DIRECTORATE OF DISTANCE & CONTINUING EDUCATIONS

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI – 627012

OPEN AND DISTANCE LEARING(ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRMMES FROM THE ACADEMIC YEAR 2023 – 2024)

B.Sc. PHYSICS
COURSE MATERIALS
ALLIED CHEMISTRY – I
JECH31

By

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Unit - I Chemical Bonding and Nuclear Chemistry 08 Hours

Chemical Bonding: Molecular Orbital Theory - bonding, antibonding and non - bonding orbitals. M. O diagrams for Hydrogen, Helium, Nitrogen; discussion of bond order and magnetic properties. Nuclear Chemistry: Fundamental particles - Isotopes, Isobars, Isotones and Isomers - Differences between chemical reactions and nuclear reactions - group displacement law. Nuclear binding energy - mass defect - calculations. Nuclear fission and nuclear fusion - differences - Stellar energy. Applications of radioisotopes - carbon dating, rock dating and medicinal applications.

Unit - II Industrial Chemistry 07Hours

Fuels: Fuel gases: Natural gas, water gas, semi water gas, carbureted water gas, producer gas, CNG, LPG and oil gas (manufacturing details not required). Silicones: Synthesis, properties and uses of silicones. Fertilizers: Urea, ammonium sulphate, potassium nitrate, NPK fertilizer, superphosphate, triple superphosphate.

Unit - III Fundamental Concepts in Organic Chemistry 07 Hours

Hybridization: Orbital overlap hybridization and geometry of CH_4, C_2H_4, C_2H_2 and C_6H_6. Polar effects: Inductive effect and consequences on Ka and Kb of organic acids and bases, electromeric, mesomeric, hyper conjugation and steric - examples and explanation. Reaction mechanisms: Types of reactions – aromaticity - aromatic electrophilic substitution; nitration, halogenation, Friedel - Craft’s alkylation and acylation. Heterocyclic compounds: Preparation, properties of pyrrole and pyridine.

Unit - IV Thermodynamics and Phase Equilibria 07 Hours

Thermodynamics: Types of systems, reversible and irreversible processes, isothermal and adiabatic processes and spontaneous processes. Statements of first law and second law of thermodynamics. Carnot’s cycle and efficiency of heat engine. Entropy and its significance. Free energy change and its importance (no derivation). Conditions for spontaneity in terms of entropy and Gibbs free energy. Relationship between Gibbs free energy and entropy. Phase Equilibria: Phase rule - definition of terms in it. Applications of phase rule to water system. Two component system - Reduced phase rule and its application to a simple eutectic system (Pb-Ag).

Unit - V Analytical Chemistry 07 Hours

Introduction qualitative and quantitative analysis. Principles of volumetric analysis. Separation and purification techniques: extraction, distillation and crystallization. Chromatography: principle and application of column, paper and thin layer chromatography.

Text Books

1. V.Veeraiyan, Text book of Ancillary Chemistry; High mount publishing house,Chennai, first edition,2009.
2. S.Vaithyanathan, Text book of Ancillary Chemistry; Priya Publications, Karur,2006.
3. S.ArunBahl, B.S.Bahl, Advanced Organic Chemistry; S.Chand and Company,

   NewDelhi, twenty third edition, 2012.
4. P.L.Soni, H.M.Chawla, Text Book of Organic Chemistry; Sultan Chand & sons, New Delhi, twenty ninth edition, 2007.

Unit I

Chemical Bonding

Chemical bonding refers to the formation of a chemical bond between two or more atoms, molecules or ions to give rise to a chemical compound.

The attractive force which holds various constituents (atoms, ions, etc.) together and stabilises them by the overall loss of energy is known as chemical bonding.

Important Theories on Chemical Bonding

Albrecht Kössel and Gilbert Lewis were the first to explain the formation of chemical bonds successfully in the year 1916. They explained chemical bonding on the basis of the inertness of noble gases.

Types of Chemical Bonds

The type of chemical bonds formed varies in strength and properties. There are 4 primary types of chemical bonds which are formed by atoms or molecules to yield compounds. These types of chemical bonds include

- Ionic Bonds
- Covalent Bonds

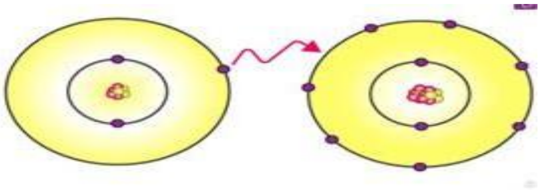
- Hydrogen Bonds
- Polar Bonds

These types of bonds in chemical bonding are formed from the loss, gain or sharing of electrons between two atoms/molecules.

Ionic Bonding

Ionic bonding is a type of chemical bonding which involves a transfer of electrons from one atom or molecule to another. Here, an atom loses an electron, which is, in turn, gained by another atom. When such an electron transfer takes place, one of the atoms develops a negative charge and is now called the anion.

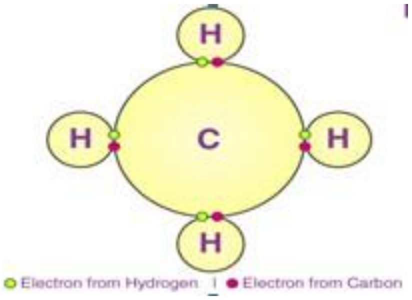
The other atom develops a positive charge and is called the cation. The ionic bond gains strength from the difference in charge between the two atoms, i.e., the greater the charge disparity between the cation and the anion, the stronger the ionic bond.



Types of Chemical Bonds – Ionic bonding

Covalent Bonding

A covalent bond indicates the sharing of electrons between atoms. Compounds that contain carbon (also called organic compounds) commonly exhibit this type of chemical bonding. The pair of electrons which are shared by the two atoms now extend around the nuclei of atoms, leading to the creation of a molecule.



Covalent Bonding

Polar Covalent Bonding

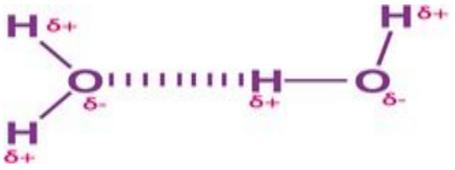
Covalent bonds can be either polar or non-polar in nature. In polar covalent chemical bonding, electrons are shared unequally since the more electronegative atom pulls the electron pair closer to itself and away from the less electronegative atom. Water is an example of such a polar molecule.

A difference in charge arises in different areas of the atom due to the uneven spacing of the electrons between the atoms. One end of the molecule tends to be partially positively charged, and the other end tends to be partially negatively charged.

Hydrogen Bonding

Compared to ionic and covalent bonding, Hydrogen bonding is a weaker form of chemical bonding. It is a type of polar covalent bonding between oxygen and hydrogen, wherein the hydrogen develops a partial positive charge. This implies that the electrons are pulled closer to the more electronegative oxygen atom.

This creates a tendency for the hydrogen to be attracted towards the negative charges of any neighbouring atom. This type of chemical bonding is called a hydrogen bond and is responsible for many of the properties exhibited by water.



Hydrogen Bonding

Molecular Orbital Theory

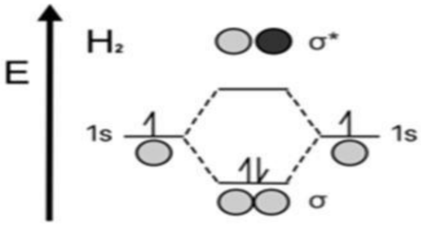
Molecular Orbital Theory is a chemical bonding theory that states that individual atoms combine together to form molecular orbitals. Due to the arrangement in Molecular Orbital Theory, **electrons** related to different nuclei are found in different **atomic orbitals**.

In molecular orbital theory, the electrons in a molecule are not assigned to individual chemical bonds between the **atoms**. Rather, they are treated as moving under the influence of the atomic nuclei in the entire molecule.

- The theory was developed by **F. Hund** and **R. S. Mulliken** at the beginning of the 20th century.
- It aimed to describe the structure and properties of different molecules.
- Molecular orbital theory turned out to be more powerful than the **valence-bond theory**.
- The orbitals described by molecular orbital theory reflect the geometries of the molecules to which it is applied.

Bonding Molecular Orbital

- Bond orbitals are commonly used in molecular orbital theory to elaborate the interactions between the atomic orbitals of two or more atoms in a molecule.
- The energy of bonding molecular orbitals is lower than the atomic orbitals to which they are bound.

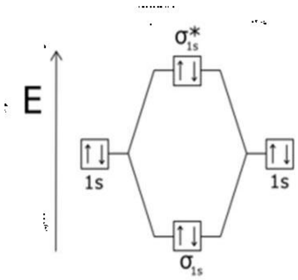


The MO diagram for dihydrogen

Antibonding Molecular Orbital

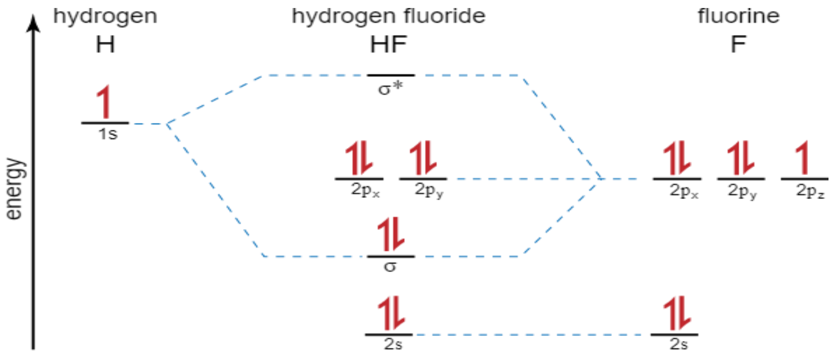
- In chemical bonding theory, an antibonding orbital is a molecular orbital that weakens the chemical bond between two atoms and helps increase the energy of a molecule relative to a single atom
- Antibonding interactions between atomic orbitals are destructive (out-of-phase) interactions, nodal planes where the wavefunction of the antibonding orbitals between two interacting particles is zero

- Antibonding molecular orbitals have higher energies than the atomic orbitals to which they bind



Non-Bonding Molecular Orbital

- A non-bonding orbital, also known as a non-bonding molecular orbital, is a molecular orbital whose electron occupation does not increase or decrease the order of the bonds between the atoms involved. Therefore, it cannot overlap and interact with the s-type valence orbital on the hydrogen atom.

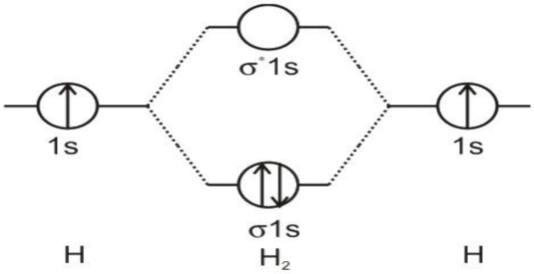


Molecular orbital for hyd

Hydrogen molecule (H_2): It is formed by the combination of two hydrogen atoms. Each hydrogen atom has ne electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in σ 1 s molecular orbital. So electronic configuration of hydrogen molecules is

$H_2 : (\sigma 1s)^2$

The molecular orbital diagram of H_2 molecules is shown in figure below.



The bond order of H_2 molecule can be calculated as follows:

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

This means that the two hydrogen atoms are bonded together by a single covalent bond. The bond dissociation energy of hydrogen molecule has been found to be 438 kJ mol^{-1} and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is diamagnetic.

Bond order

Bond order is the number of chemical bonds between a pair of atoms and indicates the stability of a bond.

For example, in diatomic nitrogen, $N \equiv N$, the bond order is 3; in acetylene, $H-C \equiv C-H$, the carbon-carbon bond order is also 3, and the $C-H$ bond order is 1.

The bond order shows the number of chemical bonds present between a pair of atoms. For instance, the bond order of diatomic nitrogen $N \equiv N$ is 3 and bond order between the carbon atoms in $H-H \equiv C-H$ is also three.

The bond order describes the stability of the bond. The molecular orbital provides an easy understanding of the concept of the bond order of a chemical bond. It quantifies the degree of covalent bonds between the atoms.

How to calculate Bond order

The Bond Order Formula can be defined as half of the difference between the number of electrons in bonding orbitals and antibonding orbitals.

Bond order=$[N_b – N_a]/2$

Where,

N_b is the number of bonding electrons

N_a is the number of antibonding electrons

Solved Example

Solution

Step 1. Write the electron configuration of C_2 molecule.

Electronic configuration of $C_2 = (\sigma 2s)^2 \ (\sigma^* 2s)^2 \ n(2px)^2 \ n(2py)^2$

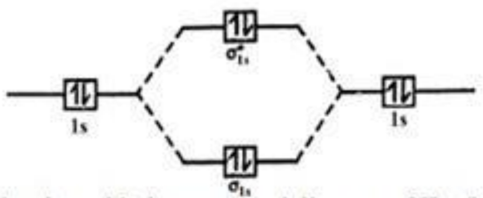
Step 2. From the above electron configuration, but the values in the formula

Bond order = (Nb – Na) / 2

=(8 – 4)/ 2

= 2

Molecular orbital energy level diagrams -Hydrogen, Hypothetical, Nitrogen, Oxygen



Molecular orbital energy level diagram of He_2 (hypothetical) molecule

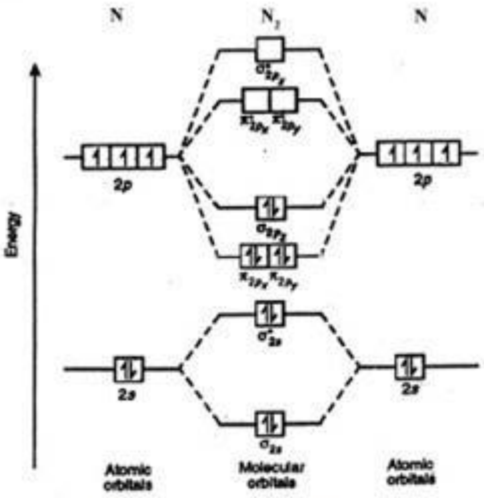


Fig. Molecular orbital energy level diagram of N_2

Molecular orbital energy level diagrams of certain diatomic Homo nuclear molecules and molecular ions

The filling of molecular orbitals is governed by the following principles.

(i)Aufbau principle

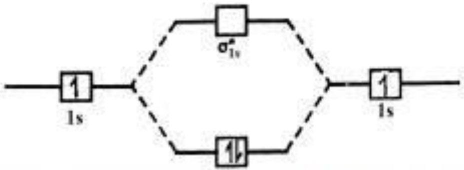
(ii)Pauli's exclusion principle and

(iii)Hund's rule of maximum multiplicity. Now, let us consider some examples of homo nuclear diatomic molecules.

1. Hydrogen molecule, H_2. It is formed by the combination of two hydrogen atoms. Each hydrogen atom in the ground state has one electron in 1s orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in lower most s1s molecular orbital. According to Pauli's exclusion principle, these two electrons should have opposite spins.

The molecular orbital electronic configuration of hydrogen molecule is (σ1s)2.

The molecular orbital energy level diagram of H_2 molecule is given in Fig..



Molecular orbital energy level diagram of H_2 molecule

The bond order of H_2 molecule can be calculated as follows.

Here, $N_b = 2$ and $N_a = 0$

Bond order = $(N_b - N_a)/2 = 2-0/2 = 2$

i. **Nature of bond** : This means that the two hydrogen atoms in a molecule of hydrogen are bonded by a single covalent bond.

ii. **Diamagnetic character** : Since no unpaired electron is present in hydrogen molecule, it is diamagnetic in nature.

2. Nitrogen molecule (N_2). The electronic configuration of nitrogen (Z=7) in the ground state is 1s2 2s2 2p1x 2p1y 2p1z . Therefore, the total number of electrons present in nitrogen molecule (N2) is 14. These 14 electrons can be accommodated in the various molecular orbitals in order of increasing energy.

$$N2 : KK(s_{2s})2\ (s^*_{2s})2\ (P2px)2\ (P2py)2\ (s2pz)2$$

Here (s1s)2 (s*1s)2 part of the configuration is abbreviated as KK, which denotes the K shells of the two atoms. In calculating bond order, we can ignore KK, as it includes two bonding and two antibonding electrons.

The molecular orbital energy level diagram of N2 is given in FIG

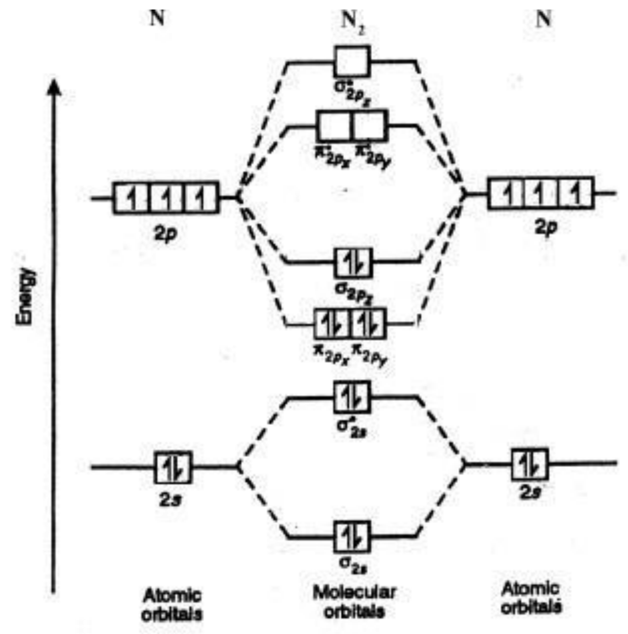


Fig. Molecular orbital energy level diagram of N_2

The bond order of N_2 can be calculated as follows.

Here, $N_b = 8$ and $N_a = 2$

∴ Bond order = $(N_b - N_a)/2 = (8-2)/2 = 3$.

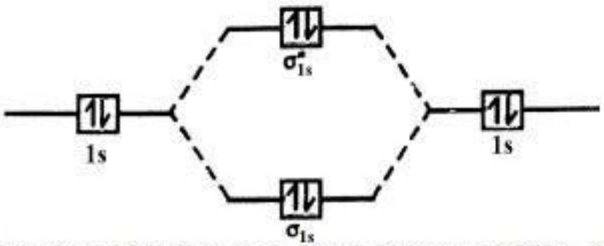
i. ***Nature of bond*** *: A bond order of 3 means that a triple bond is present in a molecule of nitrogen.*

ii. ***Diamagnetic nature*** *: Since all the electrons in nitrogen are paired, it is diamagnetic in nature.*

2. Diatomic helium molecule, He_2 (Hypothetical). The electronic configuration of helium (Z = 2) in the ground state is 1s2. As each helium atom contains two electrons, there will be four electrons in He2 molecule. Keeping in view the Aufbau principle and Pauli's exclusion principle its electronic configuration would be as follows.

He_2 : (σ 1s)2 (σ *1s)2.

The molecular orbital energy level diagram of He2 (hypothetical) is given in Fig.



Molecular orbital energy level diagram of He_2 (hypothetical) molecule

Here, $N_b = 2$ and $N_a = 2$

Bond orde = $N_b - N_a / 2 = 2 / 2 = 0$.

As the bond order for He_2 comes out to be zero, this molecule does not exist

Nuclear Chemistry

Nuclear chemistry is the study of the physical and chemical properties of elements which are influenced by changes in the structure of the atomic nucleus. It also deals with the energy released from nuclear reactions and its uses.

Types of Radiations

Unlike a normal chemical reaction that forms molecules, nuclear reactions result in the transformation of one element into another. This property of nuclear reactions is used in nuclear power plants to gather nuclear energy. The three common types of radiations are explained below.

Alpha Radiation

It is the emission part of an alpha particle from an atom's nucleus. The α particle includes two protons and two neutrons and is much similar to Helium (He)nucleus $^4He_2$. When an atom emits an α particle, the atomic mass of an atom decreases by 4 units.

$$^{238}_{92}U \rightarrow {}^{4}_{2}He + {}^{234}_{90}Th$$

Beta Radiation

When an atom emits a β particle, the mass of the atom will not change. The atomic number will increase by one.

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

Gamma Radiation

It involves the emission of electromagnetic energy from an atom’s nucleus. During gamma radiation, no particles are emitted and thus it does not cause the transmutation of atoms.

$$^{60}_{27}\mathrm{Co} \rightarrow {}^{60}_{28}\mathrm{Ni} + {}^{0}_{-1}e + 2\,{}^{0}_{0}\gamma$$

Stimulated nuclear reactions

While most elements undergo radioactive decay naturally, nuclear reactions can be stimulated artificially. Such types of reactions are mentioned below.

- **Nuclear fission:** It is the type of reaction where the atom’s nucleus splits into smaller parts releasing a huge amount of energy in the process.
- **Nuclear fusion:** It is a type of reaction where two or more elements fuse together to form a larger element, releasing a large amount of energy in the process.

Who discovered the Neutron?

James Chadwick discovered the neutron particle. A breakthrough came when it was shown that the bombardment of Beryllium with alpha particles from a radioactive source yielded penetrating but non-ionizing radiation. Such neutral radiation confounded the scientists since the only known neutral radiation was photons. Had it been a photon, the neutral radiation would exit the beryllium atom with far more energy than it does.

Neutron

The answer to this puzzle was provided by **James Chadwick**, who boldly stated that this was a new type of fundamental particle that is neutral, and he called them **Neutrons**. From the conservation of energy and momentum, he was able to derive with considerable accuracy the mass of this new particle. He found that the mass of a neutron was very close to that of a proton.

$\mathbf{M_N} = 1.00866\ \mathrm{u} = 1.6749 \times 10^{-27}\ \mathrm{kg}$

So now the nucleus had another resident, and the proton-neutron pair was called a Nucleon. The discovery of Neutron led to a better understanding of atomic mass and atomic number also with isotopes which is what radioactivity is based on!

- Z – Atomic Number = number of protons/ electrons
- N – Neutron Number = Number of Neutron
- A – Atomic Mass Number = Z + N = Total number of protons and neutrons

So now the elements of the periodic table had a new form of representation;

For example, the nucleus of a Uranium atom is represented by a $^{235}U_{92}$, which means that one atom of Uranium 235 contains 235 nucleons, of which 92 are protons, and the rest 143 are neutrons.

Isotopes

Isotopes are variants of a particular element with different numbers of neutrons. For example, the two isotopes of Uranium are, $^{235}_{92}U$ and $^{239}_{92}U$. You will see here that the number of protons is the same in both the isotopes, but they contain 143 and 147 neutrons, respectively. The presence of an extra neutron significantly changes the behaviour of that particular atom. There are two different types of isotopes, stable and radioactive. Stable isotopes can exist in their free state without breaking down spontaneously. Radioactive isotopes are too unstable to sustain themselves, and they spontaneously break down into two lighter daughter elements with the

Isobars

Isobars are elements that have the same number of nucleons (sum of protons and neutrons). The series of elements with 40 Mass numbers serve as a good example; ${}^{40}_{16}S$, ${}^{40}_{17}Cl$, ${}^{40}_{18}Ar$, ${}^{40}_{19}K$, and ${}^{40}_{20}Ca$. The nucleus of all the above-mentioned elements contain the same number of particles in the nucleus but contain varying numbers of protons and neutrons.

Isotones

Isotones are atoms that have the same neutron number but different proton number. For example, ${}^{36}_{16}S$, ${}^{37}_{17}Cl$, ${}^{38}_{18}Ar$, ${}^{39}K$, and ${}^{40}_{19}Ca$ are all isotones of 20 since they all contain 20 neutrons.

Nuclear energy and Radioactivity relies on the unstable isotopes of heavy elements to tap the explosive power of the nucleus. The discovery of one fundamental particle unlocked such amazing doors for humanity

Isotopes

- Isotopes are referred to as atoms with different densities of neutrons in the very same chemical substance.
- As a result, whereas **isotopes** from the same chemical substance have an identical atomic number, they have distinct atomic weights.
- The atomic number of a particular atom is determined by the density of protons in that atom. The mass of protons in a chemical substance is constant.
- As a result, the atomic number of different atoms hailing from alike chemical substances is comparable to one another.
- Isotopes are thus atoms from the same chemical substance.
- The atomic mass can be determined by the aggregate amount of neutrons and protons. The atomic masses of **isotopes** differ.
- Isotopes of the same chemical substance have similar chemical activity, but their physical qualities differ.
- There are **isotopes** of almost every chemical substance. There are almost 275 confirmed isotopes of around 81 stable chemical components.
- There are both stable isotopes and radioactive isotopes of each chemical element.

- The label of an isotope is derived from the chemical component's nomenclature and the isotope's atomic weight. Helium's two **isotopes**, for instance, are designated as "helium-4" & "helium-2."

Isobars

- Isobars are referred to atoms from distinct chemical components. As a result, atomic numbers remain fundamentally different.
- **Isobars** are referred to atoms with equal atomic masses from distinct chemical substances. The total of an atom's neutrons and protons is known as its atomic mass. A nucleon is defined as a neutron or a proton. Isobars contain an equal amount of nucleons as one another.
- Since various chemical components have a varying number of atoms, the atomic numbers of their isobars also differ.
- According to the Mattauch rule of isobars, if two neighbouring components from the periodic table contain **isotopes** with an alike mass number (known as isobars), at least one isotope would definitely be radioactive.
- Whenever three successive isobars occur, the first, as well as final **isobars**, are generally stable, but the intermediate one might suffer radioactive decay.
- The isobar series seems to be a grouping of isotopes having identical atomic masses.

Isotones

Isotones are referred to as the atoms of various elements with the same density of neutrons in their nucleus. **Isotones** possess various atomic numbers (owing to the varying density of protons in their nucleus) and atomic masses. We can express it as mentioned below:

Z is the atomic number

A is referred to the atomic mass

The number of neutrons is denoted by the symbol N.

A is not equal to Z but (A-Z)=N for every isotone in a single series.

What is Chemical Reaction?

A chemical reaction is the process by which atoms or molecules rearrange themselves to form new substances. In a chemical reaction, atoms of one element can combine with atoms of another element to form molecules. These new molecules can have different properties than the atoms that formed them.

What is Nuclear Reaction?

A nuclear reaction is the process of rearranging the nuclei of atoms. The process can release energy in the form of radiation, such as light or heat. In a nuclear reaction, a small amount of mass is converted into a large amount of energy.

Difference between a Chemical Reaction and Nuclear Reaction

Chemical reactions and nuclear reactions are two different types of reactions. A chemical reaction is a process that changes one or more substances into different substances. A nuclear reaction is a process that changes the nucleus of an atom.

A chemical reaction is a process that changes one or more substances into different substances. In a chemical reaction, the atoms in the substances are rearranged. In a nuclear reaction, the nucleus of an atom is rearranged.

One difference between chemical reactions and nuclear reactions is that nuclear reactions can release energy. Chemical reactions do not release energy.

Another difference between chemical reactions and nuclear reactions is that nuclear reactions can cause radiation. Chemical reactions do not cause radiation.

Nuclear reactions are more dangerous than chemical reactions. Nuclear reactions can cause radiation, which can be harmful to people. Chemical reactions do not cause radiation, and are therefore safer

Group Displacement Law:

Group Displacement Law – α-particle or β-particle. When an α – particle is lost, a new element with a lower atomic number and a lower mass number is produced, according to Soddy, Fajans, and Russell (1911-1913). When the β-particle is lost, a new element with an atomic number more significant than one is created.

The results of group displacement law have been summarised as:

- The new element is created when an α – particle is expelled to the left of the parent element in the periodic table; this happens because the atomic number is decreased by 2.
- The new element is formed when a β-particle is emitted one position to the right of the parent element in the periodic table. This happens because the atomic number is increased by 1.
- The daughter element in the periodic table moves one group to the left of the parent element when a positron is emitted.

Calculating of number of α and β particles in a radioactive displacement transformation:

Parent element Daughter element $Z_1AM_1 \rightarrow Z_2BM_2$

Number of α – particles => Change in mass number/4 = $(M_1-M_2)/4$

Number of β-particles = Let us assume 'x' β-particles and 'y' α – particles be emitted

Atomic number of parent element – 2y + x = Atomic number of daughter element

$Z1 - 2y + x = Z2$

Therefore, $x = (Z2 - Z1 + 2y)$

Group Displacement Law Example

The number of α-particle or β-particle released during the nuclear transition must be determined. It may be accomplished in the following manner:

$a=b+4x$ or

x=a-b

—— equation i

C = d+2x-y —— equation ii

Where x = no. of a-emitted, y = no. of b-emitted

substituting the value of x from eq. I and eq. ii we get,

Nuclear binding energy is the energy required to split an atom's nucleus into protons and neutrons. Mass defect is the difference between the predicted mass and the actual mass of an atom's nucleus. The binding energy of a system can appear as extra mass, which accounts for this difference.

Nuclear Binding Energy and the Mass Defect

A neutron has a slightly larger mass than the proton. These are often given in terms of an atomic mass unit, where one atomic mass unit (u) is defined as 1/12th the mass of a carbon-12 atom.

Particle	**Mass (kg)**	**Mass (u)**	**Mass (Mev/c^2)**
1 atomic mass unit	1.660540 x 10^{-27} kg	1.000 u	931.5 MeV/c^2
neutron	1.674929 x 10^{-27} kg	1.008664 u	939.57 MeV/c^2
proton	1.672623 x 10^{-27} kg	1.007276 u	938.28 MeV/c^2
electron	9.109390 x 10^{-31} kg	0.00054858 u	0.511 MeV/c^2

Einstein's famous equation relates energy and mass:

$E = mc^2$

You can use that to prove that a mass of 1 u is equivalent to an energy of 931.5 MeV.

Something should strike you as strange about the table above. The carbon-12 atom has a mass of 12.000 u, and yet it contains 12 objects (6 protons and 6 neutrons) that each have a mass greater than 1.000 u, not to mention a small contribution from the 6 electrons.

This is true for all nuclei, that the mass of the nucleus is a little less than the mass of the individual neutrons, protons, and electrons. This missing mass is known as the mass defect, and represents the binding energy of the nucleus.

The binding energy is the energy you would need to put in to split the nucleus into individual protons and neutrons. To find the binding energy, add the masses of the individual protons, neutrons, and electrons, subtract the mass of the atom, and convert that mass difference to energy. For carbon-12 this gives:

Mass defect = m = 6 * 1.008664 u + 6 * 1.007276 u + 6 * 0.00054858 u - 12.000 u = 0.098931 u

The binding energy in the carbon-12 atom is therefore 0.098931 u * 931.5 MeV/u = 92.15 MeV.

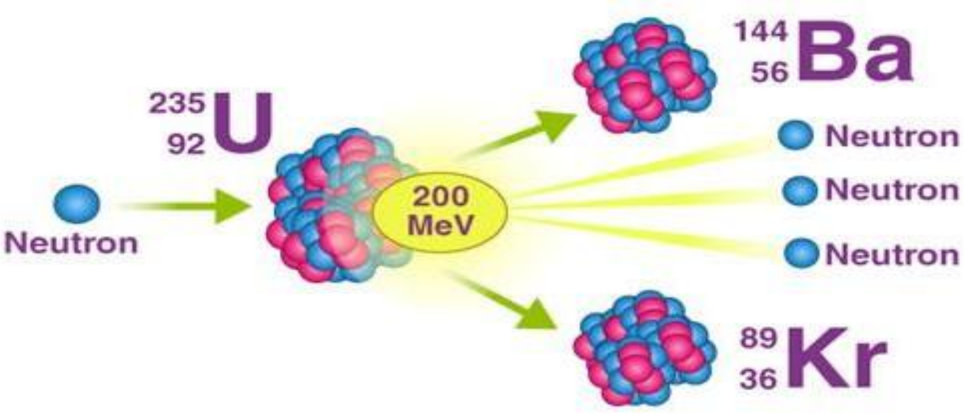
In a typical nucleus the binding energy is measured in MeV, considerably larger than the few eV associated with the binding energy of electrons in the atom. Nuclear reactions involve changes in the nuclear binding energy, which is why nuclear reactions give you much more energy than chemical reactions; those involve changes in electron binding energies.

