MAA OMWATI DEGREE COLLAGE ,HASSANPUR

B.Sc -2nd sem

Inportant notes

Sub-fundamental chemistry-2

Session- 2024-25 **Mr Devinder**

NON aqueous Solvents

What is a Solvent?

A solvent is a chemical substance that dissolves another chemical substance to form a solution of a homogeneous mixture. The solvent is the component in the solution that is present in the largest amount and determines the physicochemical form of the substance as either solid, liquid or gas. Solvents are usually but not necessarily always liquids and can also be gases or solids.

The organic solvents share a common structure; Organic solvents are both hydrophobic and hydrophilic in nature, volatile and of low molecular weight and exist in liquid form at room temperature. The solvent is the part that normally consists of more than 50 % of a solution, whereas the solvent is the part that is blended into the solvent. Typically, this is less than 50 % of the solution.

Solvent Classifications

Organic solvents and inorganic solvents are two types of solvents. Inorganic solvents don't contain the element carbon. The most common inorganic solvents are water, and liquid ammonia whereas organic solvents, such as alcohols, glycol ethers, contain carbon and oxygen in their structure.

1. Polar Solvents

A polar solvent is a type of solvent that has large partial charges or dipole moments. The bonds between the atoms have very different but measurable electronegativities. A polar solvent can dissolve ions and other polar compounds.

Polar solvents are strong dipolar molecules that, as an interface form, also use hydrogen bonding. Polar solvents also often work by breaking the solute's covalent bonds, inducing ionisation of the solute.

The most common solvents used in drug delivery systems are polar solvents, including, among others, water and alcohol. Other polar solvents, such as alcohols, aldehydes and sugar ketones and other compounds of -OH groups, are typical solutes for which polar solvents are used.

2. Nonpolar Solvents

Nonpolar Solvents possess little or no dipolar character. Although they tend to be unable to independently form dipoles, they can utilize induced dipole-induced dipole interactions for dissolving appropriate solutes.

Nonpolar solvents have dielectric constants between 1 and 20 and include fixed oils, carbon tetrachloride and chloroform among others. Ionic and polar solutes have little to no solubility in nonpolar solvents. However, oils, fats and fatty acids dissolve well in nonpolar solvents.

3. Aprotic Solvents

Aprotic solvents do not release protons , but may act either as a simple solvent , where polarity as measured by the dielectric constant is significant , or they may act as a proton acceptor i.e. aprotic basic. Aprotic solvents are polar compounds of liquid that contain no dissociable atoms of hydrogen. Chemical bodies such as O-H and N-H bonds are absent from these solvents. Therefore, hydroxyl groups (-OH) and amine groups ($-NH_2$) are absent from aprotic solvents and are unable to form hydrogen bonds.

Aprotic solvents share with protic solvents the ability of ion dissolving. There is a lack of acidic hydrogen in these solvents, thus no major release of hydrogen ions. Polar aprotic solvents have dielectric constant values that are minimal or moderate. A moderate polarity is seen by these solvents.

4. Protic Solvents

A protic solvent is made up of molecules that may serve as donors of hydrogen-bonds. Examples of protic solvents contain water, alcohol, and carboxylic acids. Solvents that are unable to serve as donors to hydrogen-bonds are considered aprotic solvents. Examples of aprotic solvents include ether, methylene chloride and hexane.

Compounds that can be described by the general formula ROH are polar protic solvents. The polarity of the polar protic solvents occurs from the O-H bond dipole. Combined with the small size of the hydrogen atom, the large difference in the electronegativity of the oxygen and the hydrogen atom warrants the isolation of molecules comprising the OH group from those polar compounds which do not.

For one, vinegar is an acetic acid solution in water. It can be impossible to tell which substance is the solute and which is the solvent in a two-liquid solution. In addition, the solvent is the material found in the largest quantity. In vinegar, the solvent is water and the solute is acetic acid.

1.

❖GENERAL CHARACTERISTICS OF NON AQUEOUS SOLVENT

1. **Electrolyte Solutions:** Solutions that conduct electricity are known as electrolyte solutions. Since salt's dissociated ions can travel freely in a solution when it dissolves, they allow a charge to flow. When salt is mixed with a solvent like water, electrolyte solutions are created. An electrolyte is a salt or ionisable molecule that permits that solution to conduct electricity when dissolved in a solution.
2. **Strong and Weak Electrolytes:** An electrolyte is a salt or ionisable molecule that permits a solution to conduct electricity. A charge can flow because a salt's dissociated ions can travel freely in a solution when it dissolves. A strong electrolyte dissociates into its constituent ions in solution, whereas a weak electrolyte remains fundamentally undissociated. Weak electrolytes include acetic acid, which is also a weak acid.
3. **Nonelectrolyte Solutions:** Nonelectrolytes are substances that do not ionise in water. As a result, nonelectrolyte-containing liquids do not conduct electricity. Covalent bonds, rather than ionic ones, typically hold nonelectrolytes together. Glucose or $C_6H_{12}O_6$ is an example of a nonelectrolyte. Although glucose (sugar) dissolves quickly in water, it is classified as a nonelectrolyte because it does not break into ions in the solution and does not conduct electricity.

Application of HSAB to predict the direction of Inorganic reactions:

HSAB principle is used to predict the outcome of few of the reactions. We can predict whether a reaction proceeds to the right or left based on soft or hard acid/base interactions.

1) The reaction between AsF_3 and PI_3 is possible and proceeds to the right since As^{3+} is softer than P^{3+} and I^- is softer than F^-.

$$AsF_3 + PI_3 \longrightarrow AsI_3 + PF_3$$

Remember that both As^{3+} and P^{3+} are soft but relatively As^{3+} is softer due to larger size.

2) The reaction between MgS and BaO as shown below is possible since Mg^{2+} is harder acid than Ba^{2+} and O^{2-} is harder base than S^{2-}.

$$MgS + BaO \longrightarrow MgO + BaS$$

3) P_2F_4 can be prepared by treating PF_2I with mercury as shown below.

$2PF_2I + 2Hg$ ------>□ $Hg_2I_2 + P_2F_4$

In this reaction, it is iodine rather than fluorine that is removed from PF_2I.

Explanation: Hg_2^{2+} ion is a soft acid that prefers soft base I^- rather than hard base F^-.

Solubility in water:

The compound formed due to soft acid-soft base combination is more covalent and less soluble in polar solvents like water. For example, Silver iodide, AgI is insoluble in water as it has covalent nature since it is the combination of soft acid, Ag^+ and soft base, I^-.

On the other hand, Lithium iodide, LiI is the result of a combination of Li^+ (hard acid) and I^- (soft base). Thus it is polar covalent and thus soluble in water.

❖ Occurrence of Noble Gases:

Helium:

- Helium is believed to have been formed during the formation of universe.
- Most of the helium is formed by nuclear fusion in the sun.
- Though there is continuous creation of new helium; the abundance of helium is not sufficiently large on earth.

Uses:

- Use of helium in balloon, due to its low density.
- Helium is used for cooling super magnets.
- Helium is also used as a protective gas in production of silicon and germanium crystals.
- Helium is also used in gas chromatography

Neon:

- Neon is produced by the fusion reaction taking place in stars.
- Its rare on Earth, like that of helium, is due to its relative lightness.
- Neon is monatomic, making it lighter than nitrogen and oxygen.

Uses:

- Neon is often used on billboards as it produces a reddish-orange colour. Some lights of different colours are sometimes called neon lights.
- Liquid neon acts as a good cryogenic coolant.
- Vacuum tubes require neon gas in preferential amount.

Argon:

- Discovered by Sir William Ramsay and an English chemist, Lord Rayleigh in 1894
- In nature, argon is found in the Earth’s atmosphere, 94 ppm, and in igneous rocks, 0.04 ppm. The isotopes found in nature are 36Ar , 38Ar, 40Ar

Uses:

- Due to its inertness, it is used in electric bulbs where it does not react with filament.
- It is widely used in welding and cutting.
- Low energy bulbs contain mercury and argon. When electric current pass it glows.

Krypton:

- The profusion of krypton in the atmosphere is thought to be about 0.000108 to 0.000114 percent. The element is also formed in the Earth’s crust when uranium and other radioactive elements decay.

Uses:

- High-power, flashing airport runway lights
- Krypton-based bulbs serve as excellent white light source for photographic flashes in burst shot photography
- It is used in MRI/CT techniques.

Xenon:

- The Earth’s atmosphere contains about 0.1 ppm of xenon. Studies designate that the atmosphere of Mars may comprise about the same quantity of xenon, perhaps 0.08 parts per million. The element is not identified to transpire in the Earth’s crust.

Uses:

- Xenon, an example of noble gas. Over the years, a number of appreciated uses for members of the noble gas class of elements have evolved. Xenon is no exclusion with a number of commercially viable uses.
- The production of xenon involves the fractional distillation of liquid air.
- Xenon when limited within a vacuum tube and subjected to an electrical charge exhibits a blue glow. This consequence finds a use in both antiseptic and stroboscopic lamps. Xenon lamps are of practice in the field of laser technology, where they are used to excite ruby lasers. Electron tube technology also includes the gas.

Radon:

- Radon is present in measurable amounts in the atmosphere of earth. Hot water springs and geysers contain radon. But nowadays most of the radon is obtained through the radioactive decay chain of radium.
- Samples of radon are found from decaying Radium 226.

Uses:

- Changes in groundwater radon concentrations help in the forecast of seismic tensions.
- Radon is used X-ray and for industrial radiography.
- Radon is used for treating auto-immune diseases.

Conclusion:

The 7 elements of the periodic table which are inert in nature yet have served purpose in our day to day life. All the elements have their different uses and different applications in the life of mankind. The abundance of such noble gases have been proved beneficial for the industrial, domestic and economical purposes.

❖ PREPARRATION AND PROPERTICES OF NOBLE GASES

The noble gases, also known as the inert gases and aerogens, are the elements that belong to group 18 of the modern periodic table. The elements that belong to this group are:

- Helium (He)
- Neon (Ne)
- Argon (Ar)
- Krypton (Kr)
- Xenon (Xe)
- Radon (Rn)

Under standard conditions for temperature and pressure, all the noble gases exist in the gaseous phase. They are known to possess extremely low chemical reactivity (hence the name inert gas). This is because all the noble gases have stable electronic configurations. This is the reason why noble gases do not form molecules easily and are mostly found as mono-atomic gases.

The general electronic configuration of the noble gases can be written as ‘$\mathbf{ns^2np^6}$’. Therefore, the outermost valence shells of the noble gases can be considered as ‘full’. This is the reason behind the chemically inert nature of the group 18 elements.

❖Properties of Helium (He)

Helium is a chemical element which is denoted by the symbol He. The atomic number of helium is 2. Under standard conditions for temperature and pressure (STP), helium exists as a **colourless monoatomic gas** that does not have any distinct odour or taste. It can be noted that helium is non-toxic in small concentrations. It is the first and the lightest noble gas. Among all elements, helium is known to possess the lowest boiling point.

Helium is an s-block element which corresponds to period 1 and group 18 of the modern periodic table. The electron configuration of helium is $1s^2$. Therefore, this element has a total of 2 electrons in its valence shell. The melting point of helium is approximately equal to 0.95 Kelvin (or -272.20 degrees Celsius) when it is placed under a pressure of 2.5 MPa. Under standard conditions for temperature and pressure, the density of this element corresponds to 1.7186 grams per litre. However, in its liquid state, the density of this element is approximately equal to

0.145 grams per cubic centimetre.

Properties of Neon (Ne)

Neon is a chemical element which is denoted by the symbol Ne. the atomic number of neon is 10. Under standard conditions for temperature and pressure (STP), neon exists as a colourless mono atomic gas (similar to helium). This gas does not possess any characteristic odour. Neon is the second-lightest noble gas, the lightest being helium.

Neon belongs to group 18 and period 2 of the modern periodic table. The electron configuration of this element is [He] $2s^2 2p^6$. It holds a total of 8 electrons in its valence shell. The melting point of neon is approximately equal to 24.56 Kelvin (or -248.59 degrees Celsius). On the other hand, the boiling point of neon is equal to 27.104 Kelvin (or -246.046 degrees Celsius). At STP, the density of this gas corresponds to 0.9 grams per litre (approximately). However, in its liquid state (at a temperature equal to its boiling point), the density of neon is equal to 1.207 grams per cubic centimetre.

The triple point of neon occurs at a temperature of 24.556 Kelvin and under a pressure of 43.37 kilopascals. The enthalpy of fusion of this element is equal to 0.335 kilojoules per mole. It can be noted that the latent heat of vaporisation of neon is equal to 1.71 kilojoules per mole.

Properties of Argon (Ar)

Argon is the 3rd noble gas whose atomic number is equal to 18. This element is denoted by the symbol Ar. In the Earth’s atmosphere, argon is known to be the third-most abundant gas. Under standard conditions for temperature and pressure, argon is known to exist as a colourless gas that exhibits a violet or lilac-coloured glow when it is placed in an electric field.

Argon is a p-block element that corresponds to group 18 and period 3 of the modern periodic table. The electronic configuration of argon is [Ne]$3s^2 3p^6$. This element has a total of 8 electrons in its valence shell. The melting point of argon corresponds to 83.81 Kelvin whereas its boiling point corresponds to 87.302 Kelvin. Under standard conditions for temperature and pressure, the density of argon is roughly equal to 1.784 grams per litre.

Properties of Krypton (Kr)

Krypton is the 4th noble gas. The atomic number of krypton is 36. This element is often denoted by the symbol Kr. Under standard conditions for temperature and pressure, krypton exists as a colourless monoatomic gas that does not have any characteristic odour. This gas is also known to be tasteless.

Krypton, like argon, is a p-block element. It corresponds to group 18 and period 4 of the modern periodic table. The electron configuration of krypton can be written as $[Ar]3d^{10}4s^{2}4p^{6}$. The melting point of this element is approximately equal to 115.78 Kelvin whereas the boiling point of this element is equal to 119.3 Kelvin. At STP, the density of this element is roughly equal to 3.75 grams per litre.

Properties of Xenon (Xe)

Xenon, the 5th noble gas, has an atomic number of 54. The symbol ‘Xe’ is often employed to denote xenon. Under standard conditions, this element is known to exist as a mono atomic gas that is colourless and odourless. This p-block element corresponds to period 5 and group 18 of the modern periodic table.

The electronic configuration of xenon is $[Kr]4d^{10}5s^{2}5p^{6}$. The melting point of xenon is equal to 161.4 Kelvin whereas the boiling point of this element is equal to 165.05 Kelvin. At STP, the density of xenon is roughly equal to 5.89 grams per litre.

Properties of Radon (Rn)

Radon is a noble gas whose atomic number is 86. The symbol of this element is Rn. Under standard conditions, radon (like most other noble gases) is a colourless and odourless gas that does not have any characteristic taste. It is important to note that radon is radioactive. In fact, the most stable isotope of radon, which is ^{222}Rn, is known to have a half-life of 3.8 days.

Radon is a p-block element that corresponds to group 18 and period 6 of the modern periodic table. The electronic configuration of this element is $[Xe]4f^{14}5d^{10}6s^{2}6p^{6}$. The melting and boiling points of radon are 202 Kelvin and 211.5 Kelvin respectively.

❖ Chemical properties of Noble gases

The noble gases do not react under normal conditions. The non-reactivity of noble gases is due to the following reasons:

1. The valence shell of the noble gases is completely filled. The next available shell is of much higher energy.
2. Noble gases have very high ionization enthalpies.
3. They have large positive values of electron gain enthalpy.

Noble gases have no tendency to gain or lose electrons under ordinary conditions. This is the only reason why they do not participate in chemical reactions and remain inert. According to modern researchers, it has been seen that noble gases can be compelled to take part in a chemical reaction under certain specific conditions.

A scientist named Neil Bartlett found that PtF_6 reacts with oxygen and forms $O_2^+ [PtF_6]^-$. The ionization energy of oxygen and xenon is comparable, and so PtF_6 should react with xenon to form $Xe^+ [PtF_6]^-$. This assumption was proved to be correct and hence he succeeded in isolating the orange-yellow compound, $XePtF_6$. This compound was obtained at room temperature by the interaction of PtF_6 with xenon. This discovery of Neil Bartlett led to the further discovery of several other xenon compounds, mainly those formed with electronegative elements such as fluorine and oxygen. There are only a few compounds of Krypton. Some compounds of radon have been prepared and identified by radiotracer techniques, but their isolation has not been possible. The true chemical nature of compounds of helium, neon, and argon is still unknown.

❖ Structure and bonding in Xenon Difluoride?

Xenon Difluoride is a chemical compound with the formula XeF_2. It was discovered in the year 1962. It is a powerful fluoridating agent. XeF_2 was considered to be a possible convenient replacement for elemental fluorine especially in addition reactions to a double bond. The oxidation state of xenon in Xenon Difluoride is +2. Xenon tetrafluoride has a negligible vapour pressure at -78° and about 3 mm-Hg at room temperature. Xenon difluoride is a hazardous chemical, reacting with water moisture to form hydrofluoric acid.

Xenon Difluoride Synthesis – XeF_2

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- When a mixture of xenon and fluorine in the ratio of 2:1 is heated at 400°C in a sealed nickel vessel, XeF_2 is formed.

