

PLUS ONE CHEMISTRY



**STUDY
MATERIAL**



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HIGHER SECONDARY NATIONAL SERVICE SCHEME

1. SOME BASIC CONCEPTS OF CHEMISTRY

Laws of Chemical Combination

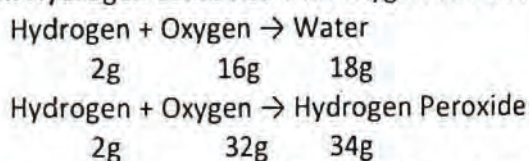
The combination of elements to form compounds is governed by the some basic laws:

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

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

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

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



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

Atomic mass

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

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

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

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

Today, 'amu' has been replaced by 'u' which is known as unified mass.

Mole concept

Mole is the unit of amount of substance. It is defined as *the amount of substance that contains as many particles as there are atoms in exactly 12 g C¹² isotope. 1 mole of any substance contains 6.022 x 10²³ atoms.* This number is known as **Avogadro number or Avogadro constant (N_A or N₀)**.

1 mol of hydrogen atoms = 6.022 × 10²³ atoms

1 mol of water molecules = 6.022 × 10²³ water molecules

1 mol of sodium chloride = 6.022 × 10²³ formula units of sodium chloride

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

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

Molar mass of oxygen = 32g

Molar mass of hydrogen = 2g etc.

Limiting reagent (Limiting reactant)

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

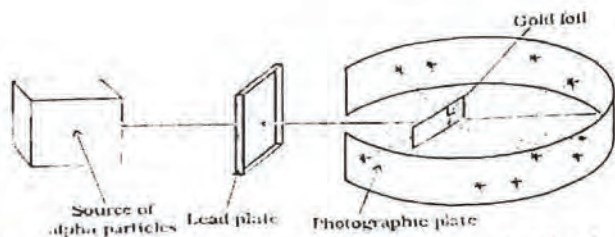
For e.g. in the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{SO}_3(\text{g})$, 2 moles of SO₂ reacts completely with 1 mole of O₂ to form 2 moles of SO₃. If we take 10 moles each of SO₂ and O₂, we get only 10 moles of SO₃ because 10 moles of SO₂ requires only 5 moles of O₂ for the complete reaction. So here SO₂ is the limiting reagent and 5 moles of O₂ remains unreacted.

2. STRUCTURE OF ATOM

Rutherford's Nuclear Model of Atom

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

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



Observations: The important observations made by Rutherford are:

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

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

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

Drawbacks or Limitations of Rutherford's atom model

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

Particle Nature of Electromagnetic Radiation:

Planck's Quantum Theory

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

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

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

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

Photoelectric effect

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

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

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

BOHR'S MODEL FOR HYDROGEN ATOM

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

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

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

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

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

Dual Behaviour of Matter – de Broglie's equation

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

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

Heisenberg's Uncertainty Principle

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

Mathematically, it can be given as in equation:

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

Orbitals and Quantum Numbers

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

1. Principal Quantum Number (n)

The following informations are obtained from n .

- It gives the size the orbit.
- It gives the energy of electron in an orbit.

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

The following informations are obtained from l .

- It gives the shape of the orbital.
- It gives the sub shell or sub level in which the electron is located.

3. Magnetic Quantum Number (m or m_l)

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

4. Spin Quantum Number (s or m_s)

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

Rules for Filling of electrons in various orbitals

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

1. Aufbau principle:

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

2. Pauli's Exclusion Principle

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

If 2 electrons have same values for n, l and m, they should have different values for s. i.e. if s = +½ for the first electron, it should be -½ for the second electron.

3. Hund's rule of maximum multiplicity

It states that *electron pairing takes place only after partially filling all the degenerate orbitals*. Orbitals having same energies are called degenerate orbitals. For example the electronic configuration of N is $1s^2 2s^2 2p_x^1 p_y^1 p_z^1$ and not $1s^2 2s^2 2p_x^2 p_y^1$.