Difference Between Nuclear Fission and Nuclear Fusion

There are two types of nuclear reactions called nuclear fission and nuclear fusion. These nuclear reactions involve the disintegration and combination of the elemental nucleus. In the case of nuclear fission, an atom divides into two or more smaller or lighter atoms. Nuclear fusion occurs when two or more atoms join or fuse together to form a large or heavier atom.

What is Nuclear Fission?

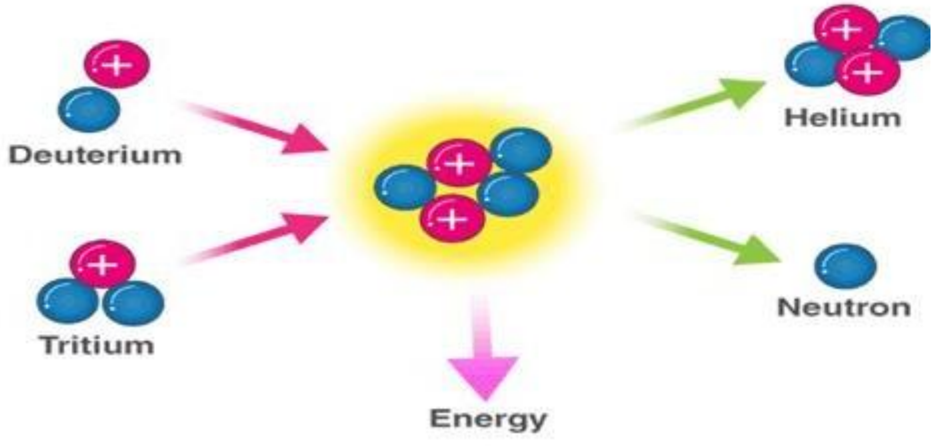
Nuclear fission is a nuclear reaction in which the nucleus of an atom is bombarded with low-energy neutrons which splits the nucleus into smaller nuclei. An abundant amount of energy is released in this process. Nuclear fission reactions are used in nuclear power reactors since it is easy to control and produces large amounts of energy.



When uranium-235 is bombarded with slow-moving neutrons, the heavy nucleus of the uranium splits and produces krypton-89 and barium-144 with the emission of three neutrons.

What is Nuclear Fusion

Nuclear fusion is a reaction that occurs when two or more atoms combine together to form to a single heavier nucleus. An enormous amount of energy is released in this process, much greater than the energy released during the nuclear fission reaction.



Nuclear_fusion

Fusion occurs in the sun where the atoms of (isotopes of hydrogen, hydrogen-3, and hydrogen-2) deuterium and tritium combine in a high-pressure atmosphere with extremely high temperatures to produce an output in the form of a neutron and an isotope of Helium. Also, the amount of energy released in fusion is way greater than the energy produced by fission.

Nuclear Fission vs Nuclear Fusion

The table below lists the various differences between nuclear fission and fusion:

Nuclear Fission	**Nuclear Fusion**
When the nucleus of an atom splits into lighter nuclei through a nuclear reaction, the process is termed nuclear fission.	Nuclear fusion is a reaction through which two or more light nuclei collide with each other to form a heavier nucleus.
When each atom splits, a tremendous amount of energy is released	The energy released during nuclear fusion is several times greater than the energy released during nuclear fission.
Fission reactions do not occur in nature naturally	Fusion reactions occur in stars and the sun
Comparatively, less energy is needed to split an atom in a fission reaction	High energy is needed to fuse two or more atoms together in a fusion reaction
Atomic bomb works on the principle of nuclear fission	Hydrogen bomb works on the principle of nuclear fusion.

The table above would have given you a clear idea about how the two terms nuclear fission and fusion vary from one another.

Nuclear Fusion and Stellar Energy:

Nuclear Fusion:

Nuclear Fusion is defined as the process in which two lighter nuclei combine together to form a heavier and stable nucleus, with the release of a large amount of energy.

Example- ${}_1H^2 + {}_1H^2 \longrightarrow {}_2He^4 + 24\ \text{MeV}$

Since the mass of a single nucleus formed is less than the sum of the masses of nuclei fused, the mass defect is converted into energy. Hence during the fusion process, a large amount of energy is released.

But the problem is how to fuse two nuclei because they would repel each other. For fusion, the parent nuclei must be within a distance of 10^{-15} m. They should be imparted high energies to overcome their repulsive forces. This is only possible at very high temperatures that are possible on the sun.

Therefore, fusion is also called a ***thermonuclear reaction***. Artificially such a high temperature (about 10^7 °C) could be produced using an atom bomb. Thus the explosion of an atom bomb can initiate nuclear fusion.

Stellar Energy:

It is the energy produced in the sun or other stars. Through thermonuclear reactions, large energy is released in which hydrogen is continuously converted into helium. According to ***Bethe*** by following two ways fusion takes place-

- Proton-Proton Cycle.
- Carbon-Nitrogen Cycle.

Proton-Proton Cycle:

Different reactions involved in the cycle are as follows-

- Two protons fuse to form deuteron.

${}_1H^1 + {}_1H^1 \longrightarrow {}_1H^2 + {}_{+1}e^0 + \text{Energy}$

- Deuteron combines with another proton to yield He-3.

$${}_1H^2 + {}_1H^1 \longrightarrow {}_2He^3 + \text{Energy}$$

- Two light He-nuclei fuses to form He-4.

$${}_2He^3 + {}_2He^3 \longrightarrow {}_2He^4 + 2\ ({}_1H^1) + \text{Energy}$$

OR

$${}_2He^3 + {}_1H^1 \longrightarrow {}_2He^4 + {}_{+1}e^0 + \text{Energy}$$

Thus the overall process is written as-

$$4\ {}_1H^1 \longrightarrow {}_2He^4 + 2\ {}_{+1}e^0 + \text{Energy}$$

The total energy released is about 26.7 MeV (27 approximately).

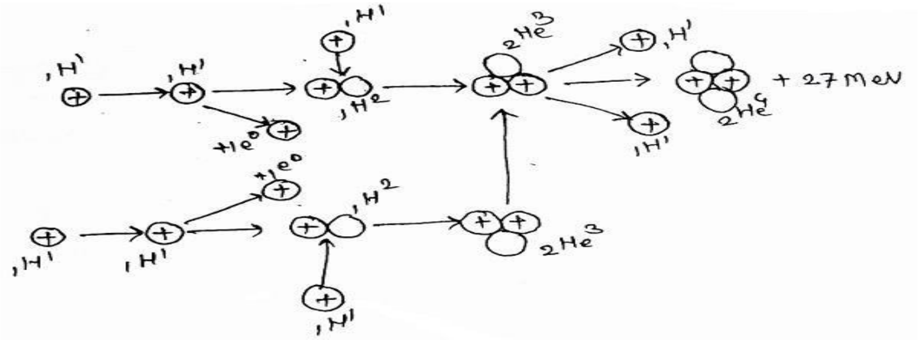


Fig. Proton-proton cycle.

Carbon-Nitrogen Cycle:

Here carbon acts as a nuclear catalyst and the different reactions involved are as follows-

$${}_6C^{12} + {}_1H^1 \longrightarrow {}_7N^{13} + E$$
$${}_7N^{13} \longrightarrow {}_6C^{13} + {}_{+1}e^0 + E$$

$${}_6C^{13} + {}_1H^1 \longrightarrow {}_7N^{14} + E$$
$${}_7N^{14} + {}_1H^1 \longrightarrow {}_8O^{15} + E$$
$${}_8O^{15} \longrightarrow {}_7N^{15} + {}_{+1}e^0 + E$$
$${}_7N^{15} + {}_1H^1 \longrightarrow {}_6C^{12} + {}_2He^4 + E$$

Thus the overall reaction is-

$$4\ {}_1H^1 \longrightarrow {}_2He^4 + 2\ {}_{+1}e^0 + E$$

The total energy released is about 26.7 MeV (27 approximately).

Electrochemical Cell (Galvanic Cell or Voltaic Cell)	Applications Of Laser And Maser
Primary Cells- Dry Cell and Mercury Cell	Nuclear Fission and Nuclear Fusion
Electrochemical Theory of Rusting and Prevention of Corrosion	Merits and Demerits of Nuclear Energy
Electrochemical Series and its Applications	Electrochemistry Notes From Tamil Board

Nuclear chemistry

Nuclear chemistry is the study of the breakup of unstable nuclei, which results in the emission of radiation and energy. There are three types of radiation; alpha (α), beta (β) and gamma (γ). Uses of radioisotopes and carbon dating

Uses of radioisotopes

Radioisotopes of elements have a wide variety of uses.

Cobalt-60	Used in medicine to treat cancer. Gamma rays can be focused on tumors.
Iodine-131	Used to treat thyroid gland (in the neck). If the gland is enlarged, iodine-131 can be absorbed and will partially destroy it.
Carbon-14	Used to date once-living materials.

Carbon dating

Every living organism contains the radioisotope carbon-14. Carbon-14 is formed when neutrons from cosmic radiation collide with nitrogen atoms in our atmosphere forming protons and carbon-14 atoms.

Carbon dioxide is responsible for carbon-14 entering the food chain.

Carbon-14 decays by beta-emission and has a half-life of 5730 years. This means that the beta-decay emissions can be monitored and the data used to calculate how long it has been since the material was alive.

What are the applications of radioisotopes?

Radioactive isotopes in medicine: Iodine - 131 is effective in locating brain tumors and in determining liver and thyroid activity. Radioactive isotopes in nuclear power plants: Uranium - 235 is used as a fuel in nuclear reactors of nuclear power plants for generating electricity.

hat is the application of radioactivity rock dating?

Radioactive dating is a method of dating rocks and minerals using radioactive isotopes. This method is useful for igneous and metamorphic rocks, which cannot be dated by the stratigraphic correlation method used for sedimentary rocks. Over 300 naturally-occurring isotopes are known.

UNIT -11

Industrial Chemistry

Industrial Chemistry as a discipline is the manufacturing art concerned with the transformation of matter into valuable materials. The Industrial Chemistry sector deals with the analysis of problems related to the procurement of industrial raw materials, the creation of solutions to these problems, and the development of better production techniques. It is a practical combination of both science and technology that aims to help human society. Thus, Industrial Chemistry finds solutions to obtain and procure natural resources and deals with developing and sustaining raw materials into improved valuable products.

Branches of Industrial Chemistry

- **Organic Industrial Chemistry:** Organic Industrial Chemistry focuses on raw materials such as rubber, cellulose, and natural fibres. It uses these materials to compose products such as diesel fuel, soaps, sugars, and fats. It also tries to obtain other compounds from these raw materials, such as hydrogen and sulfur.
- **Inorganic Industrial Chemistry:** This branch of Industrial chemistry focuses on raw materials such as water, uranium, and phosphates to produce other products such as glasses, cement, and ceramics. It is also the branch of industrial chemistry that produces metals, alloys, pigments, and even fertilizers.

What is a fuel?

According to the law of conservation of energy: Energy can neither be created nor be destroyed; it can only be changed from one form to another. Thus, we cannot produce energy to do certain work. Therefore, we use certain substances which help us to transform one form of energy into another form.

For example, when we burn paper with a matchstick, light is produced by the flame. If we analyze this closely, light energy is not created over there, it has just been produced due to the transformation of heat energy provided by the matchstick into light energy. Thus, we always need a certain substance to convert one form of energy into another for accomplishing various jobs. We call such materials as fuels. In other words, any substance that upon combustion produces a usable amount of energy is known as **fuel**. Example: fossil fuels, biogas, nuclear energy, etc.

Some properties of ideal fuel are:

- An ideal fuel is readily available.
- An ideal fuel is cheap.
- An ideal fuel burns easily in the air at a moderate rate.
- It releases a large amount of energy.
- It should not leave behind any undesirable substances which can be harmful to us.
- It should not affect the environment adversely.

Types of Fuels:

Fuels can be generally classified on the basis of two factors:

1. *On the basis of their fuels state:*
    - ***Solid Fuels***
    - ***Liquid Fuels***
    - ***Gaseous Fuels***

2. *On the basis of their occurrence:*
    - ***Natural Fuels***
    - ***Artificial Fuels***

Examples of Fuels:

Natural Fuels	**Artificial Fuels**
Solid Fuels	
Wood, Coal, Oil Shale	Tanbark, Bagasse, Straw, Charcoal, Coal, Briquettes
Liquid Fuels	
Petroleum	Oils from distillation of petroleum, Coal Tar, Shale-Oil, Alcohols, etc.
Gaseous Fuels	
Natural Gas	Coal gas, Producer Gas, Water Gas, Hydrogen, Acetylene,

	Blast Furnace Gas, Oil Gas

Solid Fuels

Solid Fuels

Fuels which are found in their solid state at room temperature are generally referred to as Solid Fuels. They were the first kind of fuel known to be used by man, basically wood to create fire. Coal was another one of the influential fuels known to man as it leads the way for the industrial revolution, from firing furnaces to running steam engines.

Advantages:

- Easier transportation and storage.
- Low production cost.
- Moderate ignition temperature.

Disadvantages:

- Large portion of energy is wasted.
- Cost of handling is high and controlling is also hard.
- Ash content is high & burn with clinker formation.

Liquid Fuel


Liquid Fuel

Most liquid fuels are derived from the fossilized remains of dead plants and animals by exposure to heat and pressure in the Earth’s crust. The fumes of the liquid fuel are flammable instead of the liquid.

Advantages:

- Higher calorific value per unit mass.
- Burn without ash, clinkers, etc.
- Controlling the combustion is easier.
- Transportation easier through pipes and stored indefinitely without loss.
- Loss of energy is comparatively lower.
- Require less furnace space for combustion.

Disadvantages:

- Cost of liquid fuel is much higher compared to solid fuel.
- Storage methods are costlier.
- Greater risk of fire hazards.
- Special burning equipment required for more efficient combustion.

Gaseous Fuel


Gaseous Fuel

Gaseous fuels occur in nature, besides being manufactured from solid and liquid fuels. Most gaseous fuels are composed of hydrocarbons, carbon monoxide, hydrogen or a mixture of them all.

Advantages:

- Transportation through pipes is easy.
- Sparking combustion is really easy.
- They have a higher heat content.
- Clean after use.
- Do Not require any special burner technology.

Disadvantages:

- Large storage tanks required.
- As they are highly inflammable, the chance for fire hazards are extremely high and strict safety measures need to be followed.

Types of fossil fuels:

- ***Coal***
- ***Oil***
- ***Natural Gas***

Nuclear Fuel

Nuclear Fuel Element

Any material consumed to give out nuclear energy is a nuclear fuel. Technically speaking, any material can be made to give out nuclear energy. But looking at its practicality and feasibility, we pick materials which do not require extreme constraints to release nuclear energy.

Most nuclear fuels contain heavy fissile elements that are capable of nuclear fission. When these fuels are struck by neutrons, they are in turn capable of emitting neutrons when they break apart. This makes possible a self-sustaining chain reaction that releases energy at a controlled rate in a nuclear reactor or with a very rapid uncontrolled rate of a nuclear weapon.

Some common examples of nuclear fuel are uranium-235 (^{235}U) and plutonium-239 (^{239}Pu).

Natural gas

Natural gas (also called **fossil gas, methane gas** or simply **gas**) is a naturally occurring mixture of gaseous hydrocarbons consisting primarily of methane in addition to various smaller amounts of other higher alkanes. Low levels of trace gases like carbon dioxide, nitrogen, hydrogen sulfide, and helium are also usually present. Methane is colorless and odorless, and the second largest greenhouse gas contributor to global climate change after carbon dioxide. So odorizers such as mercaptan (which smells like sulfur or rotten eggs) are commonly added to natural gas supplies for safety so that leaks can be readily detected.

Natural gas is a fossil fuel and non-renewable resource that is formed when layers of organic matter (primarily marine microorganisms) decompose under anaerobic conditions and are subjected to intense heat and pressure underground over millions of years. The energy that the decayed organisms originally obtained from the sun via photosynthesis is stored as chemical energy within the molecules of methane and other hydrocarbons.

Natural gas can be burned for heating, cooking, and electricity generation. It is also used as a chemical feedstock in the manufacture of plastics and other commercially important organic chemicals and less commonly used as a fuel for vehicles.

The extraction and consumption of natural gas is a major and growing contributor to climate change. Both the gas itself (specifically methane) and carbon dioxide, which is released when natural gas is burned, are greenhouse gases. When burned for heat or electricity, natural gas emits fewer toxic air pollutants, less carbon dioxide, and almost no particulate matter compared to other fossil and biomass fuels. However, gas venting and unintended fugitive emissions throughout the supply chain can result in natural gas having a similar carbon footprint to other fossil fuels overall.

Natural gas can be found in underground geological formations, often alongside other fossil fuels like coal and oil (petroleum). Most natural gas has been created through either biogenic or thermogenic processes. Biogenic gas is formed when methanogenic organisms in marshes, bogs, landfills, and shallow sediments anaerobically decompose but are not subjected to high temperatures and pressures. Thermogenic gas takes a much longer period of time to form and is created when organic matter is heated and compressed deep underground.

During petroleum production, natural gas is sometimes flared rather than being collected and used. Before natural gas can be burned as a fuel or used in manufacturing processes, it almost always has to be processed to remove impurities such as water. The byproducts of this processing include ethane, propane, butanes, pentanes, and higher molecular weight hydrocarbons. Hydrogen sulfide (which may be converted into pure sulfur), carbon dioxide, water vapor, and sometimes helium and nitrogen must also be removed.

Natural gas is sometimes informally referred to simply as "gas", especially when it is being compared to other energy sources, such as oil, coal or renewables. However, it is not to be confused with gasoline, which is often shortened in colloquial usage to "gas", especially in North America.

Natural gas is measured in standard cubic meters or standard cubic feet. The density compared to air ranges from 0.58 (16.8 g/mole, 0.71 kg per standard cubic meter) to as high as 0.79 (22.9 g/mole, 0.97 kg per scm), but generally less than 0.64 (18.5 g/mole, 0.78 kg per scm). For comparison, pure methane (16.0425 g/mole) has a density 0.5539 times that of air (0.678 kg per standard cubic meter).

WATER-GAS

The water-gas shift reaction was discovered by Italian physicist Felice Fontana in 1780. Water gas was made in England from 1828 by blowing steam through white-hot coke.

Water gas is a combustion fuel containing carbon monoxide (CO) and hydrogen gas (H_2). Water gas is made by passing steam over heated hydrocarbons. The reaction between steam and hydrocarbons produces synthesis gas.

The water-gas shift reaction can be used to reduce carbon dioxide levels and enrich hydrogen content, making water gas. The water-gas shift reaction is:

$CO + H_2O \rightarrow CO_2 + H_2$

History: The water-gas shift reaction was first described in 1780 by Italian physicist Felice Fontana. In 1828, water gas was produced in England by blowing steam across white-hot coke. In 1873, Thaddeus S.C. Lowe patented a process that used the water-gas shift reaction to enrich the gas with hydrogen. In Lowe's process, pressurized steam was shot over hot coal, with heat maintained using chimneys. The resulting gas was cooled and scrubbed before use. Lowe's process led to the rise of the gas manufacturing industry and the development of similar processes for other gases, such as the Haber-Bosch process to synthesize ammonia. As ammonia became available, the refrigeration industry rose. Lowe held patents for ice machines and devices that ran on hydrogen gas.

Production

The principle of water gas production is straightforward. Steam is forced over red-hot or white-hot carbon-based fuel, producing the following reaction:

$H_2O + C \rightarrow H_2 + CO$ ($\Delta H = +131$ KJ/mol)

This reaction is endothermic (absorbs heat), so heat must be added to sustain it. There are two ways this is done. One is to alternate between steam and air to cause combustion of some carbon (an exothermic process):

$O_2 + C \rightarrow CO_2$ ($\Delta H = -393.5$ KJ/mol)

The other method is to use oxygen gas rather than air, which yields carbon monoxide rather than carbon dioxide:

$O_2 + 2 C \rightarrow 2 CO$ ($\Delta H = -221$ KJ/mol)

Uses

Completely displaced by syngas, water gas could be applied to certain fuel cells. Used in Fischer–Tropsch process.

It reacts with producer gas to produce fuel gas.

It could also be used to gain pure hydrogen for synthesis of ammonia.

CARBURETTED WATER GAS

Water gas has a lower heat of combustion than coal gas, so the calorific value was often boosted by passing the gas through a heated retort, into which oil was sprayed. The resulting mixed gas was called *carburetted water gas*.

The average composition of carburated water gas is as follows: H_2=34-38%; CO=23-28%; saturated hydrocarbon=17-21%; unsaturated hydrocarbon=13-16%; CO_2=0.2-2.2%; N_2=2.5-5.0%. It is used as a source of heat since it has a high calorific value

Carburetted water gas:

Carburetted water gas is produced to enhance the energy value of water gas, which is ordinarily lower than that of coal gas. Water gas is carburetted by passing it through a heated retort which has been sprayed with oil

SEMI-WATER GAS

Semi-water gas is a mixture of water gas and producer gas made by passing a mixture of air and steam through heated coke. The heat generated when producer gas is formed keeps the temperature of the coke high enough to allow water gas to be formed.

Water gas shift reaction

Pure hydrogen can be obtained from water gas by using the water-gas shift reaction, after subsequent removal of the carbon dioxide formed when carbon monoxide reacts with water.

PRODUCER GAS

Producer gas is fuel gas that is manufactured by blowing a coke or coal with air and steam simultaneously.

It mainly consists of carbon monoxide (CO), hydrogen (H_2), as well as substantial amounts of nitrogen (N_2).

CNG, LPG and oil gas (manufacturing details not required)

If you're an experienced diesel technician or are considering a career in the field, you may be familiar with the various types of natural gases, which serve as an alternative to conventional petroleum-based fuels.

The world we live in today relies heavily on diesel fuel, but due to environmental concerns and cost efficiency, more and more industries are turning to CNG, LPG and LNG fuel. In the last decade, we've seen new applications for natural gas emerge in the transportation, retail and industrial sectors. As a result, it's important for today's diesel technicians to stay ahead of the curve and understand these different types of gases and how they work.

Keep reading to learn the basics of CNG, LPG and LNG fuel and how these natural gases are impacting the industry and the future of your career.

What is Compressed Natural Gas (CNG) Fuel?

In the diesel industry, you will hear the acronym CNG used quite often. You may have even seen the blue diamond CNG sticker on commercial vehicles and mass transit busses and wondered, "What is CNG fuel?

CNG stands for compressed natural gas. It is the gaseous product of petroleum and is the first product that is separated during the distillation process. CNG is odorless, tasteless and non-toxic, and is made up of 93.05% methane, nitrogen, carbon dioxide, propane and traces of ethane. It is an environmentally clean alternative fuel, as its combustion process emits a lower percentage of greenhouse gases when compared to other fuels.

While CNG fuel won’t give you the same amount of power that would come from diesel fuel, it certainly has its advantages. CNG has a high octane rating that provides a high compression ratio and is adaptable to modern engines. The combustion of CNG produces less carbon monoxide, hydrocarbons and oxides of nitrogen. Overall, this type of gas can help in reducing pollution, as it is a clean burning fuel.

Understanding LPG and LNG Fuel

In addition to CNG fuel, LPG and LNG are two other common alternatives to gas and diesel fuel. Each of these types of fuels have both similarities and differences.

LPG fuel, or liquefied petroleum gas, is a liquefied gas and is a byproduct derived while extracting crude petroleum. LPG weighs twice as much as air and is colorless, odorless and is a highly flammable explosive gas. It is comprised of propane mixed with butane, traces of propylene and butylene.

One of the advantages of LPG is that it emits less hydrocarbons, carbon monoxide and oxides of nitrogen. It also has a high octane rating and increases engine longevity. The fuel weight-to-mileage of LPG is equal to that of gasoline-operated vehicles.

LNG fuel, or liquefied natural gas, is a natural gas converted to liquid form through liquefaction. During this process, natural gas is cooled at low temperatures until it turns into a liquid, and the volume of gas is reduced by approximately 600 times.

LPG is comprised of 95% methane, and other components include nitrogen, ethane, carbon dioxide and propane. It is non-toxic and non-corrosive, resulting in less pollution. It occupies 1/600 the volume as natural gas, making it much more cost-effective for storage and transportation.

CNG VS LNG Fuel

While liquefied natural gas and compressed natural gas are similar, their delivery and storage methods are different.

LNG is frozen in order to turn it into liquid form, whereas CNG is pressurized to the point where it is very compact. LNG takes up less storage space on a vehicle than CNG, and it also offers an energy density that can be compared to diesel fuel. This makes it a common choice among many long-haul trucking companies. Using proper procedures, LNG can be converted to CNG.

On the other hand, CNG is easier to refuel than LNG, which requires special handling and equipment. CNG is also very light, so if there is a leak, it will dissipate. It has an unlimited hold time, so even if it goes unused, there is no fuel loss. This makes CNG a safer choice over LNG. CNG also has lower production costs than LNG.

Knowing about the different types of alternative fuels can benefit you greatly in your diesel career. There is a growing demand for technicians who are able to work on applications that run on these fuels, but not enough candidates who have the right skills. This skills gap is opening the door to exciting opportunities for those who are preparing for **careers in the diesel industry**.

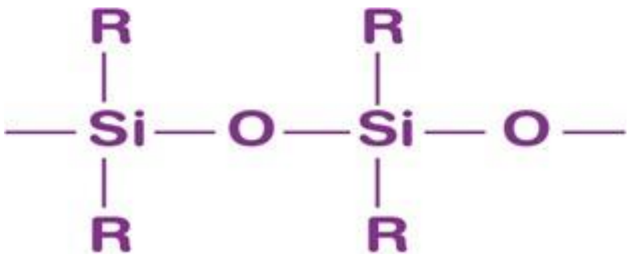
Having CNG, LPG and LNG qualifications on your resume can give you a competitive advantage and make you more valuable as a technician overall. Construction equipment, trucks, agricultural equipment and many other applications have already made the switch to natural gas, which means a new generation of technicians will be needed to keep them up and running.

Technicians who possess knowledge of alternative fuels often work for transit authorities, an engine manufacturer or dealer, and in the power generation industry. Today, nearly every manufacturer makes something that runs on natural gas. No matter where you go to work, you will most likely be exposed to working with these types of fuels—especially as their popularity grows.

Silicones

What Are Silicones?

Silicones are polymers that are also known by the name polysiloxanes. These are the polymers that involve any inert, synthetic compound made up of iterative units of siloxane. It is a chain of alternating oxygen and silicon atoms that are frequently combined with hydrogen and carbon.

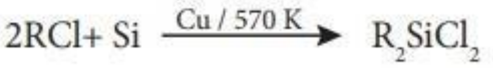


$$-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O-\overset{R}{\underset{R}{\overset{|}{\underset{|}{Si}}}}-O-$$

Silicons are the present-time class of synthetic objects and contribute to thousands of applications that offer safety and well-being in everyday life. Silicones are further a diverse family of high-performance materials that include silicone fluids, silicone polymers and reactive silanes. These materials are widely used in a variety of industrial and consumer products, and they provide essential benefits in various areas, including personal care, health care, aerospace, transportation, electronics and construction.

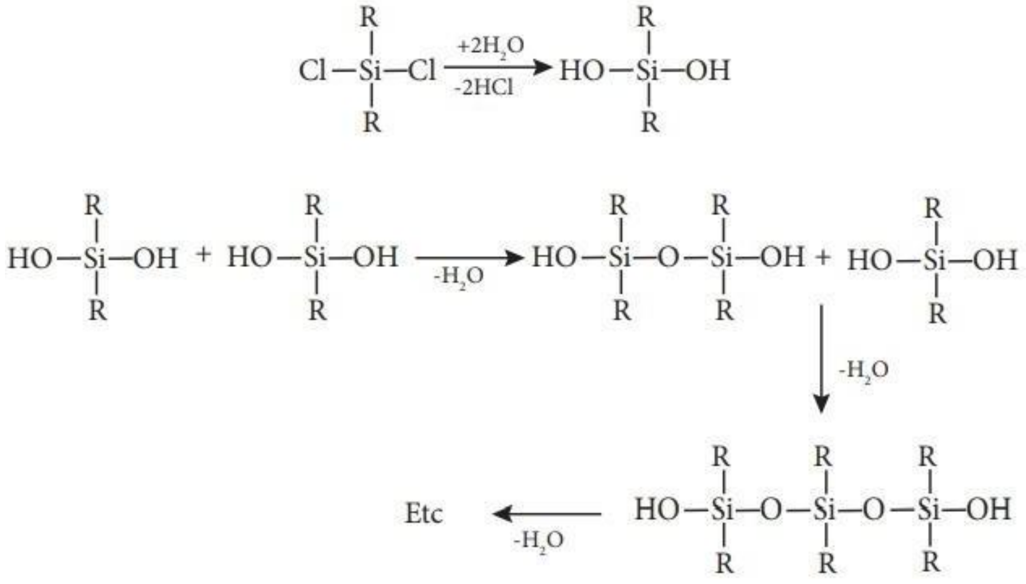
Preparation:

Generally silicones are prepared by the hydrolysis of dialkyldichlorosilanes (r_2sicl_2) or diaryldichlorosilanes Ar_2SiCl_2, which are prepared by passing vapours of rcl or arcl over silicon at 570 K with copper as a catalyst.

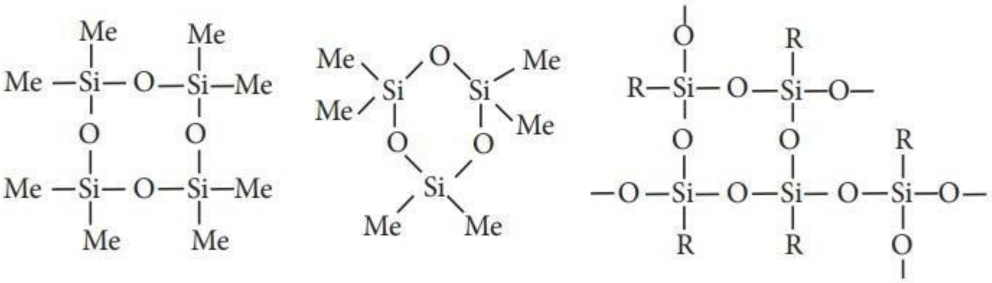


$$2RCl + Si \xrightarrow{Cu / 570 K} R_2SiCl_2$$

The hydrolysis of dialkylchloro silanes r_2sicl_2 yields to a straight chain polymer which grown from both the sides



The hydrolysis of monoalkylchloro silanes rsicl$_3$ yields to a very complex cross linked polymer.. Linear silicones can be converted into cyclic or ring silicones when water molecules is removed from the terminal –OH groups.



Properties of Silicones

Some of the common properties of silicones are as follows:

- Silicones have low thermal conductivity and chemical reactivity.
- Their toxicity is also low.
- It can repel water and form watertight seals.
- It has high resistance to oxygen, ozone, and ultraviolet (UV) light.