$Xe + F_2 \rightarrow XeF_2$

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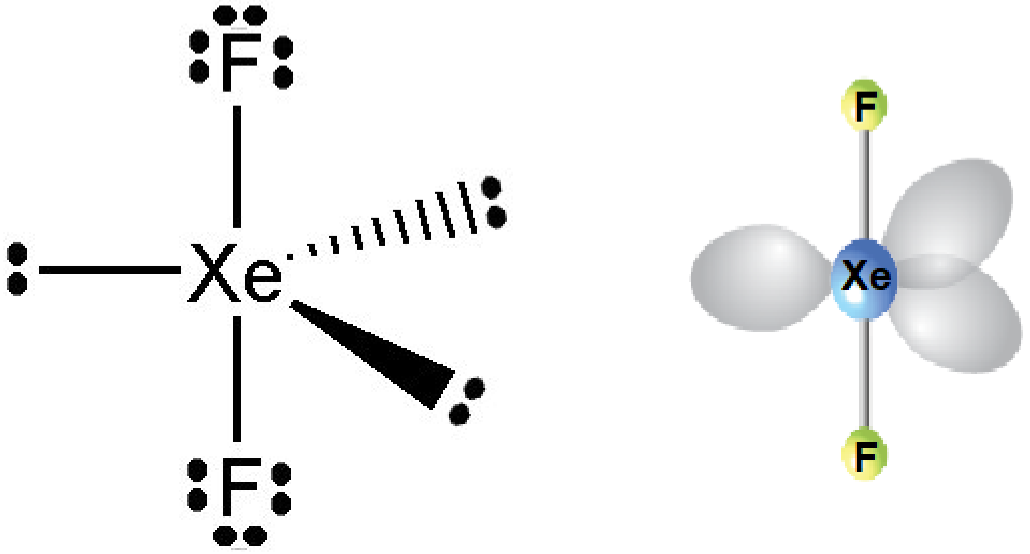
- Dioxygen difluoride reacts with xenon at about 118°C to give XeF_2.

$Xe + O_2F_2 \rightarrow XeF_2 + O_2$

Xenon Difluoride Structure – XeF_2

The structure of xenon difluoride is illustrated below.



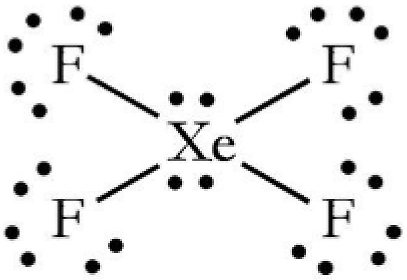
XeF2 structure features two covalent bonds between one xenon atom and two fluorine atoms. The xenon atom also holds 3 lone pairs of electrons.

Lewis Structure of XeF4

Now that we know the valence electrons of Xenon Tetrafluoride, sketching its Lewis structure will be much easier. Lewis dot structure shows the relationship between valence electrons surrounding specific atoms in a molecule. Lines denote the bonds in the structure, whereas dots denote the electrons not engaged in bond formation. Nonbonding electrons, also known as lone pairs of electrons, are electrons that do not form any bonds with other electrons.

We will put Xenon in the middle, with all the other fluorine atoms around it, since it is the least electronegative atom. Each molecular link absorbs two electrons, and since this molecule has four single bonds, eight of the 36 electrons are consumed. Begin wrapping the valence electrons around the atoms with the remaining valence electrons. One electron from the outer valence electron connected the fluorine atom to the outer valence electron.

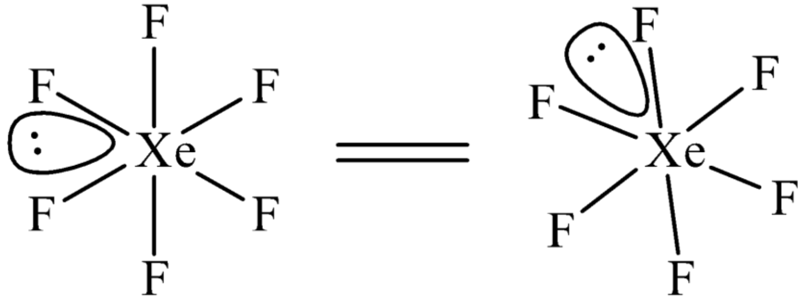
Observe that 24 electrons have already been attached to the fluorine atoms. Due to its exception from the octet rule, Xenon will become the recipient of the lone electron pairs of nonbonding electrons when atoms are atomised. Xenon combines these nonbonding electron pairs with these two nonbonding electron pairs to form a Lewis structure with two pairs of electrons lone on Xe and six nonbonding electrons on each Fluorine atom.



XeF_6 Molecular Structure

Let's understand the meaning of XeF_6 molecular geometry and bond angles meaning.

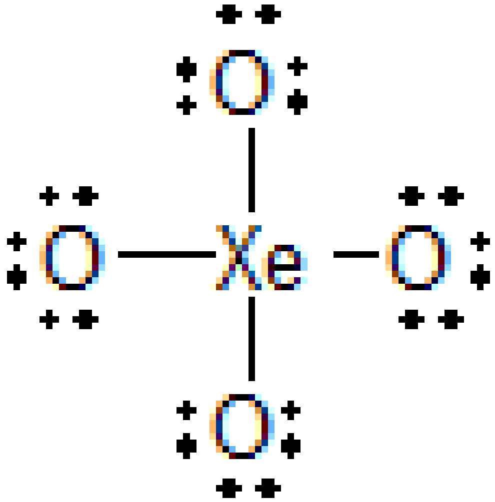
The molecular geometry of xenon hexafluoride is the arrangement of atoms in the molecule. The molecular geometry of XeF_6 is the sp^3d^3, which is also called a distorted octahedral or square bipyramidal after Hybridization. The fluorine atoms are positioned in the octahedron's vertices, while the lone pairs wander around in the space to prevent or lessen the repulsion. On the other hand, the bond angles of xenon hexafluoride describe the angle between its bonds. It describes how many lengths angles one atom of xenon hexafluoride is attached to another atom. The bond angle of xenon hexafluoride is 90° and 72°.



In XeF_6 Molecular Geometry, there are eight electrons present in the outer shell of the xenon. While combined with fluorine, six free electrons get paired with the six fluorine atoms, but two electrons of fluorine remain lonely. This resulted in the one lone pair and six bond pairs in the XeF_6 Molecular Geometry. The electrons in the valence shell of xenon become unpaired and promoted to unoccupied 5d orbitals when the fluorides of xenon develop.

XeO4 Lewis Structure (Xenon Tetroxide)

XeO4 is a chemical formula for Xenon Tetroxide. Although this molecule looks like an easy one to draw a Lewis structure for, let's not forget about Xenon that can have expanded octets despite having eight valence electrons in its outer shell.

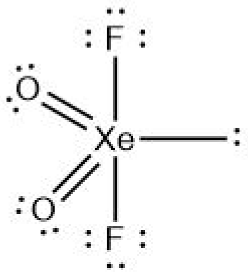


Structure of difluoro(dioxo)xenon (XeO2F2)

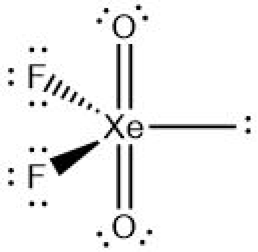
The hybridization of XeO_2F_2 by knowing the number of valence electrons and using the basic hybridization formula which is given as – Number of electrons = ½ [V+N-C+A].

Here, V will be the number of valence electrons present in the central atom (xenon).

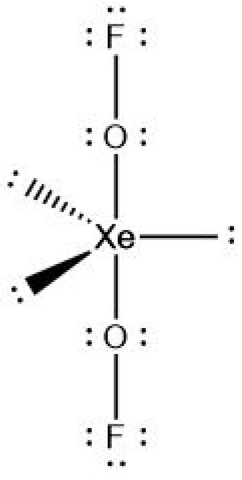
A)



B)



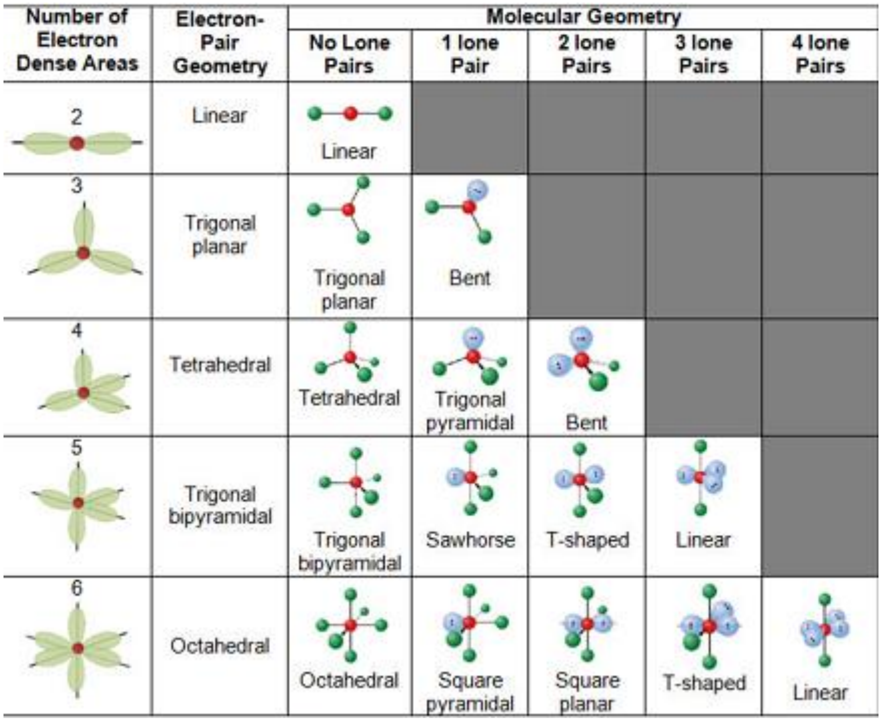
C)



What Is VSEPR Theory? Molecular shape of noble compound

The Valence Shell Electron Pair Repulsion Theory, abbreviated as VSEPR theory, is based on the premise that there is a repulsion between the pairs of valence electrons in all atoms, and the atoms will always tend to arrange themselves in a manner in which this electron pair repulsion is minimalised. This arrangement of the atom determines the geometry of the resulting molecule.

The different geometries that molecules can assume in accordance with the VSEPR theory can be seen in the illustration provided below.



Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2	Linear	Linear				
3	Trigonal planar	Trigonal planar	Bent			
4	Tetrahedral	Tetrahedral	Trigonal pyramidal	Bent		
5	Trigonal bipyramidal	Trigonal bipyramidal	Sawhorse	T-shaped	Linear	
6	Octahedral	Octahedral	Square pyramidal	Square planar	T-shaped	Linear

VSEPR Theory – Different Geometries That Molecules Can Assume

The two primary founders of the VSEPR theory are Ronald Nyholm and Ronald Gillespie. This theory is also known as the Gillespie-Nyholm theory to honour these chemists.

Postulates of VSEPR Theory

The postulates of the VSEPR theory are listed below.

- In polyatomic molecules (i.e., molecules made up of three or more atoms), one of the constituent atoms is identified as the central atom to which all other atoms belonging to the molecule are linked.
- The total number of valence shell electron pairs decides the shape of the molecule.
- The electron pairs have a tendency to orient themselves in a way that minimises the electron-electron repulsion between them and maximises the distance between them.
- The valence shell can be thought of as a sphere wherein the electron pairs are localised on the surface in such a way that the distance between them is maximised.
- Should the central atom of the molecule be surrounded by bond pairs of electrons, then the asymmetrically shaped molecule can be expected.
- Should the central atom be surrounded by both lone pairs and bond pairs of electrons, the molecule would tend to have a distorted shape.
- The VSEPR theory can be applied to each resonance structure of a molecule.
- The strength of the repulsion is strongest in two lone pairs and weakest in two bond pairs.

Limitations of VSEPR Theory

Some significant limitations of the VSEPR theory include

- This theory fails to explain isoelectronic species (i.e., elements having the same number of electrons). The species may vary in shape, despite having the same number of electrons.
- The VSEPR theory does not shed any light on the compounds of transition metals. The structure of several such compounds cannot be correctly described by this theory. This is because the VSEPR theory does not take into account the associated sizes of the substituent groups and the lone pairs that are inactive.
- Another limitation of the VSEPR theory is that it predicts that halides of group 2 elements will have a linear structure, whereas their actual structure is a bent one.

Predicting the Shapes of Molecules

The following steps must be followed in order to decide the shape of a molecule.

- The least electronegative atom must be selected as the central atom (since this atom has the highest ability to share its electrons with the other atoms belonging to the molecule).
- The total number of electrons belonging to the outermost shell of the central atom must be counted.
- The total number of electrons belonging to other atoms and used in bonds with the central atom must be counted.
- These two values must be added in order to obtain the valence shell electron pair number or the VSEP number.

6	Octahedral
7	Pentagonal Bipyramidal

Each of these corresponding shapes can also be found in the illustration provided earlier. However, the VSEPR theory cannot be used to obtain the exact bond angles between the atoms in a molecule.

Now, we will discuss each shape in detail.

Linear Shape of Molecule

- In this type of molecule, we find two places in the valence shell of the central atom.

- They should be arranged in such a manner that repulsion can be minimised (pointing in the opposite direction).
- **Example:** BeF_2

Trigonal Planar Shape of Molecule

- In this type of molecule, we find three molecules attached to a central atom.
- They are arranged in such a manner that repulsion between the electrons can be minimised (toward the corners of an equilateral triangle).
- **Example:** BF_3

Tetrahedral Shape of Molecule

- In two-dimensional molecules, atoms lie in the same plane, and if we place these conditions on methane, we will get a square planar geometry in which the bond angle between H-C-H is 90^0.
- Now, if we consider all these conditions for a three-dimensional molecule, we will get a tetrahedral molecule in which the bond angle between H-C-H is $109^028'$ (toward the corners of an equilateral triangle) CH_4

UNIT-II

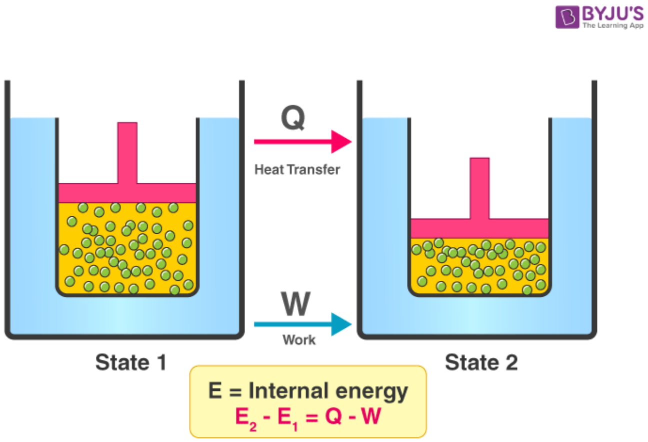
(THERMODYNAMIC)

The **first law of thermodynamics,** we need to understand the relation between heat and work and the concept of internal energy. Just like mass, energy is always conserved, i.e., it can neither be created nor destroyed, but it can be transformed from one form to another. Internal energy is a thermodynamic property of the system that refers to the energy associated with the molecules of the system, which includes kinetic energy and potential energy.

Whenever a system goes through any change due to the interaction of heat, work and internal energy, it is followed by numerous energy transfers and conversions. However, during these transfers, there is no net change in the total energy.

Similarly, if we look at the first law of thermodynamics, it affirms that heat is a form of energy. What it means is that the thermodynamic processes are governed by the principle of conservation of energy. The first law of thermodynamics is also sometimes referred to as the law of conservation of energy.

What Is the First Law of Thermodynamics?



A thermodynamic system in an equilibrium state possesses a state variable known as internal energy(E). Between the two systems, the change in the internal energy is equal to the difference of the heat transfer into the system and the work done by the system.

The first law of thermodynamics states that the energy of the universe remains the same. Though it may be exchanged between the system and the surroundings, it can’t be created or destroyed. The law basically relates to the changes in energy states due to work and heat transfer. It redefines the conservation of energy concept.

To help you understand the meaning of the first law, we can take the common example of a heat engine. In a heat engine, the thermal energy is converted into mechanical energy, and the process also is vice versa. Heat engines are mostly categorised as open systems. The basic working principle of a heat engine is that it makes use of the different relationships between heat, pressure and volume of a working fluid which is usually a gas. Sometimes phase changes might also occur involving a gas to liquid and back to gas.

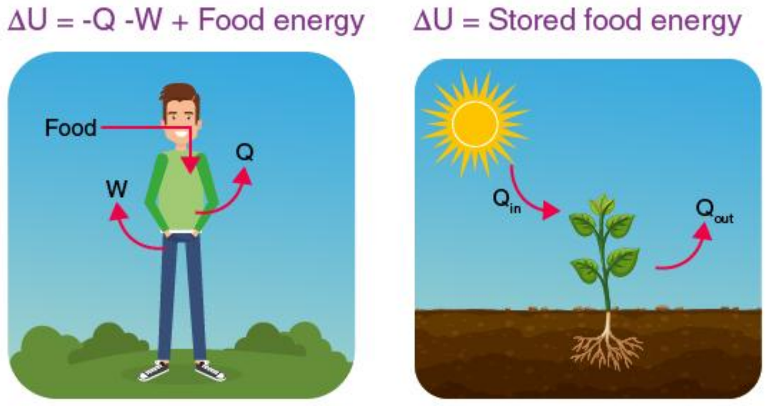
First Law of Thermodynamics Equation

The equation for the first law of thermodynamics is given as

$$\Delta U = q + W$$

Where,

- ΔU = Change in internal energy of the system
- q = Algebraic sum of heat transfer between system and surroundings
- W = Work interaction of the system with its surroundings



$\Delta U = -Q - W + \text{Food energy}$ $\Delta U = \text{Stored food energy}$

(a) (b)

Points to Remember

- For an isolated system, energy (E) always remains constant.
- Internal energy is a point function and property of the system. Internal energy is an extensive property (mass-dependent), while specific energy is an intensive property (independent of mass).
- For an ideal gas, the internal energy is a function of temperature only.

