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ENJOY CHEMISTRY

1.SOME BASIC CONCEPTS OF CHEMISTRY

<u>Some Important Points and Terms of the Chapter</u>

1. Anything which has mass and occupies space is called **matter**.
2. Matters exist in three physical states viz. solid, liquid and gas.
3. In solids, these particles are held very close to each other in an orderly fashion and there is not much freedom of movement. In liquids, the particles are close to each other but they can move around. However, in gases, the particles are far apart as compared to those present in solid or liquid states and their movement is easy and fast.
4. Solids have definite volume and definite shape.
5. Liquids have definite volume but not the definite shape. They take the shape of the container in which they are placed.
6. Gases have neither definite volume nor definite shape. They completely occupy the container in which they are placed.
7. A mixture contains two or more substances present in it (in any ratio) which are called its components.
8. A **mixture** may be homogeneous or heterogeneous.
9. In a **homogeneous mixture,** the components completely mix with each other and its composition is uniform throughout. Sugar solution and air are thus, the examples of homogeneous mixtures.
10. In **heterogeneous mixtures**, the composition is not uniform throughout and sometimes the different components can be observed. For example, the mixtures of salt and sugar, grains and pulses along with some dirt (often stone) pieces, are heterogeneous mixtures..
11. The components of a mixture can be separated by using physical methods such as simple hand picking, filtration, crystallization, distillation etc.
12. **Pure substances** have characteristics different from the mixtures. They have fixed composition, Copper, silver, gold, water, glucose are some examples of pure substances.

Glucose contains carbon, hydrogen and oxygen in a fixed ratio and thus, like all other pure substances has a fixed composition. Also, the constituents of pure substances cannot be separated by simple physical methods.

13. An **element** consists of only one type of particles. These particles may be atoms or molecules. Sodium, copper, silver, hydrogen, oxygen etc. are some examples of elements. They all contain atoms of one type. However, the atoms of different elements are different in nature. Some elements such as sodium or copper, contain single atoms held together as their constituent particles whereas in some others, two or more atoms combine to give molecules of the element. Thus, hydrogen, nitrogen and oxygen gases consist of molecules in which two atoms combine to give their respective molecules.

14. When two or more atoms of different elements combine, the molecule of a **compound** is obtained. The examples of some compounds are water, ammonia, carbon dioxide, sugar etc. the atoms of different elements are present in a compound in a fixed and definite ratio and this ratio is characteristic of a particular compound.

15. The **SI system**(Systeme International d Unités –abbreviated as SI)) has seven base units and they are listed in Table 1.1

Table 1.1 Base Physical Quantities and their Units

Base Physical Quantity	Symbol for Quantity	Name of SI Unit	Symbol for SI Unit
Length	l	metre	m
Mass	m	kilogram	kg
Time	t	second	s
Electric current	I	ampere	A
Thermodynamic temperature	T	kelvin	K
Amount of substance	n	mole	mol
Luminous intensity	I_v	candela	cd

16. **Mass** of a substance is the amount of matter present in it while **weight** is the force exerted by gravity on an object. The mass of a substance is constant whereas its weight may vary from one place to another due to change in gravity.

17. **Volume** has the units of (length)^3. So in SI system, volume has units of m^3. A common unit, litre (L) which is not an SI unit, is used for measurement of volume of liquids. 1 L = 1000 mL , 1000 cm^3 = 1 dm^3

18. **Density** of a substance is its amount of mass per unit volume SI units of density kg m^{-3} This unit is quite large and a chemist often expresses density in g cm^{-3}.

19. There are three common scales to measuretemperature — °**C (degree celsius), °F (degree Fahrenheit) and K (Kelvin)**. Here, K is the SI unit.

20. The **Kelvin scale is related to Celsius scale** as follows :K =°C+273.15

21. The °**F scale is related to Celsius** scale as follows

$$°F = \frac{9}{5}(°C) + 32$$

22. In **scientific notation (exponential Notation)** any number can be represented in the form $N \times 10^n$ where n is an exponent having positive or negative values and N can vary between 1 to 10. Thus, we can write 232.508 as 2.32508×10^2 in scientific notation. Note that while writing it, the decimal had to be moved to the *left* by two places and same is the exponent (2) of 10 in the scientific notation. Similarly, 0.00016 can be written as 1.6×10^{-4}. Here the decimal has to be moved four places to the *right* and (– 4) is the exponent in the scientific notation.

23. **Significant figures** are meaningful digits which are known with certainty. The uncertainty is indicated by writing the certain digits and the last uncertain digit. Thus, if we write a result as 11.2 mL, we say the 11 is certain and 2 is uncertain and the uncertainty would be ± 1 in the last digit. Unless otherwise stated, an uncertainty of +1 in the last digit is always understood.

24. There are certain **rules for determining the number of significant figures**. These are stated below:

a) All non-zero digits are significant. For example in 285 cm, there are three significant figures and in 0.25 mL, there are two significant figures.

b) Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point. Thus, 0.03 has one significant figure and 0.0052 has two significant figures.

c) Zeros between two non-zero digits are significant. Thus, 2.005 has four significant figures.

d) Zeros at the end or right of a number are significant provided they are on the right side of the decimal point. For example, 0.200 g has three significant figures. But, if otherwise, the terminal zeros are not significant if there is no decimal point. For example, 100 has only one significant figure, but 100. has three significant figures and 100.0 has four significant

figures. Such numbers are better represented in scientific notation. We can express the number 100 as 1×10^2 for one significant figure, 1.0×10^2 for two significant figures and 1.00×10^2 for three significant figures.

e) Counting numbers of objects, for example, 2 balls or 20 eggs, have infinite significant figures as these are exact numbers and can be represented by writing infinite number of zeros after placing a decimal i.e., 2 = 2.000000 or 20 = 20.000000

f) In numbers written in scientific notation, all digits are significant e.g., 4.01×10^2 has three significant figures, and 8.256×10^{-3} has four significant figures.

25. .**Law of Conservation of Mass** states that matter can neither be created nor destroyed.

26. **Law of Definite Proportions** states that a given compound always contains exactly the same proportion of elements by weight.

27. **Law of Multiple Proportions** states that if two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.

28. **Gay Lussac's Law of Gaseous Volumes**: This law was given by Gay Lussac in 1808. He observed that when gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.

29. In 1811, Avogadro proposed that equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

30. In 1808, Dalton published '**A New System of Chemical Philosophy**' in which he proposed the following :

    a) Matter consists of indivisible atoms.

    b) All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.

    c) Compounds are formed when atoms of different elements combine in a fixed ratio.

    d) Chemical reactions involve reorganization of atoms. These are neither created nor destroyed in a chemical reaction.

    e) Dalton's theory could explain the laws of chemical combination.

31. One **atomic mass unit** is defined as a mass exactly equal to one twelfth the mass of one carbon - 12 atom.

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

33. The **mole** is the amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon-12; its symbol is "mol." When the mole is used, the elementary entities must be specified and may be atoms, molecules, ions, electrons, other particles, or specified groups of such particles. This number of entities in 1 mol is so important that it is given a separate name and symbol. It is known as '**Avogadro constant**', denoted by N_A in honor of Amedeo Avogadro.

34. An **empirical formula** represents the simplest whole number ratio of various atoms present in a compound whereas the molecular formula shows the exact number of different types of atoms present in a molecule of a compound.

35. Many a time, the reactions are carried out when the reactants are not present in the amounts as required by a balanced chemical reaction. In such situations, one reactant is in excess over the other. The reactant which is present in the lesser amount gets consumed after sometime and after that no further reaction takes place whatever be the amount of the other reactant present. Hence, the reactant which gets consumed, limits the amount of product formed and is, therefore, called the **limiting reagent.**

36. **Mass per cent** = Mass of solute per 100 g of solution

$$= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$

It is the amount of solute in grams dissolved per 100 g of solution. e.g., 10% solution of sodium chloride means 10 g of solid sodium chloride present in 100 g of solution.

37. **Mole Fraction**: It is ratio of number of moles of a particular component to the total number of moles of all the components.

$$\text{Mole-fraction of solute} = \frac{\text{No. of moles of solute}}{\text{No. of moles of solute} + \text{No. of moles of solvent}}$$

$$x_B = \frac{n_B}{n_A + n_B} = \frac{\dfrac{W_B}{M_B}}{\dfrac{W_A}{M_A} + \dfrac{W_B}{W_B}}$$

$x_B = \dfrac{\dfrac{W_B}{M_B}}{\dfrac{W_A}{M_A}}$ in case of dilute solution $\therefore \dfrac{W_B}{M_B} << \dfrac{W_A}{M_A}$

38. **Molality (m).** It is defined as number of moles of solute (B) per 1000 g or 1 kg of solvent.

Molality (M) = $\dfrac{\text{No. of moles of solute}}{\text{Kg. of solvent}} = \dfrac{W_B}{M_A} \times \dfrac{1000}{W_B \text{ in grams.}}$

where W_A is mass of solvent.

39. **Molarity (M).** It is expressed as the number of moles of solute per litre of solution.

Molarity (M) = $\dfrac{\text{No. of moles of solute}}{\text{Litres of solution}} = \dfrac{W_B}{M_B} \times \dfrac{1000}{\text{Volume of solution in ml.}}$

where W_B is mass of solute, M_B is molar mass of solute

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2.Structure of Atom

Some Important Points and Terms of the Chapter

1. The word 'atom' has been derived from the Greek word '**a-tomio**' which means 'uncutable'or 'non-divisible'.

2. J. J. Thomson, in 1898, proposed that an atom possesses a spherical shape (radius approximately 10–10 m) in which the positive charge is uniformly distributed. The electrons are embedded into it in such a manner as to give the most stable electrostatic arrangement (Fig. 2.4, NCERT Page 5). Many different names are given to this model, for example, **plum pudding, raisin pudding or watermelon.**

3. **Rutherford's Nuclear Model of Atom**:

   a) Most of the space in the atom is empty as most of the a–particles passed through the foil undeflected.

   b) A few positively charged a– particles were deflected. The deflection must be due to enormous repulsive force showing that the positive charge of the atom is not spread throughout the atom as Thomson had presumed. The positive charge has to be concentrated in a very small volume that repelled and deflected the positively charged a– particles.

   c) Calculations by Rutherford showed that the volume occupied by the nucleus is negligibly small as compared to the total volume of the atom. The radius of the atom is about 10^{-10} m, while that of nucleus is 10^{-15} m.

   d) On the basis of above observations and conclusions, Rutherford proposed the nuclear model of atom (after the discovery of protons). According to this model :(i) The positive charge and most of the mass of the atom was densely concentrated in extremely small region. This very small portion of the atom was called nucleus by Rutherford. (ii) The nucleus is surrounded by electrons that move around the nucleus with a very high speed in circular paths called orbits. Thus, Rutherford's model of atom resembles the solar system in which the nucleus plays the role of sun and the electrons that of revolving planets. (iii) Electrons and the nucleus are held together by electrostatic forces of attraction.

