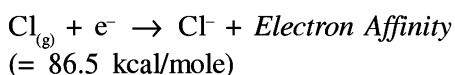
- Solid sodium sublimes to form gaseous sodium. $\text{Na}_{(s)} + \text{Sublimation Energy} \rightarrow \text{Na}_{(g)}$ (= 26 kcal/mole)
- Each sodium atom loses one electron by absorbing ionisation energy.



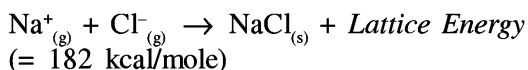
- (iii) Each chlorine molecule dissociates into two atoms of chlorine. As each sodium atom combines with one chlorine atom, only one atom of chlorine is required – only half the dissociation energy is taken.



- (iv) Each chlorine atom gains the electron (lost by sodium) and releases electron affinity energy.



- (v) Several sodium and chloride ions thus formed attract each other forming sodium chloride crystal lattice releasing lattice energy.



$$\text{Total energy absorbed} = 26 + 118 + 27$$

$$= 171 \text{ kcal/mole (steps i + ii + iii)}$$

$$\text{Total energy released} = 86.5 + 182$$

$$= 268.5 \text{ kcal/mole (steps iv + v)}$$

$$\therefore \text{net energy released} = (268.5 - 171)$$

$$= 97.5 \text{ kcal/mole}$$

So, formation of NaCl releases 97.5 kcal/mole of energy *making the bond very strong and hence stable.*



(The negative sign indicates energy is released)

Factors favouring ionic bond formation

Ionic bond formation is favoured between two atoms A and B if

- A has 1, 2 or 3 electrons in its valence shell. (i.e., A is a metal atom).
- B has 5, 6 or 7 electrons in its valence shell. (i.e. B is a non-metal atom).
- A has low ionization energy.

- (iv) B has high electron affinity.

- (v) Ionic bond between A–B has high lattice energy.

- (vi) The sum of the three energies should be negative, i.e. energy is released:

$$\text{IP} + \text{EA} + \text{LE} < 0.$$

Properties of Ionic Compounds

Ionic compounds in general exhibit the following properties.

- (a) Ionic compounds are generally *crystalline solids* at room temperature.

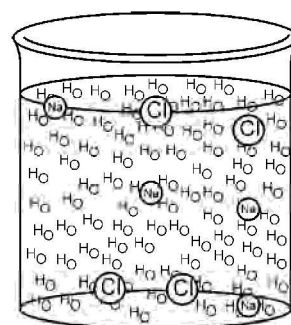
Reason – As the ions are rigidly held in the crystal lattice they lack the freedom of movement present in gases and liquids.

- (b) Ionic compounds are generally *poor conductors of electricity* in the solid state.

Reason – As the ions are held rigidly they can not move and hence cannot conduct electricity.

- (c) In the molten state or in aqueous solution, the ions can conduct electricity.

Reason – In the fused state as temperature increases, the kinetic energy of the ions increases and the electrostatic forces of attraction are overcome and the rigid network is broken. The ions are able to move and hence conduct electricity. In aqueous solution they conduct electricity as they are dissociated into ions.



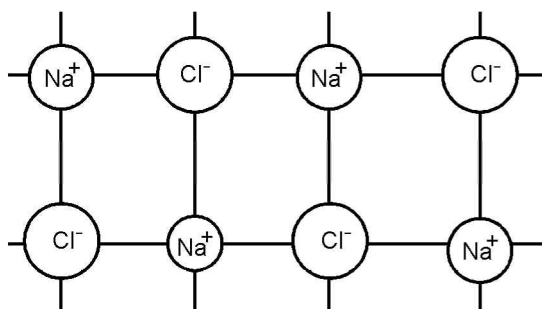
Ionic compounds conduct electricity in aqueous solution.

- (d) Ionic compounds are *hard with high melting point and boiling point.*

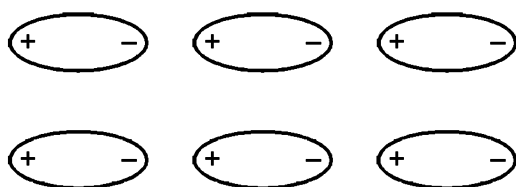
Reason – The ions attract each other with strong electrostatic forces. To overcome these forces so that the ionic compound melts, heating to high temperature is needed.

- (e) Ionic compounds are *soluble in polar solvents* and *insoluble in non-polar solvents*.

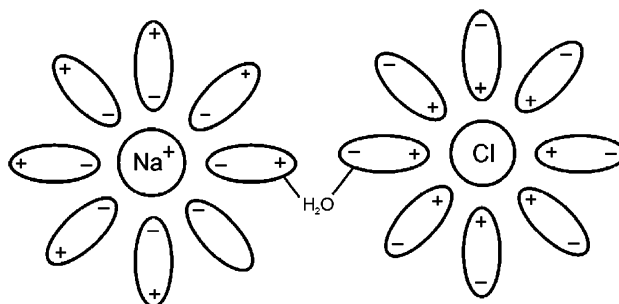
Reason – The charged polar ends of solvent molecules surround opposite charged ends of the ionic compound and pull the ions so that they dissociate.



NaCl crystal



Oppositely charged ends of solvent – water molecules



Dissociated Na^+ ion

Dissociated Cl^- ion

- (f) Ionic compounds are *very stable* due to high Lattice Energy.
 (g) Ionic compounds are *brittle*.
 (h) Ionic compounds have *high density* due to a high mass being concentrated in a small volume.
 (i) *Reactions of ionic compounds are very fast* in aqueous solutions and are instantaneous.
 Reason – Transfer of electrons takes place.

3.4 COVALENT BOND

In 1916, Lewis proposed the theory of chemical bonding based on *sharing of valence electrons*.

Covalent bonds are formed between two atoms by sharing of electrons.

On sharing electrons both the combining atoms get an inert gas configuration which gives stability to the compound formed.

Examples :

Compound	Molecule	Lewis dot representation	
Hydrogen Chloride	HCl	$\text{H} \times \ddot{\text{Cl}} :$	H—Cl
Water	H ₂ O	$\text{H} \times \ddot{\text{O}} \times \text{H}$	H—O—H
Ammonia	NH ₃	$\begin{array}{c} \text{H} \\ \times \\ \text{H} \times \ddot{\text{N}} \times \\ \times \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N} \\ \\ \text{H} \end{array}$
Methane	CH ₄	$\begin{array}{c} \text{H} \\ \times \\ \text{H} \times \ddot{\text{C}} \times \text{H} \\ \times \\ \text{H} \end{array}$	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$
Hydrogen	H ₂	$\text{H} \times \text{H}$	H—H
Oxygen	O ₂	$:\ddot{\text{O}}: \times \times \ddot{\text{O}}:$	O = O
Nitrogen	N ₂	$:\text{N}: \times \times \text{N}:$	N $\equiv$ N
Carbon Dioxide	CO ₂	$:\ddot{\text{O}}: \times \text{C} \times \ddot{\text{O}}:$	O = C = O
Other example			
Hydrogen Sulphide	H ₂ S	$\text{H} \times \ddot{\text{S}} \times \text{H}$	H—S—H
Hydrogen Cyanide	HCN	$\text{H} \times \text{C} \times \text{N}:$	H—C $\equiv$ N

Ethene	C_2H_4	$ \begin{array}{c} H & & H \\ \times & & \times \\ \times & \times & \times \\ C & \times & C \\ \times & & \times \\ H & & H \end{array} $	$ \begin{array}{c} H & & H \\ & & \\ C & = & C \\ & & \\ H & & H \end{array} $
Ethyne	C_2H_2	$ \begin{array}{c} H \times C \times \times \times C \times H \\ \times \times \times \times \end{array} $	$H-C \equiv C-H$
Ethane	C_2H_6	$ \begin{array}{c} H & & H \\ \times & & \times \\ \times & \times & \times \\ H \times C & \times & C \times H \\ \times & & \times \\ H & & H \end{array} $	$ \begin{array}{c} H & & H \\ & & \\ H-C & - & C-H \\ & & \\ H & & H \end{array} $
Phosphine	PH_3	$ \begin{array}{c} H \\ \times \\ H \times P \times \\ \times \\ H \end{array} $	$ \begin{array}{c} H \\ \\ H-P \\ \\ H \end{array} $
Phosphorous Trichloride	PCl_3	$ \begin{array}{c} :Cl: \\ \times \\ :Cl: P \times \\ \times \\ :Cl: \end{array} $	$ \begin{array}{c} Cl \\ \\ Cl-P \\ \\ Cl \end{array} $

Factors favouring covalent bond formation

Covalent bond formation is favoured :

- if the number of valence electrons of the combining atoms is 5, 6 or 7 (i.e. both the atoms are non-metals). An exception is Hydrogen which has just one valence electron yet forms covalent bonds with other atoms.
- if both the atoms have high ionization energy.
- if both the atoms have approximately equal electronegativity.

Nature of Covalent Bonds

Covalent bonds are directional bonds. They form due to overlap of valence orbitals in a particular direction.

Properties of Covalent Compounds

- (a) Most covalent compounds are *gases or liquids*. Some are soft solids. (Diamond, a very hard solid is an exception).
- (b) Most covalent compounds have *low MP and BP*. (Diamond is an exception)
- (c) Most covalent compounds are *poor conductors of electricity*. Exception is Graphite, which is a good conductor. Some covalent compounds *ionise* in aqueous solution and hence are good conductors – example HCl.
- (d) Covalent compounds are *soluble in non-polar solvents* and are *insoluble in polar solvents*.
- (e) Covalent compounds are *neither hard nor brittle*.
- (f) *Reactions of* covalent compounds are *slow*.

Classification of Covalent Bonds

Covalent bonds can be classified as follows.

- (a) Based on covalency.
- (b) Based on combining atoms
- (c) Based on electronegativity differences of the atoms: Polar Covalent Bond and Non-Polar Covalent Bonds
- (d) Based on orbital overlaps:
 - (i) Based on overlapping orbitals
 - (ii) Based on direction of overlap

(a) Based on covalency

Covalency is the number of shared *pairs of electrons* between atoms. It is never greater than 3.

If the number of shared pairs between the combining atoms is one, then the covalency of the bond is one and the bond is called Single Covalent Bond.

Examples: Molecules of hydrogen (H_2), chlorine (Cl_2) have single bonds.

If the number of shared pairs between the combining atoms is two, then the covalency of the bond is two and the bond is called Double Covalent Bond.

Example: Molecule of oxygen (O_2) has double bond.

If the number of shared pairs between the combining atoms is three, then the covalency of the bond is three and the bond is called Triple Covalent Bond.

Example: Molecule of nitrogen (N_2) has triple bond.

(b) Based on combining atoms

If both atoms in a covalent bond belong to the same element then the bond is said to be *homoatomic* (examples: H_2 , Cl_2) and if they belong to different elements then the bond is said to be *heteroatomic* (examples: HCl , NH_3)

(c) Based on Electronegativity:

Polar Covalent Bond

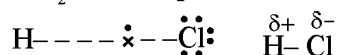
When there is a difference in electronegativity between the participating atoms, then the shared pair is attracted strongly by the more electronegative atom. Due to this, *one of the shared electrons is closer to the more electronegative atom*.

A small δ^- charge is created on the more electronegative atom.

An opposite δ^+ charge is set up on the other less electronegative atom.

Thus two small charges or poles known as *dipole* are created on the molecule. The covalent bond is therefore called *Polar covalent Bond*.

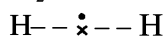
Examples: Hydrogen chloride (HCl) and water molecules (H_2O) have polar covalent bonds.



As Chlorine is more electronegative than Hydrogen, the shared pair of electrons is attracted more strongly by Chlorine. The shared pair is closer to Chlorine atom. Due to this a small negative charge is set up on Chlorine atom and a small positive charge on Hydrogen atom

Non-polar covalent bond

If however the electronegativity differences are very small or both atoms have equal electronegativity, then no dipole can be formed and such bonds are known as *non-polar covalent bonds*. Example: Hydrogen molecule (H_2) has non-polar covalent bond.



The shared pair of electrons is at equal distance from both atoms

(d) Based on orbital overlap

Concept of orbital overlap

In a covalent bond, the shared electrons are in their respective orbitals before sharing.

Example

In hydrogen molecule

- before forming the bond the shared pair of electrons are in their respective 1s orbitals.
- when they come close together, the two orbitals overlap.
- the shared pair of electrons now revolve around the two nuclei.

(iv) when covalent bonds form, sharing of electrons actually takes place by overlap of the 1s orbitals.

Characteristics of orbital overlap

- When orbitals overlap there is a redistribution of electron density (e^- density) between the two atoms.
- The extent of overlap determines the strength of the bond. More the overlap, stronger is the bond.
- The electron cloud gets concentrated nearer the more electronegative atom in the bond.
- The electron pair is attracted by two nuclei.
- The two electrons in the shared pair *spin in opposite direction*.
- The probability of finding an electron is maximum between the two nuclei.

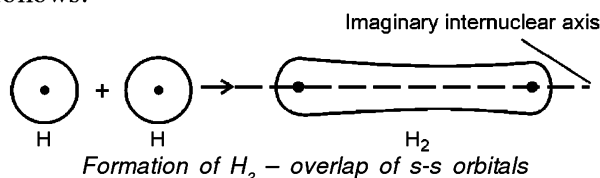
The orbital overlaps are further classified as follows.

(1) Based on participating orbitals

(i) **s-s overlap bond:** Where both the electrons in the shared pair are in s-orbitals before bonding.

Example: Hydrogen molecule - H_2

1s orbital of one H-atom overlaps with 1s orbital of the other H-atom forming an s-s overlap bond as follows:

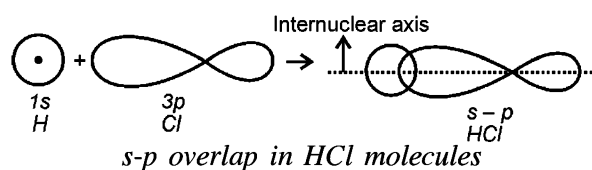


Observations: In s-s overlap, the electron cloud is symmetrical around the *imaginary* internuclear axis. The combined volume of the bonded orbitals is less than the sum of their individual volumes. Hence the molecule possesses less energy making it stable. The two electrons have opposite spin.

(ii) **s-p orbital bond:** When one of the electrons in the shared pair is in the s-orbital while the other electron of the shared pair is in the p-orbital before bonding.

Example: Hydrogen chloride - HCl

1s orbital of H-atom having 1 electron overlaps with the 3p orbital of Cl-atom having 1 electron forming an s-p overlap bond as follows.

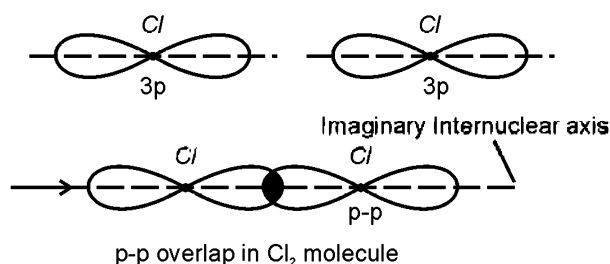


Observations: In s-p overlap the shared pair of electrons is not attracted equally by the two nuclei. The more positive nucleus attracts the shared pair more. The electron density cloud is concentrated nearer the more electronegative atom and is symmetrical around the *imaginary* inter-nuclear axis. A dipole usually develops. *If the bond is a s-p bond, the molecule is likely to be a polar covalent bond.* The two electrons that are shared have opposite spins.

(iii) **p-p orbital bond:** Both the electrons in the shared pair are in p-orbitals before bonding.

Example : Chlorine molecule- Cl_2

The 3p orbital with unpaired electron in one Cl-atom overlaps with the 3p orbital of second Cl-atom having 1 electron forming a p-p overlap bond as follows.



Observations: In p-p overlap the electron cloud is symmetrical around the *imaginary* internuclear axis and more in the central part of the molecule and less in the extremities. The combined volume of the bonded orbitals is less than the sum of their individual volumes. Hence the molecule possesses less energy making it stable. The two electrons have opposite spin.

Comparison of sigma- and pi-bonds

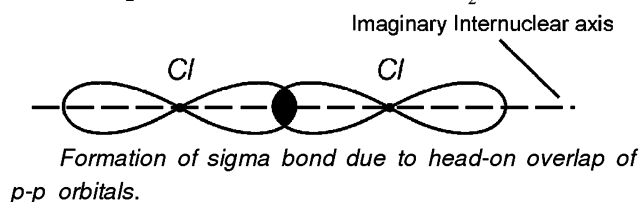
Sigma Bond	Pi Bond
(a) Formed by head-on or axial overlap.	(a) Formed by sideways or lateral overlap.
(b) Extent of overlap is large.	(b) Extent of overlap is small.
(c) Sigma bond is strong.	(c) Pi bond is weaker.
(d) Sigma bond is formed by all orbitals.	(d) Pi bonds are not formed by s-orbitals.
(e) Sigma bond can exist independently.	(e) Pi bond cannot exist independently. It is formed only after a sigma bond is formed.
(f) Electron density is symmetrical about internuclear axis.	(f) Electron density is on either side of the inter-nuclear axis.

(2) Based on direction of the overlap of the participating orbitals

(i) Sigma Bond (s-Bond)

A sigma bond is a covalent bond formed due to axial or head-on overlap of orbitals.

Example: Chlorine molecule - Cl_2 .

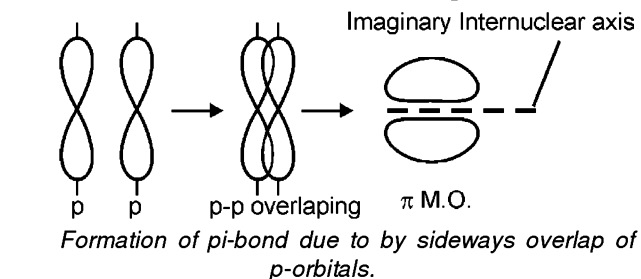


The electron density is symmetrical around the internuclear axis.

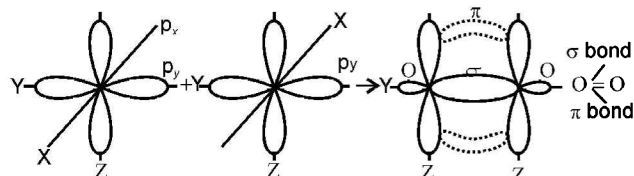
(ii) Pi Bond (p-Bond)

A pi bond is a covalent bond formed due to lateral overlap or sideways overlap of orbitals.

Example: Oxygen molecule - O_2



The electron density is on either side of the internuclear axis.



Oxygen molecule has a double bond. There are two shared pairs of electrons. One of the shared pair involves a head-on overlap of two p-orbitals. The other shared pair involves a sideways overlap of another two p-orbitals.

3.5 COORDINATE COVALENT BOND (DATIVE BONDS)

A coordinate covalent bond is a special covalent bond in which both the electrons in the shared pair are donated by one of the atoms known as the **donor**. The other atom is known as the **acceptor**.

The donor-acceptor atoms are indicated by an arrow.

Lone pair of electrons is the pair of electrons in the valence shell that belong to only one nucleus.

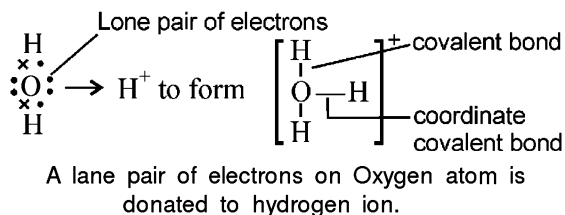
Example : In O-atom there are two lone pairs (underlined): $1s^2 \underline{2s^2} \underline{2p_x^2} 2p_y^1 2p_z^1$

Bond pair of electrons is the pair of electrons that form part of a bond and that belong to two nuclei.

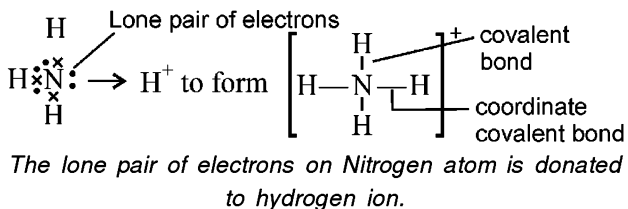
Example: In methane molecule – CH_4 , there are four bond pairs.

Examples of coordinate covalent bond.

(i) Hydronium ion



(ii) Ammonium ion

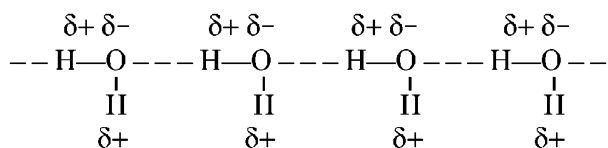


3.6 HYDROGEN BOND

Hydrogen bond is a weak bond formed due to electrostatic force of attraction between δ^+ charge on a H-atom in one molecule and the δ^- charge on a more electronegative atom usually oxygen, nitrogen, sulphur, chlorine or fluorine in another (or same) molecule.

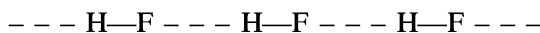
Example 1

The hydrogen bond in water is shown by dotted line in the figure below.



Example 2

The hydrogen bond in fluoride is shown by dotted line in the figure below.



Effects of Hydrogen bonding:

- (1) Hydrogen bonding causes molecules to form cluster of molecules.
- (2) Hydrogen bonding may be the reason for their physical state.
- (3) Hydrogen bonding decreases volatility and increase solubility.
 - Water is a liquid and has a high boiling point due to Hydrogen Bonds.
 - The BP of Hydrogen fluoride (19.4°C) is much less than that of water (100°C) because in Hydrogen fluoride there are only two Hydrogen bonds to be broken when compared to H_2O where there are 4 Hydrogen bonds to be broken (see above).
 - H_2S is a gas whereas H_2O is a liquid. This is because sulphur does not set up a strong enough dipole in H_2S molecule for Hydrogen bonds to form.

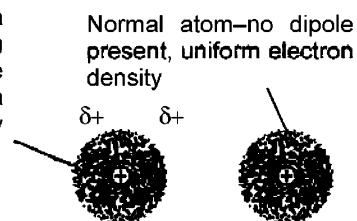
3.7 VAN DER WAAL'S FORCES

In chemical bonds, the forces of attraction are within a molecule. When two molecules come close together, they exert attractive forces that are *physical forces*.

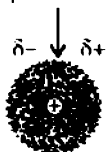
Van der Waal's forces are :

- physical forces,
- weaker forces than the chemical forces present in ionic or covalent compounds,
- very short-lived intermolecular attractive forces that exist between all kinds of atoms, molecules or ions when close and
- usually set up due to *induced dipoles*.

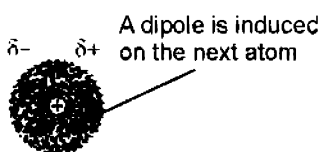
An atom in which a temporary concentration of electrons on one side of the atom sets up a dipole-electron density on one side of the atom



Due to a temporary concentration of the electrons on one side of the atom a dipole is set up on the atom



Due to a temporary dipole on one side of the atom a dipole is set up on the other atom



van der Waal's forces are forces acting between non-bonded atoms or molecules.

Explanation of van der Waal's forces

Van der Waals' forces are observed in *noble gases*. Noble gases are very stable and tend not to interact, making them difficult to *condense* into *liquid*. However, the larger the *atom* of the noble gas, the easier it is to condense the gas. This is because a larger atom has a larger *electron cloud*. Due to temporary disturbance, the electron cloud gets deformed, leaving a slight negative charge on one side of the major axis and a slight positive charge on the other. (The cloud is spherical if averaged over longer times.) The dipole induces the same shift in neighbouring atoms inducing dipoles in one atom after the other. Unlike charges attract, and the induced dipoles are held together by small dispersed forces called Van der Waal's forces.

Applications of van der Waal's Forces

- van der Waal's forces cause inert gases and halogens to condense to liquids when cooled.
- Gases show deviation from Gas Laws due to van der Waal's forces.
- Some crystals are soft and have low MP as the atoms / molecules are held only by weak van der Waal's forces.

Example: Graphite.

3.8 DESCRIBING BONDS

Several terms are used to describe a bond completely.

Beside lone pairs and bond pairs and the type of bonds that exist in the atoms, ions or molecules the following terms are used to describe bonds.

Central atom is the atom at the centre of the molecule.

Bond angle is the angle formed by the extreme atoms and the central atom.

Shape of molecule – In a molecule, there are repulsions between lone pair-lone pair, lone pair-bond pair and bond pair-bond pair. It is these repulsive forces and the actual geometry of the participating orbitals that are responsible for the molecule having a specific bond angle in each molecule. The bond angle plays a key role in determining the shape the molecule will have.

Some molecules, their bond angles and respective shapes are given below.

Molecule	Bond Angle	Bond shape
(1) H ₂ O	104°30"	V-shaped molecule
(2) CO ₂	180°	Linear molecule
(3) CH ₄	109°28"	Tetrahedral
(4) NH ₃	107°17"	Pyramidal

3.9 INTRODUCTION TO THE CONCEPT OF HYBRIDISATION

While the orbital overlap concept explains satisfactorily the formation of various molecules it cannot explain the geometry and shape of various molecules.

For example it cannot explain precisely why BeCl₂ is linear, CH₄ is tetrahedral, water is V-shaped.

Similarly in CH₄ molecule there is one s-s bond and three p-p bonds, yet the bond length of each of the four C-H bonds is same.

To explain this Pauling and Slater introduced a hypothetical concept called **hybridisation**.

According to them, any number of orbitals of an atom *which differ in energy slightly* may mix with each other to form new orbitals called *hybrid orbitals with same energy*.

Only orbitals with almost same energy can take part in hybridisation, and the number of hybrid orbitals is always the same as the orbitals which take part in the process. Also, it is only the orbitals which undergo hybridisation and *not* the electrons.

Example: Orbitals of nitrogen atom (2s²2p_x¹2p_y¹2p_z¹) hybridise to give 4 hybrid orbitals out of which one of them has 1 pair of electrons and the other three have one electron each.

These hybrid orbitals spread out as far as possible giving symmetry (and shape) to the molecule. Distortions if any will be due to the hybrid orbitals having lone pair of electrons.

Example: Both ammonia – (NH_3 is pyramidal) and methane – (CH_4 is tetrahedral) have four hybrid orbitals but the shapes are different.

3.10 IMPORTANT POINTS TO REMEMBER

- * Complete transfer of one or more electrons from one atom to another will lead to the formation of ionic or electrovalent bond.
- * Sharing of electrons will lead to the formation of covalent bond.
- * The energy of the molecule is less than the sum of the energies of atoms present in the molecule.
- * Covalent bond is formed by the overlap of two pure atomic or two hybridized or one hybridized and one atomic orbital.
- * Strong bond is formed by the maximum overlap of orbitals.
- * End-on-end overlap of orbitals lead to the formation of sigma (σ) bond and partial overlap of orbitals lead to the formation of pi (π) bond.
- * σ bond is stronger than π bond.
- * Sigma bond exists independently.
- * π bond has no independent existence. It exists only in the presence of a sigma bond.
- * In a double bond one sigma and one π bond are present.
- * In a triple bond one sigma and two π bonds are present.
- * s-s overlap is present in H_2 .
- * p-p overlap is present in F_2 , Cl_2 , Br_2 and I_2 .
- * s-p overlap is present in HF , HCl , HBr and HI .
- * Molecules having single bonds have only σ bonds.
- * Molecules having single bond are H_2 , F_2 , Cl_2 , Br_2 , I_2 , BeCl_2 , etc.
- * Molecules having double bond are O_2 , ethylene (C_2H_4), CO_2 , etc.
- * Acetylene (C_2H_2), nitrogen (N_2), HCN , CaC_2 etc., have triple bonds.
- * In coordinate covalent bond, both electrons are supplied by one atom.
- * Examples of coordinate bond are, NH_4^+ , H_3O^+ etc.
- * CO_2 , BeCl_2 , and HCN have linear structures.
- * Water molecule has “V” shape.
- * NH_3 , PCl_3 and PH_3 have pyramidal shape.
- * PCl_5 and has trigonal bipyramidal structure.

EXERCISE

I. Choose the correct answer

- (1) Element x is strongly electropositive and element y is strongly electronegative. Both are univalent so the compound formed by them would be
 - (a) x^+y^-
 - (b) x^-y^+
 - (c) xy
 - (d) $x^{2+}y^-$
- (2) The most favourable condition for the formation of an ionic bond $\text{A}^+ \text{B}^-$ is high
 - (a) when the ionization energy of A and the electron affinity of B are low.
 - (b) when the ionization energy of A is high and the electron affinity of B is low
 - (c) when the ionization energy of A and the electron affinity of B are high
 - (d) when the ionization energy of A is low and the electron affinity of B is high.
- (3) Which of the following does not exhibit both ionic and covalent bonding?
 - (a) BaSO_4
 - (b) CH_3Cl
 - (c) NH_4Cl
 - (d) $\text{Ca}(\text{NO}_3)_2$
- (4) As compared to covalent compounds electrovalent compounds generally have:
 - (a) low melting points and low boiling points
 - (b) low melting points and high boiling points
 - (c) high melting points and low boiling points
 - (d) high melting points and high boiling points
- (5) During the formation of a chemical bond
 - (a) electrons in the atoms are rearranged
 - (b) energy is released
 - (c) potential energy of the atoms decreases
 - (d) all the above.
- (6) Kossel explained the formation of an ionic bond
 - (a) on the basis of electronic configuration
 - (b) on the basis of attraction between ions
 - (c) on the basis of sharing of electrons
 - (d) on the basis of the sizes of atoms
- (7) Both the ions have helium configuration in
 - (a) $\text{Na}^+ \text{O}^{2-}$
 - (b) K_2S
 - (c) LiH
 - (d) AlF_3

- (8) In the formation of an ionic bond
- electrons are transferred between metals
 - electrons are transferred from metal to non-metal
 - electrons are shared between metal and non-metal
 - electron pair is denoted by one atom
- (9) When two oppositely charged ions come near
- attractive forces act between them
 - repulsive forces act between them
 - they unite
 - both attractive and repulsive forces act
- (10) Both cation and anion have the same number of electrons in
- KBr
 - CsI
 - MgS
 - NaCl
- (11) Ionic nature of the bond is lowest in
- CaI_2
 - CaF_2
 - CaBr_2
 - CaCl_2
- (12) The main factor responsible for the formation of ionic bonds is
- high E.A. values
 - high Lattice energies
 - high electronegativity of elements
 - easy transfer of electrons
- (13) A non directional bond is
- covalent
 - ionic
 - dative
 - hydrogen
- (14) During the formation of a chemical bond between two atoms
- only force of attraction is operative
 - only force of separation is operative
 - both of the above two forces are operative
 - neither of the two forces is operative
- (15) For ionic compounds, the correct statement is
- The higher the temperature, the more the solubility
 - The higher the dielectric constant of the solvent, the more the solubility
 - The higher the dipole moment of the solvent, the more the solubility
 - The higher the lattice energy, the more the solubility
- i, ii and iii
 - ii, iii and iv
 - i, iii and iv
 - All the statements
- (16) $\text{Na(s)} + \frac{1}{2} \text{Cl}_2 \text{(g)} \rightarrow \text{NaCl(s)} + Q_1$
 $\text{Na}^+\text{(g)} + \text{Cl}^-\text{(g)} \rightarrow \text{NaCl(s)} + Q_2$ then ' Q_1 ' and ' Q_2 ' are related as
- $Q_1 = Q_2$
 - $Q_1 > Q_2$
 - $Q_1 < Q_2$
 - $Q_1 = Q_2 = 0$
- (17) The number of unit cells present in a sample of 1 mole of sodium chloride is
- 6.023×10^{22}
 - 6.023×10^{23}
 - 3.011×10^{23}
 - 1.505×10^{23}
- (18) Chemical bond is formed between the two atoms
- due to attractive forces only
 - due to repulsive forces only
 - when repulsive forces > attractive forces
 - when the energy of compound is less than the atoms
- (19) The mass of one unit cell of NaCl crystal lattice is
- 58.5 amu
 - 117 amu
 - 234 amu
 - 2.34×10^{-24}
- (20) If the electronic configuration of an element is 2, 8, 2 the types of bonds between the atoms of the element are
- covalent
 - ionic
 - metallic
 - van der Waal's forces
- 21) The electronic configuration of an element is $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5, 4s^1$. This represents its
- excited state
 - ground state
 - cationic state
 - anionic state
- 22) The number of Cl^- ions surrounding each Na^+ in NaCl crystal is
- 5
 - 7
 - 6
 - 8
- (23) Which of the following species has the highest ionization potential?
- Li^+
 - Mg^+
 - Al^+
 - Ne
- (24) Electronegativity values of three elements are $x = 1.0$, $y = 2.5$ and $z = 3.0$ what will be the nature of bond in xz and yx ?
- Ionic and coordinate
 - Covalent and coordinate
 - Ionic and polar covalent
 - All the above
- (25) Which of the following is not true about sigma bond?
- It involves axial overlap
 - It is non-directional
 - Electron cloud is cylindrically symmetrical about internuclear axis
 - It is formed by hybrid orbitals as well as pure atomic orbitals
- (26) NH_3 and BF_3 form bond readily because of the formation of
- an ionic bond
 - a covalent bond
 - hydrogen bond
 - a co-ordinate bond

- (27) Identify the molecule which has only one pi-bond.
 (a) $\text{H}-\text{C} \equiv \text{C}-\text{H}$
 (b) $\text{CH}_2 = \text{CH} - \text{CHO}$
 (c) $\text{CH}_3 - \text{CH} = \text{CH}_2$
 (d) $\text{CH}_3 - \text{CH} = \text{CH} - \text{COOH}$
- (28) The maximum number of covalent bonds by which the two atoms can be bonded to each other is
 (a) four (b) two
 (c) three (d) no fixed number
- (29) Which of the following is an incorrect statement?
 (a) A sigma bond is weaker than a pi-bond
 (b) A sigma bond is stronger than a pi-bond
 (c) A double bond is stronger than single bond
 (d) A double bond is shorter than single bond
- (30) The electronegativity values of C, H, O, N and S are 2.5, 2.1, 3.5, 3.0 and 2.5 respectively. Which of the following bonds is most polar?
 (a) $\text{C} - \text{H}$ (b) $\text{N} - \text{H}$
 (c) $\text{S} - \text{H}$ (d) $\text{O} - \text{H}$
- (31) Two electrons of one atom A and two electrons of another atom B are utilized to form a compound AB. This is an example of
 (a) polar covalent bond
 (b) non-polar covalent bond
 (c) electrovalent bond
 (d) coordinate covalent bond
- (32) Pauling's electronegativity value for elements is useful in predicting
 (a) polarity in molecules
 (b) position of element in periodic table
 (c) coordination number
 (d) dipole moments
- (33) The electrons that take part in chemical bonding are
 (a) core electrons (b) $(n - 2)$ electrons
 (c) valence shell electrons
 (d) stationary electrons
- (34) The bonds present in N_2 are
 (a) 3s (b) 2s, 1p
 (c) 1s, 1p (d) 1s, 2p
- (35) A bonding orbital has its electron cloud around the internuclear axis. It is
 (a) s (b) p
 (c) both (a) and (b) (d) neither (a) nor (b)
- (36) p orbitals can form
 (a) sigma bonds (b) pi-bonds
 (c) both bonds (d) weak bonds
- (37) The number of bonds in C_2H_4 is
 (a) 7s (b) 5s, 1p
 (c) 3s, 2p (d) 5s, 2p
- (38) p-orbitals can form
 (a) σ bonds only (b) σ and π bonds
 (c) π bonds only (d) dative bonds only
- (39) Two elements A and B contain three and six electrons respectively in the valency shell. Then the formula of the compound formed between them is
 (a) AB (b) A_2B_3
 (c) A_3B_2 (d) AB_2
- (40) The strength of bonds increases in the order
 (a) van der Waal's attraction < Hydrogen bond < Covalent bond < Ionic bond
 (b) Hydrogen bond < van der Waal's forces < Covalent < Ionic
 (c) van der Waal's forces < Hydrogen bond < ionic < Covalent
 (d) van der Waal's forces < Hydrogen bond < Ionic = Covalent
- ## II. Give one word answers
- The bond in which the electron pair is attracted by two nuclei.
 - The bond that is directional in nature
 - The bond in hydrogen chloride molecule
 - Ionic bonds are strong due to this energy
 - In ammonium molecule the acceptor is
 - The force that is responsible for liquefaction of inert gas elements.
- ## III. Match the following.
- (1) Match the properties of bonds (List 1) with the bonds (List 2).
- | List 1 | List 2 |
|--|---------------------------|
| (a) Weak electrostatic forces | (i) Pure Covalent Bond |
| (b) Ionise on dissolving in polar solvents | (ii) Ionic Bond |
| (c) Poor conductors in solid state | (iii) Polar Covalent Bond |
| (d) Equal sharing of electrons | (iv) Hydrogen Bond |
- (2) Match the molecules (List 1) with the covalency of the bonds present in the molecules (List 2).
- | List 1 | List 2 |
|-------------------|-------------|
| (a) Cl_2 | (i) one |
| (b) N_2 | (ii) two |
| (c) O_2 | (iii) three |
| (d) CH_4 | (iv) four |

(3) Match the bonds (List 1) with the property (List 2).

- | List 1 | List 2 |
|---------------------------|--|
| (a) Covalent | (i) high density |
| (b) Ionic | (ii) soft solids or gases |
| (c) Van der Waal's forces | (iii) liquefaction of inert gas elements |
| (d) Hydrogen Bond | (iv) may be responsible for physical state |

(4) Match the elements whose atomic numbers are (given in List 1) with the type of bond they are likely to form (List 2).

- | List 1 | List 2 |
|---------------------------|---------------------|
| (a) $Z = 1$ and $Z = 17$ | (i) Pure covalent |
| (b) $Z = 7$ and $Z = 7$ | (ii) Polar covalent |
| (c) $Z = 11$ and $Z = 17$ | (iii) No Bond |
| (d) $Z = 2$ and $Z = 17$ | (iv) Ionic Bond |

(5) Match the molecules in (List 1) with the bond description of the molecules (List 2).

- | List 1 | List 2 |
|----------------------------|---|
| (a) CH_4 | (i) two covalent bonds, four bond pairs |
| (b) C_2H_4 | (ii) four covalent bonds, four bond pairs |
| (c) CO_2 | (iii) three covalent bonds, five bond pairs |
| (d) C_2H_2 | (iv) five covalent bonds, six bond pairs |

(6) Match the molecules (List 1) with the types of bonds present in the molecules (List 2).

- | List 1 | List 2 |
|----------------------------|--------------------------------|
| (a) CH_4 | (i) three sigma, two pi bonds |
| (b) C_2H_4 | (ii) two sigma, two pi bonds |
| (c) CO_2 | (iii) five sigma, one pi bonds |
| (d) C_2H_2 | (iv) four sigma, no pi bonds |

IV. State whether the following statements are True or False

- (i) Ionic compounds form directional bonds.
- (ii) van der Waal's forces are responsible for the liquid state of water.
- (iii) Ammonium chloride has ionic, covalent and coordinate bonds.
- (iv) Metals form covalent bonds with non-metals.
- (v) If electronegativity difference between atoms is above 1.9 the bond is an ionic bond.

V. Find the odd one out

- (i) polar covalent bond, coordinate covalent bond, pure covalent bond, ionic bond
- (ii) nitrogen molecule, hydrogen molecule, hydrogen chloride molecule, oxygen molecule

(iii) carbon dioxide, water, ammonia, phosphorous trichloride

VI. Fill in the blanks

- (1) The force of attraction that exists between atoms is called _____.
- (2) The electrostatic force of attraction between oppositely charged ions is known as _____.
- (3) The bonds between NH_3 and H^+ in NH_4^+ and between H_2O and H^+ in H_3O^+ are _____.
- (4) CO_2 , BeCl_2 , HCN are _____, while, NH_3 is _____ molecule and H_2O is _____ molecule.
- (5) PCl_5 is _____ shaped molecule, while PCl_3 is _____ shaped molecule.
- (6) The type of overlap present in H_2 molecule is _____, whereas, it is _____ in Cl_2 , F_2 , I_2 and _____ in HF , HCl , and HBr .
- (7) The maximum number of covalent bonds formed between two atoms never exceeds _____.
- (8) A coordinate bond is a _____ covalent bond in which both electrons are provided by _____.
- (9) The number of bonds in Nitrogen molecule is _____ while in Oxygen molecule it is _____.
- (10) Pi bond can exist only with a _____, whereas _____ can have independent existence in a bond.
- (11) The strength of a sigma bond is _____ than a pi bond.
- (12) Oxygen has two _____ of electrons in water molecule and ammonia has one _____ of electrons on N-atom.
- (13) Covalency of the bond(s) present in H_2 , F_2 , Cl_2 is _____ and in O_2 , it is _____ while in N_2 it is _____.
- (14) s-orbitals cannot form _____. However, p-orbitals, d-orbitals and f-orbitals can form _____.
- (15) Molecules with single bonds have only _____ bond.

VII. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, Statement R is true; Statement R is correct explanation for statement A

Choose B if Statement A is true, Statement R is true; Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D if Statement A is false, Statement R is true

- (1) **Statement –A:** The crystal network of ions is the unit cell.

Statement –R: The unit cell is the smallest unit of the network.

- (2) **Statement –A:** The covalency in Oxygen is two.

Statement –R: Covalency is said to be two in oxygen as two electrons form a pair.

- (3) **Statement –A:** Covalent Bond forms due to sharing of electrons.

Statement –R: All bonds form due to orbital overlap.

- (4) **Statement –A:** The electrons in a shared pair must have opposite spin.

Statement –R: If the electrons have parallel spin they are more stable.

- (5) **Statement –A:** Ionic Bond forms between metal and non-metal atoms.

Statement –R: Metal atoms lose electrons while non-metal atoms gain electrons.

- (6) **Statement –A:** The boiling point of water is quite high at 100°C.

Statement –R: Water is a liquid with high specific heat capacity.

- (7) **Statement –A:** Liquefaction of Inert Gas Elements is difficult.

Statement –R: Liquefaction of Inert Gas Elements is due to van der Waal's forces.

- (8) **Statement –A:** Sigma bonds are weaker than pi bonds.

Statement –R: Electron density is symmetrical around the inter-nuclear axis in sigma bond.

- (9) **Statement –A:** Release of Lattice Energy is responsible for the strength of Ionic Bonds.

Statement –R: On release of lattice energy the crystal lattice network becomes more stable.

- (10) **Statement –A:** The number of electron pairs in a covalent bond never exceeds three.

Statement –R: The geometry of the bond formation will not allow four pairs of electrons to be shared between two atoms.

VIII. Choose the correct word from those mentioned in brackets to fill the blank.

- (i) A double bond has one _____ bond and one _____ bond. (sigma / pi)
- (ii) A triple bond has one _____ bond and two _____ bonds (sigma / pi).

- (iii) An axial overlap of orbitals results in a _____ bond whereas a lateral overlap of orbitals results in formation of _____ bond. (pi / sigma)
- (iv) Generally a covalent bond is formed between two _____ atoms and an ionic bond is formed between _____ and _____ atoms. (metal / non-metal)
- (v) Electrons in _____ take part in bonding. (penultimate shell / valence shell)
- (vi) $ns^2 np^6$ is known as _____ configuration. (duplet / octet)
- (vii) Octet Rule says atoms or ions that have octet configuration are _____. (stable / inert)
- (viii) The number of electron pairs shared between two atoms in a covalent bond is known as _____. (covalency / valency)
- (ix) A covalent bond is formed due to overlap of two orbitals each containing one electron with _____ spin. (same / opposite)
- (x) If electronegativity difference is equal or greater than 1.9, the bond is _____. If it is smaller than 1.9 it is _____, and if it is very smaller than 1.9 it is _____ (covalent, ionic, polar covalent)

IX. Read the paragraph carefully and answer the questions that follow.

The solubility of a compound in a solvent depends on the nature of both the compound and the solvent. Ionic compounds are soluble in polar solvents like water and insoluble in non-polar solvents like Carbon disulphide. On dissolution ionic compounds undergo only dissociation into ions. Polar covalent compounds however undergo ionisation on dissolution. In ionic compounds before dissolution ions already exist – only separation takes place on dissolution. In polar covalent compounds ions do not exist – they form only on dissolution.

(1) Water is a polar solvent due to

- (a) lone pair bond pair repulsions
- (b) electronegativity difference between H and O atoms
- (c) V-shape of the molecule
- (d) all three

(2) NaCl dissociates into ions on dissolution whereas HCl ionizes on dissolution

- (a) NaCl is ionic while HCl is polar covalent compound
- (b) water is a polar compound
- (c) HCl is a gas, NaCl is a solid
- (d) all three

(3) Alcohol (an organic compound having the formula C_2H_5OH) dissolves in water due to

- electronegativity difference between O and H atoms in $-OH$ radical
- both being liquids
- boiling point of alcohol being low
- none of these

(3) Why are ionic bonds formed between metal and non-metal atoms?

(4) Ionic compounds have high density and melting points. Why?

(5) Ionic compounds are poor conductors of electricity in the solid state but excellent conductors in the liquid state. Why?

(6) Every bond has partial ionic and partial covalent character. Explain.

(7) Once a co-ordinate covalent bond is formed it cannot be distinguished from a pure covalent bond as the electrons cannot be differentiated. Explain.

X. Answer the following questions.

(1) Why do some elements exist in the free state while others exist as compounds?

(2) How do atoms acquire duplet or octet configuration?

KEY TO EXERCISE

- I.** (1) a (2) d (3) b (4) d (5) d (6) a (7) c (8) b (9) d (10) b
 (11) a (12) b (13) b (14) c (15) a (16) c (17) d (18) d (19) c (20) c
 (21) b (22) c (23) a (24) c (25) b (26) d (27) c (28) c (29) a (30) d
 (31) a (32) b (33) c (34) d (35) a (36) c (37) b (38) b (39) b (40) a
- II.** i. all types of covalent bonds ii. all types of covalent bonds iii. polar covalent bond
 iv. lattice energy v. hydrogen ion vi. van der Waal's forces
- III.** 1. a-iv b-iii c-ii d-i 2. a-i b-iii c-ii d-i 3. a-ii b-i c-iii d-iv
 4. a-ii b-i c-iv d-iii 5. a-ii b-iv c-i d-iii 6. a-iv b-iii c-ii d-i
- IV.** i. false ii. false iii. true iv. false v. true
- V.** i. ionic bond ii. hydrogen chloride molecule iii. carbon dioxide
- VI.** 1. Chemical Bond 2. Ionic Bond 3. Dative Bonds
 4. linear shaped, pyramidal shaped, V-shaped 5. trigonal bi-pyramidal, bi-pyramidal
 6. s-s overlap, p-p overlap, s-p overlap 7. three 8. modified, one atom
 9. one sigma bond and two pi bonds, one sigma bond and one pi bond.
 10. sigma bond, sigma bond 11. stronger 12. lone pair, lone pair
 13. Single bond, Double bonds, Triple bonds 14. pi bonds, pi bond 15. sigma bonds
- VII.** 1. D 2. B 3. C 4. C 5. A 6. B 7. B 8. D 9. A 10. A
- VIII.** i. sigma, pi ii. sigma, pi iii. sigma, pi
 iv. non-metal, metal, non-metal v. valence vi. octet vii. stable viii. covalency ix. opposite
 x. ionic, polar covalent, covalent
- IX.** 1. d 2. a 3. a

4

Alkali Earth Metals

4.0 INTRODUCTION

The known elements have been classified in the Modern Periodic Table into Groups and Periods. The metals occur to the left side of the Periodic Table while the non-metals are to the right. The first two groups are Group IA (called *Alkali Metals*) and Group IIA (called *Alkali Earth Metals*).

The Alkali Metals have a general valence configuration of ns^1 . They are called *Alkali Metals* because the oxides of these elements dissolve in water to give alkalis or soluble hydroxides. They are highly electropositive and extremely reactive. They are not found in the free state. Hydrogen, a non-metal belongs to this group. The elements in Group IA are hydrogen (H), lithium (Li), sodium (Na), potassium (K), cesium (Cs) and francium (Fr).

The Alkali Earth Metals have a general valence configuration of ns^2 . They are called Alkali Earth Metals because the oxides of these elements dissolve in water to give alkalis or soluble hydroxides; besides these elements occur in the earth's surface as sulphates and chlorides.

This chapter deals with Alkali Earth Metals. A comparison with Alkali Metals is inevitable as these two groups of elements lie side by side in the Periodic table.

4.1 STUDY OF GROUP IIA ELEMENTS

The elements in Group IIA are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). All elements in the group are metals.

4.2 PHYSICAL PROPERTIES AND THEIR GRADATION

- Density decreases up to Calcium after which it increases. Alkali Earth Metals have higher density than Group IA metals.
- They have higher MP and BP than Group IA elements. There is no regular trend within the group.
- They are hard but can be cut with a sharp knife.

- They belong to s-block as the differentiating electron enters s-orbital. They have ns^2 valence configuration.
- They exhibit +2 valency.
- They are malleable, ductile and good conductors of electricity.
- Their reactivity increases from Beryllium to Barium. (Radium, the last element in the group, is radioactive).
- Atomic volume increases from top to bottom.

Radius in Angstrom units

Be	Mg	Ca	Sr	Ba	Ra
1.12	1.60	1.97	2.15	2.22	–

- As they have no unpaired electrons, they are *diamagnetic* and form *colourless compounds*.
- Ionisation energy decreases as we move down the group.

	Be	Mg	Ca	Sr	Ba	Ra
I_1 values (eV)	9.3	7.6	6.1	5.7	5.2	5.3
I_2 values (eV)	18.2	15.0	11.8	11.0	10.0	10.1

- Electropositive character increases from top to bottom. IE decreases. However, since Be is least electropositive so tendency to form Be^{2+} ions is less. Its compounds are covalent while other elements in this group form ionic compounds.
- Though $I_2 > I_1$, the Alkali Earth Metals have a tendency to form divalent ions instead of *monovalent* ions. The divalent ions are extensively hydrated releasing hydration energy. The energy released makes the divalent ion more stable. The hydration energy released is greater than the extra energy required to pull out the second electron.

$$M - 1e^- \rightarrow M^+ \quad (I_1 - \text{energy absorbed})$$

$$M^+ - 1e^- \rightarrow M^{2+} \quad (I_2 - \text{energy absorbed})$$

$$M^{2+} + x H_2O \rightarrow [M(H_2O)_x]^{2+} \quad (\text{Hydration Energy} - \text{energy released})$$
- Electronegativity of Alkali Earth Metals is

small and decrease from beryllium to barium.

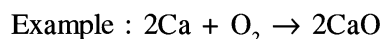
- (xiv) *Flame colouration*: When these elements are kept in a flame, the electrons absorb energy and jump to higher energy levels. When reverting to lower energy levels they give out the extra energy in the form of visible light of specific colours. Their characteristic colours are given below.

Calcium	–	brick red
Strontium	–	crimson
Barium	–	apple green
Radium	–	red

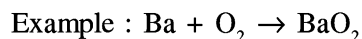
4.3 CHEMICAL PROPERTIES AND THEIR GRADATION

Group IIA elements are very reactive. Group IIA elements do not occur free in nature and occur as sulphates, carbonates or silicates. However, they are less reactive than Group IA elements.

- (i) (a) All Alkali Earth Metals except barium and radium combine with oxygen forming *monoxides*.



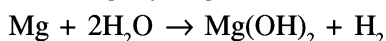
- (b) The tendency to form peroxides increases as we go down the group. Barium and radium give higher oxides, called *peroxides*.



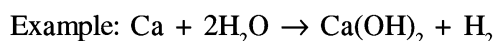
(ii) Action with water

The ease with which the alkali earth metals react with water increases as we move down the group.

- Beryllium has no action on cold or hot water.
- Magnesium reacts slowly with boiling water liberating hydrogen.



- Calcium and strontium and barium react quite easily with water liberating hydrogen.



(iii) Burning in air

Alkali Earth Metals burn *in air* with a dazzling light and give the flame a specific colour forming oxides and nitrides.

Oxides

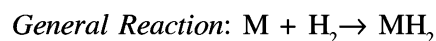
- (a) The basic nature of oxides increases as we go down the group.

BeO	–	Amphoteric
MgO	–	Weakly basic
CaO	–	Basic
SrO	–	Strongly basic
BaO	–	Strongly basic

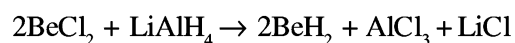
- (b) The oxides react with water releasing heat.
 (c) Solubility of the hydroxides of alkali earth metals increases from top to bottom.
 (d) Mg(OH)_2 is insoluble in water while Ba(OH)_2 is a soluble hydroxide (an alkali).

(iv) Reactions with Hydrogen

- (a) All elements of Group IIA except Be react with H_2 forming hydrides.



Note: BeH_2 is unstable and can be prepared as follows:

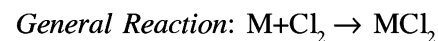


- (b) All hydrides are good Reducing Agents and react with water readily liberating hydrogen gas.



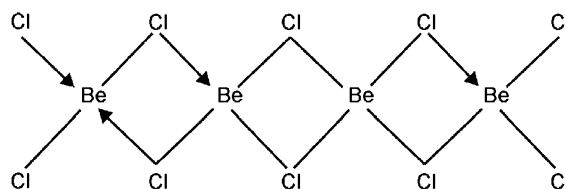
(v) Reactions with Halogens

- (a) Alkali Earth Metals react with halogens at different temperatures forming halides (MX_2).



- (b) Bond nature of halides:

- (i) All alkali earth metals (except beryllium) form ionic compounds with halogens.
 (ii) Beryllium halides are covalent. BeCl_2 forms a polymer – $(\text{BeCl}_2)_n$ at room temperature. In vapour state it exists as a linear molecules Cl-Be-Cl .



- (c) All halides are hygroscopic and form hydrated salts.

Examples: $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$

- (d) All halides except those of Be are soluble in water. However, the fluorides are almost insoluble.
- (vi) **Carbonates:** Alkali Earth Metals carbonates are insoluble in water. Their solubility decreases as we move down the group.
- (vii) **Hardness of water - Bicarbonates:** Alkali Earth Metals bicarbonates are soluble in water. They cause temporary hardness of water, which can be removed by boiling when they get converted to insoluble carbonates and so are precipitated.

4.4 ANOMALOUS BEHAVIOUR OF Be

The first member of Group IA, beryllium shows anomalous behaviour as it differs from other Alkali Earth Metals in several ways.

Beryllium differs from other Alkali Earth Metals as follows.

- Ionisation energy of beryllium is more than any other Alkali Earth Metals. So, the tendency of beryllium to form Be^{2+} ion is less when compared to other Group IIA elements.
- When compared to other alkali earth metals Beryllium forms covalent compounds as its electronegativity is more.
- Beryllium does not react with water
- Beryllium forms amphoteric oxide while other Alkali Earth Metal oxides are basic.
- Beryllium does not liberate hydrogen from acids while other Alkali Earth Metals liberate hydrogen.
- Beryllium is extremely hard when compared to other Alkali Earth Metals.

Reasons for anomalous behaviour of beryllium

The reasons for anomalous behaviour of beryllium are :

- small size of beryllium atom and ion
- presence of only 2 electrons in $(n - 1)$ shell—other alkali earth elements have more than 2
- higher hydration energy of beryllium
- higher electronegativity of beryllium

4.5 ORES OF ALKALI EARTH METALS

Group IIA elements are called alkali earth metals as these elements occur in the earth's surface as sulphates and chlorides (besides the fact that the

oxides of these elements dissolve in water to give alkalis). The Alkali Earth Metals are found as the following ores.

Beryl	$\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$
Barytes	BaSO_4
Carnalite	$\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$
Dolomite	$\text{CaCO}_3 \cdot \text{MgCO}_3$
Epsom salt	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Magnesite	MgCO_3

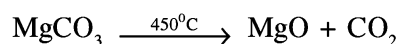
Extraction of Magnesium from its ore (see box)

- Ore:** Magnesite or Carnalite ores are used.
- Reduction method:** Electrolytic reduction.
Chemical method of reducing Mg^{2+} to free Mg is very difficult and hence not preferred.
- Metallurgy:** The ore is dressed and concentrated.

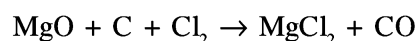
Depending on whether magnesite or carnalite is used the *ore is converted to magnesium chloride*.

(a) Magnesite ore:

The ore is roasted in air at 450°C when it decomposes to MgO.



The MgO is next mixed with Carbon (coke) and heated to a temperature of 1000°C . Chlorine gas is passed over the hot reactants. The oxide gets converted to chloride.



(b) Carnalite ore

Carnalite ore has the formula $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$. On simple heating of carnalite ore, it loses four water of crystallization molecules. The remaining two water of crystallization molecules are more difficult to remove.

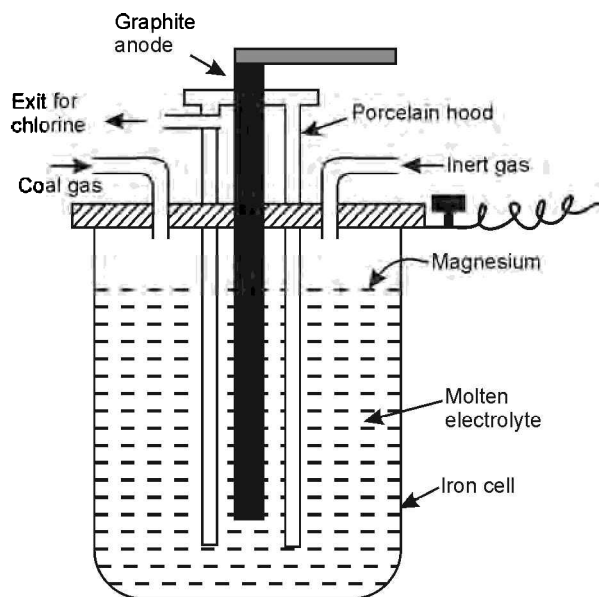


To remove the last two water of crystallisation molecules, a stream of dry hydrogen chloride gas at 350°C is passed over the product formed.



(iv) Electrolytic reduction

Flux: A flux is one or more chemicals added to the ore in its metallurgy. Anhydrous MgCl_2



Extraction of magnesium by electrolysis of fused MgCl

thus obtained is mixed with a *flux* of NaCl and KCl.

Reason for adding flux: (a) it lowers the melting point of the electrolyte significantly from above 1000°C to 700°C.

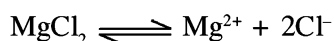
(b) it increases the conductivity of the electrolyte.

Electrodes used: The electrolyte is put in an iron pot that serves as a *cathode*.

The electrolyte is heated externally to 700°C to form a fused mass. On melting the electrolyte, a graphite rod (*anode*) in a porcelain glass tube is inserted into the electrolyte (see diagram).

Electrolysis: The electrolyte is now electrolysed.

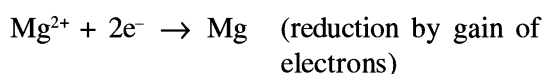
The electrolyte dissociates as follows.



At cathode

Mg^{2+} , K^+ , and Na^+ are the positive ions in the electrolyte (K^+ and Na^+ ions are present due to the dissociation of the flux).

The positively charged ions reach the cathode. At the cathode magnesium ions accept electrons more easily than potassium or sodium ions. Hence, Mg^{2+} ions are preferentially reduced.



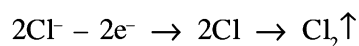
The magnesium formed at the cathode floats on the electrolyte due to two reasons.

- the temperature of the electrolyte mixture is higher than the melting point of magnesium
- the molten magnesium is less dense than the electrolyte mixture

The molten magnesium is tapped at regular intervals. It is almost 100% pure.

At anode

Chlorine ions reach the anode and are oxidised.



The chlorine gas is collected through an outlet on the porcelain tube.

Precaution: Coal gas is constantly passed over the electrolytic mixture to prevent oxidation of magnesium.

Flow chart of extraction of magnesium

Extraction of Mg	
Dressing and concentration of ore	
Magnesite Conversion to chloride (a) Roasting at 350°C: $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \uparrow$ (b) Conversion to chloride: $\text{MgO} + \text{Cl}_2 + \text{C} \rightarrow \text{MgCl}_2 + \text{CO} \uparrow$	Carnalite Conversion to chloride (a) Simple heating $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{KCl} \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}$ (b) Heating with HCl at 350°C for complete dehydration: $\text{MgCl}_2 \cdot \text{KCl} \cdot 2\text{H}_2\text{O} \rightarrow \text{MgCl}_2 \cdot \text{KCl} + 2\text{H}_2\text{O}$

The anhydrous MgCl_2 is mixed with a flux – $\text{NaCl} + \text{KCl}$ to reduce the melting point of the electrolyte and increase conductivity.

Electrolysis: Cathode: Iron pot holding the electrolyte serves as cathode.

Anode: Graphite rod kept in a porcelain tube with an outlet for the gas evolved.

Reactions at electrodes: At cathode: $\text{Mg}^{2+} + 2\text{e}^- \rightarrow \text{Mg}$
At anode: $2\text{Cl}^- - 2\text{e}^- \rightarrow 2\text{Cl} \rightarrow \text{Cl}_2 \uparrow$

Method of collection: The magnesium is in the molten state and floats on top of the electrolytic mixture. It is tapped. The chlorine gas is collected through the outlet on the porcelain tube.

Precautions: (a) Coal gas is passed over the electrolytic mixture to prevent its oxidation.

(b) The iron pot has to be heated externally to keep the temperature at 700°C so that :

(i) the electrolyte remains molten and

(ii) the magnesium forming remains in liquid state for easy tapping.

Uses of magnesium

Magnesium is used in a wide range of applications like flash lights in photography, for igniting aluminium powder in *Thermite welding*, as reducing agent in metallurgy, to remove traces of air from radio tubes and manufacture of alloys like magnalium.

4.6 IMPORTANT POINTS TO REMEMBER

- * Be, Mg, Ca, Sr, Ba and Ra belong to group IIA of the periodic table.
- * The valence electronic configuration of group IIA elements is ns^2 ($n = 1, 2, 3 \dots$)
- * Mg and Ca are abundant in nature in the form of their oxides and halides.
- * Ra is radioactive.
- * Atomic and ionic size of group IIA elements increases from Be to Ra.
- * Ionization energies and electronegativities of these elements decrease from Be to Ra.
- * M.P. and B.P of elements do not follow any regular trend.
- * Group IIA elements are very reactive and hence do not occur in elemental state.
- * These elements react with (i) water to liberate hydrogen (ii) oxygen to form oxides and (iii) halogens to form halides.
- * Oxides of these elements show basic character.
- * All group IIA elements form hydrides of the type MH_2 , which act as reducing reagents.
- * BeCl_2 is covalent. Other halides are ionic.
- * Group IIA elements are extracted from their chlorides by electrolytic reduction.
- * KCl and NaCl are added to anhydrous MgCl_2 during electrolysis to reduce the melting temperature and increase the electrical conductivity.
- * Graphite rod and iron pot act as anode and cathode respectively during the electrolysis of MgCl_2 .

EXERCISE

I. Choose the correct answer

(1) The least abundant alkaline earth metal is

- (a) Barium (b) Radium
(c) Strontium (d) Beryllium

(2) Which of the following configuration is correct for alkaline earth metals?

- (a) $1s^2 2s^2 2p^6$ (b) $1s^2 2s^2 2p^6 3s^2 3p^2$
(c) $1s^2 2s^2 2p^6 3s^2$ (d) $1s^2 2s^2 2p^3$

(3) Which of the following ions has the largest ionic radius?

- (a) Be^{2+} (b) Mg^{2+}
(c) Ca^{2+} (d) Sr^{2+}

(4) Which of the following has the highest first ionization energy?

- (a) Ba (b) Mg
(c) Ca (d) Be

- (5) In alkaline earth metals, the electrons are more firmly held to the nucleus. The correct statement is
- Ionization energy of alkaline earth metals is greater than that of alkali metals.
 - Alkaline earths are less abundant in nature
 - Reactivity of alkaline earth metals is greater than that of alkali metals
 - Atoms of alkaline earth metals are bigger in size than alkali metals
- (6) The valence shell configuration of alkaline earth metals is represented by ns^2 where n varies from
- 2 to 6
 - 2 to 7
 - 1 to 6
 - 1 to 7
- (7) Which one of the alkaline earth metals shows some anomalous behaviour?
- Ba
 - Sr
 - Ca
 - Be
- (8) Alkaline earth metals are not found free in nature because of
- Their thermal instability
 - Their low melting points
 - Their high boiling points
 - Their greater chemical reactivity
- (9) Which salt gives crimson colour in flame?
- $SrCl_2$
 - $CaCl_2$
 - $NaCl$
 - $MgCl_2$
- (10) Elements of IIA group having electronic configuration ns^2 are called alkaline earth elements because
- they only occur in earth
 - their salts form only alkaline solution
 - they all form divalent cations only
 - their oxides are basic in nature
- (11) Which of the following statements is correct?
- Alkali metals are less electropositive than alkaline earth metals
 - Alkaline earth metals are denser and harder than alkali metals
 - Alkali metals are denser and harder than alkaline earth metals
 - First ionization potential of alkali metals is more than that of alkaline earth metals
- (12) Magnesium burns in CO_2 to form
- $MgO + C$
 - $MgO + CO$
 - $MgCO_3$
 - MgO
- (13) Magnesium burns in air forming
- Mg_2O_2
 - MgO
 - Mg_3N_2 and MgO
 - Mg_3N_2
- (14) A piece of Mg ribbon was heated to redness in nitrogen atmosphere and then cooled with water. The gas evolved is
- NH_3
 - H_2
 - O_2
 - N_2
- (15) The most reactive element among the following is
- Na
 - Mg
 - Ca
 - Ba
- (16) The alkaline earth metal that forms mainly covalent compounds is
- Mg
 - Be
 - Ca
 - Ba
- (17) Beryl is
- $3BeO \cdot 3Al_2O_3 \cdot 3SiO_2$
 - $3BeO \cdot Al_2O_3 \cdot 6SiO_2$
 - $BeO \cdot Al_2O_3 \cdot SiO_2$
 - $4Al_2O_3 \cdot 6Be \cdot 10SiO_2$
- (18) Dolomite is a mineral of
- Be
 - Mg
 - Sr
 - Ba
- (19) The reason for the lower basicity of alkaline earth metals than alkali metals is
- alkali metals form ionic compounds
 - the M-OH bond strength is more for alkali metals
 - alkali metals are more electropositive than alkaline earth metals
 - alkali metals are more electronegative than alkaline earth metals
- (20) Alkaline earth metal compounds are less soluble in water than the corresponding alkali metal compounds because the alkaline earth metals have
- lower lattice energies
 - higher ionization
 - higher covalent character
 - higher ionic character
- (21) Alkaline earth metals form di-positive ions instead of uni-positive ions because
- the second ionization energy is almost double than the first ionization energy
 - uni-positive ions do not have stable configuration
 - the hydration energy of di-positive ions is more than that which compensates the higher value of the second ionization energy
 - uni-positive ions are highly hydrated
- (22) In comparison to alkali metals, alkaline earth metals are
- less reactive
 - less reducing
 - less basic
 - all the three

- (23) Which one of the following statements is correct for alkaline earth metals?
- They are diatomic and form ions of the type M^{2-}
 - They are highly electronegative elements
 - They are monoatomic and form ions of the type M^+
 - They are monoatomic and form ions of the type M^{2+}
- (24) The basic character of oxides MgO , SrO , K_2O , NiO , Cs_2O increase in the order
- $MgO > SrO > K_2O > NiO > Cs_2O$
 - $Cs_2O < K_2O < MgO < SrO < NiO$
 - $NiO < MgO < SrO < K_2O < Cs_2O$
 - $K_2O < NiO < MgO < SrO < Cs_2O$
- (25) Which of the following alkaline earth metal hydroxides is amphoteric in character?
- $Be(OH)_2$
 - $Ca(OH)_2$
 - $Sr(OH)_2$
 - $Ba(OH)_2$
- (26) Alkaline earth metal halides
- are hygroscopic in nature
 - act as dehydrating agents
 - can absorb moisture from air
 - all the above
- (27) A burning strip of magnesium is introduced into a jar containing a gas. After sometime the walls of the container is coated with Carbon. The gas in the container is
- O_2
 - N_2
 - CO_2
 - H_2O
- (28) Burning magnesium continues to burn in SO_2 forming
- MgO and MgS
 - MgO only
 - MgS only
 - $MgSO_4$
- (29) The covalent halide among the following is
- BeF_2
 - $MgCl_2$
 - $CaCl_2$
 - $BaCl_2$
- (30) Among the following amphoteric oxide is
- BeO
 - Al_2O_3
 - ZnO
 - all the above
- (31) Compared to alkaline earth metals, the alkali metals exhibit
- smaller ionic radii
 - higher boiling points
 - greater hardness
 - lower ionization energy

II. Write the name of the following ores :

- $MgCl_2 \cdot 6H_2O$
- $MgCO_3$
- $MgSO_4 \cdot 7H_2O$
- $CaCO_3 \cdot MgCO_3$
- $Be_3Al_2(SiO_3)_6$
- $BaSO_4$

III. Match the following.

- (1) Match Groups in List 1 with their general method of extraction in List 2.

List 1

List 2

- | | |
|-------------------------|-----------------------------|
| (a) Alkali Earth Metals | (i) Liquefaction |
| (b) Alkali Metals | (ii) Electrolytic Reduction |
| (c) Halogens | (iii) Vaporisation |
| (d) Nobel Gas Elements | (iv) Chemical methods |

- (2) Match the Ionisation Potential values given in List 1 with the elements of Group IIA in List 2.

List 1

List 2

- | | |
|------------|----------------|
| (a) 6.1 eV | (i) Strontium |
| (b) 9.3 eV | (ii) Magnesium |
| (c) 5.7 eV | (iii) Calcium |
| (d) 7.6 eV | (iv) Beryllium |

- (3) Match Atomic Radii given in Angstrom units in List 1 with the elements of Group IIA in List 2.

List 1

List 2

- | | |
|----------|-----------------|
| (a) 2.15 | (i) Magnesium |
| (b) 1.12 | (ii) Strontium |
| (c) 2.22 | (iii) Beryllium |
| (d) 1.60 | (iv) Barium |

IV. State whether the following statements are True or False

- Group IA metals are less electropositive than Group IIA.
- Beryllium halides are covalent compounds.
- Coke powder is put on top of the electrolyte mixture in metallurgy of magnesium to prevent heat loss.
- The radioactive Group IIA element is Francium
- Bicarbonates of Group IIA elements cause hardness of water.

V. Find the odd one out

- magnesium, beryllium, calcium, cesium, strontium
- magnesium chloride, calcium chloride, strontium chloride, beryllium chloride, barium chloride
- $MgCO_3 \cdot 7H_2O$, Fe_2O_3 , $MgCl_2 \cdot KCl \cdot 6H_2O$, $CaCO_3$, $MgCO_3$, $Be_3Al_2(SiO_3)_6$

VI. Read the passage given below and answer the questions that follow.

In the extraction of metals, the less electropositive metals are reduced by chemical methods while the more electropositive metals are reduced by electrolysis. In general ores are converted to their oxides and then reduced by chemical reducing agents. The more electropositive metals are reduced with difficulty by chemical methods. For such metals extraction by electrolytic reduction is preferred.

During electrolysis of these metal compounds, the molecules dissociate into ions. The metal ions migrate to the cathode where they get reduced by accepting electrons. However for the less electropositive metals, electrolytic reduction is relatively more expensive. The chemical method using reducing agents like Carbon or Carbon monoxide is preferred.

- (1) Metals that are easily reduced from their oxides are _____ reactive.
 - (a) more
 - (b) less
 - (c) equal
 - (d) not
- (2) In electrolysis, reduction takes place at _____ (electrode).
 - (a) cathode
 - (b) anode
 - (c) anti-cathode
 - (d) bottom
- (3) In general the electrolyte used in the electrolytic extraction of metals is in the fused state rather than an aqueous solution. This is because
 - (a) the salt is insoluble
 - (b) to keep metal dry
 - (c) water is poor conductor
 - (d) to eliminate H^+ ions

VII. Fill in the blanks.

- (i) The basic nature of oxides of Group IIA elements _____ down the group.
- (ii) Barium compounds when introduced in a flame impart it a colour _____.
- (iii) The flame colouration seen with Alkali earth metals is due to _____.
- (iv) For Group IA elements, the first ionisation energy is _____ second ionisation energy and for Group IIA elements, the second ionisation energy is _____ first ionisation energy.
- (v) The most alkaline Group IIA element is _____.

VIII. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, Statement R is true; Statement R is correct explanation for statement A

Choose B if Statement A is true, Statement R is true; Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D if Statement A is false, Statement R is true

- (1) **Statement A:** Alkali Earth Metals are more basic than corresponding Alkali Metals.

Statement R: Alkali Earth Metals ions have high hydration energy.

- (2) **Statement A:** Alkali Earth Metals show a stable +2 oxidation state.

Statement R: Alkali Earth Metals have ns^2 valence configuration.

- (3) **Statement A:** Alkali Earth Metals are less reactive than the corresponding Alkali Metals.

Statement R: Alkali Metals have very low Ionisation Potential when compared to Alkali Earth Metal.

- (4) **Statement A:** Alkali Earth Metals are extracted by electrolytic reduction.

Statement R: Alkali Earth Metals are easily reduced.

IX. Answer the following questions.

- (1) Why are Alkali Earth Metals kept in Group IIA? Why do they exhibit +2 oxidation state?
- (2) A sudden increase in IP value can be seen between an Alkali Element (Group IA) in a period and the corresponding Group IIA and Group IIIA elements in the same period. Why? Example I_1 of Na is 5.1 while that of Mg is 7.6 but that of Al in the same period is 6.0
- (3) What do Alkali Earth Metals give coloured flames.
- (4) In general $I_2 > I_1$. Yet, Alkali Earth Metals have a tendency to form, divalent rather than monovalent ions. Why?
- (5) Complete the following table to compare Alkaline Earth Metals and Alkaline Metals

Description	Alkaline Earth Metals Group IA	Alkali Metals Group II A
Electronic configuration		
Valency		
MP and BP		
Hardness		
Solubility of salts		
Flame colour		

(6) Beryllium exhibits anomalous behaviour in comparison to other group members. What is this due to?

(7) Complete the table to indicate the trends in the given physical and chemical properties as we go down Group IIA.

	Property	Trend down the group	Reason (if any)
(a)	density		
(b)	Valence configuration		
(c)	metallic nature		
(d)	basic nature		
(e)	reaction with oxygen		
(f)	reaction with halogens		
(g)	reaction with water		
(h)	solubility of hydroxides		
(i)	reaction with hydrogen		
(j)	nature of hydrides (oxidising or reducing agents)		

(8) How are Alkali Earth Metals extracted from their ores and why?