Electronic Configuration of Atoms

The distribution of electrons into various orbitals of an atom is called its *electronic configuration*. The electrons in the completely filled shells are known as *core electrons* and the electrons in the outer most shell are called *valence electrons*.

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

3. CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

Modern Periodic table

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

Periodic properties of Elements

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

1. Atomic Radius

It is defined as the distance from the centre of the nucleus to the outermost shell having electrons.

The atomic size decreases from left to right in a period. This is because in a period, the electrons are added to the same valence shell. Thus the number of shells remains same, but the effective nuclear charge increases. So the atomic radius decreases. In a given period, alkali metals (group 1) have the maximum size and halogens (group 17) have the minimum size.

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

Isoelectronic species:

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

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

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



2. Ionisation enthalpy (Δ_iH)

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

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

Its unit is kJ/mol.

Variation of Δ_iH along a period and a group

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

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

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

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

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

Periodic variation of $\Delta_{eg}H$

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

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

4. Electronegativity

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

4. CHEMICAL BONDING AND MOLECULAR STRUCTURE


The Valence Shell Electron Pair Repulsion [VSEPR] Theory

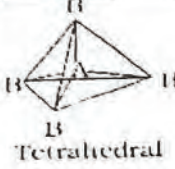


This theory was proposed by Sidgwick and Powell and later modified by Nyholm and Gillespie. The important postulates of this theory are:

- 1) The shape of the molecule depends on the number of valence shell electron pairs (VSEPRs) around the central atom.
- 2) The valence shell electron pairs repel each other.
- 3) In order to reduce the repulsion, the electron pairs stay at maximum distance.
- 4) Presence of lone pairs of electron causes distortion in the expected geometry of the molecule.

Prediction of geometry of molecules using VSEPR theory

1) Molecules containing only bond pairs of electrons

Type of Molecule	No. of VSEPs (bond pairs only)	Structure	Bond angle	Examples
AB_2 type	2	$B-A-B$ Linear	180°	$BeCl_2, HgCl_2$
AB_3 type	3	 Trigonal planar	120°	BF_3, BCl_3

AB ₄ type	4	 Tetrahedral	109°28'	CH ₄ , NH ₄ ⁺
AB ₅ type	5	 Trigonal bipyramid	120° and 90°	PCl ₅
AB ₆ type	6	 Octahedral	90°	SF ₆

Hybridisation

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

Types of hybridisation

1. **sp³ hybridisation (Tetrahedral Hybridisation)**: It is the process of inter mixing of one s-orbital and three p-orbitals to form four new orbitals having equivalent energy and shape. The 4 new orbitals formed are called sp³ hybrid orbitals. They are directed to the four corners of a regular tetrahedron with bond angle 109°28'. Each sp³ hybrid orbitals has 25% s-character and 75% p-character.

2. **sp² hybridisation (Trigonal planar hybridisation)**: It is the process of inter mixing of one s-orbital and two p-orbitals to form three new orbitals having equivalent energy and shape. The 3 new orbitals formed are called sp² hybrid orbitals. They are directed to the three corners of an equilateral triangle. So the shape of the molecule is planar triangular or trigonal planar with bond angle 120°. Each sp² hybrid orbitals has 33% s-character and 66% p-character.

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

Bond Order

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

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

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

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

Molecular Orbital Theory

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

- 1) In molecules, the electrons are present in some special type of orbitals called molecular orbitals (M.Os).
- 2) The atomic orbitals (A.Os) of comparable energy and proper symmetry combine to form molecular orbitals.
- 3) Atomic orbitals are monocentric, while molecular orbitals are polycentric. i.e. electrons present in atomic orbitals are attracted by only one nucleus. While the electrons present in molecular orbitals are attracted by more than one nuclei.
- 4) The number of molecular orbitals formed = the number of atomic orbitals combined. i.e. if 2 atomic orbitals combined, 2 molecular orbitals are formed. One is called bonding molecular orbital (BMO)