Some Examples:

Q. A gas has constant pressure in a system. There is a loss of 45 J of heat in the surroundings around the system. 450 J of work is done on the system. Find the system’s internal energy.

Solution:

$\Delta U = q+w$

$\Delta U = 45J + 450J$

$\Delta U = 495J$

In general, if we want to find the internal energy, which is denoted by ΔU, it is important to consider the relationship between the surroundings and the system. We already know, according to the law, that energy is neither created nor destroyed. Thus, we can tell that anything that is lost by the surroundings will be gained by the system. Moreover, the surrounding area will lose heat and carry out some work on the system. So if we look at q and w, they are positive in the equation, and this is mainly due to the system gaining some heat and work being done on itself.

❖ What is Heat Capacity?

The heat capacity of a substance can be defined as the amount of heat required to change its temperature by one degree.
Thermodynamics in its totality is concerned about heat. The meaning of heat today is energy in transit. Before the development of thermodynamic laws, the heat was considered as the measure of an invisible fluid, caloric, present in any matter. The capability of a substance to hold this fluid was then referred to as the heat capacity of that substance. The development in thermodynamics and dependence of heat transfer on temperature changed the definition of heat.

Modern thermodynamics defines ***heat as the measure of the total internal energy of a system.*** In order to quantify the heat energy associated with matter and its dependence on temperature, two properties were defined. These properties were named as specific heat capacity and heat capacity of the system.

❖ What is specific heat capacity?

Let’s understand the concept of specific heat capacity with the help of examples. Let’s take an equal quantity, say 1 liter, of three liquids. Water, Mustard Oil, and Mercury. The concept of specific heat is related to a body’s thermal properties. Let’s heat up these three liquids using the same stove, maintaining the same conditions in all three experiments. The liquids are at a room temperature of 20°C and need to be brought to 60°C. Will all three samples take the same amount of time?

The chances are close to none. While doing the experiment, you will notice that to undergo the same temperature rise, under the same conditions, all three liquids take different times. The mercury is heated up the fastest, followed by Mustard Oil followed then by Water. This property is measured by the heat capacity. The Heat capacity represents the change in temperature in the sample for a given amount of heat. The specific heat in SI Units is joule per kelvin (J kg^{-1}). Specific Heat Capacity which is different from Heat Capacity represents the amount of heat needed to raise the temperature of a unit mass of a substance by 1°C. The specific heat formula is;

S (Heat Capacity)=�Δ�
�=��=1��Δ�
Specific heat capacity is different from heat capacity only in the fact that specific heat capacity accounts for the mass of the body and hence it is more specific and accurate than heat capacity. The SI unit of specific heat is Joule per kelvin per kg (J kg^{-1} K^{-1}). It is important to mention that the specific heat capacity of water is 4.186 joule/gram °C which is higher than any other common substance. As a result, water plays a huge role in temperature regulation and consequently weather. If specific heat capacity is considered from the point of view of moles and not mass, that then becomes molar specific heat capacity of the substance. Molar specific heat formula is;

�=��=1��Δ�
Here, the *m* represents the number of moles of a substance and the SI unit of molar specific heat capacity is J mol^{-1} K^{-1}.

One thing we must know here is that none of the relationships discussed earlier apply in case of a phase change because the heat added or removed during a phase change does not change the temperature. The need for being specific is great. The molar specific heat capacity is not accurate enough. One of the factors we did not consider while heating the sample was whether to leave the top open to evaporation or keep it at a constant pressure. Doing one of either will definitely change the results of the experiment. To address this, scientists sub-divided specific heat capacity into two groups.

- Molar Specific Heat Capacity at Constant Pressure: If the heat transfer to the sample is done when it is held at constant pressure, then the specific heat obtain using such a method is called Molar Specific Heat Capacity at Constant Pressure.

Molar Specific Heat Capacity at Constant Volume: If the heat transfer to the sample is done when the volume of the sample is held constant, then the specific heat obtain using such a method is

❖ Relationship between Cp and Cv

Cv	Cp
Cv is the amount of heat energy that a substance absorbs or releases with the change in temperature where a volume change does not occur.	Cp is the amount of heat energy that a substance absorbs or releases with the change in temperature where a pressure change does not occur.
Volume is constant	Pressure is constant
Cv = dUdT	Cp = dHdT

Related to the internal energy of the system. Internal system is the sum of potential and kinetic energy of a system.	Related to the enthalpy of a system. Enthalpy is the energy absorbed or released. It is defined as the sum of the internal system and the product of pressure and volume.

-

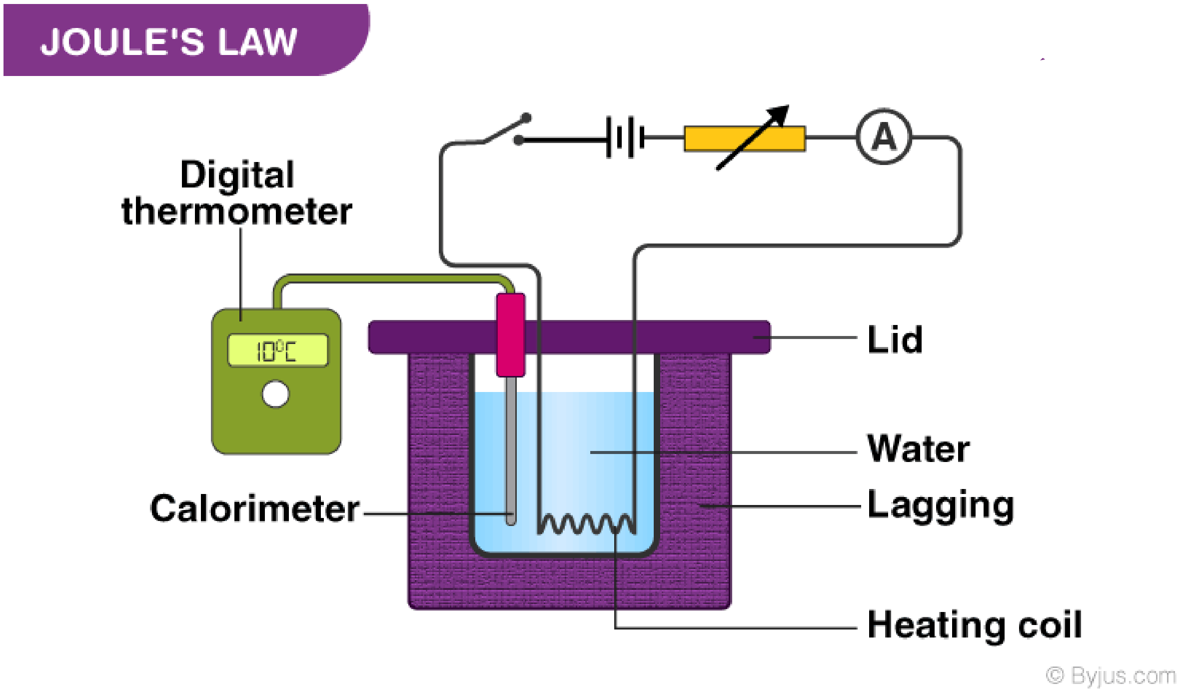
In this article, you learned about heat capacity, specific heat capacity, molar specific heat capacity, and its types

❖ Joule’s Law

We are aware of the heating impact of electric current. The heat is produced due to the collision electrons in the wire. You might have wondered about the amount of heat generated during the flow of current through a wire and the parameters and conditions it is based upon. To answer all these questions, Joule gave a formula that describes this phenomenon precisely and called it Joule’s Law.

Joule’s Law of Heating

Joule’s law is a mathematical description of the rate at which resistance in a circuit converts electric energy into heat energy.



The English physicist James Prescott discovered that the amount of heat per second that develops in a current-carrying conductor is proportional to the electrical resistance of the wire and the square of the current.

The heat that is generated because of the current flow in an electric wire is described in Joules. The mathematical expression of Joule's law is as explained below.

Joule's first law

The joule's first law shows the relationship between heat produced by flowing electric current through a conductor.

$Q = I^2 R T$

Where,

- Q indicates the amount of heat
- I show electric current
- R is the amount of electric resistance in the conductor
- T denotes time

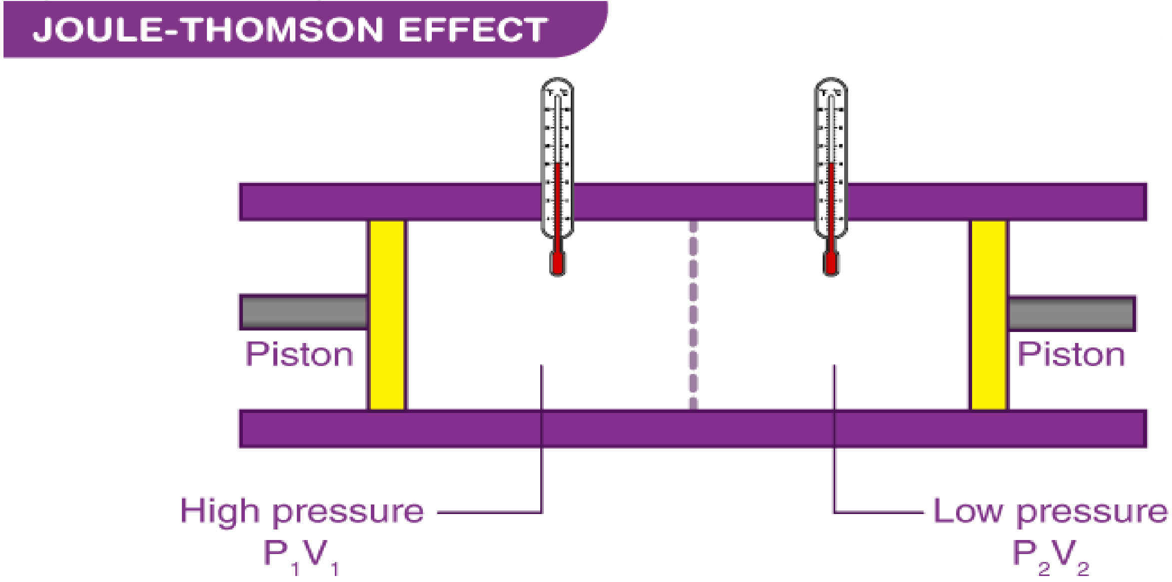
- The amount of generated heat is proportional to the wire's electrical resistance when the current in the circuit and the flow of current is not changed.

- The amount of generated heat in a conductor carrying current is proportional to the square of the current flow through the circuit when the electrical resistance and current supply is constant.

- The amount of heat produced because of the current flow is proportional to the time of flow when the resistance and current flow is kept constant.

❖ What Is Joule-Thomson Coefficient for ideal gases and real gases

The Joule-Thomson effect also known as Kelvin–Joule effect or Joule-Kelvin effect is the change in fluid's temperature as it flows from a higher pressure region to lower pressure.



According to the thermodynamic principle, the Joule-kelvin effect can be explained best by considering a separate gas packet placed in the opposite flow of direction for restriction. For the gas packet to pass through, the upstream gas needs to perform some work to push through the packet. The work equals the volume of the packet multiplied by the times of upstream pressure.

�1=�������1×�1

As the packet goes through the restriction, it has to make some room by displacing a considerable amount of the downstream gas. It includes performing the work which equals the product of packet volume and downstream pressure.

�2=�������2×�2

Due to the different effects of compressibility, the work performed upstream is not equal to the amount of work done downstream for real gases. Since depressuring is viewed as an adiabatic process, it reveals that any gas does not exchange work or heat by its surroundings, any change in internal energy has to follow the first law of thermodynamics.

�2–�1=�1–�2

Gas molecules are subjected to repulsive and attractive forces, (Van der Waals forces) as they are in random motion. When the gas pressure is lowered, i.e, the average distance between the molecules increases, the attractive forces become dominant for many gases at ambient temperature which results in an elevation in potential energy.

Most of the real gases need more work downstream at ambient temperature, due to the effects of compressibility.

�1×�1<�2×�2

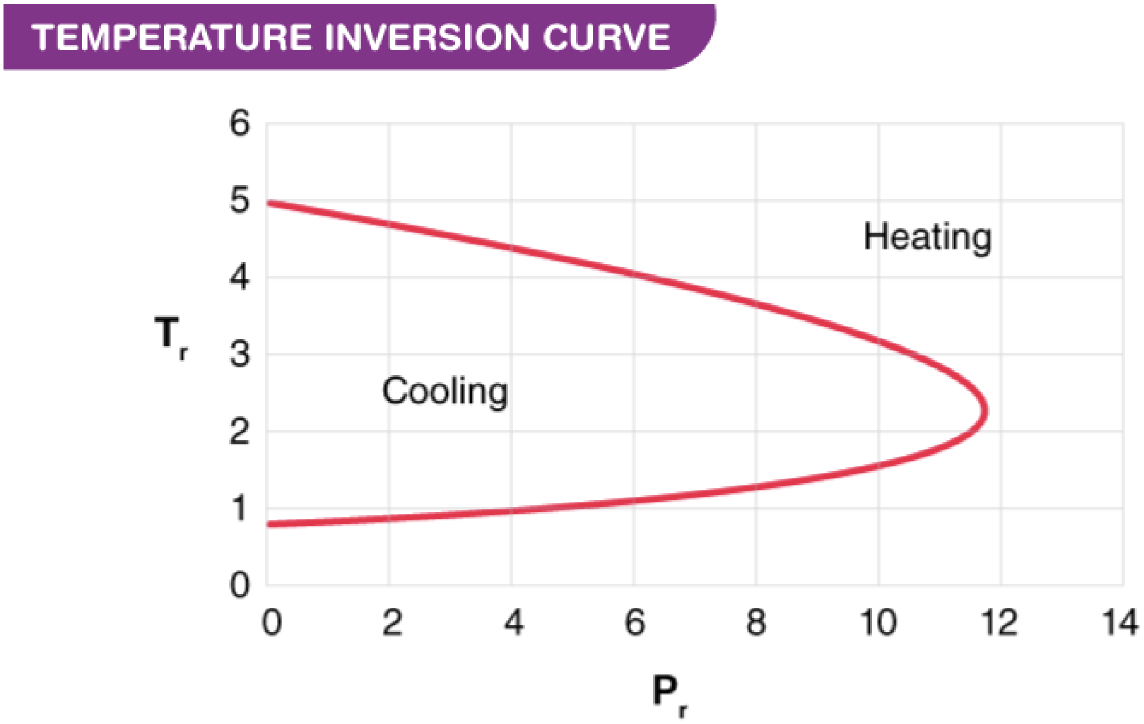
This indicates that the internal energy decreases when the gas passes through the restriction.

It can be generalized that for many real gases, the temperature decreases during a reduction in pressure, but this is not true for every gas and condition. Depressuring is an isenthalpic process which reveals that enthalpy doesn’t change. The temperature can either decrease or increase for any gas based on how the internal energy changes to maintain the enthalpy constant.

Applications of Joule-Thomson Effect

- The cooling produced in the Joule-Thomson expansion has made it a very valuable tool in refrigeration.
- The effect is applied in the Linde technique in the petrochemical industry, where the cooling effect is used to liquefy gases.
- It is also used in many cryogenic applications. For example for the production of liquid nitrogen, oxygen, and argon.
- The effect can also be used to liquefy even helium

Temperature Inversion



❖ Work and Heat

It is defined work as a force acting through a distance. It turns out that there are other equivalent definitions of work that are also important in chemistry.

When a certain volume of a gas expands, it works against an external pressure to expand (Figure 7.2 "Volume versus Pressure"). That is, the gas must perform work. Assuming that the external pressure P_{ext} is constant, the amount of work done by the gas is given by the equation

$$w = -P_{ext} \times \Delta V$$

where ΔV is the change in volume of the gas. This term is always the final volume minus the initial volume,

$$\Delta V = V_{final} - V_{initial}$$

and can be positive or negative, depending on whether V_{final} is larger (is expanding) or smaller (is contracting) than V_{initial}. The negative sign in the equation for work is important and implies that as volume expands (ΔV is positive), the gas in the system is *losing* energy as work. On the other hand, if the gas is contracting, ΔV is negative, and the two negative signs make the work positive, so energy is being added to the system.

When a gas expands against an external pressure, the gas does work.

Finally, let us consider units. Volume changes are usually expressed in units like liters, while pressures are usually expressed in atmospheres. When we use the equation to determine work, the unit for work comes out as liter·atmospheres, or L·atm. This is not a very common unit for work. However, there is a conversion factor between L·atm and the common unit of work, joules:

$$1\ \text{L·atm} = 101.32\ \text{J}$$

Heat is another aspect of energy. Heat is the transfer of energy from one body to another due to a difference in temperature. For example, when we touch something with our hands, we interpret that object as either hot or cold depending on how energy is transferred: If energy is transferred into your hands, the object feels hot. If energy is transferred from your hands to the object, your hands feel cold. Because heat is a measure of energy transfer, heat is also measured in joules.