(9) There are three positive ions that migrate to the cathode, yet only Mg^{2+} is reduced. Why?

(10) State the uses of Magnesium.

(11) In the metallurgy of magnesium, how is carnalite ore made anhydrous?

(12) How does the flux added to the electrolyte in metallurgy of Magnesium reduce the melting point and increase conductivity?

KEY TO EXERCISE										
I.	(1) b	(2) c	(3) d	(4) d	(5) a	(6) b	(7) d	(8) d	(9) a	(10) d
	(11) b	(12) a	(13) c	(14) a	(15) a	(16) b	(17) b	(18) b	(19) c	(20) c
	(21) c	(22) d	(23) d	(24) c	(25) a	(26) d	(27) c	(28) a	(29) a	(30) d
	(31) d									
II.	i. Carnalite	ii. Magnesite	iii. Epsom salt	iv. Dolomite	v. Beryl	vi. Barytes				
III.	(1) a. ii	b. ii	c. iv	d. i	(2) a. iii	b. iv	c. i	d. ii		
	(3) a. iv	b. iii	c. ii	d. i						
IV.	i. false	ii. true	iii. false	iv. false	v. true					
V.	i. cesium	ii. beryllium chloride	iii. Fe ₂ O ₃							
VI.	1. b	2. a	3. d							
VII.	i. increases rapidly	ii. apple green	iii. excited electrons returning to ground state							
	iv. lesser than, greater than	v. barium								
VIII.	1. D	2. A	3. A	4. C						

5

Metals and Metallurgy

5.0 INTRODUCTION

Out of the 80 odd metals known some metals are very useful to man in the elementary state. Iron, Aluminium, Copper, Zinc, Gold and Silver are some of the more widely useful metals. The useful metals are not found in the elementary state but as compounds. The compounds of the metals found in nature are called *minerals*. The naturally occurring minerals from which metals can be conveniently and economically extracted are called *ores*. Metallurgy is the branch of chemistry that deals with the extraction of metal from its *ore*.

5.1 CHARACTERISTICS OF METALS

In general, metals exhibit the following characteristics:

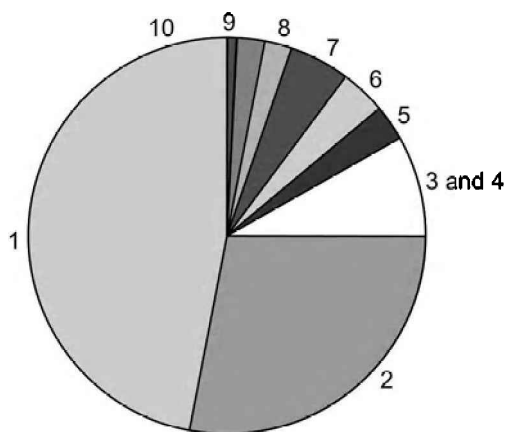
- (i) All metals are solids at room temperature excluding Mercury which is a liquid.
- (ii) Metals are good conductors of heat and electricity.
- (iii) Metals are malleable, ductile and sonorous and have lustre.
- (iv) Metals occur to the left and centre of the periodic table. Hydrogen is the only non-metal placed to the left of the periodic table.
- (v) Metals lose electrons relatively more easily when compared to non-metals to form cations. (Hydrogen is the only element which is not a metal but which also loses electrons).
- (vi) The oxides of metals are basic or amphoteric in nature (Example: Na_2O is basic while Al_2O_3 is amphoteric).

Metals

Physical Property	Metals	Exceptions
(1) Physical state:	Generally solid at room temp.	Hg, Ga
(2) Hardness:	Very hard	Na, K, Mg, Au
(3) Lustre:	When cut they shine	
(4) Density:	High	Na, K ($< \text{H}_2\text{O}$), Ca, Mg
(5) MP and BP:	High	Na, K – low MP / Ga, Hg – low BP
(6) Malleability/Ductility:	High / high	Zn, As, Sb, Bi / Zn, As, Sb, Bi, Hg
(7) Tensile strength:	High	Ga
(8) Conductivity:	High	Zn, As, Sb, Bi, Hg, Ga
(9) Atomicity:	Monoatomic	Bi, W
Chemical Property	Metals	Exceptions
(1) Valence electrons:	1,2 or 3 electrons	
(2) Formation of ions:	Form cations (lose e^-)	
(3) Oxidising action:	Oxidised so are reducing agents	
(4) Reducing action:	—	
(5) Nature of oxides:	Basic	ZnO , PbO , Al_2O_3 , SnO – Amphoteric.
(6) Action with acids:	Generally form salt and liberate H_2	Metals below H_2 in M.A.S

5.2 OCCURRENCE

The metals occur in the earth's crust as minerals or ores. The order of abundance by weight of metals in the earth's crust is Aluminium > Sodium > Calcium > Iron > Magnesium > Potassium > Titanium.



Pie chart number	Element
1	O
2	Si
3	Al
4	H
5	Na

6	Ca
7	Fe
8	Mg
9	K
10	C

Most metals exist as compounds. Only a few occur free in nature. The pie chart above shows the relative proportions of the different elements measured as weight or mass percent.

Examples of metals that occur free in nature: Copper, Silver, Gold, Platinum and Bismuth.

Differentiating between minerals and ores

Minerals are natural materials found in the earth's crust. Metals occur as oxides, carbonates, sulphides, sulphates, halides, nitrates, etc.

Ores are minerals from which metals can be extracted conveniently and economically.

Some metals like gold, silver copper and platinum occur free as they do not react easily with water, CO_2 , etc. Most metals occur in the combined state as minerals. Out of these minerals some are *ores*.

Ores, from which metals can be extracted conveniently, occur as oxides, carbonates, sulphides, sulphates, halides and nitrates, etc.

Examples of ores

Examples of oxide ores	Examples of carbonates ores
(i) Cuprite - Cu_2O (ii) Haematite - Fe_2O_3 (iii) Corundum - Al_2O_3 (iv) Cassiterite - SnO_2 (v) Magnetite - Fe_3O_4 (vi) Zincite - ZnO (vii) Lead ochre - PbO (Litharge)	(i) Limestone - CaCO_3 (ii) Siderite - FeCO_3 (iii) Magnesite - MgCO_3 (iv) Dolomite - $\text{CaCO}_3 \cdot \text{MgCO}_3$ (v) Malachite - $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ (vi) Calamine - ZnCO_3 (vii) Cerussite - PbCO_3
Examples of sulphides ores	Examples of sulphates ores
(i) Zinc Blende - ZnS (ii) Cinnabar - HgS (iii) Galena - PbS (iv) Copper pyrites - CuFeS_2 (v) Iron pyrites - FeS_2 (vi) Argentite - Ag_2S	(i) Gypsum - $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (ii) Epsom salt - $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (iii) Anglesite - PbSO_4 (iv) Barytes - BaSO_4 (v) Alunite - $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 4\text{Al}(\text{OH})_3$

Examples of halides ores	Examples of nitrates ores
(i) Rock salt - NaCl	(i) Chile Salt Petre - NaNO_3
(ii) Fluorspar - CaF_2	(ii) Bengal nitre or Petre - KNO_3
(iii) Carnalite - $\text{MgCl}_2 \cdot \text{KCl}$	Examples of hydrated oxides ores
(iv) Horn silver - AgCl	(i) Limonite- $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
(v) Cryolite - Na_3AlF_6	(ii) Bauxite- $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$

5.3 METALLURGY

Some important terms used in *metallurgy* are given below.

- Minerals** are the compounds of metals found naturally in the earth's crust.
- Ores** are minerals from which metals can be conveniently and economically extracted.
- Gangue or matrix** is the unwanted impurity in the ore such as mud, stones, sand, etc.
- Metallurgy** is a branch of chemistry which deals with the extraction of pure metal from its ore.
- Leaching** is a widely used extraction method that converts the ore into aqueous solution.
- Smelting** is the reduction of the ore in a blast furnace.
- Matte** is a term used for the molten metal sulphides formed during smelting of copper, nickel and iron ores.
- Calcination** is the roasting of ore in a limited supply of air to remove volatile impurities and make the ore porous to increase its surface area.
- Roasting** is the heating of ore to convert impurities into oxides and the ore to its oxide form.

5.4 STEPS IN METALLURGY

The process for extracting metal from the ore can be divided into four steps:

Step 1: *Dressing and concentration of ore*

Step 2: *Conversion of ore into oxide (or a suitable compound)*

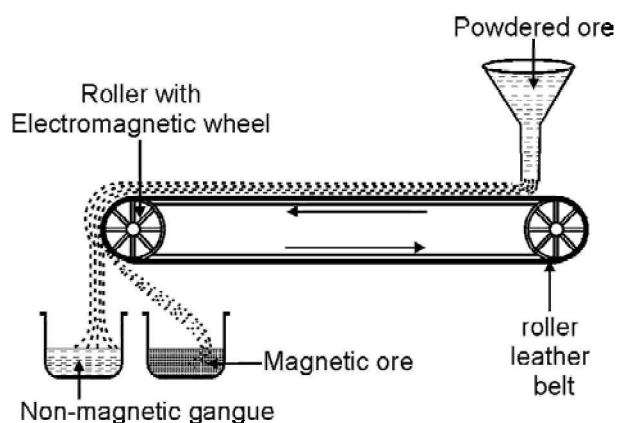
Step 3: *Extraction of metal*

Step 4: *Purification or refining of metal.*

5.5 DRESSING AND CONCENTRATION OF ORE

The ores contain a large part of gangue / matrix. The matrix has to be removed before the metal is extracted. This is done in two steps.

- Dressing:** The ore is *dressed* using one or more of the following methods:
 - handpicking, grinding and crushing, and
 - pulverising (grinding the ore to a fine powder to increase the surface area).
- Concentration:** The ore is next *concentrated* to increase the percentage of metal in the ore using one of the methods given below.
 - Electromagnetic process** used primarily for iron ores. The pulverized ore is put on a moving conveyor belt. One of the rollers of the conveyor belt is magnetic. As the pulverized ore moves over the magnetic roller, the iron ore particles get attracted till the last point on the roller and fall into a separate heap. The impurities that are non-magnetic fall vertically down in a separate heap (see schematic diagram and photo below).

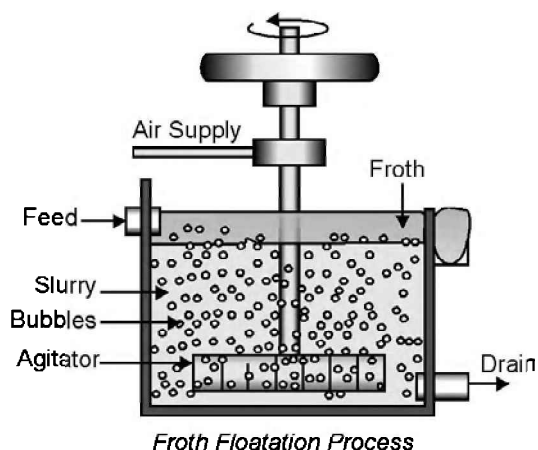


Schematic diagram showing electromagnetic separation

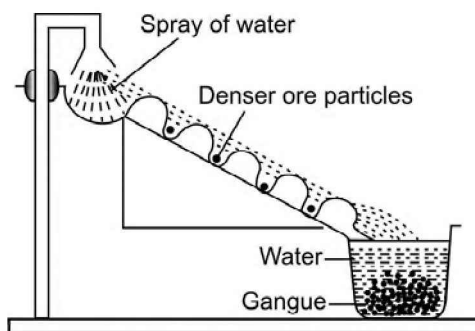


Actual photo of concentration of iron ore by electromagnetic separation

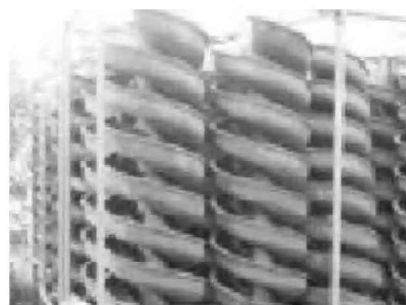
- (ii) **Froth floatation process** [used primarily for sulphide ores such as galena (PbS), zinc blende, (ZnS) and copper pyrites (CuFeS_2)]. In Froth Floatation Process, the ore is mixed with water and pine oil and churned with a strong jet of air. The pine oil wets the sulphide ore particles while water wets the remaining gangue particles. Due to churning, a froth of oil with ore concentrate is formed. The froth floats at the top and is removed and the sulphide ore recovered. The gangue is left behind at the bottom (See diagram).



- (iii) **Gravity process** (except for sulphide ores) in which the pulverized ore is poured over large tables with slanting tops and treated with a jet of water when the lighter matrix is washed away leaving the heavier ore behind (see figures).



Gravity separation using water and vibrating table



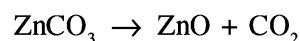
Gravity separation using water (actually photo)

5.6 CONVERSION OF ORE INTO OXIDE

The ore is next treated for the removal of volatile impurities and converted into its oxide for extraction of the metal. Two methods are outlined below.

- (i) **Calcination:** The ore is heated in a limited supply of air (taking care that the ore does not melt) to remove volatile constituents including moisture. This also makes the ore porous.

This method is used for carbonate ores and hydrated metallic oxides.

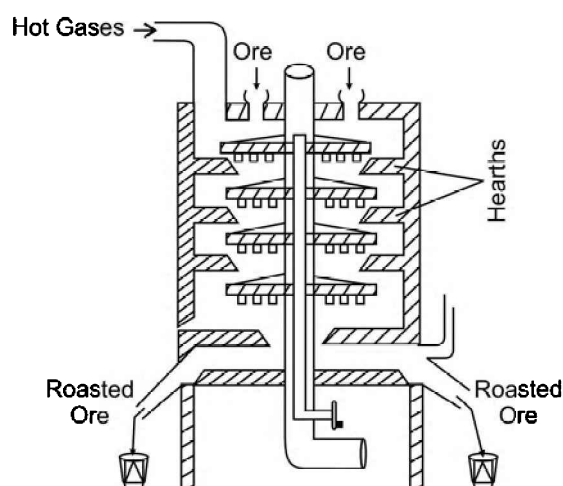


Objective achieved during calcination

- (1) Calcination removes moisture from the ore
 - (2) Calcination makes the ore porous
 - (3) Calcination expels volatile impurities.
 - (4) Calcination decomposes metallic carbonates to metallic oxides.
- (ii) **Roasting:** The ore is strongly heated to a high temperature *in excess of air* to remove volatile impurities. This converts it into oxides. This method is used for sulphide ores.

Objective achieved during roasting

- (1) Roasting removes moisture and water of crystallisation from the hydrated ores.
- (2) Roasting makes the ore porous
- (3) Roasting expels volatile impurities.
- (4) Roasting converts sulphides to oxide ores.



Multiple layered hearth furnace used for roasting.

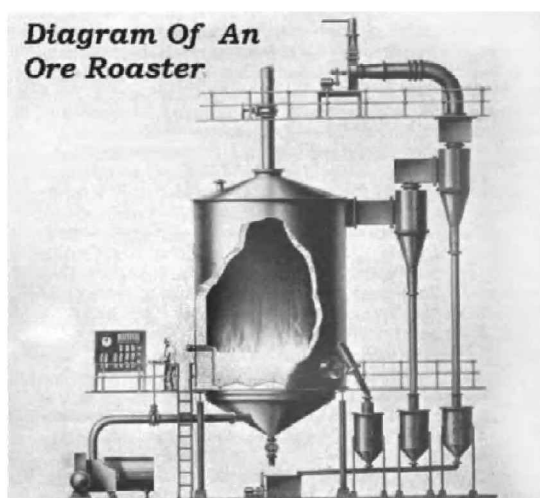
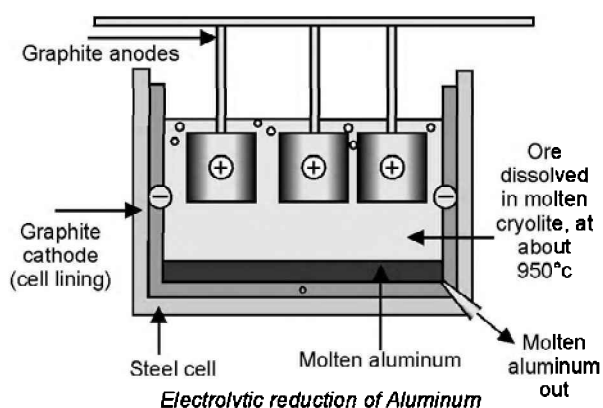


Diagram Of An Ore Roaster

5.7 REDUCTION OF ORE TO PURE METAL (EXTRACTION OF METAL)

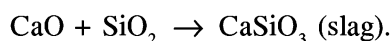
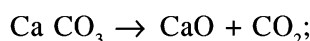
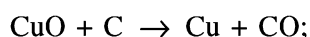
The exact method used depends on the position of the metal in the Metal Activity Series.

- (i) **Electrolytic process:** This is used for extraction of more electropositive metals like Na, K, Ca, Mg, and Al. The fused oxide or salt is used as the electrolyte. On electrolysis, the metal is deposited at the cathode (see figure).



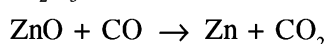
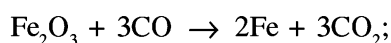
- (ii) **Reduction with Carbon:** This method is used for the metals lower in the electrochemical series like Zn, Fe, Pb, Sn and Cu. The ore is mixed with coke (reducing agent), limestone (which acts as **flux**). This mixture is then fired using a hot blast of air. Carbon reduces the metallic oxide to metal. Limestone decomposes to CaO. This CaO reacts with sand present in the ore to form Calcium silicate – **slag**. The **slag** floats on top of the liquid metal. Both are tapped separately.

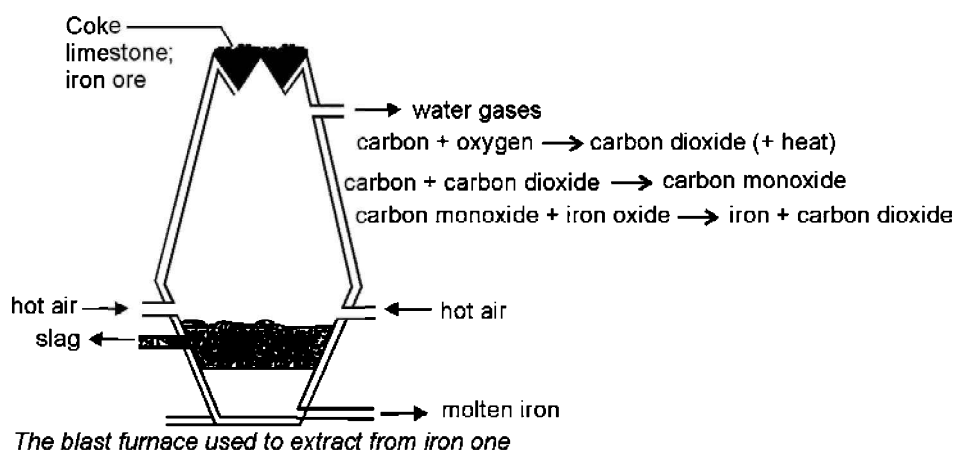
The reactions:



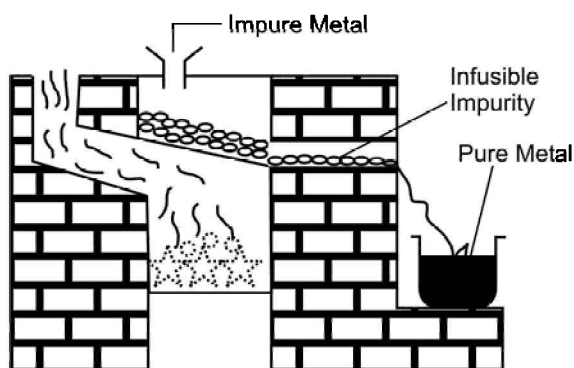
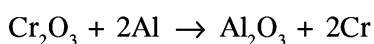
This method is commonly used for metallurgy of copper and lead.

- (iii) **Reduction using CO gas:** The reducing agent used is CO instead of C. This is used in the metallurgy of Fe and Zn.





- (iv) **Reduction using Al powder:** Metals like Cr and Mn cannot be extracted from their oxides by heating them with reducing agents like C or CO as they have strong affinity for oxygen. They can be extracted using electrolytic method or by using Al powder as reducing agent.



a hearth with a sloping floor in absence of air. The pure metal liquefies and flows down the sloping floor leaving solid impurities with higher MP behind. (Used for metals with low MP like Pb and Sn) (see figure).

Poling: Used to refine Cu. In this method, green wooden poles are used to agitate molten impure Cu. The heat of molten copper makes the green pole emit 'wood' gases which reduce Cu_2O to Cu.

Oxidation: Oxygen is blown through molten iron when impurities like C, As, S, etc., are oxidized to form their gaseous products and are blown out.

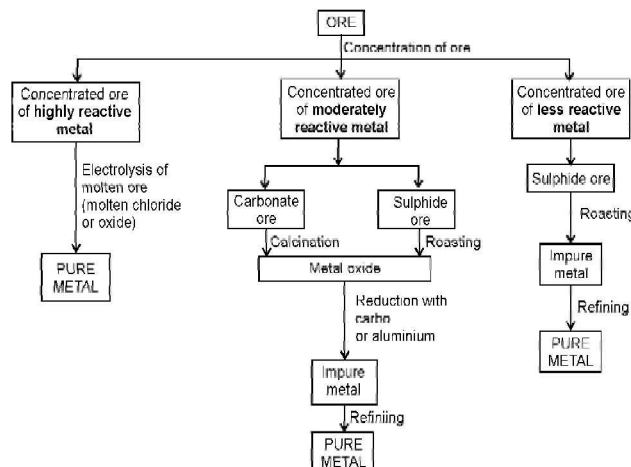
Electrolytic Refining: The impure metal is made the anode and suspended in an electrolyte containing a soluble salt of the same metal. The cathode is made of a thin strip of the pure metal. On electrolysis, the pure metal is deposited on the cathode. The impurities pass into the solution or are deposited near the anode as Anode mud. (Used for Cu, Sn, Pb, Al). (See figure below).

5.8 PURIFICATION AND REFINING OF METALS

Metals extracted by the above methods contain small quantities of impurities. The impurities can be other metals or their oxides and non-metals and gases. They are further refined as follows:

Distillation: The impure metal is strongly heated in absence of air when the metal vaporizes leaving the impurities behind. The vapours are condensed to get pure metal. (This method is used for metals with low Melting Point like Zn and Hg).

Liquation: The solid impure metal is heated in



EXERCISE

1. Differentiate between a mineral and an ore.
2. Enlist the methods of dressing and concentration of an ore. Mention the reasons for dressing and concentration.
3. Name three ores each that have the metal as carbonate, sulphate and oxide.

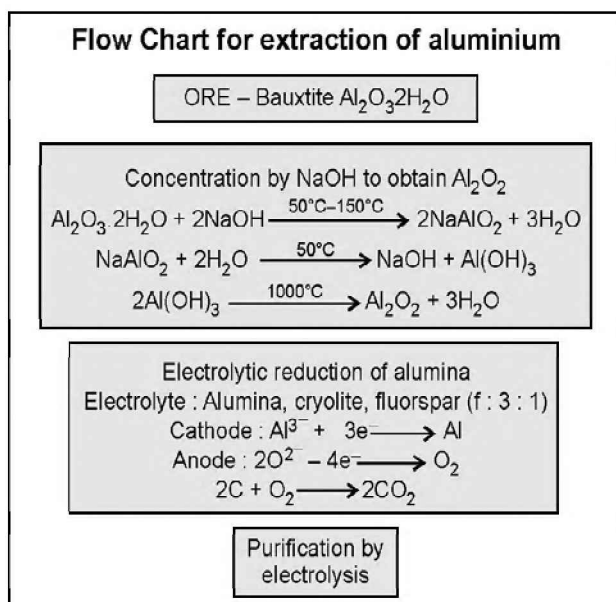
5.9 METALLURGY OF ALUMINIUM (Hall's Process)

The metallurgy of Aluminium by *Hall's process* is outlined.

Ore: Bauxite ($\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$).

Method: The ore is converted to alumina (pure Al_2O_3) and electrolytically reduced.

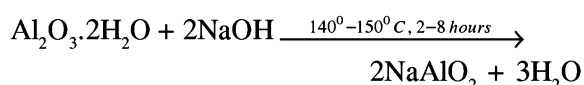
After dressing of ore and concentration by Gravity process the ore is pulverized and heated to remove volatile impurities.



Step 1: Conversion of ore to alumina by Baeyer's process

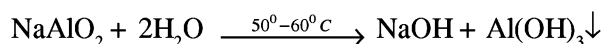
The powdered ore is heated with a concentrated solution of sodium hydroxide (NaOH) under pressure for 2 – 8 hours. The impurities mainly, ferric oxide (Fe_2O_3) and silicon dioxide (SiO_2), being *basic oxides*, do not react with NaOH and settle as a precipitate called *red mud* and is removed by filtration.

Step 2: Aluminium oxide (Al_2O_3) present in the ore, being an *amphoteric oxide* reacts and forms a soluble salt – sodium aluminate.

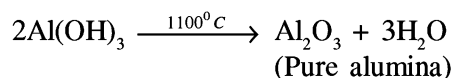


The sodium aluminate is diluted with water and mildly heated to a temperature of 50 – 60°C when

aluminium hydroxide - Al(OH)_3 precipitates out.



The aluminium hydroxide, Al(OH)_3 is next filtered. The NaOH obtained as filtrate is re-used. The precipitate is washed, dried and heated to 1100°C to get *pure alumina*.



Step 3: Reduction of alumina by electrolysis

As Aluminium has a high affinity for oxygen, alumina is a very stable compound. Alumina cannot be reduced to pure aluminium *conveniently* by using reducing agents such as carbon, carbon monoxide or hydrogen. Hence electrolytic reduction is used.

Adding flux

Alumina is mixed with flux – a mixture of chemicals. The flux used is cryolite and fluorspar.

The ratio of alumina to cryolite to fluorspar is 1:3:1.

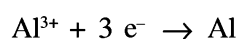
	Alumina (Al_2O_3)	–	20%
Flux ratio	Cryolite (Na_3AlF_6)	–	60%
	Fluorspar (CaF_2)	–	20%

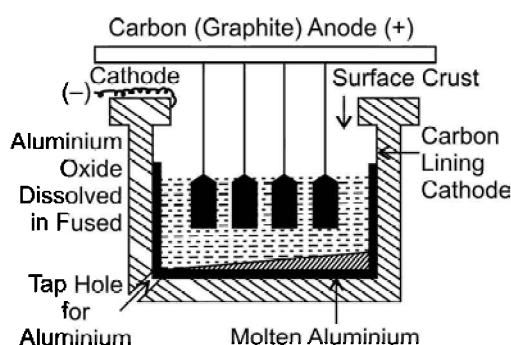
Reason for adding flux: The flux is added to the ore to :

- (i) increase its conductivity by providing more ions
- (ii) reduce the melting point of the electrolyte to 950°C from 2050°C of the pure alumina so that fuel can be saved
- (iii) to facilitate dissolution of alumina as the flux melts before the alumina.

Electrolytic reduction

The mixture is heated to 900°C when it melts. The mixture is now put in an iron pot and reduced by electrolysis. The positive ions in the mixture are Na^+ , Ca^{2+} and Al^{3+} . The positive ions move towards the cathode. At the cathode, aluminium is preferentially discharged.



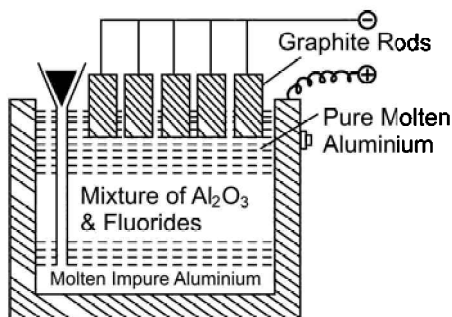


Reason for preferential discharge of aluminium ions at cathode

Metals lower in the Electrochemical Series are preferentially discharged at the cathode during electrolysis, as these metal ions will have **higher reduction potential – the tendency to gain electrons**. Due to the lower position of Aluminium in the Electrochemical Series, aluminium is discharged preferentially at the cathode.

As Melting Point of Aluminium is 660°C , the discharged aluminium is in the molten state. Aluminium being heavier than the electrolyte mixture sinks to the bottom. As more Aluminium gets discharged at the cathode, the concentration of alumina decreases during electrolysis. This decreases the conductivity of the electrolyte. To indicate this, a bulb is connected. When the bulb glows more brightly more alumina is added.

Step 4: Refining is done by further electrolysis. The process uses an electrolytic cell which contains three layers of molten substance of differing densities. Molten impure aluminium forms the bottom layer and serves as anode, while pure aluminium serves as cathode in the top layer. The middle layer consists of a mixture of fluorides of sodium, barium and aluminium. On electrolysis, aluminium from the middle layer passes to the top layer. An equivalent amount of aluminium shifts from the lower layer to the middle layer. Pure aluminium floats on the top and is tapped regularly.



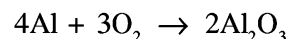
Properties of aluminium

Physical properties

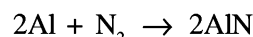
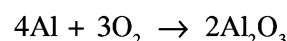
- Aluminium is a silvery white metal with good lustre. Over time it appears dull due to formation of an oxide layer.
- Aluminium is a strong metal with high tensile strength.
- Aluminium is ductile and malleable.
- Aluminium is a good conductor of heat and electricity.
- Aluminium melts at 660°C and boils at 2050°C .

Chemical Properties

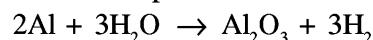
- Aluminium reacts with oxygen in the air forming a layer of aluminium oxide on its surface.



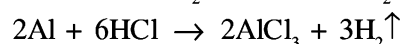
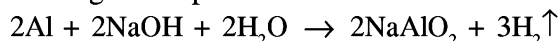
On heating to 800°C Aluminium burns with a bright light forming both Aluminium oxide and Aluminium nitride.



- Pure Aluminium reacts with steam liberating hydrogen. Ordinary aluminium does not react as it is rendered passive due to an oxide layer.

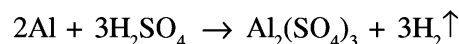


- Aluminium reacts with strong bases and acids showing its amphoteric nature.

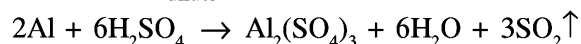


The reaction is slow in the beginning due to the oxide layer. After the layer gets dissolved the main reaction proceeds faster.

With dilute and concentrated sulphuric acid, aluminium liberates hydrogen and sulphur dioxide respectively.



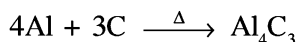
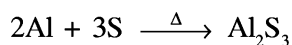
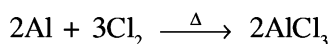
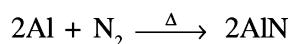
dilute



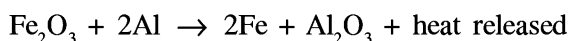
concentrated

Dilute and concentrated nitric acid makes aluminium passive due to the formation of the oxide layer.

- Aluminium reacts with non-metals like nitrogen, chlorine, sulphur, and carbon as follows.



- (e) Reducing property: Aluminium is a good reducing agent. Aluminium reduces ferric oxide (Fe_2O_3) when ignited to iron in an extremely exothermic reaction. The reduced iron will be in the molten form.



Uses of aluminium

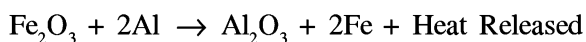
Aluminium is used in making alloys as it is light, strong and corrosion resistant.

As Aluminium is light, malleable, ductile with high tensile strength it is used in making cooking utensils, window and door frames, thin foils for wrapping food articles, etc.

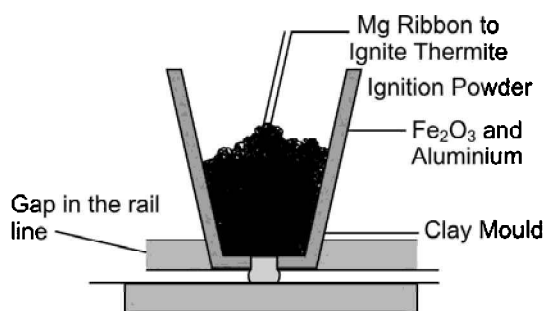
Aluminium is used in making ammonal an explosive (aluminium powder with ammonium nitrate).

Aluminium is used in **Thermite welding**: Thermite is a mixture of three parts ferric oxide and one part Al powder.

When this is heated the more reactive Al displaces Fe.



The heat released is so high that it can melt the iron. This is used to weld railway lines.



5.10 METALLURGY OF IRON

The metallurgy of iron is outlined below.

Ores: Haematite (Fe_2O_3), Limonite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), Magnetite (Fe_3O_4), Siderite (FeCO_3), iron pyrites (FeS_2) and copper pyrites (CuFeS_2).

Method: The ore is converted to oxide and reduced with CO.

The dressed ore is concentrated by electromagnetic process and then by gravity processes.

The ore is next roasted in excess of air.

Roasting has the following benefits:

- (i) removes volatile impurities,
- (ii) oxidises ferric oxide to ferrous oxide,
- (iii) converts carbonate ores into oxide and
- (iv) the ore mass becomes porous.

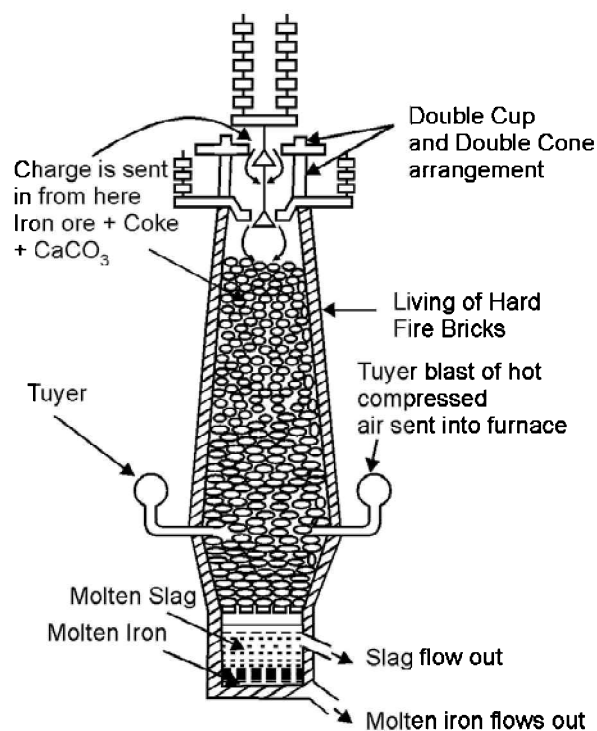
Next, the ore is smelted by reduction in a blast furnace.

The ore is mixed with coke and limestone (CaCO_3) in the ratio 3 : 2 : 1. This mixture is called **charge**.

CO acts as reducing agent, while limestone acts as flux.

Blast Furnace

Blast furnaces differ in construction. The one used in the production of iron consists of a chimney



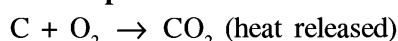
Blast furnace for the manufacture of cast iron

like structure (usually 24-30 m high) made of iron or steel and lined with firebrick. It is narrow at the top, increasing in diameter downward, but narrowing again at the bottom. The blast furnace is a specially constructed huge tower with ceramic bricks lining the inner walls to prevent corrosion. The charge is dropped from the **top of the furnace**, while hot, compressed air is sent from the tuyeres (pronounced tweezer) **at the bottom**.

Reactions

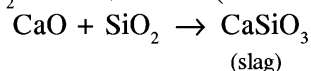
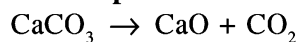
The reactions that take place in the blast furnace are as follows:

Lower part of blast furnace:



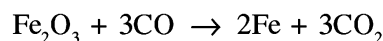
The hot CO_2 rises up the tower.

Middle part of blast furnace:

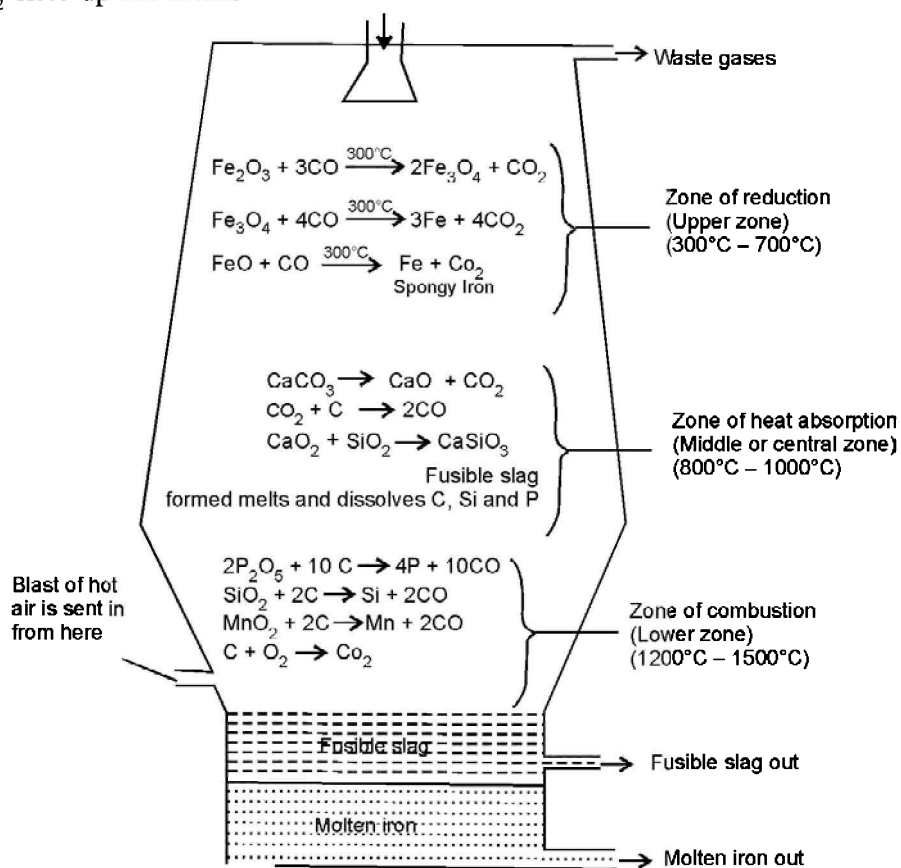


The slag trickles down the blast furnace.

Upper part of blast furnace:



Melting point of iron is 1200°C . Iron melts as it reaches the lower part of the furnace along with slag. In the lower part of the furnace the slag also melts. The slag being lighter floats on the molten iron. Both the slag and the molten iron are tapped separately.



Reaction taking place in the blast furnace

Types of iron

Cast Iron is most impure form of iron containing Carbon, Sulphur, Phosphorous and Manganese as impurities. It is hard and brittle.

Pig Iron: When molten cast iron is suddenly cooled it changes to *Pig Iron*.

Wrought Iron is the *purest form of iron* and contains least amount of Carbon and other impurities.

Steel is a mixture of iron with carbon and other elements. (See table)

Bessemer Converter: Pig Iron is converted to steel in a special furnace called *Bessemer Converter* (see diagram). A blast of hot air is forced into molten pig iron. This oxidises all the impurities. The air supply is cut off. Calculated amount of a *Spiegel* (an alloy of carbon and manganese) is added to form *steel*.

Alloys of iron

ALLOYS OF IRON	METALS PRESENT	% COMPOSITION
(a) Spiegeleisen	(a) Fe, Mn, C	(a) 74, 20, 6
(b) Stainless steel	(b) Fe, Cr, Ni, C	(b) 73, 18, 8, 1
(c) Manganese steel	(c) Fe, Mn, C	(c) 84, 15, 1
(d) Tungsten steel	(d) Fe with Tungsten (W)	(d) 90, 10
(e) Chrome Steel	(e) Fe with Cr	(e) 96, 4
(f) Vanadium Steel	(f) Fe with V	(f) 99.5, 0.5

Hardening and Tempering of steel:

When steel is heated to a temperature of 750°C to 800°C and then suddenly cooled by plunging into cold water or cold oil, the cooled steel is brittle and cannot withstand sharp jerks. This process is called **hardening**.

If the hardened steel is heated to a controlled temperature between 220°C to 300°C and then allowed to cool very slowly over four hours its hardness remains the same but the steel becomes more **tensile**, i.e., it becomes capable of bearing heavy loads or strain without breaking. This process is called **Tempering** or **Annealing**. During tempering the atoms of the metal arrange in such a way that they can take strain.

The various applications of the end products and the temperature to which they are heated during tempering and annealing are listed below.

Temperature	Use
300°C	In manufacture of springs
290°C	In manufacture of screwdrivers
270°C	In manufacture of drill knives
245°C	In manufacture of scissors
220°C	In manufacture of blades

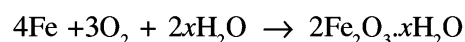
Properties of iron

Physical properties

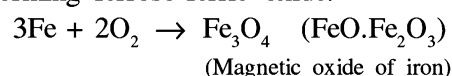
- It is a heavy metal (sp. gr. 7.9)
- It is malleable and possesses high tensile strength.
- It is a good conductor of heat and electricity
- It can be magnetised.
- It melts at 1535°C.

Chemical properties

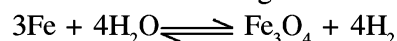
- With dry air, iron has no reaction, but moist air turns iron into rust over time.



With hot air, iron burns giving green sparks forming ferrous-ferric oxide.

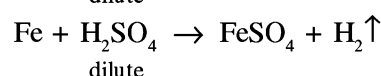
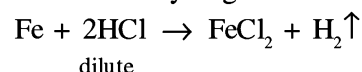


- With steam iron forms magnetic oxide of iron

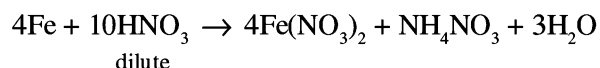


- With dilute acids

Iron forms respective salts with dilute acids with liberation of hydrogen.

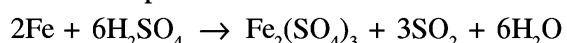


With cold dilute nitric acid, ammonium nitrate is also formed.



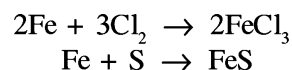
- With concentrated acids

Iron reacts with concentrated sulphuric acid to liberate sulphur dioxide.

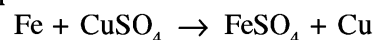


Iron reacts with concentrated nitric acid and becomes passive due to the fact that conc. nitric acid is a powerful oxidising agent – it forms a protective layer of ferric oxide over the surface of iron preventing further reaction (Passivity).

- With non-metals iron reacts as follows:



- Iron displaces other less reactive metals from the aqueous solution of their salts.



Uses of iron

Iron is used in the manufacture of drain pipes, manhole covers, railings, shutters, gates, machine

parts, etc. Steel an alloy of iron is used in buildings, machines, automobiles and in other devices.

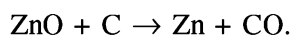
5.12 METALLURGY OF ZINC

Zinc is one of the strategic non-ferrous metal next only to Aluminium and Copper. It plays a very important role in the country's economy and development. Modern life is inconceivable without zinc. It provides the most cost-effective and environmentally efficient method of protecting iron and steel from corrosion.

The most important raw material for the production of zinc is the sulphide ore from which zinc is extracted. The metallurgy of Zinc is outlined below.

Ores: Zincite (ZnO), Zinc Blende (ZnS) and Calamine (ZnCO₃).

Method: The dressed ore is concentrated by froth flotation if it is Zinc Blende else by Gravity process. Next the ore is roasted in excess air when it gets converted to oxide. The oxide is reduced by coke.



When carbon burns in air, carbon dioxide is formed which tends to convert zinc back to its oxide. To avoid this zinc vapours are absorbed in lead. The two are later separated by distillation. The CO formed as a by-product is used as fuel for heating. The zinc so obtained is impure and is called *spelter*. The impure *spelter* is purified by controlled distillation or electrolysis.

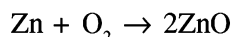
Properties of zinc

Physical properties

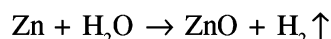
- (a) Zinc is a bluish white metal, hard and brittle that becomes malleable and ductile at 100°C.
- (b) Zinc has good tensile strength
- (c) Zinc melts at 419°C.
- (d) Zinc is a good conductor of heat and electricity.

Chemical Properties

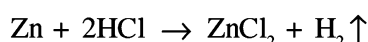
- (a) Zinc does not react with dry air but when heated to above 500°C in moist air it burns with a bluish flame forming zinc oxide.



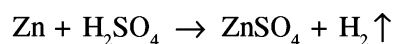
- (b) Zinc has no reaction with cold water. With steam it liberates hydrogen.



- (c) With dilute acids zinc forms respective salts with the liberation of Hydrogen.



Dilute



Dilute

But with dilute nitric acid zinc forms nitric oxide.



Dilute

- (d) With concentrated nitric and sulphuric acid, nitrogen dioxide and sulphur dioxide respectively are formed.

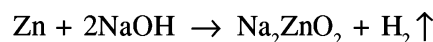


Concentrated

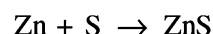
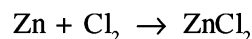


Concentrated

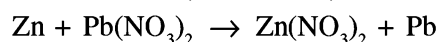
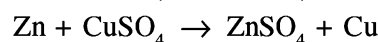
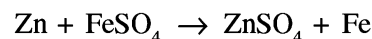
- (e) With alkalis, zinc exhibits amphoteric nature.



- (f) With non-metals zinc reacts as follows.



- (g) Zinc displaces other less reactive metals from aqueous solution of their salts.



(But, $\text{CaCl}_2 + \text{Zn} \rightarrow$ No reaction as calcium is more reactive than zinc).

Uses of Zinc

- (a) **Galvanisation:** The process of coating iron sheets with zinc metal to prevent rusting is called **galvanization**. When Zinc is coated over iron, it acts as a sacrificial metal getting preferentially oxidized to iron. This prevents the oxidation of iron and formation of rust.
- (b) Zinc is used to make alloys like brass, bronze and German silver.
- (c) Zinc is used as an electrode in dry cells. The outer coating of dry cells is made of zinc.
- (d) Zinc is used in special printing.
- (e) Zinc is used as a reducing agent.
- (f) Zinc is used in drugs and dyes.
- (g) Zinc is used in cosmetics and face creams.

5.12 OTHER ALLOYS

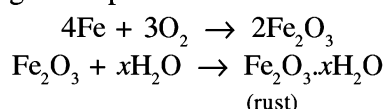
Alloy	Metals present	Percentage composition	Usage
Duralumin (Dural)	Al, Cu, Mg, Mn	95, 4, 0.5, 0.5	Aircraft frames, windows
Magnalium	Al, Mg,	95, 5	Cheap balances
Y-Metal	Al, Cu, Ni, Mg	93, 4, 2, 1	Currency coins
Alnico	Al, Fe, Ni, Co	20, 50, 20, 10	Strong magnets
Aluminium Bronze	Al, Cu	10, 90	Statues
Bronze	Cu, Zn, Sn	80, 10, 10	Metals, statues
Brass	Cu, Zn	70, 30	Utensils, decorative hardware
German Silver	Cu, Zn, Ni	40, 30, 30	Decorative articles, heaters
Bell metal	Cu, Sn	80, 20	Bells, gongs
Solder	Sn, Pb	50, 50	Welding, fuse

5.13 CORROSION – A SPECIAL DISCUSSION

Metal surfaces are liable to react with oxygen, carbon dioxide, moisture and other pollutants in the atmosphere. This is the main reason why metals corrode. While most metals suffer corrosion, some metals are more corrosive.

- (a) **Corrosion of Iron:** Iron corrodes over time when exposed to moist air forming a powdery coating of brown rust. Over time, the entire piece of iron rusts. Rusting is the corrosion of iron.

Rusting takes place as follows:



Conditions for rusting: Presence of air or oxygen and moisture are essential. Presence of only oxygen without moisture or vice-versa cannot form rust.

Prevention of rusting:

- (i) **Coating** the iron surface with a paint or oil or grease prevents moist oxygen from coming in contact with the metal and thus effectively prevents rusting of iron.
- (ii) **Galvanisation:** Iron is blasted with fine sand to make the surface rough and dipped in molten zinc and then cooled. A thin layer of zinc forms on the iron surface. Since zinc is more reactive than

iron, it acts as a sacrificial metal and is preferentially oxidised thus preventing oxidation of iron.

- (iii) **Electroplating** with tin, nickel or chromium also prevents rusting.
- (iv) **Alloying** (mixing iron in its molten state with other metals) prevents rusting. Stainless steel is an alloy of iron with Cr or Ni.
- (b) **Corrosion of Aluminium:** Aluminium sheets appear dull in colour due to the formation of a thin oxide layer. This oxide layer actually prevents aluminium from further corrosion.
- (c) **Corrosion of Copper:** Copper over a period of time reacts slowly with CO_2 and water to form a greenish coat of basic copper carbonate $[\text{Cu}(\text{OH})_2 \cdot \text{CuCO}_3]$ corroding it. It is a very slow process.
- (d) **Corrosion of Silver:** Tarnishing of silver happens over time due to the formation of a thin *sulphide* layer (not oxide as silver is relative non-reactive). Air contains very minute amounts of H_2S or SO_2 as pollutants. This reacts with silver articles forming sulphide (Ag_2S). So, silver blackens over time. Simple heating and polishing removes this layer.
Gold normally is resistant to corrosion as it is non-reactive.
Titanium is another metal which is resistant to corrosion. **It is a future metal.**

EXERCISE

I. Choose the correct answer

1. Malachite and azurite are _____ ores of copper.
 - (a) oxide
 - (b) carbonate
 - (c) sulphide
 - (d) silicate
2. Which of the following is not found in native state?
 - (a) Pt
 - (b) Cu
 - (c) Au
 - (d) Na
3. Cassiterite ore is used to extract
 - (a) Fe
 - (b) Sn
 - (c) Au
 - (d) Pb
4. The metal never found in free state is
 - (a) Au
 - (b) Ag
 - (c) Pt
 - (d) Zn
5. Carbonate or hydroxide ores are generally converted to their oxides by
 - (a) roasting
 - (b) calcination
 - (c) smelting
 - (d) fluxing
6. Copper pyrites ore is concentrated by
 - (a) Electromagnetic method
 - (b) Gravity separation
 - (c) Froth floatation method
 - (d) all the above methods
7. Calamine is
 - (a) CaCO_3
 - (b) ZnCO_3
 - (c) MgCO_3
 - (d) $\text{CaCO}_3 + \text{MgCO}_3$
8. Which one of the following is not a method of concentration of an ore?
 - (a) Gravity separation
 - (b) Froth floatation process
 - (c) Electromagnetic separation
 - (d) Smelting
9. Most abundant element in the earth's crust by weight is
 - (a) oxygen
 - (b) silicon
 - (c) aluminium
 - (d) iron
10. The rocky and silicon matter associated with an ore is called
 - (a) slag
 - (b) mineral
 - (c) matrix or gangue
 - (d) flux
11. The process of removing lighter gangue particles by washing in a current of water is called
 - (a) gravity separation
 - (b) liquation
 - (c) leaching
 - (d) cupellation
12. Gravity separation method is based upon
 - (a) preferential washing of ores and gangue particles
 - (b) difference in densities of ore particles and impurities
 - (c) difference in chemical properties of ore particles and impurities
 - (d) none of these
13. In the froth floatation process for the purification of minerals the particles float because
 - (a) they are light
 - (b) they are insoluble
 - (c) their surface is preferentially wetted by oil
 - (d) they bear an electrostatic charge
14. Froth floatation process for the concentration of ores is an illustration of the practical application of
 - (a) adsorption
 - (b) absorption
 - (c) coagulation
 - (d) sedimentation
15. Among the following statements the incorrect one is
 - (a) calamine and siderite are carbonates
 - (b) argentite and cuprite are oxides
 - (c) zinc blende and iron pyrites are sulphides
 - (d) malachite and azurite are ores of copper
16. In the blast furnace during the extraction of iron the temperature attained in the hearth is nearly
 - (a) 400°C
 - (b) 1000°C
 - (c) 1500°C
 - (d) 2000°C
17. Refractory metals are used in construction of furnaces because
 - (a) they can withstand high temperature
 - (b) they are chemically inert
 - (c) their melting point is high
 - (d) none of these
18. Which one of the following is used as conditioner in froth floatation process
 - (a) pine oil
 - (b) sodium ethyl xanthate
 - (c) sodium carbonate
 - (d) olive oil
19. During extraction of a metal the ore is roasted if it is a
 - (a) sulphate ore
 - (b) sulphide ore
 - (c) carbonate ore
 - (d) oxide ore

20. A common metal that is used for the extraction of some metals from their oxides is
 (a) Cr (b) Fe
 (c) Mn (d) Al
21. Extraction of metals from sulphide ores is done by
 (a) electrolysis (b) smelting
 (c) hydrometallurgy (d) roasting
22. The substance widely used to remove silica present as impurity, from the ore is
 (a) CaO (b) P_2O_5
 (c) SiC (d) Na_2CO_3
23. To remove basic impurities from the ore the substance generally used is
 (a) SiO_2 (b) P_2O_5
 (c) CaO (d) $CaCO_3$
24. During smelting an additional substance is added to form a fusible product. It is known as
 (a) slag (b) mud
 (c) gangue (d) flux
25. Extraction of aluminium from aluminium oxide (Al_2O_3) is best done by
 (a) electrolytic reduction of Al_2O_3
 (b) reduction of Al_2O_3 with carbon
 (c) reduction of Al_2O_3 with sodium
 (d) reduction of Al_2O_3
26. Calcination is the process of heating the ore
 (a) in inert gas
 (b) in the presence of air
 (c) in limited supply of air
 (d) in the presence of CaO and MgO
27. To which of the following ores, calcination process is not applicable
 (a) $CaCO_3$ (b) $Al_2O_3 \cdot H_2O$
 (c) $CaCO_3 \cdot Ca(OH)_2$ (d) ZnS
28. Smelting is usually carried out in
 (a) blast furnace (b) open hearth furnace
 (c) muffle furnace (d) electric furnace
29. Slag is a product of
 (a) flux and coke
 (b) coke and metal oxide
 (c) flux and impurities
 (d) metal and flux
30. The most electropositive metals are isolated from their ores by
 (a) high temperature reduction with carbon
 (b) self-reduction
 (c) thermal decomposition
 (d) electrolysis of fused ionic salts
31. In the roasting of ZnS, products are
 (a) $ZnO + SO_2$ (b) $ZnO + ZnSO_4 + SO_2$
 (c) $ZnCl_2$ (d) $Zn + SO_2$
32. Which of the following process is used for concentration of ores and for refining metals?
 (a) liquation (b) leaching
 (c) distillation (d) poling
33. Zinc is obtained on large scale by
 (a) electrolysis of $ZnCl_2$
 (b) reduction of ZnO
 (c) precipitation with Ag
 (d) any of these methods.
34. The main ore of iron is its
 (a) chloride (b) sulphate
 (c) nitrate (d) oxide
35. Most abundant ore of iron is
 (a) magnetite (b) haematite
 (c) limonite (d) pyrites
36. Mark the wrong statement among the following. The iron ore after washing is roasted with a little coal in excess of air. During roasting
 (a) moisture is removed
 (b) S and As are removed in the form of their volatile oxides
 (c) any ferrous oxide is oxidised to ferric oxide
 (d) the mass becomes compact and thus makes it suitable for any reduction to metallic iron.
37. The reducing agent added in the extraction of iron from oxide ore of iron is
 (a) coke (b) carbon
 (c) carbon monoxide (d) zinc
38. The iron obtained from blast furnace is
 (a) pig iron (b) silver
 (c) soft iron (d) steel
39. In the middle part of blast furnace, iron ore is treated with limestone to remove
 (a) C (b) CaO
 (c) SiO_2 (d) Fe_2O
40. In the manufacture of iron from haematite, limestone acts as
 (a) a reducing agent (b) flux
 (c) slag (d) gangue
41. In which of the following percentage of carbon is maximum
 (a) pig iron (b) cast iron

- (c) wrought iron
(d) pig iron and wrought iron
42. The purest form of commercial iron is
(a) pig iron (b) cast iron
(c) wrought iron (d) pig iron and cast iron
43. Spiegeleisen is an alloy is
(a) Fe, Mn, C (b) Fe, Mg, C
(c) Mn, C, Zn (d) Fe, Mn, Mg
44. Hydrated magnesium chloride on strong heating gives finally
(a) MgCl_2 (b) MgO
(c) Mg(OH)Cl (d) Mg_2OCl_2
45. The reaction not involved in the concentration of bauxite ore by Hall's process is
(a) $\text{Al}_2\text{O}_3 + \text{Na}_2\text{CO}_3 \rightarrow 2 \text{NaAlO}_2 + \text{CO}_2$
(b) $2\text{NaAlO}_2 + 3\text{H}_2\text{O} + \text{CO}_2 \rightarrow 2\text{Al(OH)}_3 + \text{Na}_2\text{CO}_3$
(c) $2\text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$
(d) $\text{AlN} + 3\text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \text{NH}_3$
46. In the electrolytic reduction of alumina, the anodic product is
(a) Al (b) Na
(c) O_2 (d) H_2
47. In the purification of bauxite by Hall's process
(a) The bauxite ore is heated with concentrated NaOH solution at 150°C
(b) the bauxite ore is heated with NaHCO_3
(c) the bauxite ore is mixed with coke and heated at 1800°C in a current of N_2
(d) the bauxite ore is fused with Na_3AlF_6
48. 'X' is substance which combines chemically with impurities associated with the ore to form easily fusible mass 'Y'. Here X and Y are
(a) flux, slag (b) slag, flux
(c) gangue, slag (d) reductant, flux
49. A mixture of Al_2O_3 and Fe_2O_3 can be separated by using
(a) sodium hydroxide (b) cold water
(c) ethyl alcohol (d) boiling water
50. Regarding the electrolysis of Alumina the correct statements are :
(A) Cryolite is added to reduce the fusion temperature
(B) Impure aluminium is mixed with copper and silicon to increase the density
(C) Fluorspar is added to reduce the fusion temperature
(D) Electrolyte is mixture of fluorides of sodium, Barium and Aluminium saturated with Alumina

- (a) only B, C and D are correct
(b) only A, C and D are correct
(c) only A, B and D are correct
(d) only C is correct

II. Name the process indicated

- (i) Sulphide ores are concentrated by
(ii) Bauxite is concentrated by
(iii) Strong heating in a plentiful supply of air
(iv) Strong heating in a limited supply of air
(v) The reduction method suitable for highly electropositive metals from their ores

III. Match the following.

1. List - I (mineral) List - II (type of mineral)

- | | |
|---------------|----------------|
| (1) Haematite | (i) carbonate |
| (2) Carnalite | (ii) oxide |
| (3) dolomite | (iii) sulphate |
| (4) Anglesite | (iv) chloride |

Correct match is

- | | 1 | 2 | 3 | 4 |
|-----|------|-------|-------|-------|
| (a) | (ii) | (iv) | (i) | (iii) |
| (b) | (i) | (ii) | (iii) | (iv) |
| (c) | (ii) | (iii) | (iv) | (i) |
| (d) | (i) | (iv) | (iii) | (ii) |

2. List - 1

List - II

- | | |
|------------------|--|
| (1) Liquefaction | (i) Volatile metals with non-volatile impurity |
| (2) Poling | (ii) Metal with its metal oxides as impurity |
| (3) Cupellation | (iii) Metal with easily oxidised impurities |
| (4) Distillation | (iv) Metal and impurities differ in M.P |

The correct match is

- | | 1 | 2 | 3 | 4 |
|-----|------|-------|-------|------|
| (a) | (i) | (ii) | (iii) | (iv) |
| (b) | (iv) | (iii) | (ii) | (i) |
| (c) | (iv) | (ii) | (iii) | (i) |
| (d) | (i) | (ii) | (iv) | *iii |

3. Various types of zone in the blast furnace are given in the list - I and reactions take place in the extraction of iron are given in list - II

2. List - 1

List - II

- | | |
|-----------------------------|--|
| (1) Zone of reduction | (i) $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$ |
| (2) Zone of heat absorption | (ii) $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$ |
| (3) Zone of fusion | (iii) $\text{Fe}_2\text{O}_3 + 3\text{CO} \rightarrow 2\text{Fe} + 3\text{CO}_2$ |

The correct match is

	1	2	3
(a)	(i)	(ii)	(iii)
(b)	(iii)	(ii)	(i)
(c)	(ii)	(iii)	(i)

**4. List – I
(concentration method)**

- | | |
|-------------------------|--|
| (1) Hydraulic washing | (i) difference in solubility of gangue and ore particles in a specific substance |
| (2) Magnetic separation | (ii) difference in wetting property of ore and gangue particle |
| (3) Froth floatation | (iii) difference in gravities of ore and gangue particles |
| (4) Leaching | (iv) difference in magnetic property of gangue and ore particles |

The correct match is

	1	2	3	4
(a)	(ii)	(iv)	(iii)	(i)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(i)	(iv)	(iii)	(iv)
(d)	(iii)	(iv)	(ii)	(i)

IV. State whether the following statements are True or False

- A mineral need not be an ore
- An ore cannot be a mineral
- All ores are not minerals
- All minerals are ores

V. Find the odd one out

- Corundum, Cassiterite, Barytes, Magnetite, Zincite
- Calcination, gravity separation, froth floatation, magnetic separation

VI. Fill in the blanks

- In froth floatation process which of the following is added _____
- The process of protecting iron by coating with zinc is called _____
- A common metal widely used in electrical cables and kitchenware is _____
- The percentage of carbon in steel is approximately _____
- Steel is heated to below red heat and then

cooled slowly to prepare for special applications. This process refers to _____

- Colourless solutions of KNO_3 , AgNO_3 , $\text{Zn(NO}_3)_2$, ZnSO_4 are placed separately in four different test tubes and a strip of copper is dipped in each one of these. The solution that will turn blue is _____

VII. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, Statement R is true; Statement R is correct explanation for statement A

Choose B if Statement A is true, statement R is true; Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D if Statement A is false, statement R is true

- Statement A:** In the extraction of Mg from fused anhydrous MgCl_2 , air gap of the electrolytic cell is replaced by inert gas.

Statement R: Oxidation of Mg metal is to be prevented during its extraction by electrolytic reduction of anhydrous MgCl_2 .

- Statement A:** Magnesium metal can easily be extracted from sea water rather than sodium metal.

Statement R: Mg(OH)_2 is less soluble in water than NaOH.

VIII. Answer the following questions.

- Differentiate between roasting and calcination. How are they beneficial in metallurgy?
- Given below are terms used in metallurgy. Identify the step in which each of these terms occur.
Poling, electrolytic reduction, calcination, gravity separation, distillation, liquation, handpicking, flux, gangue, matrix.
- Write the equations involved in the concentration of bauxite to pure alumina by both methods.
- What is the flux used in the metallurgy of aluminium? What is its role?
- Write a brief outline of metallurgy of zinc and iron with reactions. What is the reducing agent in each?
- Certain metals are extracted by electrolytic methods while others are extracted by chemical methods. When is a particular method used?

- (7) Differentiate between the following forms of iron: Cast iron, Pig iron, Wrought iron and Steel.
- (8) (a) Name three alloys of tin (Sn).
(b) Differentiate between brass and bronze.
- (9) Why is the alloy alnico used for making strong magnets? (Hint: see its composition)
- (10) Tempering of steel increases its tensile strength. This is done so that in its end use it can bear heavy strain. How is tempering done?
- (11) Gold and titanium do not undergo corrosion. Why?
- (12) Can Aluminium be galvanised with zinc to prevent its corrosion and why?
- (13) Sulphide ores are roasted while carbonate ores are calcined before reduction. State why?
- (14) Outline the method of preparing steel in a Bessemer Converter.

KEY TO EXERCISE								
I.	1. b	2. d	3. b	4. d	5. b	6. c	7. b	8. d
	9. a	10. c	11. a	12. b	13. c	14. a	15. b	16. c
	17. a	18. b	19. b	20. d	21. b	22. a	23. c	24. d
	25. a	26. c	27. d	28. a	29. c	30. d	31. a	32. a
	33. b	34. d	35. b	36. d	37. a	38. a	39. c	40. b
	41. a	42. c	43. a	44. b	45. d	46. c	47. d	48. a
	49. a	50. b						
II.	(i) froth floatation		(ii) Gravity separation		(iii) Roasting			
	(iv) calcination		(v) electrolytic reduction					
III.	1. a	2. c	3. b	4. d				
IV.	(i) true	(ii) false	(iii) false	(iv) false				
V.	(i) barytes	(ii) calcination						
VI.	(i) pine oil	(ii) galvanisation	(iii) Cu					
	(iv) 2%	(v) annealing	(vi) AgNO ₃					
VII.	1 A	2. A						

6

Acids and Bases

6.0 INTRODUCTION

In ancient times, if a substance was sour to taste it was called an acid. If it was bitter to taste it was called a base. A substance that was neither an acid nor a base was called a salt if the acid and the base formed it on reacting chemically.

Around 1800, many French chemists, including Antoine Lavoisier, incorrectly believed that all acids contained oxygen. Indeed the modern German word for oxygen is *Sauerstoff* (sour substance). Early English chemists on the other hand believed all acids contained hydrogen. The word 'Acid' comes from the Latin *acidus* meaning "sour," but in chemistry the term acid has a more specific meaning. Bases can be thought of as the chemical opposite of acids. Bases and acids are seen as opposites because the effect of an acid is to increase the hydronium ion (H_3O^+) concentration in water, whereas bases relatively reduce this concentration. Bases react with acids to produce water and salts.

6.1 PROPERTIES OF ACIDS AND BASES

Acids exhibit the following properties.

- Acids are sour to taste.
- Acids turn moist blue litmus red.
- Some acids are more corrosive than others.
- Acids liberate hydrogen on reaction with metals above [H] in the Metal Activity Series.
- Acids react with carbonates and bicarbonates giving effervescence of CO_2 .
- Acids react with bases giving salt and water.
- Some acids are good conductors of electricity.

Bases exhibit the following properties.

- Bases are soapy to touch and bitter in taste.
- Bases turn moist red litmus blue.
- Bases react with acids giving salt and water.
- Some bases are good conductors of electricity.

6.2 ACID-BASE THEORIES

Classification of acids and bases on the basis of their properties is difficult. Three important theories of acids and bases are given below. These theories help us to understand and study acids and bases better.

Theories of acids and bases

- Arrhenius' Theory
- Bronsted-Lowry Theory and
- Lewis Theory.

Each theory studies acids and bases with respect to the definition, strength and neutralisation. Each theory has its own uses and limitations. These are studied below.

6.3 ARRHENIUS' THEORY

According to Arrhenius' theory,

An acid is any substance that contains hydrogen and ionizes in aqueous solution to give H^+ ions and a base is any substance that contains hydroxyl radical and ionises in aqueous solution to give OH^- ions.

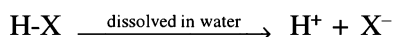
Thus, an acid has the general formula H-X and a base has the general formula M-OH .

Examples of Arrhenius' acids: HCl , HNO_3 , H_2SO_4 , HSO_3^-

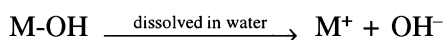
Examples of Arrhenius' bases: NaOH , KOH , Ca(OH)_2 .

Explanation of the theory

According to the theory, an acid dissociates in water to give H^+ ions. The H^+ ions in the aqueous solution of acids are responsible for the acidic properties.



Similarly, a base dissociates in water to give OH^- ions. The OH^- ions in the aqueous solution of bases are responsible for the basic properties.

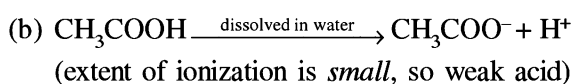
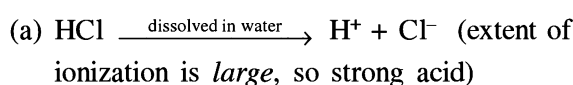


Strength of acids and bases

According to Arrhenius' theory, an acid is said

to be strong if it *ionizes or dissociates to a large degree in aqueous solution*. A base is said to be strong if it ionizes or dissociates to a large degree in aqueous solution.

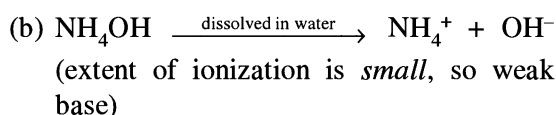
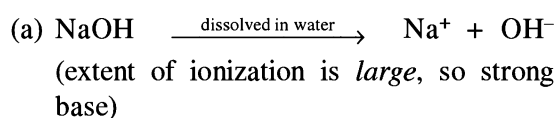
- (i) A strong acid gives more H^+ ions when compared to a weak acid. A strong acid is completely dissociated into ions. There are no whole molecules of undissociated acid present in aqueous solution. A weak acid does not dissociate completely into ions. *There are whole molecules of undissociated acid present in aqueous solution along with the dissociated ions.*



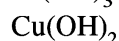
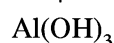
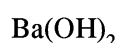
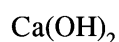
Examples: **Strong acids** **Weak acids**



- (ii) A strong base gives more OH^- ions when compared to a weak base. A strong base is completely dissociated into ions. There are no whole molecules of undissociated base present in aqueous solution. A weak base does not dissociate completely into ions. *There are whole molecules of undissociated base present in aqueous solution along with the dissociated ions.*



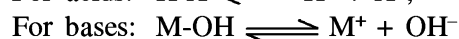
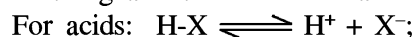
Examples: **Strong bases** **Weak bases**



Equilibrium in aqueous solution

For an aqueous solution of a weak acid or base, *equilibrium exists between dissociated and undisso-*

ciated molecules as follows. The equilibrium is shown using a double direction arrow.



But, in aqueous solution of a *strong* acid or base, no equilibrium exists *as all the acid / base molecules dissociate*. There are no undissociated molecules hence no equilibrium is possible.

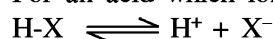
Dissociation Constant, K

The degree of dissociation of an acid or base can be estimated by its dissociation constant. Strong acids have large K_a values and vice-versa. Strong bases have large K_b values and vice-versa.

Meaning of square brackets

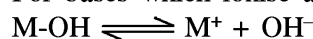
Dissociation constant measures the strength of an acid / base.

For an acid which ionise as



Dissociation constant, $K_a = \frac{[\text{H}^+][\text{X}^-]}{[\text{HX}]}$

For bases which ionise as



Dissociation constant, $K_b = \frac{[\text{M}^+][\text{OH}^-]}{[\text{MOH}]}$

The symbols inserted in between square brackets are to be read as follows.

$[\text{H}^+]$ - Concentration of H^+ ions.

$[\text{OH}^-]$ - Concentration of OH^- ions.

$[\text{H}_2\text{O}]$ - Concentration of H_2O .

Concentration is usually expressed in moles / litre.

As dissociation is almost total in strong acids and bases, *no equilibrium exists* and K_a and K_b values cannot be found. Strong acids/bases like HCl , KOH do not have K_a / K_b values as they are fully dissociated.

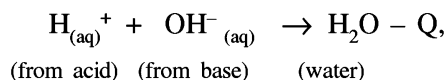
Neutralisation

When an acid reacts with an *equivalent* amount of base, both the acid and base lose their properties to form a neutral solution of salt and water with the release of heat energy. The reaction is called a *Neutralisation Reaction* and the heat energy released is called *Heat of Neutralisation*.

Consider a neutralisation reaction in which an acid H-X and base M-OH dissociate in water. The following dissociation take place.



According to Arrhenius' theory, the neutralisation reaction is given by the equation :



where Q is the heat of neutralization.

Heat of Neutralisation is the heat energy released in a neutralisation reaction per mole. It is a constant and is numerically equal to 13.7 kcal / mole.

If the acid or base or both are weak, then *the Heat of Neutralisation will be less than 13.7 kcal / mole* as a part of this heat is utilized to further dissociate the weak acid or weak base into ions.

Uses of Arrhenius' Theory

- (1) It is found that all strong acids and bases release the same Heat of Neutralisation. This proves that Arrhenius' theory is correct.
- (2) The definitions in Arrhenius' theory are quite simple and well accepted till today.
- (3) Quantitative measurements are possible according to Arrhenius' theory from the dissociation constant formulae.

Limitations of Arrhenius' theory

- (1) Arrhenius' theory is limited to behaviour of acids and bases in aqueous solutions and not in non-aqueous media. For example hydrogen chloride dissolved in water turns blue litmus red but dissolved in benzene does not do so. Arrhenius' theory cannot satisfactorily explain this discrepancy.
- (2) Many substances do not have H^+ yet they behave as acids. For example, aqueous solutions of salts like NH_4Cl , $(\text{NH}_4)_2\text{SO}_4$ turn blue litmus red. Certain oxides like CO_2 and NO_2 turn moist blue litmus red. Arrhenius' theory cannot explain why though there is no H^+ , these substances exhibit acidic properties.
- (3) Many substances do not have OH^- yet they behave as bases. For example, aqueous solutions of salts like Na_2CO_3 , CH_3COONa turn red litmus blue. Certain oxides like CaO turn moist red litmus blue. Arrhenius' theory cannot explain why though there is no OH^- , these substances exhibit basic properties.

6.4 BRONSTED – LOWRY THEORY

Bronsted – Lowry Theory tries to overcome the limitations' of Arrhenius' Theory.

According to *Bronsted – Lowry Theory*

'Acids are proton donors, while bases are proton acceptors.'

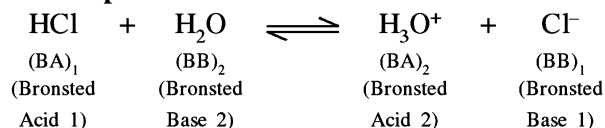
Example of Bronsted acids: HCl , HNO_3 , CH_3COOH , H_2SO_4 , H_3PO_4 furnish H^+ ions when dissolved in water and are Bronsted acids.

Example of Bronsted bases : NH_3 accepts H^+ ions to form ammonium ions and is a Bronsted base.

Neutralisation

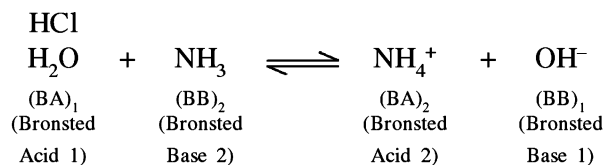
According to Bronsted Lowry theory, *a neutralisation reaction is a transfer of a proton from an acid to a base.*

Example 1:



HCl is a Bronsted acid as it donates a proton (H^+). Water is a Bronsted base as it accepts the proton.

Example 2 :



Ammonia (NH_3) is a Bronsted base as it accepts a proton (H^+). Water is a Bronsted acid as it donates a proton.

