

FIRST YEAR HIGHER SECONDARY EXAMINATION

FOCUS AREA Notes for +1 CHEMISTRY (All Chapters)

1. SOME BASIC CONCEPTS OF CHEMISTRY

Laws of Chemical Combination

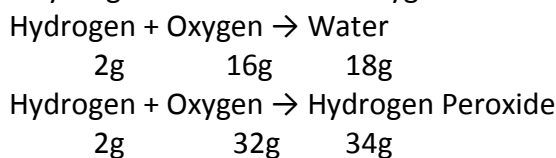
The combination of elements to form compounds is governed by the some basic laws:

1. **Law of Definite Proportions (Law of definite composition):** This law was proposed by **Joseph Proust**. It states that *a given compound always contains exactly the same proportion of elements by weight. Or, the same compound always contains the same elements combined in a fixed ratio by mass.*

Illustration: Carbon dioxide can be formed in the atmosphere by various methods like respiration, burning of fuels, reaction of metal carbonates and bicarbonates with acid etc. All these samples of CO₂ contain only two elements Carbon and Oxygen combined in a mass ratio 3:8.

2. **Law of Multiple Proportions:** This law was proposed by **John Dalton**. It states that *if two elements can combine to form more than one compound, the different masses of one of the elements that combine with a fixed mass of the other element, are in small whole number ratio.*

Illustration: Hydrogen combines with oxygen to form two compounds – water and hydrogen peroxide.



Here, the masses of oxygen (i.e. 16 g and 32 g) which combine with a fixed mass of hydrogen (2g) bear a simple ratio, i.e. 16:32 or 1: 2.

Atomic mass

Atomic mass of an element is a number that expresses how many times the mass of an atom of the element is greater than 1/12th the mass of a C¹² atom.

For e.g. atomic mass of Nitrogen is 14, which means that mass of one N atom is 14 times greater than 1/12th the mass of a C¹² atom.

Atomic mass unit (amu): 1/12th the mass of a C¹² atom is called atomic mass unit (amu).

$$\begin{aligned} \text{i.e. } 1 \text{ amu} &= 1/12 \times \text{mass of a C}^{12} \text{ atom} \\ &= 1.66 \times 10^{-24} \text{ g} \\ &= 1.66 \times 10^{-27} \text{ kg} \end{aligned}$$

Today, 'amu' has been replaced by 'u' which is known as unified mass.

Average atomic mass: Almost all the elements have isotopes. So we can calculate an average atomic mass of an element by considering the atomic mass of the isotopes and their relative abundance.

For e.g. chlorine has two isotopes ³⁵Cl and ³⁷Cl in the ratio 3:1.

So the average atomic mass Cl = (3x35 + 1x37)/4 = 35.5

Molecular mass:

Molecular mass is the sum of atomic masses of the elements present in a molecule. It is obtained by multiplying the atomic mass of each element by the number of its atoms and adding them together.

For e.g. molecular mass of H₂SO₄ is calculated as: 2 x 1 + 32 + 4 x 16 = 98 u.

Formula mass:

In the case of ionic compounds (like NaCl), there is no discrete (separate) molecules. Here the positive ions and the negative ions are arranged in a three-dimensional structure. So we can calculate only formula mass

by taking molecular formula of the compound.

Mole concept

Mole is the unit of amount of substance. It is defined as *the amount of substance that contains as many particles as there are atoms in exactly 12 g C^{12} isotope*. **1 mole of any substance contains 6.022×10^{23} atoms**. This number is known as **Avogadro number or Avogadro constant (N_A or N_0)**.

1 mol of hydrogen atoms = 6.022×10^{23} atoms

1 mol of water molecules = 6.022×10^{23} water molecules

1 mol of sodium chloride = 6.022×10^{23} formula units of sodium chloride

Molar mass: The mass of one mole of a substance in gram is called its molar mass (gram molecular mass).

The molar mass in grams is numerically equal to molecular mass in u.

Molar mass of oxygen = 32g

Molar mass of hydrogen = 2g etc.

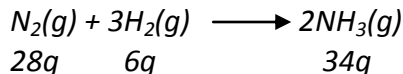
Limiting reagent (Limiting reactant)

It is the reagent that limits a reaction. Or, the reagent which is completely consumed in a chemical reaction is called limiting reagent or limiting reactant.

For e.g. in the reaction $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$, 2 moles of SO_2 reacts completely with 1 mole of O_2 to form 2 moles of SO_3 . If we take 10 moles each of SO_2 and O_2 , we get only 10 moles of SO_3 because 10 moles of SO_2 requires only 5 moles of O_2 for the complete reaction. So here SO_2 is the limiting reagent and 5 moles of O_2 remains unreacted.

Q) A reaction mixture for the production of NH_3 gas contains 250 g of N_2 gas and 50 g of H_2 gas under suitable conditions. Identify the limiting reactant if any and calculate the mass of NH_3 gas produced. (3)

Ans: Nitrogen reacts with Hydrogen to form ammonia according to the equation,



i.e. 28g N_2 requires 6g H_2 for the complete reaction.

So 250g N_2 requires, $6 \times 250/28 = 53.57g$ H_2 .

But here there is only 50g H_2 .

So we have to consider the reverse case.

i.e. 6g H_2 requires 28g N_2 .

So 50g H_2 requires $28 \times 50/6 = 233.33g$ N_2

Here H_2 is completely consumed. So it is the limiting reagent.

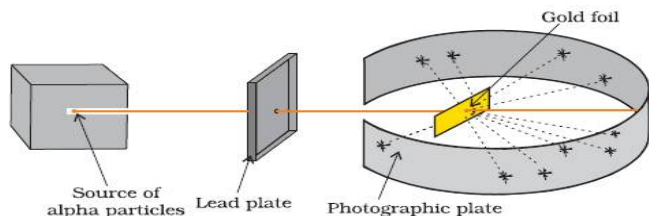
Amount of ammonia formed = $50 \times 233.33 = \underline{\underline{283.33 g}}$

2. STRUCTURE OF ATOM

Rutherford's Nuclear Model of Atom

Rutherford proposed an atom model based on his α -particle scattering experiment. He bombarded a very thin gold foil with α -particles.

The Experiment: A stream of high energy α -particles from a radioactive source was directed at a thin gold foil. The thin gold foil was surrounded by a circular fluorescent zinc sulphide screen. Whenever α -particles struck the screen, a tiny flash of light was produced at that point.



Observations: The important observations made by Rutherford are:

1. Most of the α - particles passed through the gold foil without any deviation.
2. A small fraction of the α -particles was deflected by small angles.
3. A very few α - particles (~ 1 in 20,000) bounced back, that is, were deflected by nearly 180° .

Conclusions: From the above observations, Rutherford made the following conclusions:

1. Since most of the α -particles passed through the foil without any deviation, most space in the atom is empty.
2. A few positively charged α - particles were deflected. This is because the positive charge of the atom is concentrated in a very small volume at the centre called nucleus.
3. The volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.

On the basis of above observations and conclusions, Rutherford proposed **the nuclear model (Planetary model) of atom**. According to this model:

1. All the positive charge and most of the mass of the atom are concentrated in an extremely small region called nucleus.
2. Electrons are revolving round the nucleus with a very high speed in circular paths called orbits.
3. Electrons and the nucleus are held together by electrostatic forces of attraction.

Drawbacks or Limitations of Rutherford's atom model

1. Rutherford's model cannot explain the stability of the atom.
2. He could not explain the electronic structure of atom.

Particle Nature of Electromagnetic Radiation:

Planck's Quantum Theory

The important postulates of quantum theory proposed by **Max Planck** are:

1. Atoms and molecules could emit or absorb energy not in a continuous manner, but discontinuously in small packets of energy called quanta or photons.
2. The energy (E) of each quantum of radiation is proportional to its frequency (ν).

It is expressed by the equation, **$E = h\nu$**

Where 'h' is known as Planck's constant and its value is 6.626×10^{-34} J s.

Photoelectric effect

It is the phenomenon of ejection of electrons by certain metals (like potassium, rubidium, caesium etc.) when light of suitable frequency incident on them. The electrons ejected are called photoelectrons.

This phenomenon was first observed by H Hertz. The important characteristics of photoelectric effect are:

1. The electrons are ejected from the metal surface as soon as the beam of light strikes the surface. i.e., there is no time lag between the striking of light beam and the ejection of electrons from the metal surface.
2. The number of electrons ejected is proportional to the intensity or brightness of light.
3. For each metal, there is a minimum frequency known as threshold frequency [ν_0], below which photoelectric effect is not observed.
4. The kinetic energy of the ejected electrons is directly proportional to the frequency of the incident light.

Explanation of photoelectric effect

A satisfactory explanation to photoelectric effect was first given by Albert Einstein using Planck's Quantum theory. According to him, when a photon of sufficient energy strikes the metal surface, it transfers its energy to the electron of the atom of the metal instantaneously and the electron is ejected without any time lag. A part of the energy is used to eject the electron from the metal surface (i.e. to overcome the attractive force of the nucleus [work function, $h\nu_0$]) and the other part is given to the ejected electron in the form of kinetic energy. Greater the energy possessed by the photon, greater will be transfer of energy to the electron and greater the kinetic energy of the ejected electron.

Since the striking photon has energy equal to $h\nu$ and the minimum energy required to eject the electron is $h\nu_0$ (also called work function, W_0) then the difference in energy ($h\nu - h\nu_0$) is transferred as the kinetic energy of the photoelectron.

According to law of conservation of energy, the kinetic energy of the ejected electron is given by

$$\text{K.E} = h\nu - h\nu_0$$

$$\text{Or, } h\nu = h\nu_0 + \frac{1}{2} m_e v^2$$

Where m_e is the mass of the electron and v is the velocity of the ejected electron.

A more intense beam of light contains larger number of photons, so the number of electrons ejected is also larger.

Atomic spectrum

Line Spectrum of Hydrogen

When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers. The first five series of lines are **Lyman, Balmer, Paschen, Brackett and Pfund series**. Among these lines, the Balmer series is the only series that we can be visible (since it lies in the visible region).

Johannes Rydberg proposed an equation for finding the wave number of the different lines in Hydrogen spectrum. The expression is:

$$\bar{\nu} = 1/\lambda = 109677 (1/n_1^2 - 1/n_2^2) \text{ cm}^{-1}$$

Where $n_1 = 1, 2, 3, \dots$ and $n_2 = n_1 + 1, n_1 + 2, \dots$

The different spectral lines, their n_1 and n_2 values and their spectral region are:

| Series | Spectral region | n_1 | n_2 |
|----------|-----------------|-------|-----------|
| Lyman | Ultra violet | 1 | 2,3,4.... |
| Balmer | Visible | 2 | 3,4,5.... |
| Paschen | Infra red | 3 | 4,5,6.... |
| Brackett | Infra red | 4 | 5,6,7.... |
| Pfund | Infra red | 5 | 6,7,8.... |

BOHR'S MODEL FOR HYDROGEN ATOM

The general features of the structure of hydrogen atom and its spectrum was first explained by Niels Bohr. The important postulates of his theory are:

1. The electron in the hydrogen atom can move around the nucleus in circular paths of fixed radius and energy. These paths are called orbits or stationary states or allowed energy states. These energy levels are numbered as 1,2,3 etc or as K, L, M, N, etc. These numbers are known as **Principal quantum numbers**.

- The energy of an electron in an orbit does not change with time. However, when an electron absorbs energy, it will move away from the nucleus (i.e. to a higher energy level) and when it loses energy, it will move towards the nucleus (i.e. to a lower energy level).
- The radius of orbits can be given by the equation: $r_n = a_0 n^2$ where $a_0 = 52.9$ pm. Thus the radius of the first stationary state is 52.9 pm (called the Bohr radius). As n increases, the value of r will increase.
- The energy of electron in an orbit is given by the expression: $E_n = -R_H (1/n^2)$, where $n = 1, 2, 3, \dots$ and R_H is a constant called Rydberg constant. Its value is 2.18×10^{-18} J. The energy of the lowest state (the ground state) is given by $E_1 = -2.18 \times 10^{-18}$ J. As the value of n increases, the energy of the electron also increases.
- The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE , is given by:

$$\nu = \frac{\Delta E}{h} = \frac{E_2 - E_1}{h}$$

Where E_1 and E_2 are the energies of lower and higher energy levels respectively. This expression is commonly known as *Bohr's frequency rule*.

- The angular momentum of an electron is an integral multiple of $h/2\pi$. i.e. $m_e v r = \frac{nh}{2\pi}$

Where m_e is the mass of electron, v is the velocity of electron and r is the radius of Bohr orbit. $n = 1, 2, 3, \dots$. Thus an electron can move only in those orbits whose angular momentum is an integral multiple of $h/2\pi$. So only certain fixed orbits are allowed.

Significance of negative energy of electron

When the electron is free from the influence of nucleus, its energy is taken as zero. In this situation, the electron is at the orbit with $n = \infty$. When the electron is attracted by the nucleus and is present in orbit n , the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in equation.

Explanation of Line Spectrum of Hydrogen

According to Bohr atom model, radiation is absorbed if the electron moves from lower energy to higher energy level and radiation is emitted if the electron moves from higher orbit to lower orbit. The energy gap between the two orbits is given by equation:

$$\Delta E = E_2 - E_1$$

$$\text{But } E_1 = \frac{-R_H}{n_1^2} \quad \text{and} \quad E_2 = \frac{-R_H}{n_2^2}$$

$$\text{Therefore, } \Delta E = R_H \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \\ = 2.18 \times 10^{-18} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

The frequency associated with the absorption and emission of the photon can be given as

$$\nu = \frac{\Delta E}{h} = \frac{R_H}{h} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \\ = \frac{2.18 \times 10^{-18}}{6.626 \times 10^{-34}} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}$$

$$= 3.29 \times 10^{15} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{The wave number } (\bar{\nu}) = \frac{1}{\lambda} = \frac{\nu}{c} = \frac{R_H}{hc} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}$$

$$= \frac{3.29 \times 10^{15}}{3 \times 10^8} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\}$$

$$= 1.09677 \times 10^7 \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \text{ m}^{-1} = 109677 \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \text{ cm}^{-1}$$

In case of absorption spectrum, $n_2 > n_1$ and the term in the bracket is positive and energy is absorbed. On the other hand, in case of emission spectrum $n_1 > n_2$, ΔE is negative and energy is released.

Limitations of Bohr Atom Model: Bohr atom model could explain the stability and line spectra of hydrogen atom and hydrogen like ions (e.g. He^+ , Li^{2+} , Be^{3+} etc). But it has the following limitations:

1. It could not explain the fine spectrum of hydrogen atom.
2. It could not explain the spectrum of atoms other than hydrogen.
3. It was unable to explain the splitting of spectral lines in the presence of electric field (**Stark effect**) and in magnetic field (**Zeeman effect**).
4. It could not explain the ability of atoms to form molecules by chemical bonds.
5. It did not consider the wave character of matter and Heisenberg's uncertainty principle.

Dual Behaviour of Matter – de Broglie's equation

de Broglie proposed that like radiation, matter also show both particle and wave nature. This is known as dual behaviour of matter. i.e. electrons should have momentum as well as wavelength. He gave the following relation between wavelength (λ) and momentum (p) for material particles.

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

Where m is the mass of the particle, v is the velocity and p is the momentum. The above equation is known as **de Broglie's equation**.

Just like electromagnetic radiations, an electron beam also undergoes diffraction. This is an evidence for the wave nature of electrons. An electron microscope works on the principle of wave nature of electron.

According to de Broglie, every moving object has a wave character. The wavelengths associated with ordinary objects are so short (because of their large masses) that their wave properties cannot be detected. The wavelengths associated with electrons and other subatomic particles (with very small mass) can be detected experimentally.

Heisenberg's Uncertainty Principle

Werner Heisenberg proposed the uncertainty principle which is the consequence of dual behaviour of matter and radiation. It states that *"it is impossible to determine simultaneously, the exact position and momentum (or velocity) of a moving microscopic particle like electron"*.

Mathematically, it can be given as in equation:

$$\Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Or,
$$\Delta x \cdot m \Delta v \geq \frac{h}{4\pi}$$

Or,
$$\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}$$

Where Δx is the uncertainty in position and Δp is the uncertainty in momentum and Δv is the uncertainty in velocity of the particle.

If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [Δv is large] and vice versa.

Significance of Uncertainty Principle

Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is not applicable to macroscopic objects. According to this Principle, we cannot determine the exact position and momentum of an electron. Thus it rules out the existence of definite paths or orbits of electrons. We can only say the probability of finding an electron at a given point.

Orbitals and Quantum Numbers

These are certain numbers used to explain the size, shape and orientation of orbitals. Or, Quantum numbers are the address of an electron. There are four quantum numbers which describe the electron in an atom. They are Principal Quantum number (n), Azimuthal Quantum number (l), Magnetic Quantum number (m or m_l) and Spin Quantum number (s).

1. Principal Quantum Number (n)

The following informations are obtained from n .

1. It gives the size the orbit.
2. It gives the energy of electron in an orbit.
3. It gives the shell in which the electron is found.
4. It also gives the average distance between the electron and the nucleus. As the value of n increases, the distance between the electron and the nucleus also increases.

The possible values of n are 1, 2, 3, 4, 5 etc.

If $n = 1$ the electron is in K shell

$n = 2$ the electron is in L shell

$n = 3$ the electron is in M shell and so on.

2. Azimuthal Quantum Number [Subsidiary or orbital angular momentum Quantum number] (l)

The following informations are obtained from l .

1. It gives the shape of the orbital.
2. It gives the sub shell or sub level in which the electron is located.
3. It also gives the orbital angular momentum of the electron.

For a given value of n , l can have n values ranging from 0 to $n - 1$. That is, for a given value of n , the possible value of l are : $l = 0, 1, 2, \dots, (n-1)$.

For example, when $n = 1$, value of l is only 0. For $n = 2$, the possible value of l can be 0 and 1. For $n = 3$, the possible l values are 0, 1 and 2.

$l = 0$ represents s orbital, $l = 1$ represents p orbital, $l = 2$ represents d orbital and $l = 3$ represents f orbital

The number of sub shells in a principal shell is equal to the value of n . For example,

When $n = 1$, $l = 0$. i.e. K shell contains only one sub shell - s sub shell

when $n = 2$, $l = 0$ and 1. i.e. L shell contains two sub shells - s and p sub shells

when $n = 3$, $l = 0, 1$ and 2. i.e. M shell contains three sub shells – s, p and d sub shells

when $n = 4$, $l = 0, 1, 2$ and 3. i.e. N shell contains four sub shells – s, p, d and f sub shells

3. Magnetic Quantum Number (m or m_l)

It gives information about the orientation of orbitals in space. For a given ' l ' value, there are $2l+1$ possible values for m and these values are given by :

$m = -l$ to 0 to $+l$

Thus for $l = 0$, $m_l = 0$ [$2(0)+1 = 1$]. i.e. s sub shell contains only one orbital called s orbital.

For $l = 1$, $m_l = -1, 0$ and $+1$ [$2(1)+1 = 3$]. i.e. p subshell contains three orbitals called p orbitals (p_x, p_y and p_z).

For $l = 2$, $m_l = -2, -1, 0, +1$ and $+2$, [$2(2)+1 = 5$]. i.e. d subshell contains five orbitals called d orbitals ($d_{xy}, d_{xz}, d_{yz}, d_{x^2-y^2}$ and d_z^2)

4. Spin Quantum Number (s or m_s)

It is the only experimental Quantum number and it gives the spin orientation of electrons. This spin may be either clockwise or anticlockwise. So the values for s may be $+\frac{1}{2}$ or $-\frac{1}{2}$. $+\frac{1}{2}$ represents clock-wise spin and $-\frac{1}{2}$ represents anticlock-wise spin.

Rules for Filling of electrons in various orbitals

The filling of electrons into the orbitals of different atoms takes place according to the 3 rules - aufbau principle, Pauli's exclusion principle and the Hund's rule of maximum multiplicity.

1. Aufbau principle:

The German word aufbau means 'build up'. The building up of orbitals means the filling up of orbitals with electrons. It states that **the orbitals are filled in order of their increasing energies**. In other words, electrons first occupy the lowest energy orbital and then to higher energy orbitals.

This rule has two sub rules:

- The various orbitals are filled in the increasing order of their $(n+l)$ value.
- If two orbitals have the same $(n+l)$ values, the orbital with the lower n value is filled first.

The increasing order of orbitals is as follows:

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s...

2. Pauli's Exclusion Principle

It states that **no two electrons in an atom can have the same set of four quantum numbers**. i.e. an orbital can accommodate a maximum of only 2 electrons with opposite spin.

If 2 electrons have same values for n , l and m , they should have different values for s . i.e. if $s = +\frac{1}{2}$ for the first electron, it should be $-\frac{1}{2}$ for the second electron.