4. The number of protons present in the nucleus is equal to atomic number (Z).the nucleus is equal to atomic number (Z).i.e.   **Atomic number (Z)** = number of protons in the nucleus of an atom = number of electronsin a nuetral atom

5. Protons and neutrons present in the nucleus are collectively known as nucleons. The total number of nucleons is termed as **mass number (A)** of the atom.mass number (A) = number of protons (Z) + number of neutrons (n)

6. **Isobars** are the atoms with same mass number but different atomic number for example, $_6C^{14}$and $_7N^{14}$. On the other hand, atoms with identical atomic number but different atomic mass number are known as **Isotopes**. e.g. $_6C^{14}$ $_6C^{13}$ $_6C^{12}$ & $_{17}Cl^{35}$,$_{17}Cl^{37}$

7. **Drawbacks of Rutherford Model** According to the electromagnetic theory of Maxwell, charged particles when accelerated should emit electromagnetic radiation (This feature does not exist for planets since they are uncharged). Therefore, an electron in an orbit will emit radiation, the energy carried by radiation comes from electronic motion. The orbit will thus continue to shrink. Calculations show that it should take an electron only 10^{-8} s to spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.

8. The frequency (ν), wavelength (λ) and velocity of light (c) are related by the equation (2.5). **c = ν λ** The other commonly used quantity specially in spectroscopy, is the wavenumber (ν⁻). It is defined as the number of wavelengths per unit length. Its units are reciprocal of wavelength unit, i.e., m^{-1}.

9. H. Hertz performed a very interesting experiment in which electrons (or electric current) were ejected when certain metals (for example potassium, rubidium, caesium etc.) were exposed to a beam of light . The phenomenon is called Photoelectric effect. **For photoelectric effect :** $h\nu = h\nu^0 + 1/2\, m\upsilon^2$

10. **Planck's quantum theory.**   *(i)* The energy is radiated or absorbed by a body not continuously but discontinuously in form of small packets.

(ii) Each packet is called quantum. In case of light, the quantum is called 'photon'. The energy of quantum is directly proportional to the frequency (ν) of the radiation. E ∝ ν E = *hν*, Where *'h'* is Planck's constant. Its value is 6.625×10^{-34} Joule second.

11. The spectrum of radiation emitted by a substance that has absorbed energy is called an **emission spectrum**. Atoms, molecules or ions that have absorbed radiation are said to be "excited". To produce an emission spectrum, energy is supplied to a sample by heating it or irradiating it and the wavelength (or frequency) of the radiation emitted, as the sample gives up the absorbed energy, is recorded.

12. An **absorption spectrum** is like the photographic negative of an emission spectrum. A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths.

13. **Line Spectrum of Hydrogen**: When an electric discharge is passed through gaseous hydrogen, the H_2 molecules dissociate and the energetically excited hydrogen atoms produced emit electromagnetic radiation of discrete frequencies. The hydrogen spectrum consists of several series of lines named after their discoverers.

Series	n_1	n_2	Spectral region
Lyman	1	2,3……	Ultraviolet
Balmer	2	3,4………	Visible
Paschen	3	4,5……..	Infrared
Brackett	4	5,6…….	Infrared
Pfund	5	6,7…….	Infrared

The Swedish spectroscopist, Johannes Rydberg, noted that all series of lines in the hydrogen spectrum could be described by the following expression :

$$\bar{v} = 109{,}677 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \text{ cm}^{-1}$$

14. **Bohr's Model For Hydrogen Atom**

   a) The electron in the hydrogen atom can move around the nucleus in a circular path of fixed radius and energy. These paths are called orbits, stationary states or allowed energy states. These orbits are arranged concentrically around the nucleus.

   b) An electron can move only in those orbits for which its angular momentum is integral multiple of h/2∏ that is why only certain fixed orbits are allowed.The angular momentum of an electron in a given stationary state can be expressed as in equation

$$m_e \, vr = n.\frac{h}{2\pi} \qquad n = 1,2,3\dots$$

   c) The energy of an electron in the orbit does not change with time. However, the electron will move from a lower stationary state to a higher stationary state when required amount of energy is absorbed by the electron or energy is emitted when electron moves from higher stationary state to lower stationary state . The energy change does not take place in a continuous manner.

   d) The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by ΔE, is given by :

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

15. Bohr's theory can also be applied to the ions containing only one electron, similar to that present in hydrogen atom. For example, He^+ Li^{2+}, Be^{3+} and so on. The energies of the stationary states associated with these kinds of ions (also known as hydrogen like species) are given by the

$$E_n = -2.18 \times 10^{-18} \left(\frac{Z^2}{n^2} \right) J$$

and radii by the expression

$$r_n = \frac{52.9(n^2)}{Z} pm$$

expression

16. **Limitations of Bohr's Model**: It fails to account for the finer details (doublet, that is two closely spaced lines) of the hydrogen atom spectrum observed by using sophisticated spectroscopic techniques. This model is also unable to explain the spectrum of atoms other than hydrogen, for example, helium atom which possesses only two electrons. Further, Bohr's theory was also unable to explain the splitting of spectral lines in the presence of magnetic field (**Zeeman effect**) or an electric field (**Stark effect).**

17. **Dual Behaviour of Matter**: The French physicist, de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties.

18. The **de Broglie relation**. :de Broglie relation state that the wavelength associated with a moving object or an electron is inversely proportional to the momentum of the particle.

$\lambda = \dfrac{h}{mv} = \dfrac{h}{p}$ where p is the momentum of particle $= mv$.

19. **Heisenberg's Uncertainty Principle**. It is not possible to determine the position and velocity simultaneously for a sub-atomic particle like electron at any given instant to an arbitary degree of precision. Consequently, it is not possible to talk of path of the electron in which it moves. If ' Δx' is uncertainty in position and ' ΔP' is uncertainty in momentum then

$$\Delta x . \Delta P \geq \frac{h}{4\pi}$$

20. **Orbital.** It is a region or space where there is maximum probability of getting electron.

21. **Quantum numbers.** They are used to get complete information about electron, i.e., location, energy, spin, etc. These quantum numbers also help to designate the electron present in an orbital.

22. **Principal quantum number.** It specifies the location and energy of an electron. It is measure of the effective volume of the electron cloud. It is denoted by 'n'. Its possible values are 1, 2, 3,4 …..

23. **Angular momentum quantum number.** It is also called 'azimuthal quantum number'. It determines the shape of the orbital. It is denoted by 'l'. The permitted values of 'l' are 0, 1, 2, etc., upto n–1. For a given value of n, $l = 0$ to $n – 1$ '. e.g., if value of n is 4, l can have values 0, 1, 2, 3. It determines angular momentum. $mvr = \sqrt{l(l+1)}\dfrac{h}{2\pi}$

24. **Magnetic quantum number.** It is denoted by 'm' and its value depends on value of 'l' since magnetism is due to angular momentum. It determines the magnetic orientation of an orbital, i.e., the direction of orbital relative to magnetic field in which it is placed. Its permitted values are $-l$ to $+l$ including zero, e.g., when $l = 1$, then $m = -1, 0, +1$. It has total number of values equal to $2l + 1$.

25. **Spin quantum number.** It indicates, the direction in which electron revolves. Spin is magnetic property and is also quantized. It has two permitted values $+\frac{1}{2}$ or $-\frac{1}{2}$. The spin angular momentum of an electron is constant and cannot be changed.

26. **(n+l) rule**: The relative order of energies of various sub-shells in a multi-electron atom can be predicted with the help of (n+l) rule (also called Bohr-Bury rule)According to this rule a sub-shell with lower values of (n+l) has lower energy.In case two sub-shell has equal value of (n+l), the sub-shell with lower value of n has lower energy

27. **Pauli's Exclusion Principle.** No two electrons in an atom can have all the four quantum numbers same. It can also be stated as – An orbital can have maximum two electrons and they must be of opposite spin quantum numbers.

28. **Aufbau principle.** Electrons are filled in the various orbitals in the increasing order of their energies, *i.e.*, orbital having lowest energy will be filled first and the orbital having highest energy will be filled last.**Increasing energy ofatomic orbitals for multi-electron atoms**
$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s$

29. **Hund's rule of maximum multiplicity.** No electron pairing takes place in *p, d* and *f* orbitals until each orbital in the given sub-shell contains one electron, *e.g.,* N (7) has electronic configuration $1s^2\, 2s^2\, 2p_x^1\, 2p_y^1\, 2p_z^1$ according to Hund's rule and not $1s^2\, 2s^2\, 2p_x^2\, 2p_y^1$.

30. The valence electronic configurations of Cr and Cu, therefore, are $3d^5\, 4s^1$ and $3d^{10}4s^1$ respectively and not $3d^4\, 4s^2$ and $3d^9 4s^2$. It has been found that there is extra stability(Stability of Completely Filled and Half Filled Subshells) associated with these electronic configurations.

31. **Three orbitals of 2p subshell** ($2p_x$, $2p_y$, and $2p_z$ orbitals).

p_x p_y p_z
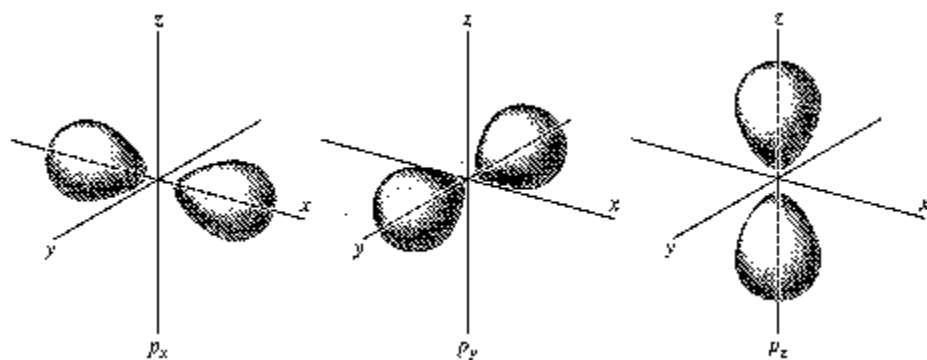
32. **Five orbitals of 3d subshell** ($3d_{xy}$, $3d_{yz}$, $3d_{zx}$ $3d_{x^2-y^2}$ and $3d_{x^2}$ orbitals).
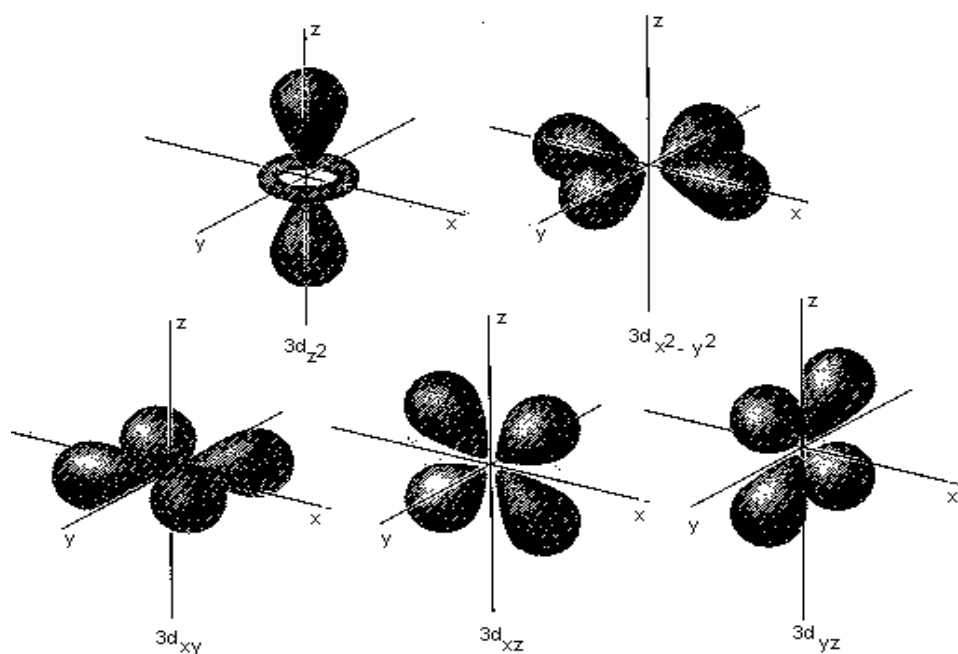
$3d_{z^2}$ $3d_{x^2-y^2}$

$3d_{xy}$ $3d_{xz}$ $3d_{yz}$

Some Important Points and Terms of the Chapter

1. **Dobereiner's Triads**:In 1817 a German chemist Doberneiner identified certain groups of three elements. These groups of three elements having similar properties was called triads. When three elements were arranged in order of their increasing atomic masses, the atomic mass of the middle element was roughly the mean of the atomic masses of the other two element

2. **New Lands Law of octaves**:When elements were arranged in order of their increasing relative atomic masses. The properties of every eight elements were similar to the first one, like the eighth note of a musical scale.This repetition in the properties of elements is just like the repetition of eighth node in an octave of music.