- It has both electrically insulative and conductive properties.
- It has high gas permeability and high thermal stability
- They are superior solvents for organic compounds.

If silicone is burned in the presence of oxygen, solid silica (silicon dioxide, sio_2) is formed as a white powder as well as char and various gases. This white powder is often called silica fume.

- ✓ **Uses:**
  - Silicones are used for low temperature lubrication and in vacuum pumps, high temperature oil baths etc...
  - They are used for making water proofing clothes
  - They are used as insulting material in electrical motor and other appliances
  - They are mixed with paints and enamels to make them resistant towards high temperature, sunlight, dampness and chemicals.

What are Fertilizers?

Fertilizers are additional substances supplied to the crops to increase their productivity. These are used by the farmers daily to increase the crop yield. These fertilizers contain essential nutrients required by the plants, including nitrogen, potassium, and phosphorus. They also enhance the water retention capacity of the soil and increase its fertility.

Types Of Fertilizers

Fertilizers are mainly classified into two main types, **organic** and **inorganic** fertilizers.

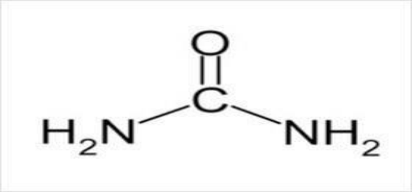
Organic Fertilizers

Natural fertilizers derived from plants and animals are known as organic fertilizers. By adding carbonic molecules necessary for plant growth, it enriches the soil. Organic fertilizers boost the amount of organic matter in the soil, encourage microbial reproduction, and alter the physical and chemical composition of the soil. It is regarded as one of the essential elements for foods that are green.

Organic fertilizers can be obtained from the following products:

- Agricultural Waste
- Livestock Manure
- Industrial Waste
- Municipal Sludge

UREA (46% N)



Fertilizers provide three primary nutrients: Nitrogen (N), Phosphorus (P) and Potassium (K). Nitrogen supports vegetative growth. Phosphorus improves roots and flowering. Potassium strengthens resistance to environmental assaults, from extreme temperatures to pest attacks.

Urea is the most important nitrogenous fertilizer in the market, with the highest Nitrogen content (about 46 percent). It is a white crystalline organic chemical compound. Urea is neutral in ph and can adapt to almost all kinds of soils. It is a waste product formed naturally by metabolizing protein in humans as well as other mammals, amphibians and some fish. Urea is widely used in the agricultural sector both as a fertilizer and animal feed additive.

The main function of Urea fertilizer is to provide the plants with nitrogen to promote green leafy growth and make the plants look lush. Urea also aids the photosynthesis process of plants. Since urea fertilizer can provide only nitrogen and not phosphorus or potassium, it’s primarily used for bloom growth.

Advantages of Urea Fertilizer

- Superior Nitrogen content
- Low production cost, as source is natural
- Non-flammable and risk-free storage
- Wide application range, for all types of crops and soils
- Neutral ph and harmless to crops and soil

How to Use Urea Fertilizer?

- Urea should be applied at the time of sowing. It should not come in contact with the seeds. It also can be applied as a top dressing.
- Since Urea is highly Nitrogen-concentrated, it should be used in combination with earth or sand before its application.
- Urea should not be applied when the soil contains free water or likely to remain wet for three or four days after application.

Ammonium sulfate preparation

- Ammonium sulfate is made by treating ammonia with sulfuric acid:
- $2 NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$
- A mixture of ammonia gas and water vapor is introduced into a reactor that contains a saturated solution of ammonium sulfate and about 2% to 4% of free sulfuric acid at 60 °C. Concentrated sulfuric acid is added to keep the solution acidic, and to retain its level of free acid. The heat of reaction keeps reactor temperature at 60 °C. Dry, powdered ammonium sulfate may be formed by spraying sulfuric acid into a reaction chamber filled with ammonia gas. The heat of reaction evaporates all water present in the system, forming a powdery salt. Approximately 6,000 million tons were produced in 1981.

- Ammonium sulfate also is manufactured from gypsum ($CaSO_4·2H_2O$). Finely divided gypsum is added to an ammonium carbonate solution. Calcium carbonate precipitates as a solid, leaving ammonium sulfate in the solution.
- $(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3$
- Ammonium sulfate occurs naturally as the rare mineral mascagnite in volcanic fumaroles and due to coal fires on some dumps

Properties

- Ammonium sulfate becomes ferroelectric at temperatures below –49.5 °c. At room temperature it crystallises in the orthorhombic system, with cell sizes of a = 7.729 å, b = 10.560 å, c = 5.951 å. When chilled into the ferrorelectric state, the symmetry of the crystal changes to space group pna

Uses

- The primary use of ammonium sulfate is as a fertilizer for alkaline soils. In the soil the ammonium ion is released and forms a small amount of acid, lowering the ph balance of the soil, while contributing essential nitrogen for plant growth. The main disadvantage to the use of ammonium sulfate is its low nitrogen content relative to ammonium nitrate, which elevates transportation costs.
- It is also used as an agricultural spray adjuvant for water-soluble insecticides, herbicides, and fungicides. There, it functions to bind iron and calcium cations that are present in both well water and plant cells. It is particularly effective as an adjuvant for 2,4- D (amine), glyphosate, and glufosinate herbicides.

Potassium Nitrate - KNO_3

Potassium Nitrate (KNO_3)

KNO_3 is a chemical compound with the chemical name Potassium Nitrate.

Potassium nitrate also called ***saltpetre or nitre*** is a white solid soluble in water formed by fractional crystallisation of sodium nitrate and potassium chloride solutions. It occurs naturally as nitre in rocks in India, South Africa and Brazil. When heated it decomposes to give the nitrite and oxygen. Unlike sodium nitrate it is non-deliquescent. Potassium nitrate is used in gunpowder, fertilisers and in the laboratory preparation of nitric acid.

Potassium nitrate is the most common desensitising agent in over-the-counter dentifrices. At a concentration of 5%, potassium nitrate in conjunction with sodium or monofluorophosphate fluoride significantly reduces symptoms within 2 weeks of daily use. Potassium ions penetrate the length of the dentinal tubule and block the repolarization of the nerve ending.

Frequent and regular application of a potassium nitrate dentifrice is necessary to avoid recurrence of symptoms, maintain a high abundance of extracellular potassium ions, and maintain the interdental nerves in a hyperpolarized state. Potassium nitrate, often called saltpetre, occurs as an efflorescence in caverns and on soils in arid regions.

Synthesis of Potassium Nitrate (KNO_3)

Potassium nitrate is a salt. It is prepared by neutralising acid. When potassium hydroxide neutralises nitric acid potassium nitrate is formed.

$$KOH + HNO_3 \rightarrow KNO_3 + H_2O$$

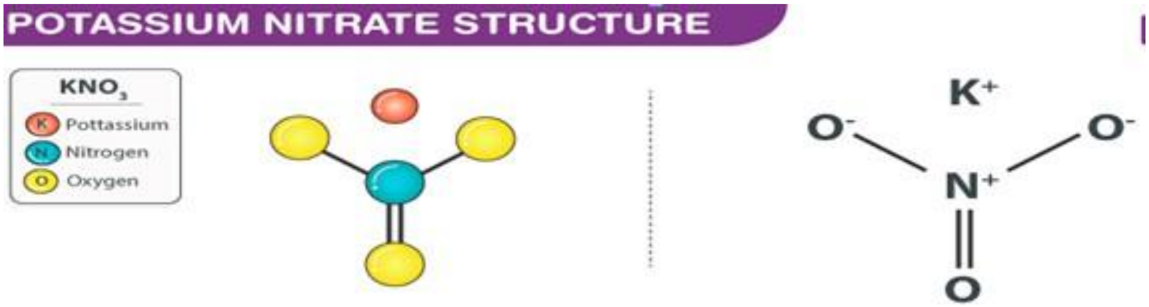
Neutralising nitric acid always makes ***"nitrate"*** salts. Other acids make other types of salts.

Potassium nitrate contains potassium (a soft, light, and silver metal), oxygen, and nitrogen (a colourless and odourless gas). It is an alkali metal nitrate because it is an ionic salt of potassium ions K^+ ions and nitrate ions NO_3^-. It is solid white or sometimes white to dirty grey in colour. Potassium nitrate is soluble in hot water. This compound releases oxygen when heated or decomposed. It is a strong oxidising agent It is widely used in the removal of stumps, fireworks, fertilisers, etc. It is a major constituent of black powder and food preservation techniques.

Properties of Potassium Nitrate – KNO_3

KNO_3	Potassium Nitrate
Molecular Weight/ Molar Mass	101.1032 g/mol
Density	2.109 g/cm^3
Boiling Point	400 °C
Melting Point	334 °C

Potassium Nitrate structure (KNO_3 Structure)



Potassium Nitrate Structure

Potassium Nitrate (KNO_3) Uses

- It is used as a form of fertiliser as it contains all the macronutrients needed for the plants to grow.
- It is used as gunpowder in explosives such as bombs, grenades, etc.
- Used in the manufacturing and production of cigarettes.
- It is used extensively used in the preservation of hides
- It has medicinal applications such as a diuretic in medicine
- Used in toothpaste to make the teeth less sensitive to pain

- Used in the food industry to preserve meat against microbial agents

Nutritional Value of Potassium Nitrate

Potassium nitrate is effectively absorbed. The synergistic interaction of K^+ and NO_3– makes it easier for the plant to absorb both nutrients through its roots. Additionally, the negative charge of nitrate and the positive charge of potassium have an affinity for one another, which reduces the likelihood of soil particles being absorbed and prolongs the time that they are available to plants.

Potassium nitrate boosts a plant's defence resistance against diseases. Short-chain carbohydrates and non-protein nitrogen buildup, which serves as a barrier against bacteria, fungi, nematodes, and viruses, are removed. Potassium nitrate enhances soil water absorption, encourages the commencement and ramification of the root system, and makes plants more drought-tolerant.

Potassium nitrate's potassium content stops water loss. Because potassium controls the opening and shutting of the stomata, it helps plants use less water by reducing transpiration. Additionally, supplying plants with enough potassium boosts their ability to absorb water from the soil. The salt buildup is prevented by potassium nitrate. Potassium nitrates take the place of the need for more water to remove salts from the soil.

Potassium Nitrate (KNO_3) Health Hazards

- **Potential exposure –** Potassium Nitrate is used in chemical analysis, as a food additive in fertilisers in medications as a vasodilator and as an antidote for cyanide poisoning.
- **Short term exposure –** Potassium nitrate can affect when breathed in. Contact can cause eye and skin burns. Breathing the dust or mist can irritate the nose, throat and lungs and may cause coughing with phlegm. Higher exposures can cause pulmonary edema, a medical emergency that can be delayed for several hours. This can cause death.
- **Long term exposure –** Repeated skin contact causes dermatitis, drying and cracking. May cause lung irritation, bronchitis may develop. There is limited evidence that potassium nitrite may damage the developing foetus.

- **Medical surveillance –** If symptoms develop or overexposure is suspected, the following may be useful, blood test for methemoglobin. Lung function tests. Consider chest X-ray after acute overexposure.
- Potassium nitrate is an inorganic salt which has a molecular KNO3 formula. This is a common form of nitrate which has been used for numerous uses as a component, including agricultural preservatives, fertilisers, tree stump removal, rocket propellants, and fireworks.
- Potassium nitrate is a common active ingredient that exerts an anti-sensitive effect in toothpaste. It offers enhanced protection against the painful sensitivity of the teeth to ice, sun, acids, sweets or touch.

The letters "NPK" on a fertilizer label stand for nitrogen, phosphorus, and potassium, the three primary nutrients plants need to grow. The numbers on the label indicate the ratio (by percentage) of nitrogen, phosphorus, and potassium in the fertilizer container.

Even if you do not see the letters N-P-K, but you see a set of three numbers, for example, 5-10-5, you can correctly assume it stands for 5% nitrogen, 10% phosphorus, and 5% potassium, always in that order. This fertilizer contains 20% nutrients; the remaining 80% is minor nutrients or fillers. Plants need about 16 nutrients; some they get from the air and water, and others are nutrients like iron, calcium, and chlorine from soil.

Nitrogen

Nitrogen, the first number referenced in an NPK sequence, plays a key role in a plant's coloring and chlorophyll production, making it an important factor in leaf development. Fertilizers high in nitrogen are often used for grass or other plants where green foliage growth is more important than flowering. At the opposite end of the spectrum, gardeners sometimes encounter the problem of nitrogen depletion—the yellowing of typically green plants often indicates a nitrogen deficiency.

Phosphorus

The middle number in an NPK series refers to the percentage of phosphorous in the fertilizer product. Phosphorus plays a key role in the growth of roots, blooming, and fruiting, which is why it is an essential nutrient for your plants in spring. Phosphorus contributes to many fundamental plant processes, such as rooting and seed formation.

Potassium

The final number in the major ingredients listing gives the percentage of potassium in the product. Potassium contributes to the overall health and vigor of plants. It is known to help strengthen plants' ability to resist disease, assist in the movement of water and nutrients in the plant, and can be especially important in areas that experience cold or dry weather.[2]

Other Ingredients

In addition to the major nutrients that are usually noted on the front label, most fertilizers also include additional ingredients that are listed on a side or back label. This may include other nutrients like calcium, magnesium, iron, micronutrients, and even the percentage of organic matter and fillers. Although the minerals and micronutrients are less critical than the major nutrients, a good fertilizer product will include small amounts of other ingredients as well.

Types of NPK Fertilizers

Balanced Fertilizers

A fertilizer listed as "10-10-10" is considered a balanced or "complete" fertilizer because its nitrogen, phosphorus, and potassium proportions are equal. Meanwhile, a fertilizer labeled "10- 0-10" is an "incomplete fertilizer."

Incomplete Fertilizers

An incomplete fertilizer is not necessarily inferior to a complete fertilizer. Identifying the right fertilizer for your needs depends on a variety of circumstances. If your soil already has an excess of one of the three nutrients in NPK, you could be harming some of your plants by adding more of it to the soil—in this case, an incomplete or unbalanced fertilizer may be the right choice.

For this reason, it is important to test your soil before applying fertilizer. Otherwise, whenever you add anything to your soil, the effect (whether positive or negative) is left to chance.

Organic Fertilizers

Organic fertilizer ingredients are soil nutrients from plant, animal, or mineral sources. Products labeled as "organic fertilizers" must specify which nutrients are organic and must be identified as synthetic or natural by percentage. For example, the label might read, "20 percent of nitrogen (6 percent synthetic, 14 percent organic)."

Organic fertilizer sources might include manure, alfalfa meal, kelp, blood and bone meal, fish emulsion, cottonseed, sewage sludge, soft rock phosphate, and green sand.

What Does "Organic" Mean in Fertilizer

Technically speaking, "organic" material is anything that contains carbon atoms. The modern definition of "organic" means it doesn't contain anything synthetic; however, "organic fertilizers" may have natural or synthetic materials, but the percentages of each must be marked. So, if what you want is "non-synthetic fertilizer," read the label carefully for all ingredients before purchasing since the term "organic" does not cover it.

Worthy of note: Organic fertilizers made wholly from natural ingredients often have lower concentrations of the three major nutrients, so you will often need to use larger amounts. The upside is they usually contain many additional nutrients that feed the plant and the soil. It is strongly recommended that if you are only using commercial synthetic fertilizer, supplement it with some type of organic matter, such as compost or manure, for more holistic soil health.

Superphosphate

Triple superphosphate is a component of fertilizer that primarily consists of monocalcium phosphate, $Ca(H_2PO_4)_2$. Triple superphosphate is obtained by treating phosphate rock with phosphoric acid. Traditional routes for extraction of phosphate rock uses sulfuric acid gives **single superphosphate**, an approximate 1:1 mixture of $Ca(H_2PO_4)_2$ and $CaSO_4$ phosphogypsum). **Double superphosphate** refers to some average of triple- and single superphosphate, resulting from the extraction of phosphate rock with a mixture of phosphoric and sulfuric acids.

Many fertilizers are derived from triple superphosphate, e.g. By blending with ammonium sulfate and potassium chloride. Typical fertilizer-grade triple superphosphate contains 45% $p_2o_5$eq, single superphosphate 20% $p_2o_5$eq.

Triple Superphosphate

Triple superphosphate (TSP) was one of the first high-analysis phosphorus (P) fertilizers that became widely used in the 20th century. Technically, it is known as calcium dihydrogen phosphate and as monocalcium phosphate, $[Ca(H_2PO_4)_2 .H_2O]$. Despite its excellent history as a P source, its use has declined as other P fertilizers have become more popular.

Production

The concept of TSP production is relatively simple. Manufacturers make nongranular TSP typically by reacting finely ground phosphate rock with liquid phosphoric acid in a cone-type mixer. Granular TSP is made similarly, but the resulting slurry is sprayed as a coating onto small particles to build granules of the desired size. The product from both production methods then cures for several weeks as the chemical reactions are slowly completed. The chemistry and process of the reaction will vary somewhat depending on the properties of the phosphate rock.

Agricultural use

TSP has several agronomic advantages that made it such a popular P source for many years. It has the highest P content of dry fertilizers that don't contain nitrogen (N). Over 90 percent of the total P in TSP is water soluble, so it becomes rapidly available for plant uptake. As soil moisture dissolves the granule, the concentrated soil solution becomes acidic. TSP also contains 15 percent calcium (Ca), providing an additional plant nutrient.

A major use of TSP is in situations where several solid fertilizers are blended together for broadcasting on the soil surface or for application in a concentrated band beneath the surface. It’s also desirable for fertilization of leguminous crops, such as alfalfa or beans, where no additional N fertilization is needed to supplement biological N fixation.

Management practices

The popularity of TSP has declined because the total nutrient content ($N + P_2O_5$) is lower than ammonium phosphate fertilizers such as monoammonium phosphate, which by comparison contains 11 percent N and 52 percent phosphorous pentoxide (P_2O_5). Costs of producing TSP can be higher than ammonium phosphates, making the economics for TSP less favorable in some situations.

All P fertilizers should be managed to avoid losses in surface-water runoff from fields. Phosphorus loss from agricultural land to adjacent surface water can contribute to undesired stimulation of algae growth. Appropriate nutrient management practices can minimize this risk.

Non-agricultural uses

Monocalcium phosphate is an important ingredient in baking powder. The acidic monocalcium phosphate reacts with an alkaline component to produce carbon dioxide, the leavening for many baked products. Monocalcium phosphate is commonly added to animal diets as an important mineral supplement of both P and Ca.

UNIT III

The Fundamental Concepts in Organic Reaction Mechanism

Fission of a Covalent Bond

A covalent bond can undergo Fission in two ways:

- **Homolytic Fission:** Also referred to as Homolysis, Homolytic fission refers to the process wherein each of the atoms acquires one of the bonding electrons.
- **Heterolytic Fission:** Also referred to as Heterolysis, Heterolytic Fission refers to the

process wherein when the bond is broken, one of the atoms acquires both of the bonding electrons.

In case B is more electronegative than A, further to acquires both the bonding electrons and becomes negatively charged. The products of heterolytic fission are ions.

Organic Reaction Mechanism: Inductive Effect

The frequently observed electron displacement effects in the substrate molecules are as following: it is a permanent effect which comes into existence when an electron is withdrawing or an electron donating group is attached to a chain of singly bonded carbon atoms.

The displacement of sigma-electrons along a saturated carbon chain due to the presence of an electron withdrawing group or electron repelling group at one end of the chain resulting in the development of partial positive or partial negative charges in the decreasing order of magnitude is called an inductive effect or I effect.

Organic Reaction Mechanism: Electromeric Effect

Electromeric effect or E effect refers to the complete transfer of the shared pair of pie electrons of multiple bonds to one of the shared atoms in the presence of an attacking reagent.

Resonance Effect (Mesomeric Effect)

Resonance refers to the phenomenon in which a molecule is represented by several electronic structures which do not differ much in their energy contents and are obtained by the oscillation of pie electrons. Such structures are called canonical forms and the molecule is said to be a resonance hybrid of these canonical forms.

The permanent effect involving the transfer of electron relayed through pie electrons of multiple bonds in a chain of carbon atoms in a molecule is called the mesomeric effect. The mesomeric effect is a permanent effect and comes into existence in the following two cases:

- when electron withdrawing or electron pumping group is in conjugation with a pie bond.
- when an atom or group having at least one lone pair of electron is in conjugation with a pie bond.

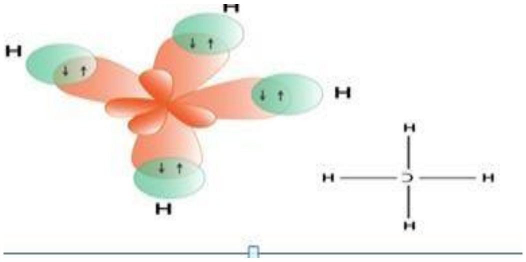
Hybridization of CH4 (Methane)

In order to understand the hybridization of CH_4 (methane), we have to take a look at the atomic orbitals which are of different shape and energy that take part in the process. The type of hybridization involved with CH4 is sp^3. We will discuss in detail how this hybridization occurs below.

Name of the Molecule	Methane
Molecular Formula	CH_4
Hybridization Type	sp^3
Bond Angle	109.5^o
Geometry	Tetrahedral

What is the Hybridization of Methane?

When we talk about CH4 it is basically a combination of 1 carbon and 4 hydrogen atoms. However, to form this compound the central atom carbon which has 4 valence electrons obtain more electrons from 4 hydrogen atoms to complete its octet. When the electrons are shared between carbon and hydrogen there is a formation of a covalent bond or bonds to be more accurate.



Now coming to the hybridization of methane, the central atom carbon is sp^3 hybridized. This is because one 2s orbital and three 2p orbitals in the valence shell of carbon combine to form four sp^3 hybrid orbitals which are of equal energy and shape. Further, four H atoms also use these four sp^3 hybrid orbitals of carbon to form C-H sigma bonds which ultimately leads to the formation of the methane molecule.

Important Points to Remember

- Each sp^3 hybrid orbital of carbon overlaps 1s-orbital of hydrogen to C-H sigma bonds.
- The hybridization involves the mixing of 1 s orbital and 3 p orbitals and there are no lone pairs.
- The sp^3 hybrid orbitals are of equal energy and shape. They contain one unpaired electron each.

CH_4 Molecular Geometry and Bond Angles

We have already discussed the bond formation and hybridization process above. Determining CH_4 molecular geometry should be easier. In methane, the four hybrid orbitals are located in such a manner so as to decrease the force of repulsion between them. Nonetheless, the four orbitals do repel each other and get placed at the corners of a tetrahedron. CH_4 has a tetrahedral shape. The sp^3 hybrid orbitals have a bond angle of 109.5^o.

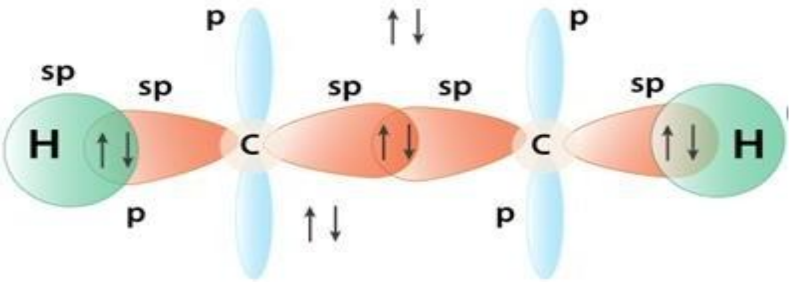
Hybridization of C_2H_2 - Acetylene (Ethyne)

Students will find the explanation of hybridization of C_2H_2 (ethyne) on this page. The type of hybridization that exists in this chemical compound is sp type. To understand the process students have to learn about the bonding and the orbitals. We will discuss everything in detail below.

Name of the Molecule	Acetylene or Ethyne
Molecular Formula	C_2H_2
Hybridization Type	sp
Bond Angle	180^o
Geometry	Linear

What is the Hybridization of Ethyne?

When we break down ethyne molecules it basically consists of 2 CH molecules. However, we will take first take both carbon and hydrogen molecule separately and draw their orbital diagrams. When we do this we will see that carbon has 6 electrons and hydrogen has one electron.



Now, if we see the electronic configuration of carbon in its ground state it will be represented as $1s^2\,2s^2\,2p^2$. When it gets into an excited state, one of the electron from 2s orbital will move or jump to the 2pz orbital and the electronic configuration will change to $1s^2\ 2s^1\ 2px^1 2py^1\ 2pz^1$. Meanwhile, the CH molecule has only 1 hydrogen atom, therefore the $2s^1$ and the $2pz^1$ orbitals get hybridised. This further leads to the formation of 4 sp hybridized orbitals wherein each CH molecule will form 2 hybridized sp orbitals.

During hybridization, C-C sigma bond is formed when one sp orbital overlaps from each of the carbons and two C-H bonds are created when second sp orbital on each carbon overlaps with 1s orbital of hydrogen. In this, the carbon atom will have two half-filled 2p orbitals. These two pairs of p orbitals do not participate in the hybridization and instead form two pi bonds resulting in the creation of a triple bond.

Important Points to Remember

- In the formation of C_2H_2, the carbon atom needs extra electrons to form 4 bonds with hydrogen and other carbon atoms. As a result, one $2s^2$ pair is moved to the empty 2pz orbital.
- The 2s orbital in each carbon hybridizes with one of the 2p orbitals and forms two sp hybrid orbitals.
- Ethyne has a triple bond between the two carbon atoms.

C_2H_2 Molecular Geometry and Bond Angles

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

As a result of the double bond C_2H_2 molecular geometry is linear with a bond angle of 180^0

Hybridization of C_2H_4 - Ethene (Ethylene)

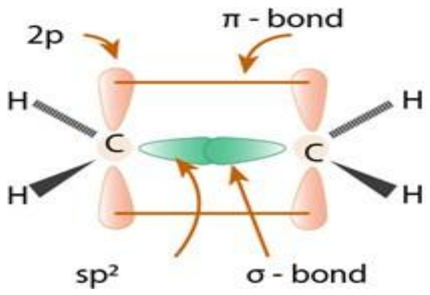
To know about the hybridization of C_2H_4 (ethene or ethylene) students have to recognize or understand the number of bond and the orbitals present in the molecule. This will help in determining the hybridization type and other details. C_2H_4 is sp^2 hybridized.

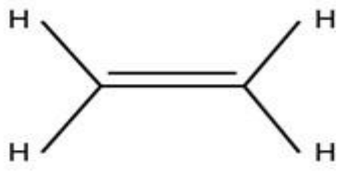
Name of the Molecule	**Ethene or Ethylene**
Molecular Formula	C_2H_4
Hybridization Type	sp^2
Bond Angle	120^o
Geometry	Planar

What is the Hybridization of Ethene?

Let us look at how the hybridization of ethene (ethylene) occurs. When we look at the molecules of C_2H_4 it has 2 CH molecules and 4 H molecules. The carbon atom consists of 6 electrons and hydrogen has 1 electron.

During the formation of $CH_2=CH_2$, the electronic configuration of carbon in its ground state ($1s^2\ 2s^2\ 2p^1\ 2p^1$) will change to an excited state and change to $1s^2\ 2s^1\ 2px^1 2py^1\ 2pz^1$. In the excited state, since carbon needs electrons to form bonds one of the electrons from $2s^2$ orbital will be shifted to the empty 2pz orbital to give 4 unpaired electrons.





Ethene

Meanwhile, out of 2s, 2px, 2py, and 2pz orbitals in carbon, only 2px, 2py, and 2s take part in hybridization. One 2pz orbital remains unchanged. This leads to the formation of three sp^2 hybridized orbitals. The hybrid orbitals look like sp^3 orbitals, but they are sp^2 orbitals as they are fatter and shorter.

The molecular orbitals after hybridization now form different bonds between the electrons. One carbon atom overlaps the sp^2 orbital of another carbon atom to form $sp^2 – sp^2$ sigma bond. The two sp^2 hybrid orbitals get overlapped by two hydrogen atoms containing unpaired electrons. A pi bond is formed by the unhybridized 2pz orbitals of each carbon atom.

Important Points To Remember

- In ethene molecule, the carbon atoms are sp^2 hybridized. One unpaired electron in the p orbital remains unchanged.
- In ethylene, each carbon combines with three other atoms rather than four.
- There is a formation of a sigma bond and a pi bond between two carbon atoms.

C_2H_4 Molecular Geometry And Bond Angles

C2H4 molecular geometry is said to be planar in structure while the sp^2 orbitals are placed at a bond angle of 120^o.

Hybridization of Benzene (C_6H_6)

The hybridization of benzene is said to be sp^2 type. Benzene consists of 6 carbon and 6 hydrogen atoms where the central atom usually is hybridized. Here, carbon is the central atom.

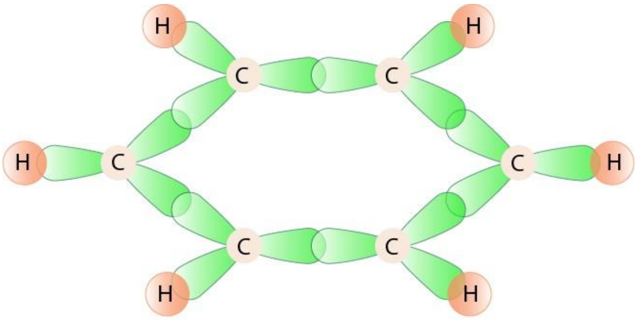
Students will understand all the mechanisms involved in the occurrence of hybridization in this lesson. We will look at the details below.

Name of the Molecule	Benzene
Molecular Formula	C_6H_6
Hybridization Type	sp^2
Bond Angle	120^o

Geometry	Trigonal Planar

What is the Hybridization of Benzene?

Before we talk about the hybridization of C_6H_6 let us first understand the structure of benzene. This chemical compound is made from several carbon and hydrogen atoms. However, to form benzene, the carbon atoms will need one hydrogen and two carbons to form bonds. Further, the carbon atom lacks the required number of unpaired electrons to form the bonds. At this stage its electronic configuration will be $1s^2$, $2s^2$, $2px^1$, $2py^1$. What happens next is the promotion of one $2s^2$ electron pair to the empty 2pz orbital.



σ bond framework

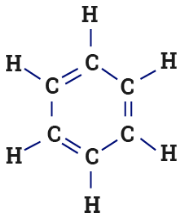
During this, the carbon atom will enter into an excited state and the electron configuration will also change to become $1s^2$, $2s^1$, $2px^1$, $2py^1$, $2pz^1$. Now when the electron is promoted from the 2s to the empty 2p orbital, we will get 4 unpaired electrons. These electrons will be used in the formation of the bonds. For, hybridisation to occur the outer orbitals are used. Three of the carbon orbitals are used rather than all four. In this, 1 s orbital and two p orbitals are hybridized and form three sp^2 hybridized orbitals. Each of the carbon atoms will form sigma bonds with two other carbons and one hydrogen atom.

Important Points to Remember

- Benzene is a combination of carbon and hydrogen atoms.
- The hybridization is sp^2 type.

- During the hybridization of benzene, each carbon atom forms different bonds with two other similar carbon atoms instead of just one.

Benzene Molecular Geometry and Bond Angles



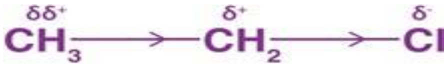
The carbon atoms in the benzene ring are arranged in a trigonal planar geometry. The hybrid orbitals are arranged at an angle of 120° to each other in a plane while the p orbitals are at right angles to them.