3. Hund's rule of maximum multiplicity

It states that **electron pairing takes place only after partially filling all the degenerate orbitals**.

Orbitals having same energies are called degenerate orbitals. For example the electronic configuration of N is $1s^2 2s^2 2p_x^1 p_y^1 p_z^1$ and not $1s^2 2s^2 2p_x^2 p_y^1$.

Electronic Configuration of Atoms

The distribution of electrons into various orbitals of an atom is called its *electronic configuration*.

The electrons in the completely filled shells are known as *core electrons* and the electrons in the outer most shell are called *valence electrons*.

Stability of Completely Filled and Half Filled Subshells

For atoms having half filled or completely filled electronic configurations have extra stability compared to other atoms. This is due to their symmetrical distribution of electrons and greater exchange energy.

For example, the electronic configuration of Cr is $[\text{Ar}] 3d^5 4s^1$ and not $3d^4 4s^2$. This is due to the extra stability of half filled d^5 configuration. Similarly, for Cu the electronic configuration is $[\text{Ar}] 3d^{10} 4s^1$ and not $3d^9 4s^2$. This is due to the extra stability of fully filled d^{10} configuration.

3. CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Modern Periodic table

Henry Moseley's work on the atomic spectra of elements proved that atomic number is the most fundamental property. Based on this observation, he proposed a periodic law, which states that "*the properties of elements are the periodic functions of their atomic numbers*". This is known as **Modern Periodic law**.

Based on modern periodic law, numerous forms of periodic tables have been proposed. The most commonly used is the **long form of periodic table**.

In this periodic table, the elements are arranged in the increasing order of their atomic number. It contains **7** horizontal rows called **periods** and **18** vertical columns called **groups**. Elements having similar outer electronic configurations are arranged in same group or family. The groups are numbered from 1 to 18. Due to the similar outer electronic configuration and same valency, the elements present in the same group have similar properties.

There are 7 periods in Modern periodic table. The period number corresponds to the highest principal quantum number of the elements. The *first period* contains 2 elements (H and He). Here the subshell filled is 1s. This period is called *very short period*.

The *second period* contains 8 elements (Li to Ne). Here the subshells filled are 2s and 2p. The *third period* also contains 8 elements (Na to Ar). Here the subshells filled are 3s and 3p. These 2 periods are called *short periods*.

The *fourth period* contains 18 elements (K to Kr). Here the subshells filled are 4s, 3d and 4p. The *fifth period* also contains 18 elements (Rb to Xe). Here the subshells filled are 5s, 4d and 5p. These 2 periods are called *long periods*.

The *sixth period* contains 32 elements (Cs to Rn). Here the subshells filled are 6s, 4f, 5d and 6p. This period is the longest period in the periodic table and is called the *Monster period*. The *seventh period* is an incomplete period. It can also accommodate 32 elements. Here the subshells filled are 7s, 5f, 6d and 7p.

The 14 elements each of sixth and seventh periods are placed in separate rows below the main body of the periodic table. These are together called **inner transition elements**. The 14 elements of sixth period (from cerium to lutetium) are called *Lanthanides or Lanthanones or Lanthanoids or rare earths*. The 14 elements of seventh period (from thorium to lawrencium) are called *Actinides or Actinones or Actinoids*.

The Modern periodic table is divided into 4 blocks based on the subshell in which the last electron enters. They are s block, p block, d block and f block.

Periodic properties of Elements

The properties which repeat after a regular interval are called periodic properties. Some of the important periodic properties of elements are atomic radius, ionic radius, ionization enthalpy, electron gain enthalpy, electronegativity etc.

1. Atomic Radius

It is defined as the distance from the centre of the nucleus to the outermost shell having electrons. Atomic radius of individual atoms cannot be determined. So it is expressed in any of the following methods:

- Covalent radius*: It is half of the inter nuclear distance between two covalently bonded (single bonded) atoms. It is used to express the atomic radius of non-metal atoms.
For e.g. the distance between 2 Cl atoms in Cl₂ molecule is 198 pm. So its covalent radius is 99 pm.
- Metallic radius*: It is the half of the inter nuclear distance between two metallic ions in a metal crystal.
- van der Waal's radius*: It is defined as the half of the inter nuclear distance between two non bonded atoms of separate molecules in the solid state.

Atomic radius is commonly expressed in picometre (pm) or angstrom (Å) unit. It is measured by x-ray diffraction method or by spectroscopic method.

Variation of atomic radius along a group and a period

The atomic size decreases from left to right in a period. This is because in a period, the electrons are added to the same valence shell. Thus the number of shells remains same, but the effective nuclear charge

increases. So the atomic radius decreases. In a given period, alkali metals (group 1) have the maximum size and halogens (group 17) have the minimum size.

In a group, the atomic radius increases from top to bottom. This is because of the increase in no. of shells and shielding effect. (In atoms with higher atomic number, the inner electrons partially shield the attractive force of the nucleus. So the outer electrons do not experience the full attraction of the nucleus and this is known as shielding effect or screening effect).

Atomic radius of noble gases is larger than that of halogens. This is because noble gases are monoatomic. So van der Waal's radius is used to express the atomic radius which is greater than covalent radius.

Ionic radius

It is defined as the half of the inter nuclear distance between cations and anions of an ionic crystal. The variation of ionic radius is same as that of atomic radius.

Generally a cation is smaller than its parent atom (e.g. Na^+ is smaller than Na atom). This is because a cation has fewer electrons, but its nuclear charge remains the same as that of the parent atom.

An anion is larger than its parent atom (e.g. Cl^- is larger than Cl atom). This is because the addition of one or more electrons would result in an increased electronic repulsion and a decrease in effective nuclear charge.

Isoelectronic species:

Atoms and ions having the same number of electrons are called isoelectronic species.

E.g. O^{2-} , F^- , Ne, Na^+ , Mg^{2+} etc. (All these contain 10 electrons)

Among isoelectronic species, *the cation with greater positive charge will have the smaller radius*. This is because of their greater effective nuclear charge. *The anion with greater negative charge will have the larger radius*. Here the effective nuclear charge is less and the repulsion between electrons is greater. So the ion will expand in size.

2. Ionisation enthalpy ($\Delta_i H$)

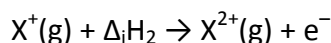
It is defined as the energy required to remove an electron from the outer most shell of an isolated gaseous atom in its ground state.

It may be represented as:
$$\text{X}_{(g)} + \Delta_i H \rightarrow \text{X}^+_{(g)} + e^-$$

Its unit is kJ/mol.

The energy required to remove the first electron from the outer most shell of a neutral atom is called *first ionisation enthalpy ($\Delta_i H_1$)*
$$\text{X}_{(g)} + \Delta_i H_1 \rightarrow \text{X}^+_{(g)} + e^-$$

Second Ionisation enthalpy ($\Delta_i H_2$) is the amount of energy required to remove an electron from a unipositive ion.



Energy is always required to remove an electron from an atom or ion. So $\Delta_i H$ is always positive.

The second ionisation enthalpy is always higher than first ionization enthalpy. This is because it is more difficult to remove an electron from a positive charged ion than from a neutral atom.

Similarly third ionisation enthalpy is higher than second ionisation enthalpy and so on.

i.e. $\Delta_i H_1 < \Delta_i H_2 < \Delta_i H_3 \dots\dots\dots$

As the ease of removal of electron increases, the ionisation enthalpy decreases.

Factors affecting ionisation enthalpy

The important factors which affect ionisation enthalpy are:

- Atomic size:* Greater the atomic size (atomic radius), smaller will be the ionisation enthalpy.
- Nuclear charge:* The value of ionisation enthalpy increases with nuclear charge.
- Shielding effect:* As the shielding effect increases, the electrons can easily be removed and so the ionisation enthalpy decreases.
- Presence of half filled or completely filled orbitals* increases ionisation enthalpy.

Variation of Δ_iH along a period and a group

Along a *period*, ionisation enthalpy *increases* from left to right. This is because of the *decrease in atomic radius and increase in nuclear charge*. Thus alkali metals have the least Δ_iH and noble gases have the most.

Down a *group*, Δ_iH *decreases due to increase in atomic radius and shielding effect*. Thus among alkali metals, lithium has the least Δ_iH and francium has the most.

In the second period of modern periodic table, *the first ionisation enthalpy of Boron is slightly less than that of Beryllium*. This is because of the completely filled orbitals in Be ($1s^2 2s^2$).

Similarly *the first ionisation enthalpy of N is greater than that of Oxygen*. This is because N has half filled electronic configuration ($1s^2 2s^2 2p^3$), which is more stable and so more energy is required to remove an electron.

3. Electron gain enthalpy ($\Delta_{eg}H$)

It is the heat change (enthalpy change) when an electron is added to the outer most shell of an isolated gaseous atom. It can be represented as $X_{(g)} + e^- \rightarrow X^-_{(g)}$

Its unit is kJ/mol. It may be positive or negative depending on the nature of the element. For most of the elements, energy is released when electron is added to their atoms. So $\Delta_{eg}H$ is negative. Noble gases have large positive electron gain enthalpy because of their completely filled (stable) electronic configuration. As the ease of addition of electron increases, electron gain enthalpy becomes more negative.

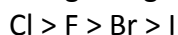
The factors affecting Electron gain enthalpy are atomic size, nuclear charge, shielding effect and electronic configuration. As the atomic size increases $\Delta_{eg}H$ decreases. When nuclear charge increases, electron gain enthalpy increases and become more negative. As the shielding effect increases, $\Delta_{eg}H$ decreases (or, becomes less negative). Presence of half filled or completely filled orbitals makes $\Delta_{eg}H$ less negative.

Periodic variation of $\Delta_{eg}H$

From left to right across a *period*, $\Delta_{eg}H$ become *more negative*. This is *because of decrease in atomic radius and increase in nuclear charge*. So the ease of addition of electron increases and hence the $\Delta_{eg}H$. Down a *group*, $\Delta_{eg}H$ becomes less negative *due to increase in atomic radius and shielding effect*.

Electron gain enthalpy of fluorine is less negative than chlorine. This is because, when an electron is added to F, it enters into the smaller 2^{nd} shell. Due to the smaller size, the electron suffers more repulsion from the other electrons. But for Cl, the incoming electron goes to the larger 3^{rd} shell. So the electronic repulsion is low and hence Cl adds electron more easily than F. Due to the same reason $\Delta_{eg}H$ of Oxygen is less negative than S.

Thus in modern periodic table, alkali metals have the least $-ve$ $\Delta_{eg}H$ and halogens have the most $-ve$ $\Delta_{eg}H$. Among halogens, the negative $\Delta_{eg}H$ decreases as follows.



The negative electron gain enthalpy is also called electron affinity.

4. Electronegativity

Electronegativity of an atom in a compound is the ability of the atom to attract shared pair of electron of electrons. It is not a measurable quantity and so it has *no* unit. There are different scales for measuring the Electronegativity of elements. Some of them are Pauling scale, Mulliken – Jaffe scale, Allred-Rochow scale etc. The most commonly used is the **Pauling Electronegativity scale** proposed by Linus Pauling.

Electronegativity depends on atomic size and nuclear charge. As the atomic radius increases, electronegativity decreases. Greater the nuclear charge, greater will be the electronegativity. Generally electronegativity increases across a period and decreases along a group. So in modern periodic table, F has the maximum electronegativity and Fr has the minimum electronegativity. *In Pauling Scale, electronegativity of F is 4.0 and that of Oxygen is 3.5.*

The electronegativity of an element is *not constant*. It varies depending on the element to which it is bound. It is directly related to the non-metallic character of elements. *An increase in electronegativity across a period indicates an increase in non-metallic character and decrease in metallic character.*

4. CHEMICAL BONDING AND MOLECULAR STRUCTURE

The attractive force that binds the atoms together in a molecule is called a chemical bond. . It is formed either by the transfer of electrons or by the sharing of electrons.

Covalent bond

A bond formed by the mutual sharing of electrons between two or more atoms is called covalent bond. It may be a single bond, double bond or triple bond. *A covalent bond formed by the sharing of one pair of electron is called a single bond. A double bond is formed when 2 pairs of electrons are shared between 2 atoms and a triple bond is formed when 3 pairs of electrons are shared between two atoms.* The double and triple bonds are together called **multiple bonds**.

The shapes of molecules

Covalent bonds are directional in nature. i.e. they are directed to some specified positions in space. So covalent compounds have definite shapes.

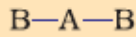
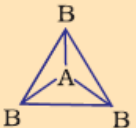
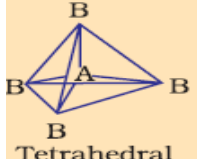
The Valence Shell Electron Pair Repulsion [VSEPR] Theory

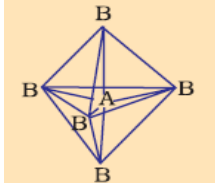
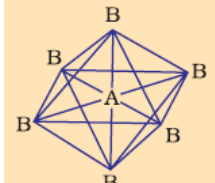
This theory was proposed by Sidgwick and Powell and later modified by Nyholm and Gillespie. The important postulates of this theory are:

- 1) The shape of the molecule depends on the number of valence shell electron pairs (VSEPRs) around the central atom.
- 2) The valence shell electron pairs repel each other.
- 3) In order to reduce the repulsion, the electron pairs stay at maximum distance.
- 4) Presence of lone pairs of electron causes distortion in the expected geometry of the molecule.
- 5) The repulsion between two lone pairs of electrons is different from those between two bond pairs or between a lone pair and bond pair. The repulsion decreases in the order lone pair - lone pair > lone pair - bond pair > bond pair - bond pair.
- 6) As the angle between the electron pairs increases, the repulsion decreases.

Prediction of geometry of molecules using VSEPR theory

1) Molecules containing only bond pairs of electrons

| Type of Molecule | No. of VSEPs (bond pairs only) | Structure | Bond angle | Examples |
|----------------------|--------------------------------|--|------------|--|
| AB ₂ type | 2 |  Linear | 180° | BeCl ₂ , HgCl ₂ |
| AB ₃ type | 3 |  Trigonal planar | 120° | BF ₃ , BCl ₃ |
| AB ₄ type | 4 |  Tetrahedral | 109°28' | CH ₄ , NH ₄ ⁺ |

| | | | | |
|----------------------|---|---|--------------|------------------|
| AB ₅ type | 5 | Trigonal bipyramid  | 120° and 90° | PCl ₅ |
| AB ₆ type | 6 | Octahedral  | 90° | SF ₆ |

II) Molecules containing both bond pairs and lone pairs

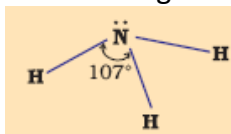
The presence of lone pairs of electron causes distortion in the shape of the molecules.

| Type of molecule | Total no. of VSEPs | No. of b.ps | No. of l.ps | Shape | e.g. |
|--------------------------------|--------------------|-------------|-------------|------------------|----------------------------------|
| AB ₂ E | 3 | 2 | 1 | Bent | SO ₂ , O ₃ |
| AB ₃ E | 4 | 3 | 1 | Trigonal Pyramid | NH ₃ |
| AB ₂ E ₂ | 4 | 2 | 2 | Bent | H ₂ O |
| AB ₄ E | 5 | 4 | 1 | See-saw | SF ₄ |
| AB ₃ E ₂ | 5 | 3 | 2 | T-Shape | ClF ₃ |
| AB ₅ E | 6 | 5 | 1 | Square Pyramid | BrF ₅ |
| AB ₄ E ₂ | 6 | 4 | 2 | Square Planar | XeF ₄ |

Explanation of shapes of ammonia and water molecules by VSEPR theory

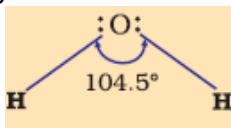
1. NH₃

In ammonia, the central atom N has 5 valence electrons (${}_7\text{N} - 2, 5$). Among these electrons, three are used for the formation of bonds with hydrogen atoms and the remaining 2 electrons stay as lone pairs. So there are 4 VSEPs. Hence the expected shape of the molecule is tetrahedral. But due to the presence of lone pairs, the shape is distorted to triangular pyramid and the bond angle changes from 109°28' to 107°.



2. H₂O

In water, the central atom O has 6 valence electrons (${}_8\text{O} - 2, 6$). Two of them are used for the formation of bonds with hydrogen atoms and the remaining 4 electrons stay as lone pairs. So there are 4 VSEPs. Hence the expected shape of the molecule is tetrahedral. But due to the presence of 2 lone pairs, the shape is distorted bent or angular or inverted v shape and the bond angle changes from 109°28' to 104.5°.



Valence Bond Theory (VB Theory)

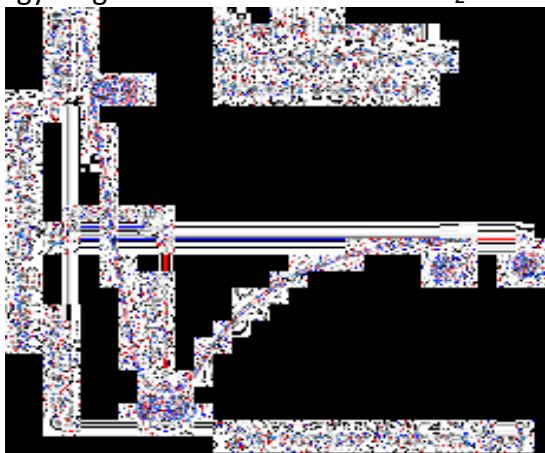
This theory was introduced by Heitler and London and later developed by Linus Pauling in order to explain the shape of molecules theoretically. VBT can be explained by considering the formation of H_2 molecule.

Consider 2 hydrogen atoms A and B with nuclei N_A and N_B and electrons e_A and e_B respectively. When the two atoms are at large distance from each other, there is no interaction between them. So their potential energy is zero. When the two atoms approach each other, new attractive and repulsive forces begin to operate.

Attractive forces arise between nucleus of one atom and electron of other atom i.e., $N_A - e_B$ and $N_B - e_A$. Similarly repulsive forces arise between electrons of two atoms ($e_A - e_B$) and nuclei of two atoms $N_A - N_B$. Attractive forces bring the two atoms close to each other whereas repulsive forces push them away.

Experimentally it has been found that the magnitude of new attractive force is more than the new repulsive forces. So the two atoms approach each other and potential energy decreases. At a particular stage, the net attractive force balances the net repulsive forces and the energy becomes minimum. At this stage, the 2 hydrogen atoms are bonded together to form a stable molecule. The distance between the two atoms at this stage is called **bond length** (74 pm). The amount of energy liberated at this stage is called **bond enthalpy**(435.8kJ/mol)

The potential energy diagram for the formation of H_2 molecule is as shown below:



Orbital overlap concept

Orbital overlapping is the process of partial interpenetration of atomic orbitals. The important characteristics of orbital overlapping are:

1. A covalent bond is formed by the overlapping of half filled atomic orbitals present in the valence shell of atoms.
2. The overlapping orbitals should contain electron with opposite spin.
3. As a result of overlapping, the electrons get paired and a stable covalent bond is formed.
4. The strength of a covalent bond depends on the extent of overlapping. The greater the extent of overlapping, the stronger will be the covalent bond formed.

Types of overlapping

There are two types of orbital overlapping.

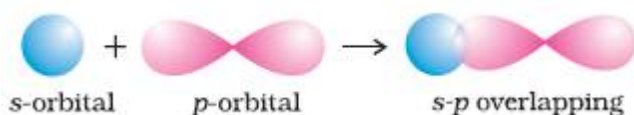
1. **Axial overlapping:**

If the overlapping of atomic orbitals take place *along inter nuclear axis*, it is called axial overlapping or end to end overlapping. A bond formed by axial overlapping is called **sigma (σ) bond**. The electrons present in sigma bond are called sigma electrons. All single bonds are sigma bonds. A sigma bond can be formed by the following ways:

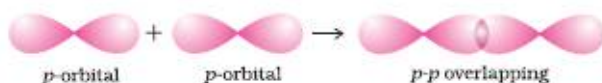
- i) s-s overlapping: Here the overlapping of two half filled s-orbitals take place along the inter nuclear axis.



- ii) s-p overlapping: It occurs with the overlapping of one half filled s-orbital and one half filled p-orbital.

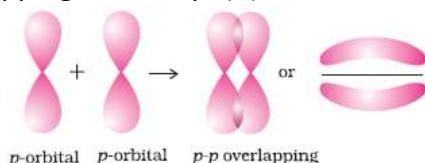


- iii) p-p overlapping: Here two half filled p-orbitals of two atoms overlap.



2. Lateral overlapping:

Here the overlapping take place perpendicular to the inter nuclear axis. The bond formed as a result of lateral overlapping is called pi (π) bond. The electrons in pi bond are called π electrons.



A π bond is always present along with σ bonds. A double bond contains one σ bond and one π bond. A triple bond contains one sigma bond and two pi bonds.

A sigma bond is stronger than a pi bond. This is because the extent of overlapping is greater in a sigma bond.