3. **Mendeleev's Periodic Law:**The physical and chemical properties of elements are the periodic function of their atomic masses.

4. **Mendeleev's Periodic Table**:When mendeleev started his work, 63 elements were known at that time. He selected hydrogen and oxygen as they are very reactive and formed compounds with most elements. Mendeleev's periodic table contains vertical columns called groups and horizontal rows called periods. There were 7 periods and 8 groups. Noble gases were not known at that time. So there was no group of noble gases.The elements in each group of the periodic tables are similar to one another in many properties. The similar properties of the elements are repeated periodically

(a).**Merits of mendeleev's classification**

- Mendeleev's periodic law predicted the existence of some elements that had not been discovered at that time

- .Could predict the properties of several elements on the basis of their position in the periodic table.

- Could accommodate noble gases when they were discovered.

(b)**Limitations of mendeleev's classification** :-

- The correct position could not be assigned to the hydrogen in the periodic table.

- Wrong order of the atomic masses of some elements could not be explained.

- The position of isotopes could not be explained.
- Uncertainty in prediction of new elements was there.

5. **Modern periodic law**: Properties of elements are the periodic function of their atomic number.

6. **Modern Periodic Table**: This table was prepared was Bohr and is based upon the electronic configuration of elements. The table consists of 18 vertical columns called groups Elements having similar outer electronic configurations in their atoms are arranged in vertical columns, referred to as groups . According to the recommendation of International Union of Pure and Applied Chemistry (IUPAC), the groups are numbered from 1 to 18 and the table consists of 7 horizontal rows called periods. The first period contains 2 elements. The subsequent periods consists of 8, 8, 18, 18 and 32 elements, respectively. The seventh period is incomplete and like the sixth period would have a theoretical maximum (on the basis of quantum numbers) of 32 elements. In this form of the Periodic Table, 14 elements of both sixth and seventh periods (lanthanoids and actinoids, respectively) are placed in separate panels at the bottom

7. **.Notation for IUPAC Nomenclature of Elements With Z > 100**

Digit	Name	Abbreviation
0	nil	n
1	un	u
2	bi	b
3	tri	t
4	quad	q
5	pent	p
6	hex	h
7	sept	s
8	oct	o
9	enn	e

8. We can classify the elements into four blocks viz., s-block, p-block, d-block and f-block depending on the type of atomic orbital that are being filled with electrons.

9. **s-Block Elements** : The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the s-Block Elements.

10. **p-Block Elements** The p-Block Elements comprise those belonging to Group 13 to 18 and these together with the s-Block Elements are called the Representative Elements or Main Group Elements. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period.

11. **d-Block Elements** These are the elements of Group 3 to 12 in the centre of the Periodic Table. These are characterised by the filling of inner d orbitals by electrons and are therefore referred to as d-Block Elements. These elements have the general outer electronic configuration $(n-1)d^{1-10}ns^{0-2}$.

12. **f-Block Elements** The two rows of elements at the bottom of the Periodic Table, called the Lanthanoids, Ce(Z = 58) – Lu(Z = 71) and Actinoids, Th(Z = 90) – Lr (Z = 103) are characterised by the outer electronic configuration $(n-2)f^{1-14}$ $(n-1)d^{0-1}ns^2$. The last electron added to each element is filled in f- orbital. These two series of elements are hence called the Inner-Transition Elements (f-Block Elements).

13. **Variation in Atomic Radius in Period**: The atomic size generally decreases across a period It is because within the period the outer electrons are in the same valence shell and the effective nuclear charge increases as the atomic number increases resulting in the increased attraction of electrons to the nucleus.
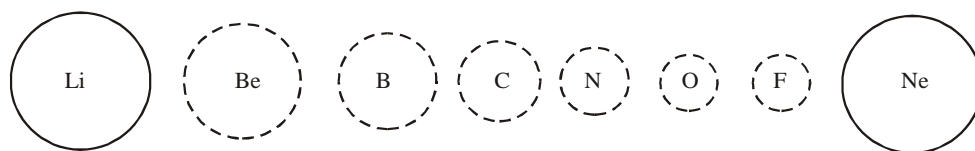
14. **Variation in Atomic Radius in Group:** Within a family or vertical column of the periodic table, the atomic radius increases regularly with atomic number as). as we descend the groups, the principal quantum number (n) increases and the valence electrons are farther from the nucleus. This happens because the inner energy levels are filled with electrons, which serve to shield the outer electrons from the pull of the nucleus. Consequently the size of the atom increases as reflected in the atomic radii.

15. The **atomic radii of noble gases** are not considered here. Being monatomic, their (non-bonded radii) values are very large. In fact radii of noble gases should be compared not with the covalent radii but with the van der Waals radii of other elements.

16. A **cation is smaller than its parent atom** because it has fewer electrons while its nuclear charge remains the same. **The size of an anion will be larger than that of the parent atom** because the addition of one or more electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge. For example, the ionic radius of fluoride ion (F^-) is 136 pm whereas the atomic radius of fluorine is only 64 pm. On the other hand, the atomic radius of sodium is 186 pm compared to the ionic radius of 95 pm for Na^+.

17. **Isoelectronic species** :Atoms and ions which contain the same number of electrons.. For example, O^{2-}, F^-, Na^+ and Mg^{2+} have the same number ofelectrons (10). Their radii would be different because of their different nuclear charges. The cation with the greater positive charge will have a smaller radius because of the greater attraction of the electrons to the nucleus. Anion with the greater negative charge will have the larger radius. In this case, the net repulsion of the electrons will outweigh the nuclear charge and the ion will expand in size.

18. **Ionization Enthalpy:** It represents the energy required to remove an electron from an isolated gaseous atom (X) in its ground state. In other words, the first ionization enthalpy for an element X is the enthalpy change ($\Delta_i H$) for the reaction depicted in equation. $X (g) \rightarrow X^+(g) + e^-$. The ionization enthalpy is expressed in units of kJ mol^{-1}. We can define the second ionization enthalpy as the energy required to remove the second most loosely bound electron; it is the energy required to carry out the reaction shown in equation $X^+(g) \rightarrow X^{2+}(g) + e^-$. Energy is always required to remove electrons from an atom and hence ionization enthalpies are always positive. The second ionization enthalpy will be higher than the first ionization enthalpy because it is more difficult to remove an electron from a positively charged ion than from a neutral atom.

In the same way the third ionization enthalpy will be higher than the second and so on. The term "ionization enthalpy", if not qualified, is taken as the first ionization enthalpy.

19. **Variation in Ionization Enthalpy in Group:** As we descend in a group the first ionization enthalpy generally decreases .Because as we go down a group, the outermost electron being increasingly farther from the nucleus, there is an increased shielding of the nuclear charge by the electrons in the inner levels. In this case, increase in shielding outweighs the increasing nuclear charge and the removal of the outermost electron requires less energy down a group.

20. **Variation in Ionization Enthalpy in Period**: The first ionization enthalpy generally increases as we go across a period. When we move from left to right in period, successive electrons are added to orbitals in the same principal quantum level and the shielding of the nuclear charge by the inner core of electrons does not increase very much to compensate for the increased attraction of the electron to the nucleus. Thus, across a period, increasing nuclear charge outweighs the shielding. Consequently, the outermost electrons are held more and more tightly and the ionization enthalpy increases across a period
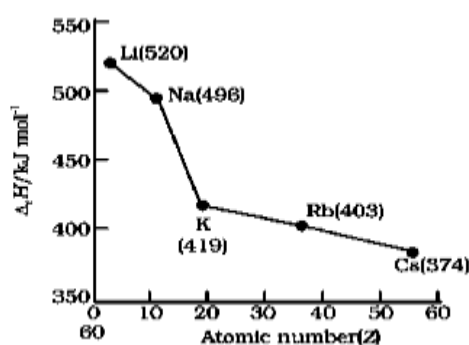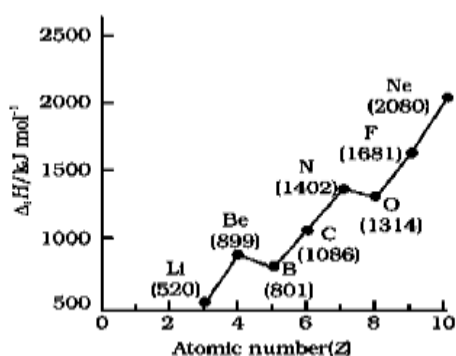
21. **Electron Gain Enthalpy**: When an electron is added to a neutral gaseous atom (X) to convert it into a negative ion, the enthalpy change accompanying the process is defined as the Electron Gain Enthalpy ($\Delta_{eg}H$). Electron gain enthalpy provides a measure of the ease with which an atom adds an electron to form anion as represented by equation. $X(g) + e^- \rightarrow X^-(g)$. Depending on the element, the process of adding an electron to the atom can be either endothermic or exothermic. For many elements energy is released when an electron is added to the atom and the electron gain enthalpy is negative. For example, group 17 elements (the halogens) have very high negative electron gain enthalpies because they can attain stable noble gas electronic configurations by picking up an electron. On the other hand, noble gases have large positive

electron gain enthalpies because the electron has to enter the next higher principal quantum level leading to a very unstable electronic configuration.

22. **Variation in electron gain enthalpies in Group & period**: The variation in electron gain enthalpies of elements is less systematic than for ionization enthalpies. As a general rule, electron gain enthalpy becomes more negative with increase in the atomic number across a period. The effective nuclear charge increases from left to right across a period and consequently it will be easier to add an electron to a smaller atom since the added electron on an average would be closer to the positively charged nucleus. We should also expect electron gain enthalpy to become less negative as we go down a group because the size of the atom increases and the added electron would be farther from the nucleus. This is generally the case. However, electron gain enthalpy of O or F is less negative than that of the succeeding element. This is because when an electron is added to O or F, the added electron goes to the smaller $n = 2$ quantum level and suffers significant repulsion from the other electrons present in this level. For the $n = 3$ quantum level (S or Cl), the added electron occupies a larger region of space and the electron-electron repulsion is much less.

23. **Electronegativity**: A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself is called electro negativity Linus Pauling, an American scientist, in 1922 assigned arbitrarily a value of 4.0 to fluorine, the element considered to have the greatest ability to attract electrons. Electronegativity generally increases across a period from left to right (say from lithium to fluorine) and decrease down a group (say from fluorine to astatine) in the periodic table.