For a given object, the amount of heat (q) involved is proportional to two things: the mass of the object (m) and the temperature change (ΔT) evoked by the energy transfer. We can write this mathematically as

$$q \propto m \times \Delta T$$ �∝� × ��

where ∝ means “is proportional to.” To make a proportionality an equality, we include a proportionality constant. In this case, the proportionality constant is labeled *c* and is called the specific heat capacity, or, more succinctly, **specific heat**:

$q = mc\Delta T$

❖ Second law of thermodynamics

The **second law of thermodynamics** puts restrictions upon the direction of heat transfer and achievable efficiencies of heat engines. The first law of thermodynamics states that the energy of the universe remains constant; though energy can be exchanged between system and surroundings, it can’t be created or destroyed.

While the first law of thermodynamics gives information about the quantity of energy transfer as a process, it fails to provide any insights about the direction of energy transfer and the quality of the energy. The first law cannot indicate whether a metallic bar of uniform temperature can spontaneously become warmer at one end and cooler at others. All that the law can state is that there will always be an energy balance if the process occurs. It is the second law of thermodynamics that provides the criterion for the feasibility of any process. A process cannot occur unless it satisfies both the first and second laws of thermodynamics.

What Is the Second Law of Thermodynamics?

The second law of thermodynamics states that:-

any spontaneously occurring process will always lead to an escalation in the entropy (S) of the universe. In simple words, the law explains that an isolated system’s entropy will never decrease over time.

Nonetheless, in some cases, where the system is in thermodynamic equilibrium or going through a reversible process, the total entropy of a system and its surroundings remains constant. The second law is also known as the Law of Increased Entropy.

The second law clearly explains that it is impossible to convert heat energy to mechanical energy with 100 per cent efficiency. For example, if we look at the piston in an engine, the gas is heated to increase its pressure and drive the piston. However, even as the piston moves, there is always some leftover heat in the gas that cannot be used for carrying out any other work. Heat is wasted, and it has to be discarded. In this case, it is done by transferring it to a heat sink or in the case of a car engine, waste heat is discarded by exhausting the used fuel and air mixture to the atmosphere. Additionally, heat generated from friction that is generally unusable should also be removed from the system.

The Second Law of Thermodynamics Equation

Mathematically, the second law of thermodynamics is represented as

$\Delta S_{univ} > 0$

Where ΔS_{univ} is the change in the entropy of the universe.

Entropy is a measure of the randomness of the system, or it is the measure of energy or chaos within an isolated system. It can be considered a quantitative index that describes the quality of energy.

Meanwhile, there are a few factors that cause an increase in the entropy of the closed system. Firstly, in a closed system, while the mass remains constant, there is an exchange of heat with the surroundings. This change in the heat content creates a disturbance in the system, thereby increasing the entropy of the system.

Secondly, internal changes may occur in the movements of the molecules of the system. This leads to disturbances which further cause irreversibilities inside the system resulting in the increment of its entropy.

Limitations,

- **Closed systems**

  The law only applies to closed systems, which are nearly impossible to create in nature.

- **Entropy**

  Entropy is a measure of disorder, but it's hard to apply the law to natural systems because it's difficult to create a truly closed system.

- **Heat engines**

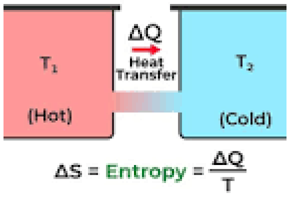
  Heat engines can't be 100% efficient because some energy is lost as waste heat.

- **Real-world heat engines**

  Real-world heat engines are less efficient than the Carnot cycle because of friction, heat loss, and irreversibilities.

- **Heat transfer**

  Heat can only travel from a hotter to a cooler zone, not the other way around.
  Explanation



The second law of thermodynamics states that entropy increases in a closed system. It also states that heat can't be converted entirely to mechanical energy.

The second law of thermodynamics helps predict whether processes are allowed to happen, even if they obey the first law of thermodynamics.

❖ Carnot Theorem

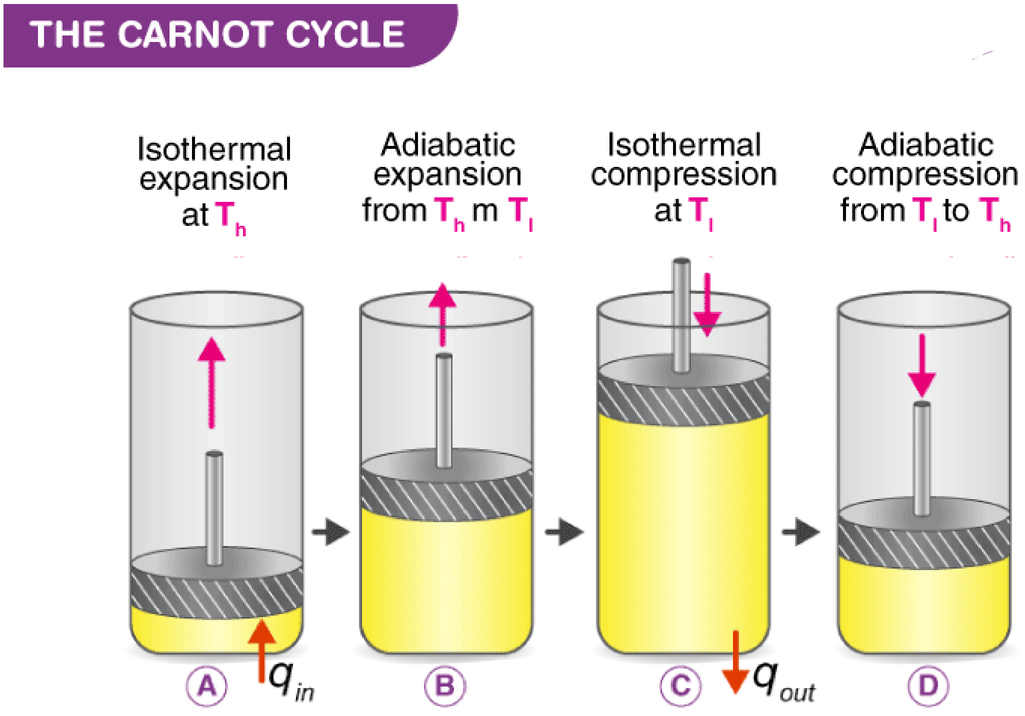
According to Carnot Theorem:

Any system working between T_1 (hot reservoir) and T_2 (cold reservoir) can never have more efficiency than the Carnot engine operating between the same reservoirs.

Also, the efficiency of this type of engine is independent of the nature of the working substance and is only dependent on the temperature of the hot and cold reservoirs.

Carnot Cycle

A Carnot cycle is defined as an ideal reversible closed thermodynamic cycle. Four successive operations are involved: isothermal expansion, adiabatic expansion, isothermal compression, and adiabatic compression. During these operations, the expansion and compression of the substance can be done up to the desired point and back to the initial state.



Following are the four processes of the Carnot cycle:

- In (a), the process is reversible isothermal gas expansion. In this process, the amount of heat absorbed by the ideal gas is q_{in} from the heat source at a temperature of T_h. The gas expands and does work on the surroundings.
- In (b), the process is reversible adiabatic gas expansion. Here, the system is thermally insulated, and the gas continues to expand and work is done on the surroundings. Now the temperature is lower, T_l.
- In (c), the process is a reversible isothermal gas compression process. Here, the heat loss q_{out} occurs when the surroundings do the work at temperature T_l.
- In (d), the process is reversible adiabatic gas compression. Again the system is thermally insulated. The temperature again rises back to T_h as the surrounding continue to do their work on the gas.

Steps involved in a Carnot Cycle

For an ideal gas operating inside a Carnot cycle, the following are the steps involved:

Step 1:

Isothermal expansion: The gas is taken from P_1, V_1, T_1 to P_2, V_2, T_2. Heat Q_1 is absorbed from the reservoir at temperature T_1. Since the expansion is isothermal, the total change in internal energy is zero, and the heat absorbed by the gas is equal to the work done by the gas on the environment, which is given as:

�1→2=�1=�×�×�1×���2�1

Step 2:

Adiabatic expansion: The gas expands adiabatically from P_2, V_2, T_1 to P_3, V_3, T_2.

Here, work done by the gas is given by:

�2→3=���−1(�1−�2)

Step 3:

Isothermal compression: The gas is compressed isothermally from the state (P_3, V_3, T_2) to (P_4, V_4, T_2).

Here, the work done on the gas by the environment is given by:

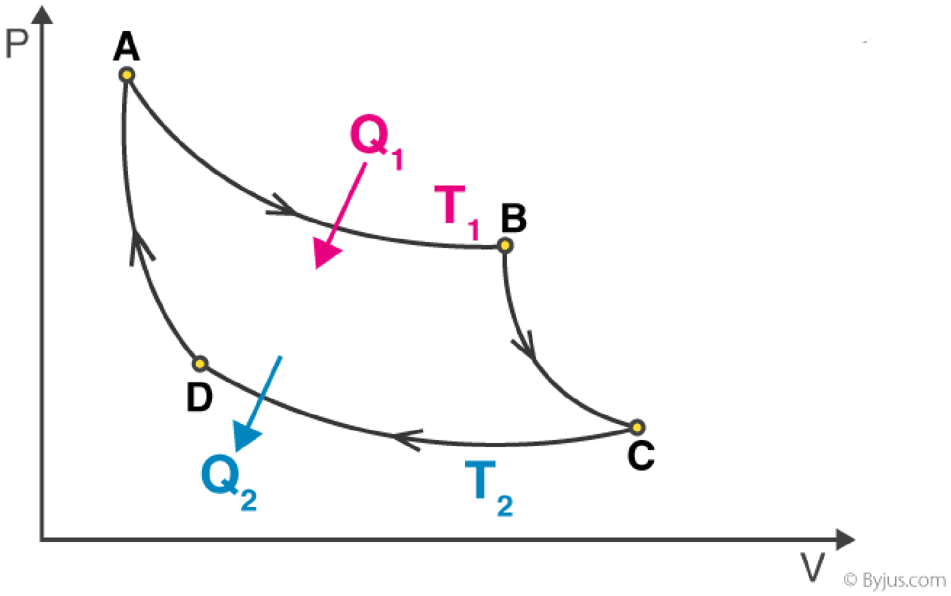
�3→4=���2���3�4

Step 4:

Adiabatic compression: The gas is compressed adiabatically from the state (P_4, V_4, T_2) to (P_1, V_1, T_1).

Here, the work done on the gas by the environment is given by:

�4→1=���−1(�1−�2)



Hence, the total work done by the gas on the environment in one complete cycle is given by:

�=�1→2+�2→3+�3→4+�4→1�=���1���2�1−���2���3�4
��������������=���������������*h*������������
���������*h*�����
��������������=��1=�1−�2�1=1−�2�1=1−�2�1���3�4���2
�1

Since the step 2–>3 is an adiabatic process, we can write $T_1V_2^{Y-1} = T_2V_3^{Y-1}$

Or,

�2�3=(�2�1)1�−1

Similarly, for the process 4–>1, we can write

�1�2=(�2�1)1�−1

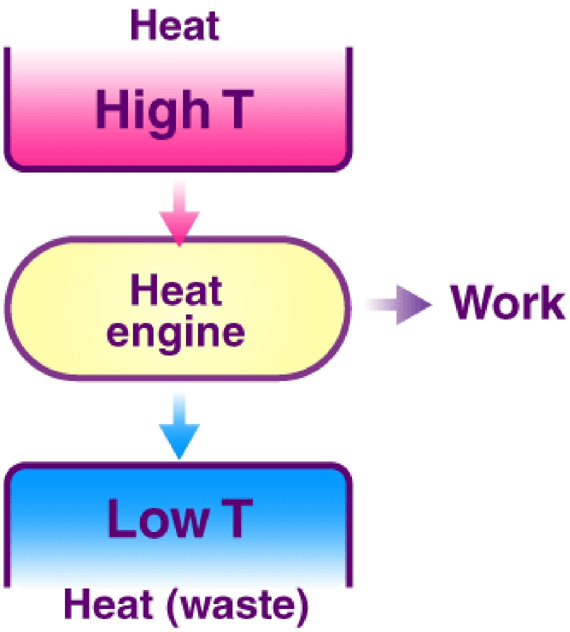
This implies,

�2�3=�1�2

So, the expression for net efficiency of Carnot engine reduces to:

❖ What is Carnot's theorem?

Carnot's theorem also known as Carnot's rule was developed by Nicolas Léonard Sadi Carnot in the year 1824, with the principle that there are limits on maximum efficiency for any given heat engine. It depends mainly on hot and cold reservoir temperatures.



Carnot's theorem states that:

- Heat engines that are working between two heat reservoirs are less efficient than the Carnot heat engine that is operating between the same reservoirs.
- Irrespective of the operation details, every Carnot engine is efficient between two heat reservoirs.
- Maximum efficiency is given as:

����=�������=1−����
Where,

T_C: absolute temperature of the cold reservoir.

T_H: absolute temperature of the hot reservoir.

η: the ratio of work done by the engine to heat drawn out of the hot reservoir.

Processes involved in thermodynamics can be carried out in the following two ways:

Reversible engine:

The efficiency of all reversible engines remains the same that works between two same heat reservoirs.

Δ�=∫��������
Where,

ΔS: change in entropy

T: temperature

∫��:���h���h���h��������h��������.
Irreversible engine:

There is no irreversible engine that is more efficient than the Carnot engine working between two same reservoirs.

Example of an irreversible engine are:

- Plastic deformation
- Friction
- Spontaneous chemical reaction

Applications of Carnot's theorem

- Carnot’s theorem finds application in engines that convert thermal energy to work.
- Refrigeration: Method of removal of heat from the at low temperature and dissipating it to a higher temperature. This is a reversible process.

Stay tuned with BYJU’S to learn more about the Carnot engine and other related topics with video lectures and interactive sessions.

UNIT - III

❖ HYDROCARBONS :-

What are Alkanes?

Alkanes are referred to as saturated hydrocarbons, that is, hydrocarbons having all carbon atoms bonded to other carbon atoms or hydrogen atoms with sigma bonds only.

As the alkanes posses weak Van Der Waals forces, the first four members, C_1 to C_4 are gases, C_5 to C_{17} are liquids and those containing 18 carbon atoms or more are solids at 298 K. They are colourless and odourless.

Physical Properties of Alkanes:-

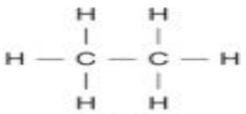
1. Structures of Alkanes:-

All the carbon atoms present in an alkane are sp^3 hybridised that is, every carbon atom forms four sigma bonds with carbon or hydrogen atoms. General configuration of alkane is C_nH_{2n+2}. They exhibit tetrahedral geometry with a bond angle of 109.47° between them.

The methane molecule has a symmetrical tetrahedral structure.

3-D representation 2-D representation

Spatial and graphical formula of methane



Ethane

$CH_3 - CH_3$

Propane

$CH_3 - CH_2 - CH_3$

2. Solubility of Alkanes:-

- Due to very little difference in electronegativity between carbon and hydrogen and the covalent nature of C-C bond or C-H bond, alkanes are generally non-polar molecules.
- As we generally observe, polar molecules are soluble in polar solvents whereas non-polar molecules are soluble in non-polar solvents. Hence, alkanes are hydrophobic in nature, that is, alkanes are insoluble in water.
- However, they are soluble in organic solvents as the energy required to overcome the existing Van Der Waals forces and the energy required to generate new Van Der Waals forces is quite comparable.

3. Boiling Point of Alkanes:-

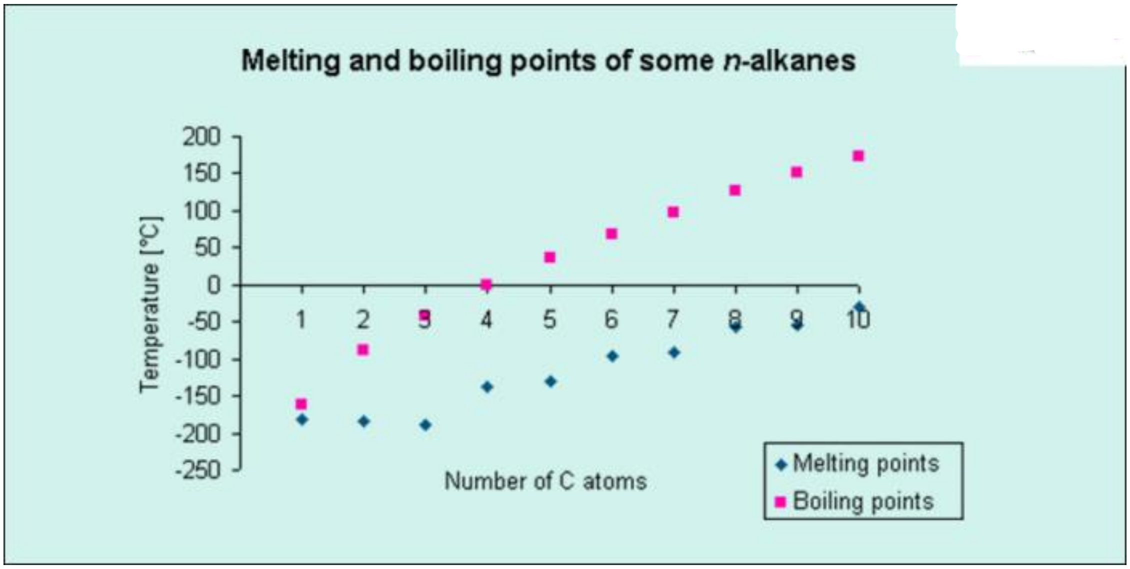
As the intermolecular Van Der Waals forces increase with the increase of the molecular size or the surface area of the molecule we observe,

- The boiling point of alkanes increases with increasing molecular weight.