Hybridisation

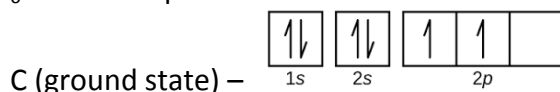
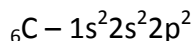
It is the process of inter mixing atomic orbitals having slightly different energies to form new orbitals having equivalent energy and identical shape. The new orbitals formed are called hybrid orbitals.

Types of hybridisation

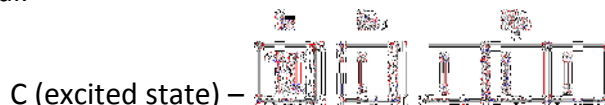
1. **sp^3 hybridisation**: It is the process of inter mixing of one s-orbital and three p-orbitals to form four new orbitals having equivalent energy and shape. The 4 new orbitals formed are called sp^3 hybrid orbitals. They are directed to the four corners of a regular tetrahedron with bond angle $109^\circ 28'$. Each sp^3 hybrid orbitals has 25% s-character and 75% p-character.

e.g. i) . **Formation of methane (CH_4)**

In CH_4 , the central atom C has the electronic configuration



In order to explain the tetra valency of C, it is suggested that one of the electrons of 2s orbital is promoted to 2p orbital.

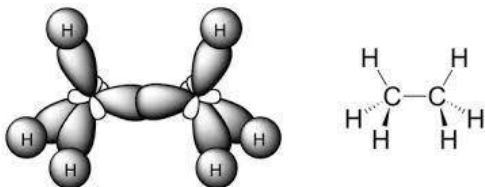


Now, one s-orbital and three p-orbitals undergo sp^3 hybridisation. These sp^3 hybrid orbitals are directed to the four corners of a regular tetrahedron with bond angle $109^\circ 28'$. Each of these sp^3 hybrid orbitals overlap with 1s orbital of H to form four C-H σ bonds.



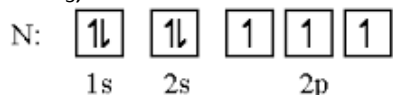
ii) Formation of ethane (C₂H₆)

In ethane, each C atom undergoes sp³ hybridisation. Out of the 4 sp³ hybrid orbitals, one of each C atom overlaps axially to form a C-C σ bond. The remaining 3 sp³ hybrid orbitals of each C atom overlap with 1s orbital of H atom to form 6 C-H σ bonds.



iii) Formation of Ammonia (NH₃) molecule

In NH₃, the central atom N has the electronic configuration 1s²2s²2p³.



The one s-orbital and three p-orbitals of N undergo sp³ hybridisation to form 4 sp³ hybrid orbitals. One of this sp³ hybrid orbitals is occupied by a lone pair and the other three sp³ hybrid orbitals overlap with 1s orbital of hydrogen to form 3 N-H bonds. Due to the greater repulsion between lone pair and bond pairs, the shape is distorted to **pyramidal** and the bond angle becomes **107°**.



iv) Formation of water (H₂O) molecule

In H₂O, the central atom O has the electronic configuration 1s²2s²2p⁴.



Now the one s-orbital and three p-orbitals of O undergo sp³ hybridisation to form 4 sp³ hybrid orbitals. Two of these sp³ hybrid orbitals are occupied by lone pairs and the other two sp³ hybrid orbitals overlap with 1s orbital of hydrogen to form 2 O-H bonds. Due to the greater repulsion between lone pairs, the shape is distorted to angular shape or bent structure or inverted 'v' shape and the bond angle becomes 104.5°.



2. **sp² hybridisation:** It is the process of inter mixing of one s-orbital and two p-orbitals to form three new orbitals having equivalent energy and shape. The 3 new orbitals formed are called sp² hybrid orbitals.

They are directed to the three corners of an equilateral triangle. So the shape of the molecule is planar triangular or trigonal planar with bond angle 120° . Each sp^2 hybrid orbitals has 33% s-character and 66% p-character.

e.g. i) **Formation of BCl_3**

Here the central atom B has the electronic configuration $1s^2 2s^2 2p^1$. In the excited state, one of the 2s electrons is promoted to vacant 2p orbital. So the configuration becomes $2s^1 2p^2$.

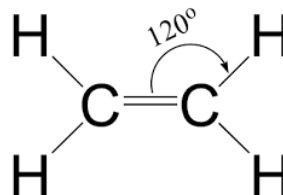
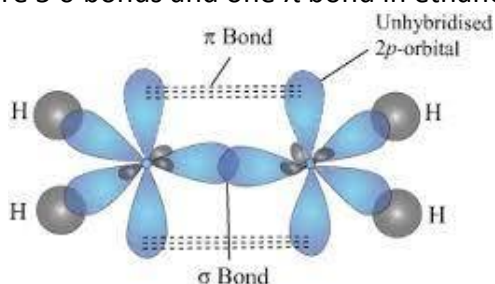
Now one s-orbital and two p-orbitals undergo hybridisation. The 3 hybrid orbitals formed overlap with 2p orbitals of Cl to form 3 B-Cl σ bonds. Since the hybridisation is sp^2 , the shape of the molecule is planar triangular with bond angle 120° .



ii) **Formation of ethane or ethylene (C_2H_4)**

In ethane, each C atom undergoes sp^3 hybridisation. Out of the 3 sp^3 hybrid orbitals, one of each C overlaps axially to form a C-C σ bond. The remaining two sp^3 hybrid orbitals of each C overlap with the 1s orbital of H to form 4 C-H σ bonds.

Now each C atom has one unhybridized p-orbital, which overlaps laterally to form a π bond. Thus there are 5 σ bonds and one π bond in ethane.

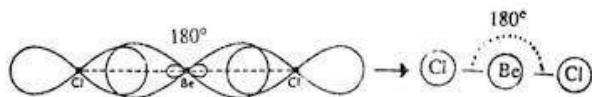


3. **sp hybridisation**: It is the process of inter mixing of one s-orbital and one p-orbital to form two new orbitals having equivalent energy and shape. The 2 new orbitals formed are called sp hybrid orbitals. They are directed in a line. So the shape is linear with bond angle 180° . Each sp hybrid orbitals has 50% s-character and 50% p-character.

e.g. i) **Formation of $BeCl_2$**

in $BeCl_2$, the central atom Be has the electronic configuration $1s^2 2s^2$. In the excited state, one of the 2s electrons is promoted to 2p level. So the configuration becomes $1s^2 2s^1 2p^1$.

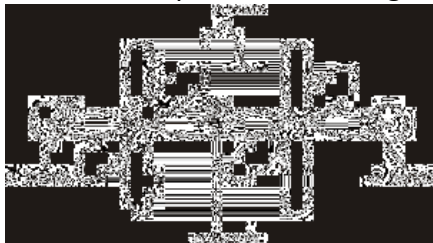
Now one s-orbital and one p-orbital undergo sp hybridisation to form 2 new sp hybrid orbitals. Each of these hybrid orbitals overlaps with the 2p orbitals of Cl to form 2 Be-Cl bonds. So the shape of the molecule is linear with bond angle 180° .



ii) **Formation of ethyne or acetylene (C_2H_2)**

In acetylene, each C atom undergoes sp hybridisation. Out of the 2 sp hybrid orbitals, one of each C overlaps axially to form a C-C σ bond. The remaining two sp hybrid orbitals of each C overlap with the 1s orbital of H to form 2 C-H σ bonds.

Now each C atom has 2 unhybridized p-orbitals, which overlap laterally to form 2 π bonds. Thus the molecule has linear shape with bond angle 180° . Here there are 3 σ bonds and 2 π bonds in ethyne.



Molecular Orbital Theory

This theory was developed by F.Hund and R.S Mulliken. The important postulates of this theory are:

- 1) In molecules, the electrons are present in some special type of orbitals called molecular orbitals (M.Os).
- 2) The atomic orbitals (A.Os) of comparable energy and proper symmetry combine to form molecular orbitals.
- 3) Atomic orbitals are monocentric, while molecular orbitals are polycentric. i.e. electrons present in atomic orbitals are attracted by only one nucleus. While the electrons present in molecular orbitals are attracted by more than one nuclei.
- 4) The number of molecular orbitals formed = the number of atomic orbitals combined. i.e. if 2 atomic orbitals combined, 2 molecular orbitals are formed. One is called bonding molecular orbital (BMO) and the other is called anti-bonding molecular orbitals (ABMO)
- 5) The BMO has lower energy and greater stability than the corresponding ABMO.
- 6) The molecular orbitals give the electron probability distribution around a group of nuclei.
- 7) The molecular orbitals are filled according to 3 rules – Aufbau principle, Pauli's exclusion principle and Hund's rule.

Formation of molecular orbitals – Linear Combination of Atomic Orbitals (LCAO) method

Molecular orbitals are formed by the combination of atomic orbitals by an approximate method known as Linear Combination of Atomic Orbitals (LCAO). According to this theory, the combinations of atomic orbitals take place by addition and subtraction of wave functions of atomic orbitals. The M.O formed by the addition of A.Os is called the bonding molecular orbital (BMO) and by the subtraction of A.Os is called the anti-bonding molecular orbitals (ABMO).

The electron density in a BMO is located between the nuclei of the bonded atoms. So the repulsion between the nuclei is very low. Therefore a BMO always possess lower energy than the combining A.Os. While in the case of an ABMO, most of the electron density is located away from the space between the nuclei. There is a nodal plane between the nuclei and hence the repulsion between the nuclei is high. So an ABMO possess higher energy than the combining A.Os. ABMO is denoted by using an asteric (*) mark.

Conditions for the combination of atomic orbitals

The combination of A.Os to form M.Os takes place only if the following conditions are satisfied:

1. The combining A.Os must have the same or nearly the same energy.
2. The combining A.Os must have the same symmetry about the molecular axis.
3. The combining A.Os must overlap to the maximum extent.

Types of molecular orbitals

M.Os of diatomic molecules are designated as σ (sigma), π (Pi), δ (delta) etc. the sigma M.Os are symmetrical about the bond axis, while the pi M.Os are not symmetrical.

Linear combination of two 1s atomic orbitals produces two M.Os – a BMO σ_{1s} and an ABMO σ^*_{1s} .

Similarly linear combination of two 2s atomic orbitals produces two M.Os – σ_{2s} and σ^*_{2s} .

If z-axis is taken as the inter nuclear axis, linear combination of two $2p_z$ orbitals produces two sigma M.Os $\sigma 2p_z$ and $\sigma^* 2p_z$.

While the combination of $2p_x$ and $2p_y$ orbitals produce M.Os which are not symmetrical about the bond axis. So two $2p_x$ orbitals produces 2 sigma M.Os – $\pi 2p_x$ and $\pi^* 2p_x$ and two $2p_y$ orbitals produce 2 M.Os – $\pi 2p_y$ and $\pi^* 2p_y$.

Energies of various M.Os

The various M.Os are filled in the increasing order of their energies (Aufbau Principle). The increasing order of energy is:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < (\pi 2p_x = \pi 2p_y) < \sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

For O_2 , F_2 and Ne_2 , the order is:

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi 2p_x = \pi 2p_y) < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z$$

Bond Order

It is defined as *the half of the difference between the number of bonding electrons (N_b) and the number of anti-bonding electrons (N_a)*.

i.e. **Bond order (B.O) = $\frac{1}{2} [N_b - N_a]$**

A molecule is stable only if the bond order is positive. (i.e. $N_b > N_a$). a negative bond order (i.e. $N_b < N_a$ or $N_b = N_a$) means an unstable molecule.

For a single bond, B.O = 1, for a double bond B.O = 2 and so on. Bond order gives an approximate measure of the bond length. In general, **as the bond order increases, bond length decreases and bond enthalpy increases**.

For molecules like He_2 , Be_2 , and Ne_2 , bond order = 0. So these molecules do not exist.

Magnetic nature

If all the M.Os in a molecule are doubly occupied, the substance is diamagnetic. i.e. that substance is repelled by an external magnetic field. If one or more M.Os are singly occupied, it is paramagnetic. i.e. it is attracted by an external magnetic field. E.g. O_2 molecule.

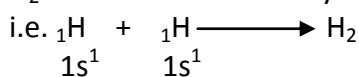
Molecular orbital Diagram

The representation of various M.Os in the increasing order of energy is called M.O diagram.

Bonding in Some Homonuclear Diatomic Molecules

1. Hydrogen Molecule (H_2)

H_2 molecule is formed by the combination of two Hydrogen atoms.



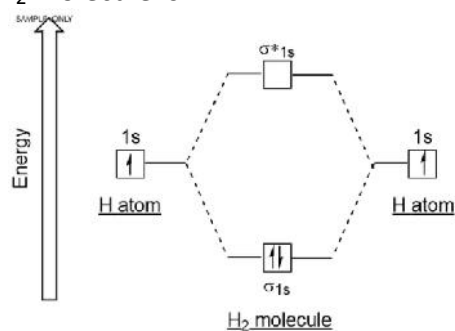
Total no. of electrons in H_2 molecule = 2

So its M.O configuration is $\sigma 1s^2$

Bond order of H_2 molecule = $\frac{1}{2} [N_b - N_a] = \frac{1}{2} [2 - 0] = 1$

i.e. in H_2 molecule, two hydrogen atoms are bonded together by a single bond.

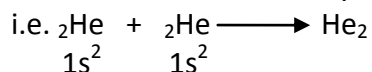
M.O diagram for H_2 molecule is:



Due to the absence of unpaired electrons in M.Os, H_2 molecule is diamagnetic.

2. Helium Molecule (He_2) Molecule

He_2 molecule is formed by the combination of two Helium atoms.



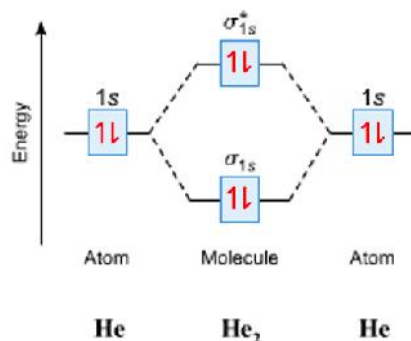
Total no. of electrons in He_2 molecule = 4

So its M.O configuration is = $\sigma 1s^2 \sigma^* 1s^2$

Bond order of He_2 molecule = $\frac{1}{2} [N_b - N_a] = \frac{1}{2} [2 - 2] = 0$

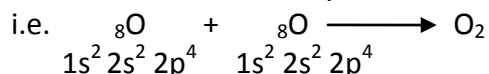
Since B.O is zero, He_2 molecule does not exist.

Its M.O diagram is:



3. Oxygen (O_2) molecule

O_2 molecule is formed by the combination of two Oxygen atoms.



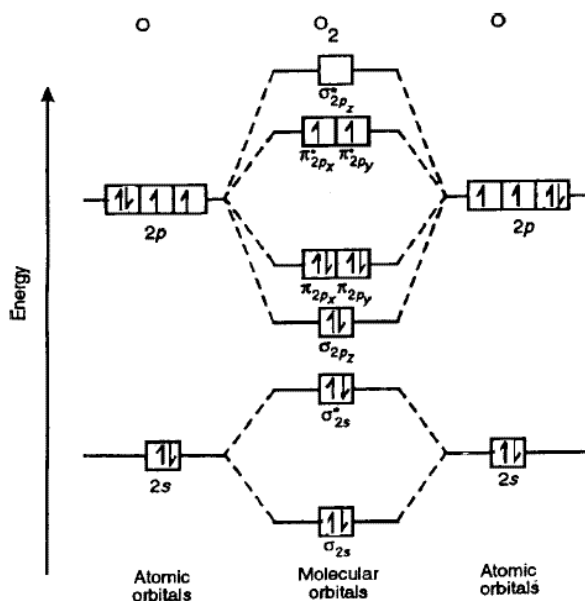
Total no. of electrons in O_2 molecule = 16

So its M.O configuration is = $\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 \pi 2p_y^2 \pi^* 2p_x^1 \pi^* 2p_y^1$

Bond order of O_2 molecule = $\frac{1}{2} [N_b - N_a] = \frac{1}{2} [10 - 6] = \frac{1}{2} \times 4 = 2$

i.e. in O_2 molecule, two Oxygen atoms are bonded together by a double bond.

Its M.O diagram is:



Due to the presence of unpaired electrons, O_2 molecule is paramagnetic.

5. STATES OF MATTER

Gas Laws

These are some relationships connecting the measurable properties of gases like pressure (P), temperature (T), volume (V) and number of moles (n). These are:

1) Boyle's Law (Pressure – Volume Relationship)

It states that at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure. Mathematically,

$$P \propto 1/V$$

$P = k \times 1/V$, where k is the proportionality constant.

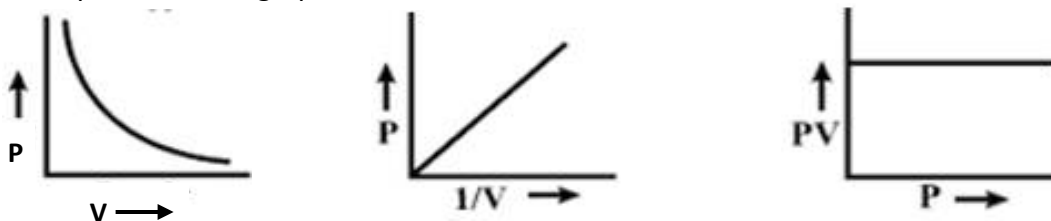
Or, $PV = k$, a constant

Consider a fixed amount of gas at constant temperature T. Let V_1 & P_1 are its initial volume and pressure respectively. Let the gas undergoes expansion, so that its final volume and pressure becomes V_2 and P_2 .

Then according to Boyle's law,

$$P_1V_1 = P_2V_2$$

If we plot graphs between pressure against volume, pressure against 1/volume and PV against P at constant temperature, the graphs obtained are as follows:



These graphs are obtained at constant temperature and so they are called **isotherms**.

We know that density = mass/volume

$$\text{i.e., } d = m/V$$

If we put value of V in this equation from Boyle's law equation, we get the relationship,

$$d = (m/k) \times p$$

i.e. At constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.

2) Charles' Law (Temperature – Volume Relationship)

It states that at constant pressure, volume of a fixed mass of gas is directly proportional to its temperature.

Mathematically, $V \propto T$

$$\text{Or, } V = k \times T$$

$$\text{Or, } V/T = k, \text{ a constant}$$

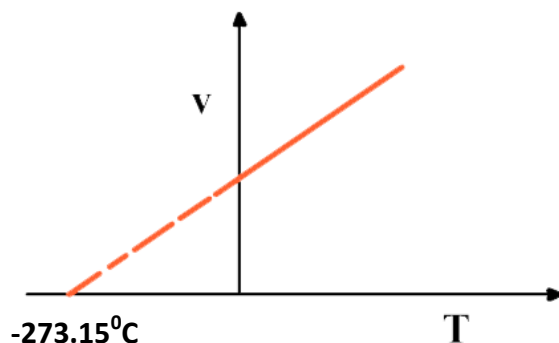
Consider a fixed amount of gas at constant pressure P. Let V_1 be its volume at a temperature T_1 and V_2 be its volume at a temperature T_2 .

Then according to Charles' law:

$$V_1/T_1 = V_2/T_2$$

Graphical Representation of Charles' law

If volume is plotted against temperature at constant pressure, the graph obtained is as follows.



Since the graph is obtained at constant pressure, it is called **isobar**.

If we extend the graph to temperature axis (X-axis), the graph will meet at -273.15°C . At this temperature, the volume of the gas becomes zero. This lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **Absolute zero of temperature** and the scale of temperature based on absolute zero is called **Absolute scale of temperature**. All gases become solid or liquid before reaching this temperature.

3) Avogadro Law (Volume – no. of moles or Amount Relationship)

It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of moles or molecules. This means that at constant temperature and pressure, the volume of a gas is directly proportional to its number of moles (n) or molecules (N).

i.e., $V \propto n$, the number of moles

or, $V = k \times n$, where k is a constant

We know that number of moles (n) = mass in gram (w)/molar mass (M)

i.e., $n = w/M$

So the above equation becomes:

$$V = k \times w/M$$

Or, $M = k \times w/V$

Or, $M = k \times d$

Or, $M \propto d$

i.e., the density of a gas is directly proportional to its molar mass.

Standard Temperature and Pressure (STP)

Standard temperature and pressure (also called NTP, the normal temperature and pressure) means 273.15 K (0°C) temperature and 1 bar pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level. At STP, molar volume of an ideal gas is 22.71 L mol^{-1} .

IDEAL GAS EQUATION

The combination of the three gas laws (Boyle's law, Charles' and Avogadro law) give a single equation which is known as **ideal gas equation**.