24. **Anomalous Properties of Second Period Elements**: The first element of each of the groups 1 (lithium) and 2 (beryllium) and groups 13-17 (boron to fluorine) differs in many respects from the other members of their respective group. For example, lithium unlike other alkali metals, and beryllium unlike other alkaline earth metals, form compounds with pronounced covalent character; the other members of these groups predominantly form ionic compounds. In fact the behaviour of lithium and beryllium is more similar with the second element of the Group 1, 2 ,13, 14, 15, 16 ,17. following group i.e., magnesium and aluminum, respectively. This sort of similarity is commonly referred to as **diagonal relationship** in the periodic properties. The anomalous behaviour is attributed to their small size, large charge/ radius ratio and high electronegativity of the elements. In addition, the first member of group has only four valence orbitals (2*s* and 2*p*) available for bonding, whereas the second member of the groups have nine valence orbitals (3*s*, 3*p*, 3*d*). As a consequence of this, the maximum covalency of the first

member of each group is 4 (e.g., boron can only form $[BF_4]^-$, whereas the other members of the groups can expand their valence shell to accommodate more than four pairs of electrons e.g., aluminum forms $[AlF_6]^{3-}$). Furthermore, the first member of *p*-block elements displays greater ability to form $p\prod - p\prod$ multiple bonds to itself (e.g., $C = C$, $C \equiv C$, $N = N$, $N \equiv N$) and to other second period elements (e.g., $C = O$, $C = N$, $C \equiv N$, $N = O$) compared to subsequent members of the same group.

4.Chemical bonding and Molecular Structure

Some Important Points and Terms of the Chapter

1. **Lewis dot structures** are shorthand to represent the valence electrons of an atom. The structures are written as the element symbol surrounded by dots that represent the valence electrons.

2. **Covalent Bonds**- The bond formed between two atoms by mutual sharing of electrons between them so as to complete their octets or duplets. When two atoms share one electron pair they are said to be joined by a single covalent bond.e.g H_2 If two atoms share two electron pairs of electrons, the covalent bond between them is called a double bond. e.g O_2 If two atoms share three electron pairs of electrons, the covalent bond between them is called a double bond. e.g N_2

3. **Octet Rule-** Kossel and Lewis in 1916 developed an important theory of chemical combination between atoms known as electronic theory of chemical bonding. According to this, atoms can combine either by transfer of valence electrons from one atom to another or by sharing of valence electrons in order to attain their octet. This is known as octet rule.

4. **Limitations of octet rule-**

a) Incomplete octet of the central atom: In some compounds the number of electrons surrounding the central atom is less than eight. This is especially the case with elements having less than four valence electrons.   Examples-   LiCl ,$BeCl_2$, BCl_3

b) Odd-electron molecules: In molecules with an odd number of electrons like nitric oxide, NO and nitrogen dioxide, the octet rule is not satisfied for all the atoms.

c) The expanded octet :   Elements in and beyond the third period of the periodic table have, apart from 3s and 3p orbitals, 3d orbitals also available for bonding. In a number of compounds of these elements there are more than eight valence electrons around the central atom. This is termed as the expanded octet. Some of examples of such compounds are: PF_5, SF_6.

d) This theory does not account for the shape of molecules.

5. **Electrovalent bond or Ionic Bond**: The chemical bond as result of transfer of electron from one atom(electropositive) to another atom (electronegative).Ionic bonds will be formed more easily between elements with comparatively low ionization enthalpies and elements with comparatively

high negative value of electron gain enthalpy. Most ionic compounds have cations derived from metallic elements and anions from non-metallic elements.

6. **Formation of Ionic Bond**

$$M(g) \rightarrow M^+(g) + e^-;$$
$$\text{Ionization enthalpy}$$
$$X(g) + e^- \rightarrow X^-(g);$$
$$\text{Electron gain enthalpy}$$
$$M^+(g) + X^-(g) \rightarrow MX(s)$$
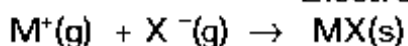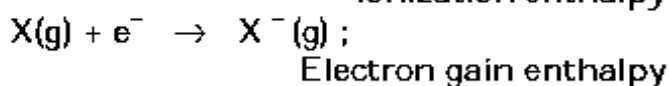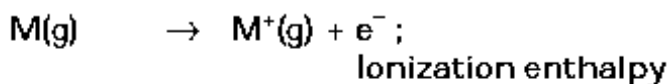
7. **Bond length** is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

8. **Bond Angle:** It is defined as the angle between the orbital containing bonding electron pairs around the central atom in a molecule/complex ion. It gives some idea regarding the distribution of orbital around the central atom in a molecule/complex ion and hence it helps us in determining its shape

9. **Bond enthalpy**: It is defined as the amount of energy required to break one mole of bonds of a particular type between two atoms in a gaseous state. The unit of bond enthalpy is kJ mol^{-1}

10. **Bond Order :** The Bond Order is given by the number of bonds between the two atoms in a molecule. E.g.: Bond Order of O_2= 2. With increase in bond order, bond enthalpy increases and bond length decreases.

11. **Resonance**: According to the concept of resonance, whenever a single Lewis structure cannot describe a molecule accurately, a number of structures with similar energy, positions of nuclei, bonding and the non- bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately

12. **Polarity of bonds:** In case of heteronuclear molecules like HCl, the shared pair of electron between the two atoms gets displaced more towards chlorine since the electronegativity of chlorine is far greater than that of hydrogen. The resultant covalent bond is called a polar covalent bond.

13. **Dipole moment**: As a result of polarization, the molecule possesses the dipole moment which can be defined as the product of charge and the distance between the centers of positive and negative charge. It is usually designated by a Greek letter 'μ'. Mathematically, it is expressed as follows:

    Dipole moment (μ) = charge (Q) X   distance of separation (r)

14. **VSEPR Theory**

- The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
- Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
- These pairs of electrons tend to occupy such positions in space that minimize repulsion and thus maximise distance between them.
- The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
- A multiple bond is treated as if it is a single electron pair and the two or three electron pairs of a multiple bond are treated as a single super pair.
- Where two or more resonance structures can represent a molecule, the VSEPR model is applicable to any such structure.
- The repulsive interaction of electron pairs decrease in the order: Lone pair (lp) – Lone pair (lp) > Lone pair (lp) – Bond pair (bp) > Bond pair (bp) –Bond pair (bp)
- **Geometry of Molecules** on the basis of VSEPR Theory

Bond pair	Lone pair	Shape	Examples
2	0	Linear	$BeCl_2$
3	0	Trigonal Planar	BCl_3
2	1	Bent	SO_2
4	0	Tetrahedral	CH_4
3	1	Pyramidal	NH_3, ,PH_3,
2	2	V-shape	H_2O
5	0	Trigonal bipyramidal	PCl_5
4	1	See saw	SF_4
3	2	T-shaped	CIF_3,
2	3	Linear	XeF_2
5	1	Square pyramidal	CIF_5, IF_5
4	2	Square planar	XeF_4,
6	1	Distorted Octahedral	XeF_6

15. **Hybridization:** It can be defined as the process of intermixing of the orbitals of slightly different energies so as to redistribute their energies, resulting in the formations of new set of orbitals of equivalent energies and shape.

- **Salient Features of hybridization :**
- The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- The hybridised orbitals are always equivalent in energy and shape.
- The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement.

16. **Types of Hybridisation**

- **sp hybridisation**- This type of hybridisation involves the mixing of one s and one p orbital resulting in the formation of two equivalent sp hybrid orbitals.e.g.$BeCl_2$
- **sp^2 hybridisation**- In this hybridisation there is involvement of one s and two p-orbitals in order to form there equivalent sp^2 hybridised orbitals. e.g.BCl_3
- **sp^3 hybridisation**- When there is mixing of one s and three p-orbitals of the valence shell to form four sp^3 hybrid orbitals of equivalent energies and shape. e.g.CH_4

17. **Molecular orbital.** It gives electron probability distribution around a group of nuclei in a molecule. They are filled in the same way as atomic orbitals. Molecular orbitals are formed by linear combination of atomic orbitals.

18. **Bonding molecular orbital.** A molecular orbital that is formed by addition overlap (*i.e.,* when the lobes of atomic orbitals overlap with the same sign) of two atomic orbitals is known as *bonding molecular orbital.* It is represented as

$\Psi_{MO} = \Psi_A + \Psi_B$ Its energy is lower than the atomic orbitals from which it is formed. It favours bonding.

19. **Anti-bonding molecular orbital.** A molecular orbital that is obtained by the subtraction overlap (*i.e.,* when the lobes of atomic orbitals overlap with the opposite sign) of two atomic orbitals is know as *anti-bonding molecular orbital.* It is represented as

$\Psi^*_{MO} = \Psi_A - \Psi_B$ Its energy is higher than the atomic orbitals from which it is formed. It does not favour bonding.

20. Bond order. It is defined as half of the difference between number of electrons in bonding and anti-bonding orbitals, *i.e.,* B.O. = ½ (N_b – N_a) 'where N_b are number of electrons in bonding orbitals' and N_a are number of electrons in anti-bonding orbitals. Bond order helps in estimating stability of atom.

21. Relationship between electronic configuration and molecular behaviour :

(a)   If N_b is greater than N_a, the molecule is stable.

(b)   The molecule is unstable if N_a is greater than N_b.

(c)   The molecule is also unstable if N_a is equal to N_b because anti-bonding effect is stronger than bonding effect.

22. Sigma (σ) molecular orbitals. A molecular orbital which is formed from the overlap of two *s* atomic orbitlas or head to head overlap of one *s* and *p*-atomic orbitals or head to head overlap of two *p*-atomic orbitals, is known as *sigma molecular orbital.*

23. pi (π) molecular orbitals. A molecular orbital which is formed by lateral overlap of two parallel *p*-orbitals is known as *pi(π) molecular orbital.*

24. Conditions for the Combination of Atomic Orbitals. The linear combination of atomic orbitals takes place only if the following conditions are satisfied :

(i)   The combining atomic orbitals must have same or nearly same energy.

(ii)   The combining atomic orbitals must have the same symmetry about the molecular axis. By convention, z-axis is taken as the molecular axis.

(iii) The combining atomic orbitals must overlap to the maximum extent. Greater the extent of overlapping, the greater will be electron density between the nuclei of a molecular orbital.

25. Energy level Diagrams for Molecular Orbitals. The increasing order of energies of various molecular orbitals for O_2 and F_2 is given below.

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi 2\overset{*}{p}_x = \pi 2\overset{*}{p}_y < \sigma 2\overset{*}{p}_z$$

However, this sequence of energy levels of molecular orbitals is not correct for remaining molecules Li_2, Be_2, B_2, C_2, N_2. For instance, it has been observed experimentally that for molecules such as B_2, C_2, N_2 etc., the increasing order of energies of various molecular orbitals is

5/6

$$\sigma 1s < \overset{*}{\sigma} 1s < \sigma 2s < \overset{*}{\sigma} 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \overset{*}{\pi 2} p_x = \overset{*}{\pi 2} p_y < \overset{*}{\sigma 2} p_z$$

The important characteristic feature of this order is that the energy of $\sigma 2p_z$ **molecular orbital is higher than that of** $\pi 2p_x$ **and** $\pi 2p_y$ **molecular orbitals** in these molecules.

5.States of Matter

Some Important Points and Terms of the Chapter

1. **Intermolecular forces** are the forces of attraction and repulsion between interacting particles (atoms and molecules). This term does not include the electrostatic forces that exist between the two oppositely charged ions and the forces that hold atoms of a molecule together i.e., covalent bonds. Attractive intermolecular forces are known as van der Waals forces, in honour of Dutch scientist Johannes van der Waals (1837-1923).