Thus, in each acid-base reaction, *two acid-base pairs* are involved: $\text{BA}_1\text{-BB}_1$ and $\text{BA}_2\text{-BB}_2$. Each pair differs by 1 proton - H^+ .

A neutralisation reaction does not necessarily produce salt and water. It however produces two acid-base pairs. According to this theory, water can behave as a Bronsted acid or Bronsted base depending on the reaction.

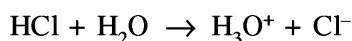
Conjugate acid-base pair is an acid base pair, which differ by a proton and are formed by mutual transfer of a proton.

The acid loses a proton (H^+). The resulting ion has a tendency to accept H^+ back, thus behaving as a *conjugate base*. The base accepts a proton (H^+). The resulting ion has a tendency to lose the H^+ behaving as a *conjugate acid*.

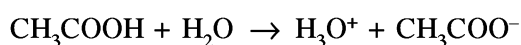
Practice Exercise: (a) Identify the conjugate base of H_2SO_4 , HNO_3 , H_2CO_3 , H_3PO_4 and HSO_3^-
 (b) Identify the conjugate acid of OH^- , CH_3COO^- , HCOO^- , ClO^- and ClO_3^- , HPO_4^{2-} , SO_4^{2-} .

Water can behave as a Bronsted acid and Bronsted base.

According to this theory, water can behave as a Bronsted acid or Bronsted base depending on the reaction.



(Water behaving as a Bronsted base – accepting a proton)



(Water behaving as a Bronsted acid – donating a proton)

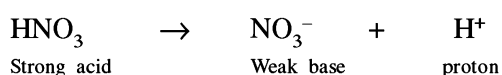
Strength of acids and bases

According to Bronsted and Lowry theory, a strong acid (SA) has a greater tendency to donate a proton than a weak acid (WA), while a strong base (SB) has a greater tendency to accept a proton than a weak base (WB). The strength of a Bronsted acid / base depends on the solvent. A more polar solvent like water makes the acid / base stronger.

Conjugate of WA is a SB.

The conjugate of a strong acid is a weak base and that of a weak acid is a strong base.

Example 1:



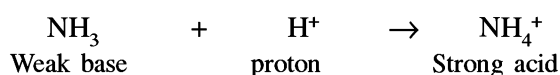
Example 2:



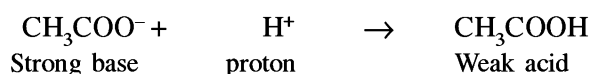
Conjugate of WB is a SA.

The conjugate of a weak base is a strong acid and that of a strong base is a weak acid.

Example 1:



Example 2:



Limitations of theory

- (1) Bronsted Lowry theory explains neutralisation reactions only in terms of proton transfer.

According to this theory the reaction $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$ is not a neutralisation reaction.

- (2) Bronsted Lowry theory explains the behaviour of acids or bases only when dissolved in solvents that have H - atoms.

6.5 LEWIS THEORY

According to Lewis acid-base theory

'An acid is a molecule or ion that can accept a pair of electrons to form a dative bond'

and *'A base is a molecule or ion that can donate an electron pair to form a dative bond'*.

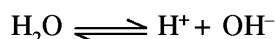
Examples: Lewis acids - H^+ , BF_3

Lewis bases - H_2O , NH_3

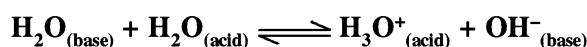
This theory will be studied in more detail in higher classes.

6.6 IONIC PRODUCT OF WATER, K_w

Water ionises to a very weak extent as follows.



Since a proton (H^+) cannot exist independently, this equation is actually written as



The water molecules are in equilibrium with ionised water molecules.

The equilibrium constant, K of this reaction is given by

$$K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Rearranging, $K_c[\text{H}_2\text{O}] = [\text{H}^+][\text{OH}^-]$

As, water dissociates to a very little extent concentration of water is almost a constant,

i.e., $[\text{H}_2\text{O}] = \text{constant}$. So, K_w , a product of these two constants - K_c and $[\text{H}_2\text{O}]$, is also a constant.

K_w is known as the Ionic product of water

Ionic product of water, K_w is the product of H^+ and OH^- ion concentration in an aqueous solution or pure water at a given temperature. The value of Ionic product at 25°C is 1×10^{-14}

Some simple facts

- (i) In pure water, concentration of both ions i.e. $[\text{H}^+]$ and $[\text{OH}^-]$ are equal.

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7} \text{ moles / l.}$$

- (ii) The ionic product of water changes with temperature.

(iii) In acids, $[H^+] > [OH^-]$.

So, $[H^+] > 1 \times 10^{-7}$ moles / l

Also, $[OH^-] < 1 \times 10^{-7}$ moles / l.

(iv) In bases, $[H^+] < [OH^-]$

So, $[H^+] < 1 \times 10^{-7}$ moles / l

Also, $[OH^-] > 1 \times 10^{-7}$ moles / l.

(v) But in all aqueous solutions whether acids, bases or salts *and* in pure water the product of $[H^+]$ and $[OH^-]$ or ionic product is a constant at 25°C.

$$K_w = [H^+] [OH^-] = 1 \times 10^{-14} \text{ at } 25^\circ\text{C}.$$

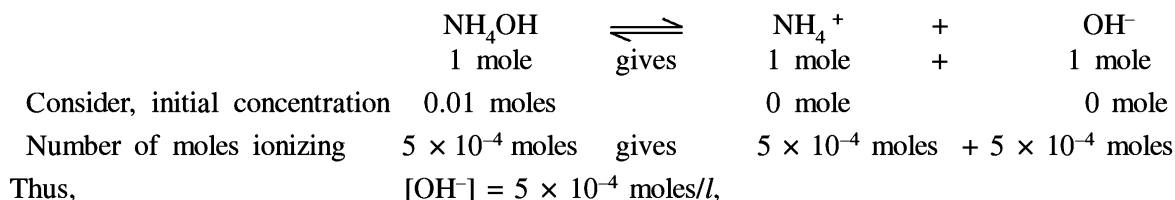
SOLVED PROBLEMS

(1) A 0.01M ammonia solution is 5% ionized. Find the concentration of $[H^+]$ and $[OH^-]$ at 25°C.

Ans: Ammonia solution (NH_4OH) is a weak base and so weakly ionized.

0.01M NH_4OH has 0.01 moles/l at 25°C.

Since it is 5% ionized (given), 5% of the moles ionize, i.e., 5% of 0.01 = 5×10^{-4} moles ionise as follows

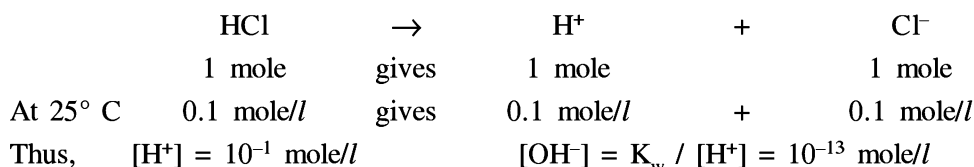


And,

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{5 \times 10^{-4}} = 2 \times 10^{-11} \text{ moles/l}$$

(2) Find the $[H^+]$ and $[OH^-]$ of 0.1M HCl at 25°C.

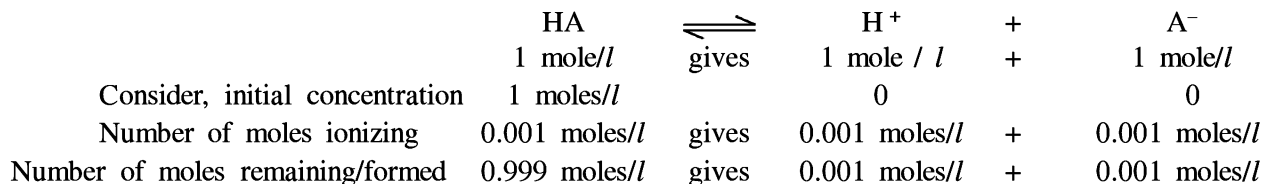
Ans: HCl is a strong acid and hence is fully ionized as



(3) The degree of dissociation of an acid H-A is 0.1%. Calculate the dissociation constant.

Ans: H-A is a weak acid dissociating 0.1%. Consider, 1M of the acid.

1 M of the acid has 1 mole/l which is 0.1% dissociated, i.e., 0.1% of 1mole/l = 0.001 moles/l dissociates.



$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.001 \times 0.001}{0.999} = \frac{1}{999} \times 10^{-3} = 1 \times 10^{-6}$$

(4) Calculate the $[H^+]$ of 0.001M NaOH aqueous solution.

Ans: NaOH is a strong base ionizing fully.

So 0.001M NaOH ionizes to give 0.001M Na^+ and 0.001M OH^- ions

Thus, $[OH^-] = 1 \times 10^{-3}$ mole / l

and
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1 \times 10^{-14}}{1 \times 10^{-3}} = 1 \times 10^{-11} \text{ moles/l}$$

(5) Calculate the $[OH^-]$ of 1M HCl aqueous solution.

Ans: HCl is a strong acid ionizing fully.

So, 1M HCl ionizes to give 1M H^+ and 1M Cl^- ions.

Thus, $[H^+] = 1 \text{ mole/l}$ or $1 \times 10^0 \text{ mole/l}$

and
$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1 \times 10^{-14}}{1 \times 10^0} = 1 \times 10^{-14} \text{ moles/l}$$

6.7 pH AND pOH

Since concentration of H^+ and OH^- are expressed in exponential form of the order 10^{-14} , to avoid very small numbers, the concentration are converted to negative logarithms called pH and pOH.

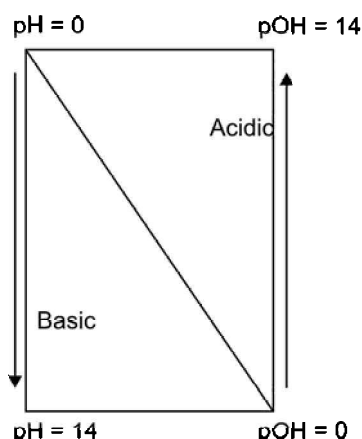
The negative log of $[H^+]$ and $[OH^-]$ is known as pH and pOH respectively.

Significance of pH and pOH

(i) For pure water $[H^+] = [OH^-] = 10^{-7} \text{ moles/l}$.

$$\begin{aligned} \text{pH} &= -\log[H^+] \\ &= -\log(10^{-7}) \\ &= 7 \end{aligned}$$

$$\begin{aligned} \text{similarly, pOH} &= -\log(10^{-7}) \\ &= 7 \end{aligned}$$



(ii) For any aqueous solution $[H^+][OH^-] = 10^{-14}$.

$$\text{pH} + \text{pOH} = 14$$

$$\text{pH} = 14 - \text{pOH}$$

$$\text{and pOH} = 14 - \text{pH}$$

(iii) For acids $\text{pH} < 7$ (but > 0).

(iv) For bases $\text{pH} > 7$ (but < 14)

(v) Lower the pH, higher the pOH – more the acidic nature.

(vi) Higher the pH, lower the pOH – more the basic nature.

(vii) For acids $\text{pOH} > 7$ (but < 14)

(viii) For bases $\text{pOH} < 7$ (but > 0).

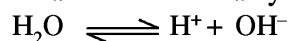
(ix) For neutral solutions $\text{pH} = \text{pOH} = 7$.

6.8 SALT HYDROLYSIS

When a salt is dissolved in water, it dissociates into ions. The cation and anion of the salt reacts with the ionised water molecules. This is called *hydrolysis*.

When a salt A-B, is added to pure water, it dissociates $A-B \rightleftharpoons A^+ + B^-$

Pure water ionizes weakly as



Hydrolysis of salts results in aqueous solutions that show differences in nature.

(i) Some salts like NH_4Cl have acidic nature (turn blue litmus red).

(ii) Some other salts like CH_3COONa have basic properties (turn red litmus blue).

(iii) Yet other salts like $NaCl$ form neutral solutions (have no effect on litmus).

The nature of A^+ and B^- will determine whether the solution will be acidic or basic.

Salts are formed when an acid and base react with each other. There are four possible permutations depending on strength of the acid and base:

(a) Salts formed when WA reacts with SB

(b) Salts formed when WA reacts with WB

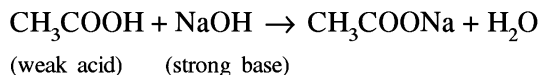
(c) Salts formed when SA reacts with WB

(d) Salts formed when SA reacts with SB

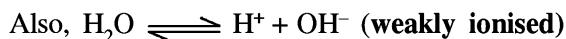
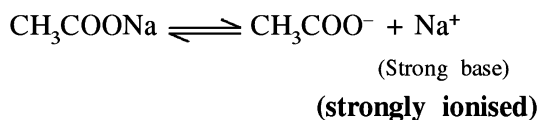
SA = strong acid
SB = strong base
WA = weak acid
WB = weak base

(a) Hydrolysis of salt formed by a WA and SB:

Consider a salt formed by a weak acid and a strong base.

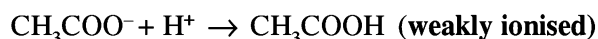


When the salt is dissolved in water the ions formed are



As the conjugate of a WA (CH_3COOH) is a SB (CH_3COO^-), the SB seeks protons.

CH_3COO^- ions **tend to combine in aqueous solution** as follows:



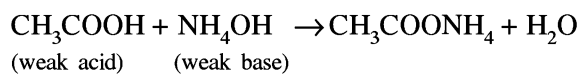
H^+ ions thus, leave the solution to form whole molecules of acetic acid.

Due to this, there is a relative increase in $[\text{OH}^-]$.

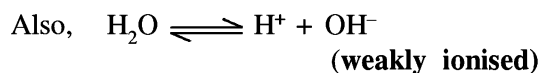
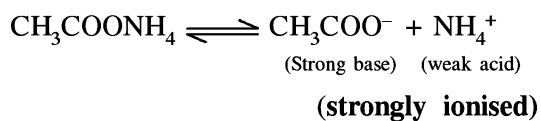
So, the salt solution is basic turning red litmus blue.

(b) Hydrolysis of salt formed by a WA and WB:

Consider a salt formed by a weak acid – CH_3COOH and a weak base – NH_4OH .



When the salt is dissolved in water the ions formed are



As the conjugate of a WB (NH_4OH) is a SA (NH_4^+), the SA seeks OH^- ions.

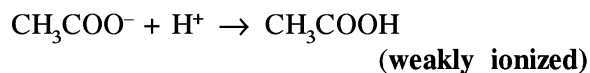
NH_4^+ ions **tend to combine in aqueous solution** as follows:



Step 1: OH^- ions leave the solution to form whole molecules of ammonium hydroxide.

As the conjugate of a WA (CH_3COOH) is a SB (CH_3COO^-), the SB seeks protons.

CH_3COO^- ions **tend to combine in aqueous solution** as follows:



Step 2: H^+ ions leave the solution to form whole molecules of acetic acid.

Thus, both OH^- ions (step 1 above) and H^+ ions (step 2 above) leave the solution to form whole molecules of ammonium hydroxide and acetic acid respectively.

Thus, there is **no relative increase or decrease in either $[\text{H}^+]$ or $[\text{OH}^-]$. Thus, the salt solution is neutral.**

As a general rule hydrolysis of a salt formed by

- SB + WA results in a basic solution
- WB + SA results in an acidic solution
- WB + WA results in a neutral solution
- SB + SA results in a neutral solution

PRACTICE EXERCISE

- Predict the nature of the aqueous solutions by outlining the hydrolysis of the salt formed by
 - SA + WB
 - SA + SB (take suitable examples)
 - State whether the following salts are acidic, basic or neutral by preparing a chart as shown
- | Salt | Parent acid | Parent base | Nature of aq. salt solution |
|----------------------|--------------------|--------------------|-----------------------------|
| (1) NaClO | HClO (WA) | NaOH (SB) | basic |
| (2) NaHCO_3 | | | |

6.9 TYPES OF SALTS

There are 6 types of salts.

- (a) *Normal salts* are formed by replacing all the replaceable H^+ ions from an acid by basic radical(s). The salt has no replaceable H-atoms.

Examples: $NaCl$, K_2SO_4 , $CaCO_3$.

- (b) *Acid salts* are formed by partial replacement of the replaceable H^+ ions in an acid by a basic radical. The salt has replaceable H-atoms.

Examples: $NaHSO_4$, $NaHCO_3$, $Ca(HCO_3)_2$

- (c) *Basic salts* are formed by incomplete neutralisation of a base.

Examples: $Cu(OH)Cl$ (basic copper chloride), $Pb(OH)NO_3$

- (d) *Double salts* are formed when two simple salts crystallize out of a mixture of a saturated solution of the two salts.

Examples:

Potash alum – $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$,
Mohr's salt – $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$,

Dolomite – $CaCO_3 \cdot MgCO_3$

- (e) *Mixed salts* are salts that contain two or more acidic or basic radicals.

Examples: $NaKSO_4$, Na_2KPO_4 , $Ca(OC)Cl$

- (f) *Complex salts* are salts that have a simple ion and a complex ion.

Examples:

$NaAg(CN)_2$ – Sodium argento cyanide,

$K_3Fe(CN)_6$ – Potassium ferricyanide.

6.10 COMMON ION EFFECT

When a solution of a weak acid or base is added to the saturated solution of a strong electrolyte containing a common ion, the dissociation of the weak acid or base is suppressed.

E.g.: $NH_4OH \rightleftharpoons NH_4^+ + OH^-$
(weakly ionized)

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$ (strongly ionized)

When NH_4OH is added to a saturated solution of NH_4Cl , there is a relative increase in concentration of NH_4^+ , causing the equilibrium in the weakly ionized NH_4OH reaction to shift backwards suppressing its ionisation further.

Application of Common Ion Effect: If to a saturated solution of $NaCl$, HCl is added, $NaCl$ comes out of the solution. This method is used to purify and crystallize $NaCl$ in its manufacture.

6.11 BUFFER SOLUTIONS

Buffers are solutions that resist pH change even if a small amount of strong acid or strong base is added.

There are two types of buffers.

- (1) *Acid buffers* are prepared by mixing a weak acid and its salt with a strong base.

Example: $CH_3COOH + CH_3COONa$.

- (2) *Basic buffers* are prepared by mixing a weak base and its salt with a strong acid.

Example: $NH_4OH + NH_4Cl$.

Explanation of buffering action

The buffering action of buffers is explained as follows.

Acid buffer: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
 $CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

There are two possible situations:

- (a) a little amount of strong acid is added.

- (b) a little amount of strong base is added.

- (a) Addition of SA to a buffer **should** decrease the pH. But there is no change in pH.

Reason: When an acid is added $[H^+]$ increases. But since CH_3COO^- is a SB it seeks protons.

$CH_3COO^- + H^+ \rightarrow CH_3COOH$.

This is a weak acid that is weakly ionized. So, the increase in $[H^+]$ is nullified as the excess H^+ ions are removed by forming whole molecules of CH_3COOH .

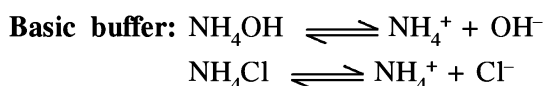
- (b) Addition of SB to a buffer **should** increase the pH. But there is no change in pH.

Reason: When a base is added $[OH^-]$ increases. But since OH^- is a SB it seeks protons.

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

So, the increase in $[OH^-]$ is nullified as the excess OH^- ions are removed by reacting with molecules of CH_3COOH .

Thus, overall pH does not change whether a strong acid or base is added to an acidic buffer.



There are two possible situations:

- (a) add a little amount of strong acid
- (b) add a little amount of strong base.
- (a) Addition of SA **should** decrease the pH. But there is no change in pH.

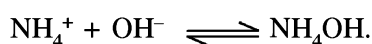
Reason: When an acid is added $[\text{H}^+]$ increases. But since $[\text{H}^+]$ is a SA, it accepts $[\text{OH}^-]$



Thus, there is no change in pH.

- (b) Addition of SB **should** increase the pH. But there is no change in pH.

Reason: When a base is added $[\text{OH}^-]$ increases. But since NH_4^+ is a SA, it accepts $[\text{OH}^-]$



Thus, overall pH does not change whether a strong acid or base is added to a basic buffer.

Applications of Buffers

- (1) Blood is the best buffer. Its pH = 7.35.
 When acid concentration increases, the buffering action is

$$\text{H}^+ + \text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3$$
 Thus excess H^+ ions are removed.
 When base concentration increases, the buffering action is

$$\text{OH}^- + \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{HCO}_3^-$$
 Thus excess OH^- ions are removed
- (2) Industry: Buffers are used in the manufacture of paints, ink, dyes, paper, drugs, antibiotics, leather, and laundry soap.
- (3) Agriculture – Soil testing to maintain the pH of soil for maximum yield of crops.

6.12 INDICATORS

Indicators are weak organic acids/bases used to find the nature of solution by specific colour change.

Indicators are of two types:

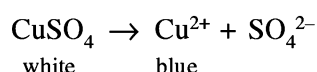
- (a) *Acidic Indicators*
- (b) *Basic Indicators*

The specific colour changes that some indicators show when added to acid / base are given below.

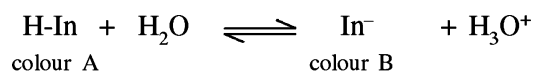
Indicator	Acids	Bases
<i>Litmus</i>	Blue → Red	Red → Blue
<i>Methyl Orange</i>	Red	Yellow
Phenolphthalein	Colourless	Pink

Action of indicators

Indicators are weak organic acids. They work on the principle, that a whole molecule exhibits a particular colour when compared to the ion. As an example, anhydrous CuSO_4 is white while the Cu^{2+} ion is blue in colour.



Acid Indicators are denoted by the symbol H-In as they have H^+ in the molecule and ionize in aqueous solution as:

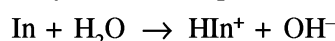


If the indicator is added to an acid, due to increase in $[\text{H}^+]$, the equilibrium shifts backward, and the colour exhibited is of the whole indicator molecule H-In, i.e., colour A.

If the indicator is added to a base, due to H_3O^+ getting neutralized by OH^- ion, the equilibrium shifts forward and the colour exhibited is of the indicator ion In^- , i.e., colour B.

Example: Phenolphthalein is an acid indicator. Let its formula be H-In. The whole indicator molecule is colourless while the ion (In^-) is pink.

Basic indicators are denoted by the symbol, In and they ionize in aqueous solution as follows:



If the indicator is added to an acid, due to increase in $[\text{H}^+]$, the equilibrium shifts forward, and the colour exhibited is of the indicator ion (H-In^+).

If the indicator is added to a base, due to increase in $[\text{OH}^-]$ the equilibrium shifts backward and colour exhibited is of the indicator, In.

Example: Methyl orange (In) is yellow and its ion (H-In^+) is red.

6.13 SOME USEFUL FACTS

- (1) *Alkalis* are bases that are soluble in water. *All alkalis are bases, but all bases are not alkalis.*

Examples: NaOH is both a base and an alkali, but, $\text{Al}(\text{OH})_3$ is a base but not an alkali.

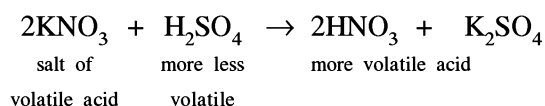
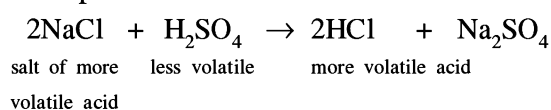
- (2) Classification of acids based on composition:
- (i) **Hydro-acids** have hydrogen and a non-metallic element other than oxygen in them.
Example: H_2S , HCl , HI , HCN .
Oxy-acids have hydrogen, oxygen and one more element in them.
Example: HNO_3 , H_2SO_4 , H_3PO_4 .
- (3) *Concentration of an acid or base* is a measure of the water present in it. An acid or base with very little water is called *concentrated* and more water than acid is called *dilute*. In general if concentration is less than 1 mole/l, it is called dilute acid/base.
- (4) *Strength of an acid or base* is a measure of the extent of dissociation, α and is different from concentration. Larger the extent of dissociation, α , stronger is the acid. In general if $\alpha > 30\%$, it is called a strong acid / base.
- (5) The strongest acid is HClO_4 . Some more strong acids: H_2SO_4 , HNO_3 , HCl , HClO_4 .
The conjugates of these acids will be weak bases.
- (6) Some weak acids: H_2CO_3 , H_3PO_4 , H_2SO_3 , H_2S , HCN , HCOOH , CH_3COOH , $(\text{COOH})_2$.
- (7) Volatile acids have BP below 100°C . H_2SO_4 has a BP of 398°C and is the least volatile acid. Other examples: HCl , HNO_3 , H_2SO_3 .
- (8) The volatility of $\text{HCN} < \text{HCl} < \text{CH}_3\text{COOH}$.
- (9) Examples of non-volatile acids: H_3PO_4 , H_2SO_4 .
- (10) **Constant Boiling Mixture:** Dilute HNO_3 can be concentrated by slow heating so that water evaporates. But it cannot be concentrated above 68% by this method as it forms a *constant boiling mixture* having a BP of 121°C where the entire water acid mixture boils off together.
- (11) **Constant Boiling Mixtures:** Some hydro-

acids cannot be concentrated beyond a certain percentage by boiling as they form a Constant Boiling Mixture – both the acid and water boil off together. Some examples

HCl	22%
H_2SO_4	98%
HNO_3	68%

- (12) Solid-state acids: H_3PO_4 , $(\text{COOH})_2$, H_3BO_3
 (13) Some gaseous state acids: H_2S
 (14) **Displacement rule:** As a general rule a more volatile acid is displaced from its salt by a less volatile acid.

Examples:



- (15) Strength of some acids:
 $\text{HClO}_4 > \text{HI} > \text{HBr} > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$
- (16) Classification of acids on basicity
Basicity of an acid is the number of replaceable Hydrogen ions (H^+) in its molecule.
 Examples:
 Monobasic acids – HCl , HNO_3 , CH_3COOH
 Dibasic acids – H_2SO_4 , H_2SO_3 , $(\text{COOH})_2$
 Tribasic acids – H_3PO_4 , H_3PO_3
- (17) Classification of bases on acidity
Acidity of a base is the number of replaceable Hydroxyl radicals (OH^-) in its molecule.
 Examples:
 Monoacidic bases –
 NaOH , KOH , LiOH , NH_4OH
 Diacidic bases –
 $\text{Ca}(\text{OH})_2$, $\text{Zn}(\text{OH})_2$, $\text{Pb}(\text{OH})_2$
 Triacidic bases – $\text{Al}(\text{OH})_3$, $\text{Cr}(\text{OH})_3$

SOLVED PROBLEMS

(Useful information : $\log 2 = 0.3010$; $\log 5 = 0.6990$, $\log 3.3 = 0.5185$).

1. Calculate the pH of the following solutions with $[\text{H}^+]$ concentrations 10^{-3}M , $5 \times 10^{-9}\text{M}$, 10^{-13}M .

Ans: (a) $\text{pH} = -\log[\text{H}^+] = -\log(10^{-3}) = 3\log 10 = 3 \times 1 = 3$

(b) $\text{pH} = -\log[\text{H}^+] = -\log(5 \times 10^{-9}) = -\log 5 + 9\log 10 = -0.6990 + 9 = 8.301$

(c) $\text{pH} = -\log[\text{H}^+] = -\log(10^{-13}) = 13\log 10 = 13 \times 1 = 13$

2. Calculate the pH of 0.5M HCl and 0.005M H₂SO₄

Ans: All the given acids are strong acids and hence fully ionized.

HCl is strong acid. Since it is monobasic, $[H^+] = \text{molarity of acid} = 0.5 \text{ moles/l} = 5 \times 10^{-1}$

$$\text{pH} = -\log(5 \times 10^{-1}) = -\log 5 + \log 10 = -0.699 + 1 = 0.301$$

H₂SO₄ is strong acid. Since 1 mole of H₂SO₄ gives two moles of H⁺ ions, 0.005 moles will give 2×0.005 moles of H⁺ ions.

$$\text{pH} = -\log(2 \times 0.005) = -\log(0.01) = -\log(10^{-2}) = 2\log 10 = 2$$

3. Calculate pH of 0.5M NaOH solution, 0.002M Ba(OH)₂.

Ans: NaOH is strong base. Since it is monoacidic, $[OH^-] = \text{molarity of base} = 0.5 \text{ moles/l} = 5 \times 10^{-1}$

$$\text{Thus, pOH} = -\log(5 \times 10^{-1}) = 0.301 \quad \text{pH} = 14 - 0.301 = 13.699$$

Ba(OH)₂ is strong base. Since 1 mole of H₂SO₄ gives two moles of H⁺ ions, 0.002 moles will give 2×0.002 moles of OH⁻ ions.

$$\text{pOH} = -\log(4 \times 10^{-3}) = -\log 2^2 + 3\log 10 = -2\log 2 + 3 = -2 \times 0.3010 + 3 = 3 - 0.6020 = 2.398$$

$$\text{pH} = 14 - 2.398 = 11.602$$

4. Calculate the pH and $[OH^-]$ of 0.1M HNO₃.

Ans: As HNO₃ is strong acid, pH = 1 and pOH = 13

5. Calculate the pH of a solution containing 4gm of NaOH in 500ml.

Ans: Number of moles = $m/M = 4/40 = 0.1$

$$\text{Molarity} = \text{moles per litre} = 0.1/0.5 = 0.2M$$

Since, NaOH is monobasic, molarity = $[OH^-] = 0.2 \text{ moles/l}$

$$\text{pOH} = -\log(2 \times 10^{-1}) = -\log 2 + 1 = -0.3010 + 1 = 0.699$$

$$\text{pH} = 14 - \text{pOH} = 14 - 0.699 = 13.301$$

6. Calculate the pH of a mixture of equal volumes of N/10 NaOH and N/20 HCl. (Assume 1 l of solution.)

Ans: 1 litre of N/10 NaOH has 0.1 g equivalent of NaOH

1 litre N/20 HCl has 0.05 g equivalent of HCl.

Since 1 g equivalent of any acid neutralizes 1 g equivalent of any base always,

NaOH is clearly in excess by $0.1 - 0.05$ g equivalent = 0.05 g equivalent.

This is present in 2 l of solution as 1 l of NaOH was added to 1 l of HCl.

Thus, Normality of NaOH (which is in excess) = $0.05 \text{ g equivalent}/2 \text{ l} = 0.025N$

Since acidity of NaOH = 1, Normality = Acidity $\times$ Molarity

$$\text{Molarity of NaOH} = \text{Normality of NaOH} = 0.025M$$

Since NaOH is strong base it is fully ionized; it is also mono-acidic

$$[OH^-] = \text{molarity} = 0.025, \text{pOH} = -\log 0.025 = -\log(5^2 \times 10^{-3}) = -2\log 5 + 3 = -2 \times 0.699 + 3 = 3 - 1.398 = 1.602 \text{ and } \text{pH} = 14 - 1.602 = 12.398$$

7. Calculate the pH of aq solutions containing 100ml of 1N HCl and 60ml of 1N NaOH assuming complete ionization.

Ans: Number of g equivalent in HCl = $1 \times 0.1 = 0.1$ gram equivalent.

Number of g equivalent in NaOH = $1 \times 0.06 = 0.06$ gram equivalent

HCl is in excess by $0.1 - 0.06 = 0.04$ gram equivalent. This excess is present in (100 + 60) ml of solution.

Since basicity of HCl is 1, Molarity = Normality = $0.04/0.16 = 1/4 = 0.25\text{M}$

Since HCl is strong acid and fully ionized, $[\text{H}^+] = \text{molarity} = 0.25 \text{ moles/l.}$

$$\text{pH} = -\log 0.25 = -\log (5^2 \times 10^{-2}) = -2\log 5 + 2 = 2 - 2 \times 0.699 = 2 - 1.398 = 0.602$$

8. At 90°C $[\text{H}_3\text{O}^+]$ in pure water is 10^{-4} . Calculate the K_w of pure water at 90°C .

Ans: H^+ is a proton and cannot exist independently. It combines with water molecule forming hydronium ion.
 $\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+$.

Thus, the $[\text{H}^+] = [\text{H}_3\text{O}^+]$ Also, in pure water, $[\text{H}^+] = [\text{OH}^-]$

$$K_w = [\text{H}^+] [\text{OH}^-] = [\text{H}_3\text{O}^+] [\text{OH}^-] = 10^{-4} \times 10^{-4} = 10^{-8} \text{ at } 90^\circ\text{C}.$$

6.14 IMPORTANT POINTS TO REMEMBER

- * Acids turn blue litmus red and bases turn red litmus blue.
- * Acids are formed when non-metal oxides are dissolved in water.
- * Bases are formed when metallic oxides are dissolved in water.
- * Acids react with bases, metals, metallic oxides, carbonates and bicarbonates.
- * Bases produce metallic oxides on heating.
- * According to Arrhenius' theory, acids produce H^+ ions and bases produce OH^- ions in aqueous media.
- * Combination of H^+ and OH^- ions is called neutralization.
- * One of the limitations of Arrhenius' theory is that it could not cover all acids and bases.
- * Water ionizes only to a small extent to produce H^+ and OH^- ions.
- * The product $[\text{H}^+] [\text{OH}^-]$ is called ionic product of water K_w . The value of $K_w = 1 \times 10^{-14}$ at 25°C .
- * pH was introduced by Sorensen $\text{pH} = -\log [\text{H}^+]$
- * pH of acids is between 0 and 7 and that of bases is between 7 and 14.
- * Neutral solution has a pH of 7.
- * Completely ionized acids and bases are called strong acids and strong bases respectively.
- * Incompletely ionized acids and bases are called weak acids and weak bases respectively.
- * The heat liberated when one mole of strong acid or H^+ ions react with one mole of strong base or OH^- ions is called heat of neutralization.
- * For a reaction between strong acid and strong base the heat of neutralization is $13.7 \text{ kcal mol}^{-1}$.
- * For a reaction involving weak acid or weak base, the heat of neutralization is less than $13.7 \text{ kcal mol}^{-1}$.

EXERCISE

I. Choose the correct answer

1. Which of the following is an Arrhenius' acid?

(a) NH_3 (b) SO_2
(c) AlCl_3 (d) HNO_3

2. Arrhenius' theory could not explain the acidic nature of

(a) HCl (b) HCOOH
(c) H_2S (d) CO_2

3. Which of the following species acts as Bronsted base but not as Bronsted acid?

(a) CH_3COOH (b) HCO_3^-
(c) H_2PO_2^- (d) H_2PO_3^-

4. Conjugate acid of HPO_4^{2-} is

(a) H_3PO_4 (b) H_2PO_4^- (c)
 PO_4^{3-} (d) HPO_4^{2-}

5. Conjugate base of HSO_4^- is

(a) H_2SO_4 (b) $\text{H}_2\text{SO}_4^{2-}$
(c) SO_4^{2-} (d) H^+

6. Which aqueous solution will have the largest pOH?

(a) MgCl_2 (b) $\text{Mg}(\text{HCO}_3)_2$
(c) CH_3COONa (d) NaNO_3

7. Among the following, relatively weak base is (Hint: acidic nature decreases down a group in the periodic table)
- (a) F^- (b) Cl^-
(c) Br^- (d) I^-
8. Which of the following is not a conjugate acid – base pair?
- (a) $HPO_4^{2-}; PO_4^{3-}$ (b) $H_2PO_4^-; HPO_4^{2-}$
(c) $H_2PO_4^-; H_2PO_4$ (d) $H_2PO_4^-; PO_3^{2-}$
9. In aqueous solution, HCl and HNO_3 are equally strong. This is because
- (a) their basicities are same
(b) both are any acids of non-metal
(c) both have lower molecular weights
(d) ionisation of water
10. Strength of a weak acid or a weak base depends upon its
- (a) temperature (b) nature of solvent
(c) degree of dissociation (d) all the above
11. In the reaction $CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^-$, H_3O^+ acts as
- (a) weak acid (b) weak base
(c) strong acid (d) strong base
12. Which of the following is an acidic salt?
- (a) Na_3PO_4 (b) Na_2HPO_3
(c) NaH_2PO_2 (d) NaH_2PO_4
13. Which of the following is a normal salt?
- (a) Na_3PO_4 (b) $CaSO_4$
(c) Na_2CO_3 (d) all the above
14. Which of the following does not turn blue litmus red?
- (a) $1M HCl$ (b) pure and dry HCl
(c) dil. HCl (d) conc. HCl
15. Which of following is relatively strong base in aqueous solution?
- (a) $NaOH$ (b) $Ca(OH)_2$
(c) $Ba(OH)_2$ (d) all are equally strong
16. Which of the following failed to explain the relative strength of acids and bases?
- (a) Arrhenius' theory (b) Bronsted theory
(c) Lowry theory (d) Lewis theory
17. Which of the following is wrong?
- (a) All Bronsted bases are Lewis bases
(b) All Lewis acids are Bronsted acids
(c) All Arrhenius' acids are Bronsted acids
(d) All Arrhenius' bases are Bronsted bases
18. The number of conjugate acid base pairs present in the aqueous solution of H_3PO_3 is
- (a) 2 (b) 3
(c) 4 (d) 5
19. H_2CO_3 ionises in two stages as given below. The number of conjugate acid–base pairs in the reaction is _____
- $$H_2CO_3 + H_2O \longrightarrow H_2O^+ + HCO_3^- \quad \text{and}$$
- $$HCO_3^- + H_2O \longrightarrow H_3O^+ + CO_3^{2-}$$
- (a) 2 (b) 3
(c) 4 (d) 5
20. The units of ionic product of water is
- (a) mole/ lit (b) mole/kg
(c) $\text{mole}^2 \text{ lit}^{-2}$ (d) no units
21. At $100^\circ C$, the value of pK_w is
- (a) 14 (b) < 14
(c) > 14 (d) $pH - pOH$
22. At $25^\circ C$, for an acid
- (a) $[H^+] > 10^{-7} M$ (b) $[OH] < 10^{-2} M$
(c) $pH < 7$ (d) all the above
23. At $298 K$, the $[H_3O^+]$ of a solution is $2 \times 10^{-8} M$. The nature of the solution is
- (a) acidic (b) basic
(c) neutral (d) cannot be predicted
24. Ionic product of water depends on
- (a) volume of water
(b) amount of salt in water
(c) temperature
(d) all the above
25. At a given temperature, when an acid is added to water then the value of K_w
- (a) decreases (b) increases
(c) remains same
(d) first decreases then increases
26. At any temperature, the proton concentration of water is
- (a) $10^{-7} M$ (b) $< 10^{-7} M$
(c) $> 10^{-7} M$ (d) $\sqrt{K_w}$
27. The value of ionic product of water increases with increase in
- (a) acidic nature of solution
(b) basic nature of solution
(c) temperature
(d) volume of the solution
28. pH of a solution is given by
- (a) $pH = -\log [H^+]$ (b) $pH = \log \frac{1}{[H^+]}$
(c) $pH = pK_w - pOH$ (d) all the above

- 29. pH of a solution is independent of**
- temperature
 - nature of the solution
 - degree of dissociation of acid (or) base
 - volume of the solution
- 30. Which of the following is wrong?**
- At any temperature pH of water is exactly equal to 7
 - At 25°C, the pH of an acid is less than 7
 - At 25°C, the pH of a base is greater than 7
 - At 25°C, the pOH of water is equal to 7
- 31. The pH of an aqueous solution is zero. Then the nature of the solution is**
- slightly acidic
 - strongly acidic
 - neutral
 - basic
- 32. Among the following**
- pH of water decreases with increase in temperature
 - pH of water decreases by the addition of base
 - pH of water increases by the addition of acid
 - at any temperature pH of water is equal to $pK_w/2$
- all are correct
 - (ii), (iii), (iv) are correct
 - (i) and (ii) are correct
 - (i), (ii) and (iii) are correct
- 33. At any temperature, pH + pOH is equal to**
- 7
 - 0
 - 14
 - pK_w
- 34. Among the following**
- on dilution, the pH of an acid increases
 - a solution with pH = 5 is 100 times more basic than a solution with pH = 3
 - a solution with pH = 8 is 1000 times more acidic than a solution with pH = 11
 - the pH of 10^{-9} M KOH is slightly greater than 7
- all are correct
 - (i), (iv) are only correct
 - (i), (ii), (iii) are only correct
 - all are wrong
- 35. Each 10^{-3} M of following four acids are taken. Their pH values are given in brackets. Which of the following is relatively strong acid?**
- A (3.6)
 - B (4.2)
 - C (5.4)
 - D (6.8)
- 36. For a strong acid**
- K_a is very high
 - pK_a is very low
 - $[H^+]$ is very high
 - all the above
- 37. Which of the following is a weak electrolyte?**
- CH_3COONa
 - CH_3COOH
 - KOH
 - H_2SO_4
- 38. Which of the following is the best conductor of electricity?**
- 1M HNO_3
 - 1M H_2CO_3
 - 1M H_3PO_4
 - 1M H_2SO_4
- 39. Which of the following is wrong?**
- degree of dissociation of a weak electrolyte increases with dilution
 - increase in temperature increases the ionisation
 - strong electrolytes are ionised completely even at moderate concentration
 - addition of NH_4Cl to NH_4OH increases the ionisation of the latter.
- 40. Which of the following does not affect the degree of ionisation?**
- Temperature
 - Current
 - Nature of solvent
 - Concentration
- 41. At infinite dilution, the percentage ionisation of both strong and weak electrolytes is**
- 1%
 - 20%
 - 50%
 - 100%
- 42. Aqueous solution of salt of strong acid and weak base**
- undergoes cationic hydrolysis
 - is acidic in nature
 - has pH less than 7
 - all the above
- 43. The compound whose 0.1 M solution is basic is**
- Ammonium acetate
 - Ammonium chloride
 - Ammonium sulphate
 - Sodium acetate
- 44. Which of the following shows relatively higher pH?**
- Aqueous NaCl
 - Aqueous NH_4Cl
 - Aqueous Na_3PO_4
 - Aqueous KOH
- 45. Aqueous solution of salt of weak acid and strong base**
- has $[H^+] < [OH^-]$
 - is basic in nature
 - has pH greater than 7
 - all the above
- 46. Aqueous solution of KCl is neutral because**
- K^+ undergoes hydrolysis
 - Cl^- undergoes hydrolysis
 - both K^+ and Cl^- undergo hydrolysis
 - no hydrolysis takes place

47. Dissociation of CH_3COOH is suppressed by adding

- (a) HCl (b) H_2SO_4
(c) CH_3COONa (d) any of the above

48. Ionisation of NH_4OH is suppressed by the addition of NH_4Cl , because

- (a) NH_4Cl is a salt of WB and SA
(b) NH_4Cl is a salt of strong base and weak acid
(c) Of the common ion effect of NH_4^+ ion
(d) None of the above

49. The H^+ ion concentration of a solution is $4 \times 10^{-5}\text{M}$. Then the OH^- ion concentration of the same solution is

- (a) $4 \times 10^{-5}\text{ M}$ (b) $2.5 \times 10^{-9}\text{ M}$
(c) $1.0 \times 10^{-7}\text{ M}$ (d) $2.5 \times 10^{-10}\text{ M}$

50. The $[\text{OH}^-]$ of $0.005\text{ M H}_2\text{SO}_4$ is

- (a) $2 \times 10^{-12}\text{ M}$ (b) $5 \times 10^{-3}\text{ M}$
(c) 10^{-2} M (d) 10^{-12} M

II. Give one word answers

- The temperature at which the pH of pure water is 7.
- The heat released in a neutralisation reaction is called :
- The name of the strongest oxyacid is :
- sum of pH and pOH
- value of pK_w at 25°C

III. Match the following. More than one match or no matches is possible.

- | | |
|---|-----------------------------------|
| 1. Acid | Basicity |
| (a) oxalic acid ($\text{C}_2\text{O}_4\text{H}_2$) | (i) one |
| (b) formic acid (HCOOH) | (ii) three |
| (c) acetic acid ($\text{C}_2\text{H}_4\text{O}_2$) | (iii) two |
| (d) phosphoric acid | (iv) four |
| 2. Base | Acidity |
| (a) Basic copper chloride $[\text{Cu}(\text{OH})\text{Cl}]$ | (i) one |
| (b) NaOH | (ii) two |
| (c) NH_4OH | (iii) three |
| (d) $\text{Al}(\text{OH})_3$ | (iv) zero |
| 3. List I | List II |
| (a) strong acid | (i) low dissociation |
| (b) weak acid | (ii) high dissociation |
| (c) organic acids | (iii) very, very low dissociation |
| (d) pure water | (iv) very low dissociation |

IV. State whether the following statements are True or False

- The pH of HCl acid whose $[\text{H}^+] = 10^{-8}\text{ moles / l}$ is 8.
- The conjugate of acetate ion is a strong acid.
- The conjugate of OH^- is H_2O .
- SO_2 turns moist blue litmus red and hence is an Arrhenius' acid.
- The value of ionic product is independent of temperature but dependent on molar concentrations of H^+ and OH^- .

V. Pick the correct word(s) that fills the blank from the options given.

- A solution with $\text{pH} = 4$ is 100 times more acidic than a solution with pH equal to ____ ($6 / 2$).
- The pH of solutions A, B, C, D are respectively 9.5, 2.5, 3.5, and 5.5. The most acidic solution is ____ (A / B / C / D)
- Urine normally has pH of 6.0. A patient eliminates 1.3 litres of urine per day. The number of moles of H^+ ions he eliminates in a day is ____ ($1.3 \times 10^{-3} / 1.3 \times 10^{-6}$)

VI. Fill in the blanks

- The ionic product of water is 10^{-14} . The H^+ ion concentration in 0.1 M NaOH solution is ____.
- The number of H_3O^+ ions present in 10 ml of water at 25°C is ____.
- At some high temperature, K_w of water is 10^{-10} , and then pH of water at the same temperature is ____.
- Four grams of NaOH solid are dissolved in just enough water to make 1 litre of solution. The $[\text{H}^+]$ of the solution is ____.
- The pH of HCl is 3. Then the pH of NaOH solution having same molar concentration is ____.
- The pH of a solution is 3.0. This solution is diluted by 100 times. Then the pH of the resulting solution is ____.
- The amount of NaOH to be added to 100 ml of HCl solution whose pH is 1, to get pH of 7 is ____.

VII. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, Statement R is true; Statement R is correct explanation for statement A

Choose B if Statement A is true, statement R is true;
Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D if Statement A is false, statement R is true

- (1) **Statement A:** HCl is not acidic in benzene.

Statement R: Benzene does not accept protons.

- (2) **Statement A:** All Bronsted bases are Lewis bases.

Statement R: A species that accepts a proton should necessarily donate a lone pair of electrons.

- (3) **Statement A:** pH of an aqueous solution of acetic acid remains unchanged on the addition of sodium acetate.

Statement R: Dissociation of acetic acid is suppressed by the addition of sodium acetate due to common ion effect.

- (4) **Statement A:** At 90°C, the pH of pure water is less than 7.

Statement R: Ionic product of water increases with increase in temperature.

- (5) **Statement A:** The pH of a solution changes from 5 to 8 when the solution is diluted by 1000 times.

Statement R: When the concentration H^+ ion decreases 10 times, then pH of the solution increases by one unit.

- (6) **Statement –A:** Ionic Product of water increases with temperature.

Statement –R: The extent of dissociation of water increases with temperature

- (7) **Statement –A:** Sulphuric acid cannot be concentrated beyond 98% by simple boiling.

Statement –R: Sulphuric acid decomposes above this concentration.

- (8) **Statement –A:** The Heat of Neutralisation when a weak acid is neutralised with a strong base will be above 13.7 kcal/mole.

Statement –R: The strong base furnishes more OH^- ions.

- (9) **Statement –A:** A volatile acid can be prepared by displacing it from its salt by a less volatile acid.

Statement –R: A less volatile acid is dissociated less.

VIII. Solve the problems.

- (1) The pH of a 1 l solution is 2. It is diluted with water till its pH becomes 4. How much water has been added?

Hint: Assume complete ionization of the acid. $[H^+]$ will be equal to normality. Use $N_1 V_1 = N_2 V_2$. Water to be added = $V_2 - V_1$.

- (2) Calculate the amount of solute present in 1 l of NaOH given that the pH = 12.

Hint: NaOH is a strong base;

$[OH^-] = K_w/[H^+] = \text{Molarity of NaOH (as acidity} = 1);$
 $\text{wt of solute} = \text{g mol wt} \times \text{molarity}$

- (3) If chlorine gas is bubbled through pure water will the pOH increase or decrease?

(Hint : $H_2O + Cl_2 \rightarrow HCl + HClO$)

- (4) The pH of solution is increased from 3 to 6. Does its $[H^+]$ increase or decrease?

- (5) (a) What is conjugate acid of O^{2-} ?

(b) What is conjugate of azide ion?

- (6) (a) What are conjugates of NH_2^- and $H_2PO_4^{1-}$?

(b) What are the conjugates of water?

- (7) Calculate the number of moles of H^+ ions urinated by a patient who passes 1.3 l of urine a day if its pH = 6.

- (8) The gastric juice in our stomach has enough HCl to make 0.01M HCl. Find the pH of gastric juice.

- (9) If ionic product of pure water at 100°C is 10^{-12} , find the pH of water at 373K. (Hint: 373K = 100°C)

- (10) pH of a solution is 5. Its $[H^+]$ is decreased by 100 times. What is the nature of the solution?

- (11) 0.1M HCl solution is diluted 100 times. Find the pH of the solution so formed.

- (12) A solution of pH 9 is 1000 times as basic as a solution of pH 'x'. Calculate the value of 'x'.

- (13) 100 ml of N/10 NaOH solution is mixed with 100 ml of N/5 HCl and the volume is made up to 1 l. Find the pH. (Hint: Calculate the number of gm equivalents in NaOH and HCl)

- (14) Predict the nature of the solution formed by mixing 100ml of 0.5N NaOH with 200 ml of 0.2 N H_2SO_4 .

- (15) If the pH of a solution is changed from 4 to 6 what is the change in its $[OH^-]$. (Hint: use ionic product)

- (16) State the changes that take place in $[H^+]$ and $[OH^-]$ ion concentrations when an acid or base is added to pure water without changing temperature.

- (17) Find the change in pH value for every 10 fold decrease and increase in $[H^+]$.

- (18) When a drop of HCl is added to a mixture of acetic acid and sodium acetate solution, what effect will it have on pH? (Hint: see buffers)

- (19) The pH of dilute HCl whose $[H^+] = 10^{-8}$ should by definition be 8. But pH of an acid can never exceed 7. Explain.

KEY TO EXERCISE

- I.** 1. d 2. d 3. c 4. b 5. c 6. a 7. d 8. d
 9. d 10. d 11. c 12. d 13. d 14. b 15. d 16. d
 17. b 18. b 19. b 20. c 21. b 22. d 23. b 24. c
 25. c 26. d 27. c 28. d 29. d 30. a 31. b 32. c
 33. d 34. a 35. a 36. d 37. b 38. d 39. d 40. b
 41. d 42. d 43. d 44. d 45. d 46. d 47. d 48. c
 49. d 50. d
- II.** (i) 25°C (ii) heat of neutralisation (iii) per chloric acid (iv) 14 (v) 14
- III.** (1) a. (iii) b. (i) c. (i) d. (ii) (2) a. (i) b. (i) c. (i) d. (iii)
 (3) a. (ii) b. (i) c. (iv) d. (iii)
- IV.** (i) false (ii) false (iii) true (iv) false (v) false
- V.** (i) 6 (ii) B (iii) 1.3×10^{-6}
- VI.** (1) 10^{-13} M (2) 6.023×10^{14} (3) 5 (4) 10^{-13} moles/ litre (5) 11 (6) 5 (7) 0.4g
- VII.** (1) A (2) A (3) D (4) A (5) D (6) A (7) C (8) B (9) C
- VIII.** (1) 99l 10) 0.4g (2) increase (3) Decreases (4) OH^- , NH_2^-
 (5) acid - NH_3 , base - NH_2^- ; acid - H_3PO_4 , base - HPO_4^{2-} (6) 1.3×10^{-6} moles (7) pH = 2 (8) pH = 6
 (9) pH = 7 hence neutral (11) pH = 3 (12) $x = 6$ (13) pH = 1.301 (14) basic (15) 9.9×10^{-9}
 (16) $[\text{H}^+]$ increases and $[\text{OH}^-]$ decreases if acid is added and vice versa if base is added but the product of the concentration of the two ions will be same provided temperature is not changed.
 (17) decrease in $[\text{H}^+]$ increases pH by 1; increase in $[\text{H}^+]$ decreases pH by 1.
 (18) no effect as it has buffering action
 (19) In dilute HCl, ionization of water molecules also is significant. Due to water ionization the $[\text{H}^+] = 10^{-7}$. So, total $[\text{H}^+] = 10^{-8}$ (due to the acid) + 10^{-7} (due to water ionizing) = 1.1×10^{-7} . Hence pH will be slightly smaller than 7.

7

Solutions

7.0 INTRODUCTION

We have seen how matter has been classified into pure and mixed substances. A mixed substance consists of two or more pure substances mixed in any proportion by weight. The constituents in the mixture can be separated by physical methods. Mixed substances – also known as mixtures, are of two types: homogeneous mixtures and heterogeneous mixtures. A homogeneous mixture is also called *true solution* while a heterogeneous mixture is classified further into *colloids* and *suspensions*. This chapter deals primarily with *solutions*.

7.1 COMMON TERMS

A mixture has two or more components mixed physically in a random way. Some terms used in the study of mixtures are given below.

Solution: A homogeneous mixture of a substance in another substance.

Solute: The substance that is present in a relatively smaller extent in a solution.

Solvent: The substance that is present in a larger extent in a solution.

Concentration: The amount of solute dissolved in a given quantity of solvent.

Process of dissolution: The solute dissolves in the solvent giving a solution.

7.2 TYPES OF SOLUTIONS

Solutions can be classified in two ways.

- Depending on the amount of solute in the solution
- Depending on the solute particle size in solution.

(a) Based on the amount of solute

Solutions are classified based on solute quantity in solution as follows.

- Dilute solution** is a solution in which the solute quantity is small in a given mass of solvent.

- Concentrated solution** is a solution in which the solute quantity is large in a given mass of solvent.

- Saturated solution** is a solution that cannot dissolve any more solute without changing the temperature.

- Unsaturated solution** is a solution that can dissolve more solute at a given temperature.

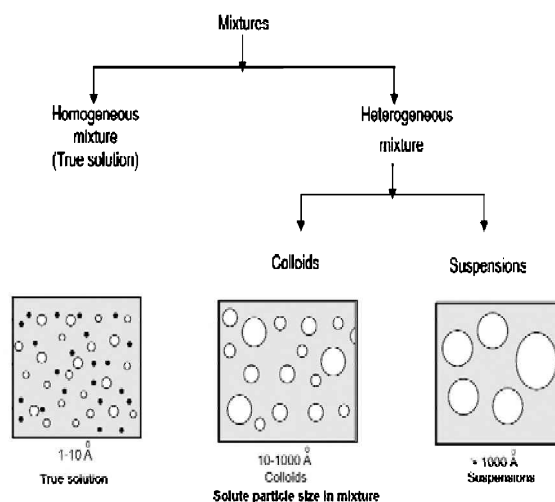
- Supersaturated solution** is a solution that has more solute than a saturated solution at a given temperature.

(b) Based on solute particle size

Mixtures are further classified into homogeneous and heterogeneous mixtures.

- Homogeneous mixtures are also called **True Solutions**. They have at least two constituents. The size of the constituent present to a lesser extent (also called solute) is of the order of $10 \text{ \AA}$ units. Its density is uniform.

- Heterogeneous mixtures also have at least two constituents. But the solute particle size is of the order of $10 - 1000 \text{ \AA}$ units in the case of **Colloids** and greater than $1000 \text{ \AA}$ units in the case of **Suspensions**.



Solute particle size in mixture

7.3 CONCEPT OF DISPERSION SYSTEMS

Dispersion system: Any medium made up of a substance distributed as minute particles (of solid, droplets of liquid or very tiny particles of gas bubbles) through another substance is called *Dispersion system*.

The substance *dispersed* is called the *Dispersed Phase* and the continuous medium around it is called *Dispersed Medium*.

For example in a solution of common salt in water,

Dispersion system is the solution
Dispersed phase is common salt
Dispersed medium is water.

Both the *Dispersed Phase* and *Dispersed Medium* can be in any physical state – solid, liquid or gas.

Example: Air is a mixture of gases in which oxygen is the smaller component and nitrogen the larger component.

- (i) In *true solutions* both *Dispersed Phase* and *Dispersed Medium* are indistinguishable and appear as one. The particle size is $1-10\text{\AA}$
- (ii) In *colloids*, *size of Dispersed Phase* (solute) is $10-1000\text{\AA}$. Two phases exist: *Dispersed Phase* and *Dispersed Medium*. Solute particle size > size of solvent particle.
- (iii) In *suspensions*, *size of Dispersed Phase* > $1000\text{\AA}$. The solute particles precipitate after sometime.

Examples of Dispersion systems:

	Dispersed Phase	Dispersed medium	Name of Colloid	Examples
(1)	Liquid	Gas	<i>Aerosol</i>	fog, mist, cloud.
(2)	Gas	Liquid	<i>Foam</i>	soap, lather, and whipped cream
(3)	Solid	Gas	<i>Aerosol</i>	smoke, dust, fumes
(4)	Gas	Solid	<i>Solid foam</i>	ice cream, rubber
(5)	Liquid	Solid	<i>Gel, Amalgam</i>	butter, boot polish
(6)	Solid	Liquid	<i>Sol</i>	paints, starch solution
(7)	Solid	Solid	<i>Solid sol</i>	coloured glass
(8)	Liquid	Liquid	<i>Emulsion</i>	milk, hair cream
(9)	Gas	Gas	—	air

7.4 PROPERTIES OF TRUE SOLUTIONS

A true solution is a homogeneous mixture and has the following characteristics.

- (a) True solution is a homogeneous mixture.
- (b) True solution is clear and transparent. The solute particles cannot be seen.
- (c) The dispersed phase and dispersed medium are indistinguishable.
- (d) True solution passes through a filter paper.
- (e) Solute can be separated from the solution by physical methods.

7.5 TYPES OF TRUE SOLUTIONS

Depending on the physical state of the solute and solvent there are several types of true solutions.

- (a) *Gaseous solutions* in which both solute and solvent are in gaseous / vapour state.

Example: Air {Oxygen is the dispersed phase and nitrogen is the dispersed medium}

- (b) *Liquid solutions* in which the solvent is a liquid and the solute can be solid, liquid or a gas.

The principle here is '*Likes dissolve likes.*'
Polar solvents dissolve polar solutes and
non-polar solvents dissolve non-polar solutes.

Examples: *Gas in Liquid* – aerated water.

Liquid in liquid – milk and water, water and alcohol.

Solids in liquids – NaCl in water, Naphtha in benzene.

- (c) *Solid solutions* in which both solute and solvent are solids.

Example: Alloys.

7.6 SOLUBILITY

We see in our daily lives that to prepare a sugar syrup or solution, sugar is dissolved in water and heated as more sugar is added.

Different substances dissolve to different extent in water. For example, for a given amount of water the maximum amount of salt that will dissolve will be different from the amount of glucose that will dissolve for the same amount of water. Not only that, the amount of salt or glucose that dissolves in the given amount of water will depend on the temperature. Increase in temperature usually increases the amount of solute that can be dissolved.

Solubility is the weight in grams of the solute that dissolves in 100 gm of a solvent at a given temperature.

Factors affecting solubility

- (i) **Nature of solvent and solute:** If both solute and solvent are polar or both are non-polar, then solubility is more.
- (ii) **Temperature:** As temperature increases, kinetic energy of both solute and solvent increases. Hence as dissolving progresses, the saturated regions disperse quickly to allow more solute to enter the solution.
- (iii) **Pressure:** Pressure has no effect on solubility of a solid in a liquid. But the solubility of a gas increases in a liquid if pressure is increased. Example, more CO_2 dissolves in water under high pressure.

The *rate of dissolving of a solute in a solvent* depends on :

- (i) **Size of particles:** *smaller the particle size more the rate of dissolution.*
- (ii) **Agitation:** *agitation increases the rate of dissolution* as it helps in dispersing the saturated regions to make way for unsaturated regions, and
- (iii) **Temperature:** *temperature in general increases the rate of dissolution* as kinetic energy of the particles increases.

7.7 SATURATED, UNSATURATED, SUPER-SATURATED SOLUTIONS

An *unsaturated solution* is a solution which **can**

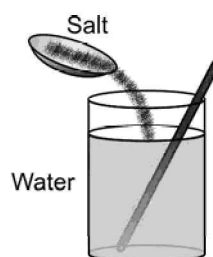
dissolve more solute at a given temperature.

A *saturated solution* is a solution which **cannot dissolve** any more solute at a given temperature.

A *supersaturated solution* is a solution which *has more solute than the solubility at the given temperature.*

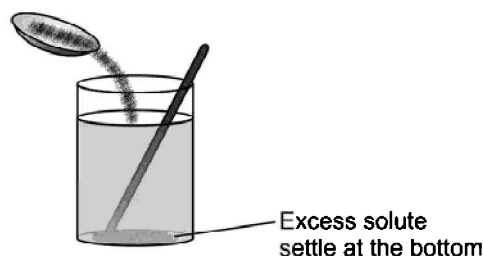
Preparing saturated solution

Take 100 ml of water in a beaker and add KNO_3 salt to it, while constantly stirring with a glass rod. Continue adding the salt till no further salt can be dissolved. Using a filter paper and funnel, filter the excess salt. The solution that forms is a saturated solution of KNO_3 at the given temperature.



An unsaturated solution

More of the solute can dissolve in the solvent at the given temperature.

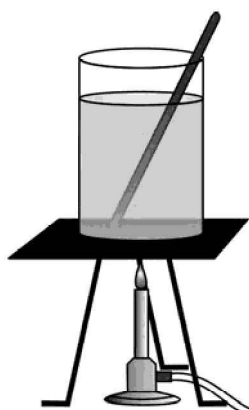


A saturated solution

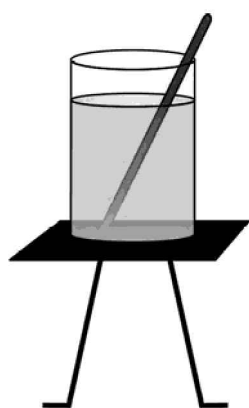
More solute cannot be dissolved at the given temperature.

Preparing supersaturated solution

Prepare 100 ml of a saturated solution of KNO_3 in pure water. Heat it slowly to around 70°C . Slowly add minute quantities of KNO_3 salt constantly stirring with a glass rod. Continue adding the salt till no further salt can be dissolved. Remove the burner to stop the heating. Allow the solution to cool without disturbing it any way. Even at room temperature the excess solute *that was added while heating to 70°C* remains in solution. The solution that forms is a supersaturated solution of KNO_3 at room temperature.



The solution is slowly heated to 70 °C, adding little quantities of the salt till no further salt dissolves.



Heating is stopped and the solution allowed to cool to room temperature without disturbing it in any way. remains in solution even though the amount is in excess of the solubility at room temperature. This solution is called supersaturated solution.

Converting saturated solution to unsaturated solution

A saturated solution can be made unsaturated in two ways:

- (i) by adding more solvent
- (ii) by changing the temperature.

Example: A saturated solution of 100 ml of KNO_3 can be made unsaturated by adding more water or by heating. In either case, the solution becomes unsaturated and can dissolve more of the salt.

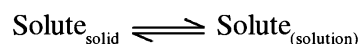
Differentiating concentrated and saturated solution

A concentrated solution is a solution in which the amount of solute is high in relation to the solvent when compared to a dilute solution. All concentrated solutions however need not be saturated solutions.

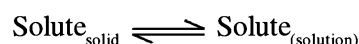
Example: Concentrated sulphuric acid has little water and more pure acid than dilute sulphuric acid.

7.8 EQUILIBRIUM IN SATURATED SOLUTION

In saturated solutions, equilibrium exists between solute particles entering the solution and those leaving the solution:



In a supersaturated solution, an unstable or metastable equilibrium exists.



The broken arrow indicates that a slight disturbance will cause the equilibrium to shift backwards causing the excess solute to come out of the solution. The disturbance can be caused by agitation or putting a single grain of solute called *seed* or scratching the sides of the container with a rod or adding some impurity. Supersaturated solutions cause rapid crystallization of excess solute when disturbed.

Crystals of many substances can be formed by first preparing supersaturated solutions and then, causing a disturbance in them when the excess solute crystallizes out.

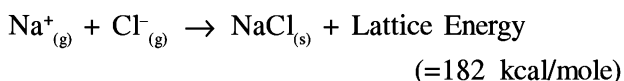
7.9 ENERGY CHANGES DURING DISSOLUTION

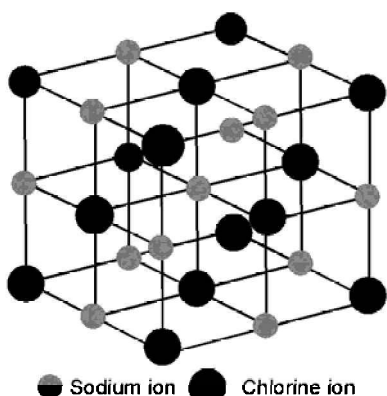
Is dissolution an exothermic or endothermic process? Whether a solute dissolves in a solvent with the release of energy or absorption of energy depends on two factors.

- (i) *Lattice Energy*
 - (ii) *Heat of Hydration.*
- (i) **Lattice Energy (LE)** is the energy released when the crystal lattice of one mole of an ionic compounds is formed.

Conversely, energy equal to *lattice energy* will have to be supplied in the form of heat energy to break lattice network of ions of one mole of the ionic compound. The later process is *endothermic*.

Example:



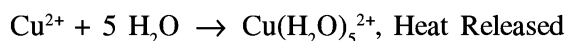


When one mole of sodium ions combine with one mole of chlorine ions, one mole of sodium chloride is formed and the energy released is 182 kcal.

To break the lattice network of ions in one mole of sodium chloride 182 kcal of energy will have to be supplied in the form of heat energy.

- (ii) **Hydration Energy (HE)** is the amount of heat released when water molecules hydrate the ions. *This process is exothermic.*

Example : When CuSO_4 dissolves in water it dissociates into copper ions and sulphate ions. Each copper ion is surrounded by 5 water molecules.



- (a) If lattice energy is greater than hydration energy, then there is a net absorption of energy and solution formed is cooler.

If $\text{LE} > \text{HE}$ dissolution is endothermic.

Examples: Substances which dissolve endothermically: KNO_3 , NaNO_3 , CuSO_4 , NH_4Cl , sugar.

- (b) If lattice energy is smaller than hydration energy, then there is a release of energy and solution formed is warmer.

If $\text{LE} < \text{HE}$ dissolution is exothermic.

Examples: Substances which dissolve exothermically: $\text{Ca}(\text{OH})_2$, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, CaSO_4

- (c) If lattice energy is equal to hydration energy then there is neither absorption nor release of energy.

If, $\text{LE} = \text{HE}$ dissolution is neither exothermic nor endothermic

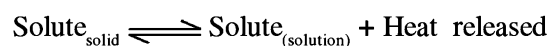
Examples: NaCl $\text{LE} = 184 \text{kcal/mole}$
 $\text{HE} = 182.8 \text{kcal/mol.}$

$\therefore \text{LE}$ is almost equal to HE .

Dissolution of NaCl in water is neither an endothermic nor an exothermic process.

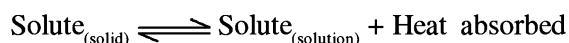
7.10 EFFECT OF TEMPERATURE ON SOLUBILITY

- (1) If *dissolution is an exothermic process in the forward direction*, then, the equilibrium will shift backwards, if temperature is increased. Hence solubility will decrease if temperature is increased.



If dissolution is exothermic then solubility will decrease if temperature is increased and vice-versa.

- (2) If *dissolution is an endothermic process in the forward direction*, then, the equilibrium will shift forward, if temperature is increased. Hence solubility will increase if temperature is increased.



If dissolution is endothermic then solubility will increase if temperature is increased and vice-versa.

- (3) If, however, dissolution is neither endothermic nor exothermic, then, the solubility will not change whether temperature is increased or decreased.

- (4) **Solubility of gases:** Solubility of gases in water *decreases* with increase in temperature.

7.11 SOLUBILITY GRAPHS

Applications of solubility graphs

Solubility graphs are used extensively in predicting the solubility of a substance at a specific temperature, forming supersaturated solutions for crystallization, etc.

- (i) A steep curve indicates rapid rise in solubility with increase in temperature.

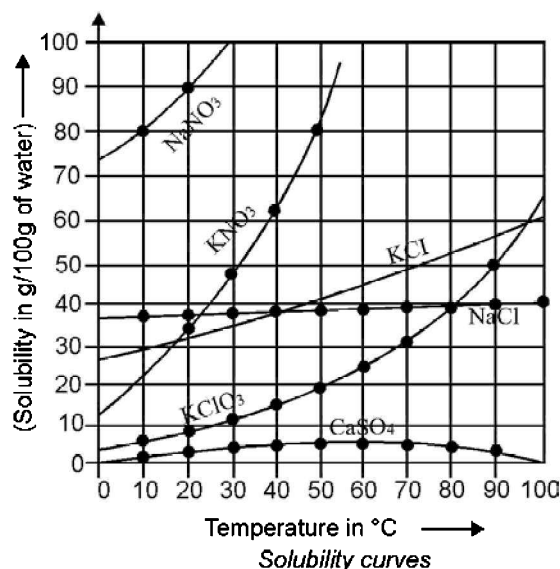
Example: KNO_3

- (ii) A flat curve indicates either a gradual or no increase in solubility with increase in temperature.

Example: LiCl , NaCl and KCl

With change in temperature, the solubility of a salt also changes. The change in solubility with temperature when plotted on a graph gives the *solubility curve* of the salt. The solubility curves of

some salts are given below.



Applications of solubility graphs

Solubility graphs are used extensively in predicting the solubility of a substance at a specific temperature, forming supersaturated solutions for crystallization, etc.

- (i) A steep curve indicates rapid rise in solubility with increase in temperature.

Example: KNO_3

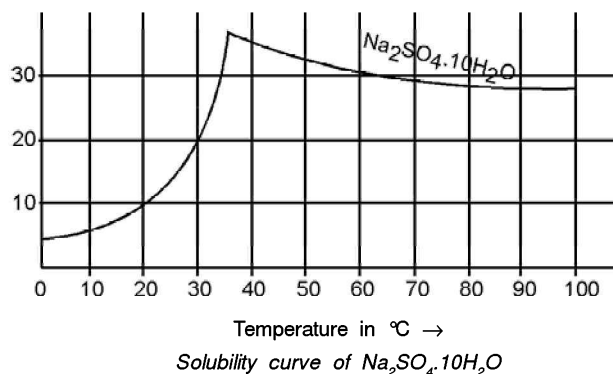
- (ii) A flat curve indicates either a gradual or no increase in solubility with increase in temperature.

Example: LiCl , NaCl and KCl

Transition temperature

A curve that first rises and then falls indicates solubility increases up to a certain temperature known as *Transition temperature* and then solubility decreases.

Example: For Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) the *transition temperature* is 32.5°C .



7.12 EXPRESSING CONCENTRATION

There are nine methods of expressing concentration.

1. Weight fraction

Wt. fraction of solute = the ratio of weight of solute to weight of solution

$$= \frac{\text{Wt. of solute}}{\text{Wt. of solution}}$$

Wt. fraction of solvent = the ratio of weight of solvent to weight of solution

$$= \frac{\text{Wt. of solvent}}{\text{Wt. of solution}}$$

2. Weight %

Wt. % of solute = the ratio of weight of solute to weight of solution expressed as a percentage

$$= \frac{\text{Wt. of solute}}{\text{Wt. of solution}} \times 100$$

Wt. % of solvent = the ratio of weight of solvent to weight of solution expressed as a percentage

$$= \frac{\text{Wt. of solvent}}{\text{Wt. of solution}} \times 100$$

3. Volume fraction

Vol. fraction of solute = the ratio of volume of solute to volume of solution

$$= \frac{\text{Vol. of solute}}{\text{Vol. of solution}}$$

Vol. fraction of solvent = the ratio of volume of solvent to volume of solution

$$= \frac{\text{Vol. of solvent}}{\text{Vol. of solution}}$$

4. Volume %

Vol. % of solute = the ratio of volume of solute to volume of solution expressed as a percentage

$$= \frac{\text{Vol. of solute}}{\text{Vol. of solution}} \times 100$$

Vol. % of solvent = the ratio of volume of solvent to volume of solution expressed as a percentage

$$= \frac{\text{Vol. of solvent}}{\text{Vol. of solution}} \times 100$$

Practice Problems on Weight and Volume fractions and percentages

- 150 ml of an aqueous solution contains 8 g NaCl. If density of solution is 1.28 g/ml, calculate wt fraction and wt% of solute. (Hint: use formula)
- Find the weights of the solute and solvent required to prepare 250g of 25% glucose solution.
- Dissolving 'X' in alcohol forms a solution. The volume % of 'X' is 20. If volume of solution is 250ml, calculate volume of alcohol and solute 'X'.
- 12 g of solute is dissolved in 200 ml of solvent. The density of the solvent is 0.895 g/ml. Express concentration in wt%.
- An aqueous solution of glucose has strength of 10%. Find the volume in which 1 g mole of it is dissolved?

- 5. Mole Fraction:** If a, b, c are three constituents in a solution
The number of moles, n of each constituent can be calculated.

For constituent, a : $n_a = \frac{m_a}{M_a}$, where m_a is its weight and M_a is its gram molecular weight.

$$\text{Mole Fraction of a} = \frac{n_a}{n_a + n_b + n_c}$$

$$\text{Mole Fraction of b} = \frac{n_b}{n_a + n_b + n_c}$$

$$\text{Mole Fraction of c} = \frac{n_c}{n_a + n_b + n_c}$$

Sum of Mole Fractions

$$= \frac{n_a}{n_a + n_b + n_c} + \frac{n_b}{n_a + n_b + n_c} + \frac{n_c}{n_a + n_b + n_c} = \frac{n_a + n_b + n_c}{n_a + n_b + n_c} = 1$$

Practice problems on Mole Fraction

- A solution of glucose is prepared by dissolving 18g of it in 200ml of water. Calculate mole fraction of glucose. (Hint: Assume density 1gm/ml).
- A gaseous mixture contains 4g of Hydrogen, 16g Oxygen and 7g Nitrogen. Calculate mole fractions of each gas.
- A gaseous mixture contains 4g of CO_2 and 4g of CH_4 . Calculate mole fraction of each gas.

- 6. Molarity (M)** is the number of moles of the solute per litre of the solution.

$$\text{M, Molarity,} = \frac{\text{no. of moles}}{\text{volume in litre}},$$

$$= \frac{m / M}{V}, \text{ where, m is wt. of solute in grams, GMW is gram mol. wt.}$$

Solved Example

What is the molarity of pure water?