According to Boyle's law: $V \propto 1/P$ (At constant T and n)

According to Charles' Law: $V \propto T$ (At constant p and n)

According to Avogadro Law: $V \propto n$ (At constant p and T)

On combining these three laws we get:

$$V \propto n \times T \times 1/P$$

Or, $V = R \times n \times T \times 1/P$ (where R is a constant called **universal gas constant**)

Or, **$PV = nRT$** (1)

This equation is known as **ideal gas equation**.

From equation (1), $R = \frac{PV}{nT}$

The value of R depends upon units in which P, V and T are measured.

Values of R in different units

| | |
|-----------------------------|------------------------------------|
| 1. L atm/K/mol | 0.0821 |
| 2. L bar/K/mol | 0.08314 (8.314×10^{-2}) |
| 3. Pa m ³ /K/mol | 8.314 |
| 4. J/K/mol | 8.314 |

Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called **equation of state**.

Relation between density and Molar mass

The ideal gas equation is $PV = nRT$

But $n = w/M$

So, $PV = wRT/M$

Or, $P = wRT/MV$

Or, $P = dRT/M$

Or, **$M = dRT/P$**

Combined Gas Law

From ideal gas equation $PV = nRT$, $\frac{PV}{T} = nR$

If temperature, volume and pressure of a fixed amount of gas vary from T_1 , V_1 and P_1 to T_2 , V_2 and P_2 then we can write, $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

This equation is known as **combined gas law**. By knowing the values of any 5 parameters, we can determine the sixth one.

KINETIC MOLECULAR THEORY OF GASES

In order to explain the gas laws theoretically Maxwell, Boltzmann, Clausius etc. put forward a theory called *kinetic molecular theory of gases or microscopic model of gases*. The important postulates of this theory are:

1. Every gas contains a large number of minute and elastic particles (atoms or molecules). The actual volume of the molecules is negligible compared to the volume of the gas.
2. There is no force of attraction between the gas particles.
3. The particles of a gas are in constant and random motion in straight line. During this motion they collide with each other and also with the walls of the container.
4. The pressure of a gas is due to the wall collisions of the particles.
5. All collisions are perfectly elastic. i.e. the total energy of particles before and after collisions remains the same.
6. At any particular time, different particles of a gas have different speed and hence different kinetic energy.
7. The average kinetic energy of gas molecules is directly proportional to absolute temperature.

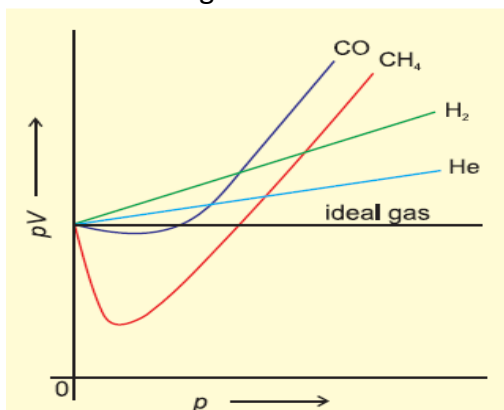
Behavior of real gases – Deviation of real gases from ideal behavior

Real gases do not obey ideal gas equation at all conditions of temperature and pressure. This can be understood from the PV against P graphs for different gases.

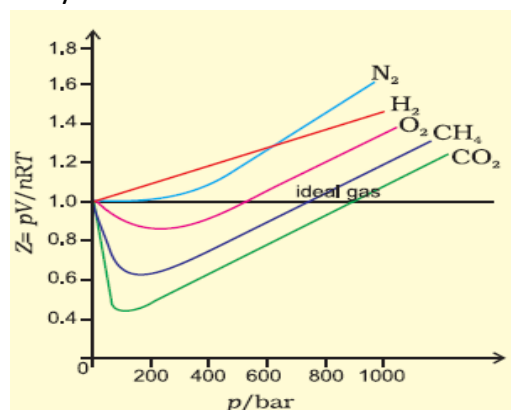
For ideal gases, PV is constant for any pressure. So the graph obtained is a straight line parallel to the pressure axis (X – axis). For H_2 and He , PV increases with increase of pressure. But for CO and CH_4 , the value of PV first decreases, reaches a minimum value and then increases.

The deviation from ideal behaviour can be measured in terms of compressibility factor Z , which is the ratio of product PV and nRT . Mathematically,
$$Z = \frac{PV}{nRT}$$

For ideal gas $Z = 1$ at all temperature and pressures. So the graph of Z vs P will be a straight line parallel to pressure axis. For real gases value of Z deviates from unity.



PV vs P graph



Z vs P graph for real & ideal gases

From the graph it is clear that all gases behave ideally at low pressure. As the pressure increases the deviation from ideal behaviour also increases.

The deviation of real gases from ideal behaviour is due to two wrong assumptions of kinetic molecular theory of gases. They are:

1. The actual volume of the molecules is negligible compared to the volume of the gas.
2. There is no force of attraction between the gas particles.

These two assumptions become wrong at *high pressure and low temperature*. When the pressure increases, the volume of the gas decreases. Then the volume of the gas molecule is also considered. At this condition, there arises inter molecular forces of attraction.

Thus real gases obey ideal gas equation at low pressure and high temperature. Or, real gases deviate from ideal behaviour at high pressure and low temperature.

By considering the above two assumptions, van der Waal proposed an equation, which is applicable to real gases. The equation is known as **van der Waal's equation** and is given as:

$$(P + n^2a/V^2)(V - nb) = nRT$$

Where P is the pressure of the gas, V is the volume, R is the universal gas constant, T is the absolute temperature, n is the no. of moles, ' a ' and ' b ' are called van der Waal's constants. ' a ' is a measure of magnitude of inter molecular attractive forces within the gas and ' b ' is related to the volume of the particles. The unit of ' a ' is $L^2atm\ mol^{-2}$ and that of ' b ' is $L\ mol^{-1}$. The term n^2a/V^2 is related to pressure correction and term ' nb ' is related to volume correction.

Boyle Temperature or Boyle Point

The temperature at which real gases obey ideal gas equation over an appreciable range of pressure is called Boyle temperature or Boyle point. It depends on the nature of the gas.

6. THERMODYNAMICS

It is a branch of science that deals with the relationship between heat and work. *Chemical thermodynamics is a branch of chemistry that deals with the heat changes associated with chemical reactions.*

Some definitions:

System and Surroundings

System is the part of the universe which is under observation or investigation. The part of the universe except system is called surroundings. The system and surroundings are separated by a boundary which may be real or imaginary.

System + surroundings → Universe

Types of systems

Depending on the ability to exchange energy and matter with the surroundings, systems are classified into three types:

1. **Open system:** It is a system that can exchange both energy and matter with the surroundings.
E.g. Hot water taken in an open vessel.
2. **Closed system:** It is a system that can exchange only energy and not matter with the surroundings.
E.g. Hot water taken in a closed vessel.
3. **Isolated system:** It is a system that cannot exchange both energy and matter with the surroundings.
E.g. Hot water taken in a thermo flask.

Extensive and Intensive Properties

Extensive properties are properties which depend on the amount of matter present in the system. Or, these are the properties which change when a system is divided.

E.g.: Volume (v), length (l), breadth (b), height (h), internal energy (U), enthalpy (H), entropy (S), Gibb's energy (G), heat capacity etc.

Intensive properties are properties which are independent of the amount of matter present in the system. Or, these are the properties which do not change when a system is divided.

E.g. : Temperature (T), Pressure (P), Volume (V), density, refractive index, molar heat capacity, viscosity, surface tension etc.

State and Path functions

A function or a property that depends only on the initial and final state of a system and not on the path followed is called a state function.

E.g. for state functions: T, P, V, U, H, S, G etc.

Path functions: These are properties which depend on the path followed also.

E.g. heat (q) and work (w)

Thermodynamic process

A process is the method (path) by which a state change occurs in a system. The different types of thermodynamic process are:

1. **Isothermal process:** It is a process that occurs at constant temperature. For this process $\Delta T = 0$ but $\Delta q \neq 0$
2. **Isobaric process:** It is a process that occurs at constant Pressure. For such a process $\Delta P = 0$
3. **Isochoric process:** It is a process that occurs at constant volume. For such a process $\Delta V = 0$
4. **Adiabatic process:** It is a process that occurs at constant heat energy. Here no heat enters into or leaves from the system. For such a process $\Delta q = 0$ but $\Delta T \neq 0$

5. **Cyclic process:** It is a process that takes place in a cyclic manner. Here the system undergoes a series of changes and finally returns to its initial state. For such a process $\Delta U=0$ and $\Delta H = 0$
6. **Reversible process:** Every process is associated with two types of forces – driving force and opposing force. Driving force favours the process while opposing force opposes it. *If the driving and opposing forces are differed by an infinitesimally small quantity the process takes place in both directions. Such a process is called reversible process. For a reversible process, the system and surroundings are always nearly in equilibrium with each other.*
7. **Irreversible process:** If the driving and opposing forces are differed by a large quantity, then the process takes place in only one direction. Such a process is called irreversible process.

Heat and Work

Heat: It is a form of energy. Heat flows from a hot body to a cold body, when there is a thermal contact between the two. When a body absorbs heat, its energy increases and when it evolves heat, its energy decreases. Thus by international convention, when heat is absorbed by a system, q becomes +ve and when heat is evolved by a system q becomes -ve.

Work: Thermodynamics mainly deal with expansion work which is the product of pressure (P) and change in volume (ΔV). i.e., expansion work (w) = $-P\Delta V$

For irreversible process, $w = -P\Delta V$ and

For reversible process, $w = -2.303nRT \log(V_2/V_1)$.

Where V_1 and V_2 are the initial and final volumes of the system respectively.

By international convention, w becomes +ve, when work is done *on* the system and w becomes -ve, when work is done *by* the system.

Free expansion: Expansion of a gas into vacuum (external pressure = 0) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

Internal Energy or Intrinsic Energy (U)

It is the energy possessed by a body. It is the sum of different types of molecular energies like translational kinetic energy, rotational kinetic energy, vibrational kinetic energy, electronic energy, nuclear energy etc.

Internal energy of a body is an extensive property and state function. We cannot calculate the exact value of internal energy, but we can calculate the change in internal energy (ΔU) during a process by using an apparatus called *Bomb Calorimeter*.

The change in internal energy (ΔU) = $U_2 - U_1$, where U_1 and U_2 are the initial and final internal energies respectively. The unit of internal energy is kJ/mol.

The internal energy of a system can change mainly by two ways:

1. By the transfer of heat
2. By doing work

First law of thermodynamics: It is same as law of conservation of energy. It states that energy can neither be created nor be destroyed. Or, the total energy in the universe is always a constant. Or, the total energy of an isolated system is always a constant.

$$\text{Mathematically } \Delta U = q + w \dots\dots\dots (1)$$

Where q is the amount of heat absorbed by the system and w is the amount of work done on the system.

If there is only expansion work, the above equation becomes $\Delta U = q - P\Delta V \dots\dots\dots (2)$ (since, $w = -P\Delta V$).

Significance of ΔU

We know that $\Delta U = q - P\Delta V$

For a process taking place at constant volume, $\Delta V = 0$. So $\Delta U = q_v$

i.e., ΔU gives the amount of heat absorbed or evolved by a system at constant volume.

Enthalpy (H)

It is the total heat content of a system. It is the sum of internal energy and pressure-volume energy of a system.

$$\text{i.e. } H = U + PV$$

It is a state function and an extensive property. i.e., whenever there is a change in enthalpy, it depends only on the initial and final values and not the path followed. If H_1 is the enthalpy of a system in the initial state and H_2 is that in the final state, then the change in enthalpy, $\Delta H = H_2 - H_1$.

The unit of enthalpy is kJ/mol. ΔH is determined by using an apparatus called calorimeter.

ΔH is negative for exothermic reactions, (reactions in which heat is evolved to the surroundings) and ΔH is positive for endothermic reactions (reactions in which heat is absorbed from the surroundings).

Relation between ΔH and ΔU

Consider a gaseous reaction taking place at constant pressure (P) and temperature (T). Let H_1 , U_1 and V_1 be the initial enthalpy, internal energy and volume respectively. Let these values change to H_2 , U_2 and V_2 respectively. Then,

$$H_1 = U_1 + PV_1 \dots\dots\dots (1)$$

And $H_2 = U_2 + PV_2 \dots\dots\dots (2)$

(2) – (1) gives: $H_2 - H_1 = (U_2 + PV_2) - (U_1 + PV_1)$

$$\text{Or, } \Delta H = (U_2 - U_1) + (PV_2 - PV_1)$$

$$\text{Or, } \Delta H = \Delta U + P(V_2 - V_1)$$

$$\text{Or, } \Delta H = \Delta U + P\Delta V \dots\dots (3)$$

From ideal gas equation, $PV = nRT$

If n_1 and n_2 are the total no. of moles of reactants and products respectively, then

$$PV_1 = n_1RT \text{ and } PV_2 = n_2RT$$

$$PV_2 - PV_1 = n_2RT - n_1RT$$

$$\text{Or, } P(V_2 - V_1) = (n_2 - n_1)RT$$

$$\text{Or, } P\Delta V = \Delta n_g RT$$

So equation (3) becomes, $\Delta H = \Delta U + \Delta n_g RT$

$$\text{Where } \Delta n_g = n_{p(g)} - n_{r(g)}$$

i.e., Δn_g = no. of moles of gaseous products – no. of moles of gaseous reactants

If $\Delta n_g = 0$, then $\Delta H = \Delta U$

If $\Delta n_g > 0$, then $\Delta H > \Delta U$

And if $\Delta n_g < 0$, then $\Delta H < \Delta U$.

Significance of ΔH

We know that $\Delta H = \Delta U + P\Delta V$ (at constant pressure) (I)

From first law of thermodynamics, $\Delta U = q - P\Delta V$

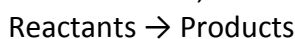
$$\text{So, } q = \Delta U + P\Delta V \dots\dots\dots (II)$$

From the equations (I) and (II), we can write, $\Delta H = q_p$

i.e. enthalpy change in a chemical reaction is equal to the amount of heat evolved or absorbed at constant pressure. This is the significance of ΔH .

ENTHALPY CHANGE OF A REACTION – REACTION ENTHALPY ($\Delta_r H$)

In a chemical reaction, reactants are converted into products and is represented by,



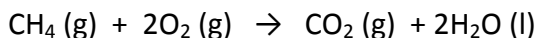
The enthalpy change during a chemical reaction is called the reaction enthalpy. It is given by the symbol $\Delta_r H$.

$\Delta_r H = (\text{sum of enthalpies of products}) - (\text{sum of enthalpies of reactants})$

$$\text{i.e. } \Delta_r H = \sum a_i \cdot H_{\text{Products}} - \sum b_i \cdot H_{\text{Reactants}}$$

Where, a_i and b_i are the stoichiometric coefficients of the products and reactants respectively in the balanced chemical equation.

For the reaction:



$$\Delta_r H = \sum a_i \cdot H_{\text{Products}} - \sum b_i \cdot H_{\text{Reactants}}$$
$$= [H_m(\text{CO}_2) + 2 \times H_m(\text{H}_2\text{O})] - [H_m(\text{CH}_4) + 2 \times H_m(\text{O}_2)]$$

Where H_m is the molar enthalpy.

Standard enthalpy of reactions ($\Delta_r H^\circ$)

The standard enthalpy of reaction is the enthalpy change for a reaction when all the substances are in their standard states. In thermodynamics, the standard state of a substance at a specified temperature is its pure form at 1 bar pressure. Usually data are taken at 298 K temperature.

Hess's Law of Constant Heat Summation

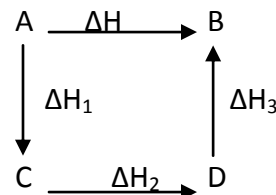
The law states that the total enthalpy change for a physical or chemical process is the same whether the reaction taking place in a single step or in several steps. Or, the total enthalpy change for a process is independent of the path followed.

Thus according to Hess's law, if a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions.

Illustration

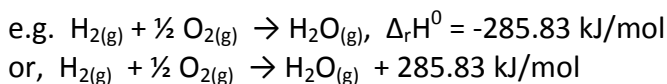
Consider a process in which the reactant A is converted to product B in a single step by involving heat change ΔH . Let the same reactant A is first converted to C, then to D and finally to B involving heat changes ΔH_1 , ΔH_2 and ΔH_3 respectively.

Then according to Hess's law: $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$



Thermochemical equations

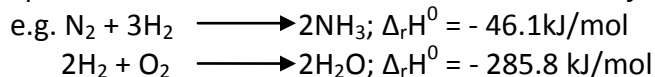
A balanced chemical equation together with the value of enthalpy of reaction is called a thermochemical equation. Here the physical state of the each of the reactants and products is also shown in bracket.



Spontaneous Process

It is a process that takes place without the help of any external agency. All natural processes are spontaneous. E.g. flow of water from high level to low level, flow of heat from hot body to cold body, inter mixing of gases, burning of fuels, melting of ice, evaporation of water etc. A spontaneous process cannot reverse its direction by its own.

Spontaneous chemical reactions are also called *feasible or probable or irreversible reactions*.



A process that takes place with the help of an external agency is called *non-spontaneous process*.

E.g. flow of water from low level to high level.

Criteria for spontaneity

During spontaneous processes like burning of fuels, flow of heat from hot body to cold body, flow of water from high level to low level etc, energy of the system decreases. So one of the criteria for spontaneity is *decrease in energy*.

But for some spontaneous processes like melting of ice, evaporation of water etc, heat is absorbed. i.e. the energy of the system increases during the process. The above processes are accompanied with

increase in disorder (entropy) of the system. Thus another criterion for spontaneity is *increase in disorderness or randomness of the system*.

Entropy (S)

It is **a measure of degree of disorderness or randomness of a system**. As the disorderness increases, entropy also increases. It is an extensive property and state function.

If S_1 is the initial entropy of a system and S_2 is its final value, then the change in entropy $\Delta S = S_2 - S_1$.

For a given substance, the solid state has the least entropy and the gaseous state has the most.

When temperature increases entropy also increases. The unit of entropy and entropy change is J/K/mol.

If a system absorbs 'q' amount of heat reversibly at a temperature T, then the change in entropy,

$$\Delta S = \frac{q_{\text{rev.}}}{T} \quad \text{Where } q_{\text{rev.}} \text{ is the amount of heat absorbed reversibly.}$$

Entropy and spontaneity

During a spontaneous process, disorderness of the system increases. Thus entropy increases and hence ΔS becomes positive.

The total entropy change for the system and surroundings is given by $\Delta S_{\text{Total}} = \Delta S_{\text{syst.}} + \Delta S_{\text{surr.}}$

For a spontaneous process, $\Delta S_{\text{Total}} > 0$

When a system attains *equilibrium*, the entropy becomes maximum and there is no further change in entropy. So $\Delta S_{\text{Total}} = 0$

If $\Delta S_{\text{Total}} < 0$, the process is non-spontaneous.

Second Law of Thermodynamics:

It can be stated as the entropy of the universe always increases during every spontaneous process.

The second law of thermodynamics explains why spontaneous reactions are so common. In exothermic reactions, heat released by the reaction increases the disorder of the surroundings. So the overall entropy change (ΔS_{Total}) is positive and hence the reaction becomes spontaneous.

Third law of Thermodynamics:

It states that the entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. The importance of this law is that we can calculate the absolute value of entropy of pure substances from thermal data alone.

Gibb's energy (G)

It is defined as *the maximum amount of available energy that can be converted to useful work*. It is a measure of free energy and hence it is also known as free energy of the reaction.

It is given by the equation, **$G = H - TS$**

It is an extensive property and a state function. If G_1 is the initial Gibb's energy and G_2 is its final value, then the change in Gibb's energy (ΔG) = $G_2 - G_1$

The unit of Gibb's energy is kJ/mol.

Relation between ΔG , ΔH and ΔS (Gibb's Equation)

We know that $G = H - TS$

So $\Delta G = \Delta H - \Delta(TS)$

$$= \Delta H - (T\Delta S + S\Delta T)$$

At constant temperature, $\Delta T = 0$.

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

The change in Gibb's energy for a system can be written as $\Delta G_{\text{syst.}} = \Delta H_{\text{syst.}} - T\Delta S_{\text{syst.}}$. This equation is known as *Gibb's equation*.