- The straight-chain alkanes are observed to have a higher boiling point in comparison to their structural isomers.

4. Melting Point of Alkanes:-

- The melting point of alkanes follows the same trend as their boiling point, that is, it increases with an increase in molecular weight.
- This is attributed to the fact that higher alkanes are solids and it’s difficult to overcome intermolecular forces of attraction between them.



It is generally observed that even-numbered alkanes have a higher trend in melting point in comparison to odd-numbered alkanes as the even-numbered alkanes pack well in the solid phase, forming a well-organised structure which is difficult to break.

Chemical Properties of Alkanes:-

Alkanes are the least reactive type of organic compound. Alkanes are not absolutely unreactive. Two important reactions that they undergo are combustion, which is the reaction with oxygen and halogenation, which is the reaction with halogens.

1. Combustion:-

A combustion reaction is a chemical reaction between a substance and oxygen that proceeds with the evolution of heat and light. Alkanes readily undergo combustion reactions when ignited. When sufficient oxygen is present to support total combustion then carbon dioxide and water are formed.

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ + energy
$2C_6H_{14} + 19O_2 \rightarrow 12CO_2 + 14H_2O$ + energy

The exothermic nature of alkane combustion reactions explains the extensive use of alkanes as fuels. Natural gas which is used in home heating is predominantly methane.

2. Halogenation:-

Halogenation of an alkane produces a hydrocarbon derivative in which one or more halogen atoms have been substituted for hydrogen atoms. An example of an alkane halogenation reaction is

$CH_3\text{-}CH_3 + Br_2 \rightarrow CH_3\text{-}CH_2\text{-}Br + HBr$

Alkane halogenation is an example of a substitution reaction, a type of reaction that often occurs in organic chemistry.

A general equation for the substitution of a single halogen atom for one of the hydrogen atoms of an alkane is

$R\text{-}H + X_2 \rightarrow R\text{-}X + H\text{-}X$

What is Halogenation Reaction?

A halogenation reaction is a chemical reaction between a substance and a halogen in which one or more halogen atoms are incorporated into molecules of the substance.

❖ What is Halogenation of Alkanes?

Halogenation of an alkane produces a hydrocarbon derivative in which one or more halogen atoms have been substituted for hydrogen atoms.

Alkanes are notoriously unreactive compounds because they are non-polar and lack functional groups at which reactions can take place. Free radical halogenation therefore provides a method by which alkanes can be functionalized.

A severe limitation of radical halogenation however is the number of similar C-H bonds that are present in all but the simplest alkanes, so selective reactions are difficult to achieve.

General Features of Halogenation of Alkanes:-

Note the following features of halogenation of alkanes.

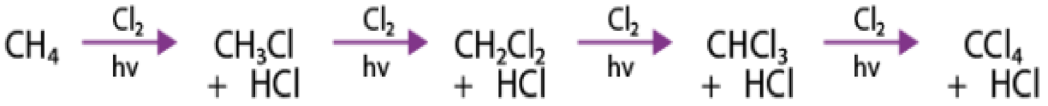
- The notation R-H is a general formula for an alkane. R in this case represents an alkyl group. Addition of a hydrogen atom to an alkyl group produces the parent hydrocarbon of the alkyl group.
- The notation R-X on the product side is the general formula for a halogenated alkane. X is the general symbol for a halogen atom.
- Reaction conditions are noted by placing these conditions on the equation arrow that separates reactants from products.

Chlorination of Methane by Substitution:-

In halogenation of an alkane, the alkane is said to undergo fluorination, chlorination, bromination or iodination depending on the identity of the halogen reactant. Chlorination and bromination are the two widely used alkane halogenation reactions. Fluorination reactions generally proceed too quickly to be useful and iodination reactions go too slowly.

Halogenations usually result in the formation of a mixture of products rather than a single product. More than one product results because more than one hydrogen atom on an alkane can be replaced with halogen atoms.

Methane and chlorine when heated to a high temperature in the presence of light react as follows.



The mechanism for this reaction takes place in three steps.

1. Initiation Step:-

The Cl-Cl bond of elemental chlorine undergoes hemolysis when irradiated with UV light, and this process yields two chlorine atoms, also called chlorine radicals.

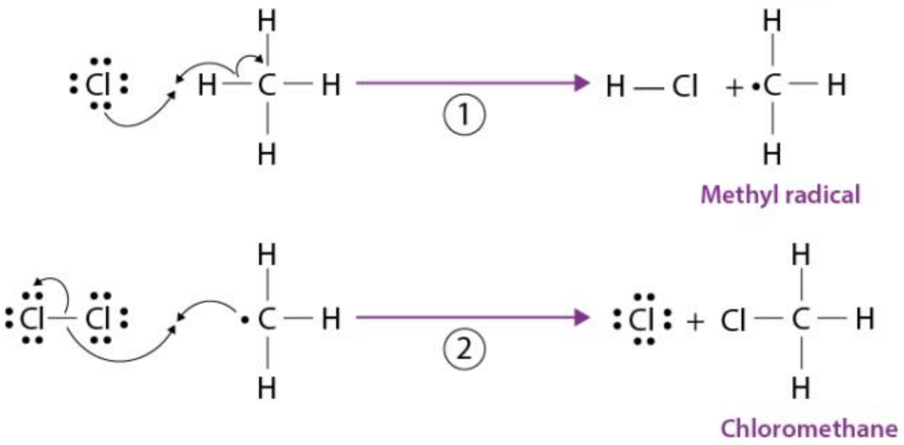
2. Propagation Step:-

A chlorine radical abstracts a hydrogen atom from methane to produce the methyl radical. The methyl radical in turn abstracts a chlorine atom from a chlorine molecule and chloromethane is formed. The second step of propagation also regenerates a chlorine atom. These steps repeat many times until termination occurs.

$$CH_3Cl + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CHCl_3 + HCl$$

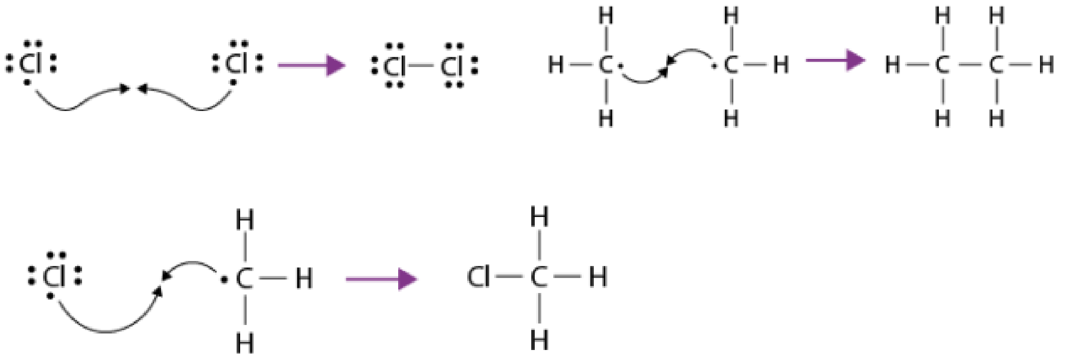
$$CHCl_3 + Cl_2 \xrightarrow[\text{light}]{\text{Heat or}} CCl_4 + HCl$$



3. Termination Step:-

Termination takes place when a chlorine atom reacts with another chlorine atom to generate Cl2, or chlorine atom can react with a methyl radical to form chloromethane which constitutes a minor pathway by which the product is made. Two methyl radicals can also combine to produce ethane, a very minor by product of this reaction.

The reaction does not stop at this step, however because the chlorinated methane product can react with additional chlorine to produce polychlorinated products.



By controlling the reaction conditions and the ratio of chlorine to methane. It is possible to favour formation of one or another of the possible chlorinated methane products.

ALKENES:-

What is Isomerism?

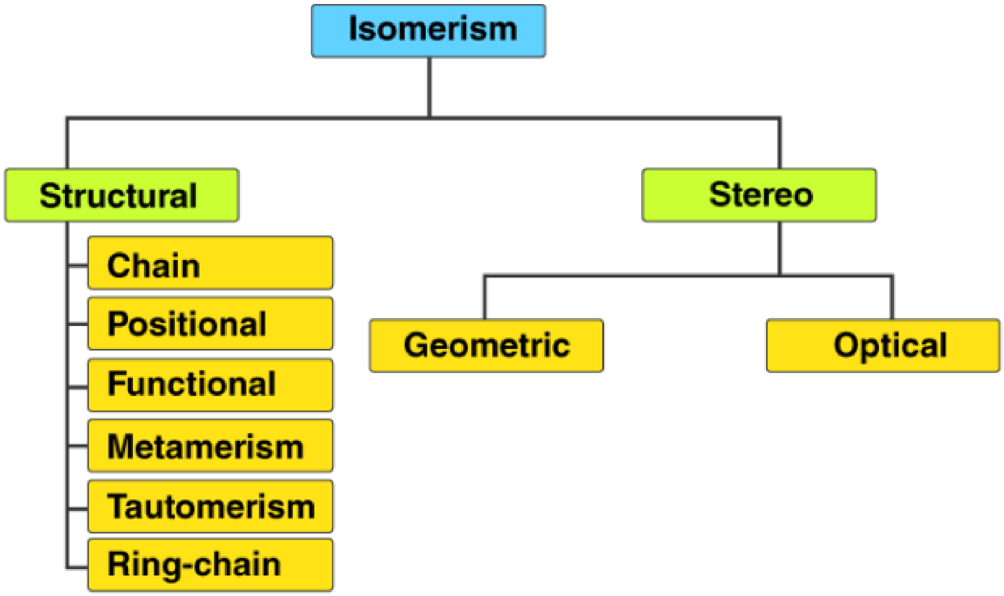
Isomerism is the phenomenon in which more than one compounds have the same chemical formula but different chemical structures.

Chemical compounds that have identical chemical formulae but differ in properties and the arrangement of atoms in the molecule are called **isomers**. Therefore, the compounds that exhibit isomerism are known as isomers.

The word “isomer” is derived from the Greek words “isos” and “meros”, which mean “equal parts”. This term was coined by the Swedish chemist Jacob Berzelius in the year 1830.

Isomerism Types:-

There are two primary types of isomerism, which can be further categorized into different subtypes. These primary types are **Structural Isomerism** and **Stereoisomerism**. The classification of different types of isomers is illustrated below.



Structural Isomerism:-

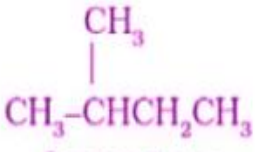
Structural isomerism is commonly referred to as constitutional isomerism. The functional groups and the atoms in the molecules of these isomers are linked in different ways. Different structural isomers are assigned different IUPAC names since they may or may not contain the same functional group.

Chain Isomerism

- It is also known as skeletal isomerism.
- The components of these isomers display differently branched structures.
- Commonly, chain isomers differ in the branching of carbon
- An example of chain isomerism can be observed in the compound C_5H_{12}, as illustrated below.

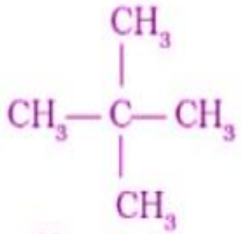
$CH_3CH_2CH_2CH_2CH_3$

Pentane



$$\begin{array}{l} \quad\;\; CH_3 \\ \quad\;\;\, | \\ CH_3{-}CHCH_2CH_3 \end{array}$$

Isopentane
(2-Methylbutane)



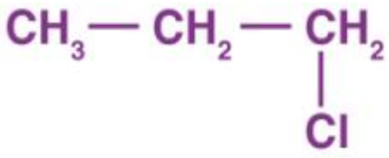
$$\begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}CH_3 \\ | \\ CH_3 \end{array}$$

Neopentane
(2.2-Dimethylpropane)

Position Isomerism:-

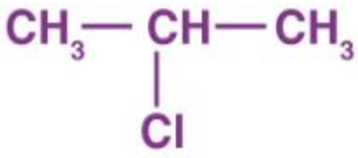
- The positions of the functional groups or substituent atoms are different in position isomers.
- Typically, this isomerism involves the attachment of the functional groups to different carbon atoms in the carbon chain.

- An example of this type of isomerism can be observed in the compounds having the formula C_3H_7Cl.



$CH_3-CH_2-CH_2-Cl$

1-Chloropropane



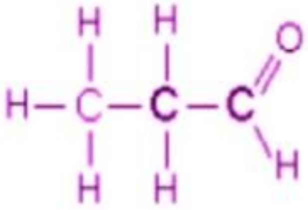
$CH_3-CH(Cl)-CH_3$

2-Chloropropane

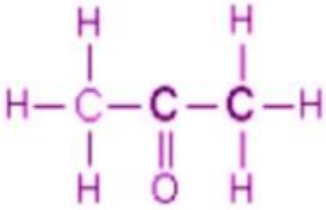
Functional Isomerism:-

- It is also known as functional group isomerism.
- As the name suggests, it refers to the compounds that have the same chemical formula but different functional groups attached to them.
- An example of functional isomerism can be observed in the compound C_3H_6O.

propanal



propanone (acetone)



Metamerism:-

- This type of isomerism arises due to the presence of different alkyl chains on each side of the functional group.
- It is a rare type of isomerism and is generally limited to molecules that contain a divalent atom (such as sulphur or oxygen), surrounded by alkyl groups.
- Example: $C_4H_{10}O$ can be represented as ethoxyethane ($C_2H_5OC_2H_5$) and methoxy-propane ($CH_3OC_3H_7$).

Tautomerism:-

- A tautomer of a compound refers to the isomer of the compound which only differs in the position of protons and electrons.
- Typically, the tautomers of a compound exist together in equilibrium and easily interchange.
- It occurs via an intramolecular proton transfer.
- An important example of this phenomenon is Keto-enol tautomerism.

Ring-Chain Isomerism:-

- In ring-chain isomerism, one of the isomers has an open-chain structure whereas the other has a ring structure.
- They generally contain a different number of pi bonds.
- A great example of this type of isomerism can be observed in C_3H_6. Propene and cyclopropane are the resulting isomers, as illustrated below.

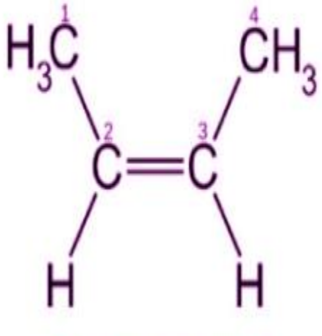
Stereoisomerism:-

This type of isomerism arises in compounds having the same chemical formula but different orientations of the atoms belonging to the molecule in three-dimensional space. The compounds that exhibit stereoisomerism are often referred to as stereoisomers.

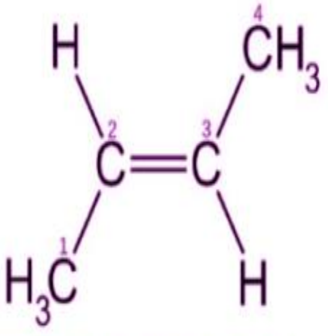
This phenomenon can be further categorized into two subtypes. Both these subtypes are briefly described in this subsection.

Geometric Isomerism:-

- It is popularly known as cis-trans isomerism.
- These isomers have different spatial arrangements of atoms in three-dimensional space.
- An illustration describing the geometric isomerism observed in the acyclic But-2-ene molecule is provided below.



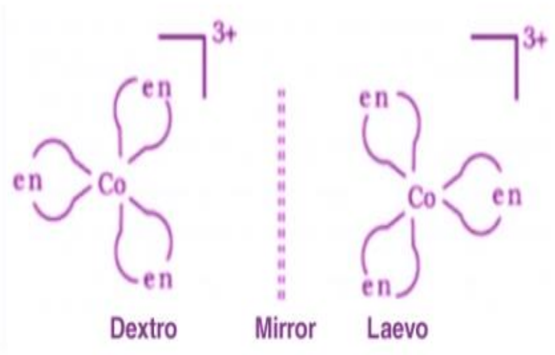
cis-but-2-ene



trans-but-2-ene

Optical Isomerism:-

- Compounds that exhibit optical isomerism feature similar bonds but different spatial arrangements of atoms forming non-superimposable mirror images.
- These optical isomers are also known as enantiomers.
- Enantiomers differ from each other in their optical activities.
- Dextro enantiomers rotate the plane of polarized light to the right whereas laevo enantiomers rotate it to the left, as



Ionization Isomerism:-

The compound which gives different ions in the solution, although they have same composition, is called ionization isomers and this property is known as ionization isomerism. Compounds which gives different ions in solution although they have same composition are called ionization isomerism. This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

One example of ionisation isomerism is $[Co(NH_3)_5SO_4]Br$ and $[Co(NH_3)_5Br]SO_4$.

❖ Saytzeff's Rule :-

Elimination reactions of some alkyl halides and alcohol will result in different alkenes, and Saytzeff's rule is used to predict the major product. The major and minor products are predicted based on the number of alkyl groups attached to the alkene.