Ans: Assuming the density of water to be 1g/cc, 1000g of water will occupy 1 l

$$\begin{aligned} \text{Number of moles in 1000g} \\ = 1000/18 = 55.56 \text{ moles} \end{aligned}$$

$$\begin{aligned} \text{Molarity of water} &= \text{Number of moles per litre} \\ &= 55.56 \text{ moles/l} = 55.56 \text{ M} \end{aligned}$$

- 7. Normality (N)** is the number of gram equivalents of the solute per litre of the

solution = $\frac{m/E}{V}$, where, m is wt. of solute in g, E is Gm. Eq. Wt.

$$\text{Normality, N} = \frac{\text{no. of gm. equivalents}}{\text{volume in litre}},$$

Calculating gram equivalents

Equivalent weight of any substance is the num-

ber of grams that combines with 8 grams of oxygen or 35.5 grams of chlorine.

Gram Equivalent Weight is the equivalent weight expressed in grams.

(i) Equivalent weight of Acid

$$E_{\text{Acid}} = \frac{\text{Formula weight of acid}}{\text{Basicity}}$$

(Number of replaceable hydrogen in the acid is called *basicity*).

Example: Equivalent weight of sulphuric

$$\text{acid} = \frac{M}{2} = \frac{98}{2} = 49$$

(ii) **Equivalent weight of Base**

$$E_{\text{Base}} = \frac{\text{Formula weight of Base}}{\text{Acidity of Base}}$$

(Number of replaceable hydroxyl groups of base is called *acidity*).

Example: Equivalent weight of calcium

$$\text{hydroxide} = \frac{M}{2} = \frac{74}{2} = 37$$

(iii) **Equivalent weight of salt**

$$E_{\text{Salt}} = \frac{\text{Formula weight of the Salt}}{\text{Total charge of the cation or anion of the salt}}$$

Example: Equivalent weight of sodium carbonate salt

$$= \frac{\text{Formula weight of the Salt}}{\text{Total charge of the cation or anion of the salt}} = 53$$

Practice problems for finding Equivalent Weight

- Calculate equivalent weights of the following elements. The atomic weights are given in brackets: Zn (65), Na (23), Ca (40), Al (27), O (16), and S (32).
- Find equivalent weights of following acids / bases / salts: H_2SO_4 , HCl , HNO_3 , $(\text{COOH})_2$, CH_3COOH , H_3PO_4 , NaOH , $\text{Ca}(\text{OH})_2$, $\text{Al}(\text{OH})_3$. The atomic weights of the elements are Na=23, C=12, O=16, H=1, S=32, Cl=35.5, N=14, P=31)

(8) **Formality** is the number of formula weights per litre of the solution. It is used for ionic compounds that have empirical formula rather than **molecular formula**.

(9) **Molality (m)** is the number of moles of solute per kilogram of the solvent.

$$\text{Molality, } m = \frac{\text{wt. of solute} \times 1000}{\text{wt. of solvent} \times \text{Gm. mol. wt. of solute}}$$

Concentration and temperature

Of the nine methods of expressing concentration

Weight fraction, wt %, mole fraction, Molality are independent of temperature as they are related to the mass and not volume of the substance.

Relationship between Normality and Molarity

Normality of a base = acidity $\times$ Molarity i.e.,
 $(N_{\text{Base}} = \text{acidity} \times M)$

Normality of an acid = basicity $\times$ Molarity i.e.,
 $(N_{\text{Acid}} = \text{basicity} \times M)$

Dilution Law

When a concentrated solution of volume, V_1 and Normality N_1 is diluted to a volume V_2 , then the normality is decreased to N_2 .

$$\therefore V_1 N_1 = V_2 N_2 \text{ -- this is called the Dilution Law.}$$

For Molarity, the relationship is $V_1 M_1 = V_2 M_2$

These formulae are used to calculate change in concentration on dilution.

Solved example

How much water is to be added to 10 ml of 10N HCl to make it exactly decinormal?

$$N_1 V_1 = N_2 V_2$$

$$10 \times 10 = 0.1 \times V_2$$

$$V_2 = 1000 \text{ ml}$$

$$\therefore \text{the amount of water to be added} = V_2 - V_1 \\ = 1000 - 10 = 990 \text{ ml.}$$

7.13 STANDARD SOLUTIONS

A standard solution is a solution whose concentration is known for a given temperature.

Preparation of 100ml of 0.1M NaOH

1st step : **Calculate the weight of solute required**

Since a 0.1 M NaOH has 0.1 mole per litre, 100 ml of the solution will have 0.01 mole of NaOH.

Since the weight of 1 mole of NaOH is 40g (its Gm. Mol. Wt.),

$$0.01 \text{ moles of NaOH will weigh } 0.01 \times 40 \text{ g} = 0.4 \text{ gm.}$$

2nd step : **Preparing the standard solution**

Weigh 0.4g of dry NaOH.

Put it in a standard conical flask of 100 ml volume. (Transfer the NaOH weighed carefully into the flask making sure nothing is left sticking to the

container.) Add a little water and stir till it dissolves. Make up the solution to the mark on the flask (100 ml). The resulting solution is 100 ml solution of 0.1M NaOH.

7.14 SOME IMPORTANT POINTS TO REMEMBER

- (i) When compared to molarity, molality is *temperature independent* as mass does not change with temperature; volume however changes. So, molality is a more accurate way for expressing concentration. In fact *when expressing molarity, the temperature should also be mentioned, as molarity changes with change in temperature.*
- (ii) *Standard solutions* are solutions whose concentration is known accurately. Standard flasks in sizes of 100 ml, 250 ml, 500 ml, 1l, etc are available in the laboratory. While taking the reading of volume the *lower meniscus* is taken.
- (iii) **Normality = acidity × Molarity** (or basicity × Molarity)
- (iv) In particular, *Formula weight* and *Formality* are used for expressing concentrations of some covalent and ionic compounds. Some covalent substances exist as macromolecules and ionic substances have empirical formula and exist as ions in solution. *Formula weight is the number of formula weights of the solute present in 1l of the solution.*

Example: A 1F solution of NaCl contains 58.5 g of NaCl in 1 l of solution.

- (v) The concept of equivalent weight is important, as

‘One equivalent of any substance will always react with one equivalent of another substance’.

Example: Equivalent weight of H_2SO_4

$$= \frac{\text{Formula weight of acid}}{\text{Basicity}} = \frac{98}{2} = 49$$

Equivalent weight of NaOH

$$= \frac{\text{Formula weight of Base}}{\text{Acidity of Base}} = \frac{40}{1} = 40$$

The balanced equation of the reaction is
 $\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$

As per balanced equation, 98 g H_2SO_4 reacts with 80 g of NaOH

Or 49 g of H_2SO_4 reacts with 40 g of NaOH

In other words, one equivalent weight of H_2SO_4 (49 g) reacts with one equivalent weight of NaOH (40 g).

- (vi) 1 equivalent = equivalent weight of substance = 1000 millequivalents.
- (vii) According to the law of normality $N_1V_1 = N_2V_2 = N_3V_3$...also, $M_1V_1 = M_2V_2$
- (viii) Mole fraction has no units, as it is a ratio. It is independent of temperature (It is an indirect measurement of wt.).
- (ix) At the boiling point of a liquid, its vapour pressure will be equal to the atmospheric pressure.

7.15 SUMMARY

- * A homogeneous mixture containing two or more substances is called a solution.
- * The component which is relatively less in quantity is called solute and the one which is comparatively large in quantity is called solvent.
- * Solute + Solvent = Solution.
- * In an aqueous solution, the solvent is water.
- * “Solubility” is defined as the maximum amount of the solute dissolved in 100 g of solvent at constant temperature.
- * Solutions are divided into (i) unsaturated (ii) saturated and (iii) supersaturated solutions based on the solubility of the solute.
- * Super saturated solutions are unstable.
- * Solubility of a substance depends on (i) the nature of solvent and solute and (ii) on temperature.
- * Concentration is defined as the amount of solute present in unit volume of solution.
- * Concentration can be expressed as (i) w% (ii) V% (iii) Molarity and (iv) Mole fraction.
- * W%, V% and Mole fraction have no units
- * The units of molarity are mol lit^{-1}
- * Molarity depends on temperature.
- * Mole fraction is independent of temperature.

$$* \text{w\%} = \frac{\text{wt. of solute}}{\text{wt. of solution}} \times 100$$

$$* V\% = \frac{\text{Vol. of solute}}{\text{vol. of solution}} \times 100$$

$$* \text{Molarity} = \frac{n}{V} \quad (V \text{ in litres})$$

* Molarity

$$= \frac{\text{wt. of solute}}{\text{gm.mol.wt. of solute}} \times \frac{l}{\text{wt of solvent}}$$

* Mole fraction

$$= \frac{\text{no. of moles of a given component}}{\text{total no. of moles of all components}}$$

* Standard solution is prepared in standard flasks.

* Some substances such as NaCl, NaNO₃, Na₂SO₄, KCl, KNO₃, FeCl₃, BaCl₂, etc., that dissolve in water dissociate completely into ions. These substances are known as “strong electrolytes”. They let current pass through their solutions.

* Some substances like CH₃COOH, NH₄OH, etc., when dissolved in water dissociate incompletely. They are called “weak electrolytes”.

* The extent of dissociation increases with increase in temperature and dilution.

* Some other substances such as sucrose, glucose, urea, etc., when dissolved in water do not dissociate. They are called “non-electrolytes”. They do not allow current to pass through their solutions.

EXERCISE

I. Choose the correct answer

- If air is taken as a binary solution, the solvent is
 - Nitrogen
 - Oxygen
 - Carbon dioxide
 - Hydrogen
- Homogeneous system among the following is
 - milk
 - sand in water
 - urea in water
 - benzene in water
- The characteristic property of solution is
 - formation of solution is a physical change
 - solute and solvent in the solution can be separated by filtration
 - solute and solvent in the solution can be separated by decantation
 - solution can be represented with a chemical formula
- The units of molarity are
 - g lit⁻¹
 - moles lit⁻¹
 - equivalents lit⁻¹
 - moles kg⁻¹
- To halve the molarity of a solution the following should be adopted
 - weight of the solute to be doubled
 - weight of the solvent to be doubled
 - volume of the solvent to be doubled
 - volume of the solution to be doubled
- The units of normality are
 - moles lit⁻¹
 - moles kg⁻¹
 - equivalents lit⁻¹
 - equivalents kg⁻¹
- Which of the following acid has the same molecular weight and equivalent weight?
 - H₂PO₂
 - H₃PO₃
 - H₃PO₄
 - H₂SO₄
- The number of glucose molecules present in 10 ml of decimolar solution is
 - 6.0×10^{20}
 - 6.0×10^{19}
 - 6.0×10^{23}
 - 6.0×10^{22}
- The volumes of 1M HCl and 5M HCl to be mixed to get 2 lit of 2M HCl are
 - 1 lit and 1 lit
 - 1.5 lit and 0.5 lit
 - 1.25 lit and 0.75 lit
 - 1.33 lit and 0.66 lit
- The concentration of a 100 ml solution containing ‘x’ grams of Na₂CO₃ is y M. The values of x and y are
 - 2.12, 0.05
 - 1.06, 0.2
 - 1.06, 0.1
 - 2.12, 0.1
- Which of the following solution is more concentrated?
 - 0.3% H₃PO₄
 - 0.3M H₃PO₄
 - 0.3m H₃PO₄
 - 0.3N H₃PO₄
- If 6 g urea (NH₂CONH₂) is dissolved in 90 g of water, the mole fraction of solute is
 - 1/5
 - 1/50
 - 1/51
 - 1/501
- A gaseous mixture contains four gases A, B, C and D. The mole fraction of gas B is 0.5. The mole fraction of gas A is
 - 0.525
 - 0.375
 - 0.625
 - 0.732
- Aqueous NaOH solution is labelled as 10% by weight. Mole fraction of the solute in it is
 - 0.05
 - 0.0476
 - 0.052
 - 0.52
- The mole percentage of oxygen in a mixture of 7 gm of nitrogen and 8 gm of oxygen is
 - 8
 - 16
 - 21
 - 50
- 100 milli moles of a solute is present in 200 ml of the solution. Then its molarity is
 - 2M
 - 1M
 - 0.5M
 - 1.5M
- 0.5 moles of a solute is present in 500 ml of the solution. Then its Molarity is
 - 1M
 - 10^{-3} M
 - 10^{-2} M
 - 10^{-1} M

18. The number of milli moles of solute present in 10 ml of decimolar solution is
(a) 1 (b) 10^{-3} (c) 10^{-2} (d) 10^{-1}
19. The number of moles of solute present in 0.5 dm^3 of 0.5M solution is
(a) 0.5 (b) 5×10^{-3} (c) 5×10^{-2} (d) 0.25
20. The weight of AgNO_3 (Mol. Wt. 170) present in 100 ml of its 0.25 M solution is
(a) 4.25 g (b) 42.5 g (c) 8.5 g (d) 2.125 g
21. 5 milli moles of solute present in how many litres of the solution will have 0.1 M
(a) 5 (b) 0.5 (c) 50 (d) 0.05
22. The volume of water to be added to convert 10 ml of decimolar HCl solution to decimolar solution is
(a) ml (b) 100 ml (c) 1000 ml (d) 990 ml
23. The molarity of water is
(a) 18 (b) 55.55 (c) 10 (d) 0.01
24. 10 milli equivalents of solute is present in 5 ml of an aqueous solution. Then its Normality is
(a) 1 N (b) 0.5 N (c) 2 N (d) 0.25 N
25. The number of equivalents of HCl in 200 ml of 0.1 N HCl solution is
(a) 2 (b) 0.2 (c) 0.02 (d) 20
26. The volume of 0.05N Na_2CO_3 solution required to neutralize 200ml of 0.02M H_2SO_4 solution is
(a) 80 ml (b) 140 ml (c) 160 ml (d) 240 ml
27. A sample of NaOH weighing 0.4 g, is added to 100 ml of 0.1N H_2SO_4 solution. The nature of the resulting solution is
(a) acidic (b) basic
(c) neutral (d) amphoteric
28. In a nearly saturated solution the solubility increases with increase in temperature. Then H sol. is
(a) + ve (b) - ve
(c) + ve (or) - ve (d) 0

II. Give one word answer

- The number of gram equivalents in one litre of solution.
- Equilibrium present in a supersaturated solution
- A solution whose concentration at a given temperature is known
- Relationship between normality and molarity of a monoacidic base or a monobasic acid

III. Match the following.

1. List – I

- | | |
|------------------------|---------------------------------|
| (A) Gaseous solution | (i) German silver |
| (B) Liquid solution | (ii) Milk |
| (C) Solid solution | (iii) Sand in water |
| (D) Colloidal solution | (iv) Aqueous Alcoholic solution |
| | (v) Air |

List – II

Correct match is

- | | 1 | 2 | 3 | 4 |
|-----|------|-------|------|------|
| (a) | (v) | (iv) | (i) | (ii) |
| (b) | (i) | (iii) | (ii) | (v) |
| (c) | (iv) | (ii) | (v) | (i) |
| (d) | (ii) | (iii) | (i) | (iv) |

2. List – I

- (A) Mole fraction
(B) Molarity
(C) Normality
(D) Molality

List – II

- (i) Number of gm. equivalents in 1000 ml of solution
(ii) Always less than one
(iii) Greater than or equal to molarity
(iv) No. of g moles present in 100ml solution
(v) No. of g moles of solute 1 kg of solvent

The correct Match is

- | | A | B | C | D |
|-----|------|-------|-------|-------|
| (a) | (i) | (ii) | (iii) | (iv) |
| (b) | (ii) | (iii) | (i) | (v) |
| (c) | (i) | (iv) | (ii) | (iii) |
| (d) | (ii) | (iv) | (iii) | (v) |

3. List – I

- (A) 0.5M H_2SO_4 solution
(B) 0.1M NaCl solution
(C) 0.2M AlCl_3 solution
(D) 0.5M H_3PO_4 solution

List – II

- (i) 0.1N solution
(ii) 1N solution
(iii) 1.5N solution
(iv) 2.0 N solution
(v) 0.6N solution

The correct Match is

- | | A | B | C | D |
|-----|------|------|------|-------|
| (a) | (ii) | (v) | (i) | (iii) |
| (b) | (iv) | (ii) | (i) | (v) |
| (c) | (ii) | (i) | (v) | (iii) |
| (d) | (v) | (iv) | (ii) | (i) |

4. Which of the following solutions is more concentrated in each pair?

I: 0.5 M KCl or 0.5 wt% in water

II: 1.75 M glucose or 1.75 m glucose in water

1

- (a) 0.5 M KCl
(b) 0.5 wt% KCl
(c) 0.5 M KCl
(d) 0.5 wt% KCl

II

- 1.75 M glucose
1.75 M glucose
1.75 m glucose
1.75 m glucose

IV. State whether the following statements are True or False

- Molality of a solution changes with temperature.
- Molarity of a solution changes with temperature.
- Normality of a solution does not change with temperature.

- (iv) Mole fraction of a solute in a solution changes with temperature.
- (v) Volume fraction of a solute in a solution changes with temperature.

V. Find the odd one out

- (i) wt%, normality, formality, volume %, volume fraction
- (ii) saturated solution, unsaturated solution, super-saturated solution
- (iii) 1N NaOH, 1M NaOH, 1m NaOH, 1F NaOH

VI. Fill in the blanks

- (i) A saturated solution _____ a concentrated solution.
- (ii) One-fourth litre of 1M NaOH has _____ gm of the salt dissolved in it.
- (iii) A supersaturated solution is unstable in the _____ direction.
- (iv) If dissolution is exothermic solubility _____ with increase in temperature.
- (v) In an aerosol, the dispersed *phase* is in _____ state and the dispersed *medium* is in _____ state.

VII. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, Statement R is true; Statement R is correct explanation for statement A

Choose B if Statement A is true, statement R is true; Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D if Statement A is false, statement R is true

- (1) **Statement A:** Any part of the solution has identical chemical and physical properties.
Statement R: Solution is always a homogeneous mixture.
- (2) **Statement A:** Molarity of a solution decreases with an increase of temperature.
Statement R: As temperature increases volumes of the solution increases
- (3) **Statement A:** Molarity of an aqueous solution at 0°C is less than the molarity of the same solution at 4°C.
Statement R: Molarity increases with an increase of temperature.
- (4) **Statement A:** Molality is independent of temperature
Statement R: There is no volume factor in the expression of molality.
- (5) **Statement A:** One molar aqueous solution is

always more concentrated than one molal aqueous solution.

Statement R: The amount of solvent in 1M solution is less than in 1m solution.

- (6) **Statement A:** Mole fraction has no units.

Statement R: Mole fraction is a ratio of number of solvent.

- (7) **Statement A:** Pressure does not have significant effect on solubility of solids in liquids.

Statement R: Solids and liquids are highly incompressible.

- (8) **Statement A:** Aquatic species are more comfortable in cold water rather than in warm water.

Statement R: The solubility of O₂ gas, increases with decrease of temperature.

VIII. Solve the following problems

1. Find the weight of KNO₃ present in 100 ml of 0.125 M solution. (Hint: Use Molarity formula)
2. Find the molarity of a solution containing 171 gms of sugar (C₁₂H₂₂O₁₁) in 4l of it.
3. Concentrated HCl contains 36.5% of HCl by weight. Its density is 1.1854 gm/ml. What is its molarity? (Hint: Take 1l (1000 ml) of conc. HCl. The wt. of the conc. HCl is 1185.4 g. Given 36.5 % of this is weight of pure HCl. Use Molarity formula to find molarity.)
4. Prepare a 100ml standard solution of 0.1M Na₂CO₃. (See Q. No. 5 in solved examples)
5. 2.65gm of Na₂CO₃ is preset in 250ml of its solution. Calculate the molarity of the solution. (Na=23, C=12, O=16) (Hint: Use formula)
6. Calculate the amount of oxalic acid (H₂C₂O₄·2H₂O) in 500 ml of 0.2 M solution. (C=12, O=16, H=1) (Hint: Use formula and use ratio of water of crystallization to calculate wt. of water)
7. Calculate the number of moles of NaOH present in 750ml of 0.4M solution. (Hint: Use formula)
8. How much of solute in each case is required to prepare 250ml of 0.01M solution of NaOH, Na₂CO₃, and H₂SO₄? (Hint: Use formula)
9. How many litres of water are to be added to 2l of 5M H₂SO₄ to make it 0.75 M solution? (Hint: Use $M_1V_1 = M_2V_2$, volume of water to be added is $V_2 - V_1$)]
10. 20ml of 8M HCl is added to 25ml of 12M HCl and made up to 1l with water. Calculate molarity of resultant solution? (Hint: Find number of moles in 20ml of 8M and also in 25ml of 12M. Add the two and divide by molecular weight to get number of moles in 1l molarity.)
11. Find the volume of 4N H₂SO₄ required to prepare 400 ml of 0.12N H₂SO₄. (Hint: $N_1V_1 = N_2V_2$)

12. Concentrated HCl contains 36.5 % HCl by weight. Find its molality. (Hint: Density of water is 1000g/l. Use formula for Molality. Compare your answer with the answer of Q. No. 3)
 13. If 100ml of 1N HCl is added to 500ml of 2M HCl. Calculate molarity and normality of the resultant solution. (Hint: Normality = Molarity for HCl. Find g equivalents of both HCl and NaOH. Find which is in excess and by how much? This value gives the number of g eq. of the excess compound which is now present in (100 + 500) ml. Find Normality and Molarity using the formula.)
 14. 1l of 0.1 M Ca(OH)_2 is added to 250ml 0.01 N Ca(OH)_2 . Calculate molarity and normality of resultant solution. (Hint: Use same method as given above)
 15. 2 moles of H_2SO_4 are dissolved in 250 ml. What is the molarity of H^+ ions in the solution? (Hint: The molarity of H_2SO_4 is the Molarity of H^+ ions as H_2SO_4 is a strong acid and is completely dissociated)
 16. 10 moles of NaOH are dissolved in 1l. Now the solution is divided in to 2 unequal parts. What is the molarity of each part? (Hint: Each part now contains proportional number of moles.)
 17. How many milli moles are present in 500 ml of 0.2 M Na_2CO_3 ? (Hint: 10^3 milli moles = 1 mole)
 18. How many milli equivalents are present in 100 ml of N/10 phosphoric acid?
 19. What is the normality of 2M sulphuric acid?
 20. What volume of 0.1M H_2SO_4 will exactly neutralize 25ml of 0.2M NaOH?
 21. What is the volume of 0.8M solution containing 0.1 mole of the solute?
 22. Calculate the number of SO_4^{2-} ions in 100 ml of 10^{-3} M H_2SO_4 .
- IX. Answer the following questions.**
- (1) What is a mixture?
 - (2) Differentiate between a saturated solution and concentrated solution.
 - (3) Differentiate between a homogeneous and heterogeneous mixture.
 - (4) How is a supersaturated solution prepared?
 - (5) In which mode of expressing the concentration is independent of temperature?
 - (6) What are the most favourable conditions for higher solubility of a gas in a liquid?
 - (7) What will be the Molarity in terms of Normality of a tribasic acid?
 - (8) What is the value of the sum of all mole fractions in a solution?
 - (9) If the vapour pressure of a liquid is equal to the atmospheric pressure, what is the temperature of the liquid called?
 - (10) What will be the effect of increasing the temperature of an aqueous solution?
 - (11) What is an amalgam?
 - (12) Which out of the following has no units: Molarity, Molality, Normality and Mole fraction?

KEY TO EXERCISE

I.	1. a	2. c	3. b	4. b	5. d	6. c	7. a	8. a
	9. b	10. c	11. b	12. c	13. b	14. b	15. d	16. c
	17. a	18. a	19. d	20. a	21. d	22. d	23. b	24. c
	25. c	26. c	27. c	28. a				
II.	(i) Normality	(ii) metastable equilibrium	(iii) Standard solution	(iv) both are equal				
III.	(1) a	(2) d	(3) c	(4) a				
IV.	(i) false	(ii) true	(iii) false	(iv) true	(v) true			
V.	(i) wt%	(ii) unsaturated solution	(iii) 1m NaOH					
VI.	(i) need not be	(ii) 10gm	(iii) backward	(iv) decreases	(v) liquid, gas			
VII.	(1) A	(2) A	(3) C	(4) A	(5) A	(6) C	(7) A	(8) A
VIII.	(1) 1.16g	(2) 0.125M	(3) 11.85M	(4) 1.06 g of given salt in 100 ml of water				
	(5) 0.1M	(6) 12.6g	(7) 0.3moles	(8) 0.1g, 0.265g, 0.245g				
	(9) 11.33l	(10) 0.46M	(11) 12 ml	(12) 15.75 Molal				
	(13) 1.83N, 1.83M	(14) 0.162N, 0.081M	(15) 8M					
	(16) same as undivided solution	(17) 100 millimoles	(18) 10 milli equivalents					
	(19) 4N	(20) 5ml	(21) 125ml	(22) 6.02×10^{19}				

8

Electrolysis

8.0 INTRODUCTION

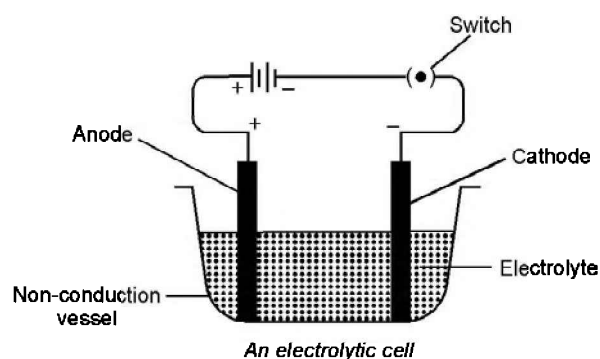
The word *Electrolysis* is made of two words, *electro* (meaning flow of electrons or electricity) and *lysis* (meaning breaking apart). Electrolysis is concerned with bringing a chemical change by using electric current. Conductors have the ability to conduct electric current unlike insulators which do not conduct electricity.

An ionic compound is formed due to the electrostatic force of attraction between oppositely charged ions. If this process is reversed, i.e., if we break the ionic compound by the passage of an electric current, the process is named as *electrolysis*. In simpler terms, *electrolysis* is the chemical decomposition of an ionic compound using electricity.

8.1 ELECTROLYTIC CELL

An electrolytic cell is one in which electrical energy is converted into chemical energy. It consists of a non-conducting vessel containing ionic compound (generally in fused state or in aqueous solution and called electrolyte) in which two graphite (or metal) rods are placed. These rods are called electrodes. The electrode connected to the *positive terminal* of a battery is called anode and the one con-

nected to the *negative terminal* of a battery is called cathode.



8.2 METALLIC AND ELECTROLYTIC CONDUCTORS

Metallic conductors

Metals allow electricity to pass through them and hence are called *conductors* while non-metals do not and hence are called non-conductors or *insulators*. Electric current flows through a metallic conductor due to flow of electrons.

Electrolytic conductors

The flow of electricity in an electrolytic conductor is due to the movement of charged ions to the oppositely charged electrodes.

Differentiating metallic and electrolytic conductors

Metallic conductors	Electrolytic conductors
(1) Flow of electricity through the conductor is due flow of electrons.	(1) Flow of electricity through the conductor is due to flow of ions.
(2) Electrons flow from negative end to positive end.	(2) Ions move towards oppositely charged electrodes.
(3) No chemical change takes place.	(3) Chemical changes take place.
(4) Mass transfer is not involved.	(4) Mass transfer is involved.
(5) Conductance decreases and resistance increases with temperature.	(5) Conductance increases with the increase of temperature due to the increase in ionic mobility and degree of dissociation of electrolyte.

8.3 TERMS USED IN ELECTROLYSIS

(i) *Electrolysis* is the process of decomposition of a chemical compound in aqueous solution or in molten state accompanied by a chemi-

cal change by passing electricity through it.

(ii) *Electrolytes* are ionic compounds that conduct electricity in molten or aqueous state. They are acids, bases or salts.

Examples: NaCl, HCl, NaOH

- (iii) *Non-electrolytes* do not ionise either in aqueous solution or in molten state. Hence they do not conduct electricity. They contain only whole molecules. *They are pure covalent compounds*. Examples: distilled water, ether, alcohol, benzene.
- (iv) *Electrolytic cell or Voltameter* is a non-conducting vessel in which electrolysis is carried out. *Electrical energy is converted to chemical energy*.
- (v) *Electro-chemical cell* is a device used to convert chemical energy into electrical energy.

Example: Daniel cell

- (vi) *Electrodes* are the metal plates, wires or rods immersed in the electrolyte through which electricity enters or leaves the electrolyte.
- (vii) *Ions* are atom(s) or group of atoms which carry a positive or negative charge. The charge which the ion carries is equal to its *Valency*.

Cations : Cations are positive ions. Cations migrate to the cathode during electrolysis. Cations are reduced by gaining electrons at the cathode.

Anions : Anions are negative ions. Anions migrate to the anode during electrolysis. Anions are oxidised by losing electrons at the Anode.

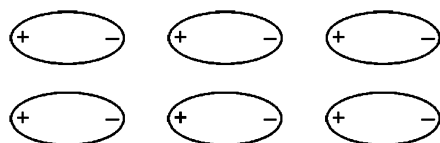
8.4 ELECTROLYTES

Flow of electricity through an electrolyte is due to the movement of charged ions to the oppositely charged electrodes. However electrolytes *will not conduct electricity* in solid state as strong electrostatic forces of attraction hold the ions and prevent their movement. Electrolytes conduct electricity in the molten or aqueous state as they *dissociate into ions*.

Dissociation of an electrolyte

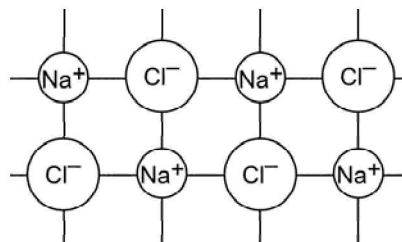
Polar solvents

Water is a polar solvent. Water molecules have oppositely charged ends.



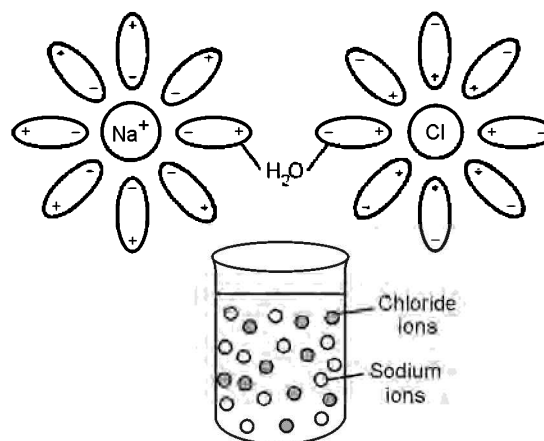
Oppositely charged ends of solvent – water molecules

In Sodium chloride crystal several sodium ions and chloride ions are held in crystal lattice.



NaCl crystal – Current cannot flow though an ionic compound in the solid state. The ions are held in a rigid network by strong electrostatic forces of attraction that prevent the ions from moving and hence electric charge cannot flow through the solid.

The negatively charged ends of several water molecules surround each sodium ion and the positively charged ends of several water molecules surround each chloride ion. The water molecules pull the ions apart *dissociating the ionic compound*.



Water molecules surround sodium and chloride ions so that the oppositely charged ends face each other. How the water molecules surround one sodium ion and one chloride ion is shown above. The water molecules pull the two ions apart *dissociating them or separating them*.

Thus, ionic compounds do not conduct electricity in solid state as strong electrostatic forces of attraction hold the ions. Ionic compounds conduct electricity in molten or aqueous state as they *dissociate into ions*.

Dissociation versus ionisation

When an ionic compound is heated strongly or dissolved in a polar solvent like water the ions separate. The ions already existed in the ionic compound. On dissolution they separate. The compound is said to *dissociate*.

When a polar covalent compound is dissolved in a polar solvent like water, it ionizes and forms ions.

The ions did not exist previous to the ionisation. Only on dissolution ions are formed. The compound is said to undergo *Ionisation*.

Ionic compounds *dissociate* on dissolving in polar solvents.

Polar covalent compound *ionise* on dissolving in polar solvents.

Example: On dissolving in water, NaCl dissociates into sodium ions and chlorine ions whereas on dissolving in water HCl ionizes into hydrogen ions and chlorine ions.

8.5 ROLE OF ELECTRODES

The electrodes carry current into the electrolyte and out of it. The cations in the electrolyte migrate

to the cathode and the anions to the anode.

Example:

Solid sodium chloride on heating dissociates as : $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

The Na^+ ions migrate to the cathode and the Cl^- ions to the anode.

At cathode: *The electric current flows into the electrolyte through the cathode.* These electrons are gained by sodium ions to form sodium atoms: $\text{Na}^+ + 1 \text{e}^- \rightarrow \text{Na}$ (**Sodium ions are oxidised**)

At anode: *The electric current flows out of the electrolyte through the anode.* These electrons are lost by chlorine ions to form chlorine: $\text{Cl}^- - 1 \text{e}^- \rightarrow \text{Cl}$ (**Chlorine ions are reduced**)

Cathode	Anode
Cathode is connected to the negative terminal of battery.	Anode is connected to the positive terminal of battery.
Cations (+ ve) ions migrate to cathode.	Anions (– ve) ions migrate to anode.
Reduction takes place at cathode.	Oxidation takes place at anode.
Current enters the electrolyte through cathode.	Current leaves the electrolyte through anode.

Inert and active electrodes

Inert electrodes are the electrodes that do not undergo any chemical change. The inert electrodes only supply electrons or take them.

Examples: Iron, Graphite, and Platinum

Active electrodes are the electrodes that undergo chemical change and have to be replaced periodically. The active electrodes supply atoms that ionise by losing electrons.

Examples: Nickel, Silver, Chromium, and Copper.

8.6 ARRHENIUS' THEORY OF IONISATION

In 1887 Arrhenius proposed his theory of ionisation.

- An electrolyte ionizes (dissociates) to give charged species called ions *when dissolved in water*.
- On ionisation the electrolyte allows the flow of electricity through it.
- The charged ions carry the electricity through the electrolyte.
- The conductivity of an electrolyte depends on

the extent of dissociation (i.e. concentration of ions).

- The number of positive ions is equal to the number of negative ions at any given moment.
- A state of electrolytic equilibrium exists between dissociated and undissociated ions.
- In non-electrolytes only molecules are present as there is no ionization / dissociation.
- Under the influence of an electric potential across the two electrodes the ions start migrating towards the respective electrodes.
- The extent of ionisation is different for different electrolytes. It is given by the equation

Degree of ionisation,

$$\alpha = \frac{\text{number of molecules that ionise}}{\text{total number of molecules before ionisation}} \times 100$$

- Degree of dissociation depends on nature of electrolyte, nature of solvent, conc. of solution, temperature, and common ion effect.
- While strong electrolytes undergo complete ionisation, weak electrolytes undergo low

ionisation at moderate concentration. The ionisation increases as dilution is increased reaching unity at infinite dilution.

- (xii) The dissociation constant of an electrolyte, $K = c \alpha^2$ where c is the concentration of the ions.
- (xiii) Strong electrolytes have large K values and vice versa.
Example: The dissociation constant of acetic acid is 1.8×10^{-5} and for HCN is 4×10^{-10} . From this it can be said that acetic acid is a stronger electrolyte than HCN.
- (xiv) Electrolytes are ionised more in polar solvents like water than in non-polar solvents like benzene.
- (xv) The degree of dissociation, α is also directly proportional to temperature.

8.7 CHARACTERISTICS OF ELECTROLYSIS

The electric cell consists of an electrolytic bath, a source of direct current (like a battery) and two electrodes, like platinum rods and the electrolyte (either fused or aqueous solution). The battery pushes electrons through the cathode into the electrolyte and 'pulls' out the electrons from the anode.

- (i) *Thus electricity is conducted in the external circuit by the flow of electrons from anode to cathode and by migrating ions under the influence of the electric potential in the electrolyte.*
- (ii) Electric energy is converted to chemical energy as follows.
- (iii) Cations migrate to cathode. They gain electrons to become neutral atoms or groups.
- (iv) Anion migrates to anode. They lose electrons to become neutral atoms or groups.
- (v) Thus, reduction takes place at the cathode and oxidation at the anode. *The overall reaction is thus a redox reaction.*
- (vi) Metal ions are discharged at the cathode and non-metal atoms at the anode.
- (vii) There are two half reactions taking place – one half at the cathode, *reduction half reaction* and another half at the anode, *oxidation half reaction*.

- (viii) In terms of heat energy, *electrolysis is endothermic reaction.*

8.8 ELECTROCHEMICAL SERIES

Metals: The electrochemical series of metals is a series in which metallic elements are arranged in *increasing order of ease of reduction*.

Metals at the top of the series lose electrons more easily than metals lower down.

Non-metals: The electrochemical series of non-metals is a series in which negative radicals or anions are arranged in *increasing order of ease of oxidation*.

Negative radicals or anions at the top of the series gain electrons more easily than those lower down.

Thus, lower metals or non-metals in the series are discharged more easily or preferentially.

Oxidation potential: The electron-losing tendency of the metal is a measure of its oxidation potential. It is measured in volts.

Reduction potential: The electron-gaining tendency of the metal ions is a measure of its reduction potential. It is measured in volts.

Electrode potential: When a metal rod is kept in a solution containing its *own ions* the metal ions are in equilibrium with the metal atoms. The electron-losing tendency of the metal atoms is equal to the electron-gaining tendency of the metal ions.

For any electrode,

$$\text{Oxidation Potential} = - \text{Reduction potential}$$

Stated simply, the ease with which an element loses electrons is equal to the difficulty with which it accepts electrons.

The Standard Reduction Potentials (ease with which electrons are gained) are tabulated in increasing order in the *electrochemical series*.

Metals with lower reduction potentials are stronger reducing agents.

All the metals above hydrogen in ECS have negative reduction potentials and can displace hydrogen from water or acids.

All elements below hydrogen in ECS have positive reduction potentials and *cannot* displace hydrogen from water or acids.

Electrochemical series

Element	Ion	Reduction Potential	
Lithium	Li ⁺	– 3.045 V	Increasing reduction potential
Cesium	Cs ⁺	– 3.045 V	
Potassium	K ⁺	– 2.925 V	
Calcium	Ca ²⁺	– 2.866 V	
Sodium	Na ⁺	– 2.714 V	
Zinc	Zn ²⁺	– 0.762 V	
Iron	Fe ²⁺	– 0.441 V	
Nickel	Ni ²⁺	– 0.250 V	
Tin	Sn ²⁺	– 0.140 V	
Lead	Pb ²⁺	– 0.126 v	
Hydrogen	H ⁺	0 V	
Copper	Cu ²⁺	+ 0.337 V	
Silver	Ag ⁺	+ 0.800 V	
		and so on	

For non-metals and anion radicals the increasing order of oxidation potentials are shown below.

SO ₄ ²⁻	Increasing ease of oxidation	Discharge with maximum difficulty
NO ₃ ¹⁻		
F ¹⁻		Anions are discharged at anode by the loss of electrons
Cl ¹⁻		
Br ¹⁻		
I ¹⁻		
OH ¹⁻		Discharge with maximum ease

8.9 PREFERENTIAL DISCHARGE OF IONS

When two or more similarly charged ions migrate to an electrode during electrolysis, the ion which is preferentially discharged depends on

- relative position of the parent atom in the Electrochemical Series
- relative concentration of ions
- nature of electrodes.

Lithium in the *given series* has the least reduction potential (least negative value)

- gains electrons with difficulty
- loses electrons most easily.

Silver in the *given series* has the highest reduction potential (highest positive value)

- gains electrons most easily
- loses electrons with difficulty.

(a) Position in ECS

If more than two different cations are present in the electrolyte, the *cation that is lower in the ECS is preferentially reduced at the cathode.*

If more than two different anions are present in the electrolyte, the *anion that is lower in the ECS is preferentially oxidised at the anode.*

Examples

If Na⁺ and Cu²⁺ ions migrate at the same time to the same cathode during electrolysis then copper ions will be preferentially discharged. This is because sodium being higher up in the ECS has a stronger tendency to lose electrons. Conversely, copper being lower in the ECS gains electrons more easily than sodium and hence copper ions are preferentially discharged.

If Cl⁻ and OH⁻ ions migrate to the same anode during electrolysis, then OH⁻ ions will be discharged preferentially as they are lower in the ECS.

(b) Concentration of ions

Higher the concentration of an ion greater is the probability of discharge even if the ion is lower in the ECS when compared to the other ion.

Examples

In dilute NaCl, concentration of H⁺ and OH⁻ ions is high. As these ions are lower than Na⁺ and Cl⁻ respectively, H⁺ and OH⁻ ions get discharged preferentially.

In concentrated NaCl solution, concentration of Na⁺ and Cl⁻ ions is high. So, even though they are higher up in the ECS than H⁺ and OH⁻ respectively, it is Na⁺ and Cl⁻ ions that are discharged.

(c) Nature of electrode

Active electrodes lose electrons and enter the solution as metal ions that migrate to the cathode.

Inert electrodes do not participate in electrolysis

at all except to allow the electrons enter the electrolyte and leave it and facilitate reduction or oxidation of the ions.

8.10 EXAMPLES OF ELECTROLYSIS

- (a) fused lead bromide
- (b) acidulated water
- (c) acidified copper sulphate using
 - (i) copper electrodes (active)
 - (ii) anode of platinum or graphite (inactive)

(a) Electrolysis of fused lead bromide:

12V, 3amp

Electrolytic cell: *Silica crucible.*

Reasons for using silica crucible:

Silica is *non-reactive, a bad conductor and can withstand high temperature.*

Electrodes used: *Graphite electrodes. (Inert electrodes)*

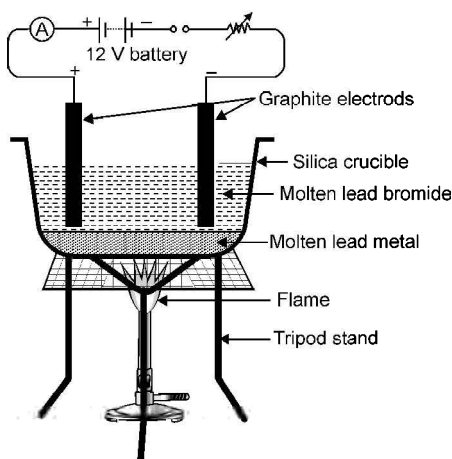
Reason for using inert electrodes: *To prevent reaction of products formed with electrodes.*

Why is platinum not used as electrode instead of graphite? *Bromine formed at anode reacts with platinum but does not react with graphite.*

Electrolyte: $PbBr_2$

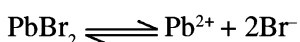
State of the electrolyte: *fused. The electrolyte is heated externally to above $380^\circ C$. MP of $PbBr_2$ is $385^\circ C$.*

Reason for the state of the electrolyte: *$PbBr_2$ in solid state is a bad conductor and poorly ionized.*



Electrolysis of molten lead bromide

Dissociation of electrolyte:



Ions present in electrolyte:

Pb^{2+} and Br^-

Ion(s) migrating to cathode: Pb^{2+}

Ion(s) migrating to anode: Br^-

Reaction at cathode: $Pb^{2+} + 2e^- \rightarrow Pb$

The reaction is *reduction*

Reaction at anode: $2Br^- - 2e^- \rightarrow 2Br \rightarrow Br_2$.

The reaction is *oxidation*.

Products obtained: At cathode: *Molten lead as the MP of lead is $327^\circ C$ (lower than that of electrolyte). As lead is denser than the electrolyte it sinks to the bottom of the electrolyte.*

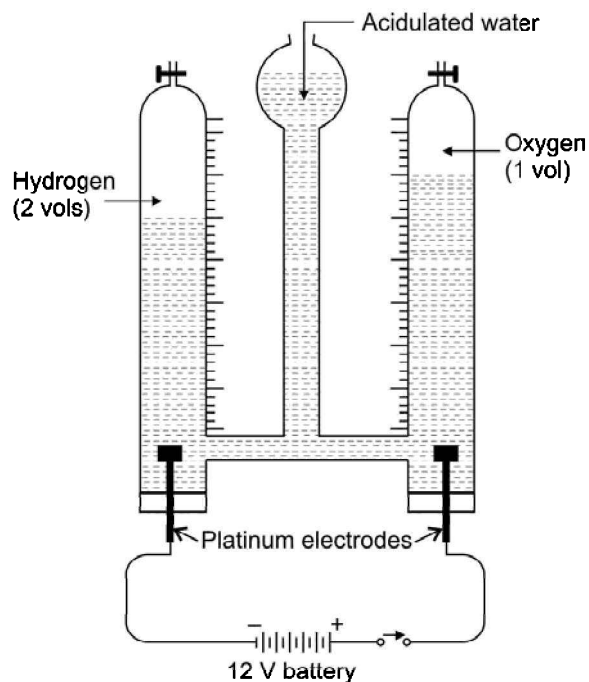
At anode: *Bromine vapours*

(b) Electrolysis of acidulated water:

12V, 3amp

Electrolytic cell: *Three interconnected glass tubes*

Electrodes: *Strips of platinum*



Electrolysis of acidulated water or dilute sulphuric acid

Reason for using inert electrodes: *To prevent reaction of products formed with electrodes*

Electrolyte: *Distilled water to which 2% sulphuric acid is added.*

Temperature of the electrolyte: *Room temperature*

Reason for adding acid to the electrolyte: *Pure*

water is bad conductor of electricity and poorly ionised.

Reason for not using dilute nitric acid instead of dilute H_2SO_4 : Nitric acid is volatile. NO_3^- ion interferes with electrolysis.

Dissociation of electrolyte: $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

$\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$

Ions present in electrolyte: H^+ , OH^- and SO_4^{2-}

Ion(s) migrating to cathode: H^+

Ion(s) migrating to anode: OH^- , SO_4^{2-}

Reaction at cathode: $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$

The reaction is *reduction*.

Reaction at anode: $4\text{OH}^- - 4\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

The reaction is *oxidation*.

Reason for preferential discharge of OH^- ion at anode: OH^- is below SO_4^{2-} in the ECS; it has a lower reduction potential.

Products obtained: Ratio of volumes of gases at cathode (hydrogen) to anode (oxygen) is 2 : 1.

At cathode: Hydrogen gas is liberated.

At anode: Oxygen gas is liberated.

(c) Electrolysis of acidified Copper sulphate using ACTIVE electrodes (copper): 12V, 3amp

Electrolytic cell: Glass container

Electrodes: Both of copper

Electrolyte: saturated CuSO_4 solution acidified with sulphuric acid

Temperature of the electrolyte: room temperature

Reason for adding acid to the electrolyte:

(a) to prevent hydrolysis of CuSO_4

(b) to make it a better conductor

Dissociation of electrolyte:

$\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$

$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

$\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$

Ions present in electrolyte: Cu^{2+} , H^+ , OH^- , SO_4^{2-}

Ion(s) migrating to cathode: Cu^{2+} , H^+

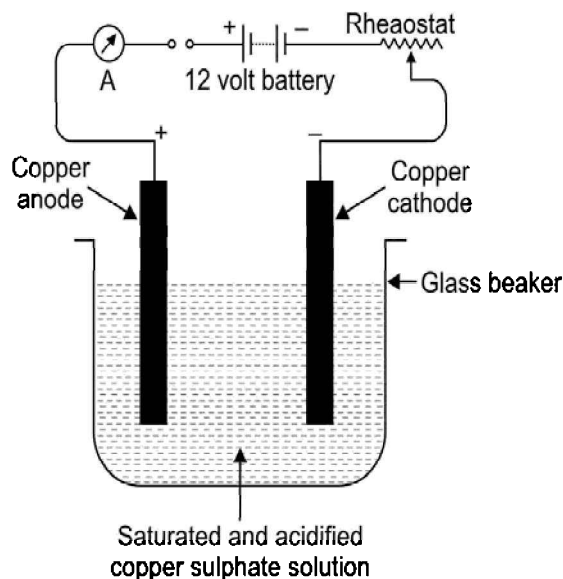
Ion(s) migrating to anode: OH^- , SO_4^{2-}

Reaction at cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

The reaction is *reduction*.

Reason for preferential discharge of Cu^{2+} ion at cathode: Cu^{2+} ions are discharged in preference to

H^+ ions as reduction potential of Cu^{2+} is lower than H^+ ions.



Electrolysis of aqueous acidified copper sulphate solution using copper electrodes

Reaction at anode: $\text{Cu} - 2\text{e}^- \rightarrow \text{Cu}^{2+}$

The reaction is *oxidation*

Reason: The ions reaching the anode are OH^- , SO_4^{2-} . But copper electrode is ionized as its reduction potential is lower than OH^- or SO_4^{2-} ions.

Reason for colour of solution remaining the same: The blue colour of the solution is due to Cu^{2+} ions. As the number of copper ions getting reduced at the cathode is equal to the number of copper atoms getting ionized at the anode the blue colour of the solution does not change.

Reason for anode being replaced periodically: As the copper atoms of the anode ionize and enter the solution, the mass of the anode decreases. After some time the anode must be replaced.

Products obtained: At cathode: Copper metal

At anode: No product formed

(d) Electrolysis of acidified copper sulphate using inert electrodes: 12V, 3amp

Electrodes used: platinum or graphite

Dissociation of electrolyte:

$\text{CuSO}_4 \rightleftharpoons \text{Cu}^{2+} + \text{SO}_4^{2-}$

$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$

$\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$

Ions present in electrolyte: Cu^{2+} , H^+ , OH^- , SO_4^{2-}

Ion(s) migrating to cathode: Cu^{2+} , H^+

Ion(s) migrating to anode: OH^- , SO_4^{2-}

Reaction at cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$

The reaction is *reduction*

Reason for preferential discharge of Cu^{2+} ion at cathode: *Cu^{2+} ions are discharged in preference to H^+ ions as reduction potential of Cu^{2+} is lower than H^+ ions.*

Reaction at anode: $4\text{OH}^- - 4\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

The reaction is *oxidation*

Reason: *The ions reaching the anode are OH^- , SO_4^{2-} . OH^- is discharged as the reduction potential of OH^- is lower.*

Reason for colour of the solution fading: *As copper ions get reduced, they leave the solution as atoms. Over a period of time, this results in the blue colour fading.*

After colour fades the electrolysis reaction changes to that of acidulated water.

The reaction at cathode is $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$

The reaction is *reduction*.

The reaction at anode: $4\text{OH}^- - 4\text{e}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2$

The reaction is *oxidation*.

Products obtained:

At the cathode copper is discharged till the colour fades. After the colour fades hydrogen is liberated due to electrolysis of water.

At the anode before and after colour fades: *Oxygen is liberated.*

8.11 APPLICATIONS OF ELECTROLYSIS

Electrolysis is used in the following applications

- Extraction of more electropositive metals like Na, K, Ca, Mg, Al.
- Electrorefining: Purification of metals like Cu, Ag and Au.
- Electroplating of a metal over another metal.
Example: Electroplating of Zinc (sacrificial metal) over iron is called galvanisation.
- Electro-printing.
- Preparation of elementary gases like H_2 , O_2 , F_2 and Cl_2 .
- Manufacture of NaOH , Na_2CO_3

Two of the important applications are discussed below.

(A) Electroplating

In electroplating a thin layer of a metal usually gold, silver or copper is deposited during electrolysis

over another metal.

The following steps are taken during electroplating.

- A saturated solution of a salt of the metal to be electroplated is taken as electrolyte (so that concentration of metal ions is high).
- The electrolyte must be acidulated with an acid that contains the same negative ions as the metal salt to prevent hydrolysis of the metal ions and improve conductivity.
- The **pure metal** that is to be electroplated is made the anode. The atoms of the metal that is to be electroplated over the object, ionise and migrate to the cathode.
- The **object** that is to be electroplated is cleaned thoroughly and made the cathode so that the deposit of the metal does not peel off over time. The positively charged cations migrate to the cathode and get reduced / deposited on the article.
- As electroplating progresses, the weight of cathode increases while that of the anode decreases.
- The anode must be replaced periodically as its weight decreases.
- A low DC current over a long time period is used so that electrolyte does not get heated up.

Examples

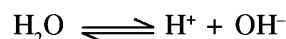
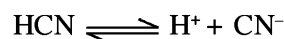
(1) Electroplating Silver

Electrolyte: A saturated solution of sodium argento cyanide - $[\text{NaAg}(\text{CN})_2]$ acidified with HCN is used as electrolyte.

Cathode: The object to be electroplated is cleaned thoroughly and used as the cathode.

Anode: A pure bar of silver is used as anode.

Reactions: Electrolytic dissociation –

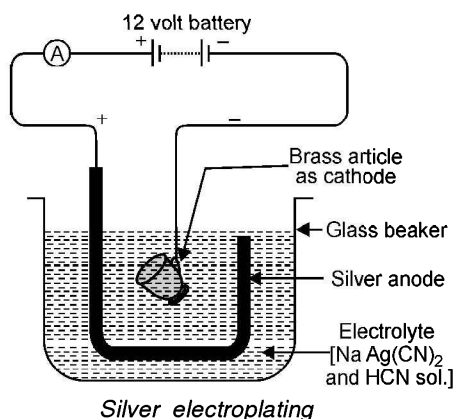


At cathode – $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$

(Silver is lower in the ECS when compared to sodium hence preferentially discharged)

At anode – $\text{Ag} - \text{e}^- \rightarrow \text{Ag}^+$

(Silver has lower reduction potential than CN^- or OH^- ions, hence silver atoms ionise)



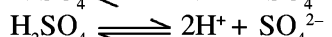
(2) Electroplating Nickel

Electrolyte: A saturated solution of nickel sulphate - $[\text{NiSO}_4 \text{ acidified with } \text{H}_2\text{SO}_4]$ is used as electrolyte.

Cathode: The object to be electroplated is thoroughly cleaned and used as cathode.

Anode: A pure bar of nickel is used as anode.

Reactions: Electrolytic dissociation –

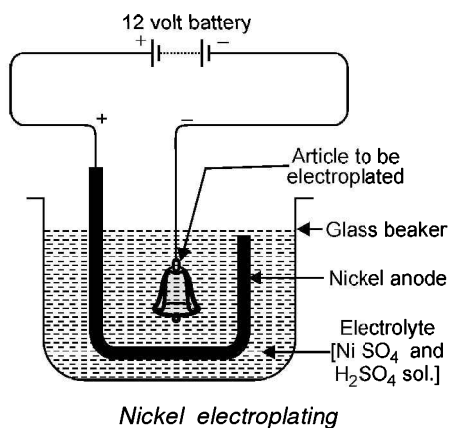


At cathode – $\text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}$

(Nickel is lower in the ECS when compared to hydrogen hence preferentially discharged)

At anode – $\text{Ni} - 2\text{e}^- \rightarrow \text{Ni}^{2+}$

(Nickel has lower reduction potential than SO_4^{2-} or OH^- ions, hence nickel atoms ionise)



(B) Electrefining

In electrefining the impurities present in an impure metal are removed by electrolysis.

The following steps are taken during electrefining.

- (i) A saturated solution of a salt of the metal to be refined is taken as electrolyte.
- (ii) The **impure metal** that is to be refined / purified is made the anode.
- (iii) A **thin wire** or piece of the pure metal is made the cathode.
- (iv) As electrefining progresses, the weight of cathode increases while that of the anode decreases.
- (v) The anode must be replaced periodically as its weight decreases.
- (vi) Impurities present in the impure metal fall below the anode and is called the **anode mud**.

Example

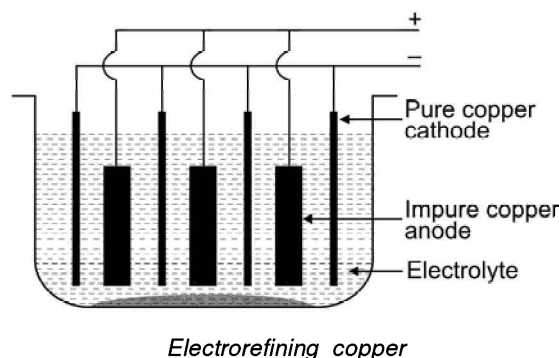
Metals like silver, nickel, lead, copper, aluminium and zinc are refined by electrefining.

Electrefining of Copper

Electrolyte: A saturated solution of CuSO_4 acidified with H_2SO_4 .

Cathode: A pure copper plate is used as cathode.

Anode: Impure copper is used as anode.



EXERCISE

I. Choose the correct answer

(1) Which one of the following is not an electrolyte?

- | | |
|-------------------------------------|---------------------|
| (a) Na_2SO_4 | (b) CuSO_4 |
| (c) $\text{C}_2\text{H}_5\text{OH}$ | (d) NaOH . |

(2) Which is a strong electrolyte?

- | | |
|-------------------|-----------------------|
| (a) acetic acid | (b) sodium acetate |
| (c) carbonic acid | (d) hydrogen cyanide. |

(3) The weak electrolyte amongst the following is

- | | |
|----------------------------|----------------------------|
| (a) NH_4OH | (b) NH_4Cl |
| (c) AgNO_3 | (d) CuSO_4 |

(4) Which one of the following is the best conductor of electricity?

- (a) Cu (b) Ag
(c) Ni (d) Sn

(5) Which one of the following is incorrect about electrochemical cell?

- (a) Electrical energy is converted to chemical energy
(b) Electrons flow from anode to cathode in external circuit
(c) Inert electrodes do not undergo chemical change
(d) The negative electrode is called anode.

(6) The extent of dissociation of an electrolyte depends on

- (a) nature of electrolyte (b) nature of solvent
(c) temperature (d) all

(7) In an electrolytic cell cathode acts as

- (a) an oxidising agent (b) reducing agent
(c) either of the two (d) none of these

(8) In an electrolytic cell the reaction at the anode is

- (a) oxidation (b) reduction
(c) electron creation (d) dehydration

(9) The article to be electroplated serves as

- (a) conductor (b) electrolyte
(c) anode (d) cathode.

(10) Molten NaCl conducts electricity due to the presence of

- (a) free electrons (b) free ions
(c) free molecules (d) atoms of Na and Cl.

(11) A solution of sodium sulphate in water is electrolysed between inert electrodes. The products at the cathode and anode are _____ and _____ respectively.

- (a) hydrogen, oxygen (b) oxygen, hydrogen
(c) oxygen, sodium
(d) oxygen, sulphur dioxide

II. Give reasons

- (i) A solution of cane sugar does not conduct electricity but a solution of sodium chloride is a good conductor.
(ii) During the electrolysis of an aqueous solution of NaCl, H^+ ions are reduced at cathode and not Na^+ ions.

III. Fill in the blanks

- (i) Molten NaCl conducts electricity due to the presence of _____
(ii) Lithium is strong reducing agent because _____
(iii) Solid NaCl is _____ conductor of electricity.

IV. Fill in the blanks :

(i) Electrolysis of fused lead bromide:

Voltage - _____ V, Current - _____ amp

Electrolytic cell is made of: _____

Reasons for using the above material of the electrolytic cell :

Electrodes: _____

Reason for using inert electrodes: _____

Why is platinum not used as electrode instead of graphite: _____

Electrolyte: _____

State of the electrolyte: _____

Temperature: _____

Reason for the physical state of the electrolyte:

Dissociation of electrolyte: _____

Ions present in electrolyte: _____

Ion(s) migrating to cathode: _____

Ion(s) migrating to anode: _____

Reaction at cathode: _____

The type of reaction is _____

Reaction at anode: _____

The type of reaction is _____

Products obtained: At cathode: _____

At anode: _____

(ii) Electrolysis of acidulated water:

Voltage _____ V, Current _____ amp

Electrolytic cell: _____

Electrodes: _____

Reason for using inert electrodes: _____

Electrolyte: _____

Temperature of the electrolyte: _____

Reason for adding acid to the electrolyte:

Reason for not using dil. nitric acid instead of dil H_2SO_4 : _____

Dissociation of electrolyte: _____

Ions present in electrolyte: _____

Ion(s) migrating to cathode: _____

Ion(s) migrating to anode: _____

Reaction at cathode: _____

The type of reaction is _____

Reaction at anode: _____

The type of reaction is _____

Reason for preferential discharge of ion at anode: _____

Products obtained:

At cathode: _____

At anode: _____

Ratio of volumes of gases at cathode (_____) to anode (_____) is _____.

(iii) Electrolysis of acidified Copper sulphate using ACTIVE electrodes (copper)

Voltage _____ V, Current _____ amp

Electrolytic cell: _____

Electrodes: _____

Electrolyte: _____

Temperature of the electrolyte: _____

Reason for adding acid to the electrolyte:

(a) _____

(b) _____

Dissociation of electrolyte: _____

Ions present in electrolyte: _____

Ion(s) migrating to cathode: _____

Ion(s) migrating to anode: _____

Reaction at cathode: _____

The type of reaction is _____

Reason for preferential discharge of _____ ion at cathode: _____

Reaction at anode: _____

The type of reaction is _____

Reason: _____

Reason for colour of solution remaining the same

Reason for anode being replaced periodically:

Products obtained:

At cathode: _____

At anode: _____

(iv) Electrolysis of acidified copper sulphate using INERT electrodes (platinum or graphite)

Voltage: _____ V, Current _____ amp

Dissociation of electrolyte: _____

Ions present in electrolyte: _____

Ion(s) migrating to cathode: _____

Ion(s) migrating to anode: _____

Reaction at cathode: _____

The type of reaction is _____

Reason for preferential discharge of _____ ion at cathode: _____

Reaction at anode: _____

The type of reaction is _____

Reason: _____

Reason for colour of solution fading:

After the colour of the electrolyte fades, electrolysis of _____ takes place.

The reaction at cathode is _____

The type of reaction is _____

Reaction at anode: _____

The type of reaction is _____

Products obtained:

At cathode: Before colour fades: _____ At anode:

Before colour fades: _____ After colour fades: _____

V. Fill in the blanks :

(i) A _____ solution of a salt of the metal to be refined is taken as electrolyte.

(ii) The _____ that is to be refined / purified is made as anode.

- (iii) A thin wire or piece of the _____ is made as cathode.
- (iv) As electrorefining progresses, the weight of cathode _____ while that of the anode _____.
- (v) The anode must be _____ periodically.
- (vi) Impurities present in the impure metal fall below the anode and is called _____.
- (vii) Electrolyte for electrorefining of silver is _____; cathode is _____.

VI. Answer the following questions.

- (1) Explain why in electroplating the metal to be electroplated is made the anode and article to be electroplated is made the cathode.
- (2) Pure NaCl is precipitated, when HCl is bubbled through conc. solution of brine. Explain why?
- (3) Differentiate between
 - (a) metallic conductor and electrolytic conductor
 - (b) anode and cathode
 - (c) ionisation and electrolysis
 - (d) electrolysis and hydrolysis
- (4) What is the difference between conductivity of Cu metal and of CuSO_4 solution?
- (5) Can we store CuSO_4 solution in a zinc vessel? Why?
- (6) Classify each of the following electrolytes as strong or weak electrolyte.
 - (i) sodium hydroxide solution
 - (ii) potassium nitrate solution
 - (iii) dil. sulphuric acid
 - (iv) acetic acid
 - (v) pure sulphuric acid
 - (vi) pure water
 - (vii) ammonia solution
- (7) Arrange the following positive and negative ions in the order in which they will be discharged in preference to other competing radicals.
At cathode: Zn^{2+} , H^+ , Mg^{2+} , Ca^{2+} , K^+ , Cu^{2+} , Na^+

At anode: Cl^- , SO_4^{2-} , OH^-

- (8) Describe what you would see at anode and cathode during electrolysis of copper (II) chloride using platinum cathode and carbon anode. Write ionic equations for the reactions at anode and cathode.
- (9) Give the products of electrolysis in
 - (a) molten lead bromide using graphite electrodes
 - (b) acidified water using platinum electrodes
 - (c) CuSO_4 using platinum electrodes
 - (d) CuSO_4 using copper electrodes
 - (e) Dil. NaCl using platinum or electrodes
 - (f) concentrated NaCl using platinum electrodes
- (10) During electroplating
 - (i) Why is direct current used?
 - (ii) Why is current of small magnitude used?
 - (iii) Why should the anode be made of the metal with which the article has to be plated?
- (11) Answer the following questions with respect to electroplating.
 - (a) Why is a saturated solution of a salt of the metal to be electroplated taken as electrolyte?
 - (b) Why should the electrolyte be acidulated with an acid that contains the same negative ions as the metal salt?
 - (c) Why is the pure metal that is to be electroplated made the anode?
 - (d) Why is the article that is to be electroplated cleaned thoroughly and made cathode?
 - (e) Why does the weight of cathode increase while that of the anode decrease as electroplating progresses?
 - (f) Why must the anode be replaced periodically?
 - (g) Why is a low DC current used for a long time period?
 - (h) What is the electrolyte used for electroplating silver?
 - (i) What is the electrolyte used for electroplating nickel?

KEY TO EXERCISE

- | | | | | | | | | | | | |
|-----------|------|------|------|------|------|------|------|------|------|-------|-------|
| I. | 1. c | 2. b | 3. a | 4. b | 5. d | 6. d | 7. b | 8. a | 9. d | 10. b | 11. a |
|-----------|------|------|------|------|------|------|------|------|------|-------|-------|
- II.**
- i. Cane sugar does not dissociate or ionise into ions but sodium chloride dissociates into ions.
 - ii. Hydrogen is below sodium in the ECS and hence preferentially discharged.
- III.**
- i. free mobile ions
 - ii. it loses electrons easily
 - iii. poor
- IV.**
- refer text
- V.**
- | | | | |
|-------------|---------------|--|--------------------------|
| i. aqueous | ii. metal | iii. pure metal | iv. increases, decreases |
| v. replaced | vi. anode mud | vii. sodium argento cyanide, thin wire of copper | |

9 Organic Chemistry

9.0 INTRODUCTION CARBON

Carbon is the third most important element on earth after Hydrogen and Oxygen for sustaining life. Carbon is the 17th most abundant element on earth. About 0.02% of earth's crust by weight is carbon.

There are over 6,00,000 Carbon compounds known.

Symbol - C, Z = 6, A = 12. Physical state: solid, non-metal.

Electronic configuration -

Ground state: $1s^2 2s^2 2p_x^1 2p_y^1$

Excited state: $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

Valency is 4.

Carbon belongs to Group IV A group and 2nd period.

Other elements of the group are Si, Ge, Sn, and Pb.

9.1 OCCURRENCE

Carbon occurs in the free as well as combined state.

Free state: Diamond and graphite are pure forms of carbon.

Charcoal, Coke and Wood are impure forms.

Combined state: Carbon occurs in combination with other elements.

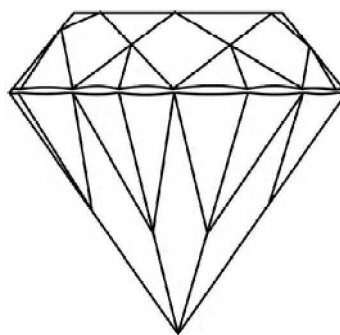
- Gaseous compounds:** CO_2 (0.03% of air is CO_2), CO (volcanic gases), hydrocarbons, natural gas, marsh gas, etc.
- Solid compounds:** Carbonates: - E.g.: CaCO_3 (lime stone, chalk), MgCO_3 (magnesite), $\text{CaCO}_3 \cdot \text{MgCO}_3$ (dolomite).
- Carbon occurs in bio-molecules such as fats, carbohydrates and proteins.

9.2 ALLOTROPES OF CARBON

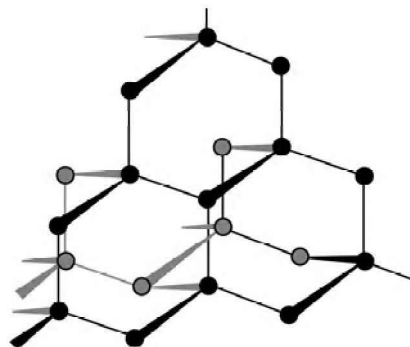
Allotropy is the phenomenon in which an element exists in two or more physical forms with same chemical properties but different physical properties. Each form is known as an *allotrope*.

The crystalline allotropes of carbon are classified as follows:

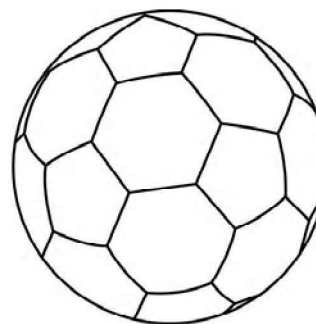
- (i) Diamond (ii) Graphite (iii) Fullerenes



Diamond



Graphite



Buckminster Fullerene

Diamond

Diamond is the purest form of carbon. Diamonds are often found near volcanoes. Diamonds are formed deep in the earth's crust where high pressure conditions are present.

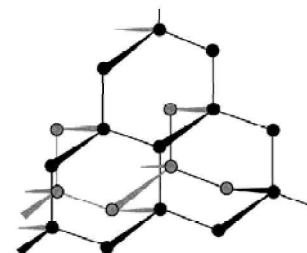
Study of Diamond		
Physical Properties	Chemical Properties	Uses
(1) Hardest naturally occurring substance. (2) Pure diamond is colourless, transparent and brittle. (3) Density is high at 3.5, due to close packing of Carbon atoms. (4) It is a poor conductor of electricity and heat as all valencies are satisfied with covalent bonding. There are no free electrons to conduct electricity. (5) The refractive index is high at 2.5. Due to high refractive index, the light ray entering a diamond crystal suffers total internal reflection, due to which it sparkles. (6) Insoluble in all solvents (7) Stable when heated in air; does not melt. (8) If heated in vacuum it changes to graphite.	(1) Inert substance as all valencies are satisfied. (2) At 900°C, it catches fire. No ash is formed indicating its purity: $C + O_2 \rightarrow CO_2$. (3) With fluorine at 750°C, it forms CF_4 . $C + 2F_2 \rightarrow CF_4$. (4) It does not react with acids or bases. (5) It reacts with sodium carbonate at very high temperature forming CO.	(1) Jewellery (2) Cutting glass (3) Drill tips (4) Watches (5) Polishing (6) Laser beam Gems Presence of impurities in diamonds gives colour to diamonds. Coloured diamonds are called <i>gems</i> . Example: <i>Emerald</i> is a gem with chromic oxide (Cr_2O_3) as impurity.

Structure of diamond

In a diamond, each carbon atom is chemically bonded to four other carbon atoms in a tetrahedral shape. The shape is rigid and hard. The distance between two carbon atoms is 1.54 Å ($1\text{Å} = 1 \times 10^{-8} \text{ cm}$) and C – C – C bond angle is $109^\circ 28'$ (see figure).

Graphite

Graphite is a greyish black solid. Graphite is also called *Black Lead* or *Plumbago*. Graphite is found in Sri Lanka and USA.

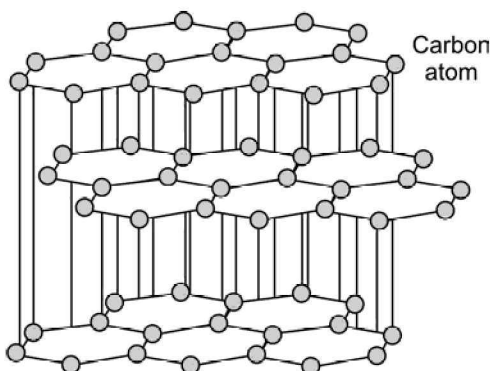


Study of Graphite		
Physical Properties	Chemical Properties	Uses
(1) Dark grey very soft solid; has metallic lustre (2) Density 2.25g/cc (3) Marks paper grey. (4) Good conductor of electricity due to free 4th electron. (5) Insoluble in solvents.	(1) Inactive element though slightly more reactive than diamond as it has one unsatisfied valency. (2) Does not burn in air. (3) In pure oxygen, it catches fire at 700°C. Some ash is formed, as it is not a very pure form of carbon. $C + O_2 \rightarrow CO_2 + \text{Heat released}$. (4) No action with acids or alkalis. (5) Reacts only with strong oxidizing agents such as boiling nitric acid, forming CO_2 . (6) Reacts with sodium carbonate at very high temperatures (fusion temperature) forming CO.	(1) Making of lead pencils. Graphite is mixed with powdered, sand and made into 'lead' pencils- more the clay harder the pencil lead. (2) As electrode (3) As a dry lubricant (4) For making refractory crucibles. (5) In nuclear reactors as a moderator that reduces the speed of neutrons.

Structure of Graphite

Every carbon atom is chemically bound to three other carbon atoms in a hexagonal ring in one plane. Each carbon atom is also bonded with *one carbon atom in the adjacent plane below and one more carbon atom in the adjacent plane above by weak van der Waal's forces*. The bonds between carbon atoms in the same plane are strong bonds while those between carbon atoms in the adjacent planes are weak. The parallel rings can thus slip over each other. This makes graphite a good lubricant.

In the same plane bond distance between adjacent carbon atoms is 1.42 Å and bond angle is 120°, while the bond length between carbon atoms in adjacent planes is 3.35 Å (see figure).

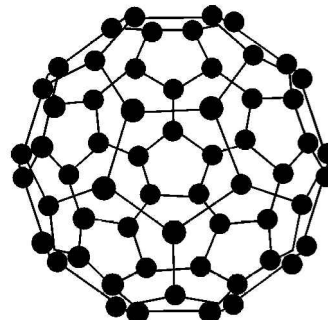


Fullerenes (Crystalline Allotrope)

Buckminster Fullerene, C₆₀ is a rare allotrope of C with 12 pentagonal and 20 hexagonal rings arranged in the shape of a football. There are a total of 60 carbon atoms arranged in 32 rings. The centre is hollow. Bond length is 1.4 Å. This allotrope has potential for use in AIDS treatment.

Fullerenes are obtained by condensing vaporized graphite.

Fullerenes are allotropes of carbon found in meteorite craters and some rocks in Russia. Fullerenes with 70, 90 and 120 carbon atoms have been discovered. Some of these Fullerenes contain atoms of other elements and are *superconductors*.



9.3 ORGANIC COMPOUNDS

The simpler compounds of carbon contain only carbon and hydrogen atoms in them and are known as *hydrocarbons*. Organic compounds can also contain other elements like O, N, S, P Cl, and Br. There are more than 6 lakh carbon compounds known. (The number of compounds without carbon is about 30,000). However, carbon containing compounds can be studied relatively easily by classifying them into aliphatic and cyclic compounds.

Catenation

Catenation is the ability of carbon to link with other carbon atoms forming long open chains or closed rings.

Catenation in carbon is *due to the following reasons*.

- Carbon has 4 electrons in valence shell
- To get octet configuration carbon atom shares these electrons with other atoms including itself.