5. STATES OF MATTER

Gas Laws

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

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

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

$$P \propto 1/V$$

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

Or, $PV = k$, a constant

2) Charles' Law (Temperature – Volume Relationship)

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

Mathematically, $V \propto T$

Or, $V = k \times T$

Or, $V/T = k$, a constant

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

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

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

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

IDEAL GAS EQUATION

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

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

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

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

On combining these three laws we get:

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

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

Or, $PV = nRT$ (1)

KINETIC MOLECULAR THEORY OF GASES

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

1. Every gas contains a large number of minute and elastic particles (atoms or molecules). The actual volume of the molecules is negligible compared to the volume of the gas.
2. There is no force of attraction between the gas particles.
3. The particles of a gas are in constant and random motion in straight line. During this motion they collide with each other and also with the walls of the container.
4. The pressure of a gas is due to the wall collisions of the particles.
5. All collisions are perfectly elastic. i.e. the total energy of particles before and after collisions remains the same.

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

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

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

6. THERMODYNAMICS

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

Some definitions:

System and Surroundings

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

System + surroundings → Universe

Types of systems

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

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

Extensive and Intensive Properties

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

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

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

E.g. : Temperature (T), Pressure (P), Molar volume (V_m), density, refractive index, molar heat capacity,

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

Mathematically $\Delta U = q + w$ (1)

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

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

Significance of ΔU

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

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

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

Enthalpy (H)

It is the total heat content of a system. It is the sum of internal energy and pressure-volume energy of a system. i.e. $H = U + PV$

Hess's Law of Constant Heat Summation

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

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

Entropy (S)

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

Second Law of Thermodynamics:

It can be stated as the entropy of the universe always increases during every spontaneous process. The second law of thermodynamics explains why spontaneous reactions are so common. In exothermic reactions, heat released by the reaction increases the disorder of the surroundings. So the overall entropy change (ΔS_{Total}) is positive and hence the reaction becomes spontaneous.

7. EQUILIBRIUM

Law of Chemical Equilibrium and Equilibrium Constant

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

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

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

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

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

Equilibrium constant for gaseous reactions

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

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

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

Relation between K_p and K_c

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

Acid – base concepts:

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

2. **The Bronsted – Lowry concept:** According to this concept acids are proton (H^+) donors and bases are (H^+) acceptors.

3. **Lewis concept:** According to this concept acids are electron pair acceptors and bases are electron pair donors.

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

Buffer Solutions

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

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

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

8. REDOX REACTIONS

These are reactions involving both oxidation and reduction.

Oxidation number (Oxidation state)

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

Rules used for the calculation of oxidation number

1. The oxidation number of all elements in the free or the uncombined state is zero. For e.g. oxidation number of H_2 , O_2 , Cl_2 , O_3 , P_4 , S_8 , Na, Mg, Al etc. is zero.
2. For simple ions, the oxidation number is equal to the charge on the ion. Thus Na^+ ion has an oxidation number of +1, Mg^{2+} ion +2, Fe^{3+} ion +3, Cl^- ion -1, O^{2-} ion -2 and so on.
3. All alkali metals have oxidation number of +1 and all alkaline earth metals have an oxidation number of +2. Aluminium shows an oxidation number of +3 in all of its compounds.
4. The common oxidation number of oxygen is -2. But in peroxides (e.g., H_2O_2 , Na_2O_2), oxidation

number of oxygen is -1 and in superoxides (e.g., KO_2 , RbO_2), it is $\frac{1}{2}$. In oxygen difluoride (OF_2) and

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

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

Types of redox reactions

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

Here either A or B or both A and B must be in the elemental form. All combustion reactions are combination redox reactions, since here one of the reactants is O_2 . Examples are:

2. **Decomposition reactions**

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

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

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

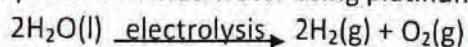
4. **Disproportionation reactions:** These are a special type of redox reaction. In a disproportionation reaction, an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances always contains an element that can exist in at least three oxidation states. The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