2. **Dipole - Dipole Forces:**Dipole-dipole forces act between the molecules possessing permanent dipole. Ends of the dipoles possess "partial charges" and these charges are shown by Greek letter *delta* (δ
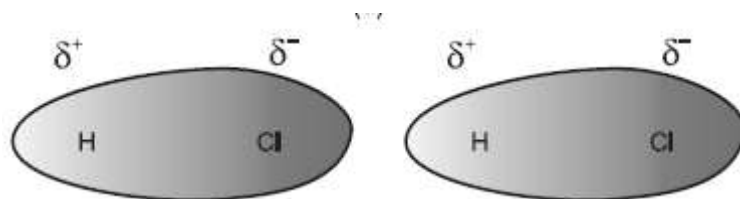
3. **Dipole -Induced Dipole Forces:** This type of attractive forces operate between the polar molecules having permanent dipole and the molecules lacking permanent dipole. Permanent dipole of the polar molecule induces dipole on the electrically neutral molecule by deforming its electronic cloud.Thus an

induced dipole is developed in the other molecule

Permanent dipole (a polar molecule)

non-polar molecule

Permanent dipole (a polar molecule)

Induced dipole in a non-polar molecule
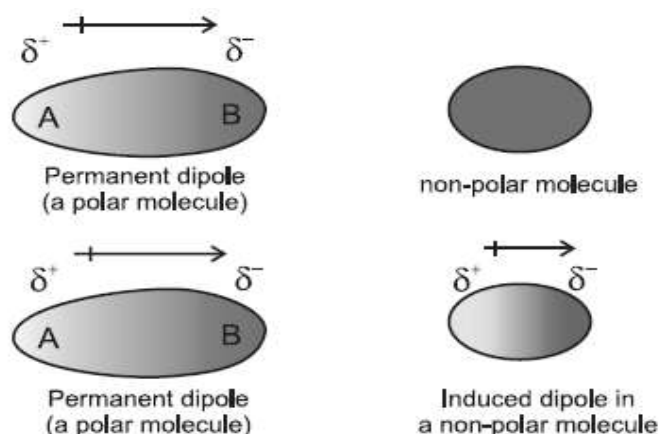
4. **Dispersion Forces or London Forces:** Atoms and nonpolar molecules are electrically symmetrical and have no dipole moment because their electronic charge cloud is symmetrically distributed. But a dipole may develop momentarily even in such atoms and molecules. This can be understood as follows. Suppose we have two atoms 'A' and 'B' in the close vicinity of each other (Fig. 5.1a NCERT page 133). It may so happen that momentarily electronic charge distribution in one of the atoms, say 'A', becomes unsymmetrical *i.e.,* the charge cloud is more on one side than the other (Fig. 5.1 b and c NCERT page 133). This results in the development of instantaneous dipole on the atom 'A' for a very short time. This instantaneous or transient dipole distorts the electron density of the other atom 'B', which is close to it and as a consequence a dipole is induced in the atom 'B'. The temporary dipoles of atom 'A' and 'B' attract each other. Similarly temporary dipoles are induced in molecules also. This force of attraction was first proposed by the German physicist Fritz London, and for this reason force of attraction between two temporary dipoles is known as **London force**. Another name for this force is **dispersion force**.

5. **Hydrogen bond**: Hydrogen bond is represented by a dotted line (– – –) while a solid line represents the covalent bond. Thus, hydrogen bond can be defined as the attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule this is special case of dipole-dipole interaction..

6. **Boyleís Law (Pressure – Volume Relationship)**: At constant temperature, the pressure of a fixed amount (i.e., number of moles n) of gas varies inversely with its volume. This is known as Boyleís law.

$p \: \alpha \: \dfrac{1}{V}$ (at constant T & V)   i.e. $p = K_1 \dfrac{1}{V}$ $pV = K_1$ $p_1 V_1 = p_2 V_2$

$$\boxed{\dfrac{p1}{V1} = \dfrac{p2}{V2}}$$

7. **Charles Law (Temperature – Volume Relationship):** It states that pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.i.e. $V \: \alpha \: T$ (at constant P & V)

$V = K_2 T$ $\dfrac{V}{T} = K_2$ $\boxed{\dfrac{V1}{T1} = \dfrac{V2}{T2}}$

8. **Gay Lussacís Law (Pressure-Temperature Relationship):** It states that at constant volume, pressure of a fixed amount of a gas varies directly with the temperature. Mathematically, . $P \: \alpha \: T$ (at constant V & n)

$p = K_3 T$ $\boxed{\dfrac{P}{T} = K_3}$

9. **Avogadro Law (Volume – Amount Relationship)**: It states that equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules. i.e. $V \: \alpha \: n$ i.e. $\boxed{V = K_4 n.}$ Since volume of a gas is directly proportional to the number of moles; one mole of each gas at standard temperature and pressure (STP)* will have same volume. Standard temperature and pressure means 273.15 K (0^oC) temperature and 1 bar (i.e., exactly 10^5 pascal) pressure

10. **Ideal gas:** A gas that follows Boyle's law, Charles' law and Avogadro law strictly.

11. **Ideal Gas Equation:** $\boxed{pV = n \, RT}$

12. **Universal Gas Constant :**R is called gas constant. It is same for all gases. R= 8.314 Pa m^3 K^{-1} mol^{-1} = 8.314 × 10^{-2} bar L K^{-1} mol^{-1} = 8.314 J K^{-1} mol^{-1}

13. **Equation of state**. $\boxed{\dfrac{P1V1}{T1} = \dfrac{P2V2}{T2}}$

14. **Density and Molar Mass of a Gaseous Substance:** $M = \dfrac{dRT}{P}$

15. **Dalton's Law of Partial Pressures:** It states that the total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases i.e., the pressures which these gases would exert if they were enclosed separately in the same volume and under the same conditions of temperature. In a mixture of gases, the pressure exerted by the individual gas is called partial pressure. Mathematically, $p_{Total} = p_1 + p_2 + p_3 + \ldots \text{(at constant } T, V)$ where pTotal is the total pressure exerted by the mixture of gases and $p1$, $p2$, $p3$ etc. are partial pressures of gases.

16. **KINETIC MOLECULAR THEORY OFGASES:**

   - Gases consist of large number of identical particles (atoms or molecules) that are so small and so far apart on the average that the actual volume of the molecules is negligible in comparison to the empty space between them. They are considered as point masses. This assumption explains the great compressibility of gases.explains the great compressibility of gases.

   - There is no force of attraction between the particles of a gas at ordinary temperature and pressure. The support for this assumption comes from the fact that gases expand and occupy all the space available to them.

   - Particles of a gas are always in constant and random motion. If the particles were at rest and occupied fixed positions, then a gas would have had a fixed shape which is not observed.

   - Particles of a gas move in all possible directions in straight lines. During their random motion, they collide with each other and with the walls of the container. Pressure is exerted by the gas as a result of collision of the particles with the walls of the container.

- Collisions of gas molecules are perfectly elastic. This means that total energy of molecules before and after the collision remains same.

17. **Behaviour Of Real Gases: Deviation From Ideal Gas:**Real gases show deviations from ideal gas law **(a)Pressure correction**: pressure exerted by the gas is lower than the pressure exerted by the ideal gas.

$$P_{ideal} = P_{real} \ + \ \frac{an^2}{V^2}$$

observed   correction
pressure   term

Here, a is a constant.

(b)Volume Correction: ($V–n$b) where nb is approximately the total volume occupied by the molecules themselves. Here, b is a constant.

18. **Van der Waals equation.equation**.:

$$\left(p+\frac{an^2}{V^2}\right)(V-nb) = nRT$$

Constants a and b are called van der Waals constants

19. **Significance of Vander wall parameter**: Vander wall parameter a is the measure of intermolecular forces while b is the measure of effective size of gaseous molecules Unit of a = bar L^3 mol^{-2} Unit of b = L mol^{-1}

20. The deviation from ideal behaviour can be measured in terms of **compressibility factor Z**, which is the ratio of product pV and nRT.

Mathematically $\boxed{Z=\dfrac{pV}{nRT}}$

21. The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or **Boyle point**.

22. **Critical temperature** (T_C)of a gas is highest temperature at which liquifaction of the gas first occurs. Liquifaction of so called permanent gase Volume of one mole of the gas at critical temperature is called **critical volume** (V_C) and pressure at this temperature is called **critical pressure** (p_C). The critical temperature, pressure and volume are called critical constants.

23. **Surface tension** is defined as the force acting per unit length perpendicular to the line drawn on the surface of liquid. It is denoted by Greek letter γ. It has dimensions of $kg\ s^{-2}$ and in SI unit it is expressed as $N\ m^{-1}$.

24. **Viscosity** is a measure of resistance to flow which arises due to the internal friction between layers of fluid as they slip past one another while liquid flows. Strong intermolecular forces between molecules hold them together and resist movement of layers past one another. Greater the viscosity, the more slowly the liquid flows. Viscosity of liquids decreases as the temperature rises because at high temperature molecules have high kinetic energy and can overcome the intermolecular forces to slip past one another between the layers.

25. **Viscosity coefficient** is the force when velocity gradient is unity and the area of contact is unit area. Thus ' η ' is measure of viscosity. SI unit of viscosity coefficient is 1 newton second per square metre ($N\ s\ m^{-2}$) = pascal second (Pa s = $1kg\ m^{-1}s^{-1}$).

6.Thermodynamics

Some Important Points and Terms of the Chapter

1. **System and the Surroundings**: A system in thermodynamics refers to that part of universe in which observations are made and remaining universe constitutes the surroundings. The surroundings include everything other than the system. System and the surroundings together constitute the universe. The wall that separates the system from the surroundings is called **boundary**

2. **Types of the System:**
   - **Open System:** In an open system, there is exchange of energy and matter between system and surroundings.
   - **Closed System** In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings.
   - **Isolated system** :In an isolated system, there is no exchange of energy or matter between the system and the surroundings

3. **State of a System**: The state of a system means the condition of the system which is described in terms of certain observable properties such as temp(T), pressure(p), volume (v), etc. of the systems. These properties of a system are called state variables.

4. **State Functions**: A physical quantity is solid to be state functions of its value depends only upon the state of the system and does not depend upon the path by which this state has been attained.

5. **Internal Energy:** a quantity which represents the total energy of the system. It may be chemical, electrical and mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the internal energy, *U* of the system.

6. **Isothermal Process**: When a process is carried out in such a manner that the temp remains constant throughout this process, it is called an isothermal process.

7. **Adiabatic Process:** Process is carried out in such a manner that no heat can flow from the system to the surrounding or vice versa.

8. **Isochoric Process:** Process during which the volume of the system is kept constant.

9. **Isobaric Process:** Process during which the pressure of the system is kept constant. .

10. The positive sign expresses that Work (w_{ad}) is positive when work is done **on** the system. Similarly, if the work is done **by** the system, wad will be negative.

11. The q is positive, when heat is transferred from the surroundings to the system and q is negative when heat is transferred from system to the surroundings.

12. **First law of Thermodynamics**: Statement: Energy can neither be created nor destroyed, however it may be converted from one form to another.

<u>or</u>

The total energy of the universe remains constant although it may undergo transformation from one to another.

Mathematical expression = $\Delta U = q + w$

13. A process or change is said to be **reversible**, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A **reversible process** proceeds infinitely slowly by a series of equilibrium states such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible processes are known as **irreversible processes**.