9.4 CLASSIFICATION OF ORGANIC COMPOUNDS

ORGANIC COMPOUNDS				
ALIPHATIC COMPOUNDS (Open chains – branched or straight)		CYCLIC COMPOUNDS (Closed chain)		
Saturated	Unsaturated	Homocyclic		Heterocyclic
(a) Alkanes	(a) Alkenes (b) Alkynes	Alicyclic Closed ring saturated with only C atoms forming the ring.	Aromatic Closed ring unsaturated with only C atoms forming the ring.	Closed ring with one or more atoms other than Carbon forming the ring.

9.5 HOMOLOGOUS SERIES

Organic compounds are classified into a series or group of compounds having some similarities in properties and formula. Such a series is known as a *Homologous Series* and each member is known as a *homologue*.

Examples of homologous series: saturated hydrocarbons and unsaturated hydrocarbons (see table above).

Characteristics of a homologous series:

- Each member can be represented by the same general formula.
- Each member differs from the next member by $-\text{CH}_2$ group (called methylene group).
- Each member differs from the next member in molecular weight by 14.
- The physical properties will be graded while the chemical properties will be similar.
- Each member in the series can be prepared by the same general method of preparation.

We will now study three homologous series of hydrocarbons

9.6 HYDROCARBONS

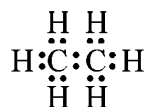
The simplest of organic compounds are the hydrocarbons. They are made up of only carbon and hydrogen atoms. One or more carbon atoms combine with each other by single bonds, double bonds or triple bonds.

Saturated hydrocarbons, and unsaturated hydrocarbons

The hydrocarbons with only single bonds between carbon atoms are *saturated hydrocarbons* whereas the hydrocarbons with double or triple bonds between carbon atoms are *unsaturated hydrocarbons*.

Illustration

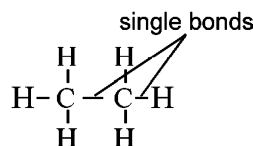
Hydrocarbons with two carbon atoms having single, double and triple bond are shown below.



All valencies of carbon are satisfied by single bonds-hence the compound is called SATURATED HYDROCARBON

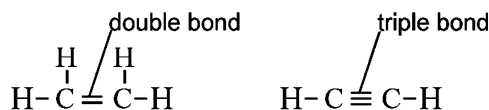


All valencies of carbon are NOT satisfied by single bonds-UNSATURATED valence bonds are there in the molecule and hence the compounds are called UNSATURATED HYDROCARBON.



SATURATED HYDROCARBON

In a Saturated hydrocarbon all valencies of carbon atom satisfied with single bonds.



UNSATURATED HYDROCARBON

In unsaturated hydrocarbon there are at least two carbon atoms with a double or triple bond between them. Such carbon atoms do not have all valencies satisfied completely.

Different methods of writing the formulae of organic compounds

There are three ways of writing the formulae of organic compounds.

Molecular Formula

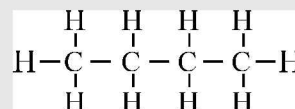
Molecular formula gives the actual number of atoms of each element.

Example: Molecular formula of butane is C_4H_{10}

Structural Formula

Structural formula gives the actual arrangement of atoms in the molecule in more detail.

Example: The structural formula of butane is



Condensed Formula

Condensed formula gives a short form of the actual linking / bonding.

Example: The condensed formula of butane is $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_3$

9.7 SATURATED HYDROCARBONS – ALKANES

The word *saturated* indicates that all valencies of every carbon atom in the hydrocarbon compound are satisfied with single covalent bonds. Saturated hydrocarbons are called **alkanes** or *paraffins*. They are the simplest of all the homologous series.

General formula: Alkanes have the general formula $\text{C}_n\text{H}_{2n+2}$.

The first five members with their formulae and names are:

	Number of carbon atom	IUPAC name	Molecular Condensed formula	Structural formula formula
1.	Methane	CH ₄	CH ₄	<pre> H H - C - H H </pre>
2.	Ethane	C ₂ H ₆	CH ₃ -CH ₃	<pre> H H H - C - C - H H H </pre>
3.	Propane	C ₃ H ₈	CH ₃ -CH ₂ -CH ₃	<pre> H H H H - C - C - C - H H H H </pre>
4.	Butane	C ₄ H ₁₀	CH ₃ -CH ₂ -CH ₂ -CH ₃	<pre> H H H H H - C - C - C - C - H H H H H </pre>
5.	Pentane	C ₅ H ₁₂	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₃	<pre> H H H H H H - C - C - C - C - C - H H H H H H </pre>

General methods of preparation of alkanes

All alkanes can be obtained by removing CO₂ from the corresponding acids or sodium salt.

Example:



Gaseous alkanes are collected by downward displacement of water.

General properties of alkanes: The main sources of alkanes are petroleum and natural gas. All alkanes can be obtained by fractional distillation of crude petroleum.

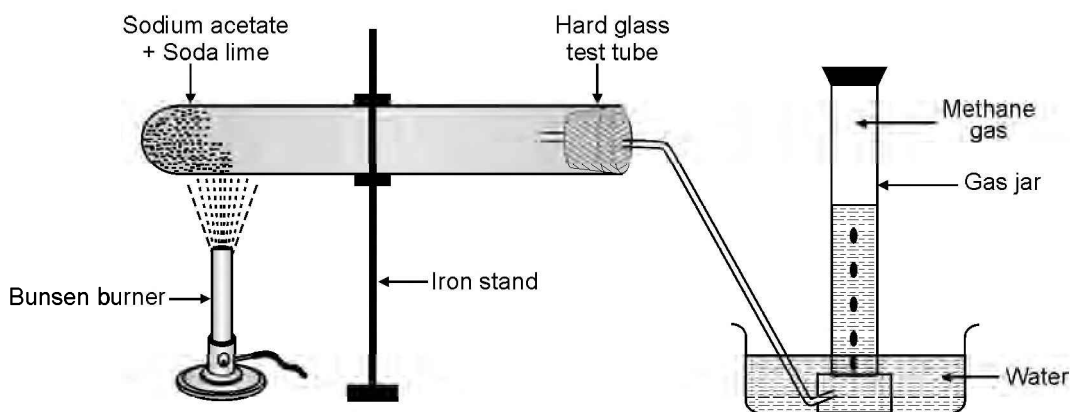
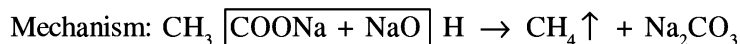
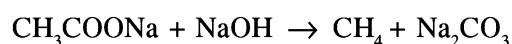
Methane

The first member of the homologous series of alkanes is Methane – CH₄. It is also called *marsh gas*.

Methane is a good fuel and occurs in natural gas, coal gas, and *gobar gas*.

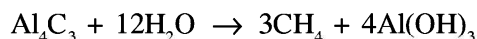
Laboratory Preparation of methane

- (1) Sodium acetate is mixed with soda lime and heated as shown. The evolved gas is collected by downward displacement of water. The reaction is



- (2) Preparation of pure methane from aluminium carbide.

When water is trickled over aluminium carbide, methane gas is formed as a product.

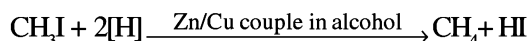


Preparing Zn / Cu couple

Zinc pieces are put into copper sulphate and allowed to stand for some time. Then the mixture is added to methyl iodide dissolved in alcohol. Methane gas is evolved slowly.

- (3) **By reduction of methyl iodide**

The reduction is carried out by putting a zinc/ copper couple in alcohol when nascent hydrogen is evolved. The nascent hydrogen reduces methyl iodide to methane.



Physical Properties of alkanes

- (1) *Physical state at room temperature*

As the number of carbon atoms increases in the chain the physical state changes from gaseous to liquid to soft solid.

Alkanes with carbon atoms

$n = 1$ to 4 are gases

$n = 5$ to 17 are liquids

- (3) **Controlled oxidation of alkanes**

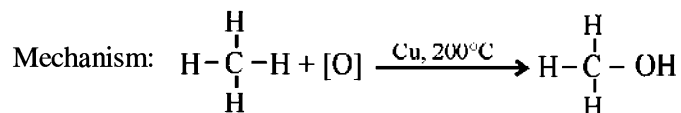
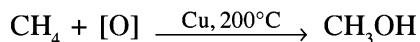
Alkanes on controlled oxidation are first oxidised to alcohols which on further oxidation get converted to aldehydes which on further oxidation get converted to carboxylic acids.

Alkane $\xrightarrow{\text{on oxidation give}}$ Alcohol $\xrightarrow{\text{on oxidation give}}$ Aldehydes $\xrightarrow{\text{on oxidation give}}$ Carboxylic acid

Example:

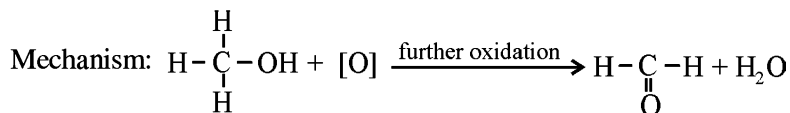
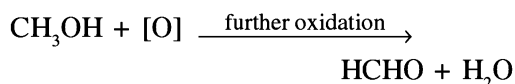
- (i) *Methane to methanol*

When methane is mixed with air, compressed and passed through a hot copper tube methanol is formed.



- (ii) *Methanol to formaldehyde*

On further oxidation with molybdenum oxide formaldehyde is formed.



$n \geq 18$ are soft solids (wax)

- (2) The melting and boiling points increase as number of carbon atoms in the chain increases.

Example:

MP of CH_4 is -182°C and BP is -162°C

($n = 1$)

MP of C_5H_{12} is -130°C and BP is 36.3°C

($n = 5$)

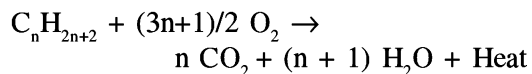
- (3) *Solubility* – Alkanes are soluble in non-polar solvents (for example benzene) and insoluble in polar solvents (for example water).
- (4) *Fuels*: All alkanes are good fuels. They burn in air releasing energy in the form of light and heat.

Chemical Properties of alkanes

- (1) **Reactivity** – As alkanes are saturated compounds they are unreactive.

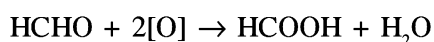
- (2) **Combustion of Alkanes** on complete combustion form CO_2 and H_2O and on incomplete combustion form CO and H_2O . The reactions are exothermic.

The general reaction is

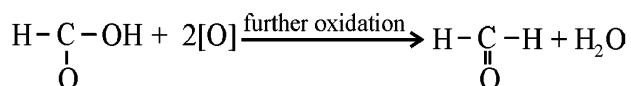


(iii) *Formaldehyde to formic acid*

On further oxidation with acidified potassium permanganate formic acid is formed.



Mechanism:



(4) **Substitution reactions**

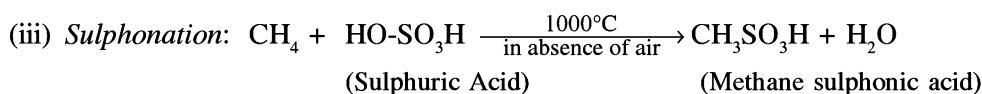
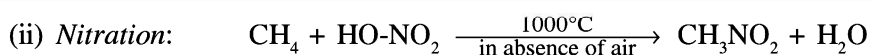
In a **substitution reaction** a more reactive atom or group of atoms substitutes H-atom in an organic compound.

Alkanes undergo substitution reactions.

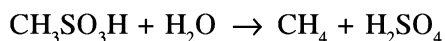
(i) *Halogenation*: Chlorine reacts with methane

Mechanism:

One Hydrogen substituted by a chlorine atom	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array} + \text{Cl}-\text{Cl} \longrightarrow \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array} + \text{H}-\text{Cl}$
Another Hydrogen atom substituted by another chlorine atom	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{H} \end{array} + \text{Cl}-\text{Cl} \longrightarrow \begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array} + \text{H}-\text{Cl}$
Third Hydrogen atom substituted by another chlorine atom	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array} + \text{Cl}-\text{Cl} \longrightarrow \begin{array}{c} \text{Cl} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array} + \text{H}-\text{Cl}$
The last Hydrogen atom substituted by one more chlorine atom	$\begin{array}{c} \text{Cl} \\ \\ \text{H}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array} + \text{Cl}-\text{Cl} \longrightarrow \begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}-\text{Cl} \\ \\ \text{Cl} \end{array} + \text{H}-\text{Cl}$



Only lower alkanes readily undergo sulphonation. The sulphonic acid thus produced again dissolves in water to give the original alkane again.

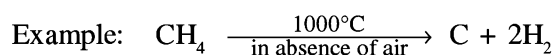
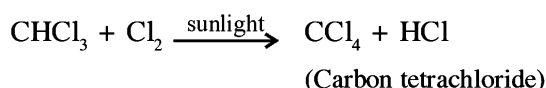
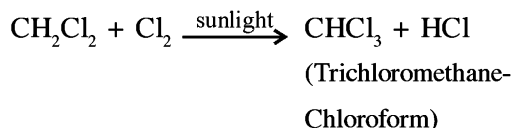
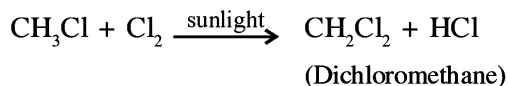
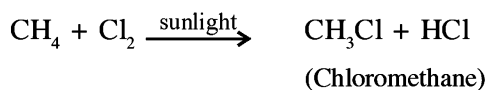


This reaction can be used to separate alkanes from a mixture of an alkane with unsaturated hydrocarbons.

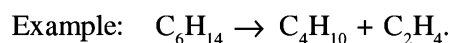
(5) **Pyrolysis** is decomposition of a compound into its constituent elements at high temperature in the absence of air.

Alkanes undergo *pyrolysis* at high temperature.

substituting each hydrogen atom forming different compounds till all hydrogen are replaced.

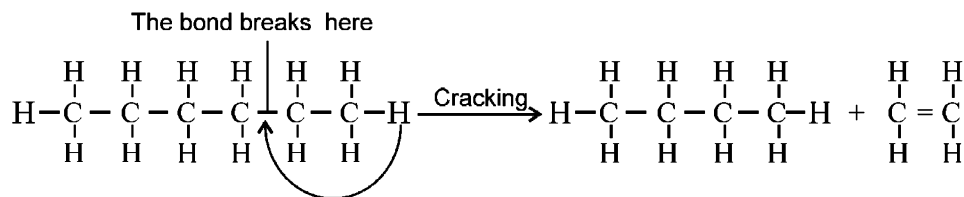


(6) **Cracking** is the breaking of a higher alkane molecule into simpler hydrocarbons either under the action of heat (*thermal cracking*) or under the influence of a catalyst (*catalytic cracking*).



Mechanism:

(7) Alkanes exhibit isomerism. This topic is discussed in the next section.



Uses of alkanes

Alkanes are used

- (i) As fuels
- (ii) Higher alkanes are used as solvents
- (iii) Manufacture of other organic compounds like alcohols.

IUPAC nomenclature Rules for naming organic compounds

- (a) The name should be simple and give an indication about the structure of the compound.
- (b) The first word (also known as root word) in name should give information on how many C atoms are there.
- (c) The words following the root word called suffixes give information on whether there are single bonds (suffix used is *-ane*) or double bonds (suffix used is *-ene*) or triple bonds (suffix used is *-yne*). A suffix also gives information about the functional group (example aldehydes have the suffix *-als*, ketones have the suffix *-ones*).
- (d) Apart from the suffixes numerical suffixes are used to show how many times atom(s) gets repeated in the molecule.
- (e) A number in the formula gives information about the number of the C atom in the chain at which a group is attached.

9.8 ISOMERISM

Isomerism: Organic compounds that have the same molecular formula but different molecular structure are said to exhibit isomerism and the different structural formulae are called isomers.

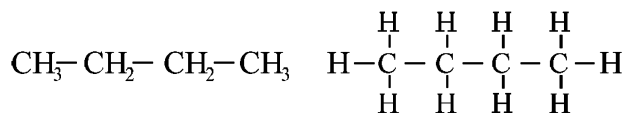
Organic compounds exhibit several types of *isomerism*.

- (1) **Structural Isomerism** – The isomers belong to the *same homologous series*. The physical properties of structural isomers may be slightly different but chemical properties will be similar.

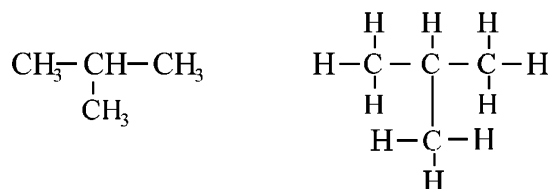
Example: Butane with molecular formula

C_4H_{10} exists in two structural forms or *isomers*.

Normal butane (C_4H_{10}) (straight chain)



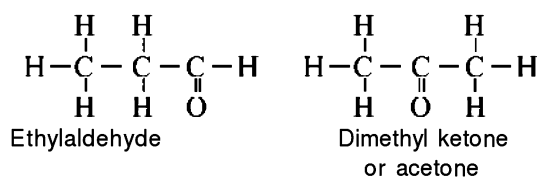
Iso-butane (branched chain)



Structural isomerism

- (2) **Functional Isomerism** – The isomers belong to *different homologous series*. The physical properties and chemical properties will be different.

Example: Ethylaldehyde ($\text{C}_2\text{H}_5\text{CHO}$) and acetone (CH_3COCH_3) have the same molecular formula $\text{C}_3\text{H}_6\text{O}$. However ethylaldehyde belongs to the homologous series of *aldehydes*, while acetone belongs to *ketones*.



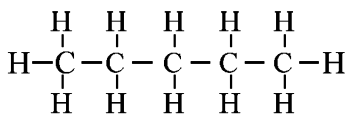
Functional isomerism

Isomerism in alkanes

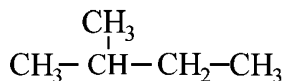
For alkanes the following isomers are possible:

- (a) Straight chains: Example: n-pentane (normal pentane)
- (b) Branched chains: There are two ways in which branching can take place.
 - (i) Single branching takes place at 2nd C-atom. The name of the alkane is suffixed with *iso-* Example: *iso*-pentane

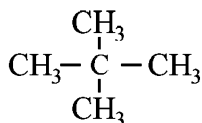
- (ii) Two branchings take place at the 2nd C-atom. The name of the alkane is suffixed with *neo*- Example: *neo*-pentane



Common Name : *n*-pentane
IUPAC Name : Pentane



Common Name : isopentane
IUPAC Name : 2-methyl butane



Common Name : *neo*-pentane
IUPAC Name : 2,2 dimethyl propane

The number of isomers that are possible for alkanes depends on the number of C-atoms.

For $n = 1, 2$ and 3 , isomerism is not possible.

For $n = 4$, the possible isomers are 2

For $n = 5$, the possible isomers are 3

For $n = 6$, the possible isomers are 5

For $n = 10$, the possible isomers are 75

For $n = 60$, millions of possible isomers are possible.

9.9 ALKYL GROUP

The remaining part in an alkane, when one H-atom is removed is called an Alkyl group (denoted by 'R-'). The naming is done by removing -ane and substituting -yl in the name.

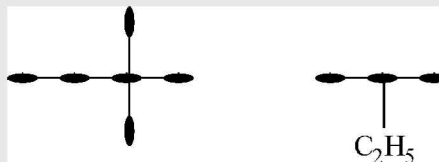
Alkane	Alkyl	Name of alkyl group
(1) Methane, CH_4	CH_3-	Methyl
(2) Ethane, C_2H_6	C_2H_5-	Ethyl
(3) Propane, C_3H_8	C_3H_7-	Propyl
(4) Butane, C_4H_{10}	C_4H_9-	Butyl
(5) Pentane, C_5H_{12}	$\text{C}_5\text{H}_{11}-$	Pentyl and so on

PRACTICE EXERCISE

- (1) Write the condensed formulae and name the 5 isomers of C_6H_{14} (hexane).

- (2) Write the condensed formulae and name any one isomers of C_7H_{16} other than *n*-heptane.

- (3) Name the following isomers:



- (4) Draw the structures of 2-methyl propane, 2,3-ethyl pentane, 2,2-methyl hexane and 2-butyl pentane.
- (5) The MP of 3 members A, B, C of a homologous series of hydrocarbons are -183°C , -138°C and -130°C . Which has lower number of C atoms?
- (6) The BP of A, B, and C are -162°C , -42.2°C and -0.5°C . Which has the highest number of C atoms?
- (7) Two alkanes A and B have 3 and 5 C-atoms. What is their physical state?
- (8) A, B, and C have the formulae CH_4 , C_3H_8 and C_8H_{18} . Which is a liquid at room temperature?
- (9) The BP of A and B are -188°C and -130°C . Which has higher mol. wt.?
- (10) Give all reactions of an alkane with 3 C- atoms with any one halogen naming all the compounds formed.
- (11) Which of these compounds belong to the same homologous series: CH_4 , C_2H_2 , C_2H_6 , C_4H_{10} , C_3H_4 , C_3H_6 ?

9.10 UNSATURATED HYDROCARBONS

An unsaturated hydrocarbon is a hydrocarbon with at least one double or triple bond.

Unsaturated hydrocarbons are of two types – those with one or more double bonds in them are called **alkenes** and those with one or more triple bonds in them are called **alkynes**.

(a) Alkenes

Alkenes are unsaturated aliphatic hydrocarbons that have at least one double bond between two carbon atoms in the chain. Alkenes are also known as **olefins**.

The general formula of alkenes is C_nH_{2n}

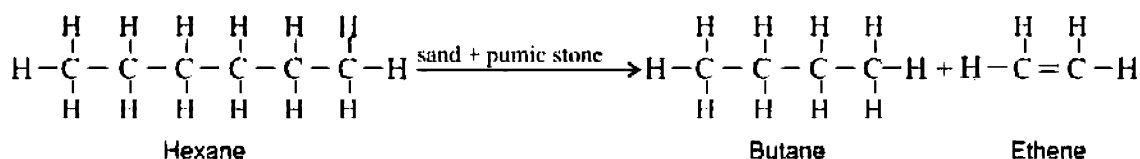
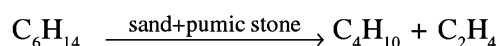
The first five members with their common names and IUPAC names are as follows :

No. of Carbon Atom	IUPAC Name	Common Name	Molecular Formula	Condensed Formula	Structural Formula
1.	Alkene with $n = 1$ does not exist. The first member starts from $n = 2$ as a minimum of two carbon atom are required for the double bond in alkenes.				
2.	Ethane	Ethylene	C_2H_4	$CH_2 = CH_2$	$\begin{array}{c} H & H \\ & \\ H-C & =C-H \end{array}$
3.	Propane	Propylene	C_3H_6	$CH_3 - CH = CH_2$	$\begin{array}{c} H & H & H \\ & & \\ H-C & -C & =C-H \\ & & \\ H & & \end{array}$
4.	(a) 1 - Butene	Butylene	C_4H_8	${}^4CH_3-{}^3CH_2-{}^2CH= {}^1CH_2$	$\begin{array}{c} H & H & H & H \\ & & & \\ H-C & -C & -C & =C-H \\ & & & \\ H & H & & \end{array}$
	(b) 2-Butene	—	C_4H_8	${}^4CH_3-{}^3CH= {}^2CH- {}^1CH_3$	$\begin{array}{c} H & H & H & H \\ & & & \\ H-C & -C & =C & -C-H \\ & & & \\ H & & & H \end{array}$

General methods of preparation

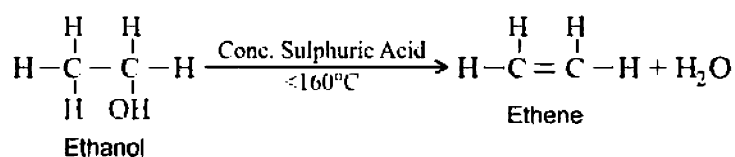
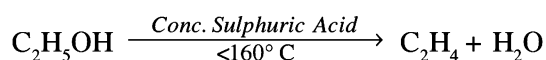
(1) By cracking of higher hydrocarbons

Hexane vapours when passed over hot sand and pumice stone undergoes cracking giving ethene.

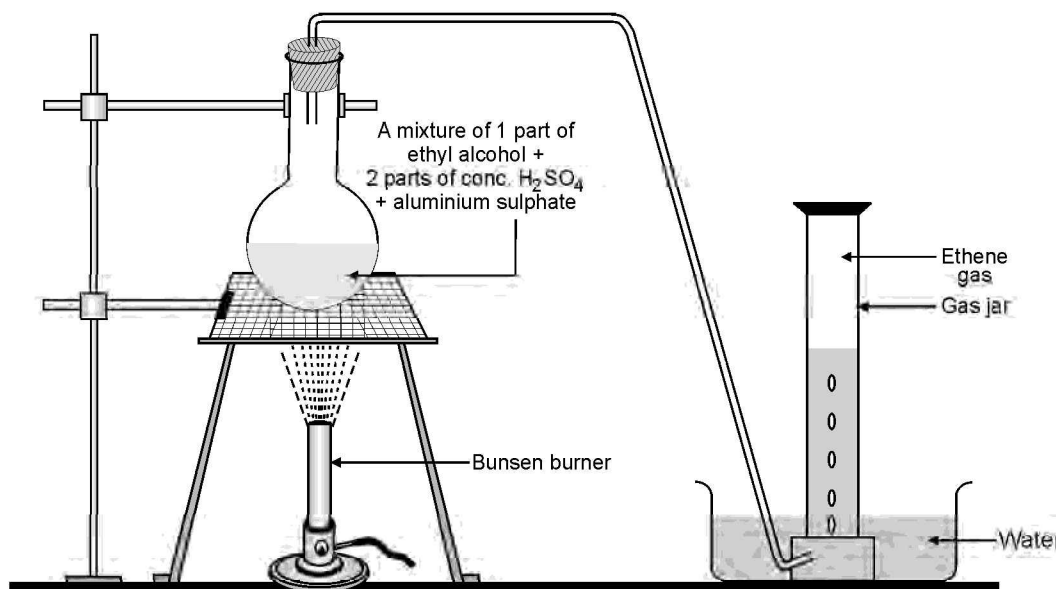


(2) Laboratory preparation of ethene—dehydration of alcohols

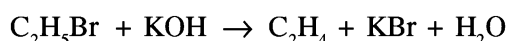
A water molecule is removed from alcohols as shown below by using a dehydrating agent like concentrated H_2SO_4 to get alkenes. A little aluminium sulphate is added to avoid frothing.



Ethene gas is collected by downward displacement of water.



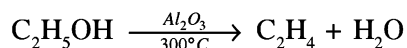
- (3) Alkyl halides are dehydrohalogenated (removing hydrogen and halogen from the compound)



(Bromo ethane) (hot, concentrated
KOH in alcohol)

- (4) **Industrial preparation of ethene**

Ethanol vapours are passed over hot alumina at 300°C.



Physical Properties

- (1) *Physical state at room temperature*

As the number of carbon atoms increases in the chain the physical state changes from gaseous to liquid to soft solid.

Alkenes with carbon atoms

$n = 2$ to 4 are gases

$n = 5$ to 15 are liquids

$n \geq 15$ are soft solids (wax)

- (2) Alkenes are soluble in non-polar solvents and insoluble in polar solvents.
(3) Most common alkene is ethene. It is a colourless and odourless gas.

Chemical Properties

- (1) **Combustion**

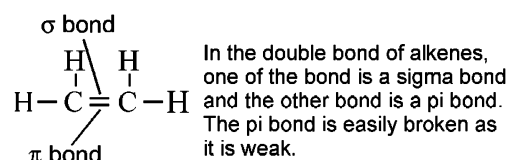
When compared to alkanes, alkenes burn with a sooty flame as they have a higher

percentage of carbon. The sooty flame is due to unburnt carbon particles.

- (2) **Reactivity**

Alkenes are more reactive than alkanes due to the presence of double bond.

Reason: The double bond comprises of one sigma and one pi bond. The pi bond in the double bond is weaker and hence easy to break. By converting the double bond to a single bond the compound becomes more stable.



- (3) **Addition reactions**

In an addition reaction a double or triple bond in an organic compound is converted to a single bond by addition of a H atom or other atom(s) to the molecule.

Thus, an addition reaction converts an unsaturated hydrocarbon to a saturated hydrocarbon.

Alkenes undergo **addition reactions**.

Alkenes undergo addition reactions with halogens, hydrogen, HCl, etc.

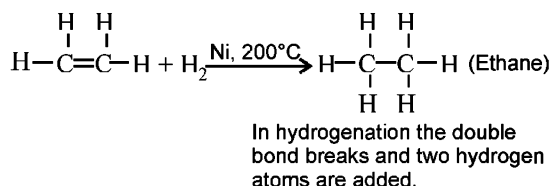
Examples:

- (i) *Addition of hydrogen*

Hydrogenation

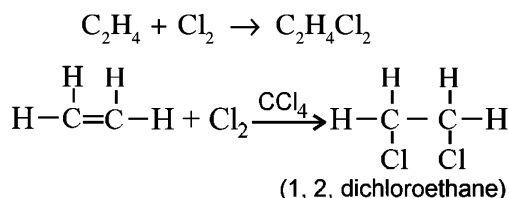
When ethene and hydrogen gases are mixed and sent over finely powdered nickel catalyst at 200°C (or platinum or palladium at ordinary temperature) the double bond breaks and two hydrogen atoms are added to form ethane.

Hydrogenation reaction – Ethene and hydrogen gases when passed over powdered nickel at 200°C from ethene

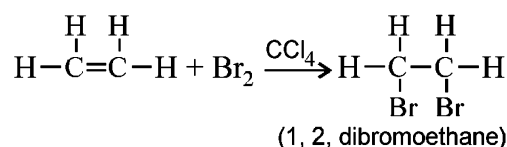


(ii) Halogenation

Addition of chlorine: Chlorine is added to ethene readily to form dichloroethane.

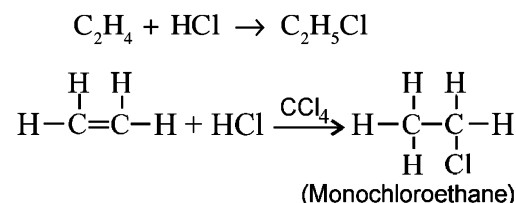


Addition of bromine: Bromine dissolved in CCl₄ has an orange colour. When ethene gas is bubbled through this solution slowly, the orange colour disappears as colourless dibromo-ethane is formed.



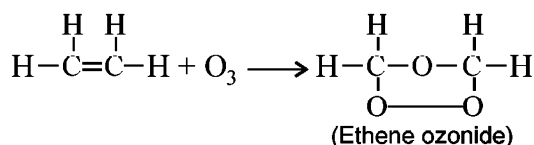
(iii) Addition of hydrogen chloride

Hydrogen chloride gets added to ethene to form chloroethane.



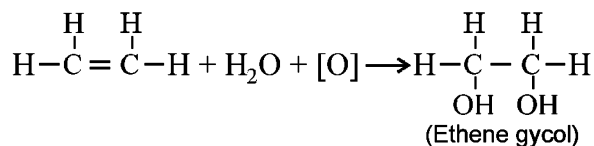
(4) Ozonolysis

Ethene reacts with ozone forming ethene ozonide.



(5) Oxidation

Ethene is oxidised in the presence of alkaline potassium permanganate to form ethylene glycol. The pink colour of KMnO₄ is decolourised. This reaction is also used as a test for double or triple bonds.

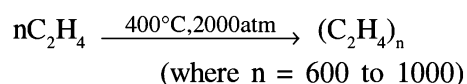


(4) Polymerisation

An alkene can undergo *self-addition reaction*. This is called *polymerisation*.

Polymerisation is the joining together of a large number of molecules of a compound to form a single large molecule called polymer. The single unit that gets repeated is called *monomer*.

Ethene polymerises to give polyethene



Test for ethene (Alkenes)

- (1) Ethene (alkenes) decolorizes reddish brown bromine water.
- (2) Ethene (alkenes) decolorizes the pink colour of alkaline KMnO₄.

- Uses**
- (1) Manufacture of organic chemicals like ethyl alcohol, glycol and synthetic fibres like polyester (terylene)
 - (2) Manufacture of plastics like polythene – used to make bags, mugs, and buckets and as insulators in cables, etc.
 - (3) Ethene is used for artificial ripening of fruits like banana, apples and oranges.
 - (4) For making mustard gas.

PRACTICE EXERCISE

- (1) What is the monomer of polyethene?
- (2) Write the equation for the hydrogenation of propene.
- (3) Give an equation in which Cl₂ is added to a hydrocarbon and an equation in which it is substituted.
- (4) What are the possible products formed when Cl₂ reacts with C₂H₄?
- (5) What are the products of combustion of ethene in sufficient and insufficient air? Write equations.
- (6) Which give unsaturated hydrocarbons on cracking: C₂H₆, C₂H₄, C₆H₁₄.

(b) Alkynes

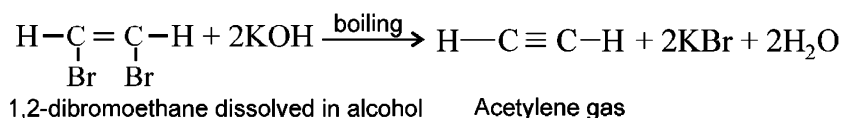
Alkynes are unsaturated aliphatic hydrocarbons with at least one triple bond in them. The general formula of alkynes is C_nH_{2n-2} . The first four members with their common names and IUPAC names are given below.

No. of Carbon Atom	IUPAC Name	Common Name	Molecular Formula	Condensed Formula	Structural Formula
1.	Alkene with $n = 1$ does not exist. The first member starts from $n = 2$ as a minimum of two carbon atoms are required for the triple bond in alkenes.				
2.	Ethyne	Acetylene	C_2H_2	$CH \equiv CH$	$H-C \equiv C-H$
3.	Propyne	—	C_3H_4	$CH_3 - C \equiv CH$	$\begin{array}{c} H \\ \\ H-C-C \equiv C-H \\ \\ H \end{array}$
4.	(a) 1-Butyne	—	C_4H_6	${}^4CH_3-{}^3CH_2-{}^2C \equiv {}^1CH$	$\begin{array}{c} H & H \\ & \\ H-C & -C & -C \equiv C-H \\ & \\ H & H \end{array}$
	(b) 2-Butyne	—	C_4H_6	${}^4CH_3-C \equiv {}^2C-{}^1CH_3$	$\begin{array}{c} H & & H \\ & & \\ H-C & -C \equiv C & -C-H \\ & & \\ H & & H \end{array}$

General method of preparation of alkynes

If 1, 2-dibromoethane is boiled with potassium hydroxide dissolved in alcohol to get ethyne. To

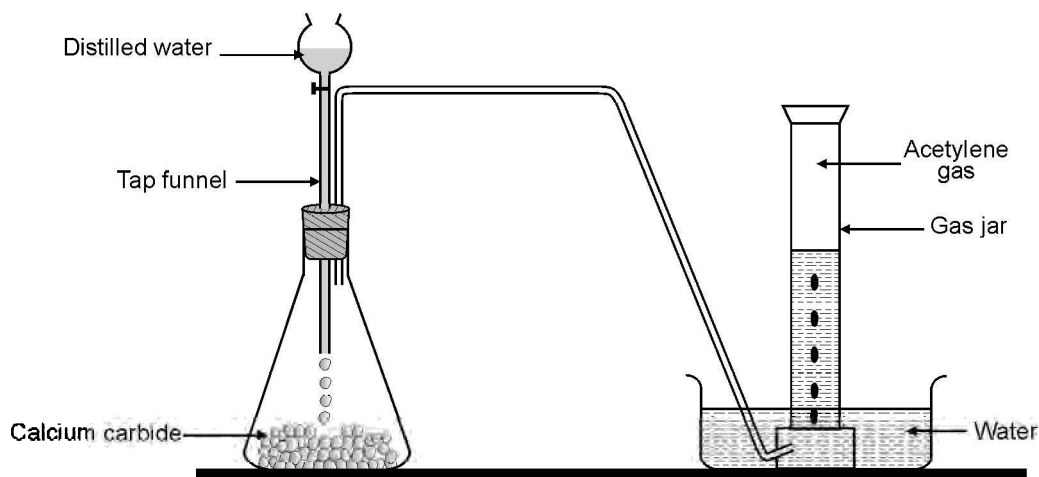
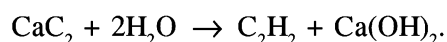
prepare other alkynes corresponding dibromoalkanes are taken.



Laboratory preparation of ethyne

The first member is ethyne (acetylene) - C_2H_2 . Ethyne is a gas with ether like odour when pure. It

can be prepared by the reaction of calcium carbide on water.



Ethyne is collected by downward displacement of water. Garlic like odour in ethyne gas prepared from calcium carbide is due to the presence of H_2S and phosphine gases.

Physical Properties of alkynes

(1) Physical state at room temperature

As the number of carbon atoms increase in the chain the physical state of alkynes changes from gaseous to liquid to soft solid.

Alkynes with carbon atoms

$n = 2$ to 4 are gases

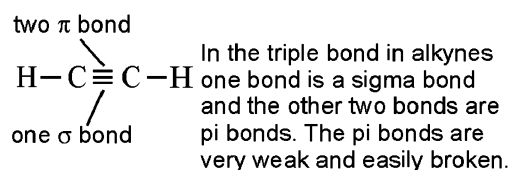
$n = 5$ to 13 are liquids

$n \geq 13$ are soft solids (wax)

- (2) Alkynes are soluble in non-polar solvents and insoluble in polar solvents.
- (3) Gaseous alkynes ($n=2$ to $n=4$) produce anesthesia when inhaled in large quantities.
- (4) Ethyne also called acetylene is a colourless gas with a slight ether-like odour.

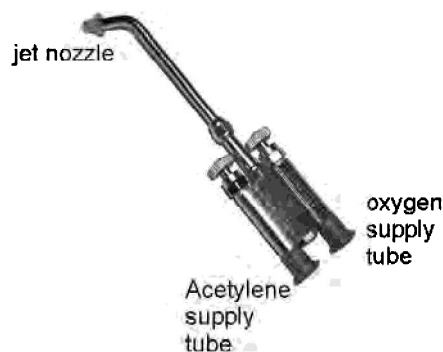
Chemical Properties of alkynes

- (1) Alkynes have the highest reactivity amongst the three types of hydrocarbons that we have seen so far. Reactivity of alkynes is more than alkanes or alkenes due to two very weak pi bonds. The weak pi bonds break freeing two valence electrons of each carbon atom. Other atoms get *added* due to bond formation with these free electrons and the product formed is saturated and hence more stable.



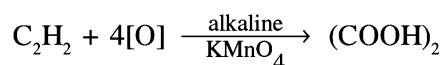
- (2) On combustion ethyne burns with a very sooty flame due to high carbon content. (C_2H_2 has 92% carbon by weight when compared to 86% in C_2H_4 and 80% in C_2H_6). Large amount of heat is released.

$$2\text{C}_2\text{H}_2 + 5\text{O}_2 \rightarrow 4\text{CO}_2 + 2\text{H}_2\text{O} + \text{heat released}$$
- (3) However if ethyne is burnt in controlled conditions by forcing it through a jet hole it burns with a blue flame at a temperature of 3000°C .



Oxy-acetylene torch achieves a temperature of 3000°C and is used for welding.

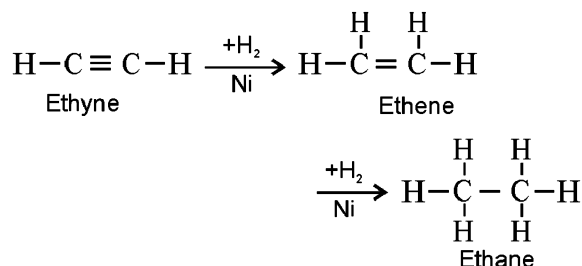
- (3) Slow oxidation of ethyne using oxidising agents produces oxalic acid.



- (4) **Addition reactions:** Alkynes undergo addition reactions as follows.

(i) Catalytic Hydrogenation

Ethyne undergoes catalytic hydrogenation in two steps to form ethane.



The triple bond in alkyne on hydrogenation gets converted to a double bond (alkene) which on further hydrogenation gets converted to a single bond (alkane)

(ii) Halogenation

When ethyne is dissolved in CCl_4 and chlorine is bubbled through it, two chlorine atoms are added first to form a double bond addition product and then another two atoms are added.

The chlorine gas gets decolorised.

When ethyne is dissolved in CCl_4 and bromine is bubbled through it, two bromine atoms are added first to form a double bond addition product and then another two atoms are added.

The bromine gas gets decolorised.

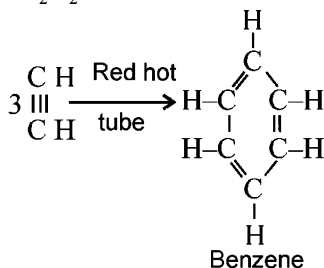
(iii) Addition of HCl

When ethyne is passed through HCl, addition products are formed in two stages.


$$\text{H}-\text{C}\equiv\text{C}-\text{H} + \text{O}_3 \longrightarrow \text{H}-\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}-\text{H}$$

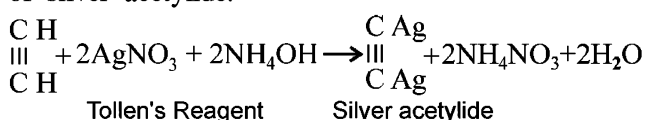
Acetylene ozonide

(a) When ethyne is passed through a red hot tube it polymerises to give benzene.



Benzene

When ethyne is passed through ammoniacal silver nitrate solution (Tollen's Reagent) in a test tube it gives a white precipitate due to the formation of silver acetylide.



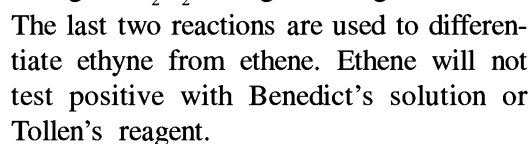
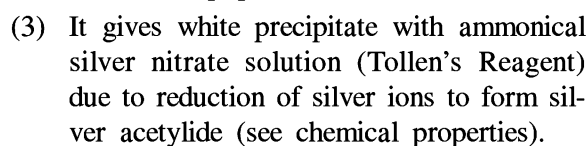
When ethyne is passed through ammoniacal cuprous chloride solution (Benedict's solution) in a test tube it gives a reddish precipitate of copper acetylide.



Cuprous
acetylide

(1) Alkynes decolourise bromine water and alkaline KMnO_4 solution.

(2) Alkynes give reddish brown precipitate with ammoniacal cuprous chloride (Benedict's solution) due to reduction of copper ions to form cuprous acetylide (see chemical properties).



Ethyne or acetylene is used

- (1) as an illuminant in special lamps.
- (2) in oxy-acetylene torches used for welding.
- (3) as a solvent.
- (4) as a starting material for making plastics, synthetic rubber, fibres.
- (5) in the manufacture of other organic chemicals like acetaldehyde, acetic acid, ethyl alcohol and Westrone ($C_2H_2Cl_4$).

Some of the chemical properties of the hydrocarbons are used as a test for their presence as follows. The actual reaction and mechanism can be referred in the text above.

	Test	Alkanes	Alkenes	Alkynes
1	Test with bromine dissolved in CCl ₄ (reddish brown colour)	No change	Decolorised	Decolorised
2	Test with alkaline KMnO ₄ (purple colour)	No change	Colour fades	Colour fades
3	Test with Tollen's Reagent	No change	No change	White precipitate
4	Test with Benedict's solution	No change	No change	Red precipitate
5	Combustion	Burns with blue flame	Burns with sooty flame	Burns with very sooty flame

9.12 FUNCTIONAL GROUPS

Functional Group is a group of atoms which is bonded to a C-atom in an organic compound and which give distinct chemical properties to the compound.

In an organic compound, the functional group determines the chemical properties while the remaining part determines the physical properties.

Some important functional groups

Alcohols have –OH group

Carboxylic acids have –COOH group

Aldehydes have –CHO group

Ketones have –CO group

Esters have –COOR group

9.13 ALCOHOLS

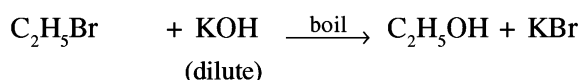
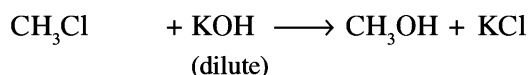
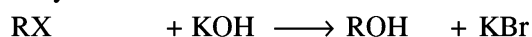
Alcohols are formed by replacing one or more hydrogen atom in an alkane with OH group. The general formula of alkyl alcohols is $C_nH_{2n+1}OH$ or $R-OH$ where R is an alkyl group. The formulae of the first five alcohols with their IUPAC names are as follows.

Common Name	Molecular formula	Abbreviated formula	Structural formula	IUPAC Name
Methyl alcohol	CH_3-OH	CH_3-OH	$\begin{array}{c} H \\ \\ H-C-O-H \\ \\ H \end{array}$	Methanol
Ethyl alcohol	C_2H_5OH	CH_3-CH_2-OH	$\begin{array}{c} H & H \\ & \\ H-C & -C-O-H \\ & \\ H & H \end{array}$	Ethanol
Propyl alcohol	C_3H_7OH	$CH_3-CH_2-CH_2-OH$	$\begin{array}{c} H & H & H \\ & & \\ H-C & -C & -C-O-H \\ & & \\ H & H & H \end{array}$	Propanol
Butyl alcohol	C_4H_9OH	$CH_3-CH_2-CH_2-CH_2-OH$	$\begin{array}{c} H & H & H & H \\ & & & \\ H-C & -C & -C & -C-O-H \\ & & & \\ H & H & H & H \end{array}$	Butanol

General methods of preparation of alcohols

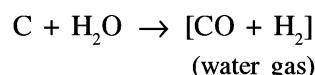
Alcohols are prepared in the laboratory by the hydrolysis of alkyl halides by boiling with dilute alkalis.

Alkyl halide + Alkali $\longrightarrow$ Alcohol + Alkali halide

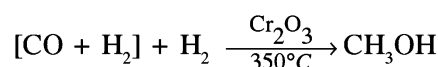


Industrial manufacture of methanol

When superheated steam is passed over white hot coke at 1000°C water gas is formed.

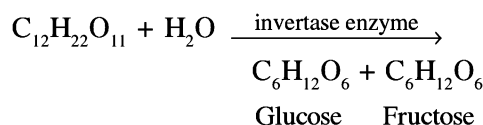


Water gas is mixed with hydrogen and passed over a catalyst – Cr_2O_3 at 350°C and 300 atmospheres forming methanol.

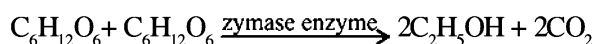


Industrial manufacture of ethanol by fermentation of sugar

Spent cane sugar juice (called *molasses*) is fermented in the presence of *invertase enzyme* to form two isomers – glucose and fructose.



When the two isomers formed are fermented further with *zymase enzyme*, ethanol is formed.



Physical properties

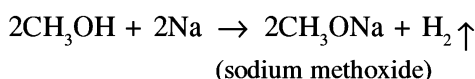
- (i) Alcohols are volatile liquids and inflammable.
- (ii) As the number of carbon atoms increases in the chain the boiling and melting point increases.

Examples: Boiling point of CH_3OH is $64.5^\circ C$ and C_2H_5OH is $78.3^\circ C$.

- (iii) Methanol and ethanol are highly soluble in water in any proportion and also in non-polar solvents.
- (iv) Methanol and ethanol are colourless with a typical smell.
- (v) They are toxic. Methanol causes blindness and is sometimes fatal.

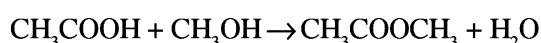
Chemical properties

- (a) With sodium metal, alcohols give effervescence of hydrogen gas. Sodium metal displaces hydrogen in the OH group.

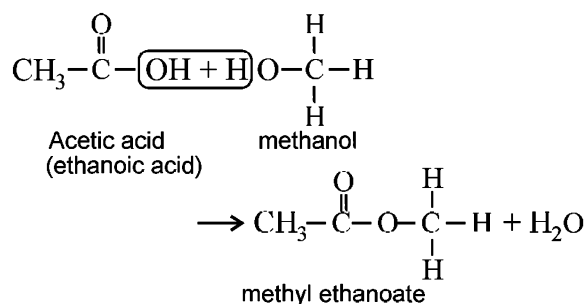


- (b) **Esterification of alcohols**

An alcohol reacts with organic acids to form sweet smelling compounds called *esters*.



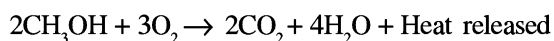
Mechanism



An esterification reaction – organic acid reacting with alcohol

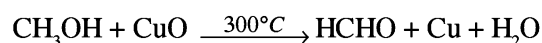
- (c) **Combustion of alcohols**

Alcohols are combustible.



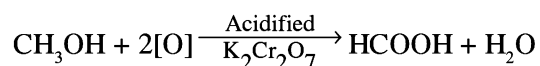
- (d) **Partial oxidation of alcohols**

Partial oxidation of alcohols forms aldehydes. When methanol vapours are passed over heated copper oxide, formaldehyde is formed.



- (e) **Complete controlled oxidation of alcohols**

Complete oxidation of alcohols forms organic acids. When methanol is added to acidified potassium dichromate, formic acid is formed.



Uses of methanol and ethanol

Uses of methanol	Uses of ethanol
(1) Methanol is a good solvent for paints and varnishes. (2) Methanol is the starting compound to manufacture formaldehyde (used for preserving biological specimens) and formic acid (used as an antiseptic and in the tanning industry).	(1) Ethanol is used in alcoholic drinks. (2) Ethanol is a good solvent for gums and resins. (3) Ethanol is used in the manufacture of other organic chemicals like acetaldehyde, acetic acid, chloroform, ether, dyes, synthetic rubber paints, varnishes, paints, perfumes, antiseptics, etc.

Abuse of methanol and ethanol

- (1) All alcoholic drinks use ethanol which causes intoxication. Prolonged use of ethanol damages the liver and kidney.
- (2) **Methylated alcohol:** Ethanol is made unfit for human consumption by adding 5% methanol. This mixture of alcohols is used by the industry primarily as a solvent.

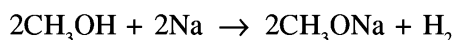
- (3) **Denatured alcohol :** To prevent misuse and abuse of ethanol, ethanol is made poisonous by adding chemicals like pyridine or copper sulphate.
- (4) **Spurious alcohol:** Spurious alcohol is prepared illegally and contains large amounts of methanol. Spurious alcohol can be prepared at very low cost by fermenting

jaggery juice. The poor sections of society fall prey to the low cost. When consumed it causes blindness and often death.

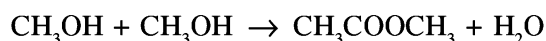
Test for alcohol

There are two tests for alcohols.

- (1) Sodium when dropped in alcohols liberates hydrogen gas.



- (2) Alcohols react with acetic acid to give very sweet smelling esters.

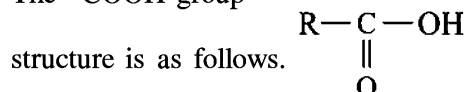


9.14 CARBOXYLIC ACIDS

Carboxylic acids are formed by replacing one or more hydrogen atom in an alkane with $-\text{COOH}$ group. The general formula of alkyl alcohols is $\text{C}_n\text{H}_{2n+1}\text{COOH}$ or $\text{R}-\text{COOH}$ where R is an alkyl group. Very common carboxylic acid is acetic acid – CH_3COOH (see below)

The formulae of the first five carboxylic acids with their IUPAC names are as follows.

The $-\text{COOH}$ group



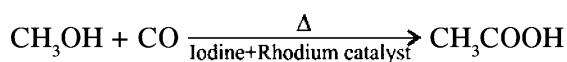
General structural formula of carboxylic acid

R has the general formula $\text{C}_n\text{H}_{2n+1}$

Alkane	IUPAC Name of acid	Common names	Molecular Formula	Structural Formula
Methane	Methanoic acid	Formic acid	HCOOH	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C}-\text{OH} \end{array} \right]$
Ethane	Ethanoic acid	Acetic acid	CH_3COOH	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}-\text{OH} \end{array} \right]$
Propane	Propanoic acid	Propionic acid	$\text{C}_2\text{H}_5\text{COOH}$	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{OH} \end{array} \right]$
Butane	Butanoic acid	Butyric acid	$\text{C}_3\text{H}_7\text{COOH}$	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}-\text{OH} \end{array} \right]$
Pentane	Pentanoic acid	Valeric acid	$\text{C}_4\text{H}_9\text{COOH}$	$\left[\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}-\text{OH} \end{array} \right]$

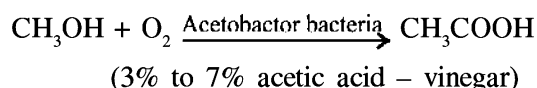
Manufacture of acetic acid

- From methanol:** Methanol vapours are mixed with carbon monoxide and passed over a heated Iodine-Rhodium catalyst.



- Preparation of vinegar**

Fermented liquor containing 10% to 15% of methyl alcohol is oxidised in the presence of a bacteria called *acetobacter* when a solution of 3% to 7% of acid is obtained. The product is called *vinegar*.



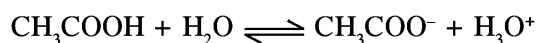
Physical properties of acetic acid

- (1) Acetic acid is a colourless, corrosive acid with a typical smell and a sour taste.
- (2) **Glacial acetic acid:** Acetic acid freezes at 16.5°C to form an icy shiny mass called glacial acetic acid.
- (3) Acetic acid is a weak acid and soluble in water in all proportions.
- (4) Acetic acid is a good solvent for iodine, sulphur, phosphorous, etc.

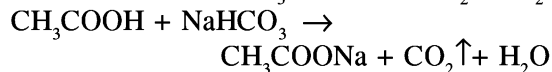
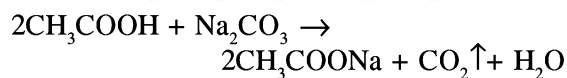
Chemical properties of acetic acid

- (1) **Acidic properties of acetic acid**

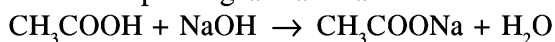
Acetic acid is a weak acid dissociating in water to form H_3O^+ ions. The H_3O^+ ions are responsible for the acidic properties.



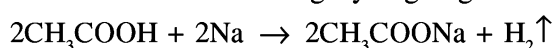
- (a) Acetic acid turns moist blue litmus red.
 (b) Acetic acid gives effervescence of CO_2 with carbonates and bicarbonates.



- (c) Acetic acid reacts with alkalis to give the corresponding acetate salts.

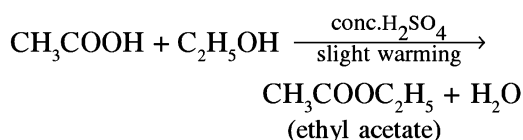


- (d) Acetic acid reacts with more electropositive metals liberating hydrogen gas.



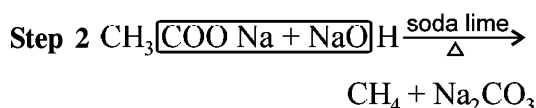
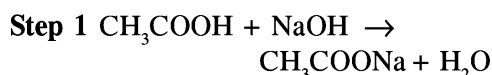
(2) Formation of esters – esterification

Acetic acid reacts with ethanol forming sweet fruity smelling esters.



(3) Decarboxylation

Decarboxylation involves removal of CO_2 from the $-\text{COOH}$ group from an organic acid. Decarboxylation is done by first converting the acid to a salt and then boiling with alkali.



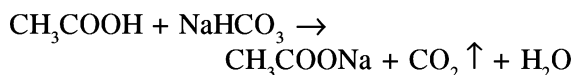
Uses of acetic acid

- (1) Acetic acid is used as a preservative as vinegar.

- (2) Acetic acid is used to make cellulose acetate used in making synthetic fibres.
 (3) Acetic acid is used as a solvent.
 (4) Acetic acid is used to make acetone, esters (for use in perfumes), drugs, dyes, etc.
 (5) Acetic acid is used to make lead acetate (for use in paints).
 (6) Aluminium acetate and chromium acetate are used as mordants in paints. Mordants fix the dye to the fabric.
 (7) Acetic acid is used as a coagulant of rubber

Test for acetic acid

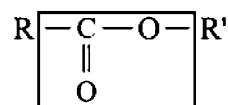
- (1) Acetic acid turns moist blue litmus red.
 (2) Acetic acid reacts with carbonates and bicarbonates to give effervescence of CO_2 .



9.15 ESTERS

The functional group in esters is $-\text{COO}-$.

The structure is



In an ester functional group in between two alkyl groups

When an alcohol reacts with an organic acid, they give esters with the general formula $\text{R}-\text{COO}-\text{R}'$, where $\text{R}-$ and $\text{R}'-$ are alkyl groups.

Some esters and the parent acid and parent alcohol from which they are formed with their IUPAC names are:

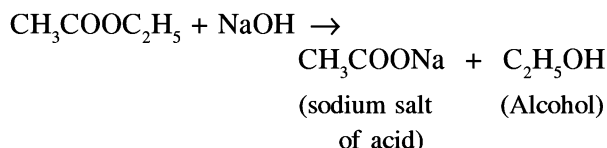
Parent Acid		Parent alcohol		Ester formula
(i) CH_3COOH	+	CH_3OH	$\rightarrow$	$\text{CH}_3\text{COOCH}_3 + \text{H}_2\text{O}$ (methyl acetate)
(ii) $\text{C}_2\text{H}_5\text{COOH}$	+	CH_3OH	$\rightarrow$	$\text{C}_2\text{H}_5\text{COOCH}_3 + \text{H}_2\text{O}$ (methyl propionate)
(iii) $\text{C}_2\text{H}_5\text{COOH}$	+	$\text{C}_2\text{H}_5\text{OH}$	$\rightarrow$	$\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$ (ethyl propionate)

Test for Esters

When phenolphthalein (pink in colour) is added to esters to which dilute NaOH is added, pink colour disappears.

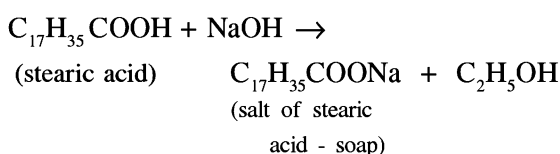
Hydrolysis of Esters

When an ester, $\text{R}-\text{COO}-\text{R}'$, is treated with NaOH , R' in the ester is replaced by Na forming a salt and also alcohol:



Saponification: When higher acids with large number of C-atoms in them (fatty acids) are hydrolysed with inorganic bases like NaOH, they form the corresponding salts of the fatty acids called *soaps* as they have cleansing action. This reaction is called **Saponification**.

Example:



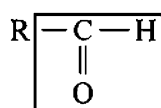
Uses of Esters

- Esters are good organic solvents and are used as such in medicines like antibiotics.
- Esters are used in plastics
- Esters have a sweet fruity smell and are used as flavours / essences in ice creams, cold drinks, etc.

Ester	Flavour
(i) Amyl acetate	Banana
(ii) Octyl acetate	Orange
(iii) Isoamyl acetate	Apple
(iv) Methyl Butyrate	Pineapple

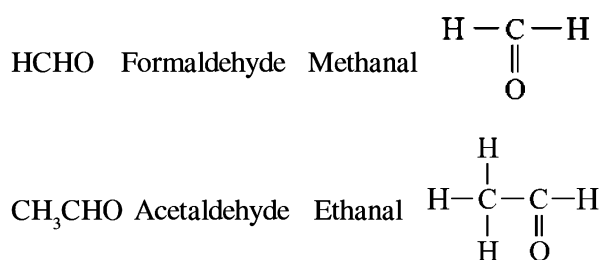
9.16 ALDEHYDES

The functional group present in aldehydes is $-\text{CHO}$. Aldehydes are known as per IUPAC rules as **Alkanals**. The structure is



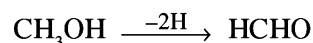
Aldehyde functional group R is an alkyl group

The names and formulae of two aldehydes are given.



General method of preparation of aldehydes

Aldehydes can be prepared by removing two H - atoms from an alcohol



Uses

- Aldehydes are used to make disinfectants.
- Aldehydes are the starting material for making *Bakelite*, which is used as an insulator.
- Aldehydes are used for silvering of mirrors.
- As formaldehyde is a gas and highly soluble in water, a 40% aqueous solution called *formalin* is used for storing biological specimens.

Test for Aldehydes

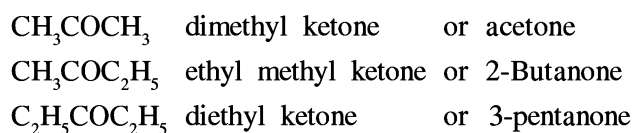
Aldehydes give a silver mirror when warmed with Tollen's Reagent (ammoniacal AgNO₃).

9.17 KETONES

The functional group is $-\text{C}=\text{O}-$ (carbonyl group). They are known as per IUPAC rules as **Alkanones**.

The general formula is $\text{R}-\overset{\text{O}}{\parallel}\text{C}-\text{R}'$. The general formula of carbonyl compounds (aldehydes and ketones) is $\text{C}_n\text{H}_{2n}\text{O}$ (where $n = 1, 2, 3, \dots$)

Ketones have a pleasant smell. Some ketones with their IUPAC names are :



Iodoform test for Ketones: On treating ketones with Iodine + NaOH they give a yellow precipitate.

9.18 SOME OTHER FUNCTIONAL GROUPS

Ethers: The functional group is $-\text{C}-\text{O}-\text{C}-$. The general formula is $\text{R}-\text{O}-\text{R}'$.

Example: Dimethyl ether is $\text{CH}_3-\text{O}-\text{CH}_3$

Amines: The functional group is $-\text{C}-\text{NH}_2$. The general formula is $\text{R}-\text{NH}_2$.

Example: Propyl amine is $\text{C}_3\text{H}_7\text{NH}_2$.

9.19 SOME IMPORTANT POINTS TO REMEMBER

- * Carbon exhibits allotropy. Diamond, graphite and fullerenes are some important allotropic forms of carbon.

- * In diamond, carbon atoms are arranged in tetrahedral structure. Each carbon is attached to four other carbon atoms.
- * In graphite, carbon atoms are arranged in hexagonal structure. Many hexagons form a graphite layer.
- * C_{60} or Buckminster fullerene has a football like structure containing pentagon and hexagon rings.
- * Carbon exhibits unique properties like catenation and isomerism
- * Petroleum, coal, wood and natural gas are the main sources of carbon compounds.
- * Distillation of petroleum gives varieties of carbon compounds.
- * Dry distillation of coal gives many important carbon compounds.
- * The compounds of carbon and hydrogen are called hydrocarbons.
- * Hydrocarbons are classified into saturated and unsaturated hydrocarbons.
- * Alkanes are saturated hydrocarbons.
- * Unsaturated hydrocarbons contain one or more double or triple bonds between carbon atoms.
- * Alkenes, alkynes and benzene are unsaturated hydrocarbons.
- * Some unsaturated hydrocarbons undergo polymerization.
- * A group of atoms in carbon compounds showing characteristic properties is called functional group.
- * Alcohol (-OH), aldehyde (-CHO), Ketone ($>C=O$), acid (-COOH), ester (-COOR) and amine ($-NH_2$) are some important functional groups.

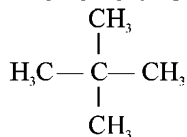
EXERCISE

I. Choose the correct answer

(1) Isobutyl group is

- (a) $CH_3 - CH_2 - CH_2 - CH_2 -$
 (b) $CH_3 - \underset{\substack{| \\ CH_3}}{CH} - CH_2 - CH_3$
 (c) $CH_3 - \underset{\substack{| \\ CH_3}}{CH} - CH_2 -$
 (d) $CH_3 - \underset{\substack{| \\ CH_3}}{\overset{\substack{CH_3 \\ |}}{C}} -$

(2) The correct IUPAC name of



- (a) Neopentane (b) Dimethyl propane
 (c) Methyl butane (d) Tertiary pentane

(3) False statement regarding Isopentane is

- (a) It has 3 CH_3 groups
 (b) It has one CH_2 group
 (c) It has one CH group
 (d) It has a carbon atom which is not bonded to hydrogen

(4) IUPAC name of $HCOOH$ is

- (a) Formic acid (b) Methanoic acid
 (c) Ethanoic acid (d) Alkanoic acid

(5) The IUPAC names of alcohol and that of aldehyde are respectively

- (a) Alkanol, alkanal (b) Alkanal, alkanol
 (c) Alkanone, Alkanal
 (d) alkanal, Alkanone

(6) The IUPAC name of acetic acid is

- (a) ethanoic acid (b) methanoic acid
 (c) vinegar acid (d) glacial acetic acid

(7) Excited state configuration of carbon is

- (a) $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^3$
 (b) $1s^2 2s^1 2p_x^2 2p_y^1 2p_z^0$
 (c) $1s^2 2s^1 2p^3$ (d) $1s^2 2s^2 2p^2$

(8) The number of possible isomeric structure for the formula C_4H_{10} is

- (a) 10 (b) 1 (c) 2 (d) 4

(9) The main source of organic compounds is

- (a) vegetable kingdom
 (b) synthetic reaction
 (c) animal kingdom (d) petroleum

(10) Which of the following organic compounds was first synthesized?

- (a) urea (b) ethylene
 (c) methane (d) acetic acid

(11) The suffixes for alcohols, aldehydes and ketones according to IUPAC system are respectively

- (a) -alc, -aid, -ket (b) -ol, -al, -ket
 (c) -ol, -al, -one (d) -coh, -aid, -one

- (12) From which of the following can ethane be prepared?
 (a) methyldehydride (b) sodium propionate
 (c) methanol (d) all of the above
- (13) A compound X produces methane when treated with water, X can be
 (a) aluminium nitride
 (b) calcium carbide
 (c) aluminium carbide
 (d) calcium phosphide
- (14) Decarboxylation of sodium propionate using soda lime produces
 (a) propane (b) ethane
 (c) methane (d) butane
- (15) Point out the compound out of the following which has the lowest boiling point
 (a) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_3$
 (b) $(\text{CH}_3)_2 - \text{CH} - \text{C}_2\text{H}_5$
 (c) $\text{CH}_3 - \text{CH}_3$
 (d) $\text{CH}_3 - \text{CH}_2 - \text{CH}_3$
- (16) Which of the following hydrocarbon is liquid at room temperature?
 (a) ethane (b) methane
 (c) hexane (d) butane
- (17) Marsh gas contains which of the following
 (a) C_2H_5 (b) CH_4 (c) H_2S (d) C_2H_4
- (18) The order of reactivity of halogens in aliphatic substitution reactions is
 (a) $\text{Br}_2 > \text{Cl}_2 > \text{F}_2$ (b) $\text{Cl}_2 > \text{Br}_2 > \text{F}_2$
 (c) $\text{F}_2 > \text{Cl}_2 > \text{Br}_2$ (d) $\text{F}_2 > \text{Br}_2 > \text{Cl}_2$
- (19) Which one of the following reagents distinguishes ethylene from acetylene?
 (a) aqueous alkaline KMnO_4
 (b) Cl_2 dissolved in CCl_4
 (c) ammoniacal Cu_2Cl_2
 (d) conc. H_2SO_4
- (20) Acetylene reacts with ammonical silver nitrate to form
 (a) Silver mirror (b) Metal silver
 (c) Silver acetate (d) Silver acetylide
- (21) Which gaseous hydrocarbon is produced when calcium carbide reacts with water?
 (a) methane (b) ethene
 (c) ethylene (d) acetylene
- (22) The product formed when acetylene is passed through red hot tube is
 (a) benzene (b) cyclohexane
 (c) neoprene (d) ethane
- (23) A metallic carbide on treatment with water gives a colourless gas which burns readily in air and gives a precipitate with ammonical silver nitrate. The gas is
 (a) methane (b) ethene
 (c) ethyne (d) propane
- (24) Ethylene may be obtained by the treatment of concentrated H_2SO_4 and X at $160 - 170^\circ\text{C}$. X is
 (a) $\text{C}_2\text{H}_5\text{OH}$ (b) CH_3OH
 (c) $\text{C}_3\text{H}_7\text{OH}$ (d) $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
- (25) Alcohol fermentation is brought about by the action of
 (a) CO_2 (b) O_2
 (c) invertase (d) yeast
- (26) A fruity smell is obtained by the reaction of ethanol with
 (a) PCl_5 (b) CH_3COCH_3
 (c) CH_3COOH (d) none of these
- (27) Methanol and alcohol are
 (a) soluble in water
 (b) soluble in water on heating
 (c) insoluble in water
 (d) insoluble in all solvents
- (28) Which of the following is not a characteristic of alcohol?
 (a) They are lighter than water
 (b) Their boiling point rise fairly uniformly with rising molecular weight
 (c) Lower members are insoluble in water and organic solvents but the solubility regularly increases with molecular mass
 (d) Lower members have a pleasant smell and burning taste, higher members are colourless and tasteless.
- (29) Ethanol containing some methanol is called
 (a) absolute spirit (b) rectified spirit
 (c) power alcohol (d) methylated spirit
- (30) Which of the following alcohol is used in beverages?
 (a) propanol (b) 2-butanol
 (c) methanol (d) ethanol
- (31) Rectified spirit is a mixture of
 (a) 95% ethyl alcohol + 5% water
 (b) 94% ethyl alcohol + 4.53% water
 (c) 94.4% ethyl alcohol + 5.43% water
 (d) 95.87% ethyl alcohol + 4.13% water.
- (32) Methanol is manufactured by passing water gas with excess of hydrogen over
 (a) platinised asbestos (b) hot COCl_2
 (c) finely divided Ni
 (d) a hot mixture of Zn and Cr_2O_3

- (33) Methyl alcohol on oxidation with acidified $K_2Cr_2O_7$ gives
 (a) CH_3COCH_3 (b) CH_3CHO
 (c) $HCOOH$ (d) CH_3COOH
- (34) The products A and B of the reaction
 $CH_3OH \xrightarrow[300^\circ C]{Cu} A \xrightarrow{NaOH} B$ are
 (a) CH_3OH (b) $HCOONa$
 (c) both (a) and (b) (d) none of these
- (35) In the esterification reaction of alcohols
 (a) H^+ of alcohols is replaced by CH_3CO group
 (b) OH^- of alcohols is replaced by CH_3CO group
 (c) H^+ of alcohols is replaced by Na metal
 (d) OH^- of alcohols is replaced by CH_3COO group
- (36) Which of the following alcohols is made by fermentation?
 (a) methanol (b) ethanol
 (c) glycol (d) propanol
- (37) Widespread deaths due to liquor poisoning is due to
 (a) pyridine (b) methyl alcohol
 (c) ethyl alcohol (d) propyl alcohol
- (38) The element which can theoretically catenate like Carbon is
 (a) Si (b) P (c) S (d) Fe
- (39) Each consecutive member in a homologous series differs by a
 (a) $-CH_2$ group (b) $-OH$ group
 (c) $-C_2H_4$ group (d) $-CH_3$ group
- (40) The general formula of alcohols is
 (a) $C_nH_{2n+2}OH$ (b) $C_nH_{2n}OH$
 (c) C_nH_{2n-2} (d) $C_nH_{2n+1}OH$
- (41) The organic equivalent of a neutralisation reaction between an acid and base is _____ reaction.
 (a) carbonation
 (b) inversion of cane sugar
 (c) esterification (d) halogenation
- (42) The first bond that is broken easily in an addition reaction is a
 (a) sigma bond (b) pi bond
 (c) single bond (d) all three
- (43) The correct order of strength of the bonds is
 (a) $C-C < C=C < C\equiv C$
 (b) $C-C > C=C < C\equiv C$
 (c) $C-C > C=C > C\equiv C$
 (d) $C-C < C=C > C\equiv C$
- (44) If ethyl alcohol is heated with conc. H_2SO_4 the product formed is
 (a) $CH_3-COOC_2H_5$ (b) C_2H_6
 (c) C_2H_4 (d) C_2H_2
- (45) Tollen's Reagent gives white precipitate with
 (a) formaldehyde (b) acetaldehyde
 (c) formic acid
 (d) all the three (a, b and c)
- (46) The colourless gas liberated when sodium reacts with methanol is
 (a) CO_2 (b) CO (c) H_2 (d) $CO + H_2$
- (47) The number of sigma and pi bonds present in ethyne molecule is
 (a) one sigma, one pi
 (b) two sigma, one pi
 (c) one sigma, two pi
 (d) two sigma, two pi
- (48) The false statement regarding homologous series is
 (a) they have the same general formula
 (b) they have same general methods of preparation
 (c) they have graded physical properties
 (d) they have different chemical properties
- (49) The compound that does not exhibit structural isomerism is
 (a) C_4H_{10} (b) C_3H_8
 (c) C_5H_{12} (d) C_6H_{14}
- (50) For complete chlorination of one mole of ethane the number of moles of chlorine gas required is
 (a) 3 (b) 6 (c) 5 (d) 4

II. Choose the correct word.

- (a) The catalyst used in the conversion of ethene to ethane is commonly _____ (iron / cobalt / nickel)
 (b) The vapour density of the seventh member of the homologous series of alkanes is _____ (100 / 50 / 25)
 (c) The isomer of pentane which has a C-atom attached to four other C-atoms is _____ (n-pentane / iso-pentane / neo-pentane)
 (d) The IUPAC name of methyl acetylene is _____. (1-butyne / propyne / ethyne)
 (e) The functional group in ethanoic acid is _____. (aldehyde / carboxyl / hydroxyl)
 (f) The alkanes form a homologous series with the general formula _____ (C_nH_{2n} / C_nH_{2n-2} / C_nH_{2n+2})

- (g) The conversion of ethanol to ethene is an example of _____ (dehydration / dehydrogenation)
- (h) Converting ethanol to ethene requires the use of _____ (concentrated hydrochloric acid / concentrated nitric acid / concentrated sulphuric acid)
- (i) The conversion of ethene to ethane is an example of _____ (hydration / hydrogenation)
- (j) The IUPAC name of the product of reaction of ethylene with hydrogen bromide is _____.
(ethyl dibromide / bromoethane dibromoethane)
- (k) All the bonds between the carbon atoms are _____ bonds in alkanes. (sigma / pi / sigma and pi)
- (l) Alkanes are _____ hydrocarbons and undergo _____ reactions. (saturated / unsaturated / addition / substitution)
- (m) Ethyne gives a red precipitate of _____ with an ammoniacal solution of _____ (CuCl / AgNO_3 / Cu_2C_2 / Ag_2C_2)
- (n) _____ are compounds that have the same molecular mass. (homologues / isomers)
- (o) Five carbon atoms can form _____ different chains. (2 / 3)
- (p) Ethane can be prepared from _____ (sodium acetate / sodium propionate).
- (q) Methane can be obtained by the action of water on _____ carbide. (aluminium / calcium)

III. Match the following.

- (1) Match the homologous series in Column I with their general formula in Column II.

Column I	Column II
(a) alkanes	(i) C_nH_{2n}
(b) simple carboxylic acids	(ii) $\text{C}_n\text{H}_{2n-2}$
(c) alkene	(iii) $\text{C}_n\text{H}_{2n+2}$
(d) alkyne	(iv) $\text{C}_n\text{H}_{2n+1}\text{COOH}$

- (2) Match the homologous series in Column I with the general tests in Column II used to identify them.