Important Concept Behind Saytzeff's Rule

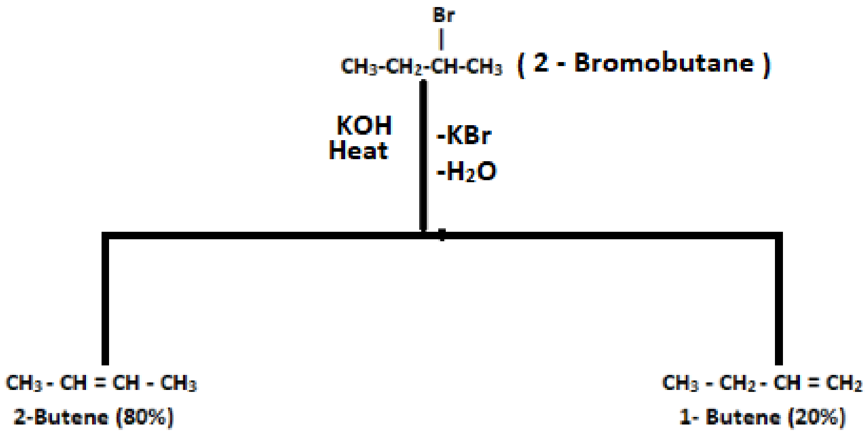
- If more than one elimination product is possible, the most substituted alkene is the most stable product (major product).
- $CH_2 = CHR < RCH = CHR < R_2C = CHR < R_2C = CR_2$

Mono < di < Tri < Tetra

Examples:

1. Dehydrohalogenation of 2-Bromobutane

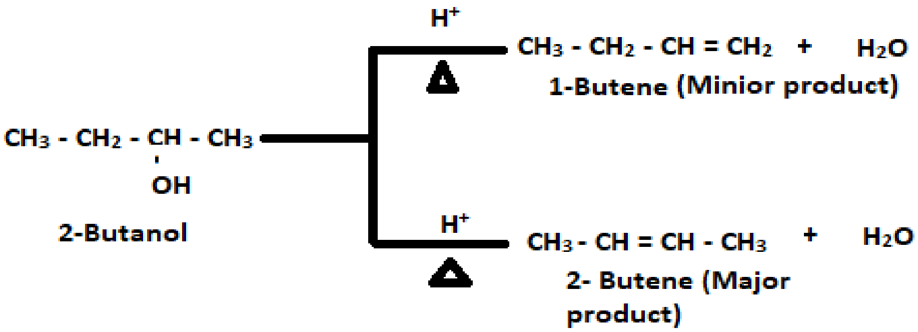
.



When 2-bromobutane undergoes a dehydrohalogenation reaction, it gives two products: 1-butene and 2-butene. Out of these two, 2-butene is a major product since it is highly substituted and more stable.

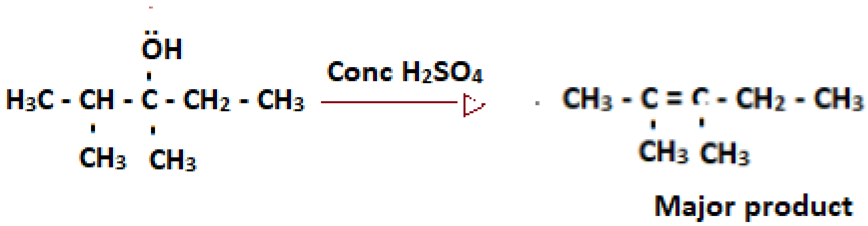
2. Dehydration of Alcohol:-

When butanol undergoes dehydration, it gives two products: 1-butene (minor product) and 2-butene (major product).



Mechanism of Elimination Reaction

Consider a dehydration reaction of 2, 3-dimethylpentan-3-ol



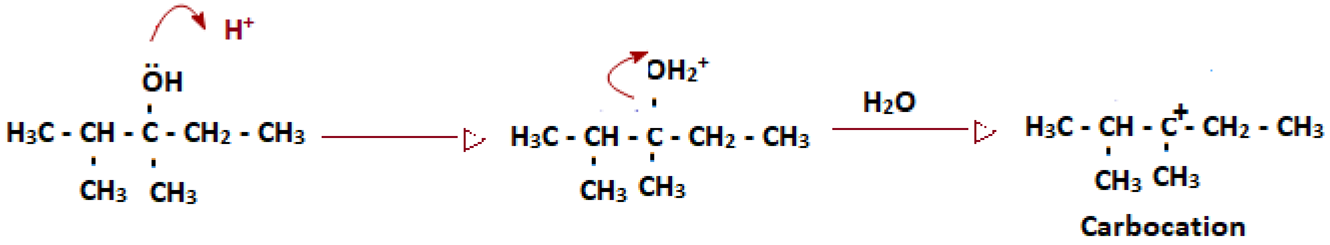
Step 1:-

Sulfuric acid ionizes to give a proton

$H_2SO_4 \rightarrow H^+ + HSO_4^-$

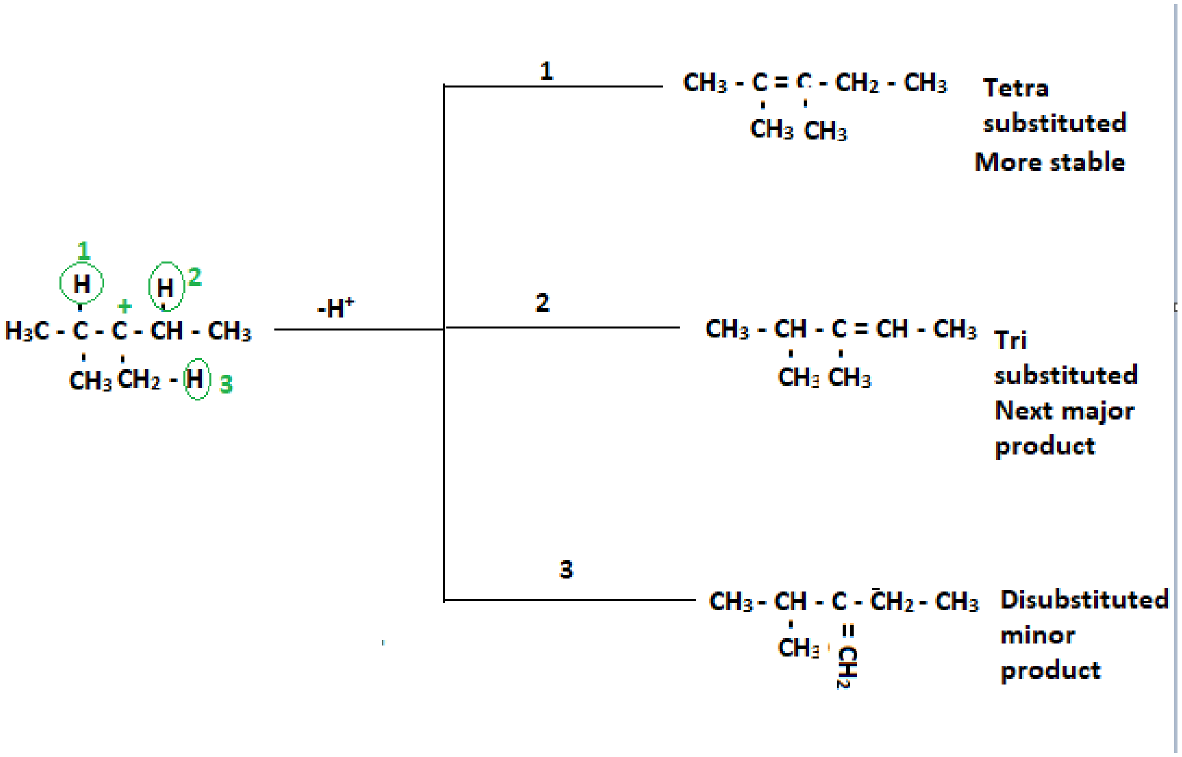
Step 2:-

Proton formed in step 1 reacts with the OH group and forms OH_2^+, and the loss of water gives a positive charge on the carbon atom and forms a tertiary carbocation.



Step 3:-

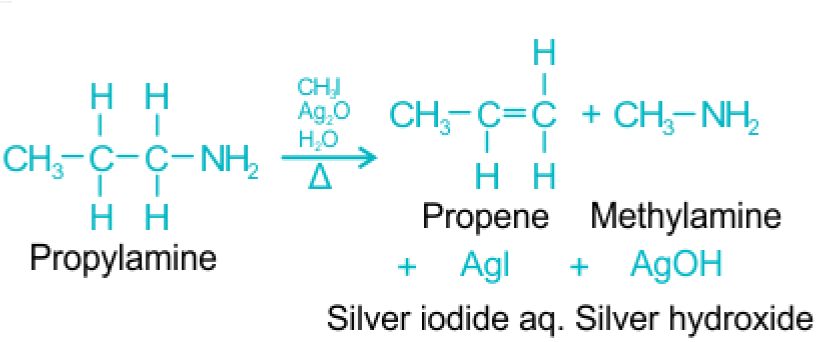
Removal of hydrogen adjacent to the tertiary carbocation gives alkene (Double bond formation). Three alkene formations are possible, as shown below:



❖ Hofmann Elimination Examples:-

These are the examples of hofmann elimination:

Preparation of propene from propyl amine take place by hofmann elimination:



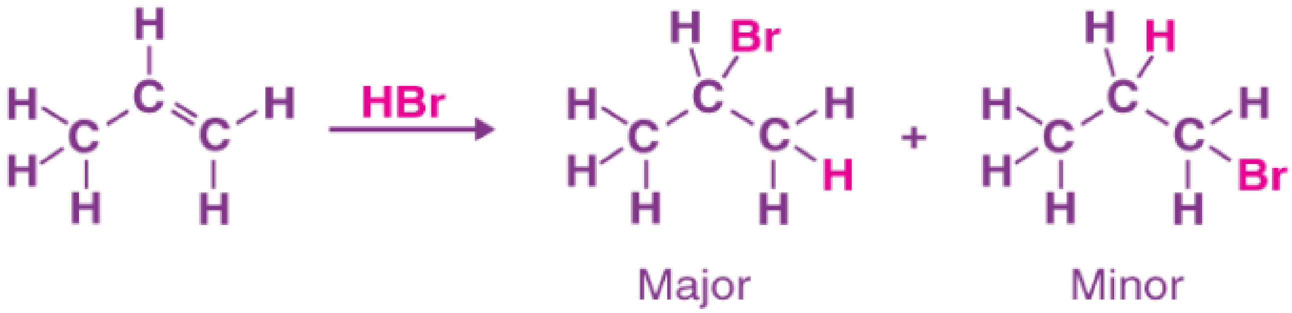
Example of Hofmann Elimination

❖ What is Markovnikov’s Rule?

When a protic acid (HX) is added to an asymmetric alkene, the acidic hydrogen attaches itself to the carbon having a greater number of hydrogen substituents whereas the halide group attaches itself to the carbon atom which has a greater number of alkyl substituents.

To simplify the rule, it can also be stated as – “Hydrogen is added to the carbon with the most hydrogens and the halide is added to the carbon with the least hydrogens”.

An example of a reaction that observes Markovnikov’s rule is the addition of hydrobromic acid (HBr) to propene, which is shown below.



It can be observed from the reaction illustrated above that the majority of the products formed obey Markovnikov's rule, whereas the minority of the products do not.

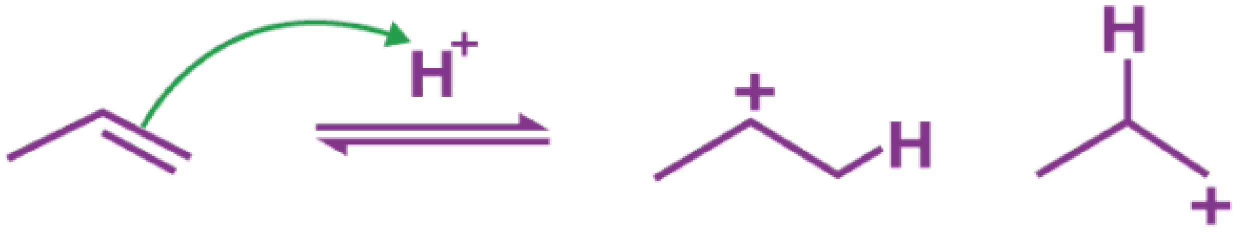
Let us consider the addition reaction wherein an alkene reacts with water to give rise to alcohol. This reaction proceeds via the formation of a carbocation. It is observed in this reaction that the hydroxyl group attaches itself to the carbon with more carbon-carbon bonds whereas the hydrogen atom attaches itself to the other carbon in the double bond, which has more carbon-hydrogen bonds.

What is the Mechanism Behind Markovnikov's Rule?

To understand this mechanism, let us consider the same example illustrated earlier, i.e. the addition reaction of hydrobromic acid with propene. The Mechanism of Markovnikov's rule can be broken down into the following two steps.

Step 1:-

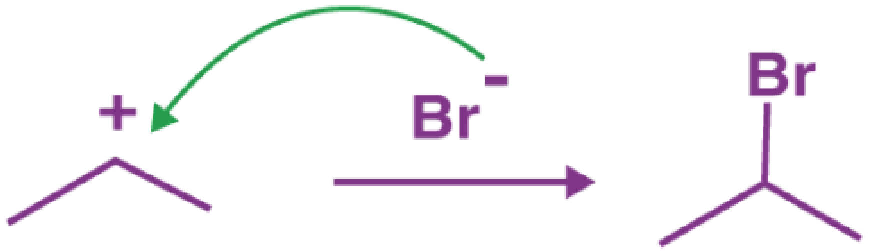
The alkene is protonated and it gives rise to the more stable carbocation as shown below.



From the illustration shown above, we can see that there are two types of carbocations that can be formed from the protonation of the alkene, one is a primary carbocation and the other is a secondary carbocation. However, the secondary carbocation is far more stable and therefore, its formation is preferred over the formation of a primary carbocation.

Step 2:-

The halide ion nucleophile now attacks the carbocation. This reaction yields the alkyl halide. Since the formation of the secondary carbocation is preferred, the major product of this reaction would be 2-bromopropane as illustrated below.



It is important to note that Markovnikov’s rule was developed specifically for its application in the addition reaction of hydrogen halides to alkenes. The opposite of ‘Markovnikov’ addition reactions can be described as Anti-Markovnikov based on the regioselectivity of the reaction.

❖ GENERAL METHODS OF PREPARATION OF ALKYNES

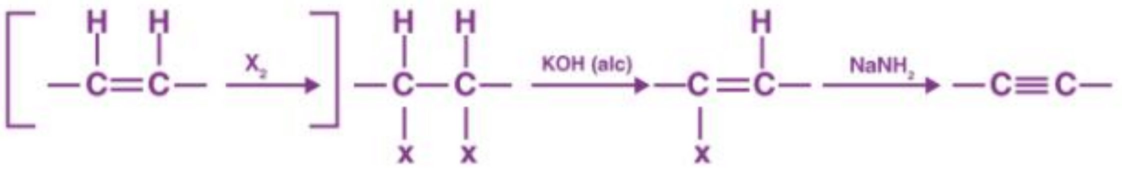
Introduction:-

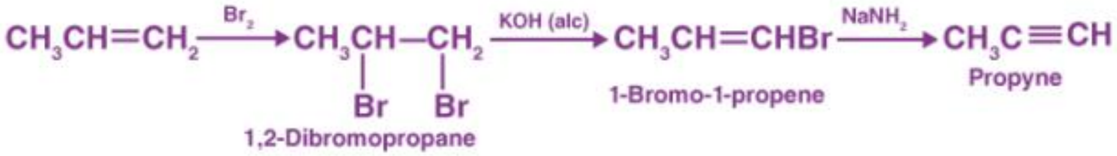
This topic explains the different methods of **preparation of alkynes from dihalides and calcium carbides**. Alkynes in organic chemistry are unsaturated hydrocarbons in which there exists, at least, a single, triple bond between the carbon-carbon atoms. The synthesis of Alkynes can be useful due to their antibacterial, antifungal and antiparasitic properties. The main reaction in the preparation of alkynes is that the ions are elimination from molecules which results in the formation of pi bonds. Usually, one of two processes are involved in the manufacturing of alkynes: the generation of the triple bond between carbon-carbon atoms or the number of molecules which contain a triple bond should be increased.

Preparation of Alkynes:-

Dehydrohalogenation of alkyl dihalides

In this method of preparation, alkenes are made to react with a halogen. Due to this reaction, a substituted alkane is obtained. Alkanes formed are further passed through alcoholic KOH in order to form substituted alkenes. It is then made to react with sodium amide to form alkynes. This process is called dehydrohalogenation as hydrogen is eliminated along with a halogen in order to obtain an alkyne.