Gibb's energy and Spontaneity of a reaction

We know that $\Delta S_{\text{Total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$ (1)

Consider a system which absorbs 'q' amount of heat reversibly at a constant temperature T and constant pressure P.

$$\text{Then, } \Delta S_{\text{surr.}} = \frac{q_p}{T}$$

But $q_p = \Delta H_{\text{surr.}}$ and $\Delta H_{\text{surr.}} = -\Delta H_{\text{system}}$. (Since, heat absorbed by the surroundings = heat evolved by the system)

$$\text{So, } \Delta S_{\text{surr.}} = \frac{-\Delta H_{\text{system}}}{T}$$

So equation (1) becomes, $\Delta S_{\text{Total}} = \Delta S_{\text{system}} - \frac{\Delta H_{\text{system}}}{T}$

On multiplying by $-T$, we get

$$-T\Delta S_{\text{Total}} = -T\Delta S_{\text{system}} + \Delta H_{\text{system}}$$

Or, $-T\Delta S_{\text{Total}} = \Delta G_{\text{system}}$. (Since, $\Delta H_{\text{system}} - T\Delta S_{\text{system}} = \Delta G_{\text{system}}$)

For a spontaneous process, ΔS_{Total} is positive. So ΔG_{system} is negative. (or, $\Delta G_{\text{system}} < 0$)

For a non-spontaneous process, ΔS_{Total} is negative, so ΔG_{system} is positive. (or, $\Delta G_{\text{system}} > 0$)

For a process at equilibrium, $\Delta S_{\text{Total}} = 0$. So, $\Delta G_{\text{system}} = 0$

Conditions for ΔG to be negative

We know that for a spontaneous process, ΔG_{system} is negative. Also $\Delta G = \Delta H - T\Delta S$.

- 1) If ΔH is negative and ΔS is +ve, ΔG is always -ve and the process is always spontaneous.
- 2) If both ΔH and ΔS are positive, ΔG will be -ve when $T\Delta S > \Delta H$. This is possible at high temperature.
- 3) If both ΔH and ΔS are negative, ΔG will be -ve when $T\Delta S < \Delta H$. This is possible at low temperature.

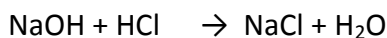
Note: If ΔH is +ve and ΔS -ve, then ΔG will be always +ve and the process will be always non-spontaneous.

7. EQUILIBRIUM

Reversible and irreversible reactions

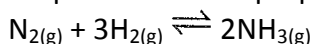
A reaction that takes place in only one direction is called an **irreversible reaction**.

e.g. Reaction between NaOH and HCl



Reversible reactions are those which take place in both directions. i.e. here reactants combined to form products and the products recombine to form reactants.

E.g. Haber process for the preparation of ammonia



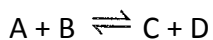
The process by which reactants are converted to products is called *forward reaction* and the process by which products recombine to form reactants is called *backward reaction*. After sometimes, the rate of forward reaction becomes equal to the rate of backward reaction and the reaction attains equilibrium. Thus *equilibrium is a state in which the rates of forward and backward reactions are equal*.

Equilibrium is dynamic in nature. i.e. at equilibrium the reaction does not stop. The reactant molecules collide to form products and the product molecules collide to form the reactants and the rates of these reactions are equal.

Law of Chemical Equilibrium and Equilibrium Constant

This law was proposed by C.M. Guldberg and Peter Waage. It states that *at constant temperature, the product of concentration of the products to that of the reactants, in which each concentration terms is raised to a power which is equal to the stoichiometric coefficients in the balanced chemical equation, has a constant value*.

For a general reversible reaction:



According to the equilibrium law, $\frac{[C][D]}{[A][B]} = K_c$

Where K_c is called the equilibrium constant.

For a general reaction, $aA + bB \rightleftharpoons cC + dD$,

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For the reaction $H_2 + I_2 \rightleftharpoons 2HI$; $K_c = \frac{[HI]^2}{[H_2][I_2]}$

For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

Equilibrium constant for the reverse reaction is the inverse of that for the forward reaction. i.e. if the equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is K_c , then that for the reverse reaction $2HI \rightleftharpoons H_2 + I_2$ is $1/K_c$.

Equilibrium constant for gaseous reactions

For a reaction involving gases, the concentration terms are replaced by partial pressures.

For example, $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$; $K_p = \frac{P_{HI}^2}{P_{H_2} \cdot P_{I_2}}$

Where K_p is called equilibrium constant in terms of partial pressure, P_{HI} , P_{H_2} and P_{I_2} are the partial pressures of HI, H_2 and I_2 respectively.

Relation between K_p and K_c

Consider a general reaction, $aA + bB \rightleftharpoons cC + dD$

The equilibrium constant in terms of concentration for this reaction is $K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$ (1)

And the equilibrium constant in terms of partial pressures is $K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b}$ (2)

From ideal gas equation, $PV = nRT$, $P = nRT/V = CRT$ (since $n/V = C$, the concentration)

Therefore, $P_A = C_A RT$, $P_B = C_B RT$, $P_C = C_C RT$ and $P_D = C_D RT$

Substitute these values in equation (2), we get

$$K_p = \frac{[C_C RT]^c \cdot [C_D RT]^d}{[C_A RT]^a [C_B RT]^b}$$

$$\text{Or, } K_p = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$\text{Or, } K_p = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b} \cdot [RT]^{(c+d)-(a+b)}$$

$$\text{Or, } K_p = K_c \cdot (RT)^{\Delta n}, \text{ where } K_c = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b}$$

And Δn is the change in no. of moles of gaseous species. i.e. $\Delta n = \text{no. of moles of gaseous products} - \text{no. of moles of gaseous reactants}$.

Special cases:

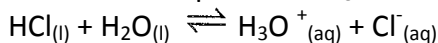
- i) If $\Delta n = 0$, then $K_p = K_c$
- ii) If $\Delta n > 0$, then $K_p > K_c$ and
- iii) If $\Delta n < 0$, then $K_p < K_c$

Acids, Bases and Salts

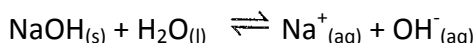
Acid – base concepts:

1. **Arrhenius concept:** According to this concept acids are substances which give hydrogen ion (H^+) or hydronium ion (H_3O^+) in aqueous solution and bases are substances which give hydroxyl ion (OH^-) in aqueous solution.

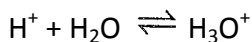
e.g. HCl is an acid since it produces H_3O^+ in aqueous solution.



e.g. for base is NaOH



Note: H^+ ions exist in water as hydronium ions (H_3O^+)



Limitations: this concept is applicable only to aqueous solutions. Also it could not account for the basicity of substances like NH_3 which do not possess OH^- ion.

2. **The Bronsted – Lowry concept:**

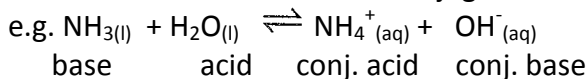
According to this concept acids are proton (H^+) donors and bases are (H^+) acceptors.

For example in the reaction $NH_{3(l)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq)} + OH^-_{(aq)}$

Here NH_3 is a base since it accepts an H^+ ion to form NH_4^+ and H_2O is an acid since it donates an H^+ ion to form OH^- . In the reverse reaction, NH_4^+ is an acid and OH^- is a base.

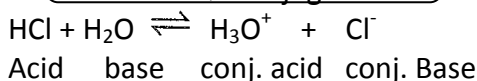
The acid base pair that differs by only one proton is called a conjugate acid – base pair.

An acid formed from a base is called conjugate acid and a base formed from an acid is called conjugate base.



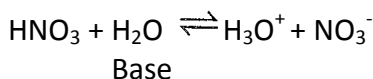
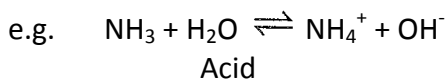
In general

| |
|---|
| Acid – $H^+ \rightarrow$ Conjugate base |
| Base + $H^+ \rightarrow$ Conjugate acid |



If the acid is strong, its conjugate base is weak and vice versa. So in the above example Cl^- is a weak conjugate base of the strong acid HCl.

Water can act both as acid and base. So it is an amphoteric substance.



3. **Lewis concept:**

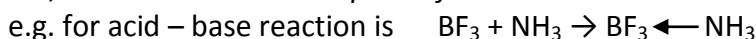
According to this concept acids are electron pair acceptors and bases are electron pair donors.

Substances which donate electron pair are called Lewis bases and substances which accept electron pair are called Lewis acids.

Example for Lewis acids are BF_3 , $AlCl_3$, H^+ , Co^{3+} , Mg^{2+} etc.

Example for Lewis bases are NH_3 , H_2O , OH^- , Cl^- , Br^- etc.

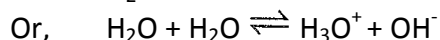
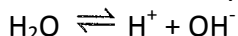
For a substance to act as Lewis acid, it should contain vacant orbitals and for a substance to act as Lewis base, it should contain lone pairs of electrons.



All cations are Lewis acids and all anions are Lewis bases.

The ionization constant of water (The ionic product of water)

Water is a weak electrolyte and hence it ionizes only partially as:



The dissociation constant, $K = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$ or, $K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$

Or, $K_w = [\text{H}^+][\text{OH}^-]$ or, $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

Where K_w is called ionization constant of water or ionic product of water. It is defined as *the product of the molar concentration of hydrogen ion (hydronium ion) and hydroxyl ion in water or in any aqueous solution.*

For pure water at 298K, $[\text{H}^+] = [\text{OH}^-] = 10^{-7}\text{M}$.

Therefore, $K_w = [\text{H}^+][\text{OH}^-] = 10^{-7} \times 10^{-7} = 10^{-14}\text{M}^2$

The value of K_w is temperature dependent.

By knowing the concentrations of H_3O^+ and OH^- ions, we can predict the nature of an aqueous solution.

If $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, the solution is acidic

If $[\text{H}_3\text{O}^+] < [\text{OH}^-]$, the solution is basic

If $[\text{H}_3\text{O}^+] = [\text{OH}^-]$, the solution is neutral

The p^H scale

p^H is defined as the negative logarithm of the hydrogen ion concentration or hydronium ion concentration in moles per litre (i.e. molarity). i.e. $p^H = -\log[\text{H}^+]$ or $p^H = -\log[\text{H}_3\text{O}^+]$

Negative logarithm of hydroxyl ion concentration in mol/L is called p^{OH} .

i.e. $p^{\text{OH}} = -\log[\text{OH}^-]$

For pure water, at 298K (25°C), $[\text{H}^+] = 10^{-7}$. Therefore p^H of pure water is 7.

The p^H scale was introduced by Sorensen. It contains numbers from 0 to 14. If the p^H is less than 7, the solution is acidic, if it is greater than 7, it is basic and if it is 7, the solution is neutral.

If the p^H is 0, 1, 2 etc., the solution is a strongly acidic and if it is 12, 13, 14 etc, it is strongly basic. The p^H of our blood is 7.4 and that of our saliva is 6.4. So blood is slightly basic and saliva is slightly acidic.

Relation between p^H and p^{OH}

We know that $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$ at 298K

Taking negative logarithm on both sides:

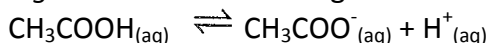
$$-\log K_w = -\log[\text{H}^+] + -\log[\text{OH}^-] = -\log 10^{-14}$$

Or, $p^{K_w} = p^H + p^{\text{OH}} = 14$

Thus by knowing the p^H , we can calculate p^{OH} as $p^{\text{OH}} = 14 - p^H$

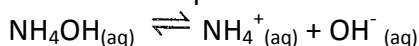
Common Ion Effect

It is the suppression of the dissociation of a weak electrolyte by the addition of a strong electrolyte containing a common ion. For e.g. consider the dissociation of acetic acid (a weak electrolyte).



If we add some sodium acetate (CH_3COONa) to the above equilibrium reaction, the concentration of acetate ion increases. Then according to Le-Chatlier's principle, the equilibrium will shift towards left or, the rate of forward reaction decreases. i.e. the dissociation rate of acetic acid decreases. This is known as common ion effect.

Another example is the dissociation of the weak base ammonium hydroxide (NH_4OH)



If we add some NH_4Cl to the above equilibrium process, the concentration of NH_4^+ increases and hence the equilibrium shifted to the left. i.e. the dissociation rate of NH_4OH decreases.

Buffer Solutions

Solution which resists the change in pH on dilution or with the addition of small amount of acid or alkali is called Buffer solution. There are two types of buffer solutions – acidic buffer and basic buffer.

Acidic buffer is a mixture of a weak acid and its salt with a strong base. E.g. a mixture of acetic acid and sodium acetate acts as an acidic buffer around p^H 4.75.

Basic buffer is a mixture of a weak base and its salt with a strong acid. E.g. a mixture of NH_4OH and NH_4Cl acts as a basic buffer around p^H 9.25.

8. REDOX REACTIONS

These are reactions involving both oxidation and reduction.

Oxidation number (Oxidation state)

Oxidation number of an element in a compound is the residual charge on the element when all the other atoms are removed from it as ions. For example oxidation number of Mn in $KMnO_4$ is the residual charge on Mn when one K atom and four O atoms removed from it as K^+ and O^{2-} ions respectively.

Rules used for the calculation of oxidation number

1. The oxidation number of all elements in the free or the uncombined state is zero. For e.g. oxidation number of H_2 , O_2 , Cl_2 , O_3 , P_4 , S_8 , Na, Mg, Al etc. is zero.
2. For simple ions, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion +2, Fe^{3+} ion +3, Cl^- ion -1 , O^{2-} ion -2 and so on.
3. All alkali metals have oxidation number of $+1$ and all alkaline earth metals have an oxidation number of $+2$. Aluminium shows an oxidation number of $+3$ in all of its compounds.
4. The common oxidation number of oxygen is -2 . But in peroxides (e.g., H_2O_2 , Na_2O_2), oxidation number of oxygen is -1 and in superoxides (e.g., KO_2 , RbO_2), it is $-\frac{1}{2}$. In oxygen difluoride (OF_2) and dioxygen difluoride (O_2F_2), the oxygen is assigned an oxidation number of $+2$ and $+1$ respectively.
5. The common oxidation number of hydrogen is $+1$. But in hydrides, H shows -1 oxidation number.
6. The common oxidation number of halogens is -1. Fluorine shows only -1 oxidation number in all of its compounds. But other halogens show positive oxidation numbers also in their oxides and oxoacids.
7. The algebraic sum of the oxidation number of all the atoms in a compound is zero.
8. In polyatomic ion, the sum of the oxidation numbers of all the atoms is equal to the charge on the ion.

Oxidation number Concept: According to this concept, *oxidation is the process of increase in the oxidation number of an element and reduction is the process of decrease in the oxidation number of an element.*

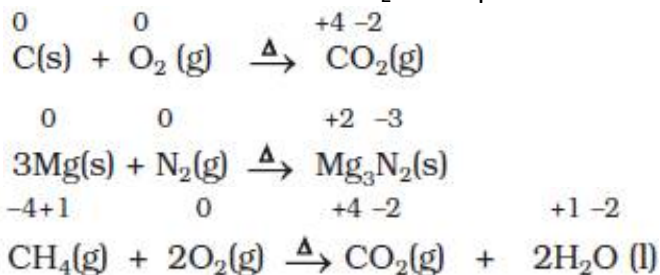
A reagent that can increase the oxidation number of an element in a given substance is called oxidising agent or oxidant and a reagent which lowers the oxidation number of an element in a given substance is called reducing agent or reductant. Oxidising agent is always reduced and reducing agent is always oxidised.

For e.g. in the reaction $CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$, the oxidation number of Zn increases from 0 to +2 and that of Cu in $CuSO_4$ decreases from +2 to 0. So Zn is oxidised and Cu in $CuSO_4$ is reduced.

Types of redox reactions

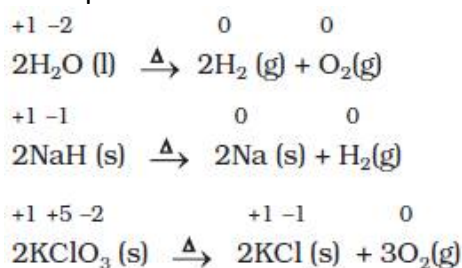
1. **Combination reactions:** A combination reaction may be denoted as $A + B \rightarrow C$

Here either A or B or both A and B must be in the elemental form. All combustion reactions are combination redox reactions, since here one of the reactants is O₂. Examples are:

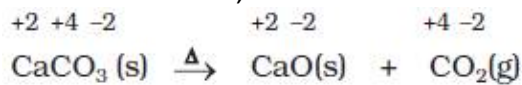


2. Decomposition reactions

Decomposition reactions are the opposite of combination reactions. It involves the breakdown of a compound into two or more components, in which at least one must be in the elemental state. It may be denoted as: C → A + B. Examples are:



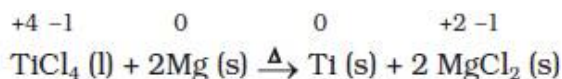
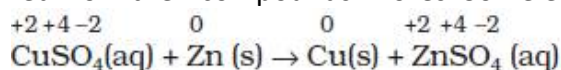
All decomposition reactions are not redox reactions. For example, decomposition of calcium carbonate is not a redox reaction, since it does not involve any change in the oxidation number.



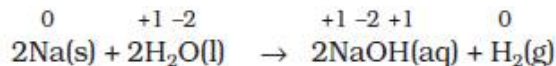
3. **Displacement reactions**: Here an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element. It may be denoted as: X + YZ → XZ + Y

Displacement reactions are divided into two - metal displacement and non-metal displacement.

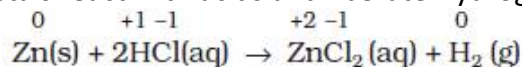
a) ***Metal displacement reactions***: Here a metal in a compound is displaced by another metal in the uncombined state. These reactions find many applications in metallurgical processes in which pure metals are obtained from their compounds in ores. Some examples are:



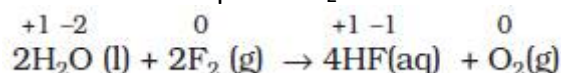
b) ***Non-metal displacement reactions***: The non-metal displacement redox reactions mainly include hydrogen displacement. All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) will displace hydrogen from cold water. Less active metals such as magnesium and iron react with steam and produce hydrogen gas.



Most of the metals react with acids and liberate Hydrogen.

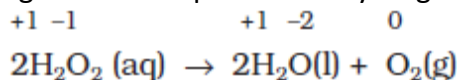


Another example is Fluorine displaces O₂ from water.



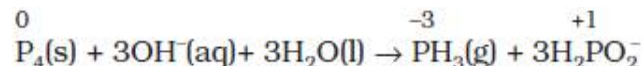
4. **Disproportionation reactions:** These are a special type of redox reaction. In a disproportionation reaction, an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances always contains an element that can exist in at least three oxidation states. The element in the reactant is in the intermediate oxidation state and both higher and lower oxidation states of that element are formed in the reaction.

E.g. The decomposition of hydrogen peroxide.



Here the oxygen of peroxide is in -1 state and it is converted to zero oxidation state in O_2 and -2 oxidation state in H_2O .

Another e.g. is:



Balancing of Redox Reactions by Half reaction method:

In this method, the redox equation is divided into 2 half reactions – oxidation half reaction and reduction half reaction. Then they are balanced separately and added together to get the net balanced equation.

The different steps involved in this method are:

Step 1: Produce unbalanced equation for the reaction in ionic form. Assign the oxidation number of each element and find out the substance oxidised and reduced.

Step 2: Separate the equation into half reactions - oxidation half reaction and reduction half reaction.

Step 3: Balance the atoms other than O and H in each half reaction individually.

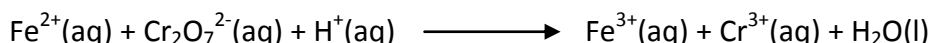
Step 4: For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms. In basic medium also add equal number of OH^- ions on both sides of the equation.

Step 5: Now balance the ionic charges. For this add electrons to one side of the half reaction. Make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate coefficients.

Step 6: Now add the two half reactions to get the overall reaction and cancel the electrons on each side.

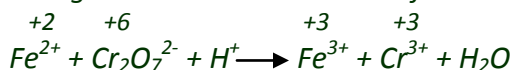
Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides.

Example: Balance the following equation by the half reaction method.



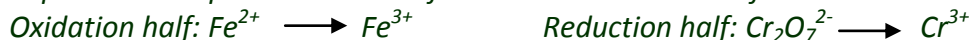
Solution

Step-1: Assign the oxidation number of each element and find out the substance oxidised and reduced.



Here Fe is oxidised and Cr is reduced.

Step-2: Separate the equation into 2 half reactions -oxidation half reaction and reduction half reaction.



Step-3: Balance the atoms other than O and H in each half reaction individually.



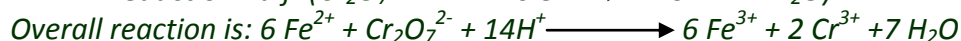
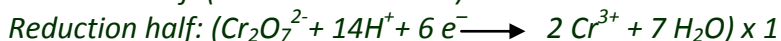
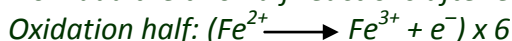
Step-4: Now balance O and H atoms. Add H_2O to balance O atoms and H^+ to balance H atoms since the reaction occurs in acidic medium.



Step -5: Now balance the ionic charges. For this add electrons to one side of the half reaction.



Step-6: Now add the two half reactions after equating the electrons.