Column I	Column II
(a) Ketones	(i) with bicarbonates give effervescence of CO_2
(b) Alkynes	(ii) with Na liberates hydrogen
(c) Alcohols	(iii) with iodine + NaOH give yellow precipitate
(d) Acids	(iv) decolourises bromine solution.

- (3) Match the functional groups given in Column I with the IUPAC names in Column II.

Column I	Column II
(a) - CHO	(i) Ether
(b) - CO -	(ii) Alkanals
(c) - C-NH ₂	(iii) Alkanones
(d) - C-O-C	(iv) Amines

- (4) Match the organic compound whose molecular formula is given in Column I with the possible homologous series the compound belongs to in Column II. More than one match is possible.

Column I	Column II
(a) $\text{C}_2\text{H}_6\text{O}$	(i) carboxylic acids
(b) $\text{C}_2\text{H}_4\text{O}_2$	(ii) ethers
(c) $\text{C}_3\text{H}_8\text{O}$	(iii) esters
(d) $\text{C}_3\text{H}_6\text{O}_2$	(iv) alcohols

IV. State whether the following statements are True or False

- (1) The main sources of organic compounds are petroleum and natural gas.
- (2) The alkane obtained by heating the sodium salt of a carboxylic acid with soda lime contains the same number of carbon atoms as in the acid.
- (3) Chloroform is trichloromethane.
- (4) Alkanes undergo polymerization reactions.
- (5) Ethane gives a red precipitate with ammoniacal CuCl .
- (6) Ethyne is more reactive than ethane.
- (7) An alkene forms an addition compound with Cl_2 .

- (8) The product of the addition reaction between $\text{CH}_3 - \text{CH} = \text{CH}_2$ and HCl is $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$.
- (9) Ethene is obtained by the dehydration of ethanol.
- (10) Alkynes do not undergo addition reactions.
- (11) Alkenes are also called olefins.
- (12) The common catalyst in the hydrogenation of alkenes and alkynes is nickel.
- (13) Both ethylene and acetylene can be used for the ripening of fruits.
- (14) All hydrocarbons are combustible.
- (15) Polyethylene ($-\text{CH}_2 - \text{CH}_2 -$)_n is an alkane.

V. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A : if Statement A is true, Statement R is true, Statement R is correct explanation for statement A

Choose B : if Statement A is true, statement R is true; Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D : if Statement A is false, statement R is true

- (1) **Statement –A :** Unsaturated compounds burn with a sooty flame.
Statement –R : The percentage of oxygen in air is decreasing.
- (2) **Statement –A :** Saturated hydrocarbons have higher calorific value compared to unsaturated hydrocarbons.
Statement –R : The percentage of hydrogen is more in saturated hydrocarbons.
- (3) **Statement –A :** Alkanes cannot undergo addition reactions.
Statement –R : Addition reactions require more energy than substitution reactions.
- (4) **Statement –A :** Alkanes with $n < 4$ do not show isomerism.
Statement –R : In alkanes with $n < 4$ number of possible positions of the atoms is only one in each case.
- (5) **Statement –A :** Alkenes and alkynes undergo substitution reaction in preference to addition reactions.
Statement –R : The double or triple bond is easier to break.

- (6) **Statement –A :** Graphite conducts electricity.

Statement –R : In graphite the fourth valency of each C-atom is loosely satisfied by weak Van der Waal's forces.

- (7) **Statement –A :** Alkenes and alkynes burn with sooty flame whereas alkanes burn with blue flame.

Statement –R : The percentage of C is more in alkenes and alkynes.

- (8) **Statement –A :** The bond at which addition takes place is unsaturated.

Statement –R : A saturated bond cannot be broken.

- (9) **Statement –A :** Diamond is a poor conductor of electricity.

Statement –R : All four valencies of each Carbon atom in diamond are satisfied by strong covalent bonds.

- (10) **Statement –A :** A sure test to distinguish between CO and CO_2 is to pass the gases through limewater.

Statement –R : Only CO_2 gas reacts with limewater.

VI. Answer the following questions.

- (1) Give the characteristics of organic compounds.
- (2) State three characteristics that show same or graded similarity and two characteristics that show variation in a given homologous series.
- (3) Name the following using IUPAC nomenclature. Also state the functional group.
 - (a) $\text{C}_2\text{H}_5 - \text{OH}$
 - (b) $\text{CH}_3 - \text{C} - \text{CH}$
 - (c) $\text{H}_3\text{C} - \text{CH} = \text{CH}_2$
 - (d) $\text{H}_3\text{C} - \text{CHO}$
 - (e) $\text{H} - \text{COOH}$
 - (f) $\text{CH}_3 - \text{COOH}$
 - (g) $\text{H}_2\text{C} = \text{CH}_2$
 - (h) $\text{C}_2\text{H}_5 - \text{Cl}$
 - (i) $\text{CH}_3 - \text{CO} - \text{CH}_3$
- (4) State which are saturated and unsaturated organic compounds.
 CH_4 , C_2H_6 , C_3H_4 , $\text{C}_3\text{H}_7\text{OH}$, HCHO
- (5) Effect the following conversions: bromoethane to ethane and cane sugar to ethanol.
- (6) State the products formed when ethene reacts with HBr , conc. H_2SO_4 , O_3 , cold dilute KMnO_4
- (7) Name the products formed when ethyne reacts HBr , ammonical cuprous chloride, and ammonical silver nitrate.

- (8) What are the controlled oxidation products of ethane?
- (9) Give a chemical test to distinguish between ethene and ethyne.
- (10) Which of the following give addition reactions: C_4H_{10} , C_2H_6 , C_2H_4 , CH_4 , C_3H_8
- (11) Why C_2H_2 decolourises bromine water but not methane?
- (12) What change is observed when bromine water is added to C_2H_6 , C_3H_6 and C_4H_6 .
- (13) What reaction takes place in oxy-acetylene torch?
- (14) If 3 unlabelled jars have C_2H_6 , C_2H_4 and C_2H_2 how would you identify the gases?
- (15) What are the chemical reactions for polymerisation in ethyne?
- (16) Which of the following decolourises bromine water: C_2H_4 , C_2H_6 , C_2H_2 , C_3H_8 , C_3H_6 ?
- (17) Write electron dot formula of ethyne.

KEY TO EXERCISE									
I.	1. c	2. b	3. d	4. b	5. a	6. a	7. c	8. c	9. b
	10. a	11. c	12. b	13. c	14. b	15. c	16. c	17. b	18. c
	19. c	20. d	21. d	22. a	23. c	24. a	25. d	26. c	27. a
	28. c	29. d	30. d	31. d	32. d	33. c	34. d	35. a	36. b
	37. b	38. a	39. a	40. d	41. c	42. b	43. c	44. c	45. d
	46. c	47. c	48. d	49. b	50. a				
II.	a. nickel	b. 50	c. neo pentane	d. propyne	e. carboxyl				
	f. C_nH_{2n+2}	g. dehydration		h. conc. sulphuric acid					
	i. hydrogenation	j. bromoethane		k. sigma	l. saturated, substitution				
	m. Cu_2C_2 , $CuCl$	n. isomers		o. 3	p. sodium propionate				
	q. aluminium								
III.	(1) a. iii	b. iv	c. ii	d. i					
	(2) a. iii	b. iv	c. ii	d. i					
	(3) a. ii	b. iii	c. iv	d. i					
	(4) a. ii, iv	b. i, iii	c. ii, iv	d. i, iii					
IV.	1. true	2. false	3. true	4. false	5. false	6. true	7. true	8. true	
	9. true	10. false	11. true	12. true	13. true	14. true	15. false		
V.	1. C	2. A	3. C	4. A	5. D	6. A	7. A	8. C	
	9. A	10. C							

10

Carbohydrates, Proteins, Fats and Oils

10.0 INTRODUCTION

Many organic compounds occur in the living world as bio-molecules. These bio-molecules fulfill various functions. Carbohydrates are organic compounds containing carbon, oxygen and hydrogen and are a source of energy for all living beings. Fats and oils are also organic compounds containing carbon, oxygen and hydrogen and are a store house of energy for all living beings. Proteins are organic compounds containing carbon, oxygen, hydrogen and nitrogen and are important for growth, development and maintenance of living tissues. This chapter deals with the chemistry of carbohydrates, proteins, oils and fats.

10.1 CARBOHYDRATES

Carbohydrates are organic compounds containing carbon, hydrogen and oxygen atoms. They are

important for metabolic activities. Carbohydrates contain carbon chains to which hydroxyl groups are attached. They also have aldehyde or ketone groups attached to the chain. Carbohydrates are therefore known as *polyhydroxy aldehydes* or *polyhydroxy ketones* (poly means many). The central chain is of carbon atoms.

Examples:

- (1) Starch - The simplest form of storing energy in plants and animals is in the form of *starch* which is a carbohydrate.
- (2) The structure of all cells is made of *cellulose* which is a carbohydrate.

Classification of carbohydrates:

Carbohydrates can be classified in two ways.

Carbohydrates		
Sugars		Non-sugars (cellulose)
Aldoses (glucose)	Ketoses (fructose)	

Carbohydrates		
Monosaccharides	Oligosaccharides	Polysaccharides

Aldoses and ketoses

Carbohydrates are classified simply by their taste into *sugars* and *non-sugars*.

Cellulose is a non-sugar carbohydrate and has the formula $(C_6H_{10}O_5)_n$ where n is a large number in the thousands.

Sugars are of two types – aldoses and ketoses.

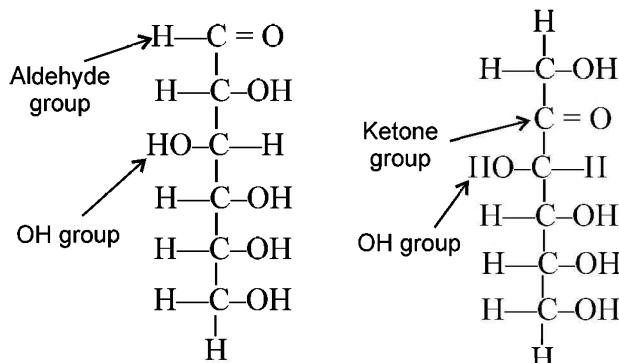
Aldoses are carbohydrates with aldehyde functional group in the molecule.

Example: Glucose

Ketoses are carbohydrates with ketone functional group in the molecule.

Example: Fructose

The structures of glucose and fructose are as follows.



Glucose	Fructose
Glucose has an aldehyde group and five OH group attached to the carbon chain. Hence Glucose is a polyhydroxy aldose.	Fructose has a ketone group and five OH groups attached to the carbon chain. Hence fructose is a polyhydroxy ketose.

Relative sweetness of sugars

All sugars are not equally sweet. Sugars are compared with sucrose which is considered as 100 on the sweetness scale. Fructose is the sweetest of all sugars.

Sugar	Relative sweetness
Sucrose	100
Glucose	74
Fructose	173
Maltose	32
Lactose	16

The other method of classifying carbohydrates is as saccharides.

(a) Monosaccharide

Monosaccharides are the simplest form of carbohydrates that cannot be *hydrolysed* further into simpler carbohydrates.

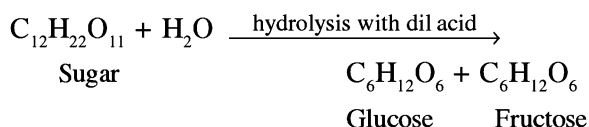
Example: glucose, fructose.

(b) Oligosaccharides: (*Oligo* = *many*) are carbohydrates that on hydrolysis give two to nine simpler carbohydrates.

Examples: Sucrose, maltose, lactose, cane sugar all with the formula – $C_{12}H_{22}O_{11}$. These carbohydrates can be hydrolysed by warming with dilute acids. On hydrolysis the above carbohydrates give two simple monosaccharides and hence are called **disaccharides**.

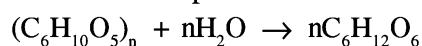
Hydrolysis of sucrose - Inversion of sugar

When sucrose is heated with dilute acids it hydrolyses into glucose and fructose. The product is called *Invert sugar* and the reaction itself is called *Inversion Reaction*.



(c) Polysaccharides: On hydrolysis they give hundreds or even thousands of simpler carbohydrates or monosaccharides.

Example: On hydrolysis of starch / cellulose dextrin is produced:



Optical activity of some carbohydrates

Many organic compounds bend light rays when they pass through them. Depending on the direction of bending they are called Dextrorotatory (if they bend the light rays to the right) or Laevorotatory (if they bend the light rays to the left). (The underlining is to make it easier to remember.

Glucose, Grape sugar or Dextrose $C_6H_{12}O_6$ is Dextrorotatory, (bends light to the right)

Fructose, Fruit sugar or Laevulose $C_6H_{12}O_6$ is Laevorotatory, (bends light to the left)

Optical isomers

Optical isomers are isomers with same formula but bend light in opposite directions when light enters them. As Glucose is Dextrorotatory and fructose is Laevorotatory, and both have the same formula ($C_6H_{12}O_6$) they are **Optical Isomers**.

Importance of carbohydrates

- (1) Carbohydrates are important products formed during photosynthesis.
- (2) Carbohydrates are important constituents of diet. They are present in several grains like rice and wheat.
- (3) Cotton and wood are primarily made up of cellulose which is another form of carbohydrate.
- Thus, it can be seen that carbohydrates are useful and important in one form or the other for food, clothing or shelter.
- (4) Some fuels are carbohydrates. For example wood can be used as a fuel.
- (5) Carbohydrates are the main source of energy for all living activity. All carbohydrates get converted to glucose which when 'burnt' in the body releases energy.

Eating carbohydrates in food provides us with energy. Some examples are given below.

Laboratory Reagents

Reagents are used in the laboratory as standard chemical substances for specific purposes like testing for the presence of other substances.

Tollen's Reagent

A mixture of $AgNO_3$ in NH_4OH is called ammoniacal silver nitrate. It is prepared by taking dilute $AgNO_3$ and adding a little amount of $NaOH$, when a grey precipitate is formed which on slowly adding NH_4OH dissolves to give ammoniacal silver nitrate.

Benedict's reagent

Benedict's solution is prepared by mixing a solution of sodium citrate and sodium carbonate with copper sulphate.

Food	Kilo calories provided by 100 gm of the food
(1) Cooked rice	110
(2) Paratha	360
(3) Green vegetables	130
(4) Bread	245
(5) Pulses	345

We require energy for various activities. The energy required to carry out some simple human activities are given below.

Activity	Calories required / 1 hour
(1) Brisk walking	288
(2) Bicycling	414
(3) Swimming (brisk)	420
(4) Running	870

Test for Glucose, Sucrose and Starch

If glucose, sucrose, and starch are kept separately in three unlabelled containers, their presence can be verified as follows using laboratory reagents.

Glucose being an aldose contains an aldehyde group.

Hence glucose will test positive, by forming a white precipitate with Tollen's reagent.

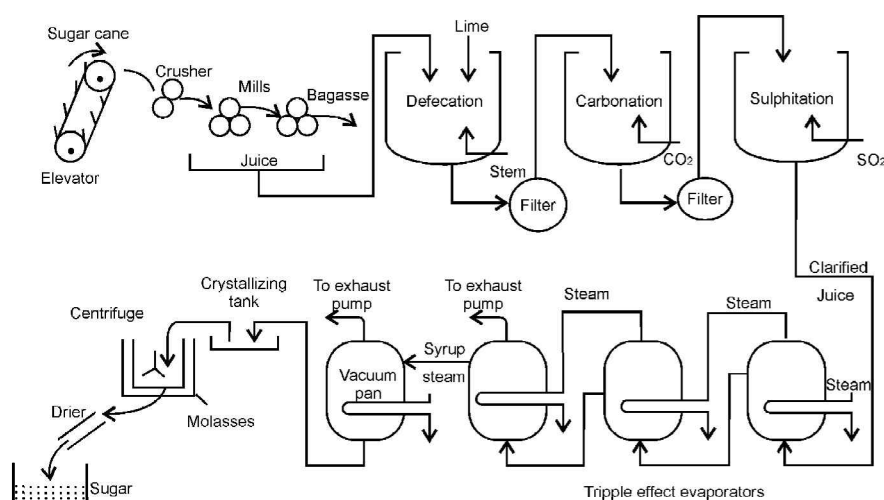
Similarly, glucose also tests positive by forming a red precipitate with Benedict's reagent. Sugar or sucrose will *test negative with both reagents*.

Iodoform Test: Presence of starch is confirmed by preparing a paste of starch and then adding hot water to get a clear solution. To this clear solution a 1% solution of iodine in alcohol is added. If starch is present, the solution turns blue.

10.2 MANUFACTURE OF SUGAR

Sugar is manufactured from sugarcane and hence called *cane sugar*. The important steps in the manufacture of sugar are as follows.

- The cane is crushed by squeezing in between heavy rollers to extract the juice. The spent cane called *bagasse* is used for manufacturing paper and cardboards or as a fuel.
- Defecation:** The cane juice will be slightly acidic. To prevent loss of sugar molecules due to hydrolysis of the juice (mainly sucrose) it is treated with lime $[\text{Ca}(\text{OH})_2]$. This process is called *defecation*. The acid gets neutralised.
- Carbonation:** Traces of excess lime, if any are removed by passing CO_2 through the juice. This process is called *carbonation*. Excess lime precipitates as carbonate.
- Sulphitation:** The juice is next treated with SO_2 to remove last traces of lime and to remove colour (bleach) of the solution. (SO_2 is a bleaching agent that bleaches by reduction).



Flow chart showing cane sugar manufacture from cane juice

- (f) **Press mud:** The precipitate obtained after defecation, carbonation and sulphitation is called *press mud*. Press mud is a very good manure and is used in the fields for farming.
- (g) **Clarified juice:** The liquid part is called *clarified juice*. Clarified juice contains 85% sugar and 15% water. The *clarified juice* is concentrated by evaporation at low pressure (nearing vacuum conditions). The *clarified juice* slowly turns into a super-saturated solution.
- (h) **Crystallisation:** The sugar is crystallized and separated by centrifugation and dried using hot air.
- (i) **Molasses:** The thick black liquid residue that is left behind is called **Molasses**. Molasses contain glucose, fructose and sucrose and other sugars to the extent of around 50-60%. It is a by-product of sugar manufacture. *Molasses are fermented to alcohol for making liquors*. Molasses are sometimes used as animal feed.

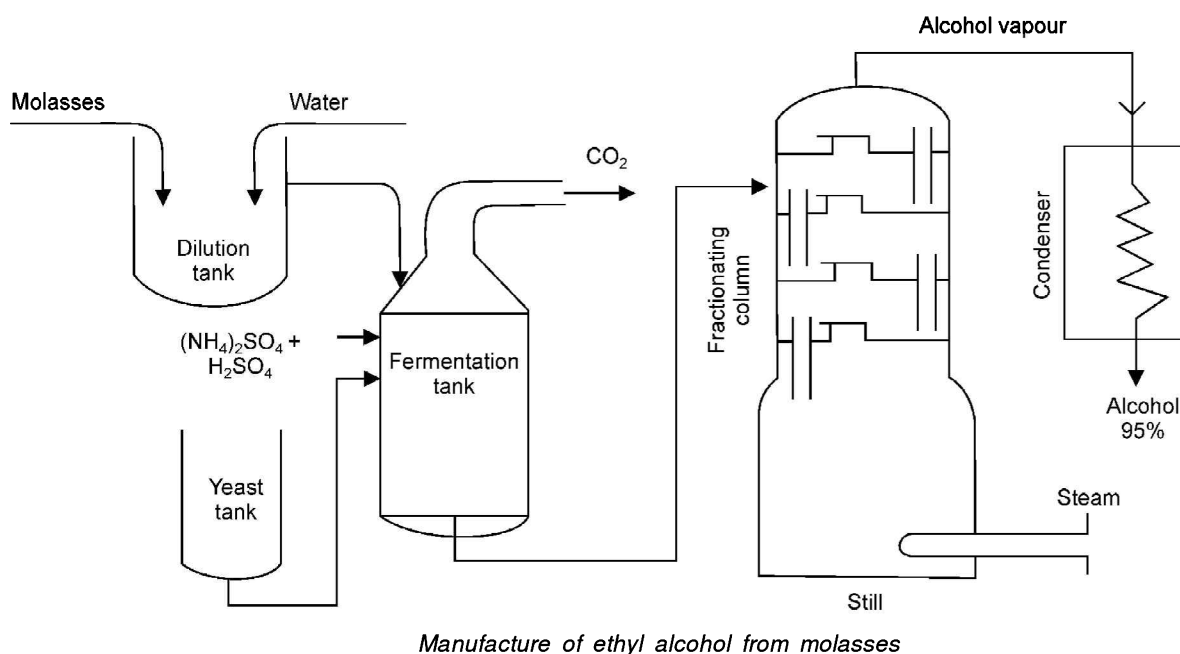
10.3 MANUFACTURE OF ALCOHOL (ETHANOL)

Ethanol is often simply called alcohol. Alcohol is manufactured on a large scale from molasses that is a by product of sugar manufacture.

The important steps in the manufacture of alcohol are as follows.

- (1) The *molasses* primarily contains glucose, fructose and sucrose in a thick solution. The molasses are diluted by adding water.
- (2) Ammonium sulphate and ammonium phosphate salts are added to the diluted mixture. This is done to allow the yeast to multiply rapidly.
- (3) Yeast is added to the mixture and the mixture is transferred to a fermentation tank.
- (4) The temperature of the mixture is maintained at 30°C for 2 to 3 days for complete fermentation.
- (5) The fermentation is done in absence of oxygen as ethyl alcohol gets oxidized to vinegar in the presence of oxygen (air).

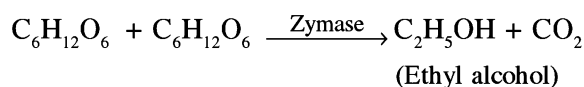
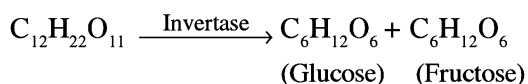
Fermentation is the process of breaking down of large molecules into small molecules by enzymatic action. **Enzymes** are bio-chemicals produced by yeast and bacteria



Fermentation reactions

Two enzymes are produced by yeast - *invertase* and *zymase* during the fermentation.

Invertase helps in the conversion of sucrose to glucose and fructose while *Zymase* helps in the conversion of these to ethyl alcohol.



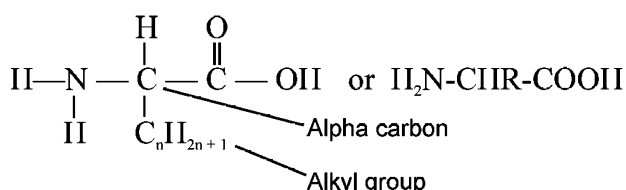
- (6) The raw product contains 15-20% alcohol (the rest being water) and is called *wash*.
- (7) The boiling point of alcohol is 35°C, while that of water is 100°C. The difference in boiling points is used to separate alcohol by *fractional distillation*.
- (8) On fractional distillation of the *wash* 96% alcohol is obtained. The 96% alcohol is called *rectified spirit*.
- (9) *Rectified spirit* is treated with lime to remove the remaining water. Pure alcohol or *absolute alcohol* (100% alcohol) is obtained.

10.4 AMINO ACIDS AND PROTEINS

Amino acids are organic compounds with carbon, hydrogen, oxygen and nitrogen atoms in them.

Amino acids have two functional groups, amine group ($-\text{NH}_2$) and carboxylic acid group ($-\text{COOH}$), attached to the carbon chain.

The general formula of amino acids is $\text{NH}_2\text{-CHR-COOH}$, where R is a hydrocarbon (that can be saturated or unsaturated).



Amino acid – structural and condensed formula

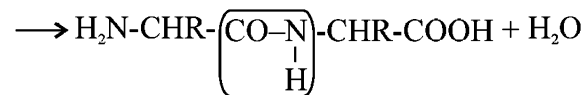
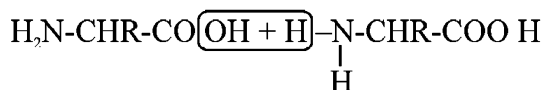
The properties of amino acids depend on the alkyl group ($-\text{R}$) attached to the carbon atom that is attached to the carboxylic acid group (see figure above). This carbon atom is known as alpha carbon atom.

Amino acids are crystalline, soluble covalent compounds with high melting points.

Polymerisation of amino acids to form peptides

When two amino acids polymerise, they eliminate a water molecule and form a peptide bond.

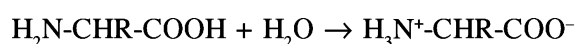
Many such amino acids join to form polypeptide. Proteins are also polypeptide molecules. Thus, amino acids are monomers of proteins.



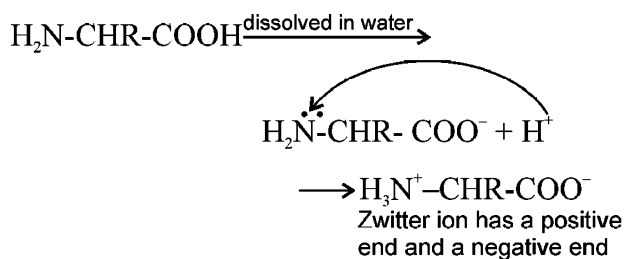
Two amino acids polymerise by eliminating a water molecule forming a peptide bond. Many such amino acids polymerise giving polypeptide.

Zwitter ion

When an amino acid is dissolved in water, the $-\text{COOH}$ group loses a proton (like acids). The H^+ ion migrates to the $-\text{NH}_2$ in the *same molecule forming a dative bond* with the lone pair of electrons on N-atom. Thus, a dipole is formed. The two poles are $-\text{COO}^-$ and $-\text{NH}_3^+$. This dipolar molecule is known as **Zwitter ion**.



Mechanism of formation of Zwitter ion

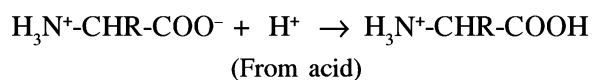


Formation of Zwitter ion

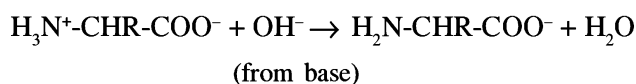
Zwitter ion is amphoteric in nature

The Zwitter ion is amphoteric in nature. It can accept or donate a proton. This results in the dipolar ion showing both acidic as well as basic properties and is responsible for the amphoteric nature of Zwitter ion.

The basic property is due to the reaction



The acidic property is due to the reaction



Essential amino acids and Non-essential amino acids

There are 26 amino acids out of which 20 amino acids are found in all proteins, while other 6 are found in special tissues. Human body can synthesise only 10 out of the 20 amino acids from the food we eat. They are thus called **non-essential amino acids** as the body can synthesise them.

The other 10 amino acids must therefore be already present in the food we eat, as we cannot synthesise the same. These amino acids are called **essential amino acids**.

All proteins are combinations of *some or all* of the 26 amino acids. For example, haemoglobin is a combination of 574 amino acids. Even if one of the amino acid is removed or changed, it makes the haemoglobin 'bad' or diseased. The haemoglobin is known as 'Sickle cell haemoglobin' and the condition is known as 'Sickle cell Anaemia'.

10.5 LIPIDS – OILS AND FATS

Lipids are waxy or oily organic compounds. They are present in all cell membranes. Lipids are classified into simple lipids and complex lipids. Simple lipids are classified into *fats / oils and waxes*. Complex lipids are classified into *phospholipids and glycolipids*. They will be discussed in higher classes.

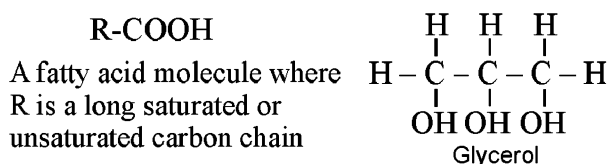
Simple lipids – fats and oils are more abundant. They are found in all living organisms.

Lipids

Simple lipids	Complex lipids
(1) fats	(1) phospholipids
(2) oils	(2) glycolipids

Generally liquid lipids are called **oils** and solid lipids are called **fats**. *Fats and oils are stored as triesters of glycerol also called triglycerides*. Triesters are formed when fatty acid reacts with glycerol.

A fatty acid molecule has a long carbon chain attached to a -COOH group. Glycerol has three OH groups substituted for H-atoms in propane molecule as shown below.



Triesters are formed when fatty organic acids react with glycerol

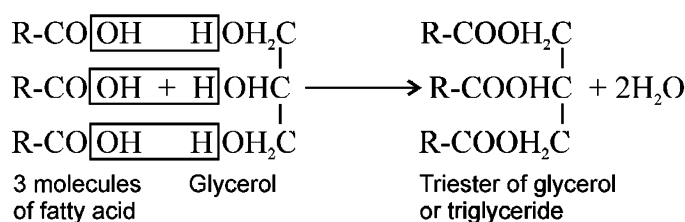
Fatty Acids

– A Saturated Fatty Acids (SFA) is a fatty acid having only single bonds.

– An Unsaturated Fatty Acid (UFA) is a fatty acid with double or triple bonds.

Number of C-atoms	Saturated Fatty Acids (SFA)– General formula $\text{-C}_n\text{H}_{2n+1}\text{COOH}$			Unsaturated Fatty Acid (UFA)– General form $\text{-C}_n\text{H}_{2n-1}\text{COOH}$		
	Name	Formula	Source	Name	Formula	Source
11	<u>L</u> auric Acid	$\text{C}_{11}\text{H}_{23}\text{COOH}$	Coconut, butter			
13	<u>M</u> yristic Acid	$\text{C}_{13}\text{H}_{27}\text{COOH}$	Coconut, whale oil	<u>M</u> yristoleic Acid	$\text{C}_{13}\text{H}_{25}\text{COOH}$	Whale oil
15	<u>P</u> almitic Acid	$\text{C}_{15}\text{H}_{31}\text{COOH}$	Butter, animal fat	<u>P</u> almitoleic Acid	$\text{C}_{15}\text{H}_{29}\text{COOH}$	Whale oil
17	<u>S</u> tearic Acid	$\text{C}_{17}\text{H}_{35}\text{COOH}$	Butter, animal fat	<u>O</u> leic Acid	$\text{C}_{17}\text{H}_{33}\text{COOH}$	Soyabean oil
17				<u>L</u> inoleic Acid	$\text{C}_{17}\text{H}_{31}\text{COOH}$	Cotton seed oil
17				<u>L</u> inoleinic Acid	$\text{C}_{17}\text{H}_{29}\text{COOH}$	Linseed oil

Mechanism of formation of triglycerides (oils and fats)

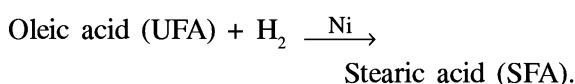


Hydrogenation of oils

Oils have unsaturated R groups while fats have saturated R groups. Oils (unsaturated) change into fats (saturated) when treated with hydrogen under high temperature and pressure in the presence of nickel as catalyst. This is called *hydrogenation of oils*.

Hydrogenation of fatty acids is an addition reaction where unsaturated fatty acids (UFA) are converted to saturated fatty acids (SFA).

Example:



Advantages of hydrogenating oils

- (1) The hydrogenated oils or fats have a higher melting point and are solids at room temperature.
- (2) Food items prepared in hydrogenated oil or fat have better taste, are preserved better and odourless.

Examples: Vanaspathi and margarine are hydrogenated oils.

Uses of Fats and Oils

- (1) **Domestic use:** cooking, hair oil, etc.
- (2) **Industrial use:** manufacture of cosmetics, soaps, paints, varnishes, leather tanning, jute, plastics and medicines.

Some specific examples and industry in which they are used are given below.

Fat / oil	Industrial use	Fat / oil	Industrial use
1. Animal fat	Soap	4. Coconut oil	Soaps, detergents
2. Linseed oil	Paints, varnishes	5. Soya bean oil	Paints, varnishes
3. Castor oil	Plastics	6. Tall oil	Soaps, Leather.

10.6 SOAPS AND DETERGENTS

Any substance that has cleansing action with water is called a detergent.

The essential function of a detergent is therefore to remove dirt. Detergents are of two types:

- (i) **Soapy detergents** that form foam
- (ii) **Non-soapy detergents** that do not form foam

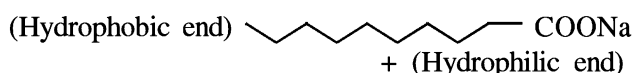
Soapy detergents are simply called *soaps* while non-soapy detergents are simply called *detergents*.

Composition of soaps

Soaps and detergents are sodium salts of fatty acids having the general formula R-COONa , where R is a saturated or unsaturated fatty chain.

Cleansing action of soap

Soap has non-ionic water-repelling end and an ionic water-loving end (Na-side). The water-hating end is called **hydrophobic end**. The dirt attaches to this end.



The water-loving end is called **hydrophilic end**. It attracts water molecules when the soap is rubbed in water forming a soluble complex **along with dirt**.

Thus the soap along with dirt is washed away. This is the reason why the water after washing looks dirty.

Examples of soap:

sodium stearate – $\text{C}_{17}\text{H}_{35}\text{COONa}$,

sodium oleate – $\text{C}_{17}\text{H}_{33}\text{COONa}$

sodium palmitate – $\text{C}_{15}\text{H}_{31}\text{COONa}$.

Manufacture of soap: The raw materials required are animal fat, caustic soda and common salt.

There are two steps involved:

- (a) Saponification or hydrolysis,
(b) Separation of salt formed.
- (a) Saponification involves boiling the fat / oil with NaOH over 2-3 hours to give sodium salt of the fatty acid.
$$\text{Fat / oil} + \text{NaOH} \xrightarrow{240^\circ\text{C, high pressure}} \text{Soap} + \text{Glycerol}.$$

(b) NaCl is added to precipitate the soap. The soap separates as a solid and floats on top. It is removed, mixed with colours and perfumes or glycerine and put in mould to form soap tablets.

The alkali used in saponification can be KOH, Mg(OH)_2 and Ca(OH)_2 instead of NaOH. The base is selected depending on end use of the soap.

Salt	Use	Salt	Use
1. K^+ salt	Toilet soap, shaving soap	4. Na^+ salt	Laundry
2. $Ca(OH)_2$, $Al(OH)_3$	Water proof texture	5. $Mg(OH)_2$	Face Powder
3. Li^+ salt	Grease	6. Glycerine	Transparent soap used in winter

Detergents vs Soaps

Hard water does not form lather with soaps easily due to dissolved calcium and magnesium ions.

Detergents react with Ca^{2+} and Mg^{2+} ions in hard water forming soluble compounds. Lather is formed easily and cleaning action is efficient. This is why detergents are used for washing and cleaning and not soaps.

Soaps however react with Ca^{2+} and Mg^{2+} ions in hard water forming insoluble compounds. The soap thus is filtered out, as precipitate preventing lather and cleaning action is inefficient.

Domestic preparation of soap

Take castor oil and add equivalent volume of NaOH.

Heat the mixture till a paste is formed. The paste is glyceryl oleate.

NaCl is now added and the solution cooled, when soap separates as solid precipitate. The soap is sodium oleate.

10.7 SOME IMPORTANT POINTS TO REMEMBER

- * The polyhydroxy aldehydes or ketones are called carbohydrates.
- * Carbohydrates can be classified in many ways.
- * They are classified as monosaccharides, disaccharides and polysaccharides based on the number of monomer units present in carbohydrates.
- * Glucose, fructose and mannose are examples of monosaccharides, sucrose and maltose are examples of oligosaccharides and starch and cellulose are examples of polysaccharides.
- * Glucose is prepared by plants by a process known as photosynthesis.
- * Glucose gives energy to the living cells.
- * Carbohydrates provide us food, clothing and shelter.

- * Glucose can be tested by Tollen's and Benedict's reagent.
- * Starch is tested with iodine solution.
- * Sugar is manufactured from sugarcane.
- * Canes are crushed to obtain juice.
- * Juice is purified by defecation, carbonation and sulphitation.
- * Juice is concentrated by evaporation of water.
- * Crystals of sugar formed by super saturation of juice are separated in centrifuges.
- * The byproducts of sugar industry are bagasse, wax, press mud and molasses.
- * Alcohol is manufactured from molasses by fermentation.
- * Fermentation is the breakdown of large molecules by microorganisms.
- * Molasses is fermented by yeast.
- * Yeast produces two enzymes, invertase and zymase.
- * Alcohol is useful in industries as solvent
- * Addiction to alcohol is harmful for health.
- * CO_2 is a byproduct of alcohol industry.
- * Amino acids contain amino (NH_2) and carboxylic acid ($COOH$) groups in a molecule.
- * Amino acids when dissolved in water form Zwitter ion. Zwitter ion is amphoteric in nature.
- * Amino acids are building blocks of proteins.
- * They are either synthesized in the living body or taken through diet.
- * Human body cannot synthesize certain amino acids called essential amino acids.
- * There are nine essential amino acids and must be supplied through diet only.
- * Proteins are polymeric compounds of amino acids.

- * The number of amino acids and their sequence make all the difference between proteins
- * Oils and fats are the trimesters of glycerol with fatty acids.
- * Lauric, stearic, oleic and linoleic acids are some examples of fatty acids.
- * Oils/fats have edible and industrial uses.

- * Oils are liquids at room temperature while fats are solids.
- * Hydrogenation of oils gives fats. Hydrogenation improves the quality of fat.
- * Soaps are salts of fatty acids.
- * Detergents produce lather even in hard water.

EXERCISE

I. Choose the correct answer

- (1) In the Tollen's test glucose reduces
 - (a) Ag metal to Ag ion
 - (b) Ag ion to Ag metal
 - (c) Cu^{2+} ion to Cu^+ ion
 - (d) Cu ion to Cu^{2+} ion
- (2) In sugar manufacture, during defecation _____ is added to remove _____.
 - (a) CO_2 , acidity
 - (b) $\text{Ca}(\text{OH})_2$, acidity
 - (c) SO_2 , acidity
 - (d) P_2O_5 , acidity
- (3) The sugar content of molasses is
 - (a) 10%
 - (b) 20%
 - (c) 50-60%
 - (d) 90%
- (4) Which of the following is the sweetest sugar?
 - (a) sucrose
 - (b) glucose
 - (c) fructose
 - (d) maltose
- (5) Glucose and fructose are isomers. The type of isomerism exhibited by them is _____ isomerism.
 - (a) structural
 - (b) optical
 - (c) functional group
 - (d) all three
- (6) The key functional group present in fats is
 - (a) ketone group
 - (b) ester group
 - (c) peptide group
 - (d) alcohol group
- (7) An alkali salt of palmitic acid is known as
 - (a) alkoxide
 - (b) ester
 - (c) soap
 - (d) epoxide
- (8) Denatured spirit is used
 - (a) as fuel
 - (b) as a drug
 - (c) as a solvent for varnishes and paints
 - (d) in food beverages
- (9) Most favourable conditions for alcoholic fermentation of sugar is
 - (a) high concentration of solution, low temperature and plenty of air supply
 - (b) low concentration of solution, high temperature and plenty of air supply
 - (c) low concentration of solution, low temperature and plenty of air supply
 - (d) high concentration of solution, low temperature and absence of air
- (10) Deaths due to liquor poisoning are mainly due to
 - (a) methyl alcohol
 - (b) ethyl alcohol
 - (c) excess CO_2
 - (d) other poisonous substances
- (11) An important by product of soap manufacture is
 - (a) sodium salts
 - (b) glycerol
 - (c) acids
 - (d) fertilizer
- (12) Long chain organic acids are called
 - (a) simple fats
 - (b) complex fats
 - (c) fatty acids
 - (d) oils
- (13) The basic difference between oils and fats is
 - (a) physical state
 - (b) presence of peptide bond
 - (c) presence of triple bond
 - (d) presence of double bond
- (14) Unsaturated fatty acids have at least one
 - (a) saturated C-atoms
 - (b) unsaturated C-atom
 - (c) dilute solutions
 - (d) none of these
- (15) Saturated fatty acids have only
 - (a) saturated C-atoms
 - (b) unsaturated C-atoms
 - (c) dilute solutions
 - (d) none of these
- (16) Hydrogenation reactions are
 - (a) Substitution reactions
 - (b) Addition reactions
 - (c) Fermentation reactions
 - (d) Neutralisation reactions
- (17) Slow decomposition of complex organic molecules into simple constituents in the presence of microorganisms is called

- (a) fermentation
(b) thermal decomposition
(c) catalytic decomposition
(d) simple decomposition
- (18) **The main gas liberated during fermentation is**
(a) CO (b) hydrogen (c) CO₂ (d) CH₄
- (19) **Zwitter ion is**
(a) acidic (b) basic
(c) amphoteric (d) neutral
- (20) **The precipitate obtained after Defecation, Sulphitation and Carbonation is called**
(a) clarified solid (b) press mud
(c) bagasse (d) molasses
- (21) **The enzyme that converts Invert Sugar to alcohol is**
(a) Invertase (b) Zymase
(c) Malt (d) Pepsin
- (22) **The raw product that contains 15-20% alcohol is called**
(a) Wash (b) rectified spirit
(c) dilute alcohol (d) spirit
- (23) **Aldoses are**
(a) polyhydroxy ketones
(b) polyhydroxy aldehydes
(c) polyhydroxy amines
(d) polyhydroxy esters
- (24) **The chief sources of edible oils is**
(a) petroleum (b) coal and coke
(c) animals and plants
(d) soaps and detergents
- (25) **Which of the following is a saturated fatty acid?**
(a) myristoleic acid (b) lauric acid
(c) palmitoleic acid (d) linoleic acid
- (26) **Detergents are useful even in hard water because**
(a) they do not react with hard water ions
(b) they react with hard water ions but do not form precipitate
(c) they destroy the hard water ions
(d) they sediment undesirable ions in hard water

II. Match the following.

- (1) Match the type of soap in Column I with the special ingredient present in it in Column II.

Column I

- (a) Deodorant soap
(b) Shaving soap
(c) Transparent soap
(d) Toilet soap

Column II

- (i) potassium salt with excess stearic acid
(ii) 3, 4, 5 tri-bromo salicylanilide
(iii) potassium salts
(iv) glycerine

- (2) Match the different intermediates in alcohol manufacture in Column I with the percentage of alcohol in Column II.

Column I

- (a) Wash
(b) Rectified Spirit
(c) Absolute Alcohol
(d) Denatured Spirit

Column II

- (i) 96% alcohol
(ii) 100% alcohol
(iii) alcohol mixed with pyridine
(iv) 15 – 20% alcohol

- (3) Match the Homologous series in Column I with the general tests in Column II used to identify them.

Column I

- (a) Amino acids
(b) Carbohydrates
(c) Alkanes
(d) Alkynes

Column II

- (i) Saturated hydrocarbons having C and H atoms only
(ii) Unsaturated hydrocarbons with C and H atoms only
(iii) Molecules having C-, H-, and O-atoms
(iv) Molecules having C-, H-, N- and O-atoms

- (4) Match the fatty acid in Column I with its formula in Column II.

Column I

- (a) Palmitoleic Acid

Column II

- (i) C₁₅H₃₁COOH

- (b) Oleic Acid
 (c) Myristic Acid
 (d) Palmitic Acid
- ii) $C_{13}H_{27}COOH$
 iii) $C_{17}H_{33}COOH$
 iv) $C_{15}H_{29}COOH$

(5) Match the carbohydrate in Column I with its description in Column II.

Column I

- (a) Glucose
 (b) Fructose
 (c) Sucrose
 (d) Cellulose

Column II

- (i) Monosaccharide, ketose
 (ii) Oligosaccharide
 (iii) Monosaccharide, aldose
 (iv) Polysaccharide

(6) Match the fatty acid in Column I with the soap it forms with NaOH in Column II.

Column I

- (a) $C_{15}H_{31}COOH$
 (b) $C_{13}H_{27}COOH$
 (c) $C_{17}H_{33}COOH$
 (d) $C_{15}H_{29}COOH$

Column II

- (i) sodium palmitoleate
 (ii) sodium oleate
 (iii) sodium palmitate
 (iv) sodium myristate

III. State whether the following statements are True or False

- (i) Glucose is a polyhydroxy ketose.
 (ii) Inversion of sugar converts sucrose to alcohol.
 (iii) Zymase ferments invert sugar to alcohol.
 (iv) Hydrogenation is invariably an addition reaction.
 (v) A soap forms lather with hard water whereas a detergent does not.

IV. Find the odd one out

- (i) sucrose, cellulose, glucose, lactose, fructose
 (ii) stearic acid, oleic acid, lauric acid, myristic acid, palmitic acid

V. Fill in the blanks

- (1) The spent cane is called _____.
 (2) _____ is used to separate the crystals of sugar and liquid juice.
 (3) _____ enzyme breaks the sucrose.
 (4) _____ enzyme breaks the glucose and fructose.
 (5) The products obtained from glucose during fermentation are _____ and _____.
 (6) _____ is the byproduct of alcohol industry.
 (7) _____ is the micro organism used for fermentation of molasses.
 (8) Sucrose is broken down into _____ and _____ during fermentation.
 (9) The formula of stearic acid is _____.

- (10) Oils are triesters of _____ and _____.
 (11) The number of monosaccharide units formed on hydrolysis of oligosaccharide is _____ to _____.
 (12) Zwitter ion is _____ in nature.

VI. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A : if Statement A is true, statement R is true, Statement R is correct explanation for statement A

Choose B : if Statement A is true, statement R is true; Statement R is not correct explanation for statement A

Choose C : if Statement A is true, Statement R is false

Choose D : if Statement A is false, statement R is true

- (1) **Statement –A:** The wash in alcohol manufacture can be concentrated by fractional distillation.
Statement –R: Alcohol has a low boiling point.
 (2) **Statement –A:** Aldoses are carbohydrates that have aldehyde group in the molecule.
Statement –R: Aldoses test negative with Tollen's Reagent.
 (3) **Statement –A:** Halogenation consists of substituting H-atoms with Cl-atoms.
Statement –R: Halogenation is an addition reaction.

- (4) **Statement –A:** $C_{17}H_{33}COOH$ is a saturated fatty acid.

Statement –R: The number of H-atoms linked to C atoms in $C_{17}H_{33}$ is minimum – i.e., 33.

- (5) **Statement –A:** For cleaning using hard water detergents are preferred.

Statement –R: Detergents are more efficacious than soaps as they form soluble salts with Ca^{2+} and Mg^{2+} .

- (6) **Statement –A:** Zwitter ion has a dative bond.

Statement –R: Zwitter ion is amphoteric in nature.

- (7) **Statement –A:** Esterification is essentially a neutralisation reaction.

Statement –2: In esterification, two alcohols react to form the ester.

- (8) **Statement –A:** Monosaccharides are simple carbohydrates that cannot be hydrolysed further.

Statement –2: Monosaccharides can be ketoses or aldoses.

VII. Answer the following questions.

- What are carbohydrates, amino acids and fats? Give the general formula or an example of each.
- How are carbohydrates classified based on their taste? Give examples of each?
- What do you understand by the term polyhydroxy aldose and polyhydroxy ketose?
- What are monosaccharide and polysaccharides?
- Mention the various steps involved in the manufacture of sugar from sugarcane.

- (6) Explain the method and purpose of defecation, carbonation and sulphitation in sugar manufacture?

- (7) What is press mud? Mention its use.

- (8) How are sugar crystals separated from juice?

- (9) What is molasses?

- (10) Write the chemical formula of ethyl alcohol?

- (11) What is meant by fermentation?

- (12) What are the enzymes produced by yeast?

- (13) What is bagasse? How is it useful?

- (14) What is clarified juice?

- (15) Why are the alcohol distilleries located at the places of much water source?

- (16) What is wash?

- (17) What is rectified spirit?

- (18) What is absolute alcohol?

- (19) What is denatured spirit?

- (20) Name the chemicals added to denature the alcohol.

- (21) Differentiate between an oil and a fat.

- (22) Write the chemical formula of oil fat.

- (23) What are the sources of oils and fats.

- (24) Mention three industrial uses of oil.

- (25) What is hydrogenation of oil?

- (26) What are the advantages of hydrogenation of oil?

- (27) What is a soap?

- (28) What is a detergent?

- (29) Write the general formula of soap and detergent?

- (30) Name 4 fatty acids?

KEY TO EXERCISE									
I.	1. b	2. b	3. c	4. c	5. d	6. b	7. c	8. c	9. d
	10. a	11. b	12. c	13. a	14. b	15. a	16. b	17. a	18. c
	19. c	20. b	21. b	22. a	23. b	24. c	25. b	26. b	
II.	(1) a. ii	b. i	c. iv	d. iii	(2) a. iv	b. i	c. ii	d. iii	
	(3) a. iv	b. iii	c. i	d. ii	(4) a. iv	b. iii	c. ii	d. i	
	(5) a. iii	b. i	c. ii	d. iv	(6) a. iii	b. iv	c. ii	d. i	
III.	i. false	ii. false	iii. true	iv. true	v. false				
IV.	i. cellulose	ii. oleic acid							
V.	1. bagasse	2. centrifugation	3. Invertase	4. zymase					
	5. alcohol and CO_2		6. press mud	7. yeast					
	8. glucose, fructose		9. $C_{17}H_{35}COOH$	10. fatty acids, glycerol					
	11. 2; 9		12. amphoteric						
VI.	(1) A	(2) C	(3) C	(4) D	(5) A	(6) B	(7) C	(8) B	

11

Stoichiometry

11.0 INTRODUCTION

The radius of the atom is of the order of 10^{-8} cm and its weight is of the order of 10^{-24} g. To deal with such small quantities is very inconvenient and difficult. To measure the radius of very small particles like the atom a more appropriate unit *angstrom unit* is used and to measure its mass *amu* is used.

The mole concept also makes chemical measurements and calculations very easy. A chemical reaction is represented in short form using a chemical equation. A chemical equation must be *balanced*. In a *balanced chemical equation* the total count of atoms of each element on the left side (reactants) is equal to the total count of atoms of each element on the right side (products side). Such a balanced chemical equation is used in calculating the weights or volumes of substances that react and the weights or volumes of the products that form. *Stoichiometry* is the branch of chemistry that deals with these calculations.

11.1 ATOMIC WEIGHT, GRAM ATOMIC WEIGHT AND GRAM-ATOM

Atomic Weight of an element is a ratio of the weight of one atom of the element to the weight of one hydrogen atom.

Gram Atomic Weight (GAW) of an element is its atomic weight expressed in grams.

Gram-atom: The weight of **one gram-atom** of an element is equal to its gram atomic weight.

Illustration 1

The **atomic weight** of carbon is 12.

The **gram atomic weight** of carbon is 12 g.

The gram atomic weight (12 g) of carbon is equivalent to **one gram-atom of carbon**.

Hence, 36 g of carbon is equivalent to 3 gram-atoms.

Conversely, 3 gram-atoms of carbon weighs 36 g.

Illustration 2

The **atomic weight** of nitrogen is 14.

The **gram atomic weight** of nitrogen is 14g.

The gram atomic weight (14g) of nitrogen is equivalent to **one gram-atom of nitrogen**.

Hence, 7 g of nitrogen is equivalent to 0.5 gram-atoms.

Conversely, 0.5 gram-atoms of nitrogen weighs 7g.

Weight of one gram atom of an element = gram atomic weight of the element

11.2 MOLECULAR WEIGHT, GRAM MOLECULAR WEIGHT AND GRAM-MOLECULE

Molecular Weight of a compound is a ratio of the weight of one molecule of the compound to the weight of one hydrogen atom.

Gram Molecular Weight (GMW) of a compound is the molecular weight expressed in grams.

Gram-molecule: The weight of **one gram-molecule** of a compound is equal to its gram molecular weight.

Illustration 1

The **molecular weight** of water is $(1 \times 2) + 16 = 18$.

The **gram molecular weight** of water is 18g.

The gram molecular weight (18g) of water is equivalent to **one gram-molecule of water**.

Hence, 108 g of water is equivalent to 6 gram-molecules.

Conversely, 6 gram-molecules of water weighs 108 g.

Illustration 2

The **molecular weight** of carbon dioxide (CO_2) is $12 + (2 \times 16) = 44$.

The **gram molecular weight** of carbon dioxide is 44g.

The gram molecular weight (44g) of carbon dioxide is equivalent to **one gram-molecule of carbon dioxide**.

Conversely, 0.25 gram-molecule of carbon dioxide weighs 11g.

**Weight of one gram molecule of a compound
= gram molecular weight of the compound**

The size of atoms and molecules is of the order of 10^{-8} cm. The weight of atoms and molecules is of the order of 10^{-24} g (see boxes).

As the weight and size of atoms and molecules are so small, dealing with a few atoms or molecules becomes very difficult as they have such small sizes and weigh so little.

To overcome this difficulty, a larger quantity called *mole* has been defined.

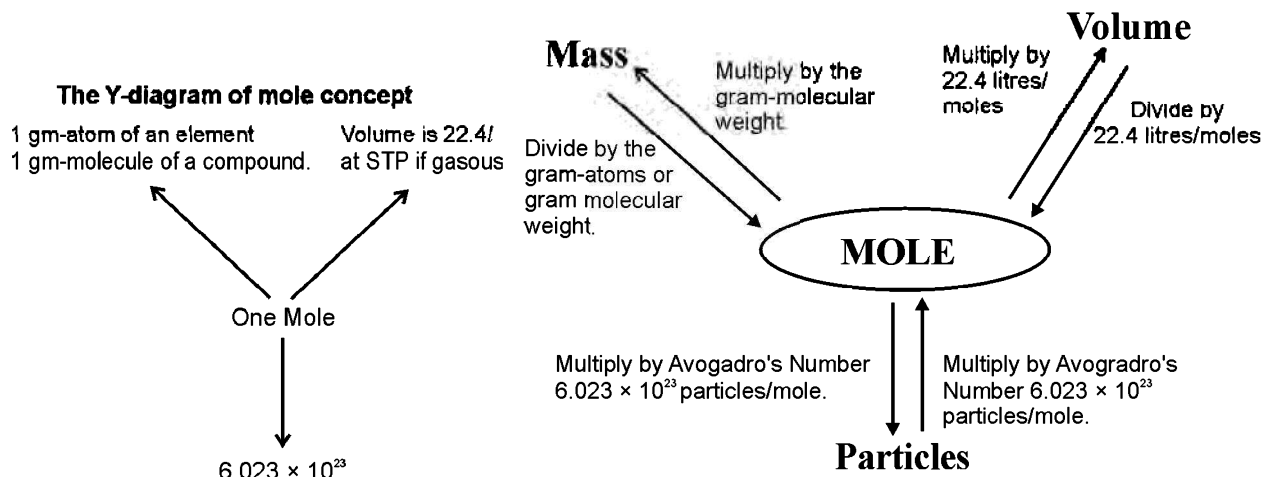
Mole: A *mole* is a number that is equal to 6.023×10^{23} . Just as 1 dozen is a number equal to 12, the mole is also a number.

This number is called **Avogadro's Number** and is denoted by N .

$$N = 6.023 \times 10^{23}$$

The mole concept gives the relationship between the mole and some of the basic quantities used in chemistry like gram-atom, gram-molecule and gram-molar volume.

The Y-diagram is an easy way to remember the relationships given by mole concept.



Using the Y-diagram above, we can state the *mole concept* as follows.

According to the *Mole Concept*

- (1) One mole of atoms (6.023×10^{23} atoms) of any element weighs 1 gram-atom.
- (2) One mole of molecules (6.023×10^{23} molecules) of any compound weighs 1 gram-molecule.

1 *mole* of atoms is equal to 6.023×10^{23} atoms.

1 *mole* of molecules is equal to 6.023×10^{23} molecules.

1 *mole* of ions is equal to 6.023×10^{23} ions.

Note: Often for the sake of simple calculations, the mole is taken as 6×10^{23} .

Imagine a length of 1metre. The length of this page is about one-third of a metre.

Imagine a length of 0.1m. (=10cm)

Next imagine a length of 0.01 metre

Next imagine 0.001metre (= 1mm)

Next imagine 0.0001 metre (0.1mm)

Next imagine a size really small:

0.0000000001m or 1 Angstrom unit - that is the order of the size of the atom!

Imagine two drops of water falling from a tap. The two drops of water weigh approximately 1gm.

Now imagine a weight of 0.1g

Next imagine a weight of 0.01g

Next imagine 0.001g

Next imagine 0.0001 g

Next imagine a size really small:

[illegible]

- (3) For gases, one mole of a gas occupies 22.4 l at STP (Standard temperature is 0°C and Standard pressure is 1 atm). This is known as **Gram Molar Volume**.

Finding the number of gram-atoms or gram-molecules

In the above diagram, to the right, simple relationships are given on how to convert one quantity into another using mole concept.

$$\text{Number of g atoms} = \frac{\text{weight in g}}{\text{Gm.At.Wt.}}$$

$$\text{Number of g molecules} = \frac{\text{weight in g}}{\text{Gm.Mol.Wt.}}$$

Loschmidt Number

1 mole of gas occupies 22.4 l at STP or 22,412 ml (to state more accurately)

Since one mole has 6.023×10^{23} molecules

22412 ml of the gas has 6.023×10^{23} molecules

∴ the number of molecules in 1 ml of gas at STP = 2.689×10^{19} per ml of gas.

This number is called **Loschmidt Number**.

Illustration 1

Consider one mole of Hydrogen.

Molecular formula of hydrogen is H_2 .

The atomic weight of hydrogen is 1.

The gram molecular weight of hydrogen is 2g.

The weight of one gram-molecule of hydrogen is 2g.

According to mole concept:

One mole of hydrogen has 6.023×10^{23} molecules of hydrogen.

One mole of hydrogen is equivalent to 1 gram-molecule of hydrogen.

One mole of hydrogen weighs 2g.

One mole of hydrogen occupies 22.4l at STP.

Since each molecule of hydrogen has two atoms of hydrogen,

One mole of hydrogen molecules has

$$2 \times 6.023 \times 10^{23} \text{ atoms} = 12.046 \times 10^{23} \text{ atoms of hydrogen.}$$

Illustration 2

Consider one mole of Helium.

Since helium is monoatomic, the molecular formula of helium is He.

The atomic weight of helium is 4.

The gram atomic weight of helium is 4g.

The weight of one gram-atom of helium is 4g.

According to mole concept:

One mole of helium has 6.023×10^{23} atoms of helium (Helium is monoatomic).

One mole of helium is equivalent to 1 gram-atom of helium.

One mole of helium weighs 4g.

One mole of helium occupies 22.4l at STP.

Illustration 3

Consider one mole of carbon dioxide.

Molecular formula of carbon dioxide is CO_2 .

The molecular weight of carbon dioxide is 44.

The gram molecular weight of carbon dioxide is 44g.

The weight of one gram-molecule of carbon dioxide is 44g.

According to mole concept:

One mole of carbon dioxide has 6.023×10^{23} molecules of carbon dioxide.

One mole of carbon dioxide is equivalent to 1 gram-molecule of carbon dioxide.

One mole of carbon dioxide weighs 44g.

One mole of carbon dioxide occupies 22.4l at STP.

Illustration 4

Consider one mole of water.

Molecular formula of water is H_2O .

The molecular weight of water is 18.

The gram molecular weight of water is 18g.

The weight of one gram-molecule of water is 18g.

According to mole concept:

One mole of water has 6.023×10^{23} molecules of water, is equivalent to 1 gram-molecule of water and weighs 18g. As water is a solid (ice) at STP we cannot calculate its volume using the mole concept.

Solved problems in mole concept

- (1) Calculate the weight of 0.4-gram atom of carbon. (C = 12)

Ans: 1gm atom of C weighs 12g

$$\therefore 0.4 \text{ gm atom weighs ? } g = 0.4 \times 12 = 4.8g$$

- (2) Calculate the weight of carbon and oxygen present in 3 moles of carbon dioxide (C=12, O=16)

Ans: 1 mole of CO_2 has 1 mole of Carbon atoms and 2 moles of Oxygen atoms.
 3 moles of CO_2 has 3 gm atoms of Carbon and 6 gm atoms of oxygen
 1 gm atom of Carbon weighs 12 g.
 3 gm atoms weighs? $\text{gm} = 3 \times 12\text{g} = 36\text{g}$
 1 gm atom of oxygen atoms weighs 16 g
 6 gm atoms of Oxygen weighs ? gm
 $= 6 \times 16 = 96 \text{ g.}$

(3) Calculate the volume occupied by 1.5×10^{22} molecules of NO_2 at NTP.

Ans: 6.023×10^{23} molecules of NO_2 at STP occupies 22.4l

1.5×10^{22} molecules NO_2 at STP occupies ? l = $\frac{1.5 \times 10^{22} \times 22.4}{6.023 \times 10^{23}} = 0.56\text{l}$

(4) Calculate the weight of 10^{24} molecules of nitric oxide. (N = 14, O = 16)

Ans: 6.023×10^{23} molecules of NO weighs (14 + 16) = 30 g

10^{24} molecules of NO weighs ? g
 $= 49.81\text{g}$

(5) What weight of calcium contains the same number of atoms as 3g of carbon? (C=12, Ca=40)

Ans: 12 g of Carbon has 6.023×10^{23} atoms
 3 g of carbon has ? atoms
 $= 1.51 \times 10^{23}$ atoms
 6.023×10^{23} atoms of calcium weighs 40 g of Ca
 1.51×10^{23} of calcium weighs ? g
 $= 10.03 \text{ g.}$

Problems on Mole Concept

- Find the weight of 4×10^{24} molecules of SO_3 gas. [S=32, O=16]
- Find the weight of 1 molecule of O_2 , 1 molecule of O_3 and 1 atom of Ag [O = 16, Ag = 108].
- Find the volumes of 0.23g of NO_2 at STP, 1.4g of CO at STP and 5.6g of N_2 at STP,
- Find the weight of 5.6dm^3 of CO_2 , 3.36dm^3 of Cl_2 gas and 7.84dm^3 of butane (C_4H_{10}) gas (at STP)

(5) Find number of moles and molecules in 6.62 g of $\text{Pb}(\text{NO}_3)_2$. [Pb=207, N=14, O=16].

(6) Find weight in g, number of moles and number of molecules in 44.8dm^3 of CO_2 gas at STP.

(7) A jar contains 7.2×10^{20} molecules of NH_3 at STP. Find number of moles, weight in g and volume in cc of the gas.

(8) A flask contains 3×10^{22} molecules of Cl_2 gas. Find number of moles, wt in g, and volume in dm^3 of Cl_2 at STP.

(9) Calculate the volume occupied by 0.5 mole of N_2 at NTP?

(10) A gas cylinder can hold 10g of H_2 or 80g of a gas under similar conditions of temperature and pressure. Find the mol. wt. of the gas.

(11) 1.12dm^3 of a gas at STP is found to weigh 3.55g. Find mol. wt. and vapour density of gas.

(12) 500cc of a gas at STP is found to weigh 0.425g. Find mol. wt. and VD of gas.

(13) A flask holds 1.75g of Hydrogen gas or 40.25g of gas 'X' under same conditions. Find mol. wt. of Gas 'X'.

(14) 4.2g of a volatile substance on sublimation has a volume of 2.4l at STP. Find molecular mass.

(15) 2.4×10^{22} atoms of an element weigh 1.32g. What would be its gram atomic weight?

(16) 11.2l of a diatomic gas weighs 16g. Find number of atoms of the element in 16g of it and the molecular mass of element.

(17) How many moles of KClO_3 on decomposition give 1 mole of oxygen?

(18) The vapour density of a gas is 35.5. Find the volume occupied by 3.55 g of the gas at NTP.

(19) What weight of nitrogen contains the same number of molecules as 11.2l of CO_2 ?

Answers to Problems on mole Concept

- 533.33g
- $5.33 \times 10^{-23}\text{g}$, $8 \times 10^{-23}\text{g}$, $18 \times 10^{-23}\text{g}$

- (3) 0.112 l , 1.12 l, 4.48 l
 (4) 11g, 10.65g, 20.3g
 (5) 0.02moles, 1.2×10^{22} molecules
 (6) 88g, 2moles, 1.2×10^{24} molecules
 (7) 0.02g, 1.2×10^{-3} moles, 26.86ml
 (8) 0.05moles, 3.55g, 1.12dm³
 (9) 11.2 l (10) 16g
 (11) 71g, 35.5 (12) 19g, 9.5
 (13) 46g (14) 39.2
 (15) 33 g (16) 6.02×10^{23} , 32
 (17) 2/3 (18) 1.12 l (19) 14g

11.5 GAY LUSSAC'S LAW OF COMBINING VOLUMES

Significant terms in

Gay-Lussac's Law of combining volumes

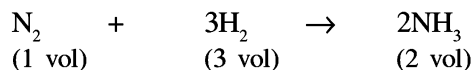
- (1) The law is applicable to reacting gases.
- (2) All volumes are measured under same conditions of temperature and pressure.
- (3) The volumes of the product are taken only if they are gaseous.

According to Gay Lussac's Law of Combining Volumes

'Whenever gases react chemically, they do so in volumes, which bear a simple ratio to each other and also to the products if they are also gaseous, provided the volumes are measured at same temperature and pressure for all the gases'.

Example 1

Consider the reaction between nitrogen and hydrogen. The balanced equation is written as

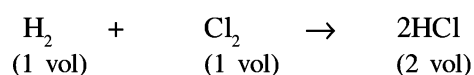


The ratio of nitrogen gas that reacts with hydrogen gas forming ammonia gas is **1 : 3 : 2**.

To illustrate, 100 ml of nitrogen gas will react with 300 ml of hydrogen gas to give 200 ml of ammonia gas.

Example 2

Consider the reaction between hydrogen and chlorine. The balanced equation is written as



The ratio of hydrogen gas that reacts with chlorine gas forming hydrogen chloride gas is **1 : 1 : 2**.

To illustrate, 100 ml of hydrogen gas will react with 100 ml of chlorine gas to give 200 ml of hydrogen chloride gas.

Solved Problems in Gay-Lussac's Law

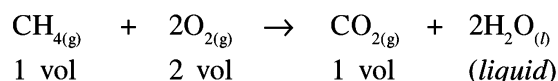
Limiting and excess reactants

A *limiting reactant* is exhausted at the end of a reaction.

An *excess reactant* is available to the extent of the excess amount at the end of the reaction.

(1) 80cc of methane is mixed with 200cc of pure oxygen at room temperature and pressure. The mixture is ignited, when it burns as given below. Find the composition of the resulting mixture, if it is cooled to room temperature. The equation of the reaction is $\text{CH}_{4(g)} + 2\text{O}_{2(g)} \rightarrow \text{CO}_{2(g)} + 2\text{H}_2\text{O}_{(l)}$

Ans: Applying Gay Lussac's law,



Ratio of CH_4 and O_2 reacting and CO_2 formed is **1 : 2 : 1**.

(Water is not considered as it is not in gaseous state at room temperature)

80 ml of CH_4 will require 160 ml of O_2 .

As the volumes that are available are 80 ml of CH_4 and 200ml of O_2 hence CH_4 is the *limiting reactant* while O_2 is the *excess reactant*.

Amount of excess O_2 is $200 - 160 = 40$ ml.

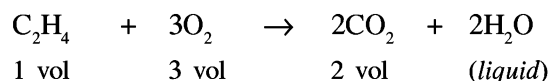
1 vol of CH_4 forms 1 vol of CO_2

80 ml of CH_4 will form ? $\text{CO}_2 = 80$ ml of CO_2

Composition of resulting mixture is 40 ml of excess O_2 and 80 ml of CO_2 formed.

(2) A mixture of C_2H_4 and O_2 is ignited. 200cc of CO_2 is collected at STP. Find amount of C_2H_4 and O_2 at STP in the original mixture. The equation of the reaction is $\text{C}_2\text{H}_4 + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$.

Ans: Applying Gay Lussac's law,



Ratio of C_2H_4 and O_2 reacting and CO_2 formed is **1 : 3 : 2**

So, if volume of CO_2 formed is 200 ml, volume of C_2H_4 required is 100 ml and volume of O_2 required is 300 ml.

This, therefore, is the composition of the reactant mixture at the start of the reaction.

11.6 AVOGADRO'S LAW

Significant terms in Avogadro's Law

- (1) The law is applicable to individual gases.
- (2) All volumes are measured under same conditions of temperature and pressure.

Avogadro's law states that

'Equal volumes of all gases contain the same number of moles under similar conditions.'

Illustration

If 1l of hydrogen gas at STP contains say, 'n' molecules, then according to Avogadro Law

1l of oxygen gas at STP has the same number of molecules, i.e., 'n' molecules

1l of nitrogen gas at STP also has the same number of molecules, i.e., 'n' molecules and

1l of CO₂ at STP will also have the same number of molecules, i.e., 'n' molecules.

Solved Problems in Avogadro's Law

- (1) 500cc of H₂ at STP contains 'n' molecules. How many molecules are present in 25cc of oxygen at STP?

Ans: Applying Avogadro Law,

500 cc of H₂ at STP has 'n' molecules

500 cc of O₂ at STP will also have 'n' molecules

25 cc of O₂ will have ? molecules = 0.05 n molecules

- (2) 6×10^{20} molecules are present in H₂ having volume V at STP. Find volume of oxygen, which has 3×10^{24} molecules at STP.

Ans: 6×10^{20} molecules of H₂ occupies 'V' volume at STP

3×10^{24} molecules of H₂ occupies ? volume = 5000V at STP

Applying Avogadro Law, at STP

3×10^{24} molecules of O₂ will also occupy 5000V

11.7 APPLICATIONS OF AVOGADRO'S LAW

Avogadro's Law can be used to calculate the following.

- (i) Find the atomicity of an elementary gas.

- (ii) Explain Gay-Lussac's Law of combining volumes.
- (iii) Give the relationship between gram molecular weight and gram molar volume
- (iv) Find the relationship between vapour density of a gas and its molecular weight.
- (v) Find the molecular formula of a gas.

(i) *To find the atomicity of an elementary gas using Avogadro's Law*

Atomicity is the number of atoms present in one molecule of an element.

Examples:

Atomicity of helium = 1

Atomicity of oxygen = 2

Atomicity of ozone = 3.

Finding the atomicity of nitrogen and hydrogen

Experimentally one volume of nitrogen combines completely with three volumes of hydrogen giving two volumes of ammonia, *all volumes being measured under similar conditions.*

Nitrogen	+	Hydrogen	→	Ammonia
1 volume		3 volumes		2 volumes

Applying Avogadro's Law since equal volumes of all gases under similar conditions have the same number of molecules,

Three volumes of hydrogen will have thrice the number of molecules as that present in one volume of nitrogen.

Similarly, two volumes of ammonia will have twice the number of molecules as that present in one volume of nitrogen.

In other words,

Nitrogen	+	Hydrogen	→	Ammonia
1 volume		3 volumes		2 volumes
1 molecule		3 molecules		2 molecules
$\frac{1}{2}$ molecule		$\frac{3}{2}$ molecules		1 molecule

The formula of ammonia is NH₃.

One molecule of ammonia has 1 atom of nitrogen. This one atom of nitrogen must have come from $\frac{1}{2}$ a molecule of nitrogen.

Hence, $\frac{1}{2}$ molecule of nitrogen $\equiv$ 1 atom of nitrogen

$\therefore$ 1 molecule of nitrogen $\equiv$ 2 atoms of nitrogen

$\therefore$ **Atomicity of nitrogen is 2.**

Similarly, one molecule of has 3 atoms of hydrogen. These three atoms of hydrogen must have come from $\frac{3}{2}$ molecules of hydrogen.

Hence, $\frac{3}{2}$ molecules of hydrogen $\equiv$ 3 atoms of hydrogen

1 molecule of hydrogen $\equiv$ 2 atoms of hydrogen

Atomicity of hydrogen is 2.

(ii) To explain Gay-Lussac's Law of combining volumes using Avogadro's Law

Experimentally one volume of nitrogen combines completely with 3 volumes of hydrogen giving two volumes of ammonia, *all volumes being measured under similar conditions.*

Equal volumes of all gases according to Avogadro's Law have same number of molecules under similar conditions.

Let one volume of gas have x molecules.

Nitrogen	+	Hydrogen	$\rightarrow$	Ammonia
1 volume		3 volumes		2 volumes
x molecules		$3x$ molecules		$2x$ molecules
1 molecule		3 molecules		2 molecules

Since the atomicity of both nitrogen and hydrogen is 2 and formula of ammonia is NH_3 , this supports the experimental data.

Thus the ratio of combining volumes of gaseous reactants and gaseous products formed are in a simple ratio:

Nitrogen : Hydrogen : Ammonia = 1 : 3 : 2.

This is in accordance with Gay-Lussac's law.

(iii) To find the relationship between gram molecular weight and gram molar volume using Avogadro's Law

According to Mole concept, equal number of moles of all gases under STP conditions occupy 22.4 l.

Since one mole of any compound has a weight equal to the gram molecular weight hence, the gram molecular weight of all gases occupy 22.4l at STP.

Also, density of 1 litre of gas at STP

$$= \frac{\text{Gram molecular weight of gas}}{\text{Gram molar volume}}$$

Thus, Gram molecular weight of a gas

= density of gas at STP $\times$ Gram molar volume

= density of gas at STP $\times$ 22.4 l

(density of gas is to expressed in gm/l)

(iv) To find the vapour density of a gas using Avogadro's law

Vapour Density is the ratio of the mass of a given volume of gas or vapour to the weight of same volume of Hydrogen under the same conditions of temperature and pressure.

By definition,

Vapour Density

$$= \frac{\text{mass of given volume of gas}}{\text{mass of same volume of hydrogen}} \quad \{\text{under similar conditions}\}$$

Since equal volumes of gases have same molecules by Avogadro's Law,

$$\begin{aligned} &= \frac{\text{mass of 'x' molecules of gas}}{\text{mass of 'x' molecules of hydrogen}} \\ &= \frac{\text{mass of 1 molecule of gas}}{\text{mass of 1 molecule of hydrogen}} \\ &= \frac{\text{mass of 1 molecule of gas}}{\text{mass of 2 atoms of hydrogen}} \\ &= \frac{\text{mass of 1 molecule of gas}}{2 \times \text{mass of 1 atom of hydrogen}} \\ &= \frac{1}{2} \times \frac{\text{mass of 1 molecule of gas}}{\text{mass of 1 atom of hydrogen}} \\ &= \frac{1}{2} \times \text{molecular weight of gas} \end{aligned}$$

$\therefore$ **Molecular weight of a gas is numerically twice the vapour density of the gas.**

$$\text{MW} = 2 \times \text{VD}$$

(v) To find the molecular formula of a gas using Avogadro's Law

Experimentally one volume of nitrogen combines completely with 3 volumes of hydrogen giving two volumes of ammonia, *all volumes being measured under similar conditions.*

Equal volumes of all gases according to Avogadro's Law have same number of molecules under similar conditions.

Let one volume of gas have x molecules.