14. **Difference between Reversible Process & Irreversible Process**

Reversible Process		Irreversible Process
1. The process is carried out infinitesimally slowly		1. It is carried out rapidly
2. At any stage, the equilibrium is not disturbed		2. Equilibrium may exist only after the completion of the process.
3. It takes infinite time for completion.		3. It takes a finite time for completion.
4. Work obtained in this process is maximum.		4. Work obtained in this process is not maximum

15. **Enthalpy, *H*:** The enthalpy *H* [Greek word *enthalpien*, heat content] is defined as : $H = U + pV$ For finite changes at constant pressure, we can write above equation as $\Delta H = \Delta U + \Delta pV$ Since *p* is constant, we can write $\boxed{\Delta H = \Delta U + p\Delta V}$ *since* $p\Delta V = \Delta n_g RT$,therefore $\boxed{\Delta H = \Delta U + \Delta n_g RT}$

16. **Extensive property**: An extensive property is a property whose value depends on the quantity or size of matter present in the system. For example, mass, volume, internal energy, enthalpy, heat capacity, etc. are extensive properties.

17. **Intensive property**: Those properties which do not depend on the quantity or size of matter present are known as intensive properties. For example temperature, density, pressure etc. are intensive properties.

18. **Specific heat capacity** is the quantity of heat required to raise the temperature of one unit mass of a substance by one degree celsius (or one kelvin). For finding out the heat, *q*, required to raise the temperatures of a sample, we multiply the specific heat of the substance, c, by the mass m, and temperatures change, ΔT as $q = c \times m \times \Delta T = C\Delta T$.

19. **Relationship between Cp and C_V for an ideal gas:** $\boxed{C_p - C_V = R}$

20. **Bomb calorimeter:** For chemical reactions, heat absorbed at constant volume, is measured in a bomb calorimeter . Here, a steel vessel (the bomb)

is immersed in a water bath. The whole device is called calorimeter. The steel vessel is immersed in water bath to ensure that no heat is lost to the surroundings. A combustible substance is burnt in pure dioxygen supplied in the steel bomb. Heat evolved during the reaction is transferred to the water around the bomb and its temperature is monitored. Since the bomb calorimeter is sealed, its volume does not change i.e., the energy changes associated with reactions are measured at constant volume. Under these conditions, no work is done as the reaction is carried out at constant volume in the bomb calorimeter. Even for reactions involving gases, there is no work done as $\Delta V = 0$. Temperature change of the calorimeter produced by the completed reaction is then converted to qV, by using the known heat capacity of the calorimeter with the help of equation (18).

21. **Enthalpy Change of a reaction**: The enthalpy change accompanying a reaction is called the reaction enthalpy. The enthalpy change of a chemical reaction is given by the symbol $\Delta_r H$.

    $\Delta_r H$ = (sum of enthalpies of products) – (sum of enthalpies of reactants).

    $\boxed{\Delta_r H = \sum a_i H_{Products} - \sum b_i H_{Reactants}}$

22. The **standard enthalpy of reaction** is the enthalpy change for a reaction when all the participating substances are in their standard states. The standard state of a substance at a specified temperature is its pure form at 1 bar. Standard conditions are denoted by adding the superscript ^{o} to the symbol ΔH, e.g., $\Delta \boldsymbol{H}^o$

23. The enthalpy change that accompanies melting of one mole of a solid substance in standard state is called **standard enthalpy of fusion or molar enthalpy of fusion**, $\Delta_{fus} H^o$. e.g. $H_2O(s) \rightarrow H_2O(l); \Delta \boldsymbol{fus H^0} = 6.00$ kJ mol^{-1} .

24. Amount of heat required to vaporize one mole of a liquid at constant temperature and under standard pressure (1 bar) is called its **standard enthalpy of vaporization or molar enthalpy of vaporization,** $\Delta_{vap} H^0$. e.g. $H_2O(l) \rightarrow H_2O(g); \Delta_{vap} H^0 = 40.79$ kJ mol^{-1}

25. **Standard enthalpy of sublimation,** $\Delta_{sub}H^0$ is the change in enthalpy when one mole of a solid substance sublimes at a constant temperature and under standard pressure (1bar). Sublimation is direct conversion of a solid into its vapour. Solid CO_2 (dry ice) sublimes at 195K with $\Delta_{sub}H^0$=25.2 kJ mol^{-1}; naphthalene sublimes slowly and for this $\Delta_{sub}H^0$=73.0 kJ mol^{-1}

26. **.**The **standard enthalpy change for the formation** of one mole of a compound from its elements in their most stable states of aggregation (also known as reference states) is called Standard Molar Enthalpy of Formation. Its symbol is $\Delta_f H^0$.

27. ..Standard enthalpy of combustion is defined as the enthalpy change per mole (or per unit amount) of a substance, when it undergoes combustion and all the **reactants and products** being in their standard states at the specified temperature.

28. **Enthalpy of atomization (symbol: $\Delta_a H^0$):** It is the enthalpy change on breaking one mole of bonds completely to obtain atoms in the gas phase. In case of diatomic molecules, like dihydrogen the enthalpy of atomization is also the bond dissociation enthalpy. In some cases, the enthalpy of atomization is same as the enthalpy of sublimation.

29. **Bond Enthalpy (symbol: $\Delta_{bond}H^0$):**
   $\Delta_r H = \sum bondenthapies_{reactants} - \sum bondenthapies_{products}$

30. **Enthalpy of Solution (symbol : $\Delta_{sol}H^0$):** Enthalpy of solution of a substance is the enthalpy change when one mole of it dissolves in a specified amount of solvent. The enthalpy of solution at infinite dilution is the enthalpy change observed on dissolving the substance in an infinite amount of solvent when the interactions between the ions (or solute molecules) are negligible.

31. **Lattice Enthalpy** The lattice enthalpy of an ionic compound is the enthalpy change which occurs when one mole of an ionic compound dissociates into its ions in gaseous state.

32. **Hess's Law**: Enthalpy change for a reaction is the same whether it occurs in one step or in a series of steps. This may be stated as follows in the form of: If a reaction takes place in several steps then its standard reaction enthalpy is the sum of the standard enthalpies of the intermediate reactions into which the overall reaction may be divided at the same temperature. $\boxed{\Delta_r H^0}$

$\boxed{=\Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3}$ For example: $C(s) +$

$1/2O_2\ (g) \rightarrow CO(g)$ $\Delta_r H^0 = -110.5\ \text{kJmol}^{-1}$ $CO(g) + 1/2O_2$

$(g) \rightarrow CO_2(g)$ $\Delta_r H^0 = -283.0\ \text{kJmol}^{-1}$ $C(s) + O_2$

$(g) \rightarrow CO_2\ (g)$ $\Delta_r H^0 = -393.5\ \text{kJmol}^{-1}$
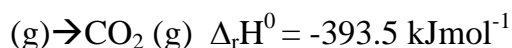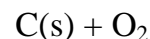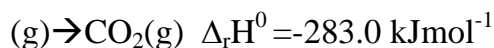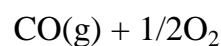
33. **Spontaneous Process**: A process which occurs by its ones i.e. Without the intervention of an outside agency.

34. **Non Spontaneous Process**: A process which can neither take place by itself nor by initiation is called a non spontaneous process.

35. Driving Force: The force which is responsible for spontaneity of a process is called the driving force.

36. Entropy(S): Entropy is a measure of randomness or disorder of the system.

37. Entropy change (ΔS): It is defined as the amount of heat (q) observed isothermally and reversibly divided by the absolute temp(T) at which the heat is absorbed.

$$\Delta S = \frac{q}{T}$$

38. Entropy of fusion : ΔS fusion $= \dfrac{\Delta H\ \text{fusion}}{T_m}$

       Where, ΔH fusion = Entropy of fusion per mole

              T_m = Melting point

$$\Delta S_{VAP} = \frac{\Delta H_{VAP}}{T_b}$$

              ΔH_{VAP} = Entropy of vaporization per mole

              T_b = Boiling point

39. Second Law Of Thermodynamics

The entropy of universe is continuously increasing due to spontaneous process taking place in it.

ΔS system + ΔS surrounding > 0

i.e. ΔS total > 0

40. <u>Gibbs Free Energy (G)</u> : It is defined as max^m amount of energy available to a system during the process that can be converted into useful work. It is a measure of capacity to do useful work.

$$\boxed{G = H - TS}$$ this equation is also known as Gibb's Helmholtz equation

G is a state function. ΔG is change in free energy.

$$\boxed{\Delta G = \Delta H - T\Delta S}$$

41. **If ΔG is negative, process is spontaneous** when $\Delta G = 0$,the process is in equilibrium if ΔG is positive, the process does not take place.

42. **Standard Free Energy Change (ΔG^0)** : It is defined as free energy change measured at 298 K and 1 atm Pressure.

43. **Standard Free energy of formation**: ($\Delta_f G^\circ$) It is free energy change when 1 mole of compound is formed from its constituting elements in their standard state.

$$\Delta_r G^\circ = \sum \upsilon_p \Delta_f G^\circ (\text{products}) - \sum \upsilon_R \Delta_f G^\circ (\text{reactants})$$

44. **Gibbs Energy Change and Work**

In case of galvanic cell, Gibbs energy change $\Delta_r G$,is related to the electrical work done by the cell.

Thus $$\boxed{\Delta_r G = -nFE_{cell}}$$

If reactants and products are in their standard states

$$\Delta_r G^\circ = -nFE^\circ cell, \text{ Here } E^\circ{}_{cell} \text{ is the standard cell potential.}$$

45. **Gibbs Energy Change and Equilibrium Constant**

$$\Delta_r G^\circ = -RT \ln K$$

$$\Delta_r G^\circ = -2.303RT \log K$$

__Some Important Formulas(Thermodynamics)__

- $\Delta U = q + w$

- $\Delta H = \Delta U + p\Delta V$

- $\Delta H = \Delta U + \Delta ngRT$

- $C_p - C_V = R$

- $\Delta_r H = \sum a_i\, H_{Products} - \sum b_i\, H_{Reactants}$

- $\Delta_r H = \sum bondenthapies_{reactants} - \sum bondenthapies_{products}$

- $.\Delta_r H^0 = \Delta_r H_1 + \Delta_r H_2 + \Delta_r H_3$

- $\Delta S\ fusion = \dfrac{\Delta H\ fusion}{Tm}$

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

- $\Delta_r G^{\circ} = \sum \upsilon_p \Delta_f G^{\circ}(products) - \sum \upsilon_R \Delta_f G^{\circ}(reactants)$

- $\Delta_r G = -nFE_{cell}$

- $\Delta_r G = -2.303RT \log K$

7 .Equilibrium

<u>Some Important Points and Terms of the Chapter</u>

1. **Equilibrium** represents the state of a process in which the properties like temperature, pressure etc do not show any change with the passage of time

2. **Chemical equilibrium:** When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products remain constant. This is the stage of chemical equilibrium. This equilibrium is *dynamic* in nature as it consists of a *forward* reaction in which the reactants give product(s) and *reverse* reaction in which product(s) gives the original reactants. Equilibrium is possible only in a closed system at a given temperature. A mixture of reactants and products in the equilibrium state is called an equilibrium mixture.

3. In a **Homogeneous system**, all the reactants and products are in the same phase. For example, in the gaseous reaction, N_2 (g) + $3H_2$(g) → $2NH_3$(g), reactants and products are in the homogeneous phase.