Preparation of acetylene from calcium carbide:-

For large-scale production of an alkyne, calcium carbide (CaC_2) is made to react with water. It is prepared by heating quicklime in the presence of coke. Quicklime is obtained by introducing limestone to heat. The reactions for the preparation of acetylene from calcium carbide are as shown below:

$CaCO_3 \rightarrow CaO + CO_2$

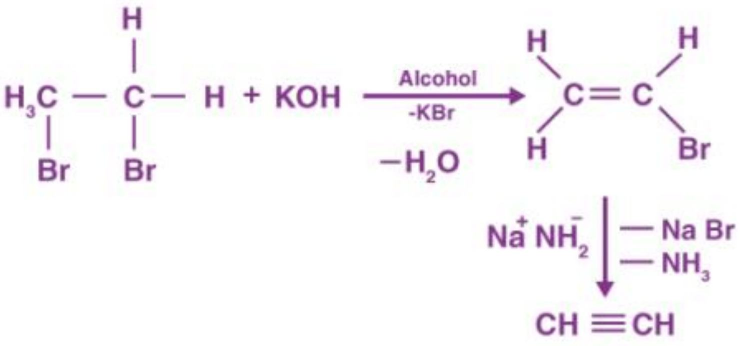
$CaO + 3C \rightarrow CaC_2 + CO$

$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

Preparation from vicinal dihalides:-

Dihalides are obtained from corresponding alkenes by the addition of halogens (Group 17 elements). Alkynes are obtained from vicinal dihalides by dehydrohalogenation which is carried out in two steps:

The first step is to prepare the unsaturated halides. The halides formed have a halogen attached to a double-bonded carbon. These halides are called vinylic halides which are not reactive in nature. These halides are made to react with the strong base which results in the formation of alkynes. Metal acetylides are used to convert small alkynes into large ones.



Preparation of alkynes from vicinal dihalides

❖ What is Electrophile?

Positively charged or neutral species are called electrophiles that are deficient in electrons and can accept a pair of electrons. These are also called species that love electrons (philic).

- The term electrophile can be split into “electro” derived from electron and “phile” which means loving.
- They are electron deficient and hence love to accept electrons (electrons loving).
- They are positively charged or neutral.
- They attract electrons. The movement of electrons depends on the density.
- They move from high-density area to low density area.

- They undergo electrophilic addition and electrophilic substitution reactions.
- An electrophile is also called Lewis acid.

What is Nucleophile?

A nucleophile is a reagent comprising an negative charge or lone pair of electrons. As a nucleophile is rich in electron, it looks for electron-deficient locations. Nucleophiles act as Lewis bases, i.e, species which can donate a pair of electrons.

- The term nucleophile can be split into “nucleo” derived from the nucleus and “phile” which means loving.
- They are electron-rich and hence nucleus loving. They are negatively charged or neutral.
- They donate electrons.
- The movement of electrons depends on the density.
- They move from low-density area to high-density area.
- They undergo nucleophilic addition and nucleophilic substitution reactions.
- A nucleophile is also called a Lewis base.

For example, as nitrogen is less electronegative than oxygen, ammonia is a stronger nucleophile than water. The lone pair of electrons on nitrogen in ammonia can be more easily given than the lone pair of electrons on oxygen in the water.

Difference between Electrophile and Nucleophile

ELECTROPHILE	**NUCLEOPHILE**
Also called Lewis acid	Also called Lewis base
They are positively charged / neutral	They are negatively charged / neutral
They undergo electrophilic addition and electrophilic substitution reactions	They undergo nucleophilic addition and nucleophilic substitution reactions
Electron-deficient	Electron-rich
It accepts a pair of an electron to form a covalent bond	It donates a pair of an electron to form a covalent bond
All carbocations are electrophiles.	All carbanions are nucleophiles.
Example: Hydronium Ion, methyl carbocation.	Example: Chloride Ion, methyl carbanion.

UNIT - IV

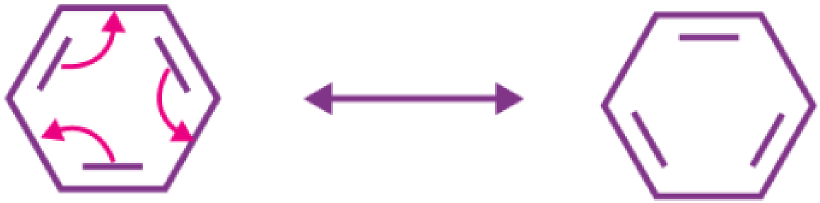
• Aromatic Hydrocarbons and Dienes :-

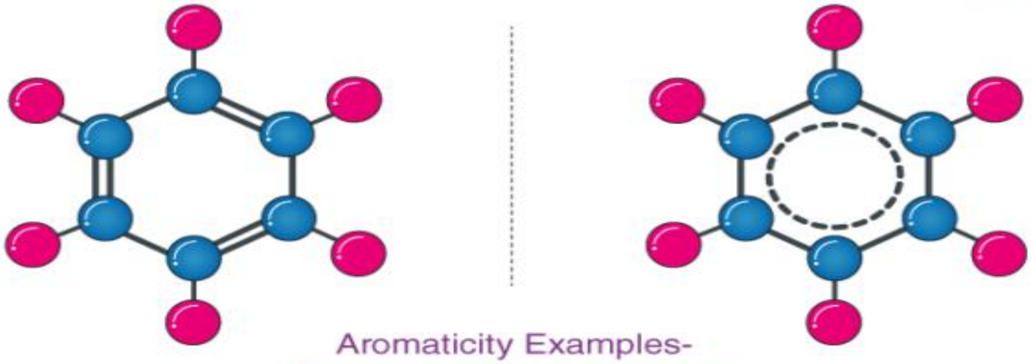
What is Aromaticity:-

Aromaticity is defined as a property of the conjugated cycloalkenes which enhances the stability of a molecule due to the delocalization of electrons present in the π-π orbitals.

Aromatic molecules are said to be very stable, and they do not break so easily and also react with other types of substances. The organic compounds which are not said to be aromatic are known as aliphatic compounds. These might be in cyclic form, but only the aromatic rings have a special kind of stability.

Aromaticity Examples:-





Aromaticity Examples-
Benzene 3D ball structure

We encounter aromaticity in our day-to-day lives. Even our bodies function with the help of certain aromatic compounds. Aromatic compounds are essential in the industry; and around 35 million tonnes of these compounds are known to be produced worldwide every year in the form of polymers and chemicals, such as nylon and polyester. These compounds are important even in the field of the biochemistry of all living things.

Most of the aromatic compounds are said to be the derivatives of benzene. The word “aromatic” in the real sense refers to the benzene derivatives, and as it was defined the way first. Also**,** there are many non-benzene kinds of aromatic compounds existing too. In the living organisms, take, for example, the very common type of aromatic ring is the DNA and RNA bases with double chains. The functional group of an aromatic compound or the substituent of it is known as an aryl group.

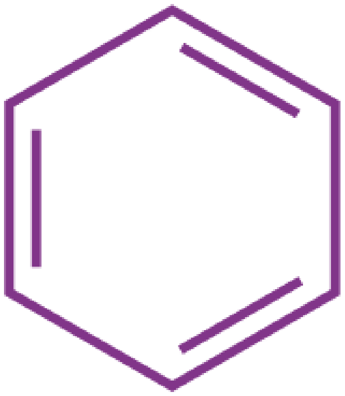
What is Huckel’s Rule?

Huckel’s Rule is used in order to estimate the aromatic qualities of any planar ring-shaped molecule in the field of organic chemistry. The supporting quantum mechanics required for the formulation of this rule was solved first by the German physical chemist and physicist Erich Armand Arthur Joseph Huckel in the year 1931.

The Huckel 4n + 2 Pi Electron Rule:-

A ring-shaped cyclic molecule is said to follow the Huckel rule when the total number of pi electrons belonging to the molecule can be equated to the formula ‘4n + 2’ where n can be any integer with a positive value (including zero).

Examples of molecules following Huckel’s rule have only been established for values of ‘n’ ranging from zero to six. The total number of pi electrons in the benzene molecule depicted below can be found to be 6, obeying the 4n+2 **π** electron rule where n=1.



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Thus, the aromaticity of the benzene molecule is established since it obeys the Huckel rule.

This rule is also justified with the help of the Pariser-Parr-Pople method and the linear combination of atomic orbitals (LCAO) method.

Generally, aromatic compounds are quite stable due to the resonance energy or the delocalized electron cloud. For a molecule to exhibit aromatic qualities, the following conditions must be met by it:

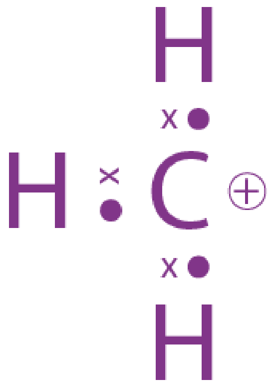
-

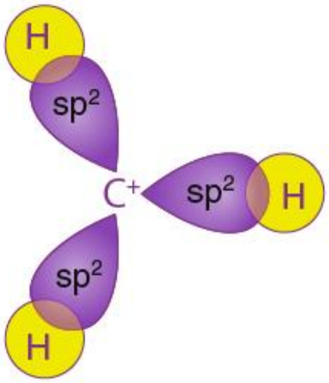
- There must be 4n + 2 **π** electrons present in a system of connected p orbitals (where the electrons are delocalized) belonging to the molecule.
- In order to meet the first condition, the molecule must have an approximately planar structure wherein the p orbitals are more or less parallel and have the ability to interact with each other.
- The molecule must have a cyclic structure and must have a ring of p orbitals which doesn’t have any sp^3 hybridized atoms.

Carbocation:-

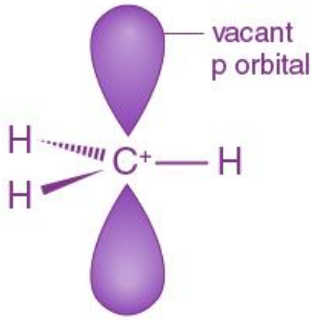
A Carbocation is a molecule in which a carbon atom has a positive charge and three bonds. We can say that, basically, they are carbon cations. Formerly, it was known as carbonium ion. Carbocation today is defined as any even-electron cation that possesses a significant positive charge on the carbon atom.

Talking about some general characteristics, the carbon cations are very reactive and unstable due to an incomplete octet. In simple words, carbocations do not have eight electrons; therefore, they do not satisfy the octet rule.





top view

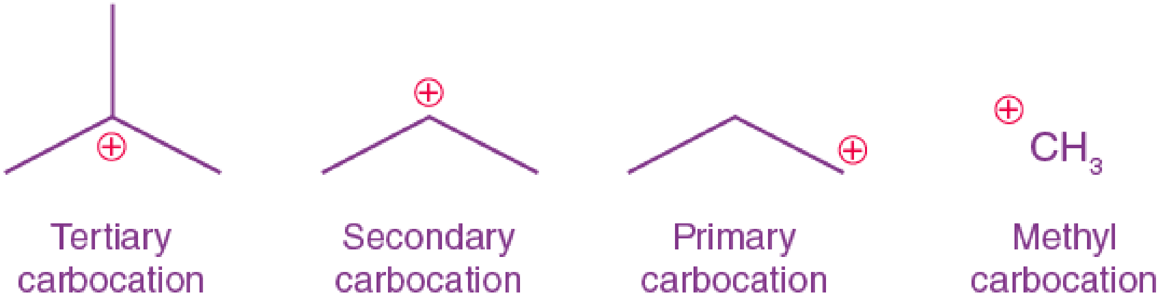


side view

Classification of Carbocation:-

The different carbocations are named on the basis of the number of carbon groups bonded to the carbon. The carbocation can be termed as methyl, primary, secondary or tertiary on the basis of how many carbon atoms are attached to it:

- Methyl carbocation: If no carbon is attached to the carbon with the positive charge, it is simply called **methyl carbocation**.
- If one, two or three carbon are attached to the carbon with the positive charge, it is called **primary carbocation, secondary carbocation, and tertiary carbonation,** respectively.



- If there is a carbon-carbon double bond next to the carbon with the positive charge, it is termed **allylic carbocation**.
- In the same way, if the carbon with the positive charge is attached to a double bond, the carbocation is termed **vinylic carbocation**. Here, the hybridization of the carbon having the positive charge is sp, and geometry is linear.
- Whenever the carbon, which consists of the positive charge, is part of a benzene ring, then the carbocation is an **aryl carbocation**.
- If the carbon having a positive charge is immediately next to a benzene ring, it is termed a **benzylic carbocation**.

Interestingly, in addition to these types, there is another type of carbocation, which is known as pyramidal carbocation. In this type, the ions consist of a single carbon atom that usually tends to hover over a four or five-sided polygon, which can be depicted as a pyramid. The 4 sided pyramidal ion will consist of a +1 charge, while the five-sided pyramid will have a +2 charge.

Formation of the CarbocationL:-

The carbocations can be formed by either of the following two fundamental steps:

- Cleavage of a bond of carbon
- Electrophilic addition

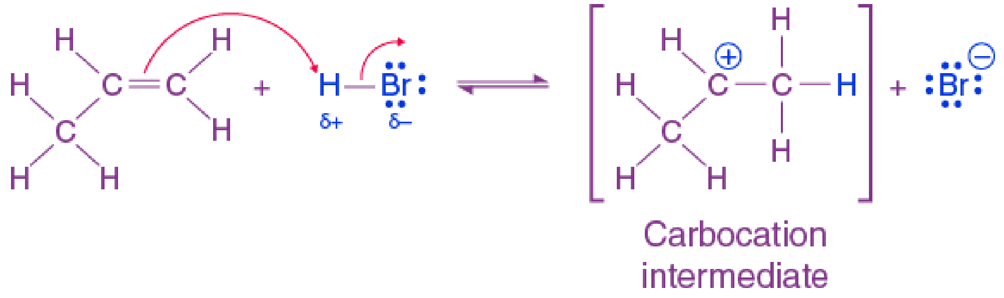
Cleavage of Bond of Carbon:-

Whenever there is a cleavage of the bond of carbon and atoms attached to it, the leaving group takes away the shared electrons, thus leaving the carbon atom as electron deficient. As a result, a positive charge is developed, forming a carbocation. The more tendency of cleavage of bond or formation of a more stable carbonation, the lower the activation energy.

In many organic reactions, such as the SN1 and E1 reactions, carbocation is formed as a reaction intermediate.

Electrophilic Addition:-

In electrophilic addition, an electrophile attacks an unsaturated point (double or triple bond), which results in the breaking of the pi bond and in the formation of a carbocation. The more stable the carbocations, the lower the activation energy and the faster the addition. Electrophilic addition to a pi bond is illustrated by the reaction of HBr (an electrophile) with propene ($CH_3CH = CH_2$).



It can be noted that the formation of the secondary carbocation is favoured over the primary carbocation because secondary carbocation is more stabilized due to resonance. This is also in accordance with Markovnikov’s Rule. Such electrophilic addition reactions are generally seen in alkenes, alkynes and benzene rings.

- ## 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.

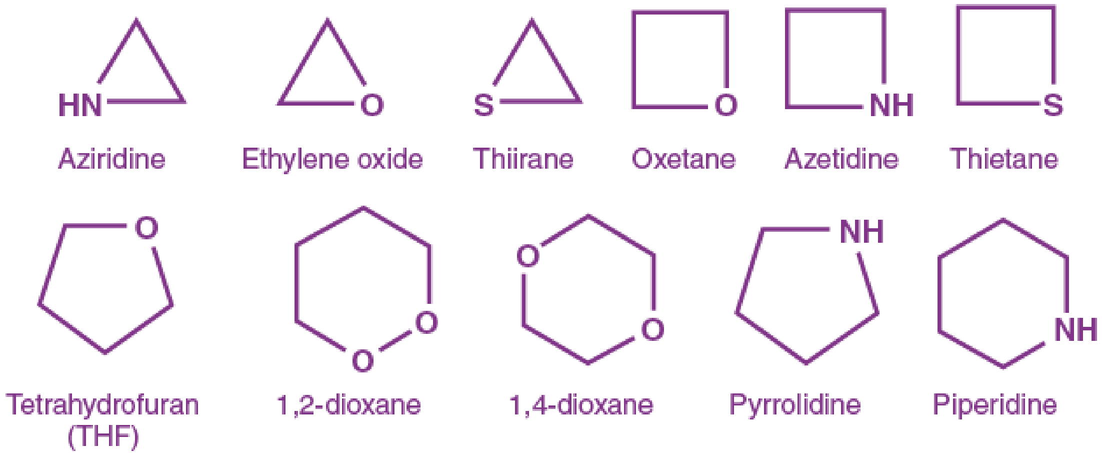
Classification of Heterocyclic Compounds:-

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

- Aliphatic Heterocyclic Compounds
- Aromatic Heterocyclic Compounds

Aliphatic Heterocyclic Compounds:-

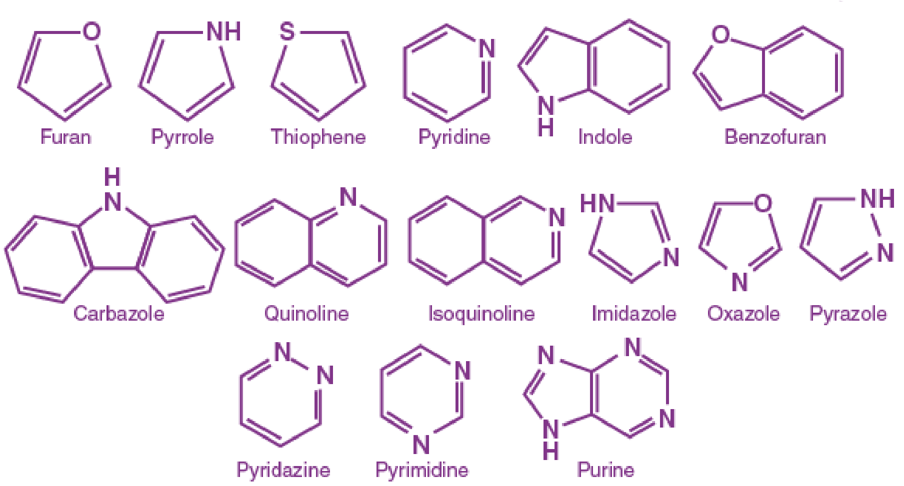
- Aliphatic heterocyclic compounds are those cyclic heterocycles that do not contain any double bond.
- The properties of aliphatic heterocyclic compounds are mainly affected due to ring strain.
- Examples of aliphatic heterocyclic compounds are Aziridine, Ethylene Oxide, Thiirane, Oxetane, Azetidine,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



Examples of aliphatic heterocyclic compounds

Aromatic Heterocyclic Compound:-

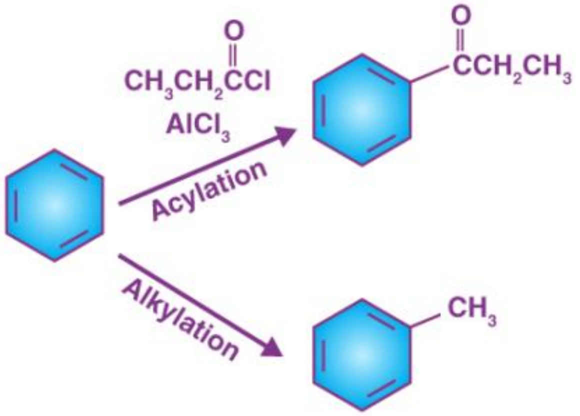
- Aromatic heterocyclic compounds, as the name suggests, are cyclic aromatic compounds.
- Aromatic Heterocyclic compounds obey Huckels Rule, i.e.
- It should be cyclic.
- It should be planar.
- It should not contain any sp3 hybridised atoms.
- It must have (4n+2) **π** electrons.
- Aromatic Heterocyclic 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

What is a Friedel-Crafts Reaction?