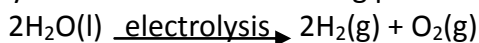
Now the equation is balanced.

9. HYDROGEN

Commercial production of Hydrogen

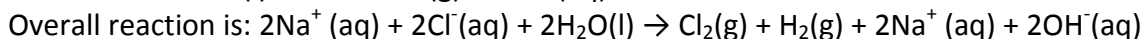
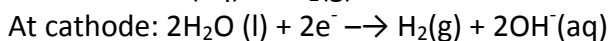
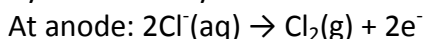
Commercially Hydrogen is prepared by the following methods:

1. Electrolysis of acidified water using platinum electrodes

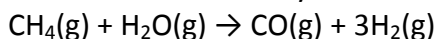


2. High purity dihydrogen is obtained by the electrolysis of warm aqueous $\text{Ba}(\text{OH})_2$ solution using nickel electrodes.

3. By the electrolysis of brine solution (NaCl solution). Here H_2 gas is obtained at the cathode.

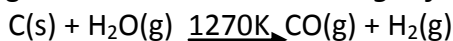


4. By the reaction of steam on hydrocarbons or coke at high temperature in the presence of catalyst.

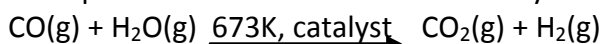


The mixture of CO and H_2 is called water gas. Since it is used for the synthesis of methanol and large number hydrocarbons, it is also called **synthesis gas or syn gas**.

Now syngas is also produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called '**coal gasification**'.



The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst. This is called **water-gas shift reaction**.



HYDRIDES

The binary compounds of hydrogen with other elements are called Hydrides. They are classified into three:

1. **Ionic or saline or salt-like hydrides:**

These are hydrides formed by s-block elements. They are crystalline, non-volatile and stoichiometric solids. They are non-conductors in the solid state but conduct electricity in the molten state or in aqueous solution state.

e.g. NaH , KH , CaH_2 , BaH_2 etc.

2. **Covalent or Molecular Hydrides:**

These are the hydrides of p-block elements. Examples are CH_4 , NH_3 , H_2O and HF . Being covalent, they are volatile compounds. Molecular hydrides are further classified into three.

(i) *electron-deficient*,

(ii) *electron-precise* and

(iii) *electron-rich hydrides*.

An electron-deficient hydride has very few electrons for writing its Lewis structure. E.g. Diborane (B_2H_6). All elements of group 13 will form electron-deficient compounds. They act as Lewis acids (i.e. they accept electron pairs).

Electron-precise compounds have the required number of electrons to write their Lewis structures. All elements of group 14 form such compounds (e.g., CH₄, SiH₄ etc.)

Electron-rich hydrides have excess electrons which are present as lone pairs. Elements of group 15 to 17 form such compounds. They behave as Lewis bases (i.e., electron donors).

3. Metallic Hydrides:

These are formed by d and f-block elements [Except the elements of group 7, 8 and 9]. Being deficient in hydrogen, they are almost non-stoichiometric. They conduct heat and electricity.

e.g. LaH_{2.87}, YbH_{2.55}, TiH_{1.5-1.8}, ZrH_{1.3-1.75}, VH_{0.56}, NiH_{0.6-0.7}, PdH_{0.6-0.8} etc.

In these hydrides the hydrogen atom is occupied in the metal lattice. So they are also called **interstitial hydrides**. Due to the property of absorption of hydrogen on interstitial sites, they are widely used as hydrogenation catalysts.

Hard and soft water

Water which does not easily form lather with soap is called hard water. It is due to the presence of calcium and magnesium salts in the form chlorides, sulphates and bicarbonates. Water free from soluble salts of calcium and magnesium is called soft water. It easily forms lather with soap.

Soaps are sodium or potassium salts of fatty acids like palmitic acid, stearic acid oleic acid etc. They react with calcium or magnesium salts presenting in hard water and form precipitates. There are two types of hardness of water – temporary hardness and permanent hardness.

Disadvantages of Hardness of water:

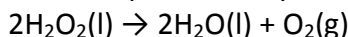
1. It results in wastage of soap.
2. It results in scale formation in boilers which ultimately results in boiler explosion.

HYDROGEN PEROXIDE (H₂O₂)

Hydrogen peroxide is an important chemical used in pollution control treatment.

Storage

H₂O₂ decomposes slowly on exposure to light.



In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark. Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.

10. The s-Block Elements

These are elements in which the last electron enters in the outermost s-orbital. They include elements of group I and II. Group I elements are Lithium (Li), Sodium (Na), Potassium (K), Rubidium (Rb), Caesium (Cs) and Francium (Fr). They are collectively called alkali metals because they dissolve in water to form strong alkalies.

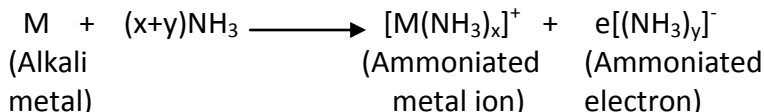
Group II elements are Beryllium (Be), Magnesium (Mg), Calcium (Ca), Strontium (Sr), Barium (Ba) and Radium (Ra). They are collectively called alkaline earth metals (except Be) because their oxides and hydroxides (except Beryllium) are alkaline in nature and are found in the earth's crust.

The general electronic configuration of s-block elements is [noble gas] ns¹ for alkali metals and [noble gas] ns² for alkaline earth metals.

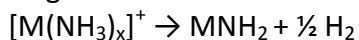
Chemical properties of Alkali metals

Solution in liquid ammonia:

The alkali metals dissolve in liquid ammonia to give deep blue solutions which are good conductors.



The blue colour of the solution is due to the ammoniated electron, which absorbs energy in the visible region and gives blue colour to the solution. The solution is paramagnetic and on standing slowly liberates hydrogen resulting in the formation of amide (MNH_2).



In concentrated solution, the blue colour changes to bronze colour and become diamagnetic.

Anomalous Properties of Lithium

Due to its small size and high polarizing power, Lithium shows some properties different from that of other alkali metals. Some of these are:

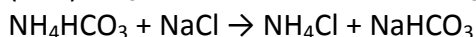
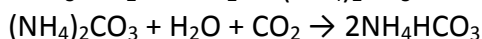
- Li is much harder and has higher melting point and boiling point than other alkali metals.
- Li is the least reactive but the strongest reducing agent among all the alkali metals.
- It forms only monoxide with oxygen.
- LiCl is deliquescent and crystallizes as a hydrate ($\text{LiCl} \cdot 2\text{H}_2\text{O}$). But the other alkali metal chlorides do not form hydrates.
- Lithium bicarbonate (LiHCO_3) is stable only in solution.
- Lithium nitrate on heating gives Li_2O , while other alkali metal nitrates decompose to form nitrite.
$$4 \text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$$
$$2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2$$
- LiF and Li_2O are comparatively much less soluble in water than the corresponding compounds of other alkali metals.

Some important compounds of Sodium

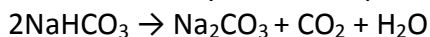
1. Sodium Carbonate [$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$] (Washing Soda)

Preparation: Solvay process

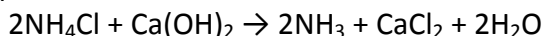
In this process, CO_2 gas is passed through concentrated NaCl solution saturated with ammonia. Ammonium carbonate first formed is converted to ammonium bicarbonate and finally reacts with NaCl to form NaHCO_3 .



Sodium bicarbonate crystals are separated and heated to get sodium carbonate.



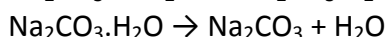
In this process, NH_3 is recovered when the solution containing NH_4Cl is treated with $\text{Ca}(\text{OH})_2$.



Note: Solvay process cannot be used for the preparation of K_2CO_3 because potassium bicarbonate (KHCO_3) is so much soluble in water that it does not get precipitated by the addition of NH_4HCO_3 to a saturated solution of KCl .

Properties:

Action of Heat: On heating, the decahydrate ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$) loses its water of crystallisation to form a monohydrate. Above 373K the monohydrate becomes completely anhydrous and changes to a white powder called "soda ash".



Uses of washing soda

- It is used in water softening, laundering and cleaning.
- It is used in the manufacture of soap, glass, borax and caustic soda.
- It is used in paper, paints and textile industries.
- It is used as a laboratory reagent.

2. Sodium bicarbonate, NaHCO₃ (Baking Soda)

It is prepared by saturating a solution of Sodium carbonate with CO₂.



Uses: i) It is a mild antiseptic for skin infection ii) It is used as a fire extinguisher.

Some Important Compounds of Calcium

1. Calcium Oxide, CaO [Quick lime]

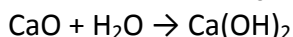
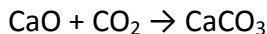
It is prepared commercially by heating lime stone (CaCO₃) in a rotary kiln (furnace) at 1070 – 1270K.



The CO₂ is removed as soon as it is formed to enable the reaction to proceed completion.

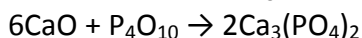
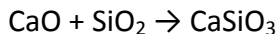
Properties:

On exposure to air, it absorbs moisture and CO₂.



The addition of limited amount of water breaks the big pieces of lime. This process is called *slaking of lime*. The product obtained is called *slaked lime*. Quick lime slaked with soda (NaOH) gives solid *soda lime* (NaOH + CaO).

Because of the basic nature of CaO, it combines with acidic oxides at high temperature to form salts. So it is used as a flux in metallurgy.

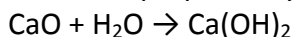


Uses:

1. It is an important primary material for the manufacture of cement and is the cheapest form of alkali.
2. It is used in the manufacture of Na₂CO₃ from caustic soda.
3. It is used in the purification of sugar and in the manufacture of dye stuffs.

Calcium Hydroxide, Ca(OH)₂ [Slaked lime]

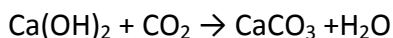
Preparation: It is prepared by adding water to quick lime.



An aqueous solution of slaked lime is known as *lime water* and a suspension of slaked lime in water is known as *milk of lime*.

Properties:

When CO₂ is passed through lime water, it turns milky due to the formation of CaCO₃. On passing CO₂ continuously, the solution becomes clear due to the formation of soluble calcium bicarbonate [Ca(HCO₃)₂]



When dry chlorine gas is passed through dry slaked lime, we get bleaching powder (a mixture of CaCl₂ & calcium hypochlorite)

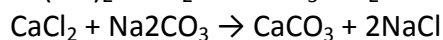
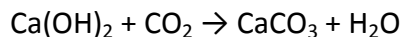


Uses:

- i) It is used in the preparation of mortar, a building material.
- ii) It is used in white washing due to its disinfectant nature.
- iii) It is used in glass making, in tanning, for the preparation of bleaching powder and for purification of sugar.

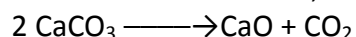
Calcium Carbonate, CaCO₃ [Lime stone]

Calcium carbonate occurs in nature in several forms like limestone, chalk, marble etc. It can be prepared by passing carbon dioxide through slaked lime or by the addition of sodium carbonate to calcium chloride.



Properties

When heated to 1200 K, it decomposes to evolve carbon dioxide.



It reacts with dilute acid to liberate carbon dioxide.



Uses: 1. It is used as a building material in the form of marble and in the manufacture of quick lime.

2. Calcium carbonate along with magnesium carbonate is used as a flux in the extraction of metals such as iron.

3. Specially precipitated CaCO_3 is extensively used in the manufacture of high quality paper.

4. It is also used as an antacid, mild abrasive in tooth paste, a constituent of chewing gum, and filler in cosmetics.

4. Calcium Sulphate (Plaster of Paris), $\text{CaSO}_4 \cdot \frac{1}{2} \text{H}_2\text{O}$

It is a hemihydrate of calcium sulphate. It is obtained when gypsum [$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$] is heated to 393 K.



Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate (CaSO_4) is formed. This is known as 'dead burnt plaster'.

It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes. During this process its volume increases. So it is used for the preparation of statues.

Uses: 1. The largest use of Plaster of Paris is in the building industry as well as plasters.

2. It is used for immobilising the affected part of organ where there is a bone fracture or sprain.

3. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

Cement

Cement was first introduced by Joseph Aspidine. It is a product obtained by combining lime (CaO) with clay which contains silica, SiO_2 along with the oxides of aluminium, iron and magnesium.

The raw materials for the manufacture of cement are limestone and clay. When clay and lime are strongly heated together they fuse and react to form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to form cement. The purpose of adding gypsum is to slow down the process of setting of the cement so that it gets sufficiently hardened.

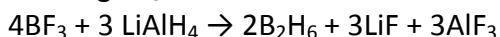
Setting of Cement: When mixed with water, the setting of cement takes place to give a hard mass. During this process the hydration of the silicates and aluminates occurs and a large amount of heat is evolved.

11. The p-Block Elements

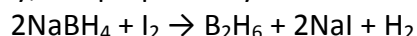
These are elements in which the last electron enters in the outer most p-subshell. They include elements of groups 13 to 18. Their general outer electronic configuration is $ns^2 np^{1-6}$ (except for He). They include metals, non-metals and metalloids.

Compounds of Boron

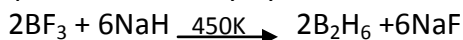
Diborane (B_2H_6): The simplest boron hydride is borane (BH_3), which exists as a dimer called Diborane (B_2H_6). It is prepared by treating BF_3 with Lithium aluminium hydride (LiAlH_4) in ether.



In the laboratory, it is prepared by the oxidation of sodium borohydride with iodine.



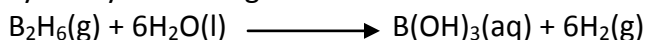
Diborane is prepared industrially by the reaction of BF_3 with sodium hydride.



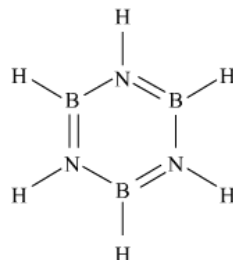
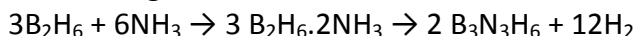
Diborane is a colourless, highly toxic gas. It catches fire spontaneously on exposure to air. It burns in oxygen to form B_2O_3 and evolve large amount of heat.



It readily hydrolysed by water to give boric acid.

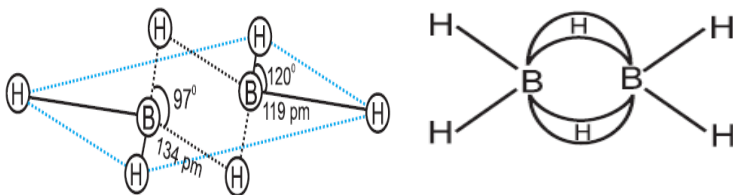


Diborane react with ammonia to form $\text{B}_2\text{H}_6 \cdot 2\text{NH}_3$ which on further heating gives **Borazine ($\text{B}_3\text{N}_3\text{H}_6$) which is commonly known as inorganic benzene**. Its structure is similar to benzene with alternate BH and NH groups.



Structure of Diborane

In diborane, each boron atoms is in sp^3 hybridisation. The two boron atoms and 4 hydrogen atoms lie in one plane. These four H atoms are called *terminal hydrogen atoms*. The other two hydrogen atoms lie one above and one below this plane. These H atoms are called *bridging hydrogen atoms*. The four terminal B-H bonds are regular two centre-two electron bonds while the two bridge (B-H-B) bonds are *three centre- two electron (3c-2e) bonds* or *banana bonds*. Thus diborane is an *electron deficient compound*.



Allotropes of Carbon

The existence of an element in two or more forms with same chemical properties but different physical properties is known as *allotropy*. Carbon exists in crystalline and amorphous allotropes. The important crystalline allotropes of Carbon are diamond, graphite and fullerene.

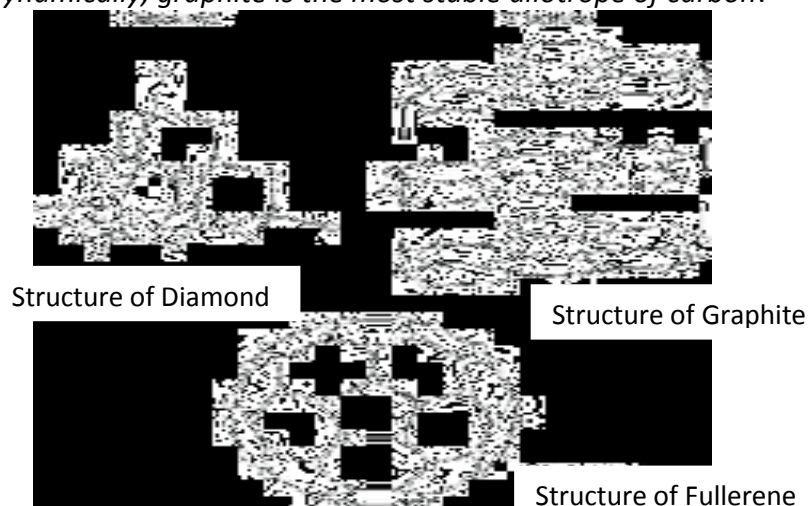
a) **Diamond**: In diamond, each carbon atom is in sp^3 hybridisation and linked to four other carbon atoms in a tetrahedral manner. So it has a rigid three dimensional network of carbon atoms. It is very difficult to break covalent bonds and, therefore, diamond is a hardest substance on the earth. It is used as an abrasive for sharpening hard tools, in making dies and in the manufacture of tungsten filaments for electric light bulbs.

b) **Graphite**: Graphite has a layered structure. Different layers are held by weak van der Waals forces of attraction. Each layer contains planar hexagonal rings of carbon atoms. Here each carbon atom is in sp^2 hybridisation and makes three C-C sigma bonds with three neighbouring carbon atoms. Fourth electron forms a π bond. These electrons are delocalised and are mobile. Therefore graphite conducts electricity. Due to layered structure, it is very soft and slippery. For this reason graphite is used as a dry lubricant in machines running at high temperature.

c) **Fullerenes:** These are the cage like spherical molecules of formula C_{60} , C_{70} , C_{76} , C_{84} etc. These are prepared by heating of graphite in an electric arc in the presence of inert gases like helium or argon.

The most commonly known fullerene is C_{60} , which is known as Buckminster fullerene. It contains twenty six- membered rings and twelve five membered rings. A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings. All the carbon atoms are equal and they undergo sp^2 hybridisation. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalised in molecular orbitals. This gives an aromatic character to the molecule.

Thermodynamically, graphite is the most stable allotrope of carbon.

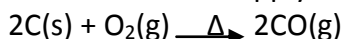


Amorphous forms of carbon are charcoal, coke and carbon black. Carbon black is obtained by burning hydrocarbons in limited supply of air. Charcoal and coke are obtained by heating wood or coal respectively at high temperature in the absence of air.

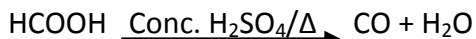
Carbon Monoxide (CO):

Preparation:

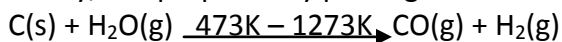
Carbon burns in limited supply of air to give CO.



By the dehydration of formic acid with conc. H_2SO_4 at 373 K.

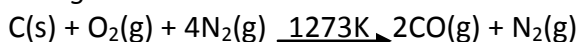


Commercially, it is prepared by passing steam over red hot coke.



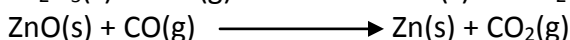
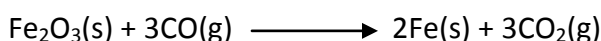
The mixture of CO and H_2 is known as *water gas* or *Syn gas*.

If instead of steam, air is passed over red hot coke, we get a mixture of CO and nitrogen commonly known as *producer gas*.



Both water gas and producer gas are used as industrial fuels.

Properties: CO is a colourless, odourless toxic gas and is insoluble in water. It is a powerful reducing agent. It reduces almost all metal oxides.



Structure: In CO, there are one sigma and two pi bonds between carbon and oxygen ($:C \equiv O:$). Because of the presence of lone pair on carbon, CO molecule acts as an electron donor and reacts with metals to form metal carbonyls.

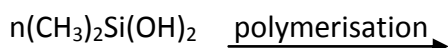
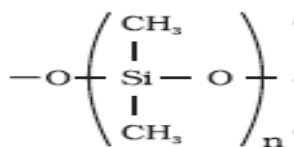
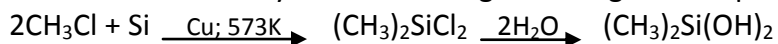
CO is highly poisonous in nature because it forms a highly stable complex with haemoglobin (carboxy haemoglobin). This prevents haemoglobin in RBC from carrying oxygen round the body. This will result in headache, weak eyesight, nervousness and even death.

Silicones:

Silicones are a group of organosilicon polymers, which have $(-R_2SiO-)$ as a repeating unit. (Where R is alkyl or aryl group).