Inductive Effect

The **inductive effect** refers to the phenomenon wherein a permanent dipole arises in a given molecule due to the unequal sharing of the bonding electrons in the molecule. This effect can arise in sigma bonds, whereas the electromeric effect can only arise in pi bonds.

What Is the Inductive Effect?

When an electron-releasing or an electron-withdrawing species is introduced to a chain of atoms (generally a carbon chain), the corresponding negative or positive charge is relayed through the carbon chain by the atoms belonging to it. This causes a permanent dipole to arise in the molecule and is referred to as the inductive effect.



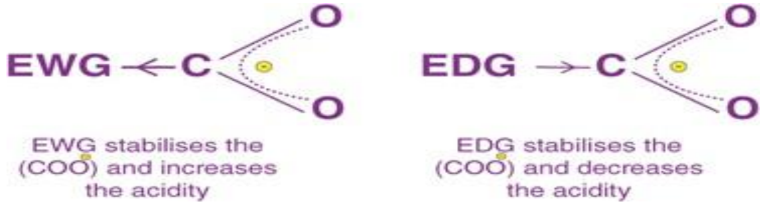
$$\overset{\delta\delta^+}{CH_3} \longrightarrow \overset{\delta^+}{CH_2} \longrightarrow \overset{\delta^-}{Cl}$$

Inductive Effect on Acidity and Basicity

Using the inductive effect, we can predict the acidity and basicity of compounds. As a generalization, it may be said that the electron-withdrawing groups (EWG) increase the acidity of a compound, and the electron-donating group decrease the acidity of a compound.

This is because, if we take the conjugate base of the acid, that is, RCOO-, if R is electron-withdrawing, then the conjugate base is stabilized via delocalization of the formed negative charge.

If R had been electron-donating, then the conjugate base would have been destabilized because of inter-electronic repulsions.



Thus, it can be said that +I groups decrease acidity (or increase basicity) and –I groups increase the acidity (or decrease basicity) of compounds.

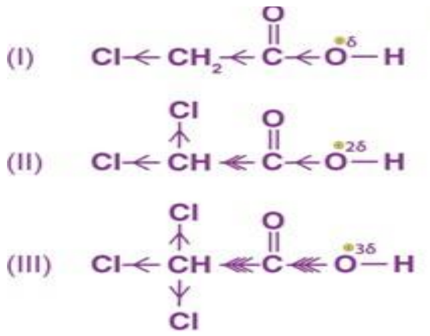
For example, formic acid (HCOOH) is more acidic than acetic acid (CH3COOH) due to the +I inductive effect of the methyl group attached to the carboxylic acid group.

$$H-\overset{\overset{O}{\|}}{C}-O-H \; > \; CH_3 \rightarrow \overset{\overset{O}{\|}}{C} \rightarrow \overset{\ominus\delta}{O}-H$$

(I) (II)

Note: If the Ka of acid is high, it is a strong acid, but if the PKa of acid is high, it is said to be a weak acid [pka = -log(ka)]. The same logic applies to bases.

Consider the acidity of mono-, di- and trichloroacetic acid.



It can be said that the presence of three Cl atoms makes oxygen highly electron deficient and, thereby, polarising the O-H bond the most. Therefore, the acidity order for the above compounds would be III > II > I.

Types of Inductive Effect

- Negative inductive effect or -I effect
- Positive inductive effect +I effect

-I Effect (Negative Inductive Effect)

When an electronegative atom, such as a halogen, is introduced to a chain of atoms (generally, carbon atoms), the resulting unequal sharing of electrons generates a positive charge which is transmitted through the chain.

This causes a permanent dipole to arise in the molecule wherein the electronegative atom holds a negative charge, and the corresponding effect is called the electron-withdrawing inductive effect or the -I effect.

+I Effect (Positive Inductive Effect)

When a chemical species with the tendency to release or donate electrons, such as an alkyl group, is introduced to a carbon chain, the charge is relayed through the chain, and this effect is called the positive inductive effect or the +I effect.

Inductive Effect on Stability of Molecules

The charge on a given atom and the charge on a group bonded to the atom plays a strong part when determining the stability of the resulting molecule as per the inductive effect.

An example of this can be observed when a group displaying the -I effect is bonded to a positively charged atom, and the positive charge on the resulting molecule is amplified, reducing its stability.

On the other hand, when a negatively charged atom is introduced to a group displaying a -I effect, the charge disparity is somewhat quenched, and the resulting molecule would be stable as per the inductive effect.

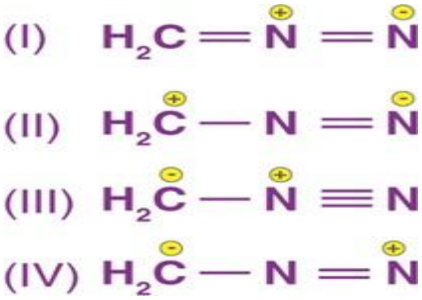
Also,

When a group displaying the -I effect is bonded to a molecule, the electron density of the resulting molecule effectively reduces, making it more likely to accept electrons and, thereby, increasing the acidity of the molecule.

When a +I group attaches itself to a molecule, there is an increase in the electron density of the molecule. This increases the basicity of the molecule since it is now more capable of donating electrons.

Applications of the Inductive Effect

Illustration 1:



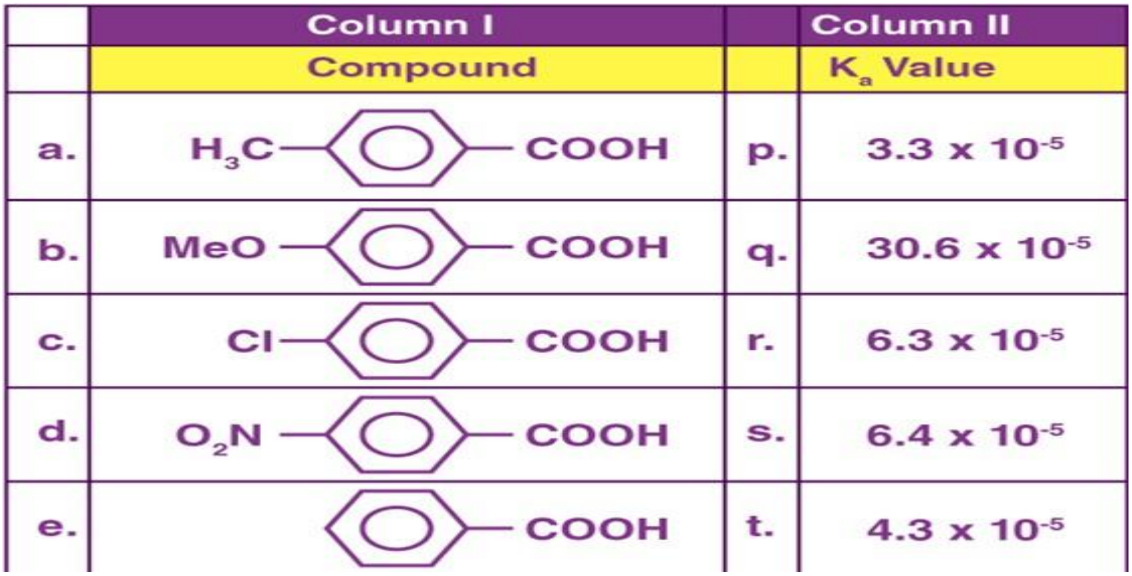
Give the stability of the following canonical forms.

Structures I and III have more covalent bonds and are more stable than II and IV. Between I and III, I is more stable because the negative charge is on an electronegative element.

Between II and IV, II is more stable because of the same reason as said above.

The order is I > III > II > IV

Illustration 2:



	Column I		Column II
	Compound		K_a Value
a.	H_3C–⌬–COOH	p.	3.3×10^{-5}
b.	MeO–⌬–COOH	q.	30.6×10^{-5}
c.	Cl–⌬–COOH	r.	6.3×10^{-5}
d.	O_2N–⌬–COOH	s.	6.4×10^{-5}
e.	⌬–COOH	t.	4.3×10^{-5}

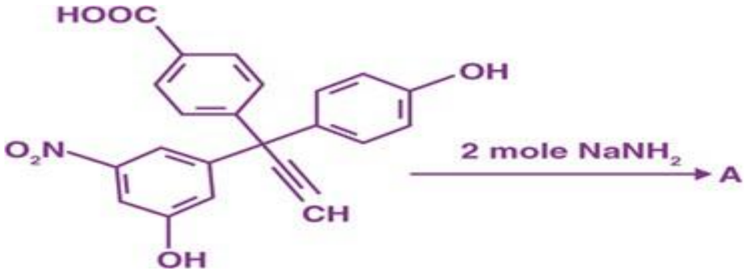
We know that EWG increases acidity and EDG decreases acidity.

-Me group is a +I group, whereas -OMe is an +R group, so –OMe decreases the acidity more strongly than -Me.

Therefore, the order is, d>c>e>a>b

Since ka is directly proportional to acidity, the answer is a→ t, b →p, c→ s, d→ q, e→ r.

Illustration 3:



Solution: $NaNH_2$ is a base; therefore, the most acidic proton of the substrate would react to form a conjugate base. The idea here is to find out the most acidic proton.

There are totally four protons, -COOH, -OH, nitro-substituted –OH and alkyne proton.

Since two moles of the base are used, two protons would react.

The order of acidity of the protons are

-COOH>-OH (Nitro substituted)>-OH> acetylenic proton

So the product would be,

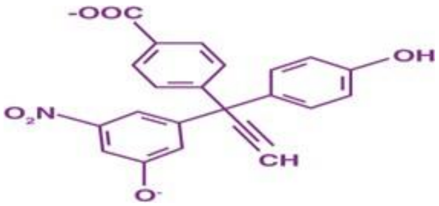
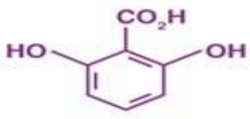
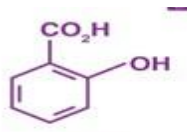


Illustration 4: The order of acidity of the following compounds is

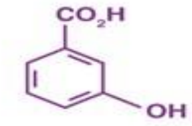
(I)



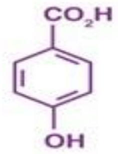
(II)



(III)



(IV)



Solution: To find out the acidity of the compounds, remove the proton and check the stability of the conjugate base formed.

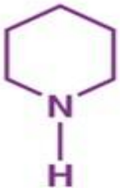
CB of structures I and II are stabilised by intramolecular hydrogen bonding (I more than II).

Between the meta and para isomer, meta would be more acidic due to the –I effect of oxygen.

Therefore, the order is I>II>III>IV

Illustration 5:

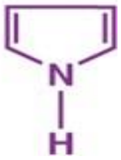
(I)



(II)

(III)

(IV)



Solution: The most basic among the four is I. This is because structures II and IV are aromatic. Between I and III, I is more basic due to the presence of an oxygen atom in III, which decreases basicity by the –I effect.

Between II and IV, II would be more basic because, in IV, the lone pair on nitrogen is delocalised to make the compound aromatic. The non-availability of the lone pair for donation makes IV the least basic.

Therefore, the order is I > III > II > IV.

Inductive Effect vs Electromeric Effect

A tabular column highlighting the key differences between the electromeric and the inductive effects can be found below.

Inductive Effect	**Electromeric Effect**
Works on sigma bonds	Works on pi bonds
The inductive effect is permanent	The electromeric effect is a temporary effect
It doesn’t require any attacking reagent	An electrophilic attacking reagent is required for this effect to arise

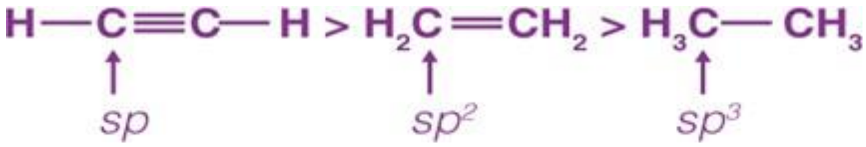
Thus, it can be understood that the +I and -I effect play a vital role in the stability, as well as the acidity or basicity of molecules.

How to Check the Acidity of Organic and Unsaturated Compounds?

To check the acidity of an organic compound, remove the proton and then check the stability of the resulting conjugate base so formed. More the stability of the conjugate base, the stronger the acid.

To check for acidity among unsaturated compounds, check the hybridisation of the carbon involved. The more the s-character on the carbon, the more its electronegativity, and hence, more the acidity.

Therefore, the most acidic amongst alkynes, alkenes and alkanes is Alkynes > Alkenes > Alkanes



$$H-\underset{\substack{\uparrow\\ sp}}{C}\equiv C-H > H_2\underset{\substack{\uparrow\\ sp^2}}{C}=CH_2 > H_3\underset{\substack{\uparrow\\ sp^3}}{C}-CH_3$$

If there is competition among two groups that are electron withdrawing via resonance and via induction, preference is given to the resonance because it affects the whole molecule.

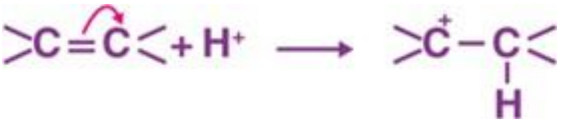
Electron displacement in an organic molecule may take place due to the presence of an appropriate attacking reagent. This kind of electron displacement leads to polarization of the bond. Some effects that feature electron displacement are the electromeric effect and hyperconjugation, a brief explanation of which is provided below:

Electromeric effect:

The electromeric effect is a temporary effect, mainly experienced in the presence of an attacking reagent in the vicinity of an organic compound having multiple bonds(a double or triple bond). In this effect, the complete transfer of a shared pair of π-electrons to one of the atoms joined by multiple bonds on the demand of an attacking reagent takes place. The effect ceases as soon as the attacking reagent is removed from the domain of the reaction. The electromeric effect is mainly categorized into two categories.

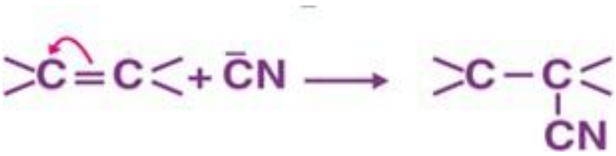
1. ***Positive Electromeric Effect (+E effect):***

   The positive electromeric effect is defined as the transfer of π−electrons of the multiple bonds to the atom with which the reagent gets attached.



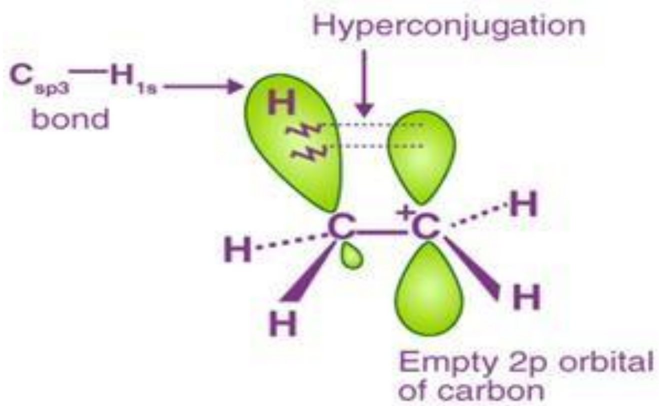
2. ***Negative Electromeric Effect (–E effect):***

   The negative electromeric effect is defined as the transfer of π−electrons of the multiple bonds to the atom with which the reagent does not get attached.



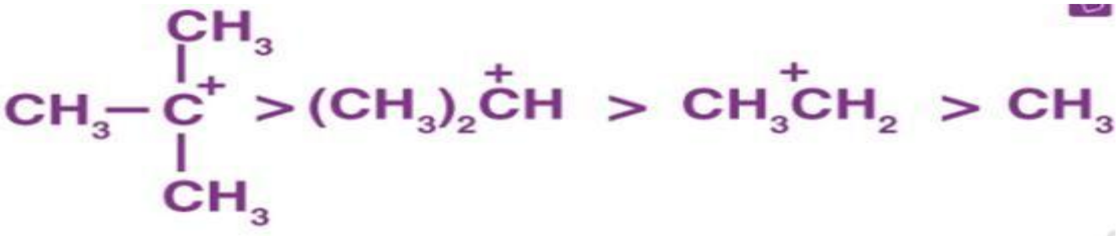
Hyperconjugation:

Hyperconjugation effect is a permanent effect in which localization of σ electrons of C-H bond of an alkyl group directly attached to an atom of the unsaturated system or to an atom with an unshared p orbital takes place.



From the above figure, we observe that one of the three C-H bonds of the methyl group can align in the plane of the empty p orbital and the electrons constituting the C-H bond in a plane with this p orbital can then be delocalized into the empty p orbital.

We also observe that the hyperconjugation stabilizes the carbocation as it helps in the dispersal of positive charges. Thus, we can say that the greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilization of the carbonation. The relative stability on the basis of hyperconjugation is given as,



$$\mathrm{CH_3-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C^{+}}}}} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > CH_3}$$

Steric effects

Steric effects are nonbonding interactions that influence the shape (conformation) and reactivity of ions and molecules. Steric effects complement electronic effects, which usually dictate shape and reactivity. Steric effects result from repulsive forces between overlapping electron clouds. Steric effects are widely exploited in applied and academic chemistry.

Steric hindrance is a consequence of steric effects. Steric hindrance is the slowing of chemical reactions due to steric bulk. It is usually manifested in *intermolecular reactions*, whereas discussion of steric effects often focus on *intramolecular interactions*. Steric hindrance is often exploited to control selectivity, such as slowing unwanted side-reactions.

Steric hindrance between adjacent groups can also affects torsional bond angles. Steric hindrance is responsible for the observed shape of rotaxanes and the low rates of racemization of 2,2'-disubstituted biphenyland binaphthyl derivatives.

Steric effects are usually smaller than electronic effects. These affect the molecule's shape and reactivity as well, but they come from the way electrons are placed in bonds.

The polarity developed between atoms of a conjugated system by the electron transfer or pi–bond electron transfer is known as the mesomeric effect. In simple terms, we can describe that the mesomeric effect occurs when π electrons move away from or towards a substituent group in a

conjugated orbital system

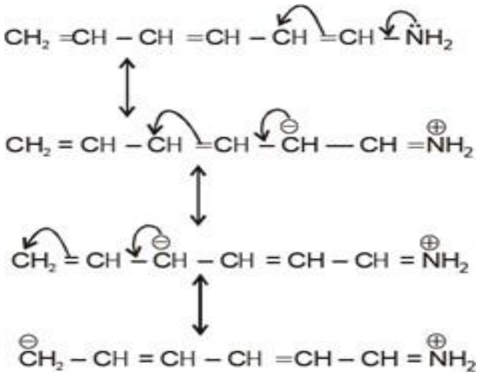
The mesomeric effect can be subdivided into two types:

- +M effect
- -M effect

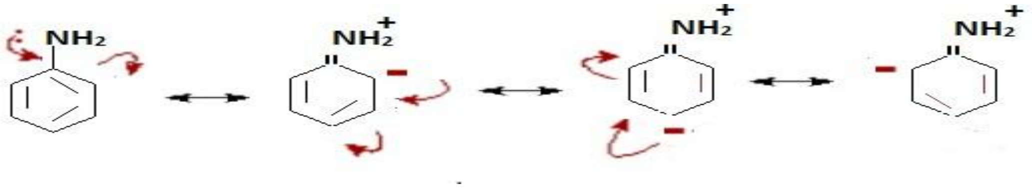
+M effect (Positive mesomeric effect)

When the electrons or the pi electrons are transferred from a particular group towards a conjugate system, thus increasing the electron density of the conjugated system, such a phenomenon is known as the (+M) effect or positive mesomeric effect.

Example 1:



Example 2:



- For the +M effect, the group should have either a lone pair of electrons or should have a negative charge.
- The +M effect gives a negative charge to the conjugate system, or it can be said that the electron density increases in the conjugate system due to this. These conjugate systems show more reactivity towards electrophiles and less reactivity towards a nucleophile.

Group showing +M effect

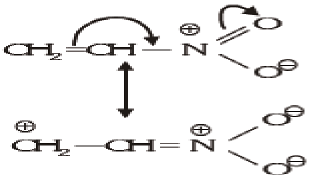
–NH, $–NH_2$,–NHR, $–NR_2$, – O, – OH, –OR, – F, – Cl, –O–COR, – NHCOR, –SH, – SR etc.

Electrophile and Nucleophile

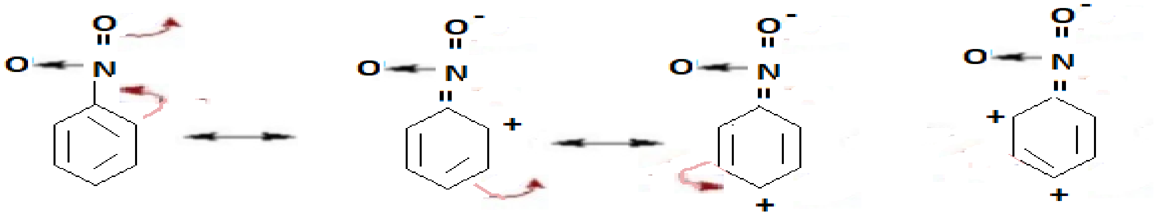
-M Effect (Negative Mesomeric Effect)

When the pi-bond electrons are transferred from the conjugate system to a particular group, the electron density of the conjugate system is decreased, then this phenomenon is known as the negative mesomeric (–M) effect.

Example 1:



Example 2:



- For the –M effect, the group should have either a positive charge or should have a vacant orbital.
- The –M effect makes the compound more reactive towards a nucleophile as it decreases the electron density in the conjugate system, and at the same time, it is less reactive towards electrophile due to the same reasons.

The group which shows the –M effect includes

$–NO_2$, –CN, –COX, $–SO_3H$, – CHO, $–CONH_2$, –COR, –COOH, –COOR etc.

Significance of Mesomeric Effect

- It describes the distribution of the charge in the compound
  and helps to decide the point at which electrophiles or nucleophiles attack.
- Useful in describing physical characteristics, such as dipole moment and bond length.

Mesomeric Effect and Resonance Effect

If two or more different structures can be drawn for a molecule or ion that have the same arrangement of atomic nuclei but differ in the distribution of electrons, this effect can be termed the resonance effect.

The different structures are called contributing or resonating structures. Not all the properties of the molecule or ion are shown by the single resonating structure, but the actual structure is a resonance hybrid of all the resonating structures.

Applications of Mesomeric Effect

Carbocation Stability

Carbocation's stability is enhanced by resonance. All the aromatic compounds are always more stable as compared to non-aromatic compounds due to the effect of resonance.

Also Read: Carbocation

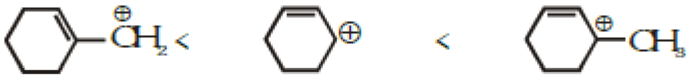
Example: Compare stability order of:

(i)

$$CH_2{=}CH{-}\overset{\oplus}{C}H_2 > CH_3{\rightarrow}CH_2{-}\overset{\oplus}{C}H_2 > CH_2{=}CH{\leftarrow}CH{-}\overset{\oplus}{C}H_2$$

Resonance effect   +I effect   – I effect

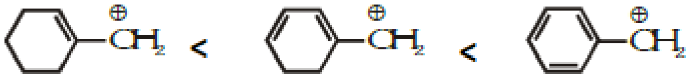
(ii)



1   2   3

1° carbocation   2° carbocation   3° carbocation

(iii)



Resonance increases, and stability increases.

Stability of Carbanion

(a) Carbanion's stability is increased by resonance.

Example: Compare stability order of:

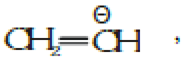
(i)

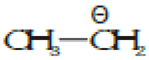
$$CH_2{=}CH{-}\overset{\ominus}{C}H_2 \;,\; CH_2{=}\overset{\ominus}{C}H \;,\; CH_3{-}\overset{\ominus}{C}H_2$$

Resonance effect

The correct order of stability is I > II > III

(ii) 
$CH_2=CH-\overset{\ominus}{C}H_2$,


$CH_2=\overset{\ominus}{C}H$,

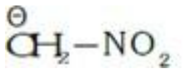

$CH_3-\overset{\ominus}{C}H_2$

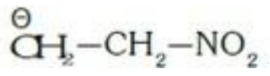
(I)   (II)

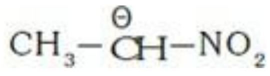
Stable by resonance   more resonance

Stability order II > I.

(iii)


$\overset{\ominus}{C}H_2-NO_2$


$\overset{\ominus}{C}H_2-CH_2-NO_2$


$CH_3-\overset{\ominus}{C}H-NO_2$

Resonance effect   no conjugation, no resonance   resonance effect and + I effect

Stability order I > III > II

Stability of Free Radicals

Electron Displacement Effects

The organic reactions are not possible until and unless some charge or polarity is developed on the reactants, and they get attached to each other. This happens only when there is a displacement of electrons, due to which polarity develops within the reactant molecules. Such effects involving the displacement of electrons in the substrate (reactant) molecules are referred to as “electron displacement effects”.

There are 4 basic electron displacement effects.

1. Inductive effect
2. Electromeric effect
3. Mesomeric effect

4. Hyperconjugation effect

Out of these four effects, the mesomeric effect is the most widely applicable and significant effect. It is also a permanent effect.

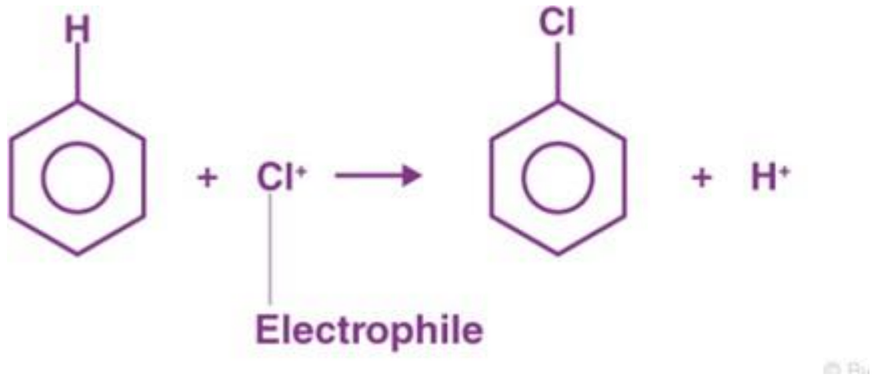
What is an Electrophilic Substitution Reaction?

An electrophilic substitution reaction is a chemical reaction in which the functional group attached to a compound is replaced by an electrophile. The displaced functional group is typically a hydrogen atom. Electrophilic substitution reactions generally proceed via a three-step mechanism that involves the following steps.

- The generation of an electrophile
- The formation of a carbocation (which is an intermediate)
- The removal of a proton from the intermediate

Types of Electrophilic Substitution Reactions

The two primary types of electrophilic substitution reactions undergone by organic compounds are electrophilic aromatic substitution reactions and electrophilic aliphatic substitution reactions. An illustration describing the electrophilic substitution of a hydrogen atom (belonging to a benzene molecule) with a chlorine atom is provided below.



Here, the chlorine cation acts as an electrophile and replaces a hydrogen atom in the benzene ring. The products formed in this electrophilic substitution reaction include a proton and a chlorobenzene molecule.

Electrophilic Aromatic Substitution Reaction

In electrophilic aromatic substitution reactions, an atom attached to an aromatic ring is replaced with an electrophile. Examples of such reactions include aromatic nitrations, aromatic sulphonation, and Friedel-Crafts reactions.

It is important to note that the aromaticity of the aromatic compound is preserved in electrophilic aromatic substitutions. Therefore, these reactions can be used to obtain aryl halides from aromatic rings and iodine, bromine, or chlorine.

Electrophilic Aliphatic Substitution Reaction

In electrophilic aliphatic substitution reactions, an electrophile replaces the functional group (generally hydrogen) in an aliphatic compound. These reactions can be classified into the following five types.

- Halogenation of ketones
- Nitrosation
- Keto-Enol tautomerism
- Insertion of a carbene into a carbon-hydrogen bond
- Diazonium coupling (aliphatic)

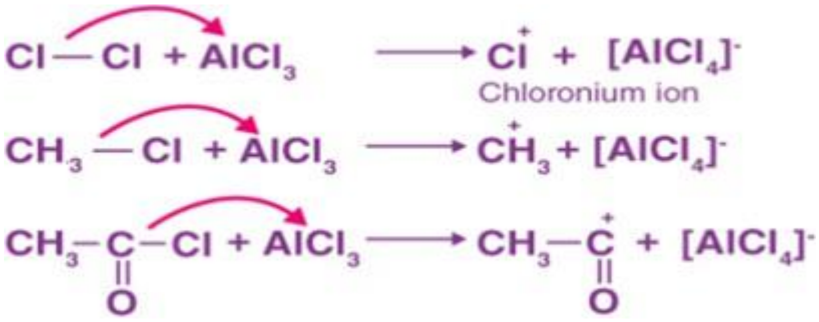
These electrophilic substitution reactions can result in an inversion of configuration if the electrophilic attack occurs at an angle of 180^o to the leaving group (attack from the rear).

Mechanism of Electrophilic Substitution Reaction

The electrophilic substitution reaction mechanism involves three steps.

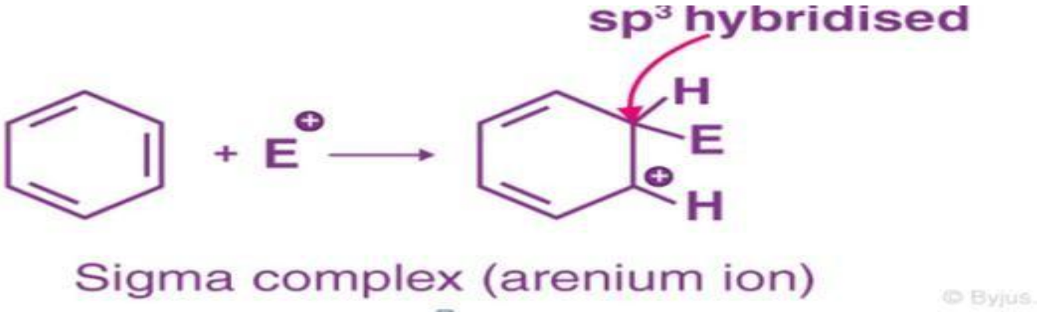
Step 1: Generation of Electrophile

Anhydrous aluminium chloride is a very useful Lewis acid in the generation of electrophile from the chlorination, alkylation, and acylation of an aromatic ring. The resulting electrophiles (from the combination of anhydrous aluminium chloride and the attacking reagent) are Cl^+, R^+, and RC^+O respectively as shown below:

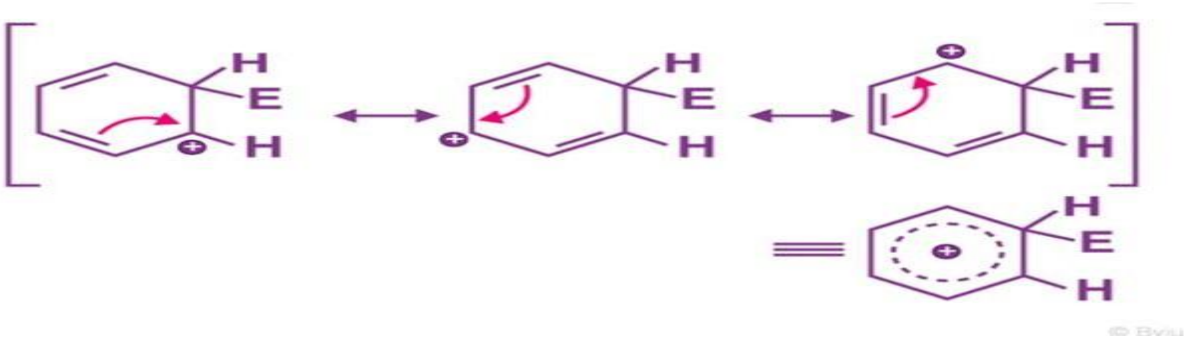


Step 2: Formation of Carbocation

The electrophile attacks the aromatic ring, forming a sigma complex or an arenium ion. One of the carbons in this arenium ion is sp^3 hybridized.