4. Equilibrium in a system having more than one phase is called **heterogeneous equilibrium.** The equilibrium between water vapor and liquid water in a closed container is an example of heterogeneous equilibrium. H_2O(l) → H_2O(g)

5. **Henry Law**:-It states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent

6. **Law of Chemical Equilibrium:** It may be stated as, at a given temperature the ratio of product of equilibrium concentration of the products to that of the reactants with each concentration terms raised to power equal to the respective stoichiometric coefficient in the balanced chemical reaction has a constant value. This constant value is known as Equilibrium constant. For a general reaction of the type $aA + bB \Leftrightarrow cC + dD$

   $Kc = [C]^c[D]^d/[A]^a[B]^b$ This expression is known as Law Of Chemical Equilibrium

7. **Relationship between Kp and Kc**: $Kp = Kc(RT)^{\Delta n}$

8. **Units of Equilibrium Constant**: The value of equilibrium constant Kc can be calculated by substituting the concentration terms in mol/L and for Kp partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For the reactions   (i)$H_2(g) + I_2(g) \rightarrow 2HI$, Kc and Kp have no unit.(ii)$N_2O_4(g) \rightarrow 2NO_2 (g)$, Kc has unit mol/L and Kp has unit bar

9. **Characteristics Of Equilibrium Constant**

   - Equilibrium constant is applicable only when concentrations of the reactants and products have attained their equilibrium state.
   - The value of equilibrium constant is independent of initial concentrations of the reactants and products.
   - Equilibrium constant is temperature dependent having one unique value for aparticular reaction represented by a balanced equation at a given temperature.
   - The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.
   - The equilibrium constant *K* for a reaction is related to the equilibrium constant of the corresponding reaction, whose equation is obtained by multiplying or dividing the equation for the original reaction by a small integer.

10. **Applications of equilibrium constant** :

    - Predict the extent of a reaction on the basis of its magnitude.

- Predict the direction of the reaction, and
- Calculate equilibrium concentrations.

11. **Le Chatelier's Principle:** It states that if a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction that tends to undo the effect of the change imposed.

- **Effect of change of concentration:** When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration change. For eg:- $H_2(g) + I_2(g) \Leftrightarrow 2HI(g)$

  If H_2 is added to the reaction mixture at equilibrium, the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction whereas H_2 is consumed i.e more of H_2 and I_2 react to form HI and finally the equilibrium shifts in forward direction.

- **Effect of change of pressure**: When the pressure is increased the equilibrium shifts in the direction in which the number of moles of the gas decreases.

  Consider the reaction, $CO(g) + 3H_2(g) \Leftrightarrow CH_4(g) + H_2O(g)$ Here, 4 mol of gaseous reactants $(CO + 3H_2)$ become 2 mol of gaseous products $(CH_4(g) + H_2O)$. so by Le Chatelier's principle. The increase in pressure will shift the equilibrium in the forward direction, a direction in which the number of moles of the gas or pressure decreases.

- **Effect of change of Temperature:** When a change in temperature occurs, the value of equilibrium constant changes. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction. The equilibrium constant for an exothermic reaction (-ve ΔH) decreases as the temperature increases. The equilibrium constant for an endothermic reaction (+ve ΔH) increases as the temperature increases. When the Temperature is increased the equilibrium shifts in the direction in of endothermic reaction.

  Consider a reaction $N_2(g) + 3H_2(g) \Leftrightarrow 2NH_3(g)$ $\Delta H = -92.38Kj/mol$

  According to Le Chatelier's principle, raising the temperature shifts the equilibrium to left (backward direction i.e direction of endothermic reaction) and decreases the equilibrium concentration of ammonia.

- **Effect of Inert Gas Addition**: If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction.

- **Effect of a Catalyst:** A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

Summary of Le Chatelier's Principle

Type of Effect or Change	Direction of Equilibrium
Addition of more reactants	Forward direction
Addition of more products	Backward direction
Increase in temperature	Towards endothermic reaction
Decrease in temperature	Towards exothermic reaction
Addition of Catalyst	No effect
Increase in Pressure	where the no. of gaseous moles are less
Decrease in Pressure	where the no. of gaseous moles are more

| Addition of Inert gas at const.Volume | No effect |
| Addition of Inert gas at const.pressure | where the no. of gaseous moles are more |

oxidation	**reduction**
1. Addition of oxygen	1. Removal of oxygen
2. Removal of hydrogen	2. Addition of hydrogen
3. Addition of an electronegative element	3. Removal of an electronegative element
4. Removal of an electropositive element	4. Addition of an electropositive element
5. Loss of electron	5. Gain of electron

Oxidation number denotes theoxidation state of an element in a compound ascertained according to a setof rules formulated on the basis thatelectron in a covalent bond belongsentirely to more electronegative element.

Calculation of oxidation number-

1. O. S. of all the elements in their elemental form (in standard state) is taken as zero O. S. of elements in Cl_2, F_2, O_2, P_4, O_3, Fe(s), H_2, N_2, C(graphite) is zero.
2. Common O. S. of elements of group one (1st) is one. Common O. S. of elements of group two (2nd) is two.
3. For ions composed of only one atom, theoxidation number is equal to the chargeon the ion.
4. The oxidation number of oxygen in most compounds is –2.While in peroxides (e.g., H_2O_2, Na_2O_2), eachoxygen atom is assigned an oxidationnumber of –1, in superoxides (e.g., KO_2,RbO_2) each oxygen atom is assigned anoxidation number of –(½).
5. In oxygendifluoride (OF_2) and dioxygendifluoride (O_2F_2), the oxygen is assignedan oxidation number of +2 and +1,respectively.
6. The oxidation number of hydrogen is +1 but in metal hydride its oxidation no. is–1.
7. In all its compounds, fluorine has anoxidation number of –1.
8. The algebraic sum of the oxidation numberof all the atoms in a compound must bezero.
9. In polyatomic ion, the algebraic sumof all the oxidation numbers of atoms ofthe ion must equal the charge on the ion.
   Stocknotation:the oxidationnumber is expressed by putting a Romannumeral representing the oxidation numberin parenthesis after the symbol of the metal inthe molecular formula. Thus aurous chlorideand auric chloride are written as Au(I)Cl andAu(III)Cl_3. Similarly, stannous chloride andstannic chloride are written as Sn(II)Cl_2andSn(IV)Cl_4.

Oxidation: An increase in the oxidationnumber
Reduction: A decrease in the oxidationnumber

Oxidising agent: A reagent which canincrease the oxidation number of an elementin a given substance. These reagents are calledas **oxidants** also.
Reducing agent: A reagent which lowers the oxidation number of an element in a givensubstance. These reagents are also called as**reductants**.
Redox reactions: Reactions which involvechange in oxidation number of the interactingspecies

Balancing of redox reactions:

Oxidation Number Method:
Write the net ionic equation for the reaction of potassium dichromate(VI), $K_2Cr_2O_7$ with sodium sulphite,Na2SO3, in an acid solution to give chromium(III) ion and the sulphate ion.
Step 1: The skeletal ionic equation is:
$$Cr_2O_7^{2-}(aq) + SO_3^{2-}(aq) \rightarrow Cr^{3+}(aq)+ SO_4^{2-}(aq)$$
Step 2: Assign oxidation numbers forCr and S
$$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) + \overset{+4\ -2}{SO_3^{2-}}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq)+ \overset{+6\ -2}{SO_4^{2-}}(aq)$$
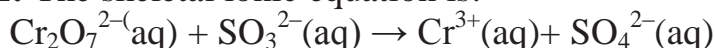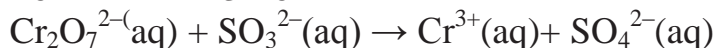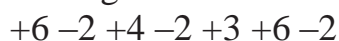
Step 3: Calculate the increase anddecrease of oxidation number, and make them equal:
$$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) + 3\overset{+4\ -2}{SO_3^{2-}}(aq) \rightarrow 2\overset{+3}{Cr^{3+}}(aq)+ 3\overset{+6}{SO_4^{2-}}(aq)$$
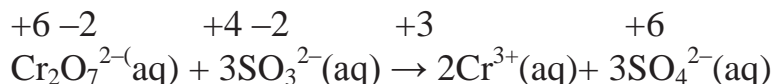
Step 4: Balance the charge by adding H^+as the reaction occurs in theacidic medium,
$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq)\ 8H^+ \rightarrow 2Cr^{3+}(aq)+ 3SO_4^{2-}(aq)$$

Step 5: Balance the oxygen atom by adding water molecule.
$$Cr_2O_7^{2-}(aq) + 3SO_3^{2-}(aq)\ 8H^+ \rightarrow 2Cr^{3+}(aq)+ 3SO_4^{2-}(aq)+ 4H_2O(l)$$
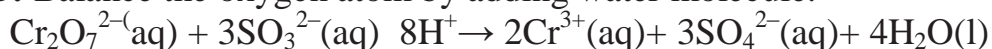
Half Reaction Method
balance the equation showing the oxidation of Fe^{2+} ions to Fe^{3+} ions by dichromate ions $(Cr_2O_7)^{2-}$ in acidic medium,wherein, $Cr_2O_7^{2-}$ ions are reduced to Cr^{3+} ions.
Step 1: Produce unbalanced equation for thereaction in ionic form :
$$Fe^{2+}(aq) + Cr_2O_7^{2-}\ (aq) \rightarrow Fe^{3+}\ (aq) + Cr^{3+}(aq)$$
Step 2: Separate the equation into halfreactions:
Oxidation half : $\overset{+2}{Fe^{2+}}\ (aq) \rightarrow \overset{+3}{Fe^{3+}}(aq)$
Reduction half :$\overset{+6\ -2}{Cr_2O_7^{2-}}(aq) \rightarrow \overset{+3}{Cr^{3+}}(aq)$
Step 3: Balance the atoms other than O andH in each half reaction individually.
$$Cr_2O_7^{2-}\ (aq) \rightarrow Cr^{3+}(aq)$$
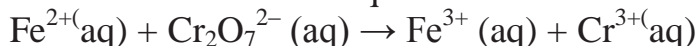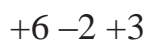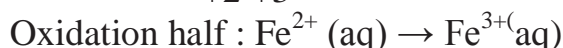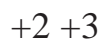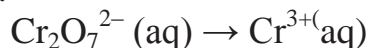
Step 4: For reactions occurring in acidicmedium, add H_2O to balance O atoms and H^+ to balance H atoms. $Cr_2O_7^{2-}$ (aq) $+14$ $H^+ \rightarrow Cr^{3+}$(aq) $+ 7H_2O$ (l)

Step 5: Add electrons to one side of the halfreaction to balance the charges. If need be,make the number of electrons equal in the twohalf reactions by multiplying one or both halfreactions by appropriate coefficients.

Fe^{2+} (aq) $\rightarrow Fe^{3+}$ (aq) + e–

$Cr_2O_7^{2-}$ (aq) + $14H^+$ (aq) + 6e– $\rightarrow 2Cr^{3+}$(aq) +$7H_2O$ (l)

$6Fe^{2+}$ (aq) $\rightarrow 6$ Fe^{3+} (aq) +6 e–
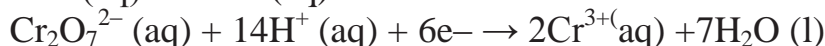
Step 6: We add the two half reactions toachieve the overall reaction and cancel theelectrons on each side. This gives the net ionicequation as :

$6Fe^{2+}$(aq) + $Cr_2O_7^{2-}$ (aq) + $14H^+$(aq) $\rightarrow$ 6 Fe^{3+}(aq) +2Cr $^{3+}$(aq) + $7H_2O$(l)
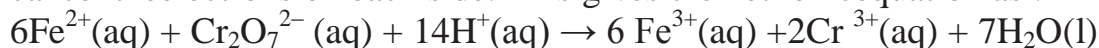
A **redox couple** is defined as havingtogether the oxidised and reduced forms of asubstance taking part in an oxidation orreduction half reaction. Represented as Zn^{2+}/Zn and Cu^{2+}/Cu.