Nitrogen + Hydrogen $\rightarrow$ Ammonia

1 volume	3 volumes	2 volumes
x molecules	$3x$ molecules	$2x$ molecules
1 molecule	3 molecules	2 molecules

Since atomicity of the nitrogen and hydrogen are two

2 atoms	6 atoms	2 molecules
or, 1 atom	3 atoms	1 molecule

Thus, one molecule of ammonia has 1 atom of nitrogen and three atoms of hydrogen.

Hence the formula of ammonia is NH_3 .

11.8 STOICHIOMETRIC CALCULATIONS

Atomic Weights of some elements

To do calculations using balanced chemical equations it will be useful to remember the atomic weights of some elements that are used often. The atomic weights of other elements can be found out from the Periodic Table or will be given in the problem.

H=1, He=4, C=12, N=14, O=16, Na=23, Mg=24, Cl=35.5, Al=27, P=31, S=32,

We will now see how to do the following calculations.

- finding percentage composition of an element in a compound,
- finding empirical formula of a compound,
- finding molecular formula of a compound if vapour density is known,
- use balanced chemical equations to do simple calculations to find
 - the weight of reactants and products and
 - volume of gaseous reactants and products.

(a) Finding percentage composition

- Calculate the percentage of hydrogen and oxygen in water.

Ans: Molecular formula of water is H_2O

Gm. Mol. Wt. = 18g

In one gram molecule, weight of hydrogen is 2g and that of oxygen is 16g

$$\% \text{ hydrogen} = \frac{2}{18} \times 100 = 11.11\% \text{ and}$$

$$\% \text{ oxygen} = 100 - 11.11 = 88.89\%$$

- Find the % of water of crystallization in Glauber's salt.

Ans: Molecular formula of Glauber's salt is $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$

$$\text{Gm. Mol. Wt. is } (46+32+64+180) = 322\text{g}$$

In one gram molecule of the salt,

weight of water = 180g

$$\therefore \% \text{ water} = 55.9\%$$

- Find the % weight of hydrogen in microcosmic salt.

Ans: Molecular formula of microcosmic salt is $\text{NaNH}_4\text{HPO}_4 \cdot 4\text{H}_2\text{O}$

The weight of one gram molecule is of the salt is $(23+14+4+1+31+64+72) = 209\text{g}$

Number of H-atoms = 13

$$\therefore \% \text{ of hydrogen} = (13 / 209)100 = 6.22\%$$

- Find the number of molecules of water of crystallization in a sample of copper sulphate crystals if 10g of hydrated salt gives 6.4g of anhydrous salt on heating. [Cu=64, S=32, O=16]

Ans: Let the hydrated salt have the formula $\text{CuSO}_4 \cdot y\text{H}_2\text{O}$

Mass of hydrated salt = 10g

Mass of anhydrous salt is 6.4g

$$\therefore \text{mass of water in the sample} = 3.6 \text{ g}$$

$$\frac{\text{Mass of water}}{\text{Mass of anhydrous salt}} = \frac{\text{Mass of water in one gm. molecule of salt}}{\text{Gram Molecular Weight of anhydrous salt}}$$

$$= \frac{18y}{64 + 32 + 64} = \frac{18y}{160} = \frac{3.6}{6.4}$$

$$y = \frac{3.6 \times 160}{6.4 \times 18} = 5 \text{ molecules}$$

(b) Finding Empirical Formula

Empirical Formula gives the simplest ratio of atoms of each element present in one molecule of a compound.

Example: Molecular formula of glucose is $\text{C}_6\text{H}_{12}\text{O}_6$.

The simple ratio of carbon, hydrogen and oxygen atoms is found as follows

$$\text{C} : \text{H} : \text{O} = 6 : 12 : 6 = 1 : 2 : 1$$

Finding number of gram atoms

The principle behind calculating empirical formula is as follows.

Consider one gram molecule of calcium carbonate with the formula CaCO_3

One gram molecule of the salt weighs

$$40 + 12 + 48 = 100\text{g}$$

Thus, 100g of the salt is distributed amongst the elements making up the compound as follows.

100g CaCO_3 has

40 g calcium $\equiv$ 1 gram atom of calcium

12 g C $\equiv$ 1 gram atom of oxygen

48 g O $\equiv$ 3 gram atoms of oxygen

Thus, the ratio of weights of the elements in one gram molecule is Ca : C : O = 40 : 12 : 48.

Also, the ratio of number of gram atoms of the elements is Ca : C : O = 1 : 1 : 3.

So, by finding the ratio of number of gram atoms of each element in a compound the empirical formula can be found.

Thus, in a compound,

Ans:

Element	% composition	Gm. At.Wt.	No. of gm-atoms = $\frac{\text{Wt}}{\text{GAW}}$	Ratio of Gm-atoms	Simple ratio of atoms
Sodium	29.11	23	$\frac{29.11}{23} = 1.27$	1.27	$\frac{1.27}{1.26} = 1$
Sulphur	40.51	32	$\frac{40.51}{32} = 1.26$	1.26	$\frac{1.26}{1.26} = 1$
Oxygen	30.38	16	$\frac{30.38}{16} = 1.9$	1.9	$\frac{1.9}{1.26} = 1.5$

Thus, the simple ratio of atoms of Na : S : O = 1 : 1 : 1.5

As atoms do not combine in fractions but in whole numbers, we multiply the ratio by two.

Therefore, the ratio of atoms is Na : S : O = 2 : 2 : 3

Thus the Empirical Formula of the compound is $\text{Na}_2\text{S}_2\text{O}_3$

(c) Finding Molecular Formula

Molecular Formula gives the actual number of atoms of different elements in a molecule of the compound.

No. of gm-atoms of an element in the compound

$$= \frac{\text{weight of the element that combines with a known weight of another element}}{\text{atomic weight of the element}}$$

If the percentage composition of each element in a compound is known then the empirical formula can be found in the following steps.

- Take 100grams of the compound.
- The weight of each element in 100 grams of the compound is tabulated.
- This weight is divided by the gram atomic weight of the element to get the number of gram atoms of that element.
- The ratio of the number of gram atoms is then *converted to a simple ratio as decimal quantities are not possible.*

Solved examples

- If the percentage composition of a compound is as given find the empirical formula: Na=29.11%, S=40.51%, O=30.38%. [Na=23, S=32, O=16]

Thus, **Mol. Formula = n (Empirical Formula)**, where n is a positive whole number.

If molecular weight of a compound is known, the value of n can be calculated.

$$n = \frac{\text{molecular weight}}{\text{empirical weight}}$$

If vapour density is known, the molecular weight of a compound and from it, the value of n can be calculated.

$$\text{molecular weight} = 2 \times \text{vapour density}$$

- Find the molecular formula of a compound having percentage composition C=26.59%,

H=2.22%, O=71.19%. Vapour density of compound is 45. [C=12, H=1, O=16]

Ans:

Element	% composition	Gm. At.Wt.	No. of gm-atoms = $\frac{Wt}{GAW}$	Ratio of Gm-atoms	Simple ratio of atoms
Carbon	26.59	12	$\frac{26.59}{12} = 2.22$	2.22	$\frac{2.22}{2.22} = 1$
Hydrogen	2.22	1	$\frac{2.22}{1} = 2.22$	2.22	$\frac{2.22}{2.22} = 1$
Oxygen	71.19	16	$\frac{71.19}{16} = 4.5$	4.5	$\frac{4.5}{2.22} = 2$

The simple ratio of atoms of C : H : O = 1 : 1 : 2

The Empirical Formula is CHO_2 .

∴ the Empirical Weight is $12 + 1 + 32 = 45$

Since, Vapour Density is 45 (given)

Molecular weight = $2 \times 45 = 90$

Thus, $n = \frac{\text{molecular weight}}{\text{empirical weight}} = \frac{90}{45} = 2$

Ans:

Thus Molecular Formula is $C_2H_2O_4$

(2) A compound has the following composition: Na=18.6%, S=25.8%, H=4.03% and O=51.58%. Find Molecular Formula of the crystalline salt assuming that all the hydrogen in the compound is in combination with oxygen as water of crystallization. Molecular weight of the compound is 248. [Na=23, S=32, H=1, O=16]

Element	% composition	Gm. At.Wt.	No. of gm-atoms = $\frac{Wt}{GAW}$	Ratio of Gm-atoms	Simple ratio of atoms
Sodium	18.6	23	$\frac{18.6}{23} = 0.81$	0.81	$\frac{0.81}{0.81} = 1$
Sulphur	25.8	32	$\frac{25.8}{32} = 0.81$	0.81	$\frac{0.81}{0.81} = 1$
Hydrogen	4.03	1	$\frac{4.03}{1} = 4.03$	4.03	$\frac{4.03}{0.81} = 5$
Oxygen	51.38	16	$\frac{51.58}{16} = 3.22$	3.22	$\frac{3.22}{0.81} = 4$

The simple ratio of atoms of Na : S : H : O = 1 : 1 : 5 : 4.

The Empirical Formula is $NaSH_5O_4$

The Empirical Weight is 124.

Since Molecular weight is 248 (given)

$n = \text{Mol. Wt.} / \text{Emp. Wt.} = 248 / 124 = 2$

Thus, Mol. Formula is $Na_2S_2H_{10}O_8$

Since it is given that all hydrogen is in combination with oxygen as water of crystallization, we can say that 10 H-atoms have combined with 5 O-atoms. ($5H_2O$)

Thus, 3 O-atoms remain. Thus the molecular formula is $Na_2S_2O_3 \cdot 5H_2O$

(d) *Problems based on chemical equations are of two types*

- (i) Problems based on weight–weight relationship
- (ii) Problems based on weight–volume relationship

Balanced Chemical Equation

A chemical equation is a symbolic representation of a chemical reaction. In a balanced chemical equation, the number of atoms of each element is the same on both sides. A balanced chemical equation is known as a stoichiometric equation.

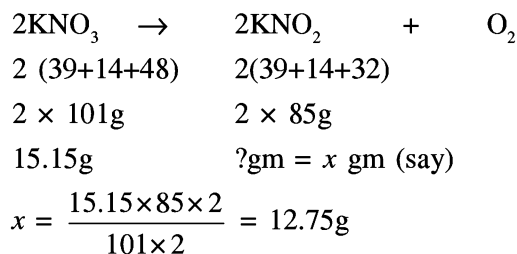
A balanced chemical equation can give information on several aspects of a chemical reaction. It conveys the following information.

- (a) it tells about the chemical nature of the reactants and products,
- (b) the direction of a chemical reaction – reversible or irreversible,
- (c) the state of matter of both reactants and products,
- (d) the ratio of weights of substances reacting and products formed,
- (e) the number of moles or molecules involved,
- (f) the volumes of reactants and products taking part or formed under similar conditions,
- (g) the conditions of a chemical reaction like temperature, pressure, catalyst used, etc.,
- (h) the energy changes that take place.

We will now do problems based on balanced chemical equations.

- (1) Find the weight of KNO_2 formed on thermal decomposition of 15.15g KNO_3 . [K=39, N=14, O=16]

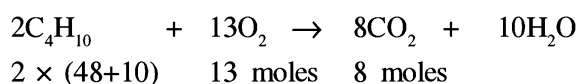
Ans:



The wt. of KNO_2 formed is 12.75g

- (2) The equation for the combustion of butane is $2\text{C}_4\text{H}_{10} + 13\text{O}_2 \rightarrow 8\text{CO}_2 + 10\text{H}_2\text{O}$. Find number of moles of oxygen needed for complete combustion of 58g of butane and the volume of CO_2 formed at STP. [H=1, C=12]

Ans: From the given data we can write the corresponding quantities in the balanced equation.



- (a) 116g of C_4H_{10} needs 13 moles of O_2
 58g of C_4H_{10} needs ? moles of O_2

$$= \frac{13 \times 58}{116} = 6.5 \text{ moles of } \text{O}_2$$

- (b) 116g of C_4H_{10} produces $8 \times 22.4 \text{ l}$ of CO_2 at STP
 58g of C_4H_{10} will produce

$$\frac{22.4 \times 8 \times 58}{116} = 89.6 \text{ litres of } \text{CO}_2 \text{ at STP}$$



EXERCISE



I. Choose the correct answer

- (1) A mole is
 - (a) The amount of substance containing the same number of chemical units as the number of atoms in exactly 12g of C^{12}
 - (b) The amount of substance containing Avogadro number of chemical units.
 - (c) The unit for expressing amount of a substance
 - (d) all the above.
- (2) The number of atoms in 7 g of nitrogen is (N=Avogadro number)
 - (a) N
 - (b) N/2
 - (c) 2N
 - (d) N/4

- (3) Which of the following has the least mass?
 - (a) One gram atom of magnesium
 - (b) 0.9 mole nitric oxide
 - (c) 22.4 lit of nitrogen at STP
 - (d) 6.02×10^{24} molecules of oxygen
- (4) The number of molecules present in 3.2g of oxygen is
 - (a) 6×10^{23}
 - (b) 1.2×10^{23}
 - (c) 6×10^{22}
 - (d) 6×10^{22}
- (5) The number of water molecules in a drop of water weighing 5 mg is
 - (a) 1.67×10^{20}
 - (b) 3.0125×10^{20}
 - (c) 6.023×10^{22}
 - (d) 1.67×10^{20}

- (6) The ratio between the number of molecules in equal masses of nitrogen and oxygen is
(a) 7 : 8 (b) 1 : 9 (c) 9 : 1 (d) 8 : 7
- (7) The ratio between the number of atoms in equal masses of Hydrogen and Helium is
(a) 1 : 2 (b) 2 : 1 (c) 1 : 4 (d) 4 : 1
- (8) The number of molecules present in 64 g of rhombic sulphur is
(a) 2N (b) 3N (c) N/4 (d) 4N
- (9) A silver coin weighs 5.4 gram ($A_g = 108$). The number of silver atoms in the coin is
(a) 1.5×10^{22} (b) 6×10^{22}
(c) 3×10^{22} (d) 4.5×10^{22}
- (10) A gaseous mixture contains oxygen and nitrogen in the ratio 1 : 4 by weight. The ratio of their number of molecules is
(a) 1 : 4 (b) 4 : 1 (c) 7 : 32 (d) 3 : 16
- (11) 1 gram-atom of oxygen is
(a) 1 gm of oxygen (b) 16g of oxygen
(c) 22.4 gms of oxygen
(d) 8g of oxygen
- (12) One mole of atoms of oxygen represents
(a) 6.02×10^{23} atoms of oxygen
(b) 16 gms of oxygen
(c) both (d) None
- (13) The density of a gas at STP is 1.2g/lit. Its molecular weight is nearly
(a) 27 (b) 54 (c) 30 (d) 16
- (14) Total number of lone pairs present in 1.5 moles of water is
(a) 3N (b) 1.5N (c) N (d) N/3
- (15) The number of ions present in 0.2 mole of sodium chloride is
(a) 0.2 N (b) 0.8N (c) 0.4N (d) 0.6N
- (16) 8g of sulphur contains the same number of atoms as
(a) 6g of sugar Charcoal
(b) 6g of Magnesium
(c) 12 g of Magnesium
(d) 3g of Magnesium
- (17) The ratio between the number of molecules in equal masses of CH_4 and SO_2 is
(a) 1 : 1 (b) 4 : 1 (c) 1 : 4 (d) 2 : 1
- (18) The volume of 1.5 gram-atoms of Helium at STP is
(a) 22.4 lit (b) 33.6 lit
(c) 44.8 lit (d) 11.2 lit
- (19) The density of a gas at STP is 1.5g/l at STP. Its molecular weight is
(a) 22.4 (b) 33.6 g (c) 33.6 (d) 44g
- (20) Rahul thinks that a mole contains 6.023×10^{24} molecules. Hence the mass of Rahul's mole of Nitrogen is
(a) 2.8 g (b) 28g (c) 280 g (d) 0.28 g
- (21) The volume of CO_2 obtained by the complete decomposition of one mole of NaHCO_3 at STP is
(a) 22.4 l (b) 11.2 l (c) 44.8 l (d) 4.48 l
- (22) The weight of oxygen required to completely react with 27 g of Al is
(a) 8g (b) 16 g (c) 32 g (d) 24 g
- (23) What volume of H_2 at NTP is required to convert 2.8 g of N_2 in to NH_3 ?
(a) 2240 ml (b) 22400 ml
(c) 6.72 lit (d) 224 lit
- (24) To get 5.6 lit of CO_2 at STP weight of CaCO_3 to be decomposed is
(a) 100 g (b) 50 g (c) 25 g (d) 75g
- (25) If 100 ml of hydrogen chloride is completely decomposed, the volume of H_2 will be
(a) 20 ml (b) 200 ml
(c) 100 ml (d) 50 ml
- (26) 26c.c of CO_2 is passed over red hot coke. The volume of CO evolved is
(a) 15 c.c (b) 10 c.c
(c) 32 c.c (d) 52 c.c
- (27) One litre of mixture of CO and CO_2 is passed over red hot coke when the volume increases to 1.6 l under the same conditions of temperature and pressure. The volume of CO in the original mixture is
(a) 400 ml (b) 600 ml
(c) 500 ml (d) 800 ml
- (28) When 10ml of H_2 and 12.5 ml of Cl_2 are allowed to react, the final mixture contains under the same conditions
(a) 22.5 ml of HCl (b) 12.5 ml of HCl
(c) 20 ml of HCl and 2.5 ml of Cl_2
(d) 20ml of HCl only
- (29) The volume of chlorine that can completely react with 100mg of hydrogen at STP is
(a) 1120 ml (b) 1.12 ml
(c) 11.2 ml (d) 112 ml
- (30) 60 gms of limestone on heating produced 22g of CO_2 . The percentage of CaCO_3 in limestone is
(a) 80% (b) 60%
(c) 83.3% (d) 87.66%
- (31) When 20ml of methane and 20 ml oxygen are exploded together and the reaction mixture is cooled to laboratory temperature. The resulting volume of the mixture is

- (a) 40 ml (b) 20 ml
(c) 30 ml (d) 10ml
- (32) 10 ml of a gaseous hydrocarbon on combustion gives 40 ml of CO_2 and 50 ml of H_2O vapour under the same conditions. The hydrocarbon is
(a) C_4H_6 (b) C_6H_{10} (c) C_4H_8 (d) C_4H_{10}
- (33) Number of water molecules present in 0.02 moles of blue vitriol (hydrated copper sulphate)
(a) 6×10^{23} (b) 6×10^{21}
(c) 6×10^{22} (d) 2.4×10^{22}
- (34) A compound contains 28% nitrogen and 72% of a metal by weight. If 3 atoms of the metal combine with 2 atoms of nitrogen, then the atomic weight of the metal is
(a) 24 (b) 28 (c) 32 (d) 42
- (35) The following gas is twice as dense as oxygen under the same conditions
(a) Ozone (b) Sulphur Trioxide
(c) Sulphur dioxide (d) Carbon dioxide
- (36) X forms an oxide X_2O_3 . 0.36 grams of X form 0.56 grams of X_2O_3 . So the atomic weight of X is
(a) 36 (b) 56.5 (c) 28 (d) 43.2
- (37) When 13.5 gm of Aluminium changes to Al^{+3} ion in solution, it loses.
(a) 18×10^{23} electrons
(b) 6.023×10^{23} electrons
(c) 3.01×10^{23} electrons
(d) 9×10^{23} electrons
- (38) Haemoglobin contains 0.33% of iron by weight. The molecular weight of haemoglobin is approximately 67200. The number of iron atoms (at. wt. of Fe = 56) present in one molecule of haemoglobin is
(a) 6 (b) 1 (c) 4 (d) 2
- (39) What is the mole percentage of O_2 in a mixture of 7g of N_2 and 8g of O_2 ?
(a) 25% (b) 75% (c) 50% (d) 40%
- (40) Which of the following has highest mass?
(a) One gram atom of Iron
(b) 5 moles of N_2
(c) 10^{24} carbon atoms
(d) 44.8 lit of He at STP
- (41) Number of gram atoms of oxygen in 48 grams of ozone is
(a) 1 (b) 3
(c) 6×10^{23} (d) 18×10^{23}
- (42) 3×10^{24} molecules represent
(a) 0.5 mole (b) 10 moles
(c) 5 moles (d) 3 moles
- (43) If N_A is Avogadro's number then number of valence electrons in 4.2g of nitride ions (N^{3-}) is
(a) $2.4 N_A$ (b) $4.2 N_A$
(c) $1.6 N_A$ (d) $3.2 N_A$
- (44) 1 amu is equal to
(a) $1/12$ of C-12 (b) $1/14$ of O-16
(c) 1g of H_2 (d) 1.66×10^{-23} kg
- (45) The density of gas A is three times that of gas B. If the molecular weight of A is M, the molecular weight of B is
(a) 3M (b) M (c) M/3 (d) M/4
- (46) If $11/2$ moles of oxygen combine with Al to form Al_2O_3 , the weight of Al used in the reaction is (Al = 27)
(a) 27g (b) 54g (c) 40.5 g (d) 81 g

II. Give one word answers

- The atomic weight expressed in grams
- The molecular weight expressed in grams
- The number of gram atoms of Ca in 100 g of CaCO_3
- The number of gram molecules in 11.2 l of helium at STP
- The volume occupied by 22.4 l of a gas at STP

III. Match the following.

Match Column A, B and C using each only once.

Column A

- 44 g of CO_2
- 2 moles
- 5.6 l of SO_3 at STP
- 6×10^{23} atoms

Column B

- 200 g of CaCO_3
- 20 g
- 22.4 l of helium
- 1 gram molecule

Column C

- $1/4$ gram molecule
- 1 mole
- at STP
- 2 gram molecules

IV. State whether the following statements are True or False

- The standard molar volume of a gas is 22.4 l
- A given mass of a noble gas contains twice the number of atoms as molecules.
- The molecular formula of a compound is a multiple of its empirical formula.
- A mole of electrons means 6.022×10^{23} electrons.
- The vapour density of a gas is twice its relative molecular mass.
- The number of moles of gas in 64 g of sulphur dioxide is 2 moles

V. Fill in the blanks

- At the same temperature and pressure, equal volumes of all gases contain the same number of _____. (atoms / molecules)
- The _____ formula of a compound is a simple multiple of its _____ formula. (empirical / molecular)
- The atomic and molecular masses of noble gas elements are _____. (same / different).
- The relative molecular masses of hydrogen, nitrogen, oxygen and chlorine are _____ their relative atomic masses. (the same as / twice / half)
- _____ mole(s) of electrons would be required to convert 1 mol of Cu^{2+} ions into metallic copper. (one / two)
- _____ mole (s) of electrons will be released when 1 mol of Fe^{2+} ions is converted into Fe^{3+} ions. (one / two)
- A compound of relative molecular mass 34 and empirical HO has the molecular formula _____. (HO / H_2O / H_2O_2).

VI. Answer the following questions.

- State Gay-Lussac's law of combining volumes.
- What is Avogadro's hypothesis?
- What do you mean by the atomicity of an element?
- What are the atomicities of hydrogen, nitrogen, oxygen, fluorine and chlorine?
- What is the relative atomic mass of an element?
- Define relative molecular mass.
- What do you understand by the term 'molar volume of a gas'?
- Define the standard molar volume of a gas.
- Is the molar volume of a gas at -10°C and 80 cm and 80 cm Hg smaller or larger than its standard molar volume?
- What is a mole?
- What is the value of Avogadro constant.
- What do you mean by the empirical formula of a compound?
- Define the vapour density of a volatile substance.
- How is the vapour density related to the relative molecular mass of a volatile substance?
- Define the term limiting reactant.
- Explain Gay-Lussac's law of combining volumes on the basis of Avogadro's hypothesis.
- What is the significance of the number 6.022×10^{23} in chemistry?
- Explain why it is essential to use a particular isotope of an element, rather than a natural sample, as a reference or standard for relative atomic and molecular masses.
- Using the example of the formation of water from hydrogen and oxygen, develop the concept of the limiting reactant.

KEY TO EXERCISE									
I.	1. d	2. b	3. a	4. c	5. a	6. d	7. d	8. c	9. c
	10. c	11. b	12. c	13. a	14. a	15. c	16. b	17. b	18. b
	19. c	20. c	21. b	22. d	23. c	24. c	25. d	26. d	27. a
	28. c	29. c	30. c	31. b	32. d	33. c	34. a	35. c	36. c
	37. d	38. c	39. c	40. b	41. b	42. c	43. a	44. a	45. c
	46. b								
II.	i. gram atomic weight		ii. gram molecular weight			iii. 5gram atoms			
	iv. $\frac{1}{2}$ gram molecule		v. gram molar volume			vi. 2 moles			
III.	a. iv-q	b. i-s	c. ii-p	d. iii-r					
IV.	i. true	ii. false	iii. true	iv. true	v. false	vi. false			
V.	1. molecules	2. molecular, empirical	3. same	4. twice	5. two	6. two	7. H_2O_2		

12 Chemistry and Industry

12.0 INTRODUCTION

Today we cannot think of living without some chemical compounds which play an important role in our daily lives. Chemistry plays an important role in sports, space research, , construction, drugs, medicines, agriculture, automobiles and numerous other fields. Most of the contribution of chemistry in daily life is not appreciated by the common man. This chapter deals with a very few of the important chemicals that make a difference to our daily lives.

12.1 CEMENT

Cement was discovered in 1824 by an English mason Joseph Aspdin. He named his cement Portland, after a rock quarry that produced very strong stone.

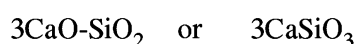


He mixed limestone and clay and heated the mixture strongly. On mixing with water and cooling the mixture became as hard as a rock – the appearance resembled a rock found in Portland and hence the name Portland cement was given to it.

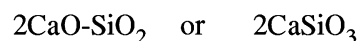
Cement is a dirty grey composite mixture. It is a heavy powder primarily made up of calcium aluminate and calcium silicates.

The approximate composition (to the extent of 90%)

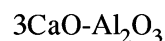
- (i) tricalcium silicate



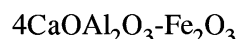
- (ii) dicalcium silicate



- (iii) tricalcium aluminate



- (iv) tetra calcium aluminoferrite



The remaining 10% of cement is made up of a mixture of oxides – mainly Na_2O , Fe_2O_3 , K_2O , MgO

Raw materials required for manufacturing cement

The raw materials required for manufacturing cement are

- (i) limestone
- (ii) clay
- (iii) gypsum

There are two methods for manufacture of cement: (i) dry process (ii) wet process.

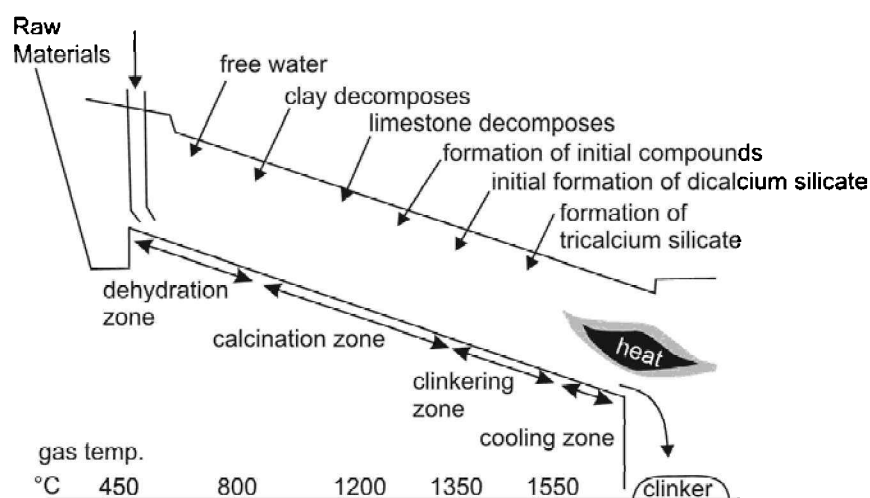
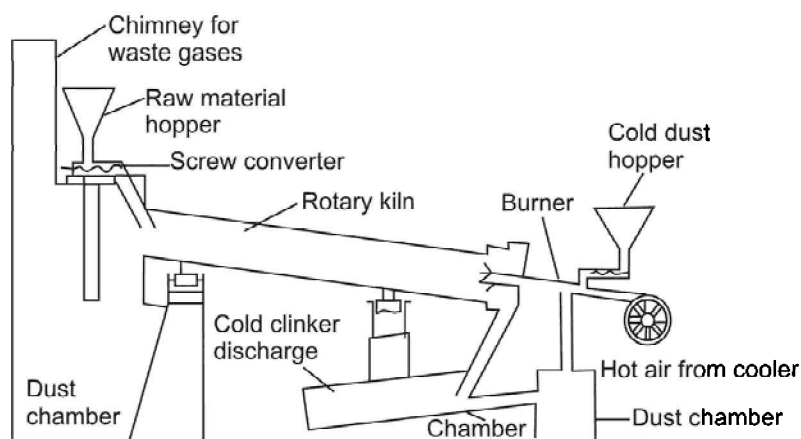
Dry Process

- (1) The *dry process* is used if the limestone is hard. The limestone is broken into small pieces and mixed with clay.
- (2) The mixture is pulverized to a fine powder. This powder is called **Raw Meal**.

Wet Process

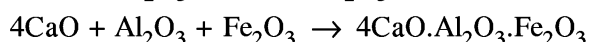
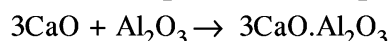
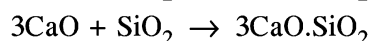
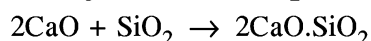
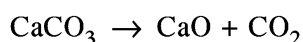
- (1) This process is used when both limestone and clay are soft. The clay is washed with water in a wash mill to remove foreign matter like flint.
- (2) The limestone is powdered and mixed with clay in the ratio 3:1.
- (3) The mixture is ground to fine powder. This powder is known as **Slurry** (it has 40% water content)

Calcination: The *raw meal* from dry process or *slurry* from wet process is heated to $1700^\circ - 1900^\circ\text{C}$ in a rotary kiln.



As the charge moves down the rotating chamber it is heated at the exit end of the chamber by a hot blast (see figures above).

Moisture gets eliminated at the upper end of the chamber where the temperatures are in the region of 450°C . In the middle of the chamber (1000°C) limestone gets decomposed with evolution of CO_2 . In the lower part of the chamber (1600°C) the following reactions take place:



The product is in the form of small grey balls called *clinker*. The *clinker* is cooled and mixed with 2-3 % of its weight of gypsum.

Reason for adding gypsum

Gypsum is added to delay the setting of the

cement while being used in the construction of buildings.

The clinker is powdered to a fine powder and packed in airtight bags and sold as *cement*.

Uses of cement

- Cement is mixed with sand and mortar for slabs of buildings, plastering and binding bricks.
- Concrete:** Cement is mixed with sand and crushed stone to form a mixture called *concrete*. *Concrete* is used for construction of bridges, roofs of buildings, etc.
- Reinforced Concrete Cement or RCC:** Steel rods, bars are embedded in the wet *concrete* to get *reinforced concrete cement (RCC)*. RCC is much stronger and used for making pillars and foundation slabs, pipes, gutters, etc.
- Mortar:** Mortar is prepared by making a thick paste of cement and sand with a little

water. The *mortar* is used to bind bricks, stones. The mortar sets to a hard mass and keeps the bricks and stones in place.

12.2 BLEACHING POWDER

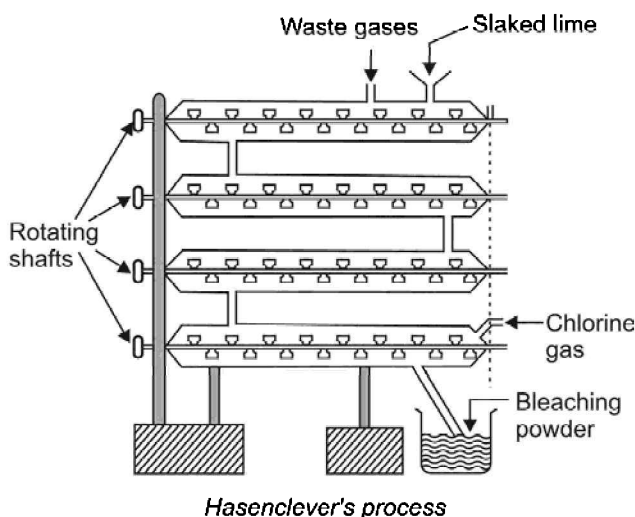
Bleaching Powder is chemically calcium oxychloride or Chloride of Lime with the formula CaOCl_2 .

Composition of bleaching powder

Bleaching powder is a mixture of two compounds - Ca(OCl)_2 and CaCl_2 or $\text{Ca}_2(\text{OCl})_2\text{Cl}_2$ or CaOCl_2 .

Manufacture

Bleaching powder is manufactured by the action of chlorine on dry slaked lime in a Hasenclever plant. The plant consists of a number of hollow horizontal cylinders made of cast iron which are fitted with shafts and connected to one another as shown below. The shafts have a large number of blades fixed along their whole lengths. The shafts having blades can be rotated inside the cylinders by connecting to a motor. The uppermost cylinder has a hopper at its top through which slaked lime is introduced into the cylinder shaft. Chlorine gas is introduced from the lower end.



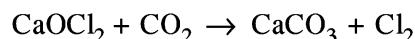
The lime is exposed to the ascending chlorine gas so that by the time it reaches the bottom it gets thoroughly saturated with the gas and gets converted completely into bleaching powder.

Properties of bleaching powder

- (i) Bleaching powder is a pale yellow powder. It smells of chlorine. It is soluble in water but the solution is unclear due to impurities.

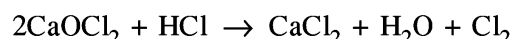
- (ii) Bleaching powder loses its chlorine when left exposed to air and loses its bleaching property.

- (iii) Bleaching powder loses its chlorine by the action of CO_2 .



- (iv) **Oxidising or bleaching properties**

In the presence of dilute acids the reaction is



The water and chlorine react to give *nascent oxygen* (atomic oxygen). This nascent oxygen reacts with coloured substance giving colourless substance.

Uses of bleaching powder

- (i) Bleaching of cotton, linen in textile industry
- (ii) Bleaching of wood pulp in paper factories
- (iii) Bleaching of washed clothes in laundry
- (iv) As an oxidising agent in many chemical industries and
- (v) for disinfecting drinking water to make water free from germs.

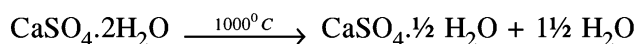
12.3 PLASTER OF PARIS

Plaster of Paris is chemically calcium sulphate hemi hydrate with the formula $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$.

The name comes because it is prepared from *gypsum* (CaSO_4) was found in Paris. It was once used in construction as cement between the bricks. Today it is used more for medicinal purpose for plastering fractured bones.

Preparation of Plaster of Paris

Plaster of Paris is prepared by heating gypsum (CaSO_4) at 100°C in a kiln. The heating is controlled so that anhydrous CaSO_4 is not obtained. The following reaction takes place.



Properties of Plaster of Paris

Plaster of Paris is a white powder. When mixed with water, crystals of gypsum are produced again. On drying it sets to a dry hard mass.

Uses of Plaster of Paris

Plaster of Paris is

- (i) used for making toys, decorative pieces, jewellery, cosmetics and statues

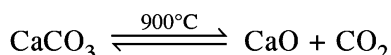
- (ii) in medicine for setting fractured bones and in dentistry to prepare moulds.
- (iii) used for giving the walls a smooth finish
- (iv) in labs to seal apparatus to make it air tight.

12.4 QUICK LIME

Quick lime has the chemical formula CaO . Limestone occurs naturally and it is used to prepare lime — a man made chemical.

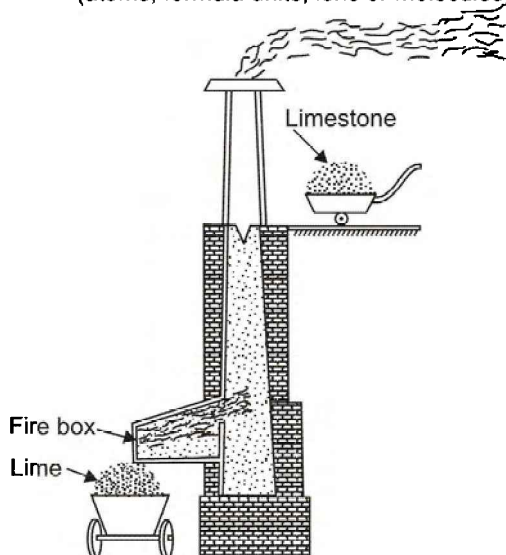
Manufacture of lime

When limestone is heated to 900°C in a kiln it changes to *Lime*.



The carbon dioxide formed is continuously removed, as the reaction is reversible.

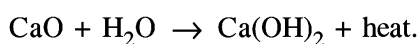
(atoms, formula units, ions or molecules)



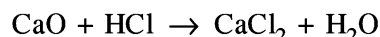
The temperature in the kiln varies from 1000°C to 1200°C . The limestone decomposes completely and is taken out at the bottom while the CO_2 escapes from the top.

Properties of lime

- (i) Pure CaO or lime is an amorphous (powdery) white solid having a MP of 2000°C .
- (ii) Lime gives a brilliant white light when heated in oxy-hydrogen flame.
- (iii) **Slaked lime:** When lime is added to water, a hissing sound is produced as it evolves a large amount of heat. The product is known as *slaked lime*.



- (iii) Lime does not react with dry HCl but reacts with moist HCl .



Uses of lime

Lime has the following uses.

- (i) Lime is used as a drying agent in the lab for drying NH_3 and alcohol.
- (ii) Lime is used in the manufacture of CaCl_2 and glass.
- (iii) Lime is used to make furnace linings.
- (iv) As slaked lime, lime is used for manufacture of Na_2CO_3 , bleaching powder and calcium carbide.
- (iv) Lime is used for white washing.

12.5 GLASS

Glass has the general formula $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 6\text{SiO}_2$. Glass is a *super cooled liquid*. One of its unique properties, is that it is transparent. Glass is obtained by the fusion of certain metal oxides with white sand. Its melting point varies with the composition. Heated glass begins to soften at a temperature far below the temperature at which it starts to melt. This property makes it suitable to be molded into various shapes.

Raw materials required for glass manufacture

The raw materials required for glass manufacture are as follows.

- (a) **Silica or sand** of uniform grain size and good purity.
- (b) **Alkaline earths** (in the form of calcium oxide, limestone, and barium carbonate). The alkaline earths are mixed to get a high refractive index of glass.
- (c) **Alkali metals** (in the form of coarse Na_2CO_3 or Na_2SO_4 to which 5% C is added as a reducing agent; potassium in the form of K_2CO_3 or KNO_3).
- (d) **Heavy metals** like litharge or red lead, zinc oxide.
- (e) **Colouring materials**
- (f) **Borax** used as a flux to increase coefficient of expansion and durability.
- (g) **Alumina** to increase resistance to sudden temperature changes.

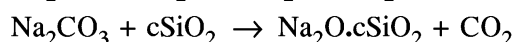
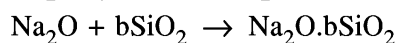
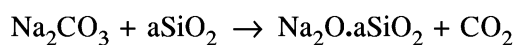
- (h) **Cullets** that are pieces of waste glass. They are required to facilitate fusion and reduce waste.

Manufacture

The raw materials used depend on the end use of glass. For ordinary glass or soda-lime glass the raw materials used are sand, washing soda and limestone.

- Fusion of raw materials:** They are mixed in proper proportion and ground together. The resulting mixture is known as *batch*.
- The batch is mixed with *cullet* and introduced into either a *pot furnace* or *tank furnace*. A tank furnace is a *reverberatory furnace* in which the molten mass forms a pool over the hearth. Heating is done using *producer gas* ($\text{CO} + \text{N}_2$) as fuel.
- The batch melts forming froth due to evolution of CO_2 and SO_2 .
- When the froth subsides, the temperature is raised and the molten glass is allowed to stand for sometime.

The reactions are:



Commercial glass is a mixture of all these silicates:



Blowing of glass

The glass can be moulded into different shapes by heating it and **blowing** manually or by machine within a few seconds.

Annealing

When hot glass is cooled suddenly, it becomes very brittle due to internal strain. If it is cooled very slowly, it becomes opaque. So passing step by step through cooling chambers in which the temperatures progressively decrease cools the molten glass at a moderate rate. This process is known as **annealing**. During annealing, the molecules of glass arrange in such a way that their inter-molecular strain remains when the article is cooled.

Finishing

This step involves cutting, grinding, polishing,

etc. after annealing.

Varieties of glass

- Soft glass or Soda glass** or common glass is the cheapest and most used. It is a mixture of sodium and calcium silicates. It fuses at relatively low temperatures. It is brittle and breaks easily. It cracks when the temperature changes suddenly. It is used for window glass, mirrors and is easily attacked by chemicals.
- Hard glass** is a mixture of potassium and calcium silicates and is used for making laboratory apparatus. It is resistant to chemicals.
- Jena glass** is a mixture of zinc and barium boro silicates and is resistant to heat, chemicals and shock.
- Pyrex glass** is a mixture of sodium and aluminium boro silicates. It has properties similar to Jena glass.
- Optical glass** is made by using red lead, potassium carbonate and sand.
- Crook's glass** contains cerium oxide, which cuts off ultraviolet light harmful to the eyes.
- Safety glass** is obtained by placing a layer of butyral plastic with a suitable adhesive between two layers of glass and cementing them by heat and pressure. It does not shatter and is used for making windshields of automobiles.
- Glass wool** is **glass fibre** obtained by forcing molten glass through tiny holes in the presence of a jet of high-pressure steam. Glass being a thermal insulator is wrapped around various articles in the form glass wool. Glass fibres are used for making fire proof clothing.
- Optical fibres** is a type of glass fibre used in telecommunications and micro surgeries as it can guide light and transmit light even if bent due to total internal reflection. They are also better conductors of electricity than copper.
- Coloured glasses:** To produce glass of different colours, different mineral substances are mixed during the process of manufacture as given below.

Red glass	$\text{Cu}_2\text{O} + \text{selenium metal}$
Green glass	$\text{CuO} + \text{Cr}_2\text{O}_3$
Yellow glass	$\text{CdS} + \text{C}$
Blue glass	$\text{CuO} + \text{CoO}$
Violet/purple glass	MnO_2

Black glass	$\text{Co} + \text{Mn} + \text{Ni}$
Milky glass	$\text{SnO} + \text{Ca}_3(\text{PO}_4)_3$
Brown glass	Fe_2O_3

12.6 MAN MADE ORGANIC COMPOUNDS

Man has synthesized many carbon containing compounds.

Synthetic Organic Compounds							
(1) Synthetic fibres			(2) Plastics		(3) Rubber		(4) Soaps / Detergents
Rayon	Nylon	Polyester	Thermoplastic	Thermo-setting plastic	Artificial	Natural (But treated chemically)	Discussed before

12.7 SYNTHETIC FIBRES

Fibres

Fibres are of two types: *Synthetic and Natural*.

Synthetic Fibres

A fibre is a special thread, which is used to make, clothes, ropes, etc. There are three important man-made fibres. They are

- Rayon** – a synthetic fibre prepared from natural raw material
- Nylon** – a pure synthetic fibre
- Polyester (Terylene)** – a pure synthetic fibre

(i) Rayon

Rayon is prepared from a natural raw material, cellulose. Cellulose has a general formula $(\text{C}_6\text{H}_{10}\text{O}_5)_n$, where n is a large number. Cotton and jute are natural cellulose fibres. Rayon is an artificially modified cellulose fibre.

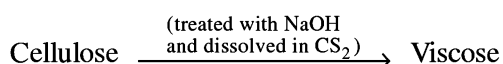
Natural source of cellulose : Wood contains large amounts of cellulose. Paper is purified form of cellulose made from wood.

Making rayon fibre by Viscose Process

The raw materials required for manufacture of rayon are cellulose in the form of paper strips or wood pulp, NaOH , CS_2 and H_2SO_4 .

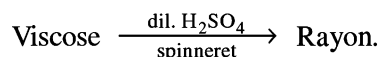
Method

Cellulose (wood pulp) is treated with NaOH and then CS_2 when a pale yellow viscous syrup called *viscose* is formed.



The viscose solution is alkaline. It is treated with

dilute H_2SO_4 for neutralisation and the *cellulose* gets *re-precipitated as rayon*. The *viscose* is forced to pass through fine jet holes of a fast rotating metal cylinder called *spinneret* into another chamber with dilute H_2SO_4 , when silk-like threads come out of the jet holes.



Rayon is a synthetic fibre consisting of purified cellulose in the form of long threads. It looks like silk and hence is also called *artificial silk*. Rayon produced by viscose process is called *Viscose Rayon*.

Uses

Rayon is used in textiles (sarees, shirts), tyres, and mixed with wool for carpets, bandages and medical dressings.

(ii) Nylon

Nylon is the first synthetic fibre made by man. Wool is a **natural** polyamide polymer whereas, nylon is a **synthetic polyamide fibre**. Nylon was first developed simultaneously in New York and LONDON. (N Y LON). When first made in 1939, 64 million pairs of women's stockings made of Nylon were sold in the first year itself.

Nylon is formed by the polymerisation of two monomers – adipic acid and hexamethylene diamine. Each of these monomers has a reactive functional group. The functional group in one monomer *has an affinity* or tendency to form a bond with the functional group present in the other monomer.

Nylon is formed by polymerization of a *dicarboxylic acid with a diamine*. The $-\text{COOH}$

group in the dicarboxylic acid has an affinity for –NH₂ group in the diamine. They join to form a *peptide bond* by *eliminating a water molecule*. When a large number of these two monomers polymerise by eliminating water molecules a *polyamide polymer* is formed. The bonding is shown below.

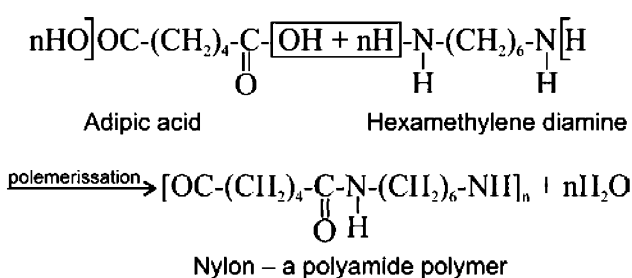
Adipic acid molecule – a dicarboxylic acid



Hexamethylene diamine molecule—A diamine



The mechanism of polymerisation



Nylon is a polyamide formed by polymerization of adipic acid with hexamethylene diamine.

Properties of nylon

- (1) Nylon is a *thermo plastic* - nylon can be cast into moulds by heating or spun into threads by passing through *spinnerets*.
- (2) Unlike natural fibres like cotton, nylon has **great strength**.
- (3) Nylon has **good elasticity**.
- (4) Nylon does not absorb water and can be drip-dried.
- (5) Nylon is wrinkle resistant and abrasion resistant (wear and tear resistant) and hence more durable.
- (6) Nylon is moth resistant, light, has finesse (smooth texture).
- (7) Nylon is inert and insoluble in most solvents.

Uses of nylon

Based on the above properties nylon finds the following uses:

- (1) Nylon is used for making of strong ropes, fishing nets, badminton racquet strings, musical instrument strings, toothbrush

bristles, paint brushes, etc., textiles like sarees, shirts, socks, etc.

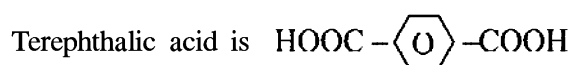
- (2) A mixture of 25% nylon and 75% wool is used for making suits and carpets.

- (3) Nylon is used in machinery parts

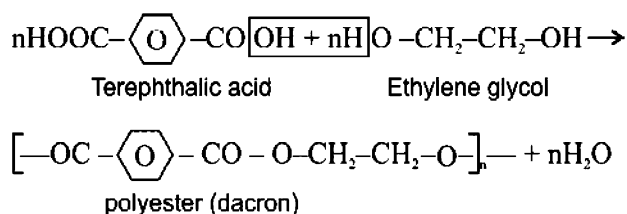
(ii) Polyester

Polyester, a synthetic fibre invented in England, is a polymer whose monomer is an ester. Polyester is prepared by condensing dicarboxylic acid with dihydroxy alcohol to form a long chain polyester.

Terylene is a polyester fibre formed by condensing terephthalic acid with ethylene glycol.



Mechanism of polymerisation



Properties of polyester

It is a **thermoplastic polymer**. It can be spun into threads.

Terylene is also known as *dacron*.

- (1) Polyester is very strong and wrinkle free
- (2) Polyester does not absorb moisture, so it dries quickly,
- (3) Polyester is moth free,
- (4) Polyester is abrasion resistant.

Uses of polyester

- (1) Polyester is used in textiles and blended textiles.
- (2) Used for making *terycot* a blend of terylene and cotton.
- (3) Used for making *terrywool* a blend of terylene and wool.
- (2) Polyester is used to make sails of sailboats as it is light and strong and does not stretch.
- (3) Polyester is used to make water hoses for fire fighting, and conveyor belts.

12.8 PLASTICS

Plastic is a synthetic material, which can be moulded into any shape and then hardened to produce a durable article. Plastics are of two types: *thermoplastics* and *thermosetting plastics*

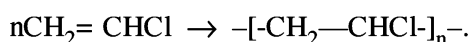
A **thermoplastic** is plastic which can be melted repeatedly moulded again into different shapes.

Examples:

- (i) Poly Vinyl Chloride (PVC)

The monomer of PVC is vinyl chloride, $\text{CH}_2=\text{CHCl}$.

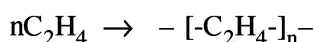
Mechanism of polymerisation



- (ii) Polyethene

The monomer of polythene is ethene, C_2H_4 .

Mechanism of polymerisation

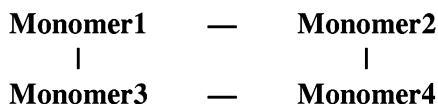


A **thermosetting plastic** is a plastic that once moulded does not become soft even when heated and hence cannot be molded again.

Example: Bakelite is a monomer of phenol formaldehyde.

Mechanism of polymerisation

In Bakelite there are cross chains between 4 monomers.



Bakelite is a good insulator and is used for making handles of electric irons, plugs, switches, etc.

12.9 RUBBER

Rubber occurs naturally and can also be synthesised.

(a) Natural rubber

Natural rubber is a natural polymer. It is obtained as *latex* from rubber trees.

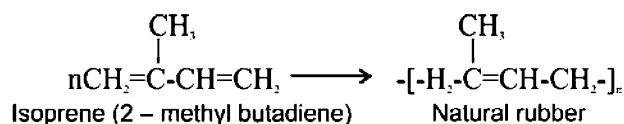
Latex is a white milky liquid containing 30-40% rubber in the form of colloidal solution in water. Latex is treated with acetic acid to coagulate the rubber component. This makes separation from the solution easier. The separated rubber is then washed and dried.

Rubber is a linear polymer of an unsaturated hydrocarbon called *isoprene*. *Isoprene* is chemically

2-methyl butadiene.

Mechanism of polymerization

The **monomer isoprene** polymerises as shown. The polymer has double bond (when rubber burns it gives off black fumes).



where $n = 11,000$ to $20,000$

Vulcanisation

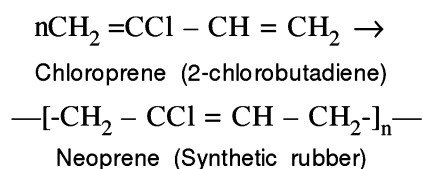
Natural rubber is soft. Vulcanisation of rubber is the treatment of rubber with hot sulphur to harden it.

Vulcanised rubber is hard, strong and elastic. It is not sticky like natural rubber. It is also more resistant to wear and tear and is insoluble. It is used in rubber bands, football bladders, gloves, and rubber tubes. Tyre rubber is prepared by hardening rubber with carbon black.

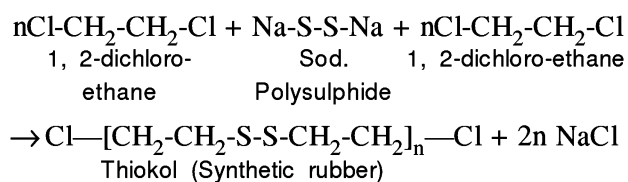
(b) Synthetic rubber

Neoprene and **Thiokol** are two synthetic rubbers.

Monomer of Neoprene is chloroprene (2-chloro butadiene). It polymerises as follows:



Monomer of Thiokol is Ethylene polysulphide. It polymerises as follows:



Neoprene is used for making insulation of cables and wires, conveyor belts and hoses for petrol delivery and transporting oil, as it does not react with oil.

Thiokol is used for making hoses and oil tank linings, chemical tank linings, engine gaskets and also as a fuel when mixed with other oxidising agents.

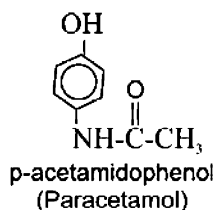
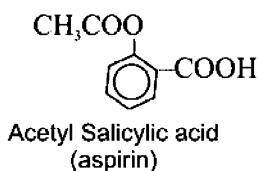
12.10 PHARMACEUTICALS

Many organic compounds are used as medicines.

Some common medicines and their uses are given below.

- (1) **Antipyretics** – Medicines used for reducing fever are called antipyretic. Some examples are aspirin and paracetamol.

Aspirin is acetyl salicylic acid. Paracetamol is acetaminophenol. The structures are shown below.



- (2) **Antibiotics** – Medicines used to control infection are called antibiotics. Some common antibiotics are penicillin with the formula $C_9H_{11}N_2O_4S-R$ and streptomycin with the formula $C_{21}H_{39}N_7O_{12}$.

12.11 DYES

Dyes are chemicals used to give a colour to textiles, foods, sweets, etc. The dyes have specific colour and can get attached to the fibre by forming bonds and remain fast so that the colour does not fade on washing.

A dye has two components –

- chromophore* that gives colour. Examples: NO_2 , NO , $N=N$, $>C=O$.
- auxochrome* that intensifies the colour and forms chemical bonds with the fabric or material. Examples: $-OH$, $-COOH$, CO_2 , H , $-NH_2$, $-NHR$, NR_2 , Cl

12.12 SOME IMPORTANT POINTS TO REMEMBER

- Cement is a mixture of calcium silicates and calcium aluminate.
- Cement is manufactured from limestone and clay.
- The heating temperature of cement is $1700 - 1900^\circ C$.
- Glass is a mixture of sodium silicate, calcium silicate and sand.
- Raw materials of glass are soda-ash, limestone and sand.
- Heating temperature of glass is $1000^\circ C$.

- Liquid glass is cooled by a special method known as annealing.
- Colour is imparted to glass by metal oxide salts.
- Ceramics are products made from clay, feldspar and sand
- Pottery or Terra-cotta are products of porous nature such as pots, jugs, etc.,
- Earthenware are glazed articles such as porcelain wall tiles, crucibles and dishes.
- Plastics are polymeric organic materials.
- Plastics are synthesized by addition or condensation polymerization.
- Plastics have domestic and industrial uses.
- Adhesives hold solid materials together by surface attachment.
- Gum – Arabic shellac, animal glue, etc., are natural adhesives.
- Urea formaldehyde, epoxy resins and silicones are some synthetic adhesives.
- Plastics with certain properties are spun into fibres known as man-made fibres.
- Melt spinning and dry spinning are two methods of spinning fibres from plastics.
- Nylon, dacron and cellulose acetate are some examples of man-made fibres.
- Cosmetics are meant for improving attraction of a person.
- Cold creams mainly contain almond-oil, bees-wax and rose-water.
- Nail polish consists of a polymeric resin plasticizer, pigments and perfumes in low boiling solvents.
- Quality of face powder depends upon opacity, slip, adherence, absorbency and fineness.
- Dyes are useful for colouring textiles.
- Chromophore and auxochrome are two groups that must be present in a dye
- Dyes are classified into acidic, basic, direct, mordant, vat, etc., depending upon the method of application of dye to the fibre.
- Drugs are substances used in prevention, diagnosis, treatment or cure of a disease

- Drugs are classified into six types based on therapeutic action. They are (i) drugs working on central nervous system (ii) drugs working on cardiovascular system (iii) drugs working on foreign

organisms (iv) chemo therapeutic drugs (v) vitamins and (vi) hormones.

- Pharmaceuticals are modified forms of drugs such as tablets, capsules, lotions, syrups, tonics and injections.

EXERCISE

I. Choose the correct answer

- (1) **Bleaching powder is**
 - (a) Sodium silicate and gypsum
 - (b) Calcium silicates and calcium aluminates
 - (c) Sand clay and feldspar
 - (d) Calcium oxychloride
- (2) **Slow cooling of glass is called**
 - (a) blowing
 - (b) condensation
 - (c) annealing
 - (d) tempering
- (4) **Chromophore**
 - (a) soaks the fibre
 - (b) binds the dye to fibre
 - (c) impart colour to the fibre
 - (d) intensifies the colour of the dye
- (5) **Raw material required for manufacture of cement is**
 - (a) limestone, clay and gypsum
 - (b) sand and limestone
 - (c) sand and clay
 - (d) gypsum and sand
- (6) **Raw material required for manufacture of glass is**
 - (a) limestone, clay and gypsum
 - (b) sand, washing soda and limestone
 - (c) sand and clay
 - (d) gypsum and sand
- (7) **Cement is a mixture of aluminates and silicates of**
 - (a) sodium
 - (b) magnesium
 - (c) calcium
 - (d) potassium
- (8) **Glass is**
 - (a) Sodium silicates
 $\text{Na}_2\text{O} \cdot a\text{SiO}_2 + \text{Na}_2\text{O} \cdot b\text{SiO}_2 + \text{Na}_2\text{O} \cdot c\text{SiO}_2$
 - (b) Calcium silicates - CaSiO_3
 - (c) Magnesium silicates - MgSiO_3
 - (d) Potassium silicates - K_2SiO_3
- (9) **The bleaching action of bleaching powder is due to formation of**
 - (a) nascent oxygen
 - (b) nascent hydrogen
 - (c) calcium chloride
 - (d) none of these
- (10) **The chemical added to delay the setting period of cement is**
 - (a) sand
 - (b) clay
 - (c) gypsum
 - (d) lime
- (11) **Cullet is added to the batch in glass manufacture to**
 - (a) reduce the melting point
 - (b) to facilitate fusion and reduce wastage
 - (c) as a catalyst
 - (d) add colour
- (12) **Annealing is**
 - (a) slow cooling of molten glass to prevent brittleness
 - (b) fast cooling of molten glass to prevent brittleness
 - (c) blowing of glass to mould it into desired shapes
 - (d) makes glass transparent
- (13) **The mixture of raw materials in manufacture of glass is called**
 - (a) cullet
 - (b) clinker
 - (c) slurry
 - (d) batch
- (14) **Round balls of cement are called**
 - (a) cullet
 - (b) slag
 - (c) clinker
 - (d) batch
- (15) **A mixture of cement, crushed stone and sand is called**
 - (a) rubble
 - (b) slurry
 - (c) concrete
 - (d) slab
- (16) **Steel rods embedded in wet concrete are called**
 - (a) steel fortified
 - (b) slab
 - (c) reinforced concrete cement
 - (d) strong cement
- (17) **Monomer of artificial rubber is**
 - (a) Isoprene
 - (b) Butadiene
 - (c) Chloroprene
 - (d) Cellulose
- (18) **Monomer of rayon is**
 - (a) Isoprene
 - (b) Butadiene
 - (c) Chloroprene
 - (d) Cellulose
- (19) **Monomer of PVC is**
 - (a) Ethene
 - (b) Ethyne
 - (c) 1-chloro ethene
 - (d) Chloro ethane
- (20) **Monomer of polythene is**
 - (a) Ethene
 - (b) Ethyne
 - (c) 1-chloro ethene
 - (d) Chloro ethane
- (21) **Rubber burns giving off dark fumes as it has**
 - (a) unsaturated carbon atoms

- (b) due to vulcanization
- (c) rubber is black in colour
- (d) lack of oxygen

(22) The polymer whose monomer is an ester is

- (a) nylon
- (b) polyester
- (c) PVC
- (d) rayon

(23) A natural polyamide fibre is

- (a) jute
- (b) cotton
- (c) wool
- (d) human hair

(24) Plastics that can be re-moulded by melting are called

- (a) thermoplastics
- (b) thermosetting plastics
- (c) synthetics
- (d) hard plastics

(25) Example of antibiotics are

- (a) aspirin and paracetamol
- (b) streptomycin
- (c) penicillin
- (d) both (b) and (c)

II. Match the following.

(1) Match the type of glass in Column I with its end use in Column II.

Column I	Column II
(a) Soft glass	(i) optical lens
(b) Optical glass	(ii) to cut off UV radiation
(c) Crook's glass	(iii) glass apparatus
(d) Hard glass	(iv) windows, mirrors

(2) Match the polymer in Column I with the monomer in Column II.

Column I	Column II
(a) Rayon	(i) terephthalic acid and ethylene glycol
(b) Polyester	(ii) cellulose unit
(c) Bakelite	(iii) isoprene
(d) Rubber	(iv) phenol formaldehyde

(3) Match the product in Column I with the raw materials required for its manufacture in Column II.

Column I	Column II
(a) Glass	(i) terephthalic acid and ethylene glycol
(b) Cement	(ii) sand, washing soda and limestone
(c) Quick lime	(iii) limestone, clay and gypsum
(d) Polyester	(iv) limestone

III. Fill in the blanks.

- (1) Cement is a mixture of _____ and _____
- (2) Raw material for cement manufacture are _____, _____ and _____.
- (3) It is prepared by mixing _____ and _____ by heating to _____ °C.
- (4) Glass is made from _____, _____ and _____ by heating to _____ °C.
- (5) Glass is _____ liquid.
- (6) Chemical formula of glass is _____
- (7) Some types of glass: _____, _____, _____, _____ and _____
- (8) Rapid cooling of glass makes it _____. Slow controlled cooling of glass is called _____.
- (9) Glass-blowing is possible with _____ glass.
- (10) The action of a chromophore (or chromogen) in a dye is to _____
- (11) Examples of chromophores: _____, _____, _____
- (12) The action of auxochrome in a dye is to _____ and _____
- (13) Examples of auxochromes: _____, _____, _____
- (14) Grey hard balls of cement are called _____
- (15) Chemicals are added to glass to give colour to it. Mention the names of the chemicals in the brackets.
Blue: _____ Green _____
Purple _____ Ruby _____
Red _____
- (16) Pulverisation means to _____

IV. Fill in the blanks

- (1) Gray hard balls of cement is called. _____
- (2) Sudden cooling of glass makes it _____
- (3) Cullet is _____
- (4) _____ gives blue colour to the glass.

- (5) _____ and _____ are examples of melt spun fibres.
- (6) Auxochrome in a dye _____ and _____
- (7) _____ softens on heating.
- (8) To reduce fever _____ are used.
- (9) Nylon is a polymer formed by polymerisation of _____ and _____
- (10) PVC is a polymer formed by polymerisation of _____

V. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, statement R is true; Statement R is correct explanation for statement A

Choose B if Statement A is true, statement R is true; Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D if Statement A is false, statement R is true

(1) **Statement –A:** Bleaching powder cannot bleach in the absence of water.

Statement –R: Bleaching action is due to release of nascent oxygen from water molecule.

(2) **Statement –A:** Quick lime is used as a drying agent.

Statement –R: Quick lime reacts quickly with water.

(3) **Statement –A:** Bakelite cannot be re-moulded.

Statement –R: Bakelite is soft.

(4) **Statement –A:** Vulcanised rubber is used for tyres.

Statement –R: Vulcanisation of rubber makes it hard.

VI. Answer the following questions.

- Mention the methods of manufacture of cement.
- What is the use of adding cullet to the raw materials of glass?
- What is a plastic? How many types are there? Give one example of each.
- What is a dye? What are its components?
- Name two chromophores. Give two examples.
- Name two auxochromes. Give two examples.
- What are pharmaceuticals? Give two examples.

KEY TO EXERCISE

- I.** 1. d 2. c 3. c 4. c 5. a 6. b 7. c 8. a 9. a
 10. c 11. b 12. a 13. d 14. c 15. c 16. c 17. a 18. d
 19. c 20. a 21. a 22. b 23. c 24. b 25. d
- II.** (1) a-iv b-i c-ii d-iii (2) a-ii b-i c-iv d-iii
 (3) a-ii b-iii c-iv d-i
- III.** (1) Calcium silicates, calcium aluminate (2) limestone, clay and gypsum
 (3) limestone, clay, 1700 – 1900°C (4) soda ash, limestone and sand, 1000°C
 (5) super cooled (6) $\text{Na}_2\text{SiO}_3 \cdot \text{CaSiO}_3 \cdot 4\text{SiO}_2$
 (7) Soda glass, Pyrex glass, Quartz glass, Flint glass and Photochromatic glass
 (8) brittle, annealing (9) Pyrex or borosilicate glass (10) impart colour to the dye
 (11) $-\text{NO}_2$, $-\text{NO}$, $-\text{N}=\text{N}-$, $\text{C}=\text{O}$, $\text{C}=\text{S}$
 (12) intensifies colour, forms chemical bonds with the fibre to attach the dye to the fibre
 (13) $-\text{OH}$, $-\text{COOH}$, $-\text{HSO}_3$, $-\text{NH}_2$, NHR , NR_2
 (14) clinker
 (15) Blue (CuSO_4); Green (Cr_2O_3); Purple (MnO_2); Ruby (AuCl_3); Red (Cu_2O)
 (16) grinding to fine powder
- IV.** 1. clinker 2. brittle 3. pieces of waste glass
 4. Copper oxide and cobalt oxide 5. rayon and nylon
 6. intensifies the colour, fixes the dye to the fabric 7. Glass 8. antipyretics
 9. adipic acid and hexamethylene diamine 10. vinyl chloride
- V.** 1. A 2. C 3. C 4. A

13 Nuclear Chemistry

13.0 INTRODUCTION

As most scientific discoveries happen, *radioactivity* was discovered accidentally by Henry Becquerel, a French physicist, in 1895. He left a little pile of a uranium mineral on a photographic plate wrapped in a thick black paper in a dark room. On developing the plate he found a dark spot on it right below the position of the pile of the mineral. The black spot on the photographic plate was in the exact shape of the uranium mineral. Becquerel concluded that the black spot on the photographic plate was caused by some rays emitted by uranium. These rays penetrated the paper wrapper and affected the photographic plate. Becquerel further found that these rays were invisible to the naked eye and are given off by not only the uranium mineral but also by metallic uranium and other uranium salts. These rays pass through thin sheets of glass or metal, produce ionization in the gases through which they pass. Becquerel called these rays as *radioactive rays*.

13.1 RADIOACTIVITY

Radioactivity is the spontaneous emission of certain radiation by radioactive elements like uranium.

Natural radioactivity is essentially due to the composition of the nucleus of the radioactive element. It is a spontaneous, irreversible process in which the radioactive substance disintegrates into new substances.

13.2 DISCOVERY OF POLONIUM AND RADIUM

A year later, in 1896, Marie Curie undertook a more systematic study of radioactive substances. She found that *pitch blende*, a mineral of uranium, was highly radioactive. The high level of radioactivity of *pitch blende* could not be satisfactorily explained by saying that it was a uranium compound. She suspected that *pitch blende* must have some new element which is the cause of the high degree of radioactive emissions.

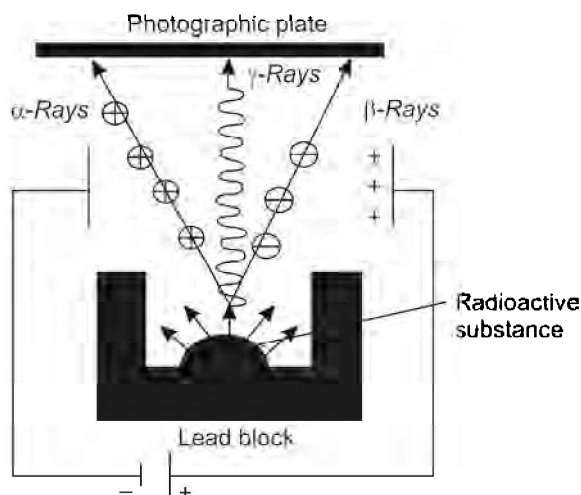
She and her husband, Pierre Curie worked together for the separation of this new hypothetical element. They took a ton of pitchblende and separated it into its constituents and found the radioactivity of each constituent. From the fraction containing bismuth they isolated a new radioactive element which they named *Polonium*, in honour of Marie Curie's native land Poland.

The wife-husband team obtained, in 1898, a few milligrams of another active element which they named *Radium* (Latin word for rays). *Radium*, the new element was found to be 30 lakh times more radioactive than uranium. The discovery of the two radioactive elements (Polonium and Radium) led to the discovery of many other radioactive elements like *Actinium*.

13.3 TYPES OF RADIOACTIVE RAYS

All radioactive emissions travel in straight lines. Rutherford found that when a strong electric field is applied perpendicular to the path of the radiations, the radiations split into three parts (see figure). One part of the radiation was deflected towards the negative plate, another part to the positive plate and the third part was not affected and continued in a straight line. Further research led to some important discoveries.

- (i) **Alpha rays [α -rays]** : The rays which are deflected towards the negative plate in the electric field must have positively charged particles. These rays were called α -rays or alpha particles. It was shown that the e/m value is same as He^{2+} particles. Alpha particles have a mass four times the mass of a hydrogen atom and two units positive charge. Thus, alpha particles are doubly charged helium ions, each ion consisting of two neutrons and two protons but no electrons.
- (ii) **Beta rays [β -rays]**: The rays which are deflected towards the positive plate in the electric field must have negatively charged particles. These rays were called β -rays or



Emission and separation of radioactive rays into α -, β -, and γ - rays in an electric field.

beta particles. The e/m ratio was shown to be the same as that of cathode ray particles. It was therefore concluded that β -rays are fast-moving electrons that carry one unit negative charge.

- (iii) **Gamma rays [γ -rays]**: The rays which are not deflected at all do not have any charged particles and are called **γ -rays** or gamma particles. It was shown that γ -rays are similar to X-rays. The rays actually travel in the form of invisible waves similar to light. The wavelengths of the rays are of the order of 10^{-8} to 10^{-11} cm. The γ -rays, unlike α -rays or β -rays, do not consist of particles with mass. Gamma rays have no mass and cannot be deflected even in the strongest electric or magnetic field which is a proof that they carry no charge.

13.4 GENERAL PROPERTIES OF RADIOACTIVE RADIATIONS

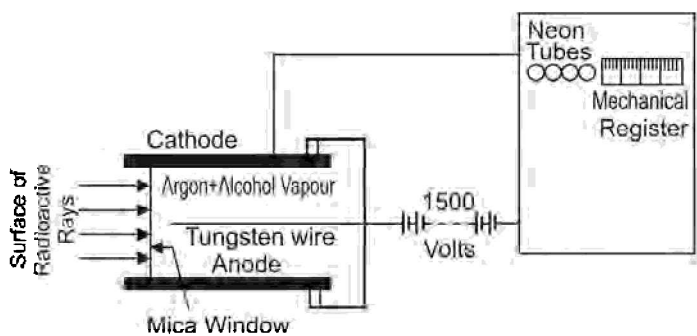
Radioactive radiations have the following properties.

- The emission of radiations is spontaneous and cannot be speeded up or slowed down by external agents like catalysts.
- The radioactive radiations travel in straight lines.
- Radioactive radiations have penetrating power. The following observations demonstrate this :
 - Radioactive radiations affect a photographic plate.

- When radioactive radiation passes through a gas it ionizes the gas.
 - Radioactive radiations cause scintillations when incident on a screen coated with zinc sulphide.
 - Radioactive radiations produce intense heat as they pass.
 - Radioactive radiations produce chemical changes.
- (d) When a radioactive substance emits radiations, *new simpler* elements are formed in an irreversible process – the new elements themselves are often radioactive.
- (e) The emission is continuous. (This is what led to their discovery).
- (f) The physical and chemical properties of radioactive elements are unaffected due to their radioactive nature.
- (g) **Electrical nature** : The three types of radioactive radiations are affected differently by electric fields. If an electric field is applied perpendicular to the path of a narrow beam of radioactive radiations, the α -rays are deflected towards the negative plate, the β -rays towards the positive plate and the γ -rays are unaffected.

13.5 DETECTION AND MEASUREMENT OF RADIOACTIVITY

A *Geiger-Muller counter* is a special device that detects and measures radioactivity. The counter consists of a copper cylinder closed at one end with a thin mica window. A tungsten wire at a high potential of more than 1500 volts is kept in the middle of the cylinder. The wire does not touch the copper cylinder. The cylinder is filled with alcohol vapour and some ionisable gas at a pressure of about 10 mm. The radioactive substance is placed outside the cylinder but near the mica window. When radioactive radiation enters the cylinder through the mica window, it causes ionization of the gas. Due to this a small ionisation current flows. This current is very small for measurement and hence it is amplified. On amplification, it causes a flash of light in a neon tube – this flash is recorded as one unit on the mechanical counter.



Geiger-Muller Counter (schematic diagram)

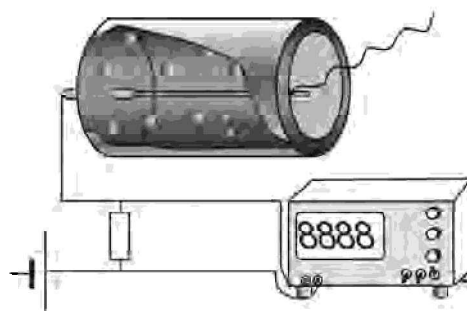


Photo of a Geiger-Muller Counter

13.6 PROPERTIES OF α -RAYS

Alpha rays exhibit the following properties.

- (i) **Velocity :** The α -rays move at high velocity ranging from 1.4×10^9 to 1.7×10^9 cm per second depending on the radioactive substance from which they are ejected. For a given radioactive substance the velocity is always the same.
- (ii) The α -rays produce intense ionization in the gas through which they pass. The alpha rays split the gaseous molecules and knock out the valence electrons of the gaseous atoms converting them to ions. Their *ionizing power* is 100 times greater than that of β -rays and 10,000 times greater than that of γ -rays.
- (iii) Alpha rays affect a photographic plate causing it to darken though the effect is feeble.
- (iv) Alpha rays have the least *penetrating power*, because α -particles while colliding with gaseous particles produce the greatest number of ions. Each collision and ionisation causes loss of energy and hence the penetrating power decreases.
- (v) Alpha-rays emitted by a radioactive material (e.g., radium salt) produce *fluorescence* when they strike a screen coated with zinc sulphide or barium platino cyanide. A tiny flash of light with a small sound or *scintillation* is produced. The fact that these scintillations are due to α -particles and not due to β - or γ -rays can be proved by interposing a thin sheet of mica between the radium salt and the fluorescent screen. Since α - rays are absorbed by mica sheet, the scintillations disappear.
- (vi) *Range of α -particles* is smallest when compared to other radiations. Scintillations from α -particles cease abruptly after they travel a certain distance through a gas or other matter. It varies from 2.70 cm for α -particles given out by uranium to 8.62 cm for those given out by polonium.
- (vii) The α -rays are *scattered* when they pass through thin sheets of mica, gold foil, etc. The divergence of α -particle from its straight line path is 2 to 3 degrees. A few particles were deflected by more than 90° . This was explained by Rutherford to be due to the repulsion between the α -particle and the nucleus of the atom, scattering the rays.
- (viii) The rays are *deflected* by electric and magnetic fields showing that they are charged particles.
- (ix) Alpha rays produce a *heating effect* in the gas they travel through. The evolution of heat is due to the collision of the particles of the radiations by other particles.
- (x) Exposure to α -rays causes incurable burns to the human body.