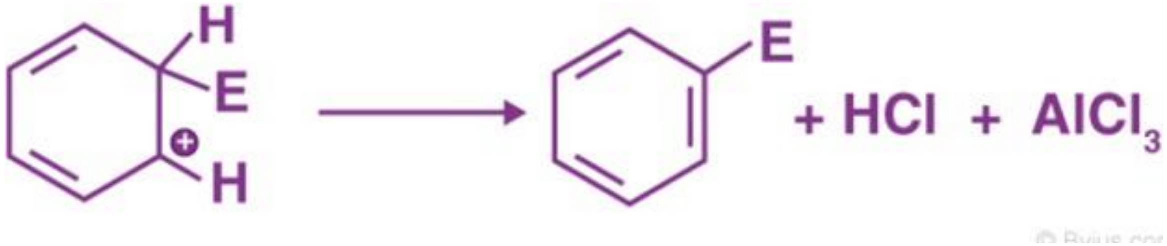


This arenium ion finds stability in a resonance structure. Since the delocalization of electrons stops at the sp^3 hybridized carbon, the sigma complex or the arenium ion loses its aromatic character.



Step 3: Removal of Proton

In order to restore the aromatic character, the sigma complex releases a proton from the sp^3 hybridized carbon when it is attacked by the $[AlCl_4]^-$. The reaction describing the removal of a proton from the sigma complex is given below:



Thus, the electrophile replaces the hydrogen atom in the benzene ring. The electrophilic substitution reaction is a very important reaction in organic chemistry as the concept is used in many organic name reactions.

In 1931, German chemist and physicist Erich Hückel proposed a theory to help determine if a planar ring molecule would have aromatic properties. His rule states that if a cyclic, planar

molecule has 4n+2 ππ electrons, it is considered aromatic. This rule would come to be known as

Hückel's Rule.

Huckel's Rule: Aromatic, Antiaromatic, and Nonaromatic

Huckel's Rule is a set of algorithms that combine the number of π electrons (N) and the physical structure of the ring system to determine whether the molecule is aromatic, antiaromatic, or nonaromatic.

The number of π electrons in an **aromatic** system can be determined by the following algorithm:

$N=4n+2$

where n is an integer.

The number of π electrons in an **antiaromatic** system can be determined by the following algorithm:

N=4n

where n is an integer.

If a compound does not have a continuous ring of conjugated p orbitals in a planar conformation, then it is nonaromatic.

Huckel's Rule is a useful first step in evaluating the potential for a ringed molecule to be aromatic. The planar requirement of the ring may require further investigation.

Four Criteria for Aromaticity

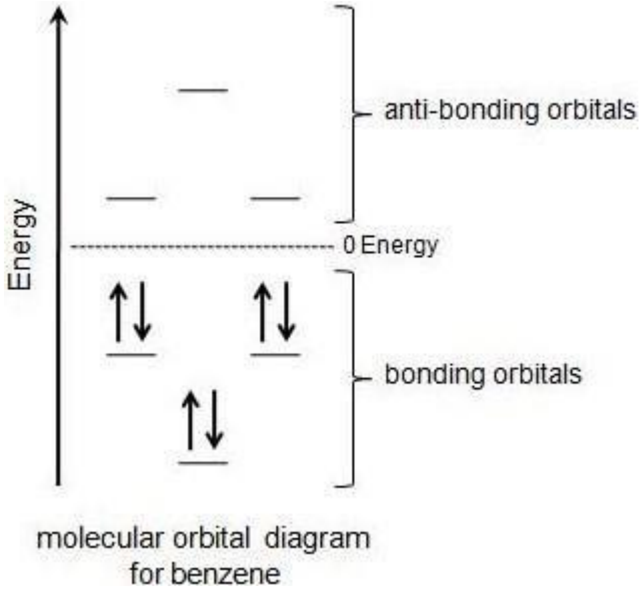
When deciding if a compound is aromatic, go through the following checklist. If the compound does not meet all the following criteria, it is likely not aromatic.

1. The molecule is cyclic (a ring of atoms)
2. The molecule is planar (all atoms in the molecule lie in the same plane)
3. The molecule is fully conjugated (p orbitals at every atom in the ring)
4. The molecule has 4n+2 ππ electrons (n=0 or any positive integer)

Why 4n+2 π� Electrons?

According to Hückel's Molecular Orbital Theory, a compound is particularly stable if all of its bonding molecular orbitals are filled with paired electrons. This is true of aromatic compounds, meaning they are quite stable. With aromatic compounds, 2 electrons fill the lowest energy molecular orbital, and 4 electrons fill each subsequent energy level (the number of subsequent energy levels is denoted by n), leaving all bonding orbitals filled and no anti-bonding orbitals occupied. This gives a total of 4n+2 π electrons. You can see how this works with the molecular orbital diagram for the aromatic compound, benzene, below. Benzene has

6 π electrons. Its first 2 π electrons fill the lowest energy orbital, and it has 4 π electrons remaining. These 4 fill in the orbitals of the succeeding energy level. Notice how all of its bonding orbitals are filled, but none of the anti-bonding orbitals have any electrons.



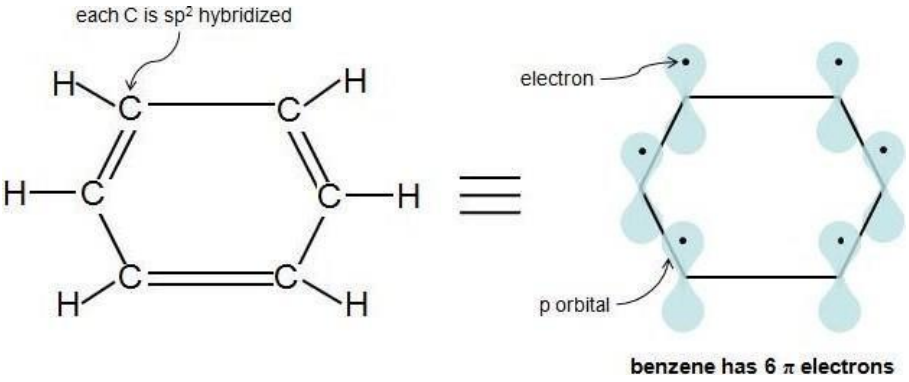
To apply the 4n+2 rule, first count the number of π electrons in the molecule. Then, set this number equal to 4n+24+2 and solve for n. If is 0 or any positive integer (1, 2, 3,...), the rule has been met. For example, benzene has six π electrons:

4n+24nn=6=4=1

For benzene, we find that n=1, which is a positive integer, so the rule is met.

How Can You Tell Which Electrons are π Electrons?

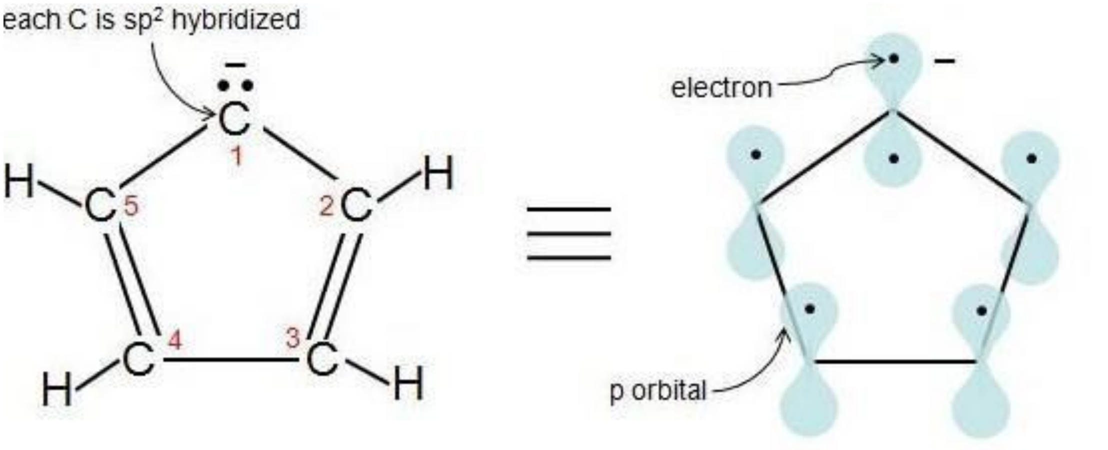
Perhaps the toughest part of Hückel's Rule is figuring out which electrons in the compound are actually π electrons. Once this is figured out, the rule is quite straightforward. Π electrons lie in p orbitals and sp^2 hybridized atoms have 1 p orbital each. So if every carbon atom in the cyclic compound is sp^2 hybridized, this means the molecule is fully conjugated (has 1 p orbital at each atom), and the electrons in these p orbitals are the π electrons. A simple way to know if an atom is sp2 hybridized is to see if it has 3 attached atoms and no lone pairs of electrons. This video provides a very nice tutorial on how to determine an atom's hybridization. In a cyclic hydrocarbon compound with alternating single and double bonds, each carbon is attached to 1 hydrogen and 2 other carbons. Therefore, each carbon is sp^2 hybridized and has a p orbital. Let's look at our previous example, benzene:



Each double bond (π bond) always contributes 2 π electrons. Benzene has 3 double bonds, so it has 6 π electrons.

Aromatic Ions

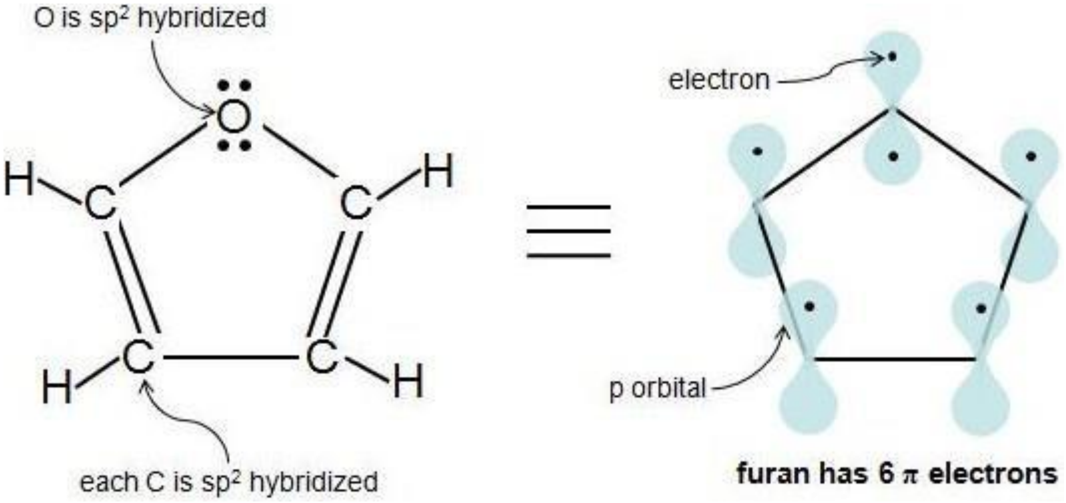
Hückel's Rule also applies to ions. As long as a compound has 4n+2 π electrons, it does not matter if the molecule is neutral or has a charge. For example, cyclopentadienyl anion is an aromatic ion. How do we know that it is fully conjugated? That is, how do we know that each atom in this molecule has 1 p orbital? Let's look at the following figure. Carbons 2-5 are sp^2 hybridized because they have 3 attached atoms and have no lone electron pairs. What about carbon 1? Another simple rule to determine if an atom is sp^2 hybridized is if an atom has 1 or more lone pairs and is attached to an sp^2 hybridized atom, then that atom is sp^2 hybridized also. This video explains the rule very clearly. Therefore, carbon 1 has a p orbital. Cyclopentadienyl anion has 6 π� electrons and fulfills the 4n+2 rule.



cyclopentadienyl anion has 6 π electrons

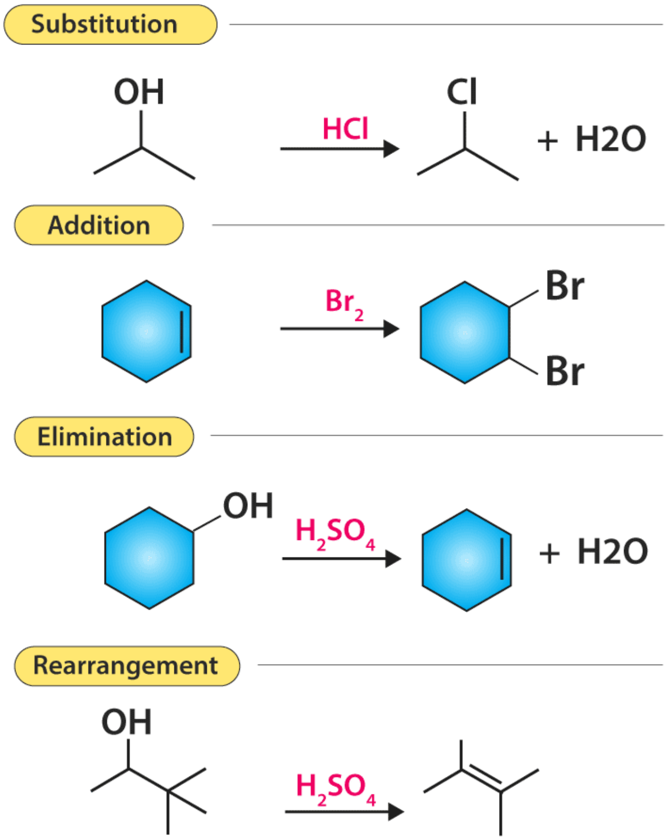
Heterocyclic Aromatic Compounds

So far, you have encountered many carbon homocyclic rings, but compounds with elements other than carbon in the ring can also be aromatic, as long as they fulfill the criteria for aromaticity. These molecules are called heterocyclic compounds because they contain 1 or more different atoms other than carbon in the ring. A common example is furan, which contains an oxygen atom. We know that all carbons in furan are sp^2 hybridized. But is the oxygen atom sp^2 hybridized? The oxygen has at least 1 lone electron pair and is attached to an sp^2 hybridized atom, so it is sp^2 hybridized as well. Notice how oxygen has 2 lone pairs of electrons. How many of those electrons are π electrons? An sp^2 hybridized atom only has 1 p orbital, which can only hold 2 electrons, so we know that 1 electron pair is in the p orbital, while the other pair is in an sp^2 orbital. So, only 1 of oxygen's 2 lone electron pairs are π electrons. Furan has 6 π electrons and fulfills the 4n+2 rule.



Types of Organic Reactions

Organic reactions are the chemical reactions that are undergone by organic compounds (the chemical compounds containing carbon). A few important types of organic reactions are illustrated below.



There are mainly five types of organic reactions:

1. Substitution reaction
2. Elimination reaction
3. Addition reaction
4. Radical reactions
5. Oxidation-Reduction Reactions.

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- Radical Reactions

Substitution Reactions

In a substitution reaction, one atom or a group of atoms is substituted by another atom or a group of atoms to form a new substance.

For example, the conversion of methane to chloromethane is a substitution reaction as hydrogen atoms are replaced by chlorine atoms.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

Elimination reaction

There are some reactions which involve the elimination or removal of the adjacent atoms or group of atoms. After this multiple bonds are formed and there is a release of small molecules as products. One of the examples of elimination reaction is the conversion of ethyl chloride to ethylene.

$$CH_3CH_2Cl \rightarrow CH_2{=}CH_2 + HCl$$

In the above reaction, the eliminated molecule is HCl, which is formed by the combination of H^+ from the carbon atom which is on the left side and Cl– from the carbon atom which is on the right side.

Addition reactions

An addition reaction occurs when two or more reactants combine to form a product without the loss of any atoms present in the reactants. Addition reaction is common in compounds that have unsaturated C-C bonds, like double (alkene) and triple (alkyne) bonds. The weaker π bond is converted into two new stronger σ bonds.

$$HCl + CH_2{=}CH_2 \rightarrow CH_3CH_2Cl$$

Radical reactions

Many of the organic reactions involve radicals. The addition of a halogen to a saturated hydrocarbon involves a free radical mechanism. There are three stages involved in a radical reaction i.e. initiation, propagation, and termination. Initially when the weak bond is broken initiation of the reaction takes place with the formation of free radicals. After that when the halogen is added to the hydrocarbon a radical is produced and finally, it gives alkyl halide.

Friedel-Crafts Reaction

Friedel-Crafts Reaction?

A Friedel-Crafts reaction is an organic coupling reaction involving an electrophilic aromatic substitution that is used for the attachment of substituents to aromatic rings. The two primary types of Friedel-Crafts reactions are the alkylation and acylation reactions. These reactions were developed in the year 1877 by the French chemist Charles Friedel and the American chemist James Crafts.

Friedel-Crafts Reaction

An illustration describing both the Friedel-Crafts reactions undergone by benzene is provided below.

It can be noted that both these reactions involve the replacement of a hydrogen atom (initially attached to the aromatic ring) with an electrophile. Aluminium trichloride ($AlCl_3$) is often used as a catalyst in Friedel-Crafts reactions since it acts as a Lewis acid and coordinates with the halogens, generating an electrophile in the process.

Friedel-Crafts Alkylation

Friedel-Crafts Alkylation refers to the replacement of an aromatic proton with an alkyl group. This is done through an electrophilic attack on the aromatic ring with the help of a carbocation. The Friedel-Crafts alkylation reaction is a method of generating alkylbenzenes by using alkyl halides as reactants.

The Friedel-Crafts alkylation reaction of benzene is illustrated below.

A Lewis acid catalyst such as $FeCl_3$ or $AlCl_3$ is employed in this reaction in order to form a carbocation by facilitating the removal of the halide. The resulting carbocation undergoes a rearrangement before proceeding with the alkylation reaction.

Mechanism

The Friedel-Crafts alkylation reaction proceeds via a three-step mechanism.

Step 1

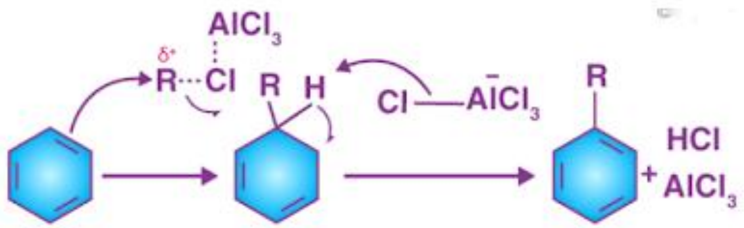
The Lewis acid catalyst ($AlCl_3$) undergoes reaction with the alkyl halide, resulting in the formation of an electrophilic carbocation.

Step 2

The carbocation proceeds to attack the aromatic ring, forming a cyclohexadienyl cation as an intermediate. The aromaticity of the arene is temporarily lost due to the breakage of the carbon-carbon double bond.

Step 3

The deprotonation of the intermediate leads to the reformation of the carbon-carbon double bond, restoring aromaticity to the compound. This proton goes on to form hydrochloric acid, regenerating the $AlCl_3$ catalyst.



An illustration describing the mechanism of the Friedel-Crafts alkylation reaction is provided above.

Friedel-Crafts Alkylation

What are the Limitations of the Friedel-Crafts Alkylation Reaction?

Some important limitations of Friedel-Crafts alkylation are listed below.

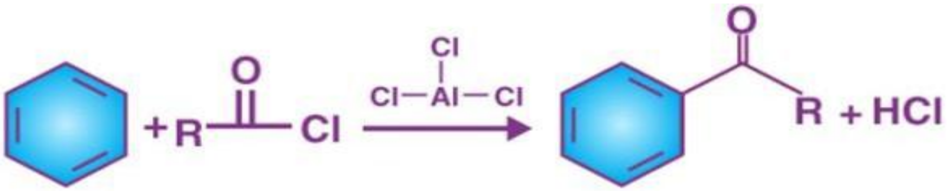
- Since the carbocations formed by aryl and vinyl halides are extremely unstable, they cannot be used in this reaction.
- The presence of a deactivating group on the aromatic ring (such as an NH_2 group) can lead to the deactivation of the catalyst due to the formation of complexes.
- An excess of the aromatic compound must be used in these reactions in order to avoid polyalkylation (addition of more than one alkyl group to the aromatic compound).
- Aromatic compounds that are less reactive than mono-halobenzenes do not participate in the Friedel-Crafts alkylation reaction.

It is important to note that this reaction is prone to carbocation rearrangements, as is the case with any reaction involving carbocations.

Friedel-Crafts Acylation

The Friedel-Crafts acylation reaction involves the addition of an acyl group to an aromatic ring.

Typically, this is done by employing an acid chloride (R-(C=O)-Cl) and a Lewis acid catalyst such as $AlCl_3$. In a Friedel-Crafts acylation reaction, the aromatic ring is transformed into a ketone. The reaction between benzene and an acyl chloride under these conditions is illustrated below.



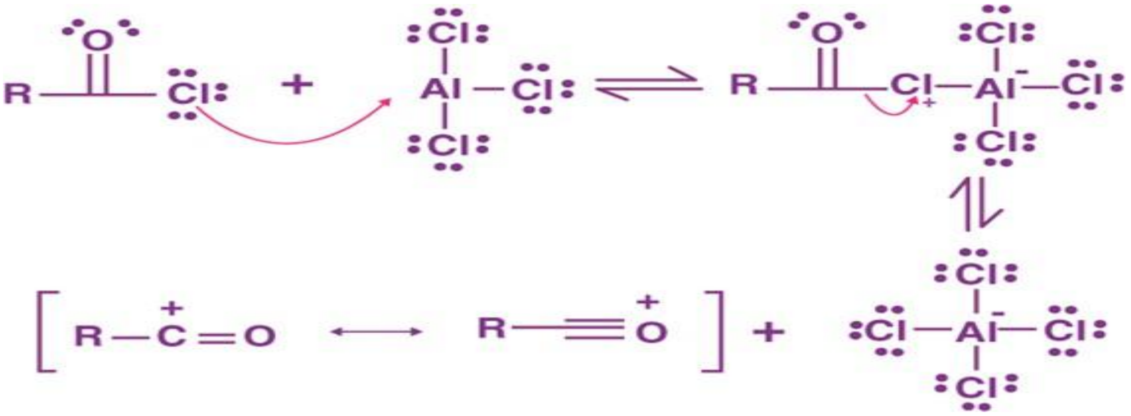
An acid anhydride can be used as an alternative to the acyl halide in Friedel-Crafts acylations. The halogen belonging to the acyl halide forms a complex with the Lewis acid, generating a highly electrophilic acylium ion, which has a general formula of RCO^+ and is stabilized by resonance.

Mechanism

Friedel-Crafts acylations proceed through a four-step mechanism.

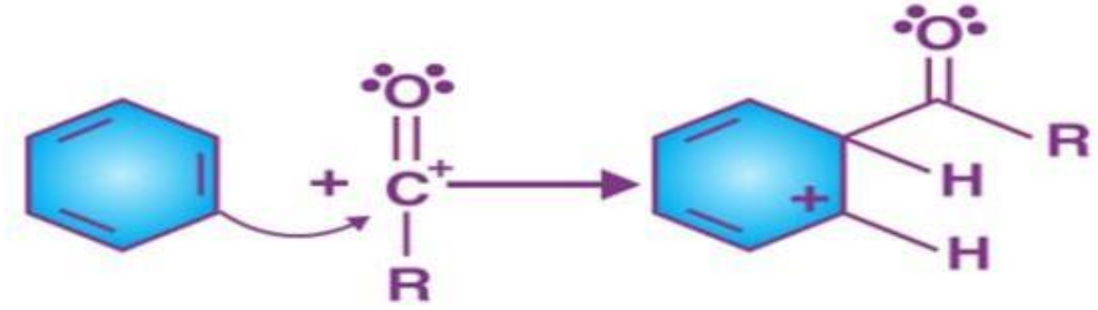
Step 1

A reaction occurs between the Lewis acid catalyst ($AlCl_3$) and the acyl halide. A complex is formed and the acyl halide loses a halide ion, forming an acylium ion which is stabilized by resonance.

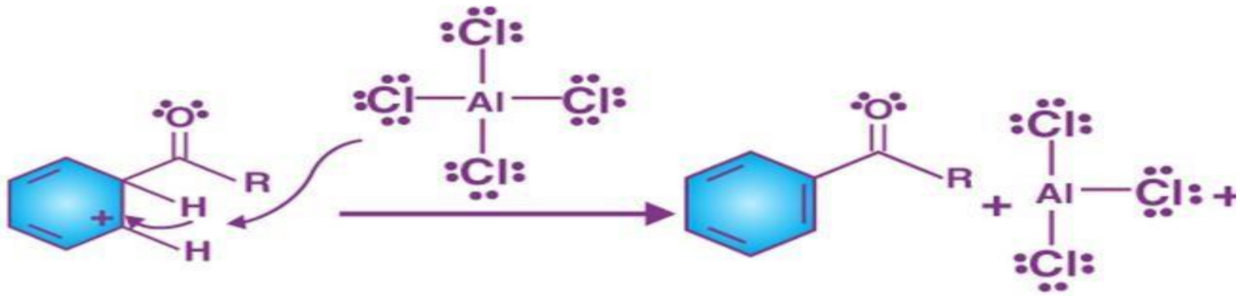


Step 2

The acylium ion (RCO^+) goes on to execute an electrophilic attack on the aromatic ring. The aromaticity of the ring is temporarily lost as a complex is formed.



Step 3



The intermediate complex is now deprotonated, restoring the aromaticity to the ring. This proton attaches itself to a chloride ion (from the complexed Lewis acid), forming HCl. The $AlCl_3$ catalyst is now regenerated.

Thus, the required acyl benzene product is obtained via the Friedel-Crafts acylation reaction.

Limitations

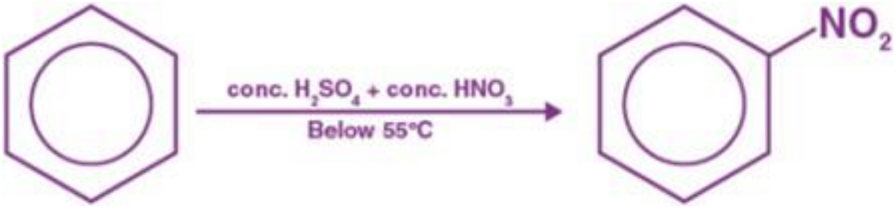
Despite overcoming some limitations of the related alkylation reaction (such as carbocation rearrangement and polyalkylation), the Friedel-Crafts acylation reaction has a few shortcomings.

- The acylation reaction only yields ketones. This is because formyl chloride (H(C=O)Cl) decomposes into CO and HCl when exposed to these conditions.
- The aromatic compound cannot participate in this reaction if it is less reactive than a mono-halobenzene.
- Aryl amines cannot be used in this reaction because they form highly unreactive complexes with the Lewis acid catalyst.

The acylations can take place on the nitrogen or oxygen atoms when amine or alcohols are used. Thus, the reaction details, mechanisms, and limitations of both Friedel-Crafts reactions are briefly discussed.

Nitration of Benzene

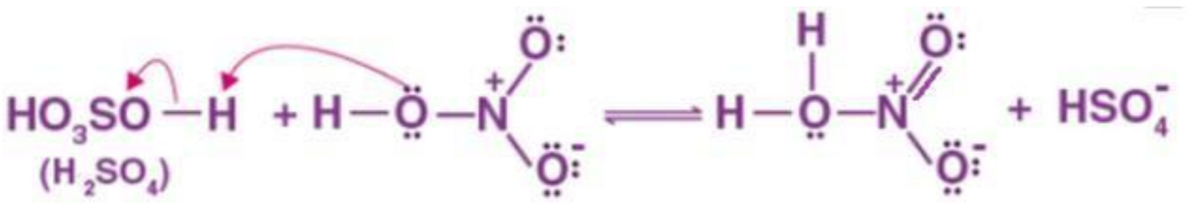
Benzene reacts with concentrated nitric acid at 323-333K in the presence of concentrated sulphuric acid to form nitrobenzene. This reaction is known as nitration of benzene.

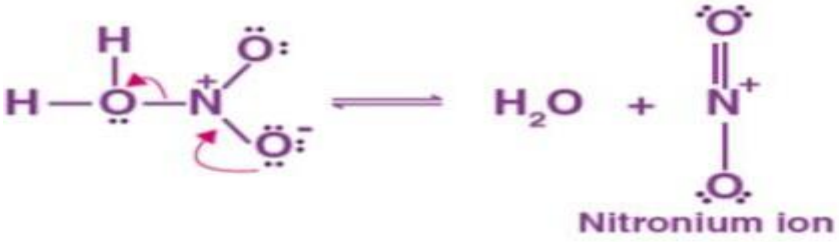


Nitration of nitrobenzene

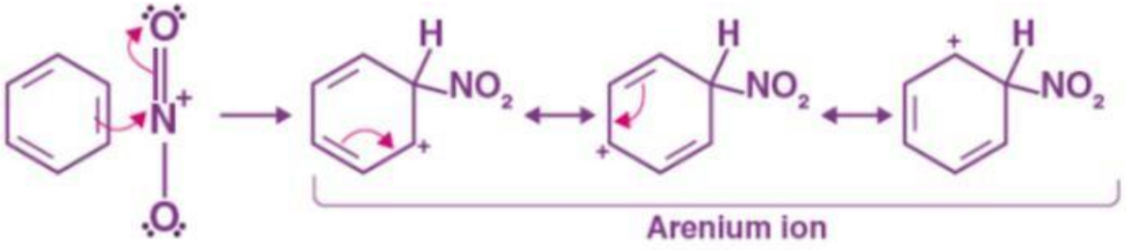
The mechanism for nitration of benzene:

Step 1: Nitric acid accepts a proton from sulphuric acid and then dissociates to form nitronium ion.

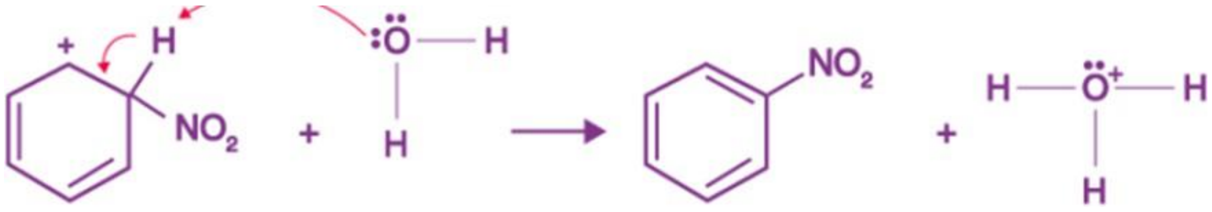




Step 2: The nitronium ion acts as an electrophile in the process which further reacts with benzene to form an arenium ion.