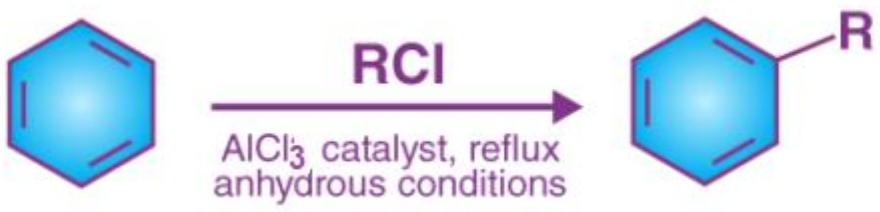
A Friedel-Crafts reaction is an organic coupling reaction involving an electrophilic aromatic substitution that is used for the attachment of substituents to aromatic rings. The two primary types of Friedel-Crafts reactions are the alkylation and acylation reactions. These reactions were developed in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



.Friedel-Crafts 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:-

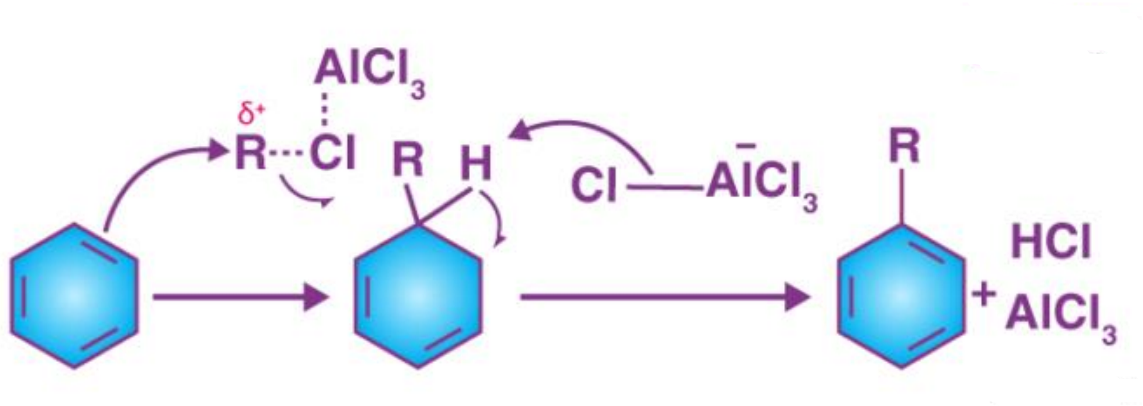
The Lewis acid catalyst ($AlCl_3$) undergoes reaction with the alkyl halide, resulting in the formation of an electrophilic carbocation.

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.

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• Limitations :-

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

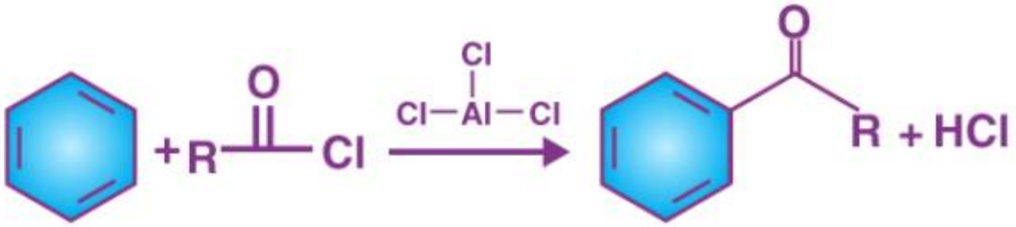
- Since the carbocations formed by aryl and vinyl halides are extremely unstable, they cannot be used in this reaction.

- 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.



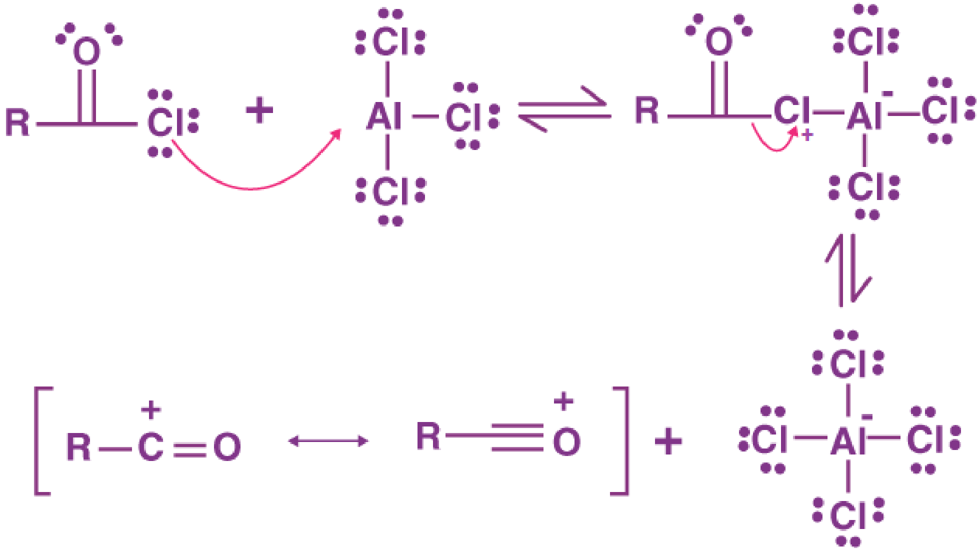
An acid anhydride can be used as an alternative to the acyl halide in Friedel-Crafts acylations. The halogen belonging to the acyl halide forms a complex with the Lewis acid, generating a highly electrophilic acylium ion, which has a general formula of RCO^+ and is stabilized by resonance.

Mechanism:-

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

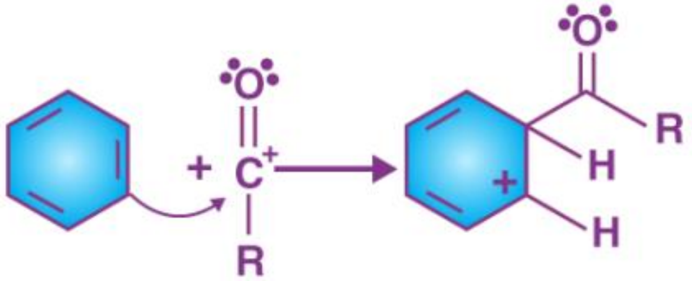
Step 1:-

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.



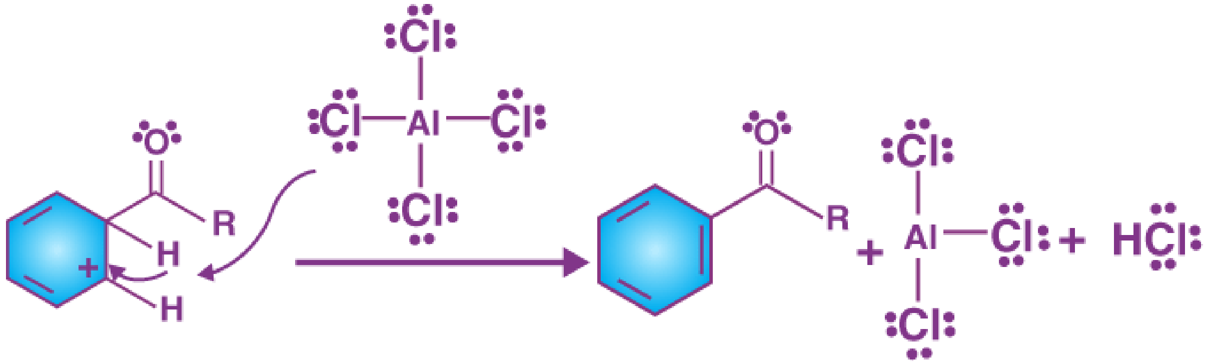
Step 2:-

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.

What is Dienes?

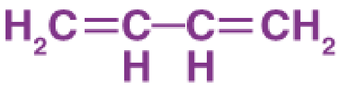
Diene is an unsaturated compound containing two double bonds between carbon atoms. Diene is used in industries as a monomer subunit of complex polymer. It is also used in Organic Synthesis.

This section will discuss the nomenclature, classes, synthesis, physical properties, chemical properties and applications of dienes.

- **Nomenclature of Diene:-**

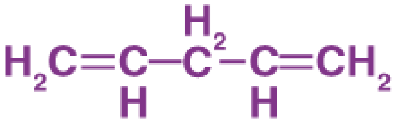
- IUPAC names Dienes in the same way as alkenes are named.
- In the end, we use diene as a suffix.
- In the beginning, we use two numbers to specify the position of two double bonds.

Example



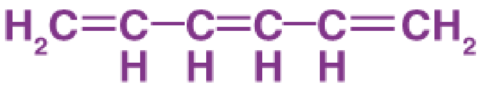
$H_2C{=}\underset{H}{C}{-}\underset{H}{C}{=}CH_2$

1,3-Butadiene



$H_2C{=}\underset{H}{C}{-}\overset{H_2}{C}{-}\underset{H}{C}{=}CH_2$

1,4-Pentadiene



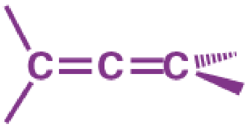
$H_2C{=}\underset{H}{C}{-}\underset{H}{C}{=}\underset{H}{C}{-}\underset{H}{C}{=}CH_2$

1,3,5-Hexatriene

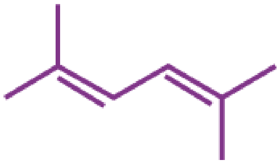
Classes of Diene:-

Based on the relative position of the double bond in the overall molecule, Dienes are classified into three classes:

- Cumulated Diene: A cumulated diene has two successive double bonds on adjacent Carbon. They are also called Allene.
- Conjugated Diene: A conjugated diene has two conjugated double bonds separated by a single bond.
- Isolated Diene: An isolated diene has two double bonds separated by two or more double bonds.



Cumulated (allenes)
The double bonds
are adjacent



Conjugated (allenes)
The double bonds are
separated by one single
bond

Isolated
The double bonds are
separated by more than
one single bond

Synthesis of Dienes:-

Dehydrohalogenation of Dihalides:-

Dienes can be prepared by Dehydrohalogenation of dihalides by successive elimination reactions.

XCH2CH2CH2CH2X→KOHalcoholH2CCHCHCH2

Dehydration of Diols:-

Dienes can be prepared by dehydration of diols by two successive elimination reactions.

OHCH2CH2CH2CH2OH→H+H2CCHCHCH2

Other Methods of Preparation of Dienes

- Butadiene is prepared in industries by thermal cracking of Butane.
- Dicyclopentadiene is prepared in industries from Coal tar.

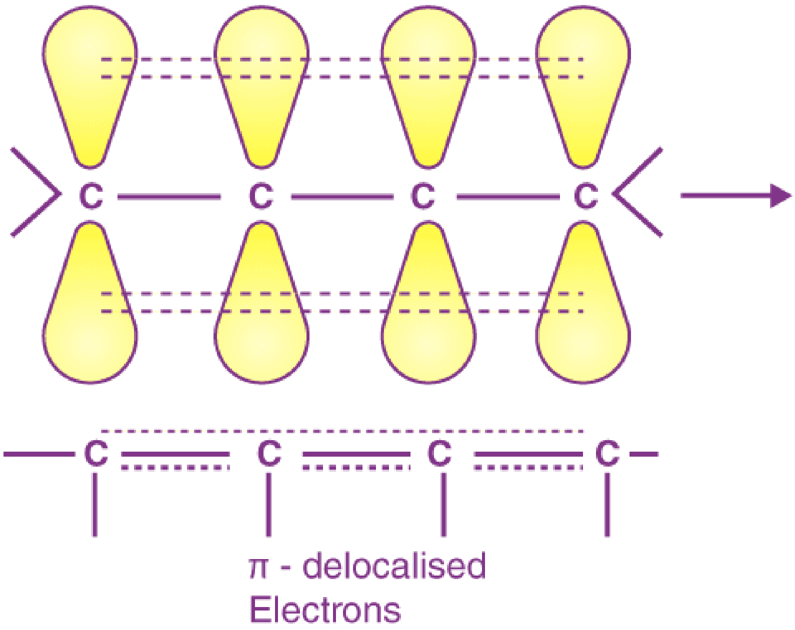
Physical Properties of Diene

Nature:

In diene, the position adjacent to a double bond is acidic. Diene’s acidic character is due to the extra stability of allyl ion due to resonance.

Stability:-

- Conjugated dienes are more stable than non-conjugated dienes because of the delocalisation of electron clouds on Carbon atoms.
- E.g. In conjugated 1,3 Butadiene, all four pi electrons are delocalised over all four Carbon atoms.
- The delocalisation of pi electrons makes the compound more stable.



Chemical Properties of Diene:-

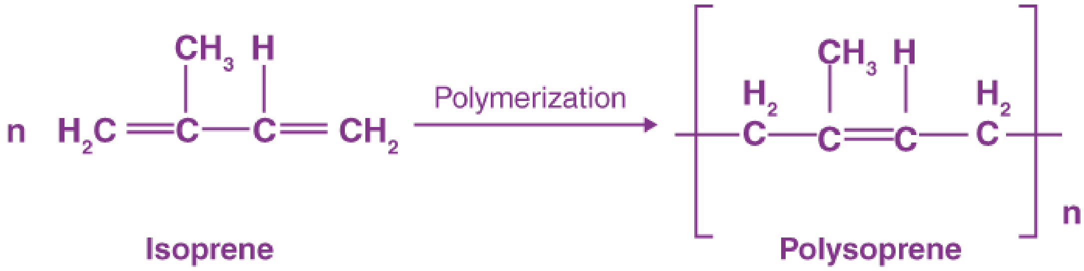
Polymerisation:-

Diene polymerises to form rubber.

- 1,3 Butadiene polymerises to form buna rubber used in tyres.

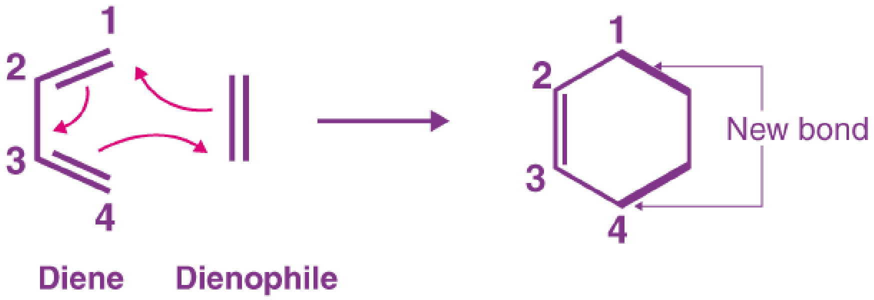
$$n(CH_2{=}CH{-}CH{=}CH_2) \xrightarrow{\text{1,4 addition}} \underset{\text{Cis or Trans}}{+CH_2{-}CH{=}CH{-}CH_2+_n}$$

- Isoprene polymerises to form natural rubber.



Cycloaddition:-

Diel- Alder Reaction is an essential reaction shown by diene. A conjugated diene reacts with substituted alkene (dienophile) to form a substituted cyclohexene derivative.



Addition of Water:-

When we add water to diene in a catalytic amount of strong acid, corresponding enol is formed.

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$CH_2=CHCH=CH_2 \rightarrow CH_3CH(OH)CH=CH_2$ (But-1-en-2-ol) + $CH_3CH=CHCH_2OH$ (But-2-en-1-ol)

Applications of Diene:-

- Dienes are widely used in industries as monomer subunits of complex polymers.
- 1,3 Butadiene polymerises to form buna rubber used in tyres.

$$n(\mathrm{CH_2{=}CH-CH{=}CH_2}) \xrightarrow{\text{1,4 addition}} \underset{\text{Cis or Trans}}{\left(\mathrm{CH_2-CH{=}CH-CH_2}\right)_n}$$