Manufacture:

When methyl chloride reacts with silicon in the presence of copper as a catalyst at a temperature 573K, dimethyl dichlorosilane $[(CH_3)_2SiCl_2]$ and other methyl substituted chlorosilanes are formed. Hydrolysis of dichlorosilane followed by condensation gives straight chain polymers.



The chain length of the polymer can be controlled by adding $(CH_3)_3SiCl$ (Trimethyl chlorosilane).

Properties:

They are water repelling in nature. They have high thermal stability, high dielectric strength and resistance to oxidation and chemicals. So they are used as sealant, greases, electrical insulators and for water proofing of fabrics. Being biocompatible they are also used in surgical and cosmetic plants.

12. ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Organic chemistry is the branch of chemistry that deals with carbon compounds. But all carbon compounds are not considered as organic compounds. (E.g. CO_2 , CO, metal carbonates, bicarbonates etc.). So organic chemistry can be defined as *the branch of chemistry that deals with hydrocarbons and their derivatives*. Hydrocarbons are the major class of organic compounds and they *contain only carbon and hydrogen atoms*. All other organic compounds are formed by replacing one or more hydrogen atoms of hydrocarbons by other atoms or groups (They are called hydrocarbon derivatives).

Nomenclature of organic compounds

An organic compound has two types of names – Common name and IUPAC name. The common name is based on the source or some properties. For e.g. citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid since the Latin word for ant is formica.

IUPAC Nomenclature of organic compounds

A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it. This name is called IUPAC name. It contains two parts – word root and suffix or prefix. The word root indicates the number of carbon atoms in the compound. The word roots for compounds containing 1 -12 carbon atoms are as follows:

| No. of C atoms | Word root | No. of C atoms | Word root |
|----------------|-----------|----------------|-----------|
| C_1 | Meth- | C_7 | Hept- |
| C_2 | Eth- | C_8 | Oct- |
| C_3 | Prop- | C_9 | Non- |
| C_4 | But- | C_{10} | Dec- |
| C_5 | Pent- | C_{11} | Undec- |
| C_6 | Hex- | C_{12} | Dodec- |

There are two types of suffixes – primary suffix and secondary suffix. Primary suffix indicates saturation or unsaturation [for alkane the primary suffix is –ane, alkene –ene and for alkyne –yne]. Secondary suffix indicates the type of functional group. Some functional groups are also indicated as prefixes.

Nomenclature of branched chain alkanes:

A branch (side chain or substituent) is obtained by removing a hydrogen atom from an alkane. The resulting group is called an **alkyl group** [alkane – H = alkyl (i.e. **word root + yl**)]. The names of some common branches are as follows:

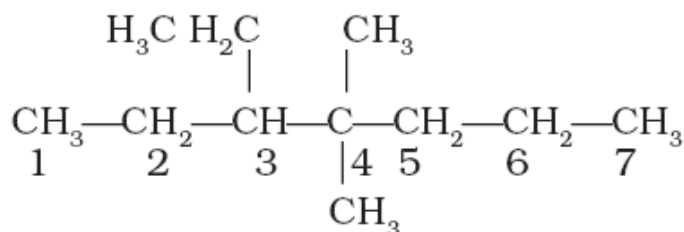
| Branch | Name |
|---|-----------------------------|
| -CH ₃ | Methyl |
| -CH ₂ -CH ₃ | Ethyl |
| -CH ₂ -CH ₂ -CH ₃ | n-propyl (normal propyl) |
| (CH ₃) ₂ CH- | isopropyl |
| -CH ₂ -CH ₂ -CH ₂ -CH ₃ | n-butyl |
| CH ₃ - $\underset{\text{ }}{\text{C}}$ -CH ₂ -CH ₃ | sec-butyl (secondary butyl) |
| (CH ₃) ₂ CH-CH ₂ - | isobutyl |
| (CH ₃) ₃ C- | tert-butyl (tertiary butyl) |
| (CH ₃) ₃ C-CH ₂ - | neopentyl |

Rules for naming branched chain alkanes:

IUPAC recommended the following rules for naming a branched chain alkane.

1. Select the longest continuous chain of carbon atoms. This chain is called parent chain or root chain. If there is more than one such chain, the chain that contains maximum number of branches is selected as the parent chain. Also identify all the branches or substituents.
2. Number the carbon atoms of the parent chain in such a way that the branched carbon atoms get the lowest possible numbers.
3. The names of alkyl groups attached as branches are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers.
4. If different alkyl groups are present, they are listed in alphabetical order. In alphabetical order, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group. The prefixes sec- and tert- are not considered to be the part of the fundamental name.
5. If two or more identical substituent groups are present then their numbers are indicated by prefixes like di (for 2), tri (for 3), tetra (for 4), penta (for 5) etc and the numbers are separated by commas. The number and word are separated by a hyphen. (The IUPAC name is written as a single word).

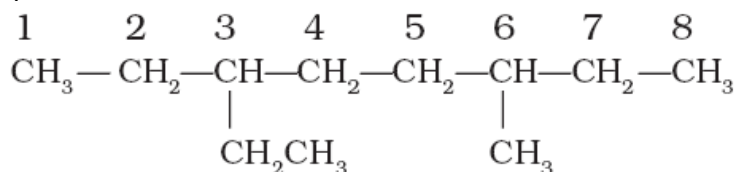
For example:



3-Ethyl-4,4-dimethylheptane

6. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing.

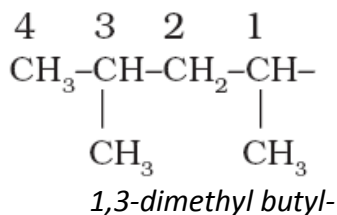
For example:



The above compound is *3-ethyl-6-methyloctane* and not *6-ethyl-3-methyloctane*.

7. While naming the branched alkyl groups, the carbon atom of the branch that attaches to the root alkane is numbered 1.

For example:



IUPAC nomenclature of compounds containing functional groups

For naming organic compounds containing functional group, the following rules are used:

1. Select the longest continuous chain containing the functional group.
2. Number the carbon atoms in such a way that the carbon to which the functional group is attached should get the lowest possible number. In the case of functional groups containing carbon atom like $-\text{CHO}$, $-\text{CN}$, $-\text{COOH}$, $-\text{CONH}_2$, $-\text{COX}$, $-\text{COOR}$ etc. the numbering should start from the carbon atom of the functional group. (i.e. carbon atom of these groups should be numbered as 1). (But for ketones, the functional group $-\text{CO}-$ should get the lowest possible number).
3. The name of the functional group is indicated by the following suffix or prefix.

| Functional group | Name of compound | Suffix/Prefix | IUPAC name |
|----------------------------|------------------|-----------------|----------------------|
| $-\text{OH}$ | Alcohol | -ol | Alkanol |
| $-\text{NH}_2$ | Amine | -amine | Alkanamine |
| $-\text{X}$ | Halo compound | Halo- | Haloalkane |
| $-\text{CHO}$ | Aldehyde | -al | Alkanal |
| $>\text{CO}$ | Ketone | -one | Alkanone |
| $-\text{COOH}$ | Carboxylic acid | -oic acid | Alkanoic acid |
| $-\text{O}-$ | Ether | Alkoxy- | Alkoxy alkane |
| $-\text{CN}$ | Nitrile | -nitrile | Alkane nitrile |
| $-\text{NO}_2$ | Nitro compound | Nitro- | Nitroalkane |
| $-\text{C}=\text{C}-$ | Alkene | -ene | Alkene |
| $-\text{C}\equiv\text{C}-$ | Alkyne | -yne | Alkyne |
| $-\text{COOR}$ | Ester | -oate | Alkyl alkanoate |
| $-\text{CONH}_2$ | Acid amide | -amide | Alkanamide |
| $-\text{COX}$ | Acid halide | -oyl halide | Alkanoyl halide |
| $-\text{SO}_3\text{H}$ | Sulphonic acid | -sulphonic acid | Alkanesulphonic acid |

In the case of suffixes, the ending $-e$ of the corresponding alkane is replaced. E.g. IUPAC name of the alcohol CH_3-OH is methanol (methane + \emptyset). But for nitriles, the $-e$ of the corresponding alkane is retained. E.g. IUPAC name of $\text{CH}_3-\text{CH}_2-\text{CN}$ is propanenitrile.

In the case of alkenes and alkynes, the suffix –ane of the alkane is replaced by –ene and –yne respectively. (i.e. word root + ene or yne). For naming alkenes or alkynes, the numbering is done in such a way that the double or triple bond should get the lowest possible number.

Some examples are:

| Compound | IUPAC Name |
|--|----------------------------------|
| $\text{CH}_3\text{-CH}_2\text{-CH=CH}_2$ | 1-Butene or, But-1-ene |
| $\text{CH}_3\text{-CH=CH-CH}_3$ | 2-Butene or, But-2-ene |
| $\text{CH}_3\text{-CH}_2\text{-C}\equiv\text{C-CH}_3$ | 2-Pentyne or Pent-2-yne |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-C}\equiv\text{CH}$ | 1-Heptyne or Hept-1-yne |
| $\text{CH}_3\text{-CH}_2\text{-OH}$ | Ethanol |
| $\text{CH}_3\text{-CH}_2\text{-CHOH-CH}_2\text{-CH}_2\text{-CH}_3$ | 3-Hexanol or Hexan-3-ol |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CHO}$ | 1-Butanal or Butanal |
| HCHO | Methanal |
| $\text{CH}_3\text{-CO-CH}_3$ | Propanone |
| $\text{CH}_3\text{-CO-CH}_2\text{-CH}_2\text{-CH}_3$ | 2-Pentanone or Pentan-2-one |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CO-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ | 4-Octanone or Octan-4-one |
| HCOOH | Methanoic acid |
| $\text{CH}_3\text{-COOH}$ | Ethanoic acid |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-COOH}$ | 1-Butanoic acid or butanoic acid |
| $\text{CH}_3\text{-CH}_2\text{-Cl}$ | 1-Chloroethane or Chloroethane |
| $\text{CH}_3\text{-CH}_2\text{-CHBr-CH}_3$ | 2-Bromobutane |
| $\text{CH}_2\text{Cl-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$ | 1-Chloropentane |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-NO}_2$ | 1-Nitropropane |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CN}$ | Butanenitrile |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CN}$ | Hexanenitrile |
| $\text{CH}_3\text{-O-CH}_3$ | Methoxymethane |
| $\text{CH}_3\text{-CH}_2\text{-O-CH}_3$ | Methoxyethane |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-O-CH}_2\text{-CH}_3$ | 1-Ethoxypropane |
| $\text{CH}_3\text{-CH}_2\text{-NH}_2$ | Ethanamine |
| $\text{CH}_3\text{-CH}_2\text{-CH(NH}_2\text{)-CH}_3$ | 2-Butanamine or Butan-2-amine |
| $\text{CH}_3\text{-CH}_2\text{-COOCH}_3$ | Methylpropanoate |
| $\text{CH}_3\text{-CH}_2\text{-COOCH}_2\text{-CH}_3$ | Ethylpropanoate |
| $\text{CH}_3\text{-CH}_2\text{-COCl}$ | Propanoylchloride |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-COBr}$ | Pentanoylbromide |
| $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CONH}_2$ | Butanamide |
| $\text{CH}_3\text{-CONH}_2$ | Ethanamide |

Nomenclature of organic compounds containing more than one functional groups (Poly functional compounds)

Here one of the functional groups is chosen as the principal functional group and the compound is named on that basis. The remaining functional groups (called subordinate functional groups) are named as substituents using the appropriate prefixes. The choice of principal functional group is made on the basis of order of preference. The order of decreasing priority for some functional groups is:

$-\text{COOH}$, $-\text{SO}_3\text{H}$, $-\text{COOR}$ (R=alkyl group), $-\text{COCl}$, $-\text{CONH}_2$, $-\text{CN}$, $-\text{CHO}$, $>\text{CO}$, $-\text{OH}$, $-\text{NH}_2$, $>\text{C}=\text{C}<$, $-\text{C}\equiv\text{C}-$

The groups like alkyl (–R), phenyl (C₆H₅–), halogens (F, Cl, Br, I), nitro (–NO₂), alkoxy (–OR) etc. are always prefix substituents.

For example if a compound contains both alcoholic and aldehydic groups, it is named as hydroxyalkanal, since here aldehydic group is the principal functional group and –OH group is the subordinate functional group.

The prefix names of some functional groups are as follows:

| Functional group | Prefix name |
|--------------------|------------------|
| –OH | Hydroxyl- |
| –NH ₂ | Amino- |
| –X | Halo- |
| –CHO | Formyl- |
| >CO | Oxo- |
| –COOH | Carboxy- |
| –O– | Alkoxy- |
| –CN | Cyano- |
| –NO ₂ | Nitro- |
| –COOR | Alkoxy carbonyl- |
| –CONH ₂ | Carbamoyl- |
| –COX | Halocarbonyl- |

While numbering the carbon chain, the principal functional group should get the lowest possible number.

Some examples are:

| Compound | IUPAC Name |
|--|---|
| CH ₃ -CHOH-CH ₂ -CO-CH ₃ | 4-Hydroxy-2-pentanone |
| CH ₂ Cl-CH ₂ -CHBr-CH ₂ -CH ₂ OH | 3-Bromo-5-chloropentan-1-ol or, 3-Bromo-5-chloro-1-pentanol |
| CH ₃ -CH ₂ -CO-CH ₂ -CH ₂ -CHO | 4-Oxohexanal |
| CH ₃ -CHNH ₂ -CH ₂ -COOH | 3-Aminobutanoic acid |
| CH ₃ -CH ₂ -CHCl-CH ₂ -CO-CH ₂ -COOH | 5-Chloro-3-oxo-heptanoic acid |

If a compound contains more than one same functional group, their number is indicated by adding the numeral prefixes di, tri, etc. before the suffix. In such cases the full name of the parent alkane is written before the suffix. However, the ending –ne of the parent alkane is dropped in the case of compounds having more than one double or triple bonds.

When both double and triple bonds are present, first give the suffix of the double bond (-en) and then that of the triple bond (-yne) [the ending –e of the suffix –ene is avoided]. While numbering the carbon chain, the lowest number is given to the multiple bonds (double and triple bonds). This may sometimes give "-yne" a lower number than "-ene". When there is a choice in numbering, the double bonds are given the lowest numbers.

Examples:

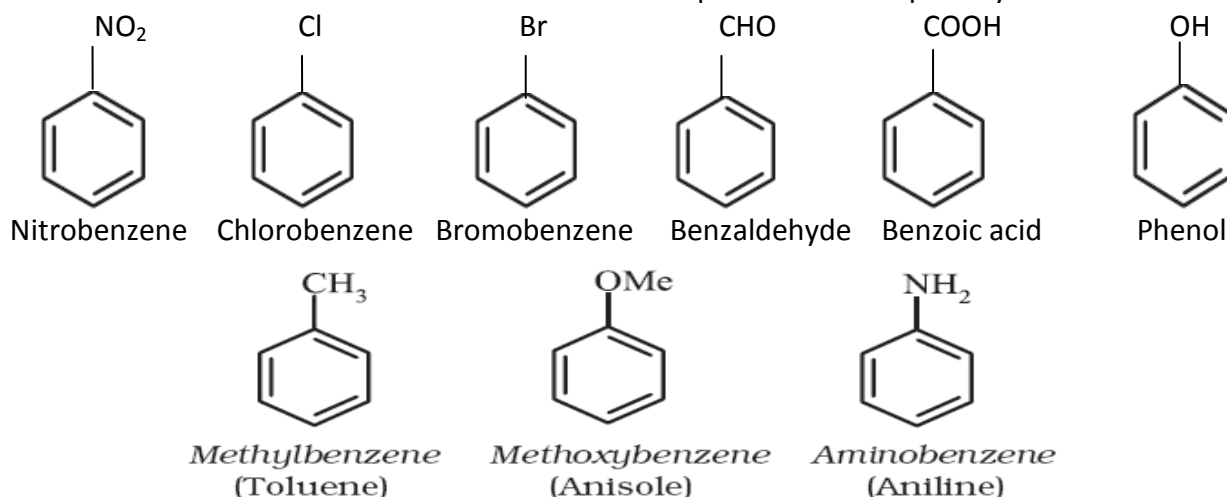
| Compound | IUPAC Name |
|--|-------------------------------------|
| CH ₂ OH-CH ₂ OH | Ethane-1,2-diol (Ethylene glycol) |
| CH ₂ OH-CHOH-CH ₂ OH | Propane-1,2,3-triol (Glycerol) |
| CHO-CHO | Ethane-1,2-dial (Glyoxal) |
| COOH-COOH | Ethane-1,2-dioic acid (Oxalic acid) |

| | |
|--|-----------------------------------|
| $\text{CH}_3\text{-CO-CH}_2\text{-CO-CH}_3$ | Pentane-2,4-dione |
| $\text{CH}_2=\text{CH-CH}=\text{CH}_2$ | 1,3-Butadiene or Buta-1,3-diene |
| $\text{CH}\equiv\text{C-CH}_2\text{-C}\equiv\text{CH}$ | 1,4-Pentadiene or Penta-1,4-diene |
| $\text{CH}_2=\text{CH-CH}_2\text{-C}\equiv\text{CH}$ | Pent-1-en-4-yne |
| $\text{CH}\equiv\text{C-CH}=\text{CH-C}=\text{CH}_2$ | Hexa-1,3-dien-5-yne |
| $\text{HC}\equiv\text{C-CH}=\text{CH-CH}_3$ | Pent-3-en-1-yne |

(The names given in the brackette are the common names)

Nomenclature of Substituted Benzene Compounds

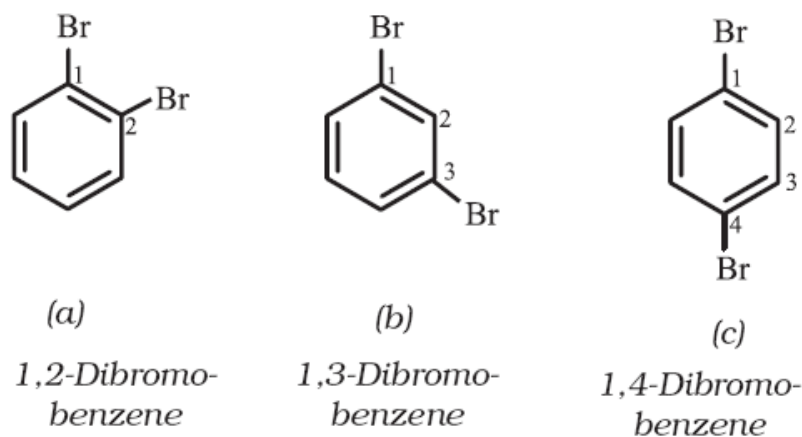
For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene. But common names of some compounds are accepted by IUPAC.



Nomenclature of di or polysubstituted benzene

If benzene ring is disubstituted, the position of substituents is indicated by numbering the carbon atoms of the ring such that the substituents get the lowest possible numbers.

Example – Dibromobenzene

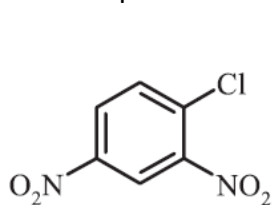


In the common system of nomenclature the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2- 1,3- and 1,4- respectively. So 1,2-dibromobenzene is named as ortho (or just o-) dibromobenzene, 1,3-dibromobenzene as meta (or just m-) dibromobenzene and 1,4-dibromobenzene as para (or just p-)dibromobenzene.

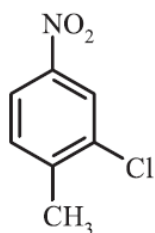
For tri - or higher substituted benzene derivatives, these prefixes cannot be used and the compounds are named by identifying substituent positions on the ring by following the lowest locant rule. In some cases, common name of benzene derivatives is taken as the base compound. Substituent of the base compound is

assigned number 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents are named in alphabetical order.

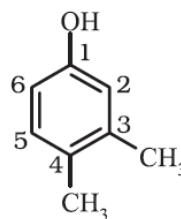
Some examples are:



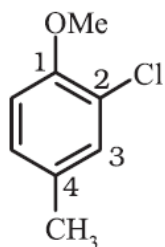
1-Chloro-2,4-dinitrobenzene



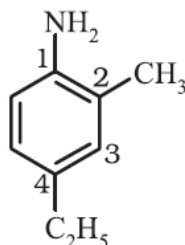
2-Chloro-1-methyl-4-nitrobenzene



3,4-Dimethylphenol



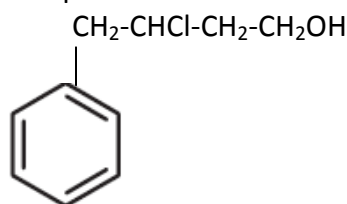
2-Chloro-4-methylanisole



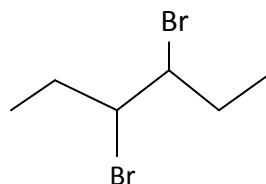
4-Ethyl-2-methylaniline

When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. The name for benzene as substituent is phenyl (C_6H_5- , also abbreviated as Ph).