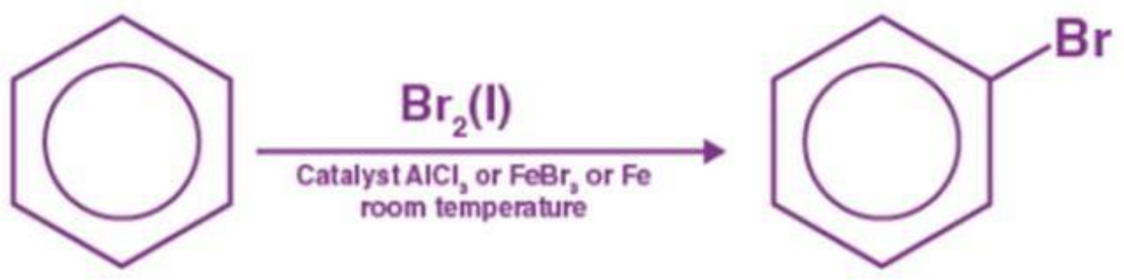
Step 3: The arenium ion then loses its proton to Lewis base forming nitrobenzene.



Halogenation of Benzene

Benzene reacts with halogens in the presence of Lewis acid like $FeCl_3$, $FeBr_3$ to form aryl halides. This reaction is termed as halogenation of benzene.

Halogenation of benzene.

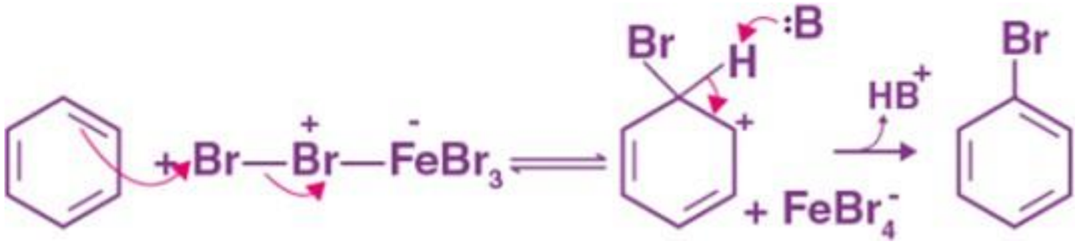


The mechanism for halogenation of benzene:

Step 1: Being a Lewis acid, FeBr3 helps in the generation of electrophile bromine ion by combining with the attacking reagent.

Generation of bromine ion

Step 2: The bromine ion acts as an electrophile in the process which further reacts with benzene to form arenium ion which finally converts to bromobenzene.



Heterocyclic Compound

Have you ever wondered how we encounter many heterocyclic compounds in our daily lives?

- Nucleic Acid that is present in the body responsible for storing and expressing genetic information, is an example of a Heterocyclic compound.
- Essential micronutrient vitamins are also an example of a heterocyclic compound.
- The majority of drugs, pesticides, dyes, and plastics are examples of heterocyclic compounds.

Table of Content

What is a Heterocyclic Compound?

A heterocyclic compound has at least two different elements as a member of its ring.

- The most common hetero atoms found on a cyclic ring are Oxygen (O), Nitrogen (N) and Sulphur (S).

Example:

- Nucleic Acid that is present in the body responsible for storing and expressing genetic information, is an example of a Heterocyclic compound.
- Essential micronutrient, Vitamins is also an example of a heterocyclic compound.

- The majority of drugs, pesticides, dyes, and plastics are examples of heterocyclic compounds.

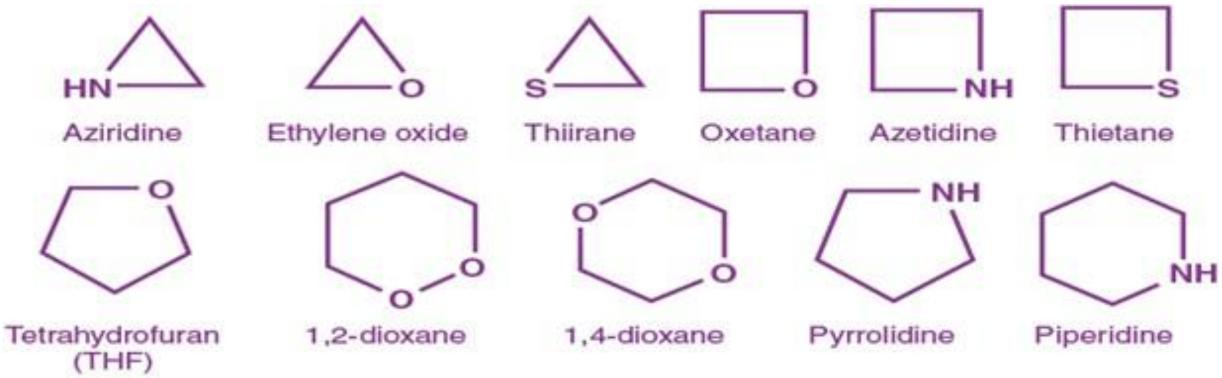
Classification of Heterocyclic Compounds

Based on the electronic arrangement, we can classify Heterocyclic compounds into two types:

- Aliphatic Heterocyclic Compounds
- Aromatic Heterocyclic Compounds

Aliphatic Heterocyclic Compounds

- Aliphatic heterocyclic compounds are those cyclic heterocycles that do not contain any double bond.
- The properties of aliphatic heterocyclic compounds are mainly affected due to ring strain.
- Examples of aliphatic heterocyclic compounds are Aziridine, Ethylene Oxide, Thiirane, Oxetane, Azetidine, Thietane, Tetrahydrofuran (THF), Dioxane, Pyrrolidine, Piperidine, etc.

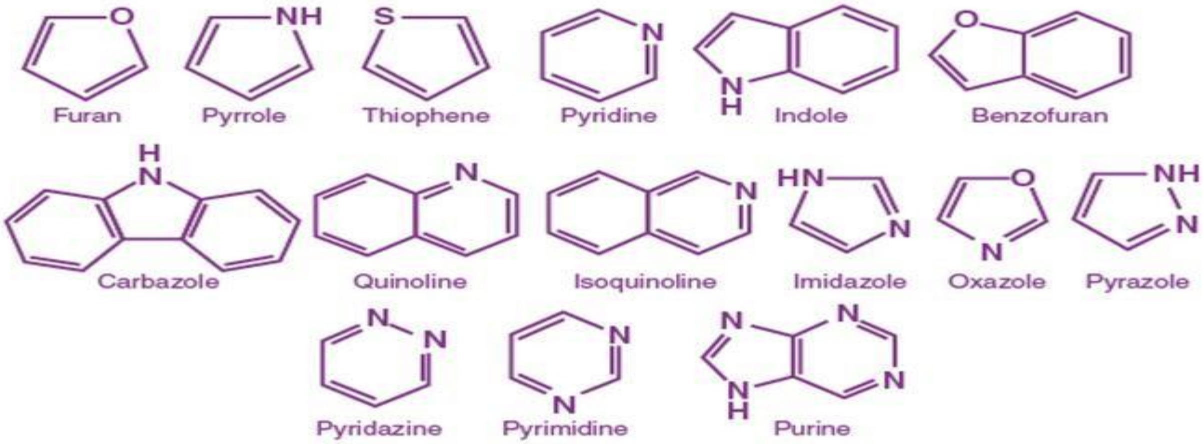


Examples of aliphatic heterocyclic compounds

Aromatic Heterocyclic Compound

- Aromatic heterocyclic compounds, as the name suggests, are cyclic aromatic compounds.
- Aromatic Heterocyclic compounds obey Huckels Rule, i.e.
- It should be cyclic.
- It should be planar.

- It should not contain any sp3 hybridised atoms.
- It must have (4n+2) **π** electrons.
- Aromatic Heterocyclic compounds are analogous to Benzene.
- Examples: Furan, Pyrrole, Thiophene, Indole, Benzofuran, Carbazole, Quinoline, Isoquinoline, Imidazole, Oxazole, Pyrazole, Pyridazine, Pyrimidine, Purine, etc.



Examples of aromatic heterocyclic compounds

Based on structure, we can classify Heterocyclic compounds into five types:

1. Three-Membered Heterocyclic Compounds
2. Four-Membered Heterocyclic Compounds
3. Five-Membered Heterocyclic Compounds
4. Six-Membered Heterocyclic Compounds
5. Condensed or Fused Heterocyclic Compounds

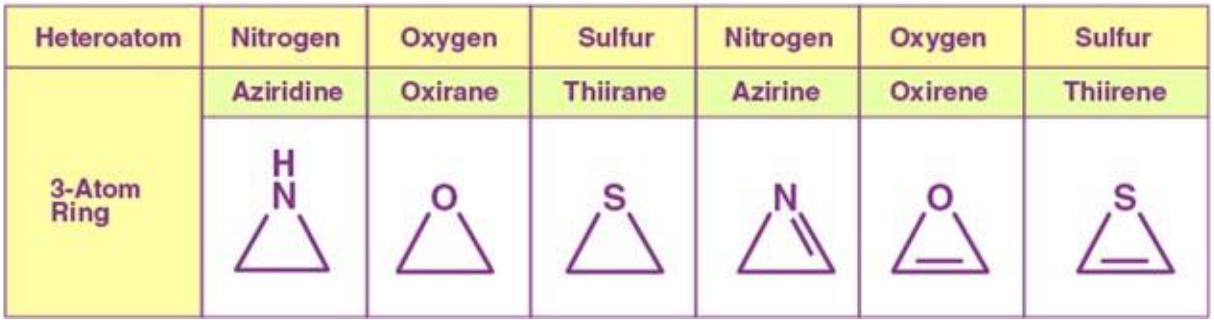
Three-Membered Heterocyclic Compounds

These heterocyclic compounds contain three atoms which may be saturated or unsaturated.

Based on the number of heteroatoms present, we can further classify them into two categories:

Heterocyclic compounds with one heteroatom.

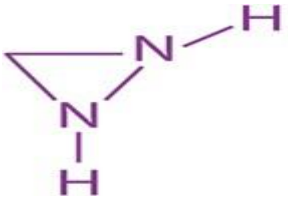
- As the name suggests, it has one heteroatom present in its ring.
- Examples: Aziridine, Oxirane, Thiirane, Azirine, Oxirene and Thiirene.

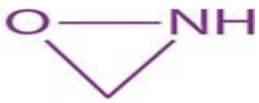


Heteroatom	Nitrogen	Oxygen	Sulfur	Nitrogen	Oxygen	Sulfur
3-Atom Ring	Aziridine	Oxirane	Thiirane	Azirine	Oxirene	Thiirene

Heterocyclic compounds with more than one heteroatom.

- As the name suggests, it has more than one heteroatom present in its ring.
- The heteroatom atom in the ring can be the same or different.
- Examples: Diaziridine and Oxiaziridine.





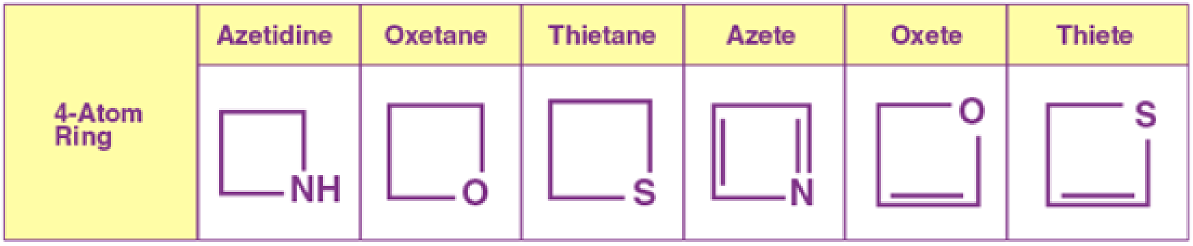
Four-Membered Heterocyclic Compounds

These heterocyclic compounds contain four atoms which may be saturated or unsaturated.

Based on the number of heteroatoms present, we can further classify them into two categories:

Heterocyclic compounds with one heteroatom.

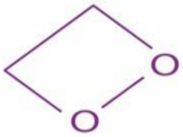
- As the name suggests, it has one heteroatom present in its ring.
- Examples: Azetidine, Oxetane, Thietane, Azete, Oxete, Thiete, etc

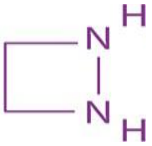


4-Atom Ring	Azetidine	Oxetane	Thietane	Azete	Oxete	Thiete

Heterocyclic compounds with more than one heteroatom.

- As the name suggests, it has more than one heteroatom present in its ring.
- The heteroatom atom in the ring can be the same or different.
- Examples: Diazetidine and Dioxetane.





Five-Membered Heterocyclic Compounds

These heterocyclic compounds are derived from Benzene by replacing a C=C bond with a hetero atom having a lone pair of electrons.

Based on the number of heteroatoms present, we can further classify them into two categories:

Heterocyclic compounds with one heteroatom.

- As the name suggests, it has one heteroatom present in its ring.
- Examples: furan, pyrrole and thiophene.

Furan Pyrrole Thiophene

Five member heterocyclic compounds with one hetero

Heterocyclic compounds with more than one heteroatom.

- As the name suggests, it has more than one heteroatom present in its ring.
- The heteroatom atom in the ring can be the same or different.
- Examples: Pyrazole, Imidazole, Oxazole, Thiazole, Triazole and Tetrazole, etc.

Five member heterocyclic compounds with two hetero atom

Six-Membered Heterocyclic Compounds

These heterocyclic compounds are derived from Benzene by replacing one of the Carbon with a hetero atom having a lone pair of electrons.

Based on the number of heteroatoms present, we can further classify them into two categories:

Heterocyclic compounds with one heteroatom.

- As the name suggests, it has one heteroatom present in its ring.
- Examples: Pyridine, Pyran, Thiopyran, etc.

Six member heterocyclic compounds with one hetero

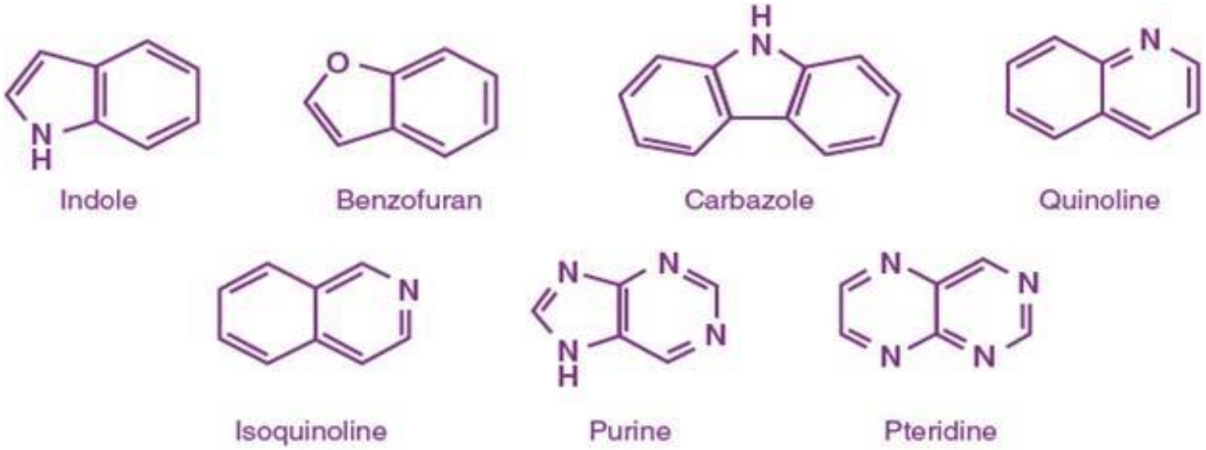
Heterocyclic compounds with more than one heteroatom.

- As the name suggests, it has more than one heteroatom present in its ring.
- The heteroatom atom in the ring can be the same or different.
- Examples: Pyridazine, Pyrimidine, Pyrazine, etc.

Six member heterocyclic compounds with more than hetero atom

Condensed or Fused Heterocyclic Compound

- Condensed or Fused Heterocyclic Compound contains two or more fused rings.
- Condensed or Fused Heterocyclic Compounds can be partly carbocyclic or partly heterocyclic.
- Examples: Indole, Quinoine, Isoquionoline, Cabazole, etc.
- Condensed or Fused Heterocyclic Compounds can also be completely heterocyclic.
- Examples: Purine, Pteridine, etc.



Fused or condensed heterocyclic compounds

Applications of Heterocyclic Compound

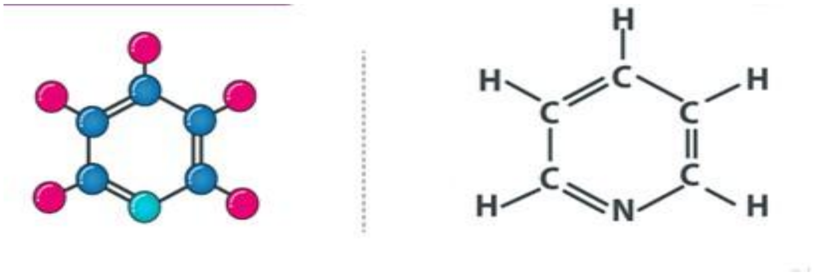
- Heterocyclic compounds are used in agrochemicals and pharmaceuticals industries.
- Heterocyclic compounds are used as starting materials in the synthesis of organic compounds.
- Heterocyclic compounds are used in corrosion inhibitors, sanitisers, anti-ordinates, and developers.
- Heterocyclic compounds are used in pesticides, dyes and plastics.

Properties of Pyridine – C_5H_5N

Pyridine and its simple derivatives are stable and relatively unreactive liquids, with strong penetrating odours that are unpleasant. Pyridine is the hydrogen derivative of this ring, it is benzene in which one CH- or methine group is replaced by a nitrogen atom. The structure of pyridine is completely analogous to that of benzene, being related by the replacement of CH with N.

C_5H_5N	Pyridine
Molecular Weight/ Molar Mass	79.1 g/mol
Density	982 kg/m³
Boiling Point	115 ℃
Melting Point	−41.6 ℃

Pyridine Structure – C_5H_5N



Structure of Pyridine – C_5H_5N

C_5H_5N Uses (Pyridine)

- It is used in the chemical industries as a very important raw material
- It is used as an antiseptic in dental care products
- It is used as a solvent which is suitable for dehalogenation
- It is used in pharmaceuticals
- It is used for antifreeze mixtures as a denaturant
- It is used as a sulfonating agent
- It is used as a reducing agent
- It is used in dyes and paints

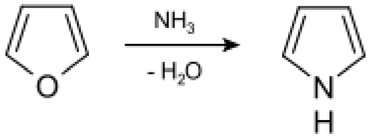
- It is used as a disinfectant
- It is used in coordination chemistry as a ligand

Pyrrole

Pyrrole is colorless liquid, Boiling point 131°C, which rapidly turns brown on exposure to air. Its odour is like that of chloroform. Pyrrole is sparingly soluble in water but dissolves in ethanol and ether.

Pyrrole is a colorless volatile liquid that darkens readily upon exposure to air, and is usually purified by distillation immediately before use.[6] Pyrrole has a nutty odor. Pyrrole is a 5-membered aromatic heterocycles, like furan and thiophene. Unlike furan and thiophene, it has a dipole in which the positive end lies on the side of the heteroatom, with a dipole moment of 1.58 D. In $CDCl_3$, it has chemical shifts at 6.68 (H2, H5) and 6.22 (H3, H4). Pyrrole is an extremely weak base for an amine, with a conjugate acid pK_a of −3.8. The most thermodynamically stable pyrrolium cation ($C_4H_6N^+$) is formed by protonation at the 2 position. Substitution of pyrrole with alkyl substituents provides a more basic molecule—for example, tetramethylpyrrole has a conjugate acid pK_a of +3.7. Pyrrole is also weakly acidic at the N–H position, with a pK_a of 16.5. As a hydrogen bonding Lewis acid it is classified as a hard acid and the ECW model lists its acid parameters as $E_A = 1.38$ and $C_A = 0.68$.

Pyrrole is prepared industrially by treatment of furan with ammonia in the presence of solid acid catalysts, like SiO_2 and Al_2O_3



Pyrrole can also be formed by catalytic dehydrogenation of pyrrolidine.

Quantitative data is numbers-based, countable, or measurable. Qualitative data is interpretation-based, descriptive, and relating to language. Quantitative data tells us how many, how much, or how often in calculations. Qualitative data can help us to understand why, how, or what happened behind certain behaviors.

UNIT-IV

Thermodynamics

Thermodynamics in physics is a branch that deals with heat, work and temperature, and their relation to energy, radiation and physical properties of matter.

To be specific, it explains how thermal energy is converted to or from other forms of energy and how matter is affected by this process. Thermal energy is the energy that comes from heat. This heat is generated by the movement of tiny particles within an object, and the faster these particles move, the more heat is generated.

Thermodynamics is not concerned about how and at what rate these energy transformations are carried out. It is based on the initial and final states undergoing the change. It should also be noted that Thermodynamics is a macroscopic science. This means that it deals with the bulk system and does not deal with the molecular constitution of matter.

Different Branches of Thermodynamics

Thermodynamics is classified into the following four branches:

- Classical Thermodynamics
- Statistical Thermodynamics
- Chemical Thermodynamics
- Equilibrium Thermodynamics

Classical Thermodynamics

In classical thermodynamics, the behaviour of matter is analysed with a macroscopic approach. Units such as temperature and pressure are taken into consideration, which helps the individuals calculate other properties and predict the characteristics of the matter undergoing the process.

Statistical Thermodynamics

In statistical thermodynamics, every molecule is under the spotlight, i.e. the properties of every molecule and how they interact are taken into consideration to characterise the behaviour of a group of molecules.

Chemical Thermodynamics

Chemical thermodynamics is the study of how work and heat relate to each other in chemical reactions and in changes of states.

Equilibrium Thermodynamics

Equilibrium thermodynamics is the study of transformations of energy and matter as they approach the state of equilibrium.

Basic Concepts of Thermodynamics – Thermodynamic Terms

Thermodynamics has its own unique vocabulary associated with it. A good understanding of the basic concepts forms a sound understanding of various topics discussed in thermodynamics preventing possible misunderstandings.

System

A thermodynamic system is a specific portion of matter with a definite boundary on which our attention is focused. The system boundary may be real or imaginary, fixed or deformable. There are three types of systems:

- **Isolated System** – An isolated system cannot exchange energy and mass with its surroundings. The universe is considered an isolated system.
- **Closed System** – Across the boundary of the closed system, the transfer of energy takes place but the transfer of mass doesn’t take place. Refrigerator, compression of gas in the piston-cylinder assembly are examples of closed systems.
- **Open System** – In an open system, the mass and energy both may be transferred between the system and surroundings. A steam turbine is an example of an open system.

Interactions of thermodynamic systems			
Type of system	Mass flow	Work	Heat
Isolated System	☓	☓	☓
Open System	✓	✓	✓

Closed System	✗	✓	✓

Surrounding

Everything outside the system that has a direct influence on the behaviour of the system is known as a surrounding.

Thermodynamic Process

A system undergoes a thermodynamic process when there is some energetic change within the system that is associated with changes in pressure, volume and internal energy.

There are four types of thermodynamic processes that have their unique properties, and they are:

- Adiabatic Process – A process where no heat transfer into or out of the system occurs.
- Isochoric Process – A process where no change in volume occurs and the system does no work.
- Isobaric Process – A process in which no change in pressure occurs.
- Isothermal Process – A process in which no change in temperature occurs.

Thermodynamic Process

A thermodynamic cycle is a process or a combination of processes conducted such that the initial and final states of the system are the same. A thermodynamic cycle is also known as cyclic operation or cyclic processes.

Thermodynamic Equilibrium

At a given state, all properties of a system have fixed values. Thus, if the value of even one property changes, the system's state changes to a different one. In a system that is in equilibrium, no changes in the value of properties occur when it is isolated from its surroundings.

- When the temperature is the same throughout the entire system, we consider the system to be in thermal equilibrium.
- When there is no change in pressure at any point of the system, we consider the system to be in mechanical equilibrium.
- When the chemical composition of a system does not vary with time, we consider the system to be in chemical equilibrium.
- Phase equilibrium in a two-phase system is when the mass of each phase reaches an equilibrium level.

A thermodynamic system is said to be in thermodynamic equilibrium if it is in chemical equilibrium, mechanical equilibrium and thermal equilibrium and the relevant parameters cease to vary with time.

Thermodynamic Properties

Thermodynamic properties are defined as characteristic features of a system, capable of specifying the system's state. Thermodynamic properties may be extensive or intensive.

- Intensive properties are properties that do not depend on the quantity of matter. Pressure and temperature are intensive properties.
- In the case of extensive properties, their values depends on the mass of the system. Volume, energy, and enthalpy are extensive properties.

What is Enthalpy?

Enthalpy is the measurement of energy in a thermodynamic system. The quantity of enthalpy equals the total heat content of a system, equivalent to the system's internal energy plus the product of volume and pressure.

Mathematically, the enthalpy, H, equals the sum of the internal energy, E, and the product of the pressure, P, and volume, V, of the system.

$H = E + PV$

What is Entropy?

Entropy is a thermodynamic quantity whose value depends on the physical state or condition of a system. In other words, it is a thermodynamic function used to measure the randomness or disorder. For example, the entropy of a solid, where the particles are not free to move, is less than the entropy of a gas, where the particles will fill the container.

Thermodynamic Potentials

Thermodynamic potentials are quantitative measures of the stored energy in a system. Potentials measure the energy changes in a system as they evolve from the initial state to the final state. Different potentials are used based on the system constraints, such as temperature and pressure.

Different forms of thermodynamic potentials along with their formula are tabulated below:

Internal Energy	$U=\int TdS-PdV+\sum i\mu idNi$
Helmholtz free energy	$F = U - TS$

Enthalpy	H = U + PV
Gibbs Free Energy	G = U + PV – TS

Thermodynamics Solved Problems

Calculate ΔG at 290 K for them followingmreaction: $2N(g)+O_2(g)+2NO_2(g)$

Solution:

Given:

ΔH = -120kJ and ΔS = -150JK^{-1}

To make the unit of ΔS the same as ΔH, we have to convert the unit of ΔS as follows:

$\Delta S=-150J/(1kJ=1000J)\Rightarrow\Delta S=-0.15kJ/K$

We know that,

$G=U+PV-TS\Rightarrow\Delta G=\Delta H-T\Delta S$

So,

$\Delta G=-120kJ-(290K)(-0.150kJ/K)\Rightarrow\Delta G=-120kJ+43kJ\Rightarrow\Delta G=-77kJ$

Therefore, ΔG is -77kJ.

Laws of Thermodynamics

Thermodynamics laws define the fundamental physical quantities like energy, temperature and entropy that characterize thermodynamic systems at thermal equilibrium. These thermodynamics laws represent how these quantities behave under various circumstances.

How many laws of thermodynamics are there?

There are four laws of thermodynamics and are given below:

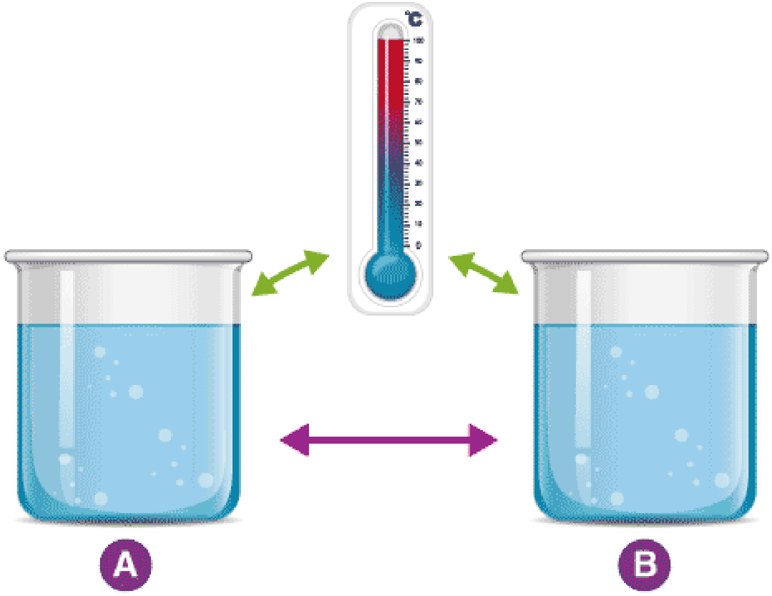
- Zeroth law of thermodynamics
- First law of thermodynamics
- Second law of thermodynamics
- Third law of thermodynamics

In the next few sections, we will discuss each of the laws of thermodynamics in detail.

Zeroth Law of Thermodynamics

The Zeroth law of thermodynamics states that if two bodies are individually in equilibrium with a separate third body, then the first two bodies are also in thermal equilibrium with each other. This means that if system A is in thermal equilibrium with system C and system B is also in equilibrium with system C, then system A and B are also in thermal equilibrium.

An example demonstrating the Zeroth Law



Consider two cups A and B, with boiling water. When a thermometer is placed in cup A, it gets warmed up by the water until it reads 100 °C. When it reads 100 °C, we say that the thermometer is in equilibrium with cup A. When we move the thermometer to cup B to read the temperature, it continues to read 100 °C. The thermometer is also in equilibrium with cup B. By keeping in mind the zeroth law of thermodynamics, we can conclude that cup A and cup B are in equilibrium with each other.

The zeroth law of thermodynamics enables us to use thermometers to compare the temperature of any two objects that we like.

First Law of Thermodynamics

First law of thermodynamics, also known as the law of conservation of energy, states that energy can neither be created nor destroyed, but it can be changed from one form to another.

The first law of thermodynamics may seem abstract, but we will get a clearer idea if we look at a few examples of the first law of thermodynamics.

First Law Of Thermodynamics Examples:

- Plants convert the radiant energy of sunlight to chemical energy through photosynthesis. We eat plants and convert the chemical energy into kinetic energy while we swim, walk, breathe, and scroll through this page.
- Switching on light may seem to produce energy, but it is electrical energy that is converted.

Second Law of Thermodynamics

Second law of thermodynamics states that the entropy in an isolated system always increases. Any isolated system spontaneously evolves towards thermal equilibrium—the state of maximum entropy of the system.

The entropy of the universe only increases and never decreases. Many individuals take this statement lightly and for granted, but it has an extensive impact and consequence.

Visualizing the second law of thermodynamics

If a room is not tidied or cleaned, it invariably becomes more messy and disorderly with time. When the room is cleaned, its entropy decreases, but the effort to clean it has resulted in increased entropy outside the room exceeding the entropy lost.

Physical Equilibrium - Types and Examples

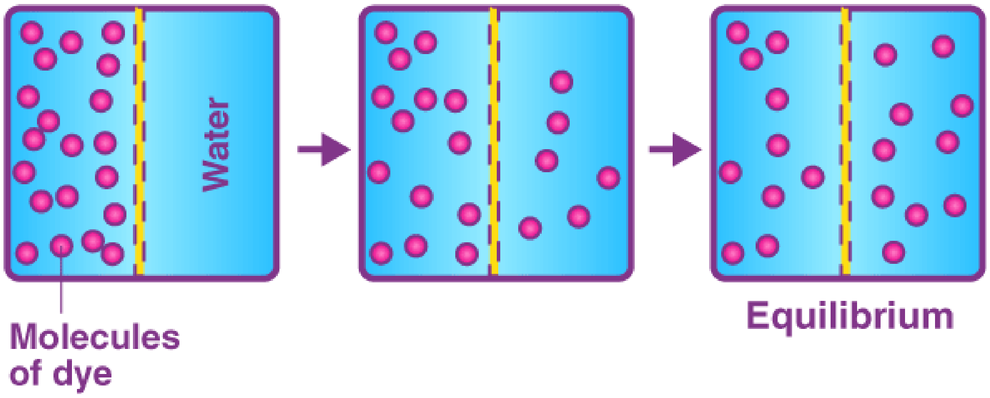
Equilibrium indicates the constancy of content and composition (as measured by colour, pressure or temperature) of an item of interest in a system, irrespective of the time period. In the equilibrium state, the rate of the forward reaction is equal to the rate of the backward reaction.