13.7 PROPERTIES OF β -RAYS

- (i) **Velocity and range of β -rays :** All β -particles do not emerge out of the nucleus with the same range and velocity. The velocities range from 1 per cent to 99 per cent of the velocity of light.
- (ii) Ionisation in air: β -rays produce ionization in air but the number of ions produced is hardly $\frac{1}{100}$ of that produced by α -rays.

Although their velocity is very large, they have a comparatively small mass and hence have very less kinetic energy.

- (iii) Penetration: β -rays can penetrate very thick matter. For example they can easily pass through 1 cm thick aluminium sheet.
- (iv) Deflection: β -rays are deflected by electric and magnetic fields. Their direction of deflection shows that they are negatively charged particles. The e/m value has been found to be constant and same as cathode ray particles. This shows that β -rays consist of electrons, the only difference being that they are of nuclear origin. In other words, they do not revolve in orbits as the extra nuclear electrons. The β -particles are obtained by splitting of nucleons.
- (v) They are readily scattered when passing through matter because of their extremely small mass.
- (vi) They affect photographic plates more strongly than α -particles.
- (vii) They produce *fluorescence* when they strike a screen coated with zinc sulphide or barium platino cyanide. They also cause small scintillations.

13.8 PROPERTIES OF γ -RAYS

- (i) Deflection : γ -rays are not deflected by electric or magnetic fields. This property shows that they are electromagnetic radiations which consist of high energy photons. They are emitted by an excited nucleus and have extremely short wavelength ranging from 0.5 Å to 0.005 Å.
- (ii) Velocity : γ -rays possess the same velocity as that of light i.e., 3×10^{10} cm/sec.
- (iii) Ionisation in gas: They ionize the gas through which they pass, although the ionization produced by them is comparatively small.
- (iv) Penetrating power : The penetrating power of γ -rays is very high as compared to that of β -rays. For example they can pass easily through a 3 cm thick iron sheet.
- (v) They produce *fluorescence* when they strike a screen coated with zinc sulphide or barium platino cyanide. They do not cause scintillations as they do not contain particles with mass.

13.9 COMPARISON BETWEEN α -, β - AND γ -RAYS

		α -rays (α -particles)	β -rays (β -particles)	γ -rays
1.	Charge and mass	It carries 2 units positive charge and 4 units mass	It carries 1 unit negative charge and negligible mass	The γ -rays are electromagnetic rays with very short wavelength (approximately 0.05 Å)
2.	Symbol	He^{2+}	${}_{-1}\text{e}^0$	${}^0\gamma^0$
3.	Action of electric field	These are deflected towards the negative plate	These are deflected toward the positive plate	These are not deflected
4.	Velocity	1.4×10^9 cm/s to 1.7×10^9 cm/s (1/10 th of velocity of light)	2.36 to 2.83×10^{10} cm/s (2.36 to 2.83×10^8 m/s)	Same as that of light 3×10^{10} cm/s (3×10^8 m/s)
5.	Ionizing power	Very high; nearly 100 times that of β -rays.	Low nearly 100 times that of γ -rays	Very low
6.	Effect on ZnS plate	They cause luminescence	Very little effect	Very little effect
7.	Penetrating power	Low	100 times that of α -particles	100 times that of β -particles
8.	Range	Very small (8 – 12 cm)	More than that of α -particles	High
9.	Nature of product	The atom of the radioactive substance that ejects an α -particle has atomic number that is 2 units <i>less</i> and mass number 4 units <i>less</i> .	The atom of the radioactive substance that ejects a β -particle has atomic number that is 1 unit <i>more</i> and <i>same</i> mass number.	There is no change in either the atomic number or the mass number.

13.10 TYPES OF RADIOACTIVITY

Radioactivity is of two types:

(i) Natural radioactivity

Naturally occurring elements like uranium, polonium, radium, etc., are constantly undergoing a spontaneous change as a result of which they emit α -, β -, or γ -rays and change into other elements. This spontaneous change is called *natural radioactivity*.

In natural radioactivity only a single nucleus is involved. Only the very heavy elements show *natural radioactivity*.

(ii) Artificial or induced radioactivity

Artificial or induced radioactivity is a process by which an element is converted into a new radioactive isotope of a known element by artificial means.

13.11 RADIOACTIVE DECAY

All radioactive substances undergo decay or disintegration. Atoms of heavy elements like uranium, thorium, polonium and radium, etc., are constantly breaking up into fresh radioactive atoms with the emission of α -, β -, γ -rays from their nuclei. In this process, the original (parent) atom disappears and gives rise to new (daughter) atoms. These new atoms are also, in general, radioactive and hence spontaneously break up in turn, thereby leading to another new element. The continuous decay to form new elements stops when an inactive element (*usually lead*) is reached. This spontaneous breaking up of the nucleus is known as *radioactive disintegration* or *radioactive decay*.

13.12 MODES OF DECAY

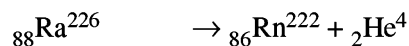
Radioactive disintegration takes place in one of the following two ways.

(i) α -particle emission

When an α -particle (${}_2\text{He}^4$) is emitted from the nucleus of an atom (called *parent element*) the nucleus of the new element formed (called *daughter element*) has mass number that is four units less and atomic number two units less because α -particle has an atomic mass of four units and nuclear charge of two units.

Illustration

An atom of radium (${}_{88}\text{Ra}^{226}$) changes on emission of an α -particle into an atom of radon (${}_{86}\text{Rn}^{222}$). The disintegration of ${}_{88}\text{Ra}^{226}$ into ${}_{86}\text{Rn}^{222}$ can be represented by a **nuclear equation** as follows.



(α -particle emitted by Radium atom to form Radon atom)

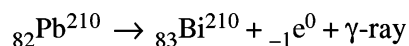
The new element Rn has mass number 222 ($226 - 4 = 222$) and atomic number 86 ($88 - 2 = 86$)

In a balanced nuclear equation, the sum of the mass numbers on the left (reactants side) is equal to the sum of the mass numbers on the right (products side). Similarly, the sum of atomic numbers on both the sides will be equal.

(ii) β -particle emission

A β -particle is an electron. It is represented as ${}_{-1}\text{e}^0$. The ejection of a β -particle is also followed by the emission of γ -rays. The emission of γ -rays is also included in the equation. When a β -particle is emitted from the nucleus of an element, the nucleus of the new element formed has the same mass number but the positive charge, i.e., the atomic number will be increased by one unit because the electron has one unit of negative charge with almost negligible mass.

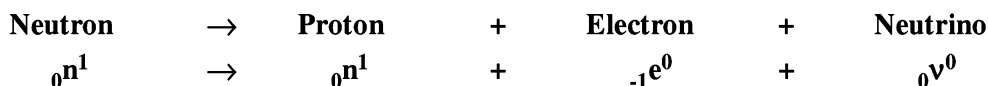
For example the transformation of lead (${}_{82}\text{Pb}^{210}$) into bismuth (${}_{83}\text{Bi}^{210}$) can be shown as



(lead atom ejects a β -particle and γ radiation to form bismuth atom)

It is now believed that in a β -particle emission, a neutron in the nucleus of the atom emitting the β -particle is converted into a proton (${}_1\text{p}^1$), an electron (${}_{-1}\text{e}^0$) and a neutrino (${}_0\nu^0$). The electron produced escapes as a β -particle leaving the proton behind in the nucleus. The increase in the atomic number of the nucleus by one unit is due to this proton left in the nucleus. This is why the atomic number increases by one. The neutrino has zero mass and charge.

Illustration



(iii) γ -ray emission

γ -rays are short wave electromagnetic radiations with no charge or mass. The emission of γ -rays from a radioactive element will not produce a new element. The emission of γ -rays results only in decrease in energy of the nucleus. The reason for γ -ray emission is that when α - or β -particle is ejected from the nucleus, the nucleus is left in an excited condition leading to the emission of γ -rays.

13.13 GROUP DISPLACEMENT LAW

According to the **Group Displacement Law**

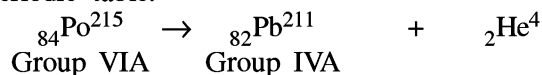
- when an α -particle is emitted from a radioactive element the new element formed is displaced two places (i.e., two groups) to the left in the periodic table as the atomic number of the new element decreases by two.
- when a β -particle is emitted, from a radioactive element the new element formed is displaced one place (i.e., one group) to the right in the periodic table as the atomic number of the new element increases by one.

Illustration

- Group Displacement Law when α -particle is emitted.*

Referring to the periodic table, we know that Polonium is in Group VIA. If polonium atom (${}_{84}^{215}\text{Po}$) emits an α -particle (${}_2^4\text{He}$) the new element formed will have atomic number 82. Again referring to the periodic table we can see that atomic number 82 is that of lead and its group is IVA. Thus there is

a *displacement* by two places to the left in the periodic table.



- Group Displacement Law when β -particle is emitted.*

Referring to the periodic table, we know that Bismuth is in Group VA. If bismuth atom (${}_{83}^{211}\text{Bi}$) emits a β -particle (${}_{-1}^0\text{e}$) the new element formed will have atomic number 84. Again referring to the periodic table we can see that atomic number 84 is that of polonium and its group is VIA. Thus there is a displacement by one place to the right in the periodic table.



Solved Examples

- Calculate the number of α - and β - particles that are emitted when ${}_{92}^{238}\text{U}$ changes into ${}_{82}^{206}\text{Pb}$.

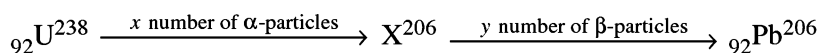
Solution: Let the number of α -particles emitted be x and number of β -particles emitted be y .

Let the emission of α - and β -particles take place in two stages as follows:

Let ${}_{92}^{238}\text{U}$ change to an intermediate element X by emitting x number of α -particles.

Let the intermediate element X emit y number of β -particles to change to ${}_{82}^{206}\text{Pb}$.

The mass number of X will be same as that Pb^{206} as X emits only β -particles (emission of β -particles does not change mass number). Thus, the mass number of X is 206. The disintegration sequence will be as follows:



$$\begin{array}{ll} \text{The mass number of X :} & \therefore 238 - 4x = 206 \\ & x = 32/4 = 8 \end{array}$$

$\therefore$ **8 α -particles are emitted.**

$$\begin{array}{ll} \text{The atomic number of X:} & \text{Since 8 particles are emitted,} \\ & \text{The atomic number of X will be} \\ & 92 - 2 \times 8 = 92 - 16 = 76 \end{array}$$

As every β -particle emission increases atomic number by 1,

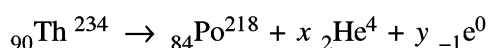
$$\therefore y = 82 - 76 = 6$$

$\therefore$ **6 β -particles are emitted.**

Thus the number of various particles emitted is 8 α -particles and 6 β -particles.

- (2) How many α - and β -particles will be emitted when ${}_{90}\text{Th}^{234}$ changes into ${}_{84}\text{Po}^{218}$?

Solution: Let the α and β particles emitted from the radioactive element be x and y .



Number of α -particles emitted:

Balancing the mass numbers on both sides we get

$$234 = 218 + x \times 4 + y \times 0$$

$$4x = 16$$

$$x = 4.$$

Thus, **number of α -particles emitted is 4.**

Number of β -particles emitted:

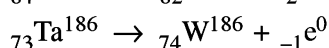
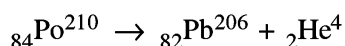
Balancing the atomic numbers on both sides we get

$$90 = 84 + 42 - y \times 1$$

$$y = 92 - 90 = 2$$

Thus, **the number of β -particles emitted is 2.**

- (3) The elements Pb and Ta belong to groups 14(IVA) and 15(VA) respectively in the periodic table. From the two nuclear reactions given below predict the groups in the periodic table to which the elements Po and W belong.



Since ${}_{82}\text{Pb}^{206}$ belonging to group 14 is formed by an alpha particle emission, the parent element Po belongs to the group that is two positions to its right, i.e., to group 16(VIA).

Since Ta belongs to group 15, so, W formed by one β -particle emission, belongs to group 16.

13.14 HALF-LIFE PERIOD

The half-life period of a radioactive substance is

the time in which half of the radioactive substance will disintegrate.

For example, it takes nearly 1620 years for half a given quantity of radium to disintegrate and change into radon. In another 1620 years, *half of the remainder* would have disintegrated leaving one-fourth of the original amount behind. *The half-life period of radium is 1620 years.*

In general, it may be said that at the end of time T , only 50% of the radioactive substance remains unchanged, at the end of $2T$, only 25%, after $3T$, only 12.5%, after $4T$, only 6.25% and at the end of $10T$, only 0.1%.

Fraction of radio active substance left after n half-lives

Suppose the fraction left after n half-lives is N and original mass of the radioactive substance is N_0 , then.

$$N = (1/2)^n N_0$$

13.15 MASS DEFECT AND BINDING ENERGY OF THE NUCLEUS

The experimental value of the atomic mass (A) of an isotope of an element is less than the sum of the masses (M) of all neutrons, protons and electrons present in one atom of that element. There is a loss of some mass in the form of energy. The mass defect is converted into energy that is released when the atom is hypothetically constructed.

The difference between the two masses is termed as **mass defect**, m .

$$\Delta m = M - A$$

The loss of mass corresponds to a release of energy as given by the Einstein equation

$$E = \text{mass} \times c^2$$

or $\Delta E = \Delta m c^2$ (where c is the velocity of light)

The energy released in the formation of a nucleus from its constituent particles is called binding energy of that nucleus.

Generally, the binding energy is expressed as *energy released per nucleon*.

Thus

Binding energy

$$= \frac{\text{Total energy released in the nucleus formation}}{\text{No. of neutrons} + \text{No. of protons}}$$

$$= \frac{\text{mass defect} \times 931.5}{\text{Mass Number}} \text{ MeV.}$$

13.16 NUCLEAR STABILITY

Nuclear stability is dependent on the composition of the nucleus, nuclear forces, mass defect, packing fraction and n/p ratio.

- (i) **Nuclear forces** bind the nucleons together. These forces are neither electrostatic nor gravitational in nature. They are independent of the charges present on the nucleons. The nucleons continuously exchange certain particles called *mesons*. The mesons bind the nucleons together. The mesons may carry positive, negative or no charge. Their main function is to bind the nucleons together. The mesons move from the neutrons to protons. The transformation of the neutrons into protons and vice-versa is due to the mesons and helps to hold the nucleons together. All mesons are unstable outside the nucleus. The number of charged particles in the nucleus however is a constant.

- (ii) **Mass defect** is the difference between the calculated *theoretical mass* of the nucleons and the observed *true mass* of the nucleons. The latter is always less than the former. The difference in mass is converted to energy according to Einstein's equation ($E=mc^2$). The energy released in the formation of a nucleus from the constituent nucleons is called binding energy. It follows that to disrupt the nucleus, we must supply it with energy equal to this binding energy.

In the conversion of mass into energy,

Loss of 1 amu mass results in the release of 931.5 MeV of energy.

(1 a.m.u. = 1.66×10^{-24} gm).

Since, A is the number of nucleons or mass number,

The average binding energy per nucleon

More the average binding energy more stable the nucleus.

Binding energy is smaller for lighter elements. It is the lowest for hydrogen. It increases with mass number reaching a maximum value of 8.7 MeV at about mass number 56 (iron). Thus, iron is thermodynamically more stable. After reaching this peak with iron the average binding energy starts decreasing with increase in mass number beyond 56. It falls to 7.57 MeV for the heavy elements like uranium.

- (iii) **Packing Fraction** gives an indication of the stability of the nucleus. It is derived mathematically as follows.

Packing Fraction

$$= \frac{\text{Isotope mass} - \text{mass number}}{\text{Mass Number}}$$

A negative PF value indicates a more stable nucleus as loss in mass is converted into energy. A positive value indicates instability of the nucleus.

- (iv) **n/p ratio:** Lighter elements up to mass numbers 40 ($Z = 20$) have equal number of neutrons and protons. The n/p ratio is thus 1 and have the most stable nuclei. For hydrogen, n/p ratio is zero. Elements with higher atomic numbers have more stable nuclei if they have a slight excess of neutrons. Excess of neutrons over protons in the nucleus increases the stability by reducing the repulsive forces between the protons and consequently increases the attractive forces within the nucleus. The n/p ratio increases to 1.6 in uranium ($Z=92$). A n/p ratio beyond 1.6 makes the nucleus unstable and the nucleus undergoes radioactive disintegration. The new elements that form on disintegration have smaller n/p ratio thus making the nucleus more stable.

SOLVED EXAMPLES

- (1) Calculate the binding energy for ${}_1\text{H}^2$ atom. The mass of one atom of ${}_1\text{H}^2$ is 2.014102 amu, where one neutron and one proton together weigh 2.01649 amu. Neglect the mass of electron.

Ans: Actual mass of ${}_1\text{H}^2 = 2.014102$ amu

Mass of neutron and proton = 2.016490 amu

Mass of defect = $2.016490 - 2.014102 = 2.388 \times 10^{-3}$ amu

$$\text{B.E} = 2.388 \times 10^{-3} \times 1.66 \times 10^{-24} \text{ g} \times (3 \times 10^{10})^2 \text{ cm}^2 \text{ sec}^{-2}$$

or $\text{B.E} = 3.56767 \times 10^{-6} \text{ erg}$

since $c = 3 \times 10^{10} \text{ cm sec}^{-1}$, $\text{amu} = 1.66 \times 10^{-24} \text{ g}$

$$\text{B.E} = \frac{3.5676 \times 10^{-6}}{10^7} \text{ Joules} \quad (1 \text{ Joule} = 10^7 \text{ ergs})$$

$$\text{B.E} = \frac{3.5676 \times 10^{-6}}{1.602 \times 10^{-19} \times 10^7} \text{ eV} \quad (1 \text{ eV} = 1.602 \times 10^{-19} \text{ J})$$

$$\text{B.E} = \frac{3.5676 \times 10^{-6}}{1.602 \times 10^{-19} \times 10^6 \times 10^7} \text{ MeV} \quad (1 \text{ MeV} = 10^6 \text{ eV})$$

$$\text{B.E} = 2.22 \text{ MeV}$$

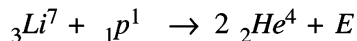
Or

$$\text{B.E} = \text{Mass defect} \times 931 \text{ MeV} \quad (1 \text{ amu} = 931 \text{ MeV})$$

$$\text{B.E} = \frac{2.388}{10^3} \times 931 = 2.22 \text{ MeV}$$

$$\text{Binding energy per nucleon} = \frac{2.22}{2} = 1.11 \text{ MeV}$$

- (2) The atomic masses of lithium, helium and proton are 7.01823 amu, 4.00387 amu and 1.00715 amu respectively. Calculate the energy evolved in the reaction.



Ans: Mass of reactants = $7.01823 + 1.00715 = 8.02538$ amu

Mass of products = $2 \times 4.00387 = 8.00774$ amu

Loss of mass = $8.02538 - 8.00774 = 0.01764$ amu

Energy evolved (E) = $0.01764 \times 931 = 16.423 \text{ MeV}$.

- (3) The half-life period of ${}_{53}\text{I}^{125}$ is 60 days. What percent of radioactive substance would be present after 180 days?

Ans: $t = 180$ days. $T = 60$ days.

$$\text{Number of half-lives, } n = \frac{\text{time elapsed}}{\text{half-life}} = \frac{180}{60} = 3$$

If 100 gm of radioactive substance is taken,

$$\text{Amount left after 3 halves} = \frac{N_0}{2^n} = \frac{100}{2^3} = 12.5 \text{ g or } 12.5\% \text{ of the original substance.}$$

13.17 RADIOACTIVE SERIES

Atoms of heavy elements like uranium, thorium, polonium and radium, etc., are constantly undergoing radioactive decay with the emission of α -, β -, γ -rays from their nuclei forming new simpler substances. The parent atom decays forming a new or daughter atom. These new atoms are also, in general, radioactive and hence spontaneously break up, in turn, thereby leading to a long chain of different radioactive elements in the form of a series until an inactive element (usually lead) is reached.

The series of elements thus obtained by the successive disintegration of the new atoms is known as **radioactive disintegration series**. There are three series of natural radioactive disintegration series. All the three series end in a stable isotope of lead. Every naturally occurring radioactive element belongs to one of the three series. They are:

- (i) Uranium series [(4n + 2) series]
- (ii) Thorium series [4n series]
- (iii) Actinium series [(4n + 3) series]

Some elements of each series emit α -particles and some others emit β -particles.

No single atom can undergo both α - and β -decays. But it is possible that at a particular stage in the series, a few atoms may undergo α -decay while other atoms undergo β -decay.

Thus at some stages two branches can be seen in the series.

(1) Uranium series [(4n + 2) series]

The parent atom is Uranium. This series is also called (4n + 2) series because the mass number of the elements of this series is given by this expression (4n + 2) in which n is a positive integer whose value decreases by one after each decay. The mass numbers of the members of this series

give a remainder of 2 when divided by 4. In this series ${}_{92}\text{U}^{238}$ is the parent element and through the successive disintegrations it is finally transformed into a stable isotope of lead, ${}_{82}\text{Pb}^{206}$ (see figure)

(2) Thorium series [4n series]

This series is also known as 4n series because mass numbers of the members of this series are divisible by 4. This series starts with ${}_{90}\text{Th}^{232}$ and ends in a stable isotope of lead ${}_{82}\text{Pb}^{208}$

(3) Actinium series [(4n + 3) series]

This series is also known as (4n + 3) series because the mass number of the elements of this series give a remainder of 3 when divided by 4. Actinium was one time thought to be the starting element of this series, but now it is known that the true starting element is ${}_{92}\text{U}^{235}$ ending up in a stable isotope of lead, ${}_{82}\text{Pb}^{207}$.

The three series showing the stepwise decays and the new elements formed which undergo further decay leading to the last stable isotope of lead is shown.

Similarities between radioactive series

There are many points of similarity between the three radioactive series:

- (i) In all three series, a product is formed which disintegrates by emitting either α - or β -particle.
- (ii) In all three series, there is an element of atomic number 86 which has the properties of an inert gas and is called *Radon*.
- (iii) The stable end product in all the three series is an isotope of lead with atomic number 82.

Radioactive Disintegration Series

Uranium Series	Thorium Series	Actinium Series
${}_{92}\text{U}^{238}$ $\downarrow -\alpha$ ${}_{90}\text{Th}^{234}$ $\downarrow -\beta$ ${}_{91}\text{Pa}^{234}$ $\downarrow -\beta$ ${}_{92}\text{U}^{234}$ $\downarrow -\alpha$ ${}_{90}\text{Th}^{230}$ $\downarrow -\alpha$ ${}_{88}\text{Ra}^{226}$ $\downarrow -\alpha$ ${}_{86}\text{Rn}^{222}$ $\downarrow -\alpha$ ${}_{84}\text{Po}^{218}$ $\swarrow -\alpha \quad \searrow -\beta$ ${}_{82}\text{Pb}^{214} \quad {}_{85}\text{At}^{218}$ $\swarrow -\beta \quad \searrow -\alpha$ ${}_{83}\text{Bi}^{214}$ $\swarrow -\alpha \quad \searrow -\beta$ ${}_{81}\text{Tl}^{210} \quad {}_{84}\text{Po}^{214}$ $\swarrow -\beta \quad \searrow -\alpha$ ${}_{82}\text{Pb}^{210}$ $\downarrow -\beta$ ${}_{83}\text{Bi}^{210}$ $\swarrow -\alpha \quad \searrow -\beta$ ${}_{81}\text{Tl}^{206} \quad {}_{84}\text{Po}^{210}$ $\swarrow -\beta \quad \searrow -\alpha$ ${}_{82}\text{Pb}^{206}$	${}_{90}\text{Th}^{232}$ $\downarrow -\alpha$ ${}_{88}\text{Ra}^{228}$ $\downarrow -\beta$ ${}_{89}\text{Ac}^{228}$ $\downarrow -\beta$ ${}_{90}\text{Th}^{228}$ $\downarrow -\alpha$ ${}_{88}\text{Ra}^{224}$ $\downarrow -\alpha$ ${}_{86}\text{Rn}^{220}$ $\downarrow -\alpha$ ${}_{84}\text{Po}^{216}$ $\swarrow -\alpha \quad \searrow -\beta$ ${}_{82}\text{Pb}^{212} \quad {}_{85}\text{At}^{216}$ $\swarrow -\beta \quad \searrow -\alpha$ ${}_{83}\text{Bi}^{212}$ $\swarrow -\alpha \quad \searrow -\beta$ ${}_{81}\text{Tl}^{208} \quad {}_{84}\text{Po}^{212}$ $\swarrow -\beta \quad \searrow -\alpha$ ${}_{82}\text{Pb}^{208}$	${}_{89}\text{Ac}^{227}$ $\downarrow -\alpha$ ${}_{87}\text{Fr}^{223}$ $\swarrow -\beta \quad \searrow -\alpha$ ${}_{88}\text{Ra}^{223}$ $\downarrow -\alpha$ ${}_{86}\text{Rn}^{219}$ $\downarrow -\alpha$ ${}_{84}\text{Po}^{215}$ $\downarrow -\alpha$ ${}_{82}\text{Pb}^{211}$ $\downarrow -\beta$ ${}_{83}\text{Bi}^{211}$ $\swarrow -\alpha \quad \searrow -\beta$ ${}_{81}\text{Tl}^{207} \quad {}_{84}\text{Po}^{211}$ $\swarrow -\beta \quad \searrow -\alpha$ ${}_{82}\text{Pb}^{207}$

13.18 SPECIAL ATOMS

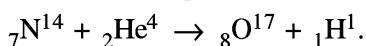
Some special atoms having some unique property are given below.

- 1 **Isotopes:** Atoms of the *same element* having same Atomic Number but different Mass Numbers are called *isotopes*. They have the same number of electrons and protons but differ in the number of neutrons. Example: Cl^{37} , Cl^{35} are isotopes.
- 1 **Isobars:** Atoms of *different elements* having different Atomic Numbers but same Mass Number are called *isobars*. They differ in the number of protons and neutrons in the nucleus, but their sum is same. Example: ${}_{19}\text{K}^{40}$ and ${}_{20}\text{Ca}^{40}$ are isobars.
- 1 **Isotones:** Atoms of *different elements* having different Atomic Numbers and Mass Numbers but the same number of neutrons are called *isotones*. Example: ${}_{19}\text{K}^{39}$, ${}_{20}\text{Ca}^{40}$ are isotones.
- 1 **Isodiaphers:** Atoms of *different elements* having different Atomic Numbers and Mass Numbers but having the same isotopic number are called *isodiaphers*. {*Isotopic Number* is $(n - p)$ or $(A - 2Z)$ }. Example: ${}_{9}\text{F}^{19}$, ${}_{11}\text{Na}^{23}$ are isodiaphers.
- 1 **Isoelectronic atoms:** Atoms having the same number of electrons. Example: N^{3-} , O^{2-} , F^{-} , Ne , Na^{+} , Mg^{2+} , Al^{3+} are all isoelectronic species as they all have 10 electrons each.
- 1 **Isosters** are molecules having the same number of atoms and electrons. Examples: N_2O and CO_2 are isosters; CO and N_2 are isosters.

13.19 ARTIFICIAL TRANSMUTATION (NUCLEAR REACTIONS)

The artificial conversion of one element into another by altering the nucleus is called *Artificial Transmutation or nuclear reaction*. Rutherford produced the first artificial transmutation when he bombarded nitrogen nucleus with alpha particles to form oxygen atom and hydrogen atom.

The nuclear equation is written as

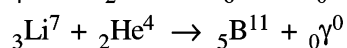
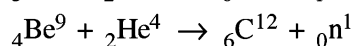
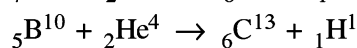
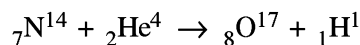


Nitrogen atom is called the *target nucleus*. Alpha particle is called projectile. The oxygen

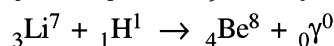
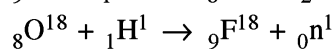
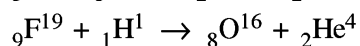
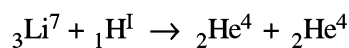
nucleus formed is called *recoil nucleus*.

Artificial transmutations can be caused using different projectiles. Two examples are given below.

(1) Transmutation by alpha particles



(2) Transmutations by protons (${}_1\text{H}^1$)



13.20 NUCLEAR REACTIONS VERSUS CHEMICAL REACTIONS

Nuclear reactions differ from chemical reactions in the following respects.

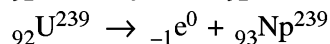
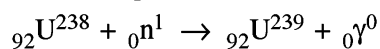
- (i) In chemical reactions *rearrangement of outermost electrons of the atom takes place while the nuclei remain unaffected*. Thus no change occurs in the atomic species taking part in the chemical reaction. In other words, no new element is formed in chemical reactions. In nuclear reactions, the numbers of nucleons present in the nucleus changes. A new element is formed. Thus nuclear reactions bring about atomic transmutation.
- (ii) The amount of energy released in nuclear reactions is million times greater than that in chemical reactions. This is because in nuclear reactions a small but measurable loss of mass takes place. This loss in mass is converted into energy in accordance with mass-energy relationship ($E = mc^2$), where m is loss in mass and c is velocity of light and E is energy produced.

13.21 PREPARATION OF TRANSURANIC ELEMENTS

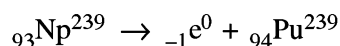
Elements after atomic number 92 are known as transuranic elements. They are artificially produced. Two examples are given below.

- (1) **Neptunium:** Neptunium is formed by bombarding ${}_{92}\text{U}^{238}$ with slow neutrons to

get ${}_{92}\text{U}^{239}$ which is radioactive with a half life of 23.5 minutes. ${}_{92}\text{U}^{239}$ disintegrates emitting beta particle and a new element called *Neptunium*.



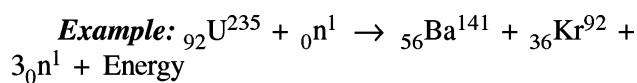
- (2) **Plutonium** is formed when ${}_{93}\text{Np}^{239}$ disintegrates emitting beta particles and *Plutonium* is formed.



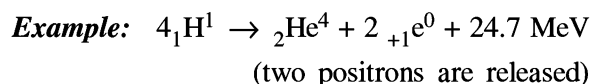
13.22 NUCLEAR FISSION AND NUCLEAR FUSION

The process in which a heavier nucleus is split

into two lighter nuclei of almost equal size with the release of a huge amount of energy is called *Nuclear Fission*.



The process in which two lighter nuclei combine to give a stable and heavier nucleus releasing large amounts of energy is called Nuclear Fusion.



The nuclear fusion reaction given in the example above is the reaction that takes place in the sun and is entirely responsible for the solar energy that sustains life.

Comparison of nuclear fission and fusion reactions

Nuclear Fission	Nuclear fusion
(1) Involves breaking of heavy nucleus into two lighter nuclei of almost equal parts.	(1) Involves fusion of two or more light nuclei to form a heavier nucleus.
(2) The heavier nucleus has to be bombarded with high energy neutrons to induce the splitting.	(2) The fusion reaction requires a very high temperature of a few million degrees to be maintained.
(3) The splitting does not continue and stops after one splitting takes place – it is a close-ended chain reaction.	(3) It is an open-ended reaction as the fusion reaction continues as long as fuel is not exhausted.
(4) For the nuclear fission to take place a minimum <i>critical mass</i> is required.	(4) No minimum mass is required for the reaction to take place as the fusion takes place only on external heating.
(5) The best use of fission reactions is for peaceful purposes like power generation.	(5) The entire energy of the universe from the sun and stars is due to nuclear fusion reactions.

13.23 APPLICATIONS OF RADIOACTIVE RADIATIONS

- (i) **In food preservation :** Nuclear radiations like γ -rays have been utilized for the preservation of food. The irradiation of food items mainly meat, poultry products, fish and fruits to destroy almost all bacteria are done by exposure to γ -rays from cobalt-60 or cesium-137. This increases the shelf life of these articles without refrigeration.
- (ii) **For industrial radiography :** Many radiation sources such as cobalt – 60, which emits γ -rays, have been used for industrial radiography i.e., for investigating

the interiors of metal castings for detecting any cracks or defects.

- (iii) **For thermonuclear power :** Radioactive substances emitting α - or β -particles have been used for the production of electric power by thermoelectric conversion. When α - or β -particles are absorbed in matter, the energy of the radiation is converted into heat which can be utilized for production of electric power. Such *radio nuclide* power generators are particularly suitable for space vehicles because of their light weight, long life and absolute reliability.

- (iv) **As a source of heat in rockets :** Radio nuclides have been used as compact sources of heat energy because of which they find many applications in spacecraft. Radio nuclides of promethium-147, polonium-210 and plutonium-238 have been used to heat hydrogen that is used as a propellant in rockets.
- (v) **For radiation chemistry :** Chemical changes initiated by radiations from radioactive substances is the basis of a newly-developed subject called *radiation chemistry* which has been applied in the production and modification of plastics.
- (vi) **For sterilization :** Gamma radiation from cobalt-60 is used in hospitals for sterilization of materials like dressings, hypodermic syringes and surgical sutures.
- (vii) **For insect control :** Population of insects which causes considerable damage to both plant crops and livestock can be controlled by irradiating the male members of these insects so that they become sterile.
- (viii) **For radiation mutations :** Radiation mutations in plants have been practiced to produce new varieties of these plants.
- (ix) **For making self-luminous paints :** Self-luminous paints for use on instruments and watch dials have been made by adding a natural α -emitting radioactive substance to phosphor.
- (x) **For elimination of static electricity :** The ionization produced by α -particles has been widely used for the elimination of static electricity which can cause serious fire and explosion hazard in the paper, textile, rubber and plastic industries.
- (xi) **Radioactive tracers** are used in studying

reaction mechanisms like photosynthesis, diagnosing diseases like brain tumour and cancerous growth, in agriculture, analytical chemistry.

- (xii) **Carbon dating :** The age of animal and plant fossils can be determined by radiocarbon dating method. This method was developed by Willard Libby who was awarded the Nobel Prize for this work.

Carbon dating

The determination of the age of a sample of wood (the time which elapsed after the death of the plant) consists of *determining the ratio of the amount of ${}_6\text{C}^{14}$ to that of ${}_6\text{C}^{12}$ in a living piece of wood and the dead piece.*

The following points will show how carbon dating is used to determine the age of fossil remains.

- (a) Carbon dioxide is made up of carbon and oxygen atoms.
- (b) *The carbon present in carbon dioxide in a given sample is a mixture of C^{14} and C^{12} isotopes which are present in a fixed ratio.*
- (c) Plants absorb carbon dioxide from the atmosphere and prepare cellulose (wood).
- (d) As long as the plant is alive, *the ratio of ${}_6\text{C}^{14}$ to ${}_6\text{C}^{12}$ atoms in the wood of the plant is the same as in the atmosphere,*
- (e) When the tree dies the ratio of ${}_6\text{C}^{14}$ to ${}_6\text{C}^{12}$ begins to decrease continuously due to the continuous decrease in the amount of ${}_6\text{C}^{14}$ in the plant. This decrease in the amount of ${}_6\text{C}^{14}$ is due to its continuous disintegration emitting β -radiations as shown:

$${}_6\text{C}^{14} \rightarrow {}_7\text{N}^{14} + {}_{-1}\text{e}^0 \quad (T = 5568 \text{ years})$$
- (f) Using special formulae and the known half life of the isotopes we can calculate the actual age of the fossil.

EXERCISE

I. Choose the correct answer

- (1) **An alpha particle is identical with**
 - (a) proton
 - (b) neutron
 - (c) helium nucleus
 - (d) electron
- (2) **Half-life period of a radioactive substance is 120 days. After 480 days, 4 g will be reduced to**
 - (a) 2
 - (b) 1
 - (c) 0.5
 - (d) 0.25

- (3) **Neutron is a fundamental particle carrying**
 - (a) charge of +1 unit mass of 1 unit
 - (b) no charge and a mass of 1 unit
 - (c) no charge and no mass
 - (d) a charge of -1 and a mass of 1 unit
- (4) **Of the following radiations, the one most easily stopped by air is**
 - (a) alpha-rays
 - (b) beta-rays
 - (c) gamma-rays
 - (d) X-rays

- (5) A magnet will cause the greatest deflection of
 (a) gamma-rays (b) beta-rays
 (c) alpha-rays (d) neutrons
- (6) ${}_{92}\text{U}^{238}$ emits an alpha-particle, the product has mass number and atomic number
 (a) 236, 90 (b) 234, 90
 (c) 238, 90 (d) 236, 90
- (7) During a beta-emission
 (a) an atomic electron is ejected
 (b) an electron which is already present within the nucleus is ejected
 (c) a neutron in the nucleus decays emitting an electron
 (d) a part of the binding energy of the nucleus is converted into an electron
- (8) The number of neutrons in the parent nucleus which gives ${}^{14}\text{N}$ on beta-emission is :
 (a) 6 (b) 7 (c) 8 (d) 14
- (9) The atom ${}_{92}\text{X}^{238}$ emits an alpha particle. The number of neutrons in the new atom will be
 (a) 138 (b) 140
 (c) 144 (d) 150
- (10) When a radioactive element loses one alpha and two beta-particles, the daughter element formed is an _____ of the parent element.
 (a) Isotope (b) Isobar
 (c) Isotone (d) Isochore
- (11) Energy is produced in a nuclear reactor by:
 (a) controlled fusion (b) uncontrolled fusion
 (c) controlled fission (d) uncontrolled fission
- (12) In a radioactive decay, an emitted electron comes from:
 (a) nucleus of the atom
 (b) inner orbital of the atom
 (c) outermost orbit of the atom
 (d) orbit having principal quantum number one
- (13) Half-life for radioactive ${}^{14}\text{C}$ is 5760 years. 200 mg of ${}^{14}\text{C}$ will be reduced to 25 mg in _____
 (a) 5760 years (b) 11520 years
 (c) 17280 years (d) 23040 years
- (14) Carbon-14 dating method is based on the fact that
 (a) carbon-14 fraction is same in all objects
 (b) carbon-14 is highly insoluble
 (c) ratio of carbon-14 and carbon-12 is constant
 (d) all the above
- (15) The half life of a radioactive isotope is three hours. If the initial mass of the isotope was 300g, the mass which remains without decaying after 18 hours would be
 (a) 4.68 g (b) 2.34 g
 (c) 1.17 g (d) 9.36 g
- (16) In nuclear fission process, energy is released because
 (a) Mass of products is more than mass of nucleus
 (b) Total binding energy of products formed due to nuclear fission is more than the parent fissionable material
 (c) Total binding energy of products formed due to nuclear fission is less than parent fissionable material
 (d) Mass of some particles is converted into energy
- (17) When an alpha-particle is removed from Ra (Group II(A)) the new element formed is of :
 (a) Group 0 (b) Group I
 (c) Group VII (d) Group III
- (18) Hydrogen bomb is based on
 (a) nuclear fusion (b) atomic fusion
 (c) atomic fission (d) nuclear fission
- (19) Heavy water used in the nuclear reactor is
 (a) water at 4°C
 (b) water containing heavy ions
 (c) D_2O
 (d) water containing CaSO_4
- (20) The binding energy of an atom is 128 MeV, the binding energy per nucleon is 8, then the number of nucleons
 (a) 4 (b) 8
 (c) 16 (d) 32
- (21) ${}_{19}\text{K}^{40}$ and ${}_{20}\text{Ca}^{20}$ are known as
 (a) isotopes (b) isobars
 (c) isotones (d) isodiaphers
- (22) The number of alpha and beta particles emitted during the reaction is ${}_{90}\text{Th}^{232} \rightarrow {}_{82}\text{Pb}^{208}$
 (a) 8 alpha and 4 beta (b) 8 alpha and 16 beta
 (c) 4 alpha and 2 beta (d) 6 alpha and 4 beta
- (23) Radioactive disintegration differs from a chemical change in being
 (a) a nuclear process
 (b) an exothermic process
 (c) a spontaneous process
 (d) a unimolecular first order reaction
- (24) The introduction of a neutron into the nucleus of an atom would lead to a change in
 (a) number of electrons also
 (b) the chemical nature of the atom
 (c) its atomic number
 (d) its atomic mass
- (25) Gamma rays are
 (a) high energy electrons
 (b) low energy electrons
 (c) high energy electromagnetic waves
 (d) high energy positrons

(26) Which of the following atoms will contain the least number of neutrons?

- (a) ${}^{238}\text{U}$ (b) ${}^{239}\text{U}$ (c) ${}^{240}\text{U}$ (d) ${}^{235}\text{U}$

(27) Gamma rays have

- (a) no mass and no charge
(b) mass only (c) charge only
(d) mass and charge both

(28) Which is the correct statement?

- (a) Isotopes are always radioactive
(b) Alpha rays are always negatively charged
(c) Beta rays are always negatively charged
(d) Gamma rays can be deflected in a magnetic field

(29) The product formed is an isobar if there is:

- (a) 1 alpha emission (b) 1 beta emission
(c) 1 alpha and 1 beta emission
(d) 1 alpha and 1 beta emission

(30) Decrease in atomic number is not observed during

- (a) alpha emission (b) beta emission
(c) positron emission (d) electron emission

II. Match the following.

(1) When a radioactive substance ${}_n\text{X}^m$ undergoes decay it forms new elements A, B, C and D as shown in Set B. Match particles emitted by X given in set A with the elements formed in Set B.

- | Set I | Set II |
|---|--------------------------------|
| (i) ${}_n\text{X}^m$ – one α -particle | (a) ${}_{(n+2)}\text{A}^m$ |
| (ii) ${}_n\text{X}^m$ – two β -particles | (b) ${}_{(n-1)}\text{B}^{m-4}$ |
| (iii) ${}_n\text{X}^m$ – one α -particle and one β -particle | (c) ${}_{(n+1)}\text{C}^m$ |
| (iv) ${}_n\text{X}^m$ – one β -particle and γ -rays | (d) ${}_{(n-2)}\text{D}^{m-4}$ |

(2) Match the particles in Set A with their origin with respect to an atom in Set B (Assume radioactive nature of atom).

- | Set I | Set II |
|---------------------------|-------------------|
| (i) cathode ray particles | (a) nucleus |
| (ii) canal ray particles | (b) valence shell |
| (iii) α -particles | (c) positive ions |
| (iv) γ -rays | (d) inner orbits |

(3) Match the special atom term in Set A with the corresponding examples in Set B.

- | Set I | Set II |
|---------------------|--|
| (i) Isotopes | (a) ${}_9\text{F}^{19}$, ${}_{11}\text{Na}^{23}$ |
| (ii) Isotones | (b) Ne, Al^{3+} |
| (iii) Isoelectronic | (c) ${}_1\text{H}^2$, ${}_1\text{H}^3$ |
| (iv) Isodiapher | (d) ${}_{19}\text{K}^{39}$, ${}_{20}\text{Ca}^{40}$ |

III. Each question contains two statements. Statement A is an Assertion Statement and Statement R is the Reason Statement. Each question has four choices out of which only one is correct. Choose the correct one.

Choose A if Statement A is true, statement R is true; Statement R is correct explanation for statement A

Choose B if Statement A is true, statement R is true; Statement R is not correct explanation for statement A

Choose C if Statement A is true, Statement R is false

Choose D if Statement A is false, statement R is true

(1) **Statement A** : β -particles are extra-nuclear electrons as they carry one unit negative charge.

Statement R : Cathode ray particles are extra-nuclear electrons with one unit negative charge.

(2) **Statement A** : When a radioactive element loses an alpha particle and two β -particles the final daughter element formed is an isotope of the parent atom.

Statement R : The atomic number of the daughter element will be same as the parent element.

(3) **Statement A** : Radioactive elements have unstable nucleus.

Statement R : The n/p ratio of radioactive elements is very large when compared to that of non-radioactive elements.

(4) **Statement A** : In nuclear fission large amount of energy is released.

Statement R : Mass defect of the products formed gets converted to energy.

KEY TO EXERCISE

- | | | | | | | | | | |
|-------------|----------|-------|--------|-------|----------|-------|--------|-------|-------|
| I. | 1. c | 2. d | 3. b | 4. a | 5. b | 6. b | 7. c | 8. c | 9. c |
| | 10. a | 11. c | 12. a | 13. c | 14. c | 15. a | 16. b | 17. a | 18. a |
| | 19. c | 20. c | 21. b | 22. d | 23. a | 24. d | 25. c | 26. d | 27. a |
| | 28. c | 29. b | 30. b | | | | | | |
| II. | (1) i. d | ii. a | iii. b | iv. c | (2) i. b | ii. c | iii. a | iv. a | |
| | (3) i. c | ii. d | iii. b | iv. a | | | | | |
| III. | 1. D | 2. A | 3. A | 4. A | | | | | |

14 Analytical Chemistry

14.0 INTRODUCTION

Analytical chemistry is the study of the chemical composition of substances. Special characteristic features of pure substances are used to establish the identity of substances whose composition is not known. Analytical chemistry consists of two main types of analysis — *qualitative* and *quantitative analysis*.

Qualitative analysis is used to identify the presence of a given element or compound in a sample.

Quantitative analysis is used to find the amount of a given element or compound in a sample.

In this chapter, we will discuss some qualitative analysis techniques. We will learn

- (i) the identification of gases
- (ii) the identifications of cations,
- (iii) the identifications of anions,
- (iv) the distinction between an acid and an alkali, and
- (v) the importance of pH in various fields.

14.1 COMMON GASES

Identifying the presence of gases has many useful aspects. By identifying the presence of certain gases we can possibly identify

- (i) the substance that is responsible for the liberation of the gas in a chemical reaction
- (ii) pollution levels in the atmosphere.

Common gases and their identification

Some common gases that we have already seen in earlier classes are water vapour, hydrogen, oxygen, carbon dioxide, sulphur dioxide, hydrogen sulphide, nitrogen, ammonia, nitrogen dioxide, chlorine, hydrogen chloride, etc. We will now see how the chemical properties of a gas can be used to identify the gas. We have already seen how the gases can be prepared in the laboratory in earlier classes.

Summary of the preparation of common gases

The laboratory preparation of these gases is tabulated below.

Gas	Detection
1. Water vapour	By boiling some water in a test tube.
2. Hydrogen	By the action of dilute H_2SO_4 on Zn pieces. $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$
3. Oxygen	(i) By strongly heating red lead (Pb_3O_4). $2\text{Pb}_3\text{O}_4 \rightarrow 6\text{PbO} + \text{O}_2 \uparrow$ (ii) By heating KClO_3 with MnO_2 . $2\text{KClO}_3 \xrightarrow{\text{MnO}_2 \text{ (catalyst)}} 2\text{KCl} + 3\text{O}_2$
4. Carbon dioxide	By the action of dilute H_2SO_4 on a carbonate or bicarbonate. $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$ $2\text{NaHCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2$
5. Sulphur dioxide	By the action of dilute H_2SO_4 on a sulphite. $\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2$
6. Hydrogen sulphide	By the action of dilute H_2SO_4 on sulphide. $\text{Na}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S}$ $\text{FeS} + \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{H}_2\text{S}$

7. Ammonia	By boiling any ammonium salt with NaOH solution. $\text{NH}_4\text{Cl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{NH}_3$
8. Nitrogen dioxide	By the action of concentrated HNO_3 on copper turnings. $\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2$ (brown gas)
9. Chlorine	By heating a mixture of NaCl, MnO_2 and concentrated H_2SO_4 . $4\text{NaCl} + \text{MnO}_2 + 4\text{H}_2\text{SO}_4 \rightarrow 4\text{NaHSO}_4 + \text{MnCl}_2 + \text{H}_2\text{O} + \text{Cl}_2$ (solid) (solid) (Concentrated)
10. Hydrogen chloride	By placing some concentrated HCl in a test tube and warming it if necessary.

14.2 ACTION ON LITMUS ON COMMON GASES

Depending on their nature, the gases that we have listed above react differently to moist litmus.

- Neutral gases:** Water vapour, hydrogen and oxygen are neutral to litmus.
- Basic gases:** Ammonia turns moist red litmus paper blue as it is basic.
- Acidic gases:** Carbon dioxide, sulphur dioxide, hydrogen sulphide, hydrogen chloride and nitrogen dioxide turn moist blue litmus red as they are acidic. Chlorine shows a similar effect but is not an acidic

gas. Chlorine reacts with water forming HCl and HClO which are acids. It is these acids that show the effect.

14.3 GASES CAN BE IDENTIFIED BY SPECIFIC TESTS

Many gases show specific and unique properties. These unique properties can be used to identify the gas as no other gas shows the property. While analyzing, the presence of a gas can be derived by logical reasoning.

The specific tests for the gases under study are tabulated below.

	Gas	Colour, odour and taste	Test	Reaction
1.	Water vapour	Colourless and odourless.	- Water vapour condenses forming a colourless liquid (water) on a cold surface - Water turns white anhydrous CuSO_4 blue - Water turns blue cobalt chloride paper pale pink – almost colourless (Soak a strip of filter paper in an aqueous solution of cobalt chloride. The strip turns almost colourless on drying. On being heated, the paper turns blue and can be used for testing again).	$\text{CuSO}_4 + 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ Anhydrous Copper sulphate (white) Hydrated Copper sulphate (blue) $\text{CoCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ Anhydrous Cobalt chloride (blue) Hydrated Cobalt chloride (pale pink)

2.	Hydrogen	Colourless and odourless	Hydrogen burns with a 'pop' sound when burnt in air.	$2\text{H}_2 + \text{O}_2 \xrightarrow{\text{kindle}} 2\text{H}_2\text{O}$
3.	Oxygen	Colourless and odourless	(i) A glowing splinter burns more brightly when introduced into a jar of oxygen. (ii) Oxygen turns alkaline pyrogallol solution brown.	
4.	Carbon dioxide	Colourless and odourless	Carbon dioxide turns limewater milky. The milkiness disappears when an excess of the gas is passed through it.	$\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ (white, insoluble) $\text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{Ca}(\text{HCO}_3)_2$ Calcium hydrogen carbonate (colourless soluble)
5.	Sulphur dioxide	Colourless, has a suffocating smell	(i) Sulphur dioxide turns lime water milky. The milkiness disappears when an excess of the gas is passed through it. (ii) Sulphur dioxide changes the colour of acidified dichromate paper (filter paper soaked in $\text{K}_2\text{Cr}_2\text{O}_7$ solution and then in dilute H_2SO_4) from orange to green. Both sulphur dioxide and carbon dioxide react similarly with limewater. However, the odour of sulphur dioxide and its reaction with $\text{K}_2\text{Cr}_2\text{O}_7$ distinguish it from carbon dioxide.	$\text{SO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaSO}_3 \downarrow + \text{H}_2\text{O}$ Calcium sulphate (white, insoluble) $\text{CaSO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HSO}_3)_2$ Calcium hydrogen sulphite (Colourless, soluble) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{SO}_2$ (orange) $\rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ (Green) Chromic sulphate
6.	Hydrogen sulphide	Colourless, smells like rotten eggs	(i) Hydrogen sulphide turns acidified dichromate paper green. Both hydrogen sulphide and sulphur dioxide turn dichromate paper green but with hydrogen sulphide a yellow deposit of sulphur is also seen. (ii) Hydrogen sulphide turns lead acetate paper black. The lead acetate test and the characteristic	$\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 + 3\text{H}_2\text{S}$ (orange) $\rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + 3\text{S}$ (green) $\text{Pb}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{S}$ (colourless) $\rightarrow \text{PbS} + 2\text{CH}_3\text{COOH}$ (black)

			smell of hydrogen sulphide distinguishes hydrogen sulphide from sulphur dioxide.	
7.	Ammonia	Colourless, has a pungent odour	(i) Ammonia produces dense white fumes when a glass rod moistened with concentrated HCl is brought near it. (ii) Ammonia turns a piece of filter paper soaked in Nessler's reagent (K_2HgI_4) brown.	$NH_3(g) + HCl(g) \rightarrow NH_4Cl$ The fumes are due to the white NH_4Cl particles suspended in air.
8.	Nitrogen dioxide	Reddish brown irritating odour	Nitrogen dioxide turns potassium iodide paper brown.	NO_2 oxidises KI to liberate I_2 , which turns the paper brown. $NO_2 \rightarrow NO + [O]$ $2KI + [O] \rightarrow K_2O + I_2$
9.	Chlorine	Greenish yellow, has a pungent odour	(i) Chlorine turns moist blue litmus paper red and then bleaches it. (ii) Chlorine turns starch – iodide paper blue. (Starch-iodide paper is prepared by first soaking a strip of filter paper in KI solution and then in starch solution)	Cl_2 is not an acidic gas, but reacts with water (moisture) to give HCl and HOCl, which are acids that act on litmus. $Cl_2 + H_2O \rightarrow HCl + HOCl$ <i>Bleaching action</i> $HOCl \rightarrow HCl + [O]$ Litmus + [O] $\rightarrow$ colourless compound $Cl_2 + 2KI \rightarrow 2KCl + I_2$ Starch + $I_2 \rightarrow$ a blue substance
10.	Hydrogen chloride	Colourless has a pungent odour	(i) Hydrogen chloride fumes in air. (ii) Hydrogen chloride produces dense white fumes when a glass rod moistened with ammonia solution (NH_4OH) is brought near it. (iii) Hydrogen chloride produces a white precipitate with $AgNO_3$ solution. The precipitate is insoluble in HNO_3 , but readily soluble in ammonia solution.	$HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$ $AgNO_3 + HCl \rightarrow AgCl \downarrow + HNO_3$ (white insoluble in HNO_3) $AgCl + 2NH_3 \rightarrow [Ag(NH_3)_2]Cl$ [diamminesilver(I) chloride] (colourless insoluble)

14.4 IDENTIFICATION OF CATIONS

The presence of some cations can be guessed though not with certainty as follows.

Colour of salts

The colour of salts gives some indication about the cation present in the salt.

<u>Colour of salt</u>	<u>Possible cations in the salt</u>
Colourless	Ca^{2+} , Zn^{2+} , Pb^{2+}
Coloured	Fe^{2+} (light green)
	Fe^{3+} (brown or reddish brown)
	Cu^{2+} (blue or bluish green)

While colour of the salt gives only a rough idea, presence of cations can be identified by using NaOH and NH_4OH solutions. The actions of NaOH and NH_4OH solutions on these cations are tabulated below.

Cation	Action of NaOH		Action of NH_4OH	
	in small amounts	in excess	in small amounts	in excess
Ca^{2+}	A white precipitate of $\text{Ca}(\text{OH})_2$ appears.	No change	No change	No change
Zn^{2+}	A white precipitate of $\text{Zn}(\text{OH})_2$ appears.	The white precipitate dissolves to form colourless Na_2ZnO_2 .	A white precipitate of $\text{Zn}(\text{OH})_2$ appears.	The white precipitate dissolves to form colourless $[\text{Zn}(\text{NH}_3)_4](\text{OH})_2$.
Pb^{2+}	A white precipitate of $\text{Pb}(\text{OH})_2$ appears.	The white precipitate dissolves to form colourless Na_2PbO_2 .	A white precipitate $\text{Pb}(\text{OH})_2$ appears.	No change
Fe^{2+}	A dirty green precipitate of $\text{Fe}(\text{OH})_2$ is formed. The precipitate slowly turns brown due to oxidation by air to $\text{Fe}(\text{OH})_3$.	No change	A dirty green precipitate of $\text{Fe}(\text{OH})_2$ is formed. The precipitate slowly turns brown due to oxidation by air to $\text{Fe}(\text{OH})_3$.	No change
Fe^{3+}	A reddish brown precipitate of $\text{Fe}(\text{OH})_3$ is formed	No change	A reddish brown precipitate of $\text{Fe}(\text{OH})_3$ is formed.	No change
Cu^{2+}	A light blue precipitate of $\text{Cu}(\text{OH})_2$ is formed, which turns black on heating due to the formation of CuO .	No change	A light blue precipitate of $\text{Cu}(\text{OH})_2$ is formed. When boiled with NaOH solution, a colourless gas with pungent odour is evolved.	The light blue precipitate is readily soluble giving an intense blue solution of $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$.

14.5 IDENTIFICATION OF ANIONS

Some common anions are carbonate (CO_3^{2-}), sulphite (SO_3^{2-}), sulphide (S^{2-}), sulphate (SO_4^{2-}), chloride (Cl^-) and nitrate (NO_3^-). One of the simple physical properties of a salt is its solubility.

Solubility of salts

Solubility of a salt in water gives us an idea of the type of salt. The common soluble and insoluble salts are given below.

Soluble in water

- (i) All nitrates
- (ii) All chlorides except Ag^+ , Hg^{2+} , Pb^{2+} , Cu^{2+} (PbCl_2 is soluble in hot water)
- (iii) All sulphates except Pb^{2+} , Ba^{2+} , Sr^{2+}

Insoluble in water

- (i) All carbonates except Na^+ , K^+ , NH_4^+
- (ii) All sulphides except Na^+ , K^+ , NH_4^+
- (iii) All sulphites except Na^+ , K^+ , NH_4^+

While solubility of a salt gives only a rough idea, presence of anions can be identified by using specific tests. Some tests for anions are tabulated below.

Anion	Experiment / test	Observation	Reaction/Explanation
(1) Carbonate	The solid is treated with dilute H_2SO_4	A colourless and odourless gas is evolved with effervescence. The gas (i) turns moist blue litmus paper red (ii) turns lime water milky (the milkiness disappears with an excess of the gas), and (iii) has no action on acidified dichromate paper.	The gas evolved is CO_2 $\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ (i) $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$ (weak acid) (ii) $\text{CO}_2 + \text{Ca}(\text{OH})_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ white $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}(\text{HCO}_3)_2$ Soluble (iii) This excludes the possibility of the gas being sulphur dioxide
(2) Sulphate	(a) An aqueous solution of the salt is treated with a BaCl_2 solution. (b) An aqueous solution of the salt is treated with a PbNO_3 solution.	A white precipitate is formed which is insoluble in dilute HCl A white precipitate is formed which is insoluble in mineral acids.	$\text{Na}_2\text{SO}_4 + \text{BaCl}_2 \rightarrow \text{BaSO}_4 + 2\text{NaCl}$ (White ppt.) $\text{BaSO}_4 + \text{HCl} \rightarrow \text{No action}$ (CO_3^{2-} or SO_3^{2-} reacts with BaCl_2 solution to give a precipitate of BaCO_3 or BaSO_3 , which is soluble in dilute HCl . The solubility of the precipitate in dilute HCl distinguishes SO_4^{2-} from CO_3^{2-} and SO_3^{2-}) $\text{Na}_2\text{SO}_4 + \text{Pb}(\text{NO}_3)_2 \rightarrow \text{PbSO}_4 + 2\text{NaNO}_3$ (insoluble in mineral acids) The gas liberated is HCl $\text{NaCl} + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HCl}$
(3) Chloride	(a) The salt is treated with concentrated H_2SO_4 and heated very slowly.	A colourless gas with a pungent odour is evolved. The gas (i) turns moist blue litmus paper red.	$\text{NaCl} + \text{NaHSO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{HCl}$ (i) HCl is a strong acid (ii) $\text{HCl}(\text{g}) + \text{NH}_3(\text{g}) \rightarrow \text{NH}_4\text{Cl}(\text{s})$

		(ii) produces dense white fumes when a glass rod moistened with ammonia solution is brought near it. (iii) produces a white precipitate when passed through AgNO_3 solution (the precipitate is insoluble in HNO_3, but soluble in ammonia solution $[\text{NH}_4\text{OH}]$)	The fumes are due to NH_4Cl particles suspended in air. (iii) $\text{HCl} + \text{AgNO}_3 \rightarrow \text{AgCl}\downarrow + \text{HNO}_3$ (white insoluble in HNO_3) $\text{AgCl} + 2\text{NH}_3 \rightarrow [\text{Ag}(\text{NH}_3)_2] \text{Cl}$ (soluble)
	(b) The salt is heated with MnO_2 and concentrated H_2SO_4. (c) A solution of the salt (if the salt is soluble in water) is treated with AgNO_3 solution.	A greenish yellow gas is evolved. The gas (i) turns moist blue litmus paper red and then bleaches it, and (ii) turns starch-iodide paper blue. A white precipitate is obtained which is (i) insoluble in HNO_3, and (ii) soluble in ammonia solution	MnO_2 oxidises HCl (produced by the action of concentrated H_2SO_4 on the chloride salt) to Cl_2. $\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + 2\text{H}_2\text{O} + \text{Cl}_2\uparrow$ (i) Cl_2 reacts with moisture to give acid: $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOCl}$ (ii) $\text{Cl}_2 + 2\text{KI} \rightarrow 2\text{KCl} + \text{I}_2$ $\text{I}_2 + \text{starch} \rightarrow \text{blue compound}$ $\text{NaCl} + \text{AgNO}_3 \rightarrow \text{AgCl} + \text{NaNO}_3$ (white insoluble in HNO_3) $\text{AgCl} + 2\text{NH}_3 \rightarrow [\text{Ag}(\text{NH}_3)_2]\text{Cl}$ (soluble, colourless)
(4) Nitrate	(a) A solution of the salt is treated with NaCl solution. (b) The salt is heated with concentrated H_2SO_4 and copper turnings.	A white precipitate is obtained. The precipitate dissolves when heated and reappears when cooled. Brown fumes are evolved which (i) turn moist blue litmus paper red, and (ii) turn potassium iodide paper brown	$2\text{NaCl} + \text{Pb}(\text{NO}_3)_2 \rightarrow \text{PbCl}_2 + 2\text{NaNO}_3$ Lead (II) chloride dissolves when heated and reappears when cooled. The gas evolved is NO_2. $\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3$ $\text{Cu} + 4\text{HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2$ (i) $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$ (ii) $3\text{NO}_2 + 2\text{KI} \rightarrow \text{KNO}_2 + \text{KNO}_3 + \text{NO} + \text{I}_2$

	(c) Ring test A Freshly prepared FeSO_4 solution is mixed with the salt. Then concentrated H_2SO_4 is added very carefully along the side of the test tube so that it forms a separate layer. The FeSO_4 solution should be freshly prepared since on standing or in contact with air Fe^{2+} is slowly oxidized to Fe^{3+}.	A brown ring is formed at the junction of the two layers.	$\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3$ The HNO_3 formed oxidizes FeSO_4 to $\text{Fe}_2(\text{SO}_4)_3$ and is itself reduced to NO. $2\text{HNO}_3 + 6\text{FeSO}_4 \rightarrow 3\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O} + 2\text{NO}$ Now, NO forms a brown compound with FeSO_4. $\text{FeSO}_4 + \text{NO} + 5\text{H}_2\text{O} \rightarrow [\text{Fe}(\text{H}_2\text{O})_3\text{NO}] \text{SO}_4$ (brown)
(5) Sulphide	The salt is treated with dilute H_2SO_4	Colourless gas with the smell of rotten eggs is evolved with effervescence. The gas turns (i) moist blue litmus paper red (ii) acidified dichromate paper green, and (iii) lead acetate paper black	The gas evolved is H_2S $\text{Na}_2\text{S} + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{S} \uparrow$ (i) H_2S is a weak acid (ii) $\text{K}_2\text{Cr}_2\text{O}_7 + 4\text{H}_2\text{SO}_4 + 3\text{H}_2\text{S}$ (orange) $\rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + 3\text{S}$ (green) A yellow deposit of sulphur is obtained. This distinguishes it from sulphur dioxide. (iii) $\text{Pb}(\text{CH}_3\text{COO})_2 + \text{H}_2\text{S}$ $\rightarrow \text{PbS} \downarrow + 2\text{CH}_3\text{COOH}$ (black) (acetic acid) This distinguishes it from sulphur dioxide.
6. Sulphite	The salt is treated with dilute H_2SO_4.	A colourless gas with a suffocating odour is evolved with effervescence. The gas (i) turns moist blue litmus paper red,	The gas evolved is SO_2 $\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2 \uparrow$ (i) $\text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3$ (sulphurous acid)

		(ii) turns limewater milky (the milkiness disappears with an excess of the gas), (iii) turns acidified dichromate paper green, and (iv) has no action on lead acetate paper.	(ii) $\text{SO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaSO}_3 + \text{H}_2\text{O}$ (Insoluble) $\text{CaSO}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(HSO}_3)_2$ (Soluble) (iii) $\text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{SO}_4 + 3\text{SO}_2$ (orange) $\rightarrow \text{K}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$ (green) This distinguishes it from CO_2 (iv) This excludes the possibility of the gas being H_2S .
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Example: Distinguish between sodium carbonate and sodium sulphite.

Solution: We can distinguish between sodium carbonate and sodium sulphite by testing for the anions as the cation is the same. The salts are labeled as Sample X and Sample Y. The following tests for anions are done.

Experiment	Observation		Inference
	Sample X	Sample Y	
The Salt is treated with dilute H_2SO_4	A colourless and odourless gas is evolved with effervescence The gas (i) turns moist blue litmus paper red. (ii) turns limewater milky (the milkiness disappears with an excess of the gas) (iii) has no action on acidified dichromate paper.	A colourless gas with suffocating odour is evolved with effervescence The gas (i) turns moist blue litmus paper red. (ii) turns limewater milky (the milkiness disappears with an excess of the gas) (iii) turns acidified dichromate paper green, and (iv) has no effect on lead acetate paper	Sample X contains the anion CO_3^{2-} Sample Y contains the anion SO_3^{2-}

Conclusion: Sample X is sodium carbonate while Sample Y is sodium sulphite

14.6 DISTINGUISHING BETWEEN AN ACID AND AN ALKALI

An acid can be distinguished from an alkali in two ways:

- by using acid-base indicators
- some specific reactions as given below.

Experiment	Observation		Inference
	With acid	With alkali	
1. The solution is treated with acid-base indicators as follows. The change in colour is noted. (i) Litmus (ii) Methyl orange (iii) Phenolphthalein	Turns blue litmus red Turns red Phenolphthalein remains colourless	Turns red litmus blue Turns yellow Turns pink	
2. The solution is treated with Na_2CO_3 or NaHCO_3	A colourless and odourless gas is evolved. The gas turns (i) moist blue litmus wine - red (ii) limewater milky	No action	CO_2 is evolved by the action of an acid on Na_2CO_3 or NaHCO_3 $\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$ $2\text{NaHCO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O} + 2\text{CO}_2 \uparrow$
3. The solution is treated with NH_4Cl and boiled	No action	A colourless gas with pungent odour is evolved The gas (i) turns moist red litmus blue. (ii) produces dense white fumes when a glass rod moistened with HCl is brought near it, and (iii) turns Nessler's reagent brown	NH_3 is evolved by the action of an alkali on an ammonium salt. $\text{NaOH} + \text{NH}_4\text{Cl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{NH}_3$

EXERCISE

I. Choose the correct answer

(1) Which of the following gases is acidic?

- (a) HCl (b) O_2
(c) NH_3 (d) H_2O

(2) Which of the following gases is basic?

- (a) NH_3 (b) H_2
(c) O_2 (d) CO_2

(3) Which of the following gases would give a black colour with lead acetate paper?

- (a) CO_2 (b) SO_2
(c) H_2S (d) HCl

(4) Which of the following compounds is formed in the ring test for nitrates?

- (a) $\text{Pb}(\text{NO}_2)_2$ (b) $\text{Ca}(\text{NO}_3)_2$
(c) $\text{FeSO}_4 \cdot \text{NO}$ (d) NH_3

(5) Which of the following compounds may be used to test for SO_4^{2-} ion?

- (a) $\text{Pb}(\text{NO}_3)_2$ (b) NaCl
(c) KNO_3 (d) $\text{Ca}(\text{NO}_3)_2$

(6) Which of the following gases will turn acidified dichromate paper green with deposit of sulphur?

- (a) SO_2 (b) H_2S
(c) SO_3 (d) Steam

(7) Which of the following compounds is responsible for the blue colour of the solution produced by the action of an excess of NH_4OH solution on CuSO_4 solution?

- (a) $\text{Cu}(\text{OH})_2$ (b) $\text{CuSO}_4 \cdot 2\text{NH}_3$
(c) CuO (d) $[\text{Cu}(\text{NH}_3)_4](\text{OH})_2$

(8) Which of the following compounds is formed when AgCl reacts with NH_4OH solution?

- (a) $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$ (b) AgOH
(c) Ag_2O (d) $\text{AgCl} \cdot 4\text{NH}_3$

II. State whether the given statement is true or false.

- Water vapour leaves blue anhydrous cobalt chloride unchanged.
- Dry chlorine is acidic.
- Lead nitrate solution remains unchanged when treated with a cold solution containing chloride ions.
- Barium chloride solution gives a white precipitate with a solution containing sulphate ions.
- Barium sulphate is soluble in dilute HCl .
- Phenolphthalein gives a pink colour with an acid.
- Methyl orange gives a yellow colour with an alkali.
- An acid gives effervescence with a carbonate or bicarbonate.
- An alkali liberates carbon dioxide gas when boiled with an ammonium salt.
- A greenish yellow gas is evolved when MnO_2 is heated with concentrated HCl .

III. Fill in the blanks. (Choose the word from the options given to fill the blank).

- The _____ gas evolved by the action of concentrated HCl on MnO_2 turns _____ paper blue. (colourless/greenish yellow/ red litmus paper/starch-iodide paper)
- FeS reacts with dilute H_2SO_4 giving a colourless gas smelling like rotten eggs that turns _____ paper black. (acidified dichromate/lead acetate)
- _____ gas turns moist red litmus blue and Nessler's reagent brown and produces dense white fumes with _____. (NH_3 / HCl)
- The liberation of _____ gas by the action of

dilute H_2SO_4 on a sulphite distinguishes it from a carbonate. ($\text{H}_2\text{S}/\text{SO}_2$)

(v) The white precipitate obtained by the action of AgNO_3 solution containing Cl^- ion is readily soluble in _____ solution. ($\text{NaOH}/\text{NH}_4\text{OH}$)

(vi) NH_4Cl is a _____ salt. (soluble / insoluble)

(vii) NaHSO_4 is a _____. (normal / acidic)

IV. Give one word answers.

- Name the compound the vapours of which turn anhydrous CuSO_4 blue and anhydrous CuCl_2 pink.
- Name the gas that turns acidified dichromate paper green and lead acetate paper black.
- Name the gas that turns limewater milky and acidified dichromate paper green.
- What colour will chlorine gas give with starch-iodide paper?

V. Answer the following questions.

- Define in terms of ionization
(a) a normal salt and (b) an acid salt
- Study the list given and answer the questions that follow by writing only the letter given against each substance.

A. Dil HCl	B. ZnSO_4
C. FeSO_4	D. NH_4Cl
E. NaCl	F. CuSO_4

 - Which two solutions give white ppt. with AgNO_3 solution?
 - Which two solutions give white ppt. with lead nitrate solution?
 - Which salt will form a red deposit when treated with zinc metal?
 - Which salt will liberate N_2 gas when warmed with sodium nitrite solution?
 - Which salt when reacted with NaOH liberates a colourless gas that produces dense white fumes with HCl gas?
- Two salts of sodium contain two different anions.
 - To one salt, conc. H_2SO_4 is added and the mixture is warmed. A colourless gas is produced which forms dense white fumes with ammonia. Identify the anion.
 - To the other salt, a few drops of BaCl_2 are added followed by a few drops of dil. HCl . The reaction produces a white precipitate. Name the anion.
- Given a solution of BaCl_2 , how will you distinguish between sodium sulphite and sodium sulphate solutions?

- (5) With the help of ammonium hydroxide solution differentiate between lead nitrate solution, zinc nitrate solution and copper nitrate solutions.
- (6) With the help of lead nitrate solution, how will you distinguish between
(a) HCl acid and nitric acid (b) solutions of sodium chloride and sodium sulphate.
- (7) Name the gases evolved in the following cases.
- Sodium sulphite is treated with dilute H_2SO_4
 - Ammonium chloride is boiled with NaOH solution.
 - Sodium chloride is heated with manganese dioxide and concentrated H_2SO_4
 - Iron (II) sulphide is treated with dilute H_2SO_4
 - Common salt is heated with concentrated H_2SO_4
 - Concentrated nitric acid is treated with copper turnings.
- (8) Name the gas produced in each of the following reactions.
- Action of concentrated HNO_3 on copper.
 - Heating $(\text{NH}_4)_2\text{SO}_4$ with NaOH solution
- (9) What is the difference between the chemical nature of an aqueous solution of hydrogen chloride and that of ammonia?
- (10) Select from the list below the gas that matches the description given in each case and answer the questions that follow.
Given list: Ammonia, chlorine, hydrogen chloride, sulphur dioxide
- Gas A is reducing agent which contains oxygen
- (a) What is the name of gas A?
- (b) What would you observe if gas A is bubbled through acidified dichromate solution?
- (ii) Gas B turns moist red litmus paper blue.
- What is the name of gas B?
 - Write the equation for the reaction that takes place when gas B is passed over heated CuO.
- (iii) When gas C is mixed with gas B dense white fumes are seen and there is no other product.
- What is the name of gas C?
 - What is the name of the product of the reaction between B and C?
- (11) Name the anion present in each of the following compounds
- Compound A when heated with concentrated H_2SO_4 gives a gas which fumes in moist air and produces dense white fumes of NH_3 .
 - When BaCl_2 solution is added to a solution of compound B, a white precipitate is formed, which is insoluble in dilute HCl.
 - The action of heat on the insoluble compound C produces a gas which turns limewater milky.
 - Compound D when warmed with dilute H_2SO_4 gives a gas that turns limewater milky and acidified dichromate solution green.
- (12) Distinguish between the following pairs compounds.
- Sodium carbonate and sodium sulphite
 - Sodium sulphite and sodium sulphide
 - Sodium carbonate and sodium sulphide
 - Potassium nitrate and potassium sulphite.

KEY TO EXERCISE

I.	1. a	2. a	3. c	4. c	5. a	6. b	7. d	8. a					
II.	1. F	2. F	3. F	4. T	5. F	6. F	7. T	8. T	9. F	10. T			
III.	(i) greenish yellow, starch-iodide paper				(ii) lead acetate		(iii) NH ₃ , HCl						
	(iv) SO ₂	(v) NH ₄ OH	(vi) soluble	(vii) acidic									
IV.	(1) water	(2) H ₂ S	(3) SO ₂	(4) blue									