9. HYDROGEN

Commercial production of Hydrogen

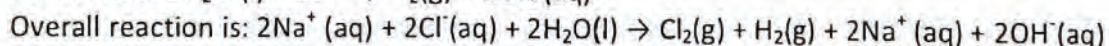
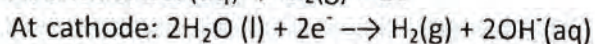
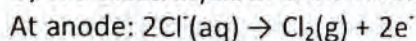
Commercially Hydrogen is prepared by the following methods:

1. Electrolysis of acidified water using platinum electrodes

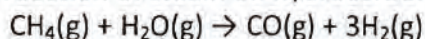


2. High purity dihydrogen is obtained by the electrolysis of warm aqueous $Ba(OH)_2$ solution using nickel electrodes.

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

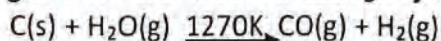


4. By the reaction of steam on hydrocarbons or coke at high temperature in the presence of catalyst.

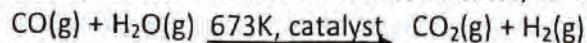


The mixture of CO and H_2 is called water gas. Since it is used for the synthesis of methanol and large number hydrocarbons, it is also called **synthesis gas or syn gas**.

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



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



HYDRIDES

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

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

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

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

2. **Covalent or Molecular Hydrides:**

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

- (i) electron-deficient,
- (ii) electron-precise and
- (iii) electron-rich hydrides.

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

Electron-precise compounds have the required number of electrons to write their Lewis structures. All elements of group 14 form such compounds (e.g., CH_4 , SiH_4 etc.)

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

3. Metallic Hydrides:

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

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

Hard and soft water

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

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

Disadvantages of Hardness of water:

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

10. The s-Block Elements

Anomalous Properties of Lithium

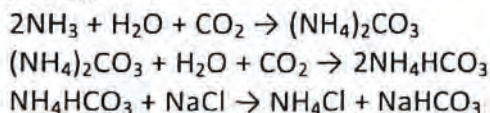
Due to its small size and high polarizing power, Lithium shows some properties different from that of other alkali metals. Some of these are:

- i) Li is much harder and has higher melting point and boiling point than other alkali metals.
- ii) Li is the least reactive but the strongest reducing agent among all the alkali metals.
- iii) It forms only monoxide with oxygen.
- iv) $LiCl$ is deliquescent and crystallizes as a hydrate ($LiCl \cdot 2H_2O$). But the other alkali metal chlorides do not form hydrates.

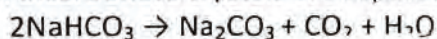
1. Sodium Carbonate [$Na_2CO_3 \cdot 10H_2O$] (Washing Soda)

Preparation: Solvay process

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



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



4. Calcium Sulphate (Plaster of Paris), $CaSO_4 \cdot \frac{1}{2} H_2O$

It is a hemihydrate of calcium sulphate. It is obtained when gypsum [$CaSO_4 \cdot 2H_2O$] is heated to 393 K. $CaSO_4 \cdot 2H_2O \xrightarrow{393K} CaSO_4 \cdot \frac{1}{2} H_2O + 3/2 H_2O$
Above 393 K, no water of crystallisation is left and anhydrous calcium sulphate ($CaSO_4$) is formed. This is known as 'dead burnt plaster'.

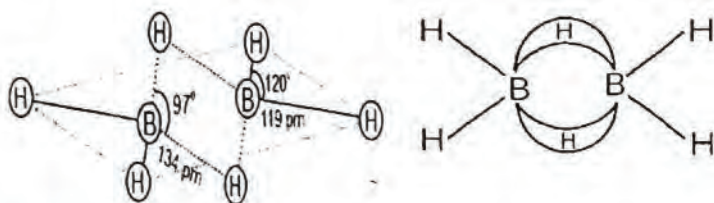
It has a remarkable property of setting with water. On mixing with an adequate quantity of water it forms a plastic mass that gets into a hard solid in 5 to 15 minutes. During this process its volume increases. So it is used for the preparation of statues.