A book on a table, liquid in a closed container, saturated solution, ionic substances in polar solvents and the manufacture of ammonia are some examples of equilibrium.

Physical Equilibrium

Physical equilibrium is defined as the equilibrium which develops between different phases or physical properties. In this process, there is no change in chemical composition. It represents the existence of the same substance in two different physical states. The physical equilibrium can be

- Phase equilibrium
- Solute-solid equilibrium
- Gas-liquid equilibrium



Type of Physical Equilibrium

- Chemical Equilibrium
- Le Chatelier’s Principle
- Equilibrium Constant

Let us now discuss the different types of physical equilibrium in detail.

Types of Physical Equilibrium

Phase Equilibrium

At 0°C, the number of water molecules becoming ice is equal to the water molecules as the ice melts to form liquid water. The rate of freezing of water is equal to the rate of melting of ice. Thus, there is an equilibrium between solid ice and liquid water.

Ice (s) $\rightleftharpoons$ Water (l)

The number of molecules of a liquid becoming vapour will be equal to the number of molecules condensing into liquid in a closed container. The rate of evaporation of liquid water is equal to the rate of condensation of water vapour. The liquid phase is in equilibrium with its own vapour phase.

Water (l) $\rightleftharpoons$ Water (g)

Solute-solid Equilibrium

When a solute in a saturated solution is in contact with an undissolved solute, the number of molecules going (depositing) out of the solution is equal to the number of molecules entering (dissolving) from the solid into the liquid. So the solute in a solution is in equilibrium with the undissolved solid.

Solute (aq) ⇌ Solute (s)

Gas-liquid Equilibrium

Gases that do not react with liquid may dissolve directly related to the pressure in the liquid. In a closed container, there is an equilibrium between the gas inside the liquid and the gas present above the liquid. In soft drinks, for example, carbon dioxide gas in the liquid is in equilibrium with the gas in the empty space of the container.

Gas (solution) ⇌ Gas (g)

Examples of Physical Equilibrium

Examples of Solid-liquid Equilibria

Consider ice and water in a perfectly insulated thermos flask at 0^0C in an open atmosphere. There will be no change in the level of water and quantity of ice, which implies that the rate of transfer of molecules from water to ice is equal to the rate of transfer of molecules from ice to water.

Hence, we can conclude that this system is in a steady state. This can be represented by the following equation:

H_2O (s)⇌ H_2O (l)

The rate of melting = The rate of freezing

Examples of Liquid-gas Equilibria

Take distilled water in a closed container and start heating. The water converts into vapour. After a certain time, we will observe that the level of water becomes constant, implying that there is no more conversion of water to vapour and vice-versa.

We can technically say that the rate of evaporation (liquid to vapour) is equal to the rate of condensation (vapour to liquid), thus achieving a steady state. This equation can be represented by the following equation:

H_2O (l) ⇌ H_2O (g)

The rate of evaporation = The rate of condensation

Examples of Solid-vapour Equilibria

This kind of equilibrium can exist only in the case of sublimates (solid directly converts to vapour). Consider heating solid iodine in a closed container. Slowly, the vessel is filled with violet-coloured vapour, and the intensity of colour increases with time.

After a certain time, the intensity of colour doesn't change with time. This implies that a steady state is attained where the rate of sublimation of solid iodine is equal to the rate of deposition of iodine vapour.

I_2 (s) ⇌ I_2 (Vapour)

The rate of sublimation = The rate of deposition

Phase Diagram

A phase diagram is a graphical representation of the various phases of a substance or mixture of substances that coexist in thermodynamic equilibrium, and undergo phase changes under different working conditions, such as temperature, pressure, or volume.

The water system is divided into three phases: ICE (S), WATER (L), and WATER VAPOUR (G) Since H_2O is the only chemical compound present, as a result, it is a one-component system.

Depiction in Phase Diagram of Water

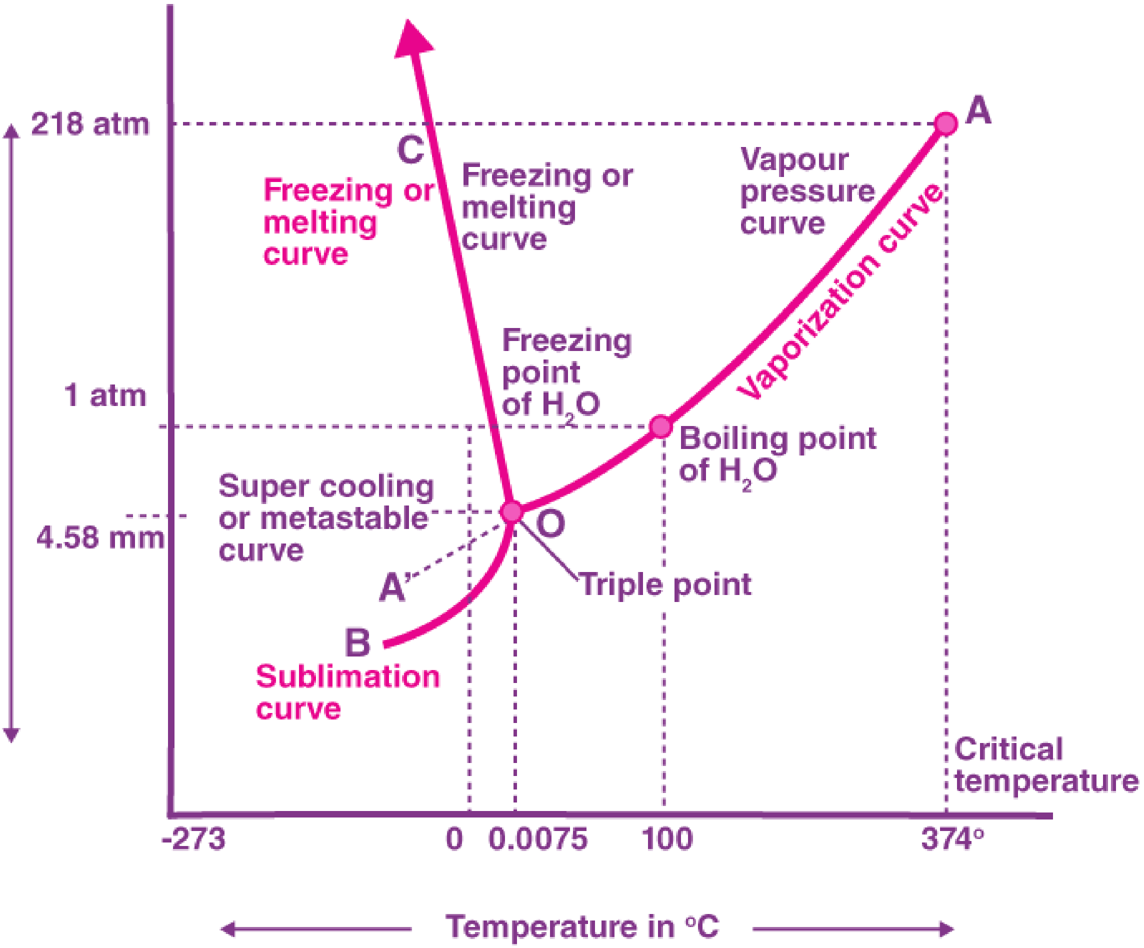
At different temperatures and pressures, a phase diagram depicts the preferred physical states of matter. Water is a liquid at typical room temperatures and pressures, but it becomes solid (i.e. ice) if the temperature is reduced below 273 K, and gaseous (i.e. steam) if the temperature is increased above 373 K at the same pressure.

Each line describes the conditions that exist when two phases coexist, but a change in temperature or pressure can cause the phases to abruptly change from one to the other.

When three lines come together, there is a 'triple point,' which is where three phases coexist but can abruptly and completely change into each other due to a change in temperature or pressure. Four lines cannot intersect at the same point.

A 'critical point' is defined as the point at which the properties of two phases become indistinguishable from one another.

Phase Diagram for Water



Curves:

1. OA- Water & Vapor

OA is the vaporisation curve. The curve OA comes to an end at A. It has a critical pressure of 218 atm and a temperature of 374°C. It represents the vapour pressure of a liquid at various temperatures.

Along the curve, two phases of water and water vapours coexist in equilibrium.

The vapour pressure is one atmosphere. The corresponding temperature in degrees Celsius is the boiling point of water, which is 100°C.

1. OB- Ice and Vapor

The OB curve is a sublimation curve. The curve OB comes to an end at B, which is the absolute zero temperature of -273°C. It depicts the vapour pressure of solid ice at various temperatures.

In equilibrium, the two phases of solid ice and water vapour coexist.

1. OC- Ice & Water

The OC curve is the fusion curve. The OC curve comes to an end at C, the critical pressure.

In equilibrium, the two phases of solid ice and liquid water coexist. The curve shows that the melting point of ice decreases as pressure increases. At one atm, the line intersects the curve at 0°C.

Areas:

The area AOC, AOB, and BOC the curves or areas between the curves represent the conditions at temperature and pressure under which a single phase, i.e., ice, water, and water vapour, can exist indefinitely.

1. BOC- Ice- denotes the solid phase.
2. COA- Water- denotes the liquid phase.
3. AOB- Vapour- denotes the gaseous phase

Triple Point:

All three curves, OA, OB, and OC, meet at point O, which is known as the triple point, where all three phases, solid, liquid, and vapour, are in simultaneous equilibrium.

At 0.0075°C and 4.58 mm Hg pressure, the triple point occurs.

Two components systems:-

Lead silver system- This system has two component and four phases. These are

1. Solid silver
2. Solid lead
3. Solution of molten silver and lead
4. Vapor

But the boiling point of Ag and Pb is completely high; the vapor phase is completely absent.Since the press has nearly no affected on equilibrium so the system can be conveniently represented by temp.-conc. diagram.

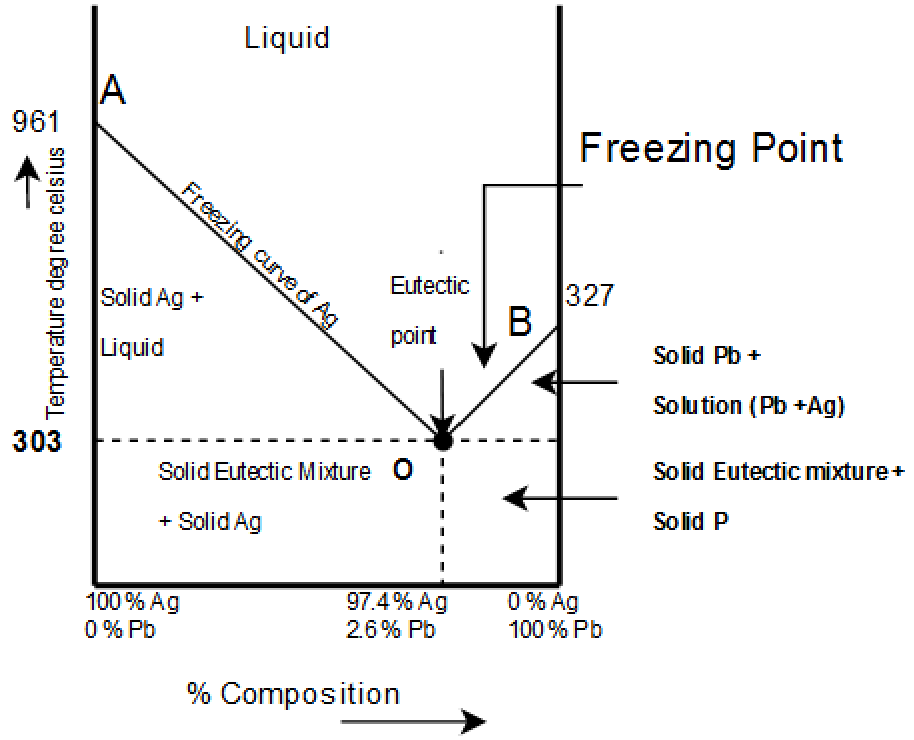
Such solid liquid system with the gas phase is absent is called condensed system.

The experimental measurements of temp and conic. in condensed system ate usually carried at under atmosphere pressure.

Since the degree of freedom in such system is reduced but one, therefore, it can be also termed as reduced phase and represented by the equation, F=C−P+1$F=C−P+1$

It is more convenient to apply to solid liquid two components condensed system e.g.-Pb-Sb, Ag-Pb, Zn-Cd

The complete temp.-conc. phase diagram of system silver-lead:



From the figure following salient features are observed:

1. The curve OA(freezing curve of Ag)
2. The curve BO(freezing curve of Pb)
3. The eutectic point 'O'
4. The Area AOB
    1. Curve AO →→Freezing curve of Hg.

i. It shows the effect on freezing point of Ag on addition of Pb in small quantities .

ii. The curve starts from (961)∘c$(961)^{\circ}c$ the M.P of Ag, where pure Ag coexists as solid and liquid(Vapors being neglected)

iii. The curve indicates that the meeting point of Ag falls gradually on adding Pb, along AO till the lowest point O(303)∘c$(303)^{\circ}c$ is reached where solution gets saturated with request to lead. At O more Pb can go in solution and consequently, the M.P. does not fall any further and if any Pb is added it separates as solid phase.

Along this curve, solid Ag and solution (Vapors being negligible) coexist and hence, according to reduced phase rule equation F=2−P+1$F=2-P+1$

i.e. system is invariant. The point O(303)∘c$(303)\circ c$ corresponds to a fixed composition of 2.62.6Ag and solution and 97.497.4 Pb and is known as eutectic composition.

On cooling the whole mass crystallizes out as such.

1. Curve BO→→Freezing curve of Pb
   i. It represents the effect on freezing point of Pb on gradual addition of small amount of Ag to it, point B is the M.P of pure Pb(−327)∘c$(-327)\circ c$
   ii. Along BO, the M.P gradually falls on addition of Ag till lowest point O is reached
   iii. At this point solution gets saturated with respect to Ag and M.P of Pb does not fall any more. List item
   iv. On cooling whole mass crystallizes out. Therefore the system is univariant like AO.

3) Point O→Eutectic point———————————————————$Point\ O\rightarrow Eutectic\ point\_$

The two curve AO and BO meet at O, where three phases solid Ag, solid Pb and their solution coexist and according phase rule. The point of O represents a fixed composition of Ag −2.6−2.6 is called eutectic composition.

At eutectic composition ^ temperature remains constant until the whole of melt solidifies in block to become solid of eutectic composition. However, further cooling results in simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point O.

Bellow temperature line there are two regions.

Eutectic solid+solid Ag in crystalline -stable

Eutectic + solid Pb in crystalline-stable.

It represents solution of Pb-Ag sample of Pb containing less than 2.6% Ag is taken at an arbitrary pt. on curve allowing mass cool temp gradually falls without any charge in composition till this point is reached to curve BO(pt may be P).

On lowering the temp lead begins to separate out of the composition varies along Pb till pt 0 is reached.On cooling whole mass solidifies into a block.

APPLICATIONS:-

1). Used in Pattison's process of desilverization of Pb.

2). If Pb is less than 2.6 Pb will separate out from soln,
If Pb is more than 2.6 Ag will separate out from

UNIT -V

When it comes to conducting data research, you’ll need different collection, hypotheses and analysis methods, so it’s important to understand the key differences between quantitative and qualitative data:

- **Quantitative data** is numbers-based, countable, or measurable. **Qualitative data** is interpretation-based, descriptive, and relating to language.

- **Quantitative data** tells us how many, how much, or how often in calculations. **Qualitative data** can help us to understand why, how, or what happened behind certain behaviors.

- **Quantitative data** is fixed and universal. **Qualitative data** is subjective and unique.

- **Quantitative research** methods are measuring and counting. **Qualitative research** methods are interviewing and observing.

- **Quantitative data** is analyzed using statistical analysis. **Qualitative data** is analyzed by grouping the data into categories and themes.

Volumetric Analysis

What is Volumetric Analysis?

Volumetric analysis is a quantitative analytical method which is used widely. As the name suggests, this method involves measurement of the volume of a solution whose concentration is known and applied to determine the concentration of the analyte.

In other words, measuring the volume of a second substance that combines with the first in known proportions is known as Volumetric analysis or titration. It is this method of quantitative analysis that allows us to determine the concentration of the analyte. The first method of Volumetric Analysis was devised and found by the French chemist Jean-Baptiste-Andre-Dumas; as he was trying to determine the proportion of nitrogen combined with other elements in organic compounds. To ensure the conversion of the nitrogen compound into pure gas, the nitrogen compound was burnt in a furnace and passed along a furnace in a stream of carbon dioxide that is passed into a strong alkali solution. The mass of the nitrogen is calculated and occupies under known conditions of pressure and volume from the sample.

Procedure for Volumetric Analysis

- ✓ A typical titration starts with a beaker or flask containing a precise volume of the analyte and small amount of indicator placed underneath a calibrated burette or pipette containing the titrant.
- ✓ The solution that needs to be analysed needs to have an accurate weighed in the sample of +/- 0.0001g of the material to be analysed.

- ✓ Choosing the right kind of material to be analysed is also very important, as choosing the wrong type of titrant will give us the wrong results. A substance that reacts rapidly and completely to produce a complete solution is chosen.
- ✓ Small quantities of titrant are added to the analyte and indicator till the indicator changes colour in reaction to the titrant saturation threshold reflects the arrival at the endpoint of the titration.
- ✓ The titration has to be continued up until the reaction is complete and the amount of reactant added is exactly the amount that is needed to complete the reaction.
- ✓ Another important step is in measuring the right volume of the standard solution since molarity is a standard metric to calculate the number of moles present in a solution.
- ✓ Based on the desired endpoint, single drops or less than a drop of the titrant makes a difference between a permanent and temporary change in the indicator.
- ✓ If the reagent or reactant that we use is to be made into a standard solution then we can weigh and dissolve the reagent into a solution, so that it is in a definitive volume within a volumetric flask.

Basic principles of volumetric analysis

- ✓ The solution to be analysed contains an unknown amount of chemicals.
- ✓ The reagent of unknown concentration reacts with a chemical of an unknown amount in the presence of an indicator (mostly phenolphthalein) to show the end-point. It's the point indicating the completion of the reaction.
- ✓ The volumes are measured by titration which completes thereaction between the solution and reagent.
- ✓ The volume and concentration of reagent which are used in the titration show the amount of reagent and solution.
- ✓ The amount of unknown chemical in the specific volume of solution is determined by the mole fraction of the equation.
- ✓ When the endpoint of the reaction is reached, the volume of reactant consumed is measured and applied to carry volumetric analysis calculations of the analyte by the following formula,

Ca= Ct Vt M / Va

Where,

Ca is the analyte concentration, typically in molarity.

Ct is the titrant concentration, typically in molarity.

V is the volume of the titrant which is used, typically in liters.

M is the mole ratio of the analyte and reactant from the balanced equation.

V is the volume of the analyte, typically in liters.

Many non-acid-base titrations are needed a constant pH throughout the reaction. Therefore, a buffer solution can be added to the titration chamber to maintain the pH value.

Puri

What is Chromatography

Chromatography is the technique for the separation, purification, and testing of compounds.
The term ***"chromatography"*** is derived from Greek, chroma meaning, ***"colour,"*** and graphein meaning "***to write."***

In this process, we apply the mixture to be separated on a stationary phase (solid or liquid) and a pure solvent such as water or any gas is allowed to move slowly over the stationary phase, carrying the components separately as per their solubility in the pure solvent.

Principles of Chromatography

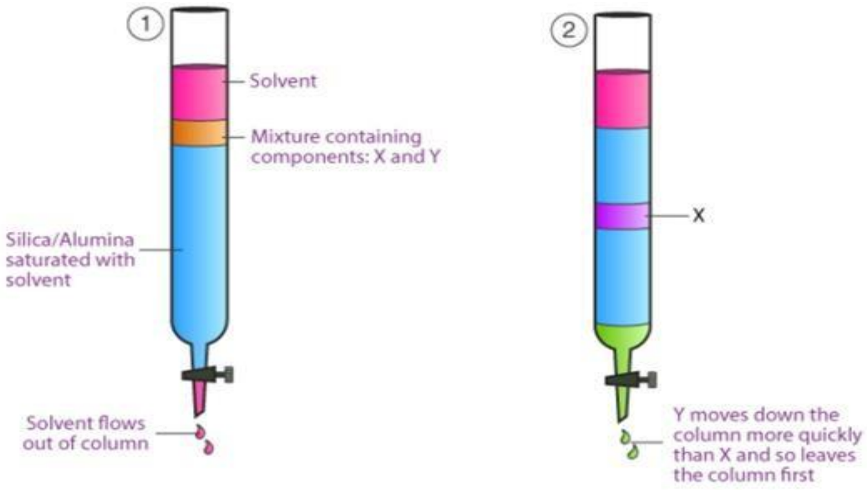
Chromatography is a separation method where the analyte is combined within a liquid or gaseous mobile phase., which is pumped through a stationary phase. Usually one phase is hydrophilic and the other is lipophilic. The components of the analyte interact differently with these two phases. Depending on their polarity they spend more or less time interacting with the stationary phase and are thus retarded to a greater or lesser extent. This leads to the separation of the different components present in the sample. Each sample component elutes from the stationary phase at a specific time called as retention time. As the components pass through the detector their signal is recorded and plotted in the form of a chromatogram.

Types of Chromatography

The four main types of chromatography are

1. Adsorption Chromatography

In the process of adsorption chromatography, different compounds are adsorbed on the adsorbent to different degrees based on the absorptivity of the component. Here also, a mobile phase is made to move over a stationary phase, thus carrying the components with higher absorptivity to a lower distance than that with lower absorptivity. The main types of chromatographic techniques that are used in industries are given as under.

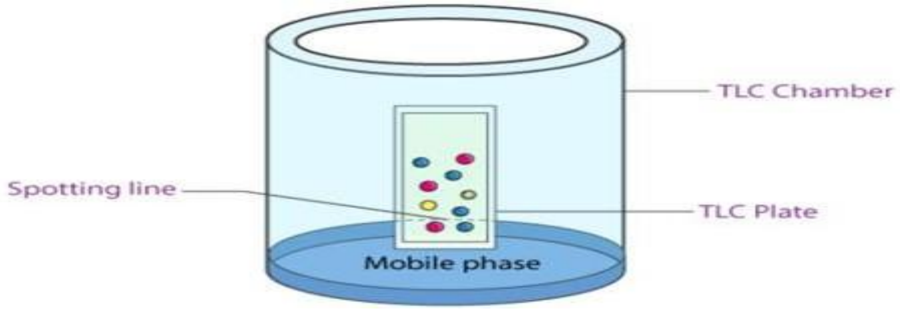


Chromatography

2. Thin Layer Chromatography

In the process of thin-layer chromatography (TLC), the mixture of substances is separated into its components with the help of a glass plate coated with a very thin layer of adsorbent, such as silica gel and alumina, as shown in the figure below.

The plate used for this process is known as chrome plate. The solution of the mixture to be separated is applied as a small spot at a distance of 2 cm above one end of the plate. The plate is then placed in a closed jar containing a fluid termed as an eluant, which then rises up the plate carrying different components of the mixture to different heights.

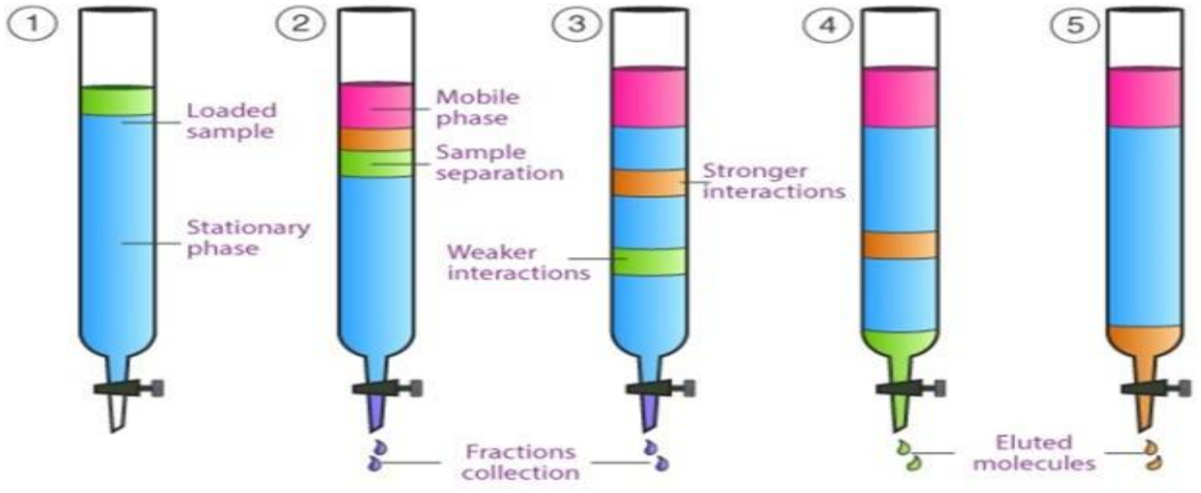


Thin Layer Chromatography

3. Column Chromatography

Column chromatography is the technique used to separate the components of a mixture using a column of suitable adsorbent packed in a glass tube, as shown in the figure below. The mixture is placed on the top of the column, and an appropriate eluant is made to flow down the column slowly.

Depending upon the degree of adsorption of the components on the wall adsorbent column, the separation of the components takes place. The component with the highest absorptivity is retained at the top, while the other flow down to different heights accordingly.

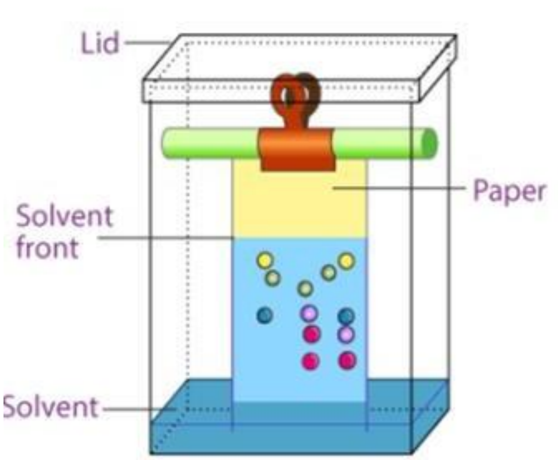


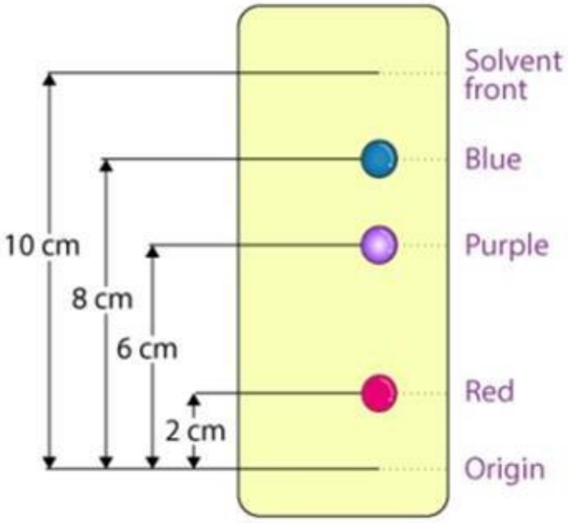
Column Chromatography

4. Partition chromatography

In this process, a continuous differential partitioning of components of a mixture into a stationary phase and mobile phase takes place. The example of partition chromatography can be seen in paper chromatography. In this process, chromatography paper is used as a stationary phase which is suspended in a mixture of solvents that act as a mobile phase.

Here, we put a spot at the base of the chromatographic paper with the mixture to be separated and as the solvent rises up this paper, the components are carried to different degrees depending upon their retention on the paper. The components are thus separated at different heights.

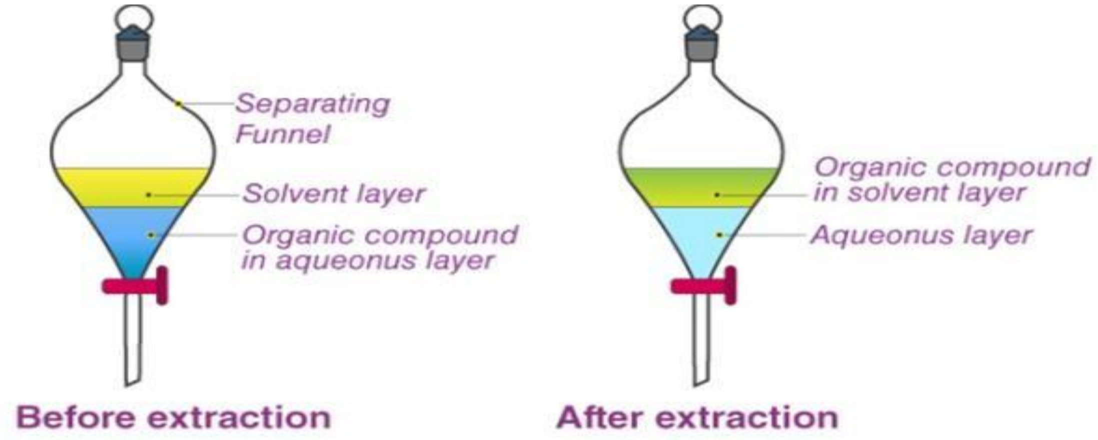




What is Differential Extraction?

Differential extraction is the method of separation of any organic component present in an aqueous solution. In this process, we use an organic solvent for which the solubility of the desired compound is more than compared to that in water. Also, the organic solvent is chosen such that it is immiscible with the aqueous solution so that it can form layers and can be separated easily using a separating funnel.

The organic compound is later recovered by the process of distillation or evaporation. The process of continuous extraction is used in cases when the solubility of the compound is less in the organic solvent.



Applications of Chromatography

In bio analytical chemistry, chromatography is mainly used for the separation, isolation and purification of proteins from complex sample matrices. In cells for example, proteins occur alongside numerous other compounds such as lipids and nucleic acids. In order to be analysed, these proteins must be separated from all the other cell components. Then the proteins of interest might have to be isolated from other proteins and purified further.

Chromatography is an essential part of almost any protein purification strategy. A number of different chromatographic techniques are used for the purification and analysis of proteins. They can be classified according to the physical principle involved in the separation process. Typical examples include reversed phase chromatography, ion exchange chromatography, affinity chromatography and size exclusion chromatography.

SEPARATION AND PURIFICATION TECHNIQUES – EXTRACTION, DISTILLATION AND CRYSTALLIZATION.

rgnic Compounds

The **purification of organic compounds** is necessary, though a complex step after its extraction from a natural source or synthesis in the laboratory. The method of purification of the organic compound depends mainly on the nature of the compound and the impurities present.