Example:



3-Chloro-4-phenyl-1-butanol



2,3-Dibromo-1-phenylpentane

Isomerism

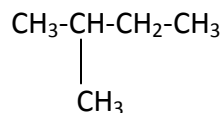
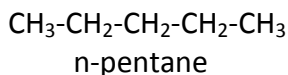
The phenomenon of existence of two or more compounds having the same molecular formula but different structural formula or spatial arrangement of atoms is known as isomerism. Such compounds are called as *isomers*. Isomers have different physical and chemical properties. Isomerism can be broadly classified into two – structural isomerism and stereo isomerism.

1. Structural isomerism

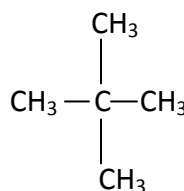
Compounds having same molecular formula but different structural formula (arrangement of atoms) are called structural isomers and the phenomenon is called structural isomerism. There are mainly four types of structural isomerism:

a) Chain Isomerism: Isomers differ in carbon chain or skeleton are called chain isomers and the phenomenon is called chain isomerism.

E.g.: Pentane (C_5H_{12})



isopentane
(2-Methylbutane)



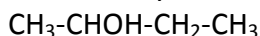
neopentane (2,2-Dimethylpropane)

b) Position isomerism: Isomers which differ in the position of the substituent or side chain are called position isomers and the phenomenon is called position isomerism.

E.g. : Alcohol with molecular formula $C_4H_{10}O$ may be 1-butanol or 2-butanol



1-Butanol



2-Butanol

c) Functional group isomerism: Isomers which differ in the functional group are called functional group isomers and the phenomenon is called functional group isomerism. This isomerism is shown by alcohols and ethers and aldehydes and ketones.

E.g. compound with the molecular formula C_2H_6O may be an alcohol ethanol (CH_3-CH_2OH) or an ether methoxy methane (CH_3-O-CH_3).

d) Metamerism: Isomers which differ in the carbon chain (alkyl groups) around the functional group are called metamers and the phenomenon is called metamerism. It is commonly shown by ethers.

E.g.: Ether with molecular formula $C_5H_{12}O$ may be methoxybutane ($CH_3-O-CH_2-CH_2-CH_2-CH_3$) or ethoxypropane ($CH_3-CH_2-O-CH_2-CH_2-CH_3$).

2. Stereo isomerism

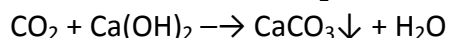
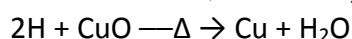
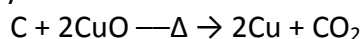
Compounds having same molecular formula but different spatial arrangement of atoms are called stereoisomers and the phenomenon is called stereoisomerism. They have same atom to atom bond. There are two types of stereo isomerism – *Geometrical isomerism and Optical isomerism*.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

An organic compound mainly contains carbon and hydrogen. Some compounds may also contain oxygen, nitrogen, sulphur, halogens and phosphorus.

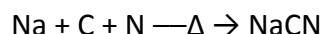
Detection of Carbon and Hydrogen

Organic compound is heated with copper (II) oxide [CuO]. Carbon present in the compound is oxidised to carbon dioxide and hydrogen to water. CO_2 can be tested by passing through lime-water, which turns milky and water can be tested with anhydrous copper sulphate, which turns blue.



Detection of Nitrogen

Nitrogen present in an organic compound is detected by "*Lassaigne's test*". Here the organic compound is fused with metallic sodium in a fusion tube, so that N in the compound is converted to cyanide.



It is then extracted by boiling with distilled water and then filtered. The filtrate is known as *sodium fusion extract*.

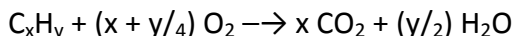
To a little of the sodium fusion extract, add freshly prepared ferrous sulphate ($FeSO_4$) solution, heated to boiling, cooled and acidified with dil. H_2SO_4 . If Nitrogen is present, a blue or green coloration or precipitate (ppt) is formed.

QUANTITATIVE ANALYSIS OF ORGANIC COMPOUNDS

The percentage composition of elements present in an organic compound is determined by the following methods:

1. Estimation of Carbon and Hydrogen

Carbon and hydrogen are estimated by **Liebig's combustion method**. In this method, a known mass of an organic compound is burnt in the presence of excess of oxygen and copper(II) oxide. Then carbon is oxidised to CO₂ and hydrogen is oxidised to H₂O.



The water so produced is absorbed in a weighed U-tube containing anhydrous calcium chloride and carbon dioxide is absorbed in another U-tube containing concentrated solution of potassium hydroxide. These tubes are connected in series. The increase in masses of calcium chloride and potassium hydroxide gives the amounts of water and carbon dioxide from which the percentages of carbon and hydrogen are calculated.

Calculations:

Let the mass of organic compound be m g, mass of water and carbon dioxide produced be m₁ and m₂ g respectively. Then,

$$\text{Percentage of hydrogen} = \frac{2 \times m_1 \times 100}{18 \times m}$$

$$\text{Percentage of carbon} = \frac{12 \times m_2 \times 100}{44 \times m} \%$$

13. Hydrocarbons

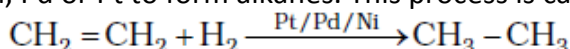
Organic compounds containing carbon and hydrogen atoms only are called hydrocarbons. Depending on the types of C-C bond, they can be classified into three – saturated, unsaturated and aromatic hydrocarbons. Saturated hydrocarbons are also called alkanes. They contain only C-C single bonds. Unsaturated hydrocarbons contain at least one carbon-carbon double bond (alkene) or carbon-carbon triple bond (alkyne). Aromatic hydrocarbons are a special type of cyclic compounds. They are also called arenes.

ALKANES

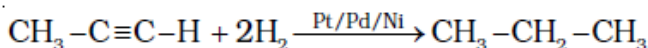
Alkanes are saturated open chain hydrocarbons containing carbon-carbon single bonds. They form a homologous series. Their general molecular formula is C_nH_{2n+2}. In alkanes, all the C atoms are sp³ hybridised. So each C atom has a regular tetrahedral shape.

Preparation of alkanes

- 1. From unsaturated hydrocarbons:** Alkenes and alkynes add Hydrogen in presence of finely divided catalysts like Ni, Pd or Pt to form alkanes. This process is called hydrogenation.



Ethene Ethane

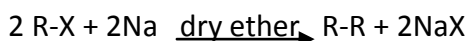


Propyne Propane

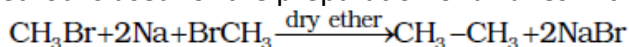
- 2. From alkyl halides**

Wurtz reaction:

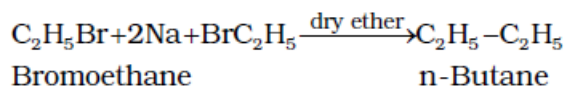
Alkyl halides react with metallic sodium in dry ether to form alkanes. This reaction is known as Wurtz reaction.



Here the alkane formed contains double the number of C atoms than that present in the alkyl halide. So this method is used for the preparation of alkanes with even number of carbon atoms.



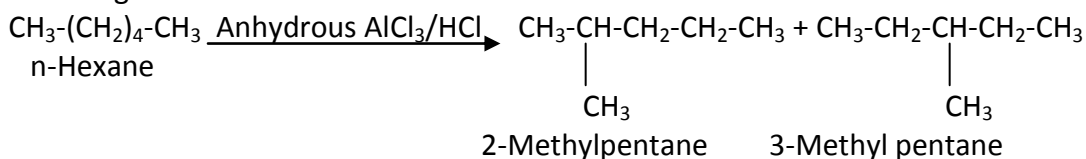
Bromomethane Ethane



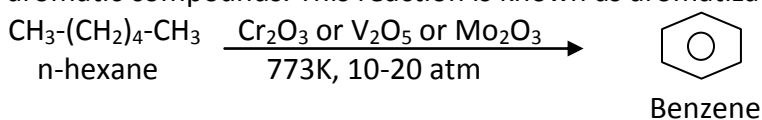
When two different alkyl halides are used, we get a mixture of alkanes.

Chemical Properties of alkanes

- 1. Isomerisation:** n-Alkanes on heating in the presence of anhydrous aluminium chloride and hydrogen chloride gas isomerise to branched chain alkanes.



- 2. Aromatization:** n-Alkanes having six or more carbon atoms on heating to 773K at 10-20 atmospheric pressure in the presence of oxides of vanadium, molybdenum or chromium supported over alumina, we get aromatic compounds. This reaction is known as aromatization or reforming.



Conformations of Alkanes

Alkanes contain carbon-carbon sigma (σ) bonds. Since, electron distribution of the sigma bonds is symmetrical around the bond axis, rotation around C–C bond is allowed. This rotation changes the spatial arrangements of atoms attached to the C atoms. These **different spatial arrangements of atoms arising due to free rotation around a C-C single bond are called conformations or conformers or rotamers.**

Conformations of ethane

Ethane contains a C-C σ bond and each carbon atom contains three hydrogen atoms. Due to free rotation of C atoms around the single bond, the spatial arrangement of hydrogen atoms attached to the C atoms change. Thus ethane can show an infinite number of conformational isomers.

If we fix one carbon atom and rotate the other, there arise two extreme cases called **eclipsed and staggered conformations.**

In *eclipsed conformation*, the hydrogen atoms attached to each carbon atoms are closed together as possible. Or, here the hydrogen atoms of the 2nd carbon atoms are exactly behind that of the first.

In *staggered conformation*, the hydrogen atoms are far apart as possible. Any conformations between eclipsed and staggered conformations are called *skew conformations.*

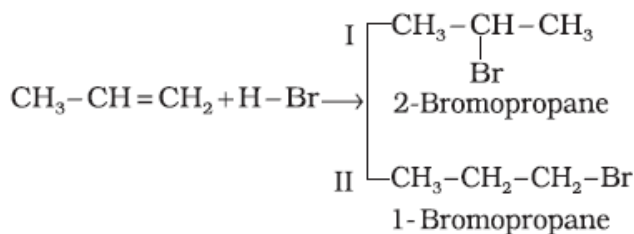
Staggered conformation is stabler than eclipsed form. This is because in staggered form, the electron clouds of carbon-hydrogen bonds are very far apart. So there is minimum repulsive forces, minimum energy and maximum stability. But in eclipsed form, the electron clouds are close to each other. So the repulsion is maximum and the stability is minimum.

Eclipsed and staggered conformations can be represented by Sawhorse and Newman projection formulas.

1. Sawhorse projections:

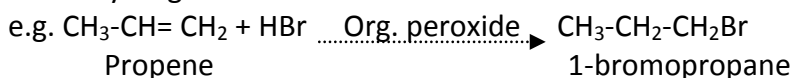
Here the molecule is viewed along the molecular axis. C–C bond is denoted by a longer straight line. The front carbon is shown at the lower end of the line and the back carbon is shown at the upper end. Each carbon has three lines attached to it corresponding to three hydrogen atoms.

Sawhorse projections of eclipsed and staggered conformations of ethane are as follows:



Here the major product is 2-bromopropane according to **Markovnikov rule**.

In presence of peroxide, addition of HBr to unsymmetrical alkenes takes place against Markovnikov rule. This is known as **peroxide or Kharash effect or anti-Markovnikov addition reaction**. i.e. here the negative part goes to more hydrogenated carbon atom.



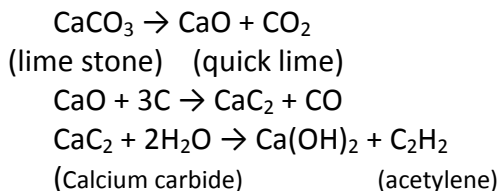
ALKYNES

They are unsaturated hydrocarbons containing at least one C≡C bond. Their general formula is $\text{C}_n\text{H}_{2n-2}$. The first member of alkyne series is ethyne commonly called acetylene (C_2H_2). Other members are considered as the derivatives of acetylene and so alkynes are also called Acetylenes. In alkynes, the triple bonded carbon atoms are sp hybridized and hence are linear.

PREPARATION

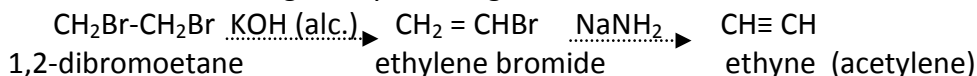
1. From Calcium carbide (CaC_2):

On large scale, ethyne is prepared by treating calcium carbide with water. Calcium carbide is prepared by heating quick lime (CaO) with coke.



2. From vicinal dihalides:

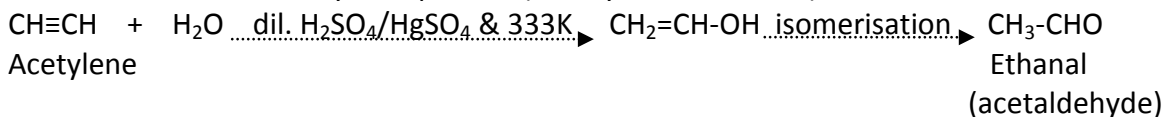
Vicinal dihalides undergo dehydrohalogenation on treatment with alcoholic KOH to form alkenes.



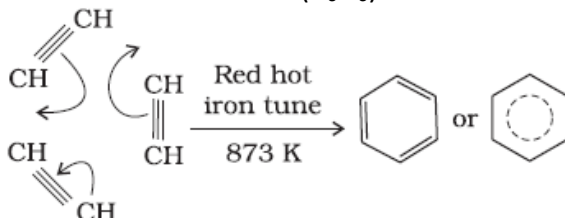
Chemical Properties of Alkynes

1. Addition of water:

On warming with water, alkynes add one molecule of water in presence of dil. H_2SO_4 and mercuric sulphate at 333K to form carbonyl compounds (aldehydes or ketones).



2. Cyclic polymerisation: Ethyne (acetylene) on passing through red hot iron tube at 873K, undergoes cyclic polymerisation to form benzene (C_6H_6).

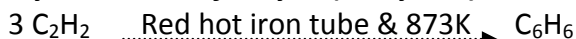


AROMATIC HYDROCARBONS (ARENES)

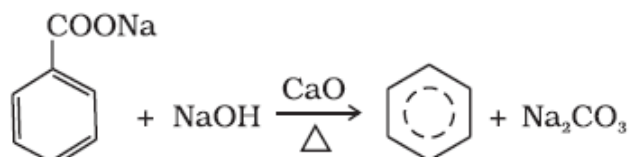
Most of the aromatic compounds have pleasant smell (aroma means pleasant smelling) and most of them contain benzene ring. Aromatic compounds containing benzene ring are called benzenoid compounds and those which do not contain benzene ring are called non-benzenoid compounds.

Preparation of Benzene

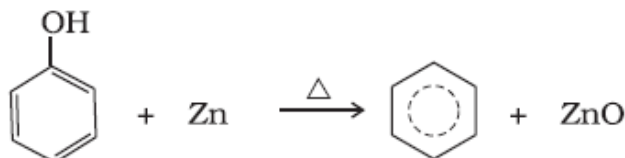
1. **Cyclic polymerisation of ethyne (acetylene):**



2. **Decarboxylation of aromatic acids:** Sodium salt of benzoic acid on heating with sodalime gives benzene.



3. **Reduction of phenol:** Phenol is reduced to benzene by passing its vapours over heated zinc dust.

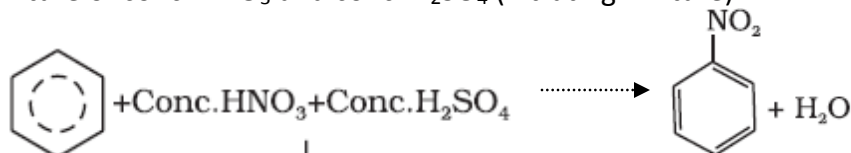


Chemical Properties

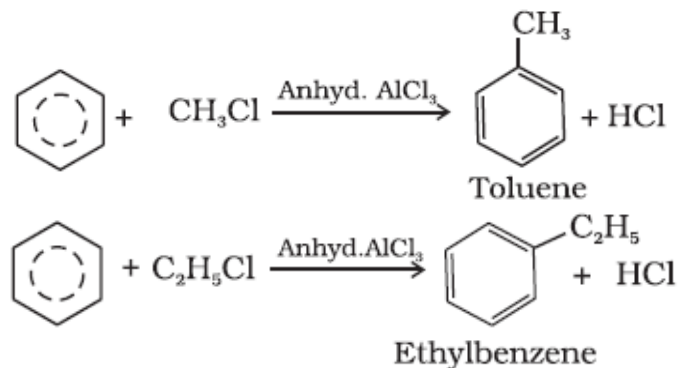
Electrophilic Substitution Reactions

These are reactions in which a weak electrophile is replaced by a strong electrophile. The important electrophilic substitution reactions are Nitration, Sulphonation, Halogenation and Friedel-Crafts alkylation and acylation.

1. **Nitration:** It is the introduction of nitro (-NO₂) group to a benzene ring. For this benzene is heated with a mixture of conc. HNO₃ and conc. H₂SO₄ (nitrating mixture).



2. **Friedel-Craft's Alkylation reaction:** It is the introduction of alkyl (-R) group to a benzene ring. Here the reagents used are alkyl halide in presence of anhydrous AlCl₃.



14. Environmental Chemistry

Environmental chemistry deals with the study of the origin, transport, reactions, effects and fates of chemical species in the environment.

Tropospheric pollution

The presence of undesirable solid or gaseous particles in the lower layer of atmosphere (Troposphere) is called tropospheric pollution.

Global Warming and Greenhouse Effect

When the concentration of carbon dioxide in the atmosphere is above the normal level (0.03%), it absorbs more infra-red radiation from the solar energy and hence the temperature of the earth's atmosphere increases. This is known as Green house effect. It results in global warming.

The gases responsible for green house effect are called green house gases. They are CO₂, methane, water -vapour, chlorofluorocarbons (CFC's), nitrous oxide and ozone.

The adverse effects of global warming and green house effect

Due to global warming, the average global temperature will increase. This will lead to the melting of polar ice caps and flooding of low lying areas all over the earth. Increase in the global temperature results in the infectious diseases like dengue, malaria, yellow fever, sleeping sickness etc.

Measures to reduce global warming

Global warming can be reduced by the following methods:

- Reduce the burning of fossil fuels by minimizing the use of automobiles.
- Plant trees and encourage afforestation.
- Avoid burning of dry leaves, wood etc.
- Aware the public about the bad effects of global warming.

Acid rain:

When the pH of the rain water drops below 5.6, it is called acid rain. Oxides of nitrogen and sulphur (e.g. SO₂ and NO₂) are mainly responsible for acid rain.

Harmful effects of acid rain

- Acid rain is harmful for agriculture, trees and plants.
- It causes respiratory ailments and skin cancer in human beings and animals.
- It affects plants and animal life in aquatic ecosystem.
- It corrodes water pipes resulting in the dissolution of heavy metals into the drinking water.
- Acid rain damages buildings and other structures made of stone or metal (e.g. The Taj Mahal).

Measures to reduce acid rain

Acid rain can be reduced by the following methods:

- Reduce the use of automobiles.
- Encourage the use of natural gas instead of coal.
- Catalytic converters must be used in motor vehicles to reduce the emission of CO and oxides of Nitrogen to the atmosphere.
- Acidity of the soil can be reduced by adding powdered limestone.
- Aware the public about acid rain.

Water Pollution

Biological Oxygen Demand (BOD)

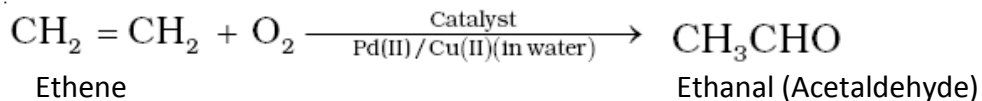
The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water is called Biochemical Oxygen Demand (BOD). The amount of BOD in the water is a measure of the amount of organic material in the water. Clean water would have BOD value of less than 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more.

Green Chemistry

Green chemistry (also called sustainable chemistry) is an area of chemistry focused on the design of products and processes that minimize the use and generation of dangerous substances.

Applications of Green Chemistry in day-to-day life

- (i) **Dry Cleaning of Clothes:** Liquefied carbondioxide, with a suitable detergent is used for dry cleaning clothes.
- (ii) **Bleaching of Paper:** Hydrogen peroxide (H₂O₂) with suitable catalyst is used for bleaching paper.
- (iii) **Synthesis of Chemicals:** Ethanal (CH₃CHO) is now commercially prepared by one step oxidation of ethene in the presence of ionic catalyst in aqueous medium.



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