- Uses:**
1. The largest use of Plaster of Paris is in the building industry as well as plasters.
 2. It is used for immobilising the affected part of organ where there is a bone fracture or sprain.
 3. It is also employed in dentistry, in ornamental work and for making casts of statues and busts.

11. The p-Block Elements

Structure of Diborane

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



Allotropes of Carbon

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

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

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

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

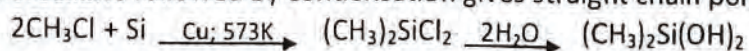
The most commonly known fullerene is C_{60} , which is known as Buckminster fullerene.

Silicones

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

Manufacture:

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



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

Properties:

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

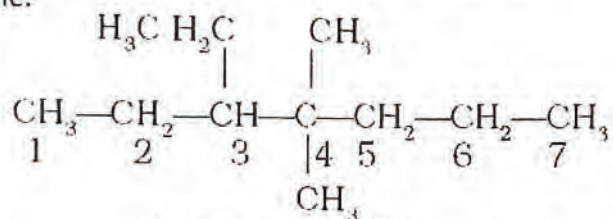
12. ORGANIC CHEMISTRY – SOME BASIC PRINCIPLES AND TECHNIQUES

Rules for naming branched chain alkanes:

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

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

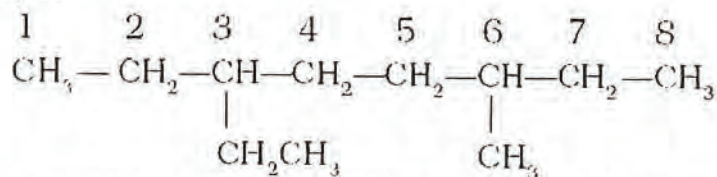
For example:



3-Ethyl-4,4-dimethylheptane

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

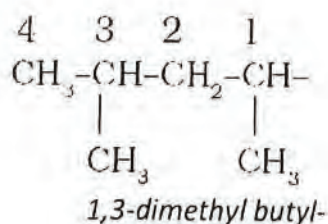
For example:



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

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

For example:



Isomerism

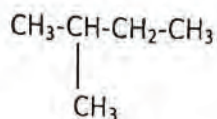
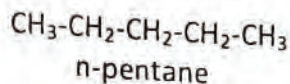
The phenomenon of existence of two or more compounds having the same molecular formula but different structural formula or spatial arrangement of atoms is known as isomerism. Such compounds are called as *isomers*. Isomers have different physical and chemical properties. Isomerism can be broadly classified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

1. Structural isomerism

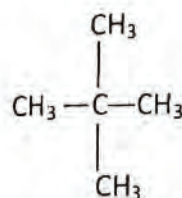
Compounds having same molecular formula but different structural formula (arrangement of atoms) are called structural isomers and the phenomenon is called structural isomerism. There are mainly four types of structural isomerism:

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

E.g.: Pentane (C₅H₁₂)



isopentane
(2-Methylbutane)



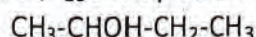
neopentane (2,2-Dimethylpropane)

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

E.g. : Alcohol with molecular formula $\text{C}_4\text{H}_{10}\text{O}$ may be 1-butanol or 2-butanol



1-Butanol



2-Butanol

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

E.g. compound with the molecular formula $\text{C}_2\text{H}_6\text{O}$ may be an alcohol ethanol ($\text{CH}_3\text{-CH}_2\text{OH}$) or an ether methoxy methane ($\text{CH}_3\text{-O-CH}_3$).

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

E.g.: Ether with molecular formula $\text{C}_5\text{H}_{12}\text{O}$ may be methoxybutane ($\text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$) or ethoxypropane ($\text{CH}_3\text{-CH}_2\text{-O-CH}_2\text{-CH}_2\text{-CH}_3$).