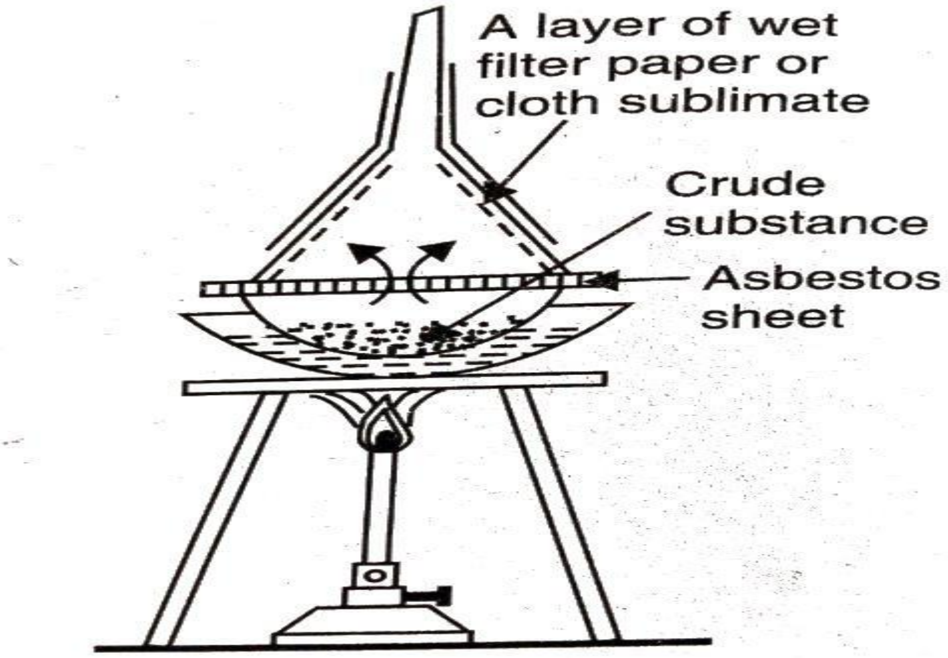
One easy method to check the purity of an organic compound is to either melt or boil it, as organic compounds tend to have sharp melting and boiling points.

Purification means the removal of unwanted impurities present in an organic compound. The general **methods of purification** are listed below:

Methods of Purification

Sublimation

Some solids can directly pass to the vapour state without going through the liquid phase. The purification technique which exploits this property is called sublimation. It is helpful in separating sublimable compounds from non-sublimable ones.



Methods of Purification – Sublimation

The substance is heated in a China dish above, and an inverted funnel is kept to collect the sublimable compounds. The funnel is kept cool so as to hasten the process. Vapours of the substance solidify on the funnel.

Check: Sublimation

Crystallisation

The principle here is that the compound and the impurities have different solubilities in a solvent. A solvent is chosen, where the compound to be purified is sparingly soluble, that is, it is sparingly soluble at a lower temperature and soluble at a higher temperature. The solution is heated to get a saturated solution, and on cooling, the crystals of the compounds are removed via filtration.

For example, crystals of benzoic acid can be crystallised with water. Benzoic acid is sparingly soluble in cold water and soluble in hot water.

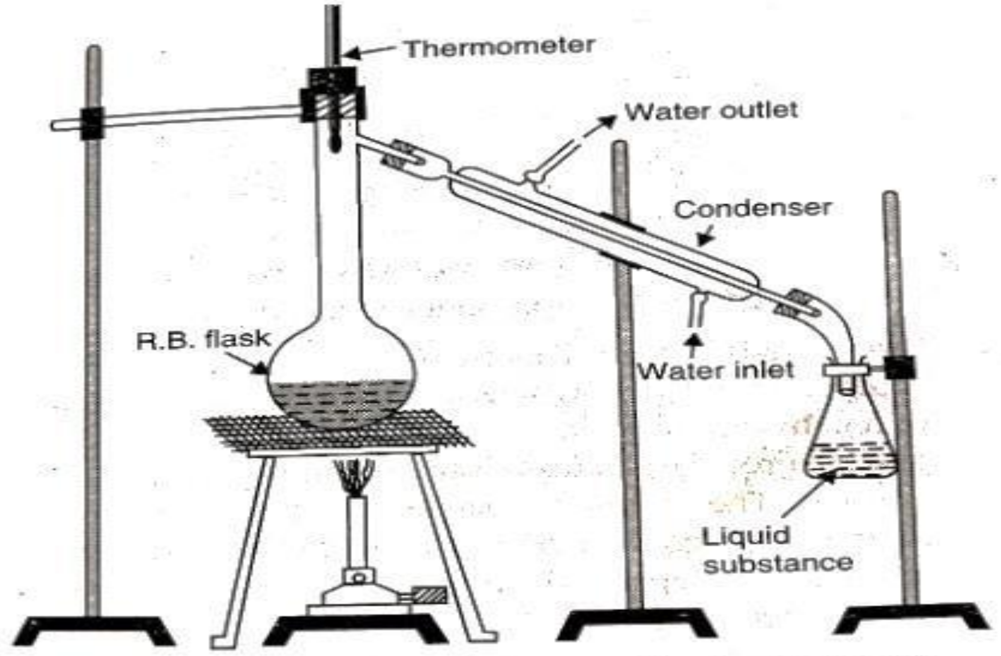
If the mixture contains impurities that have the same solubility as that of the compound to be purified, repeated crystallisation is performed.

Check: Crystallisation

Purification of Liquids

Distillation

The underlying principle behind distillation is that the mixture of liquids can be separated by the difference in their boiling points. The boiling point is defined as the temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure. This method separates volatile liquids from non-volatile liquids. The setup is given below.



(The vapours of the substance formed are condensed and the liquid is collected in a conical flask.)

Purification of Liquids – Distillation

The mixture is taken in the RB flask and boiled. The more volatile, i.e., component with a lower boiling point, evaporates faster and is collected in a separate container. A condenser is used to hasten the process of condensation.

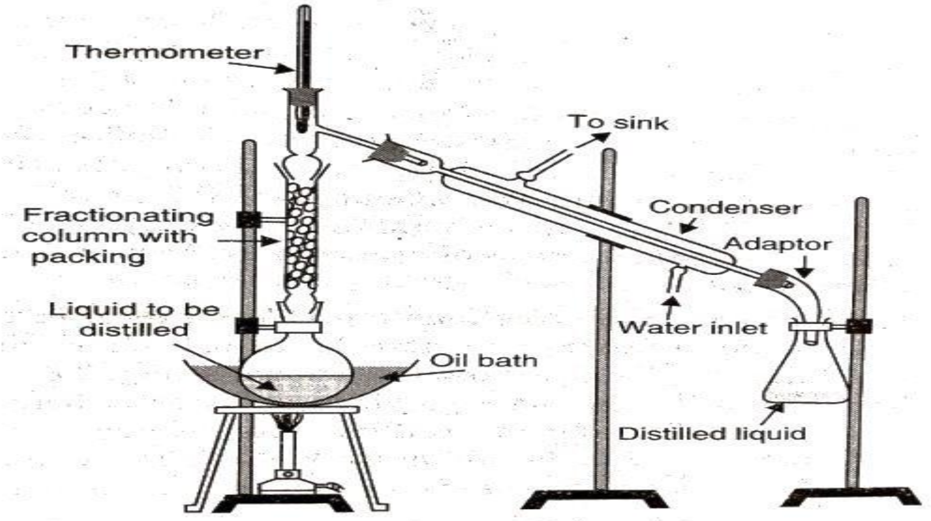
For example, a mixture of chloroform and aniline can be separated by distillation. The boiling point of chloroform is 60°C, and that of aniline is 189°C. Therefore, distillation can be used to separate a mixture of chloroform and aniline.

Check: Distillation

Fractional Distillation

This method is employed when the difference between the boiling points of the liquids isn’t much. Since the vapours of such liquids might condense together, a fractionating column is fixed to the mouth of the RB.

Check: Fractional Distillation

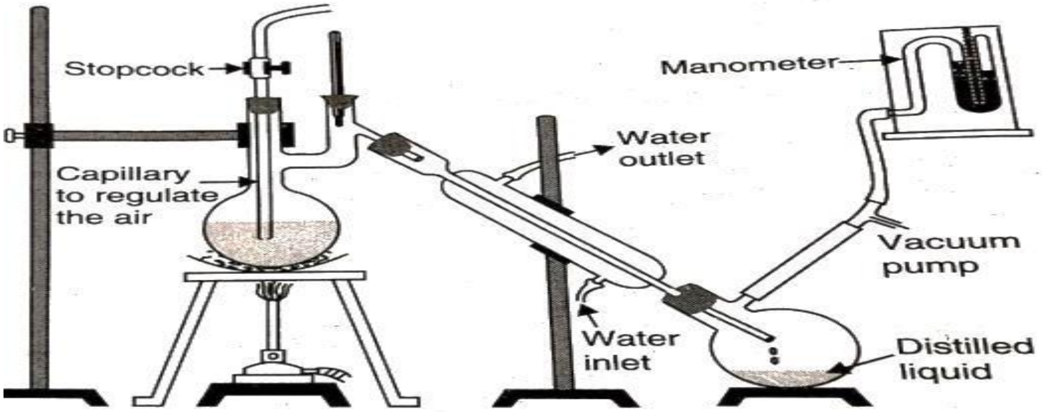


(The vapours of lower boiling fraction reach the tap of the column first followed by the vapours of higher boiling fractions.)

Purification of Liquids – Fractional Distillation

Vacuum Distillation

Since the boiling point is dependent on the atmospheric pressure, the liquids will boil at a temperature lesser than their boiling points if they were distilled in an atmosphere having lower pressure. This is achieved by using a vacuum pump. Since the atmospheric pressure is reduced, the liquids also boil faster, and hence the whole process of distillation is made fast.



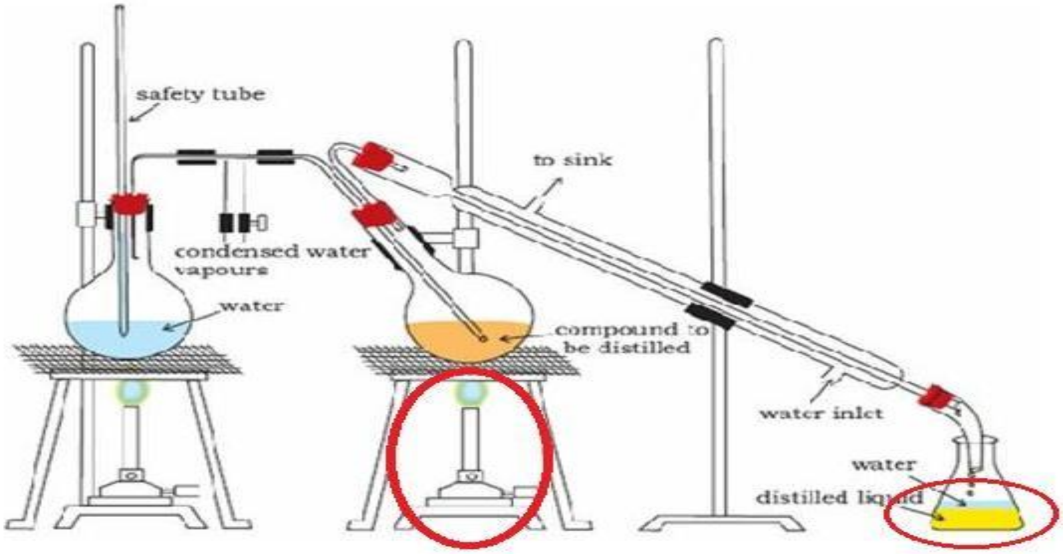
(A liquid boils at a temperature below its vapour pressure by reducing the pressure.)

Process of Vacuum Distillation

Steam Distillation

In this variant, steam is passed into the flask containing the liquids to be separated. The principle here is that the liquids will boil faster because aqueous tension (vapour pressure of water) helps in equalising the atmospheric pressure.

Total pressure = Aqueous tension + vapour pressure of liquid components



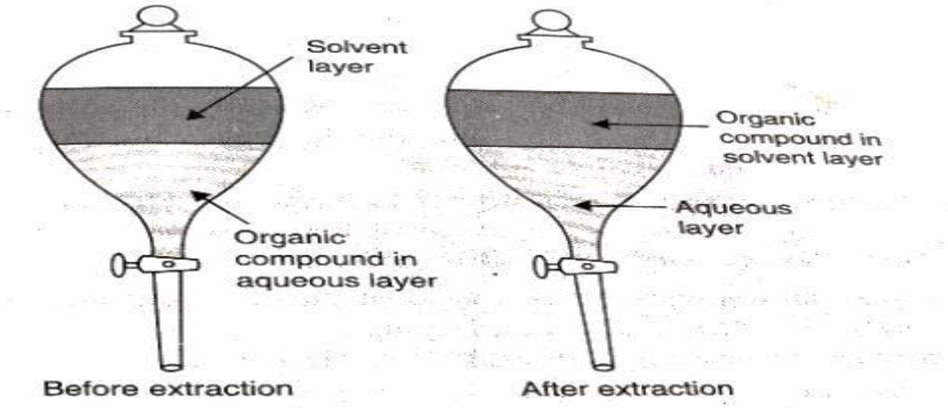
Purification of Liquids by Steam Distillation

In the absence of aqueous tension, the process of boiling would have been continued until it equalises the atmospheric pressure. Now, with the addition of steam, this process is expedited.

Differential Extraction

This method is used for immiscible liquids, that is, liquids that do not mix together. For example, oil and water are immiscible.

The immiscible liquids are taken in a separating funnel and left undisturbed. After a while, they separate out according to their specific gravities, with the heavier liquid at the bottom. Then, they are collected later.



(Extraction of compound takes place based on difference in solubility.)

Substances can also be separated according to their preferential solubilities in the liquid. For example, if phenol is to be extracted, it can be preferentially extracted using NaOH solution as one of the liquids used.

Chromatography

Chromatography is an important separation technique used to separate constituent particles of a mixture of substances to purify the compounds and check the purity of organic compounds. In this technique, on a stationary phase (solid or liquid), a mixture of substances is applied. The mixture of gas or the pure solvent is allowed to move slowly on the stationary phase. Due to this, the components of the mixture start separating from one another.

Chromatography is of two types:

- Adsorption Chromatography
- Partition Chromatography

Adsorption Chromatography

It is based on the principle that the constituents are adsorbed on an adsorbent in varying degrees. The adsorbents used are generally silica gel or alumina. When a mobile phase moves over the fixed phase, different constituents of the mixture get adsorbed at various distances over the fixed phase.

Check: Adsorption Chromatography

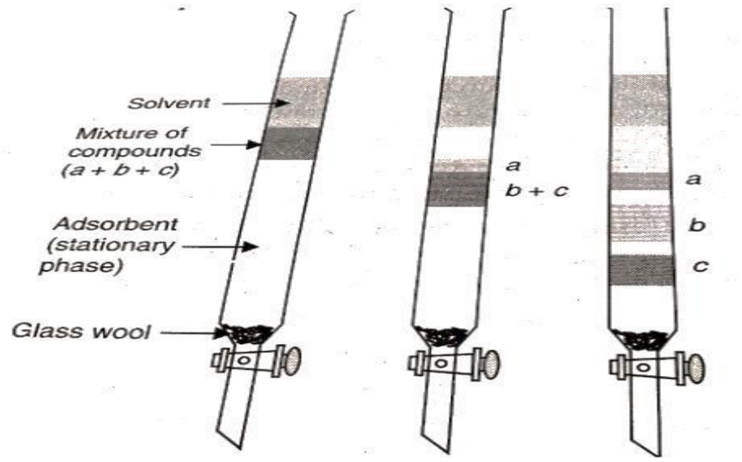
Adsorption Chromatography is further classified into:

- Column Chromatography
- Thin Layer Chromatography

Column Chromatography

Here, a mixture is separated over a column of either silica gel or alumina, packed in a glass column. The constituent with the most affinity with the fixed phase is adsorbed at the top, and so on. It is then retrieved by using an eluant. The solvent is then evaporated to get the constituent.

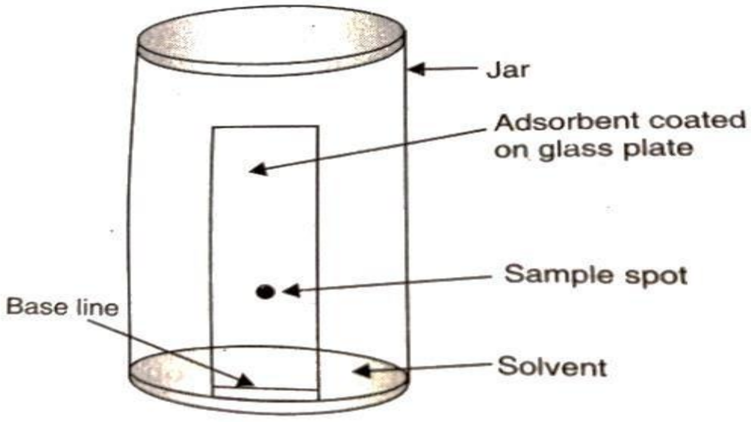
Check: Column Chromatography



Thin Layer Chromatography

Here, a sheet of alumina is taken (0.2 mm thick), over which a small spot of the mixture is placed, and it is kept in a suitable solvent. The solvent rises due to capillary action, and the constituents also rise with the solvent depending on their differential adsorption, and thereby, they are separated.

Check: Thin Layer Chromatography



Thin Layer Chromatography Principle

Like other chromatographic techniques, thin-layer chromatography (TLC) depends on the separation principle. The separation relies on the relative affinity of compounds towards both the phases. The compounds in the mobile phase move over the surface of the stationary phase. The movement occurs in such a way that the compounds which have a higher affinity to the stationary phase move slowly while the other compounds travel fast. Therefore, the separation of the mixture is attained. On completion of the separation process, the individual components from the mixture appear as spots at respective levels on the plates. Their character and nature are identified by suitable detection techniques.

Thin Layer Chromatography Diagram

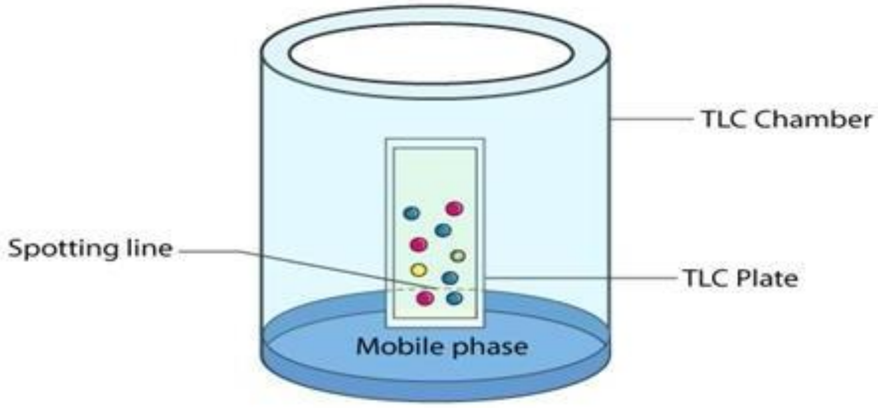


Diagram of Thin Layer Chromatography

Thin Layer Chromatography Procedure

Before starting with the Thin Layer Chromatography Experiment, let us understand the different components required to conduct the procedure along with the phases involved.

1. Thin Layer Chromatography Plates – ready-made plates are used which are chemically inert and stable. The stationary phase is applied on its surface in the form of a thin layer. The stationary phase on the plate has a fine particle size and also has a uniform thickness.
2. Thin Layer Chromatography Chamber – Chamber is used to develop plates. It is responsible to keep a steady environment inside which will help in developing spots. Also, it prevents the solvent evaporation and keeps the entire process dust-free.
3. Thin Layer Chromatography Mobile phase – Mobile phase is the one that moves and consists of a solvent mixture or a solvent. This phase should be particulate-free. The higher the quality of purity the development of spots is better.
4. Thin Layer Chromatography Filter Paper – It has to be placed inside the chamber. It is moistened in the mobile phase.

Thin Layer Chromatography Experiment

The stationary phase that is applied to the plate is made to dry and stabilize.

- To apply sample spots, thin marks are made at the bottom of the plate with the help of a pencil.
- Apply sample solutions to the marked spots.
- Pour the mobile phase into the TLC chamber and to maintain equal humidity, place a moistened filter paper in the mobile phase.
- Place the plate in the TLC chamber and close it with a lid. It is kept in such a way that the sample faces the mobile phase.
- Immerse the plate for development. Remember to keep the sample spots well above the level of the mobile phase. Do not immerse it in the solvent.

- Wait till the development of spots. Once the spots are developed, take out the plates and dry them. The sample spots can be observed under a UV light chamber.

Thin Layer Chromatography Applications

- The qualitative testing of Various medicines such as sedatives, local anaesthetics, anticonvulsant tranquilisers, analgesics, antihistamines, steroids, hypnotics is done by TLC.
- TLC is extremely useful in Biochemical analysis such as separation or isolation of biochemical metabolites from its blood plasma, urine, body fluids, serum, etc.
- Thin layer chromatography can be used to identify natural products like essential oils or volatile oil, fixed oil, glycosides, waxes, alkaloids, etc.
- It is widely used in separating multicomponent pharmaceutical formulations.
- It is used for the purification of samples and direct comparison is done between the sample and the authentic sample.
- It is used in the food industry, to separate and identify colours, sweetening agent, and preservatives
- It is used in the cosmetic industry.
- It is used to study if a reaction is complete.

Disadvantages Of Thin Layer Chromatography:

1. Thin Layer Chromatography plates do not have longer stationary phase.
2. When compared to other chromatographic techniques the length of separation is limited.
3. The results generated from TLC are difficult to reproduce.
4. Since TLC operates as an open system, some factors such as humidity and temperature can be can affect the final outcome of the chromatogram.
5. The detection limit is high and therefore if you want a lower detection limit, you cannot use TLC.
6. It is only a qualitative analysis technique and not quantitative.

Column Chromatography Principle

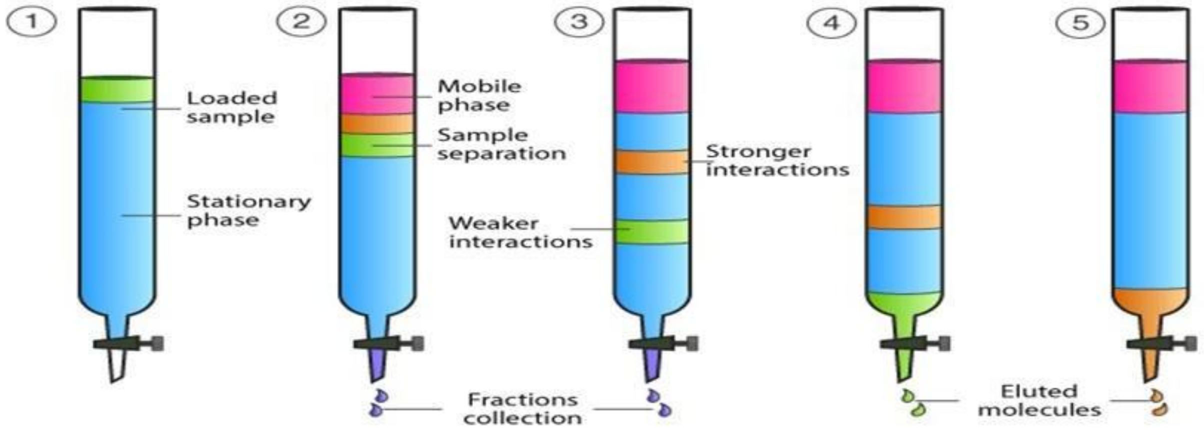
When the mobile phase along with the mixture that needs to be separated is introduced from the top of the column, the movement of the individual components of the mixture is at different rates. The components with lower adsorption and affinity to the stationary phase travel faster when compared to the greater adsorption and affinity with the stationary phase. The components that move fast are removed first whereas the components that move slowly are eluted out last.

The adsorption of solute molecules to the column occurs in a reversible manner. The rate of the movement of the components is expressed as:

R_f = the distance travelled by solute/ the distance travelled by the solvent

R_f is the retardation factor.

Column Chromatography Diagram



Column Chromatography Diagram

Elution

Elution is a chemical process that involves removing a material's ions by ion exchange with another material. The chromatographic technique of extracting an adsorbed substance from a solid adsorbing media using a solvent. The eluent is the solvent or mobile phase that passes through the column. When the polarity of the eluent matches the polarity of the molecules in the sample, the molecules desorb from the adsorbent and dissolve in the eluent.

The fraction of the mobile phase that transports the sample components is known as eluent. The mixture of solute and solvent that exits the column is known as an eluate. The eluate is made up of the mobile phase and analytes. A substance that separates and moves constituents of a mixture through the column of a chromatograph. The eluent in liquid chromatography is a liquid solvent whereas in gas chromatography is a carrier gas.

Column Chromatography Procedure

Before starting with the Column Chromatography Experiment let us understand the different phases involved.

Mobile phase – This phase is made up of solvents and it performs the following functions:

1. It acts as a solvent-sample mixture that can be introduced in the column.
2. It acts as a developing agent – helps in the separation of components in the sample to form bands.
3. It acts as an eluting agent – the components that are separated during the experiment are removed from the column
4. Some examples of solvents used as mobile phases based on their polarity are – ethanol, acetone, water, acetic acid, pyridine, etc.

Stationary phase – It is a solid material which should have good adsorption properties and meet the conditions given below:

1. Shape and size of particle: Particles should have a uniform shape and size in the range of 60 – 200μ in diameter.
2. Stability and inertness of particles: high mechanical stability and chemically inert. Also, no reaction with acids or bases or any other solvents was used during the experiment.
3. It should be colourless, inexpensive and readily available.
4. Should allow free flow of mobile phase
5. It should be suitable for the separation of mixtures of various compounds.

Column Chromatography Experiment

- The stationary phase is made wet with the help of solvent as the upper level of the mobile phase and the stationary phase should match. The mobile phase or eluent is either solvent or a mixture of solvents. In the first step the compound mixture that needs to be separated, is added from the top of the column without disturbing the top level. The tap is turned on and the adsorption process on the surface of silica begins.
- Without disturbing the stationary phase solvent mixture is added slowly by touching the sides of the glass column. The solvent is added throughout the experiment as per the requirement.
- The tap is turned on to initiate the movement of compounds in the mixture. The movement is based on the polarity of molecules in the sample. The non-polar components move at a greater speed when compared to the polar components.
- For example, a compound mixture consists of three different compounds viz red, blue, green then their order based on polarity will be as follows blue>red>green
- As the polarity of the green compound is less, it will move first. When it arrives at the end of the column it is collected in a clean test tube. After this, the red compound is collected and at last blue compound is collected. All these are collected in separate test tubes.

Column Chromatography Applications

- Column Chromatography is used to isolate active ingredients.
- It is very helpful in separating compound mixtures.
- It is used to determine drug estimation from drug formulations.
- It is used to remove impurities.
- Used to isolate metabolites from biological fluids.

Types of Column Chromatography:

1. Adsorption column chromatography – Adsorption chromatography is a technique of separation, in which the components of the mixture are adsorbed on the surface of the adsorbent.

2. Partition column chromatography – The stationary phase, as well as mobile phase, are liquid in partition chromatography.

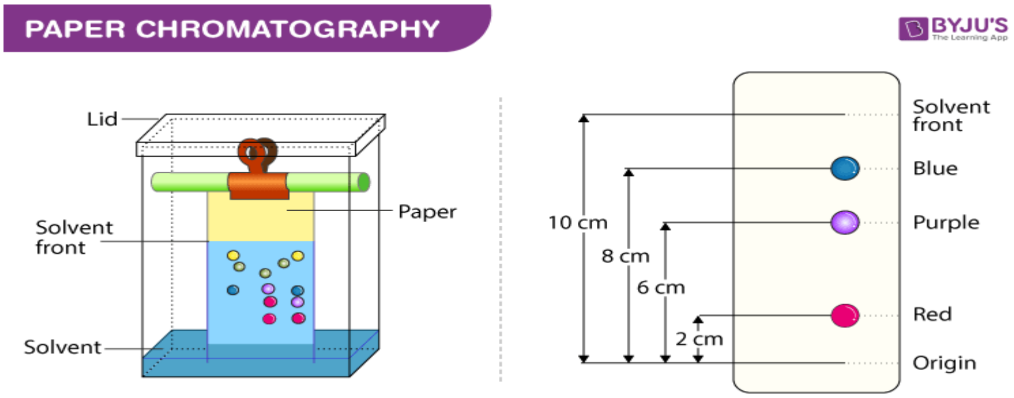
3. Gel column chromatography – In this method of chromatography, the separation takes place through a column packed with gel. The stationary phase is a solvent held in the gap of a solvent.

4. Ion exchange column chromatography – A chromatography technique in which the stationary phase is always ion exchange resin.

Paper Chromatography Principle

The principle involved can be partition chromatography or adsorption chromatography. Partition chromatography because the substances are partitioned or distributed between liquid phases. The two phases are water held in pores of the filter paper and the other phase is a mobile phase which passes through the paper. When the mobile phase moves, the separation of the mixture takes place. The compounds in the mixture separate themselves based on the differences in their affinity towards stationary and mobile phase solvents under the capillary action of pores in the paper. Adsorption chromatography between solid and liquid phases, wherein the solid surface of the paper is the stationary phase and the liquid phase is the mobile phase.

Paper Chromatography Diagram



Paper Chromatography Procedure

Below we have explained the procedure to conduct Paper Chromatography Experiment for easy understanding of students.

1. **Selecting a suitable type of development:** It is decided based on the complexity of the solvent, paper, mixture, etc. Usually ascending type or radial paper chromatography is used as they are easy to perform. Also, it is easy to handle, the chromatogram obtained is faster and the process is less time-consuming.
2. **Selecting a suitable filter paper**: Selection of filter paper is done based on the size of the pores and the sample quality.
3. **Prepare the sample:** Sample preparation includes the dissolution of the sample in a suitable solvent (inert with the sample under analysis) used in making the mobile phase.
4. **Spot the sample on the paper:** Samples should be spotted at a proper position on the paper by using a capillary tube.
5. **Chromatogram development:** Chromatogram development is spotted by immersing the paper in the mobile phase. Due to the capillary action of paper, the mobile phase moves over the sample on the paper.
6. **Paper drying and compound detection**: Once the chromatogram is developed, the paper is dried using an air drier. Also, detecting solution can be sprayed on the chromatogram developed paper and dried to identify the sample chromatogram spots.

Paper Chromatography Applications

There are various applications of paper chromatography. Some of the uses of Paper Chromatography in different fields are discussed below:

- To study the process of fermentation and ripening.
- To check the purity of pharmaceuticals.
- To inspect cosmetics.
- To detect the adulterants.
- To detect the contaminants in drinks and foods.
- To examine the reaction mixtures in biochemical laboratories.
- To determine dopes and drugs in humans and animals.

Types of paper chromatography:

1. Ascending Paper Chromatography – The techniques goes with its name as the solvent moves in an upward direction.
2. Descending Paper Chromatography – The movement of the flow of solvent due to gravitational pull and capillary action is downwards, hence the name descending paper chromatography.
3. Ascending – Descending Paper Chromatography – In this version of paper chromatography, movement of solvent occurs in two directions after a particular point. Initially, the solvent travels upwards on the paper which is folded over a rod and after crossing the rod it continues with its travel in the downward direction.
4. Radial or Circular Paper Chromatography – The sample is deposited at the centre of the circular filter paper. Once the spot is dried, the filter paper is tied horizontally on a Petri dish which contains the solvent.
5. Two Dimensional Paper Chromatography – Substances which have the same r_f values can be resolved with the help of two-dimensional paper chromatography.