13. Hydrocarbons

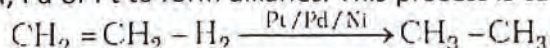
Organic compounds containing carbon and hydrogen atoms only are called hydrocarbons. Depending on the types of C-C bond, they can be classified into three – saturated, unsaturated and aromatic hydrocarbons. Saturated hydrocarbons are also called alkanes. They contain only C-C single bonds. Unsaturated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

ALKANES

Alkanes are saturated open chain hydrocarbons containing carbon-carbon single bonds. They form a homologous series. Their general molecular formula is $\text{C}_n\text{H}_{2n+2}$. In alkanes, all the C atoms are sp^3 hybridised. So each C atom has a regular tetrahedral shape.

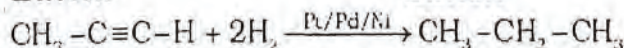
Preparation of alkanes

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



Ethene

Ethane



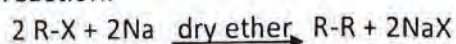
Propyne

Propane

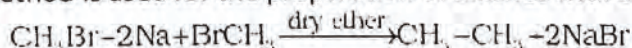
2. **From alkyl halides**

Wurtz reaction:

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

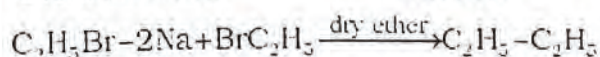


Here the alkane formed contains double the number of C atoms than that present in the alkyl halide. So this method is used for the preparation of alkanes with even number of carbon atoms.



Bromomethane

Ethane



Bromoethane

n-Butane

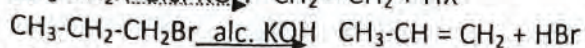
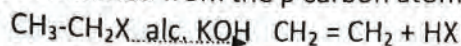
When two different alkyl halides are used, we get a mixture of alkanes.

ALKENES

PREPARATION OF ALKENES

From Alkyl halides:

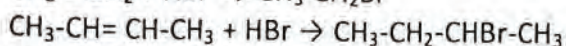
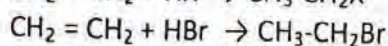
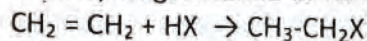
Alkyl halides (R-X) on heating with alcoholic potash, eliminate one molecule of hydrogen halide to form alkenes. This reaction is known as dehydrohalogenation i.e., removal of hydrogen halide. Since atom is eliminated from the β carbon atom, the reaction is also known as β -elimination reaction.



Chemical Properties of Alkenes

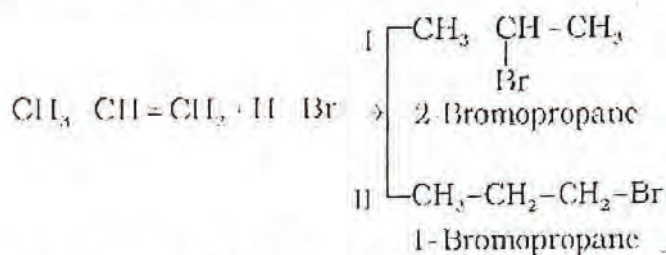
Addition of hydrogen halides:

Alkenes add hydrogen halide to form alkyl halides.



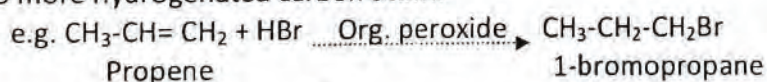
In the case of unsymmetrical alkenes, the addition takes place according to **Markovnikov's Rule (Markownikoff's rule)**. The rule states that "when an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the addendum (adding molecule) gets attached to the carbon containing lesser number of hydrogen atoms" (less hydrogenated C atom).

For e.g. when HBr is added to propene, we get 2 products – 1-bromopropane and 2-bromopropane.



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

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



14. Environmental Chemistry

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

Tropospheric pollution

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

Global Warming and Greenhouse Effect

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

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

The adverse effects of global warming and green house effect

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