❖ Electrochemical cells are the devices which are used to get electric current by using chemical reaction.
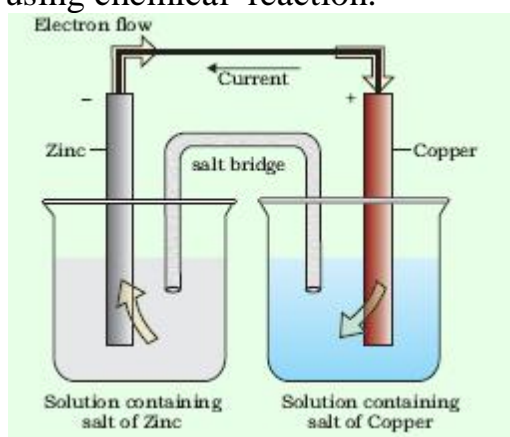
Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

The potential associated with eachelectrode is known as **electrode potential**. Ifthe concentration of each species taking partin the electrode reaction is unity (if any gasappears in the electrode reaction, it is confinedto 1 atmospheric pressure) and further thereaction is carried out at 298K, then thepotential of each electrode is said to be the**Standard Electrode Potential**.

- SHE is used to measure electrode potential and its standard electrode potential is taken as 0.00 V.

ONE MARK QUESTIONS

1. Define oxidation and reduction in terms of oxidation number.
   Ans Increase in Oxidation Number is Oxidation and decrease in Oxidation Number is called reduction.
2. What is meant by disproportionation? Give one example.
   Ans : In a disproportionation reaction an element simultaneously oxidized and reduced.
   $P_4 + 3OH^- +3H_2O \rightarrow PH_3 +3H_2PO_2^-$
3. What is O.N. of sulphur in H_2SO_4?Ans: +6
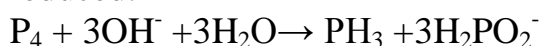
4. Identify the central atom in the following and predict their O.S.
   HNO_3
   Ans: central atom:- N; O.S. +5
5. Out of Zn and Cu which is more reactive?
   Ans: Zn.
6. What is galvanization?
   Ans: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.
7. How is standard cell potential calculated using standard electrode potential?
   Ans: $E^0_{cell} = E^0_{cathode} - E^0_{anode}$
8. What is O.S. of oxygen in H_2O_2?
   Ans: - -1.
9. The formation of sodium chloride from gaseous sodium and gaseous chloride is a redox process justify.
   Ans: Na atom get oxidize and Cl is reduced.

TWO MARKS QUESTIONS

1. Write the balanced redox reaction .
   (I) $MnO_4^-(aq) + Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + Fe^{3+}(aq)$ [acidic medium]
   (II) $Cr_2O_7^{2-} + Fe^{2+} \rightarrow Cr^{3+} + Fe^{3+}$ [Acidic medium]

   Ans:- (i) $MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O_{(l)}$
         (ii) $Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
2. Identify the strongest & weakest reducing agent from the following metals:
   .Zn, Cu, Na, Ag, Sn
   Ans: Strongest reducing agent: Na, weakest reducing agent: Ag.
3. Determine the oxidation no. of all the atoms in the following oxidants:$KMnO_4$, $K_2Cr_2O_7$ and $KClO_4$
   Ans :
       In $KMnO_4$ K = +1, Mn = +7, O = -2
       In $K_2Cr_2O_7$K = +1, Cr = +6, O = -2
       In $KClO_4$K = +1, Cl = =+7, O = -2
4. Determine the oxidation no. of all the atoms in the following species:Na_2O_2 and OF_2.
   Ans: In Na_2O_2Na = +1, O = -1
        InOF_2, F = -1, O = +2

5. Is it possible to store :
   (i) H_2SO_4 in Al container?(ii) CuSO4 solution in Zn vessel?
   Ans : (i) yes. (ii) No.
6. Calculate the standard e.m.f. of the cell formed by the combination of $Zn/Zn^{2+} \| Cu^{2+}/Cu$.
   Solution- : $E^0_{cell} = E^0_{cathode} - E^0_{anode}$
                   $=0.34 - (-0.76) = 1.10V$.
7. Identify the oxidizing and reducing agents in the following equations:

(i) MnO_4^-(aq) $+5Fe^{2+}$(aq) $+ 8H^+$(aq) $\rightarrow Mn^{2+}$(aq)$+ 5Fe^{3+}$(aq) $+ 4H_2O_{(l)}$

(ii) $Cr_2O_7^{2-} +6Fe^{2+} + 14H^+ \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$
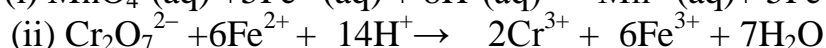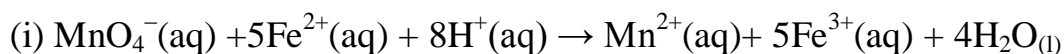
Ans : (i) O.A. $= MnO_4^-$; R.A.$= Fe^{2+}$

(ii)O.A.$=Cr_2O_7^{2-}$; R.A.$= Fe^{2+}$

8. Predict all the possible oxidation states of Cl in its compounds.

Ans:- 0, -1, +1, +3, +5, +7

9. Formulate possible compounds of 'Cl' in its O.S.is: 0, -1, +1, +3, +5, +7

Ans: Cl_2, HCl, HOCl, HOClO, $HOClO_2$, $HOClO_3$ respectively.

10. List three measures used to prevent rusting of iron.

Ans: (i) galvanization(coating iron by a more reactive metal)

(ii) greasing/oiling

(iii) painting.

THREE MARK QUESTIONS

1. Write short notes on :

(a) Electrochemical series(b) redox reactions (c) oxidizing agents

Ans :(a) Electrochemical series :- arrangement of metals(non-metals also) in increasing order of their reducing power or vice versa.

(b) Reactions in which both Oxidation and reduction take place simultaneously are REDOX REACTIONS.

(c)oxidizing agents : chemical specie which can oxidize the other one or can reduce itself.

2. Calculate O. S. of sulphur in the following oxoacids of 'S' :

H_2SO_4 ,$H_2SO_3H_2S_2O_8$and $H_2S_2O_7$

Ans : +6, +4, +6 and +6 respectively.

(calculate by considering x of 'S' and taking +1 of H, -2 0f "O" and -1 of "O" in peroxide bond.)

3. Explain role of salt bridge in Daniell cell.

Ans : (a) it completes the electric circuit in the cell.

(b) it maintains the electric neutrality in the cell.

4. Account for the followings :

(i)   sulphur exhibits variable oxidation states.

Ans. Due to the presence of vacant 'd' orbitals in 'S'

(ii) Fluorine exhibits only -1 O.S.

Ans . It is most electronegative element

(iii) oxygen can't extend its valency from 2.

Ans. Small size/unavailabilityof vacant 'd' orbitals in O

5. Balance the equation $MnO_4^- + I^- \rightarrow Mn^{2+} +I_2 + H_2O$by ion electron method in acidic medium.

Ans :Step-I Balancing of reduction half reaction by adding protons and electrons on LHS and more water molecules on RHS:

$8H^+ + MnO_4^- +5e^- \rightarrow Mn^{2+} + 4H_2O$
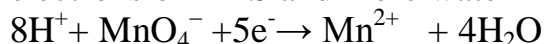
<u>Step-II</u> Balancing of oxidation half reaction by adding electrons on RHS:

$2I^- \rightarrow I_2 + 2e^-$
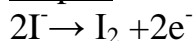
Step-III To multiply the OHR by 5; RHR by2 andto add OH & RH reactions to get overall redox reaction(cancellation of electrons of RH & OH reactions):

$$[8H^+(aq) + MnO_4^-(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)] \times 2$$

$$[2I^- \rightarrow I_2 + 2e^-] \times 5$$

$$\overline{MnO_4^-(aq) + 5Fe^{2+}(aq) + 8H^+(aq) \rightarrow Mn^{2+}(aq) + 5Fe^{3+}(aq) + 4H_2O_{(l)}}$$
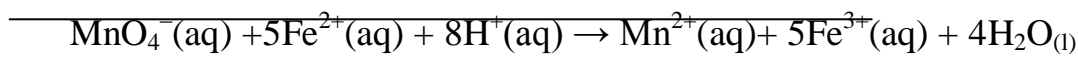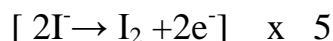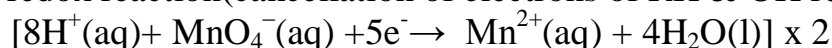
6. complete and balance the following equations:
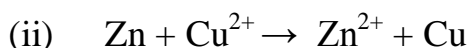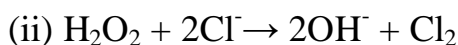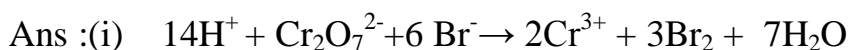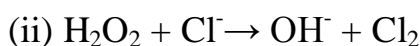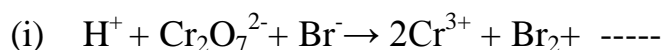
(i) $H^+ + Cr_2O_7^{2-} + Br^- \rightarrow 2Cr^{3+} + Br_2 +$ -----

(ii) $H_2O_2 + Cl^- \rightarrow OH^- + Cl_2$

(iii) $Zn + Cu^{2+} \rightarrow$?

Ans :(i) $14H^+ + Cr_2O_7^{2-} + 6\ Br^- \rightarrow 2Cr^{3+} + 3Br_2 + 7H_2O$

(ii) $H_2O_2 + 2Cl^- \rightarrow 2OH^- + Cl_2$

  (ii) $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

7. Identify the oxidizing and reducing agents in the following equations:
 (i) $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$
 (ii)$H_2 + Cl_2 \rightarrow 2HCl$
 (iii) $MnO_2 + 4HCl \rightarrow MnCl_2 + 2H_2O + Cl_2$
 Ans :(i) O.A. $=H_2SO_4$;   R.A.$=$ Fe
   (ii) O.A. $= Cl_2$; R.A.$=H_2$
   (iii)O.A. $= MnO_{2;}$ R.A. $=HCl$

8. . Arrange the following in increasing order of their reducing power:

    Cu, Ag, Au, Zn, Fe, Al, Na, Mg, Pt(SHE), Hg, Ca, K

Ans : Au, Hg, Ag, Cu, Pt(SHE), Fe, Zn, Al, Mg, Na, Ca, K
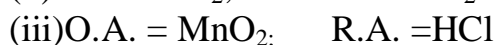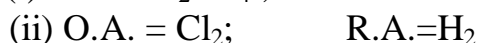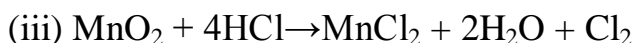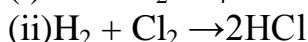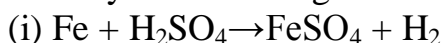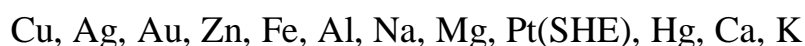
9. Indicate O.S. of each atom present in given structure of peroxodisulphuric acid
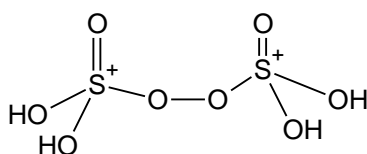
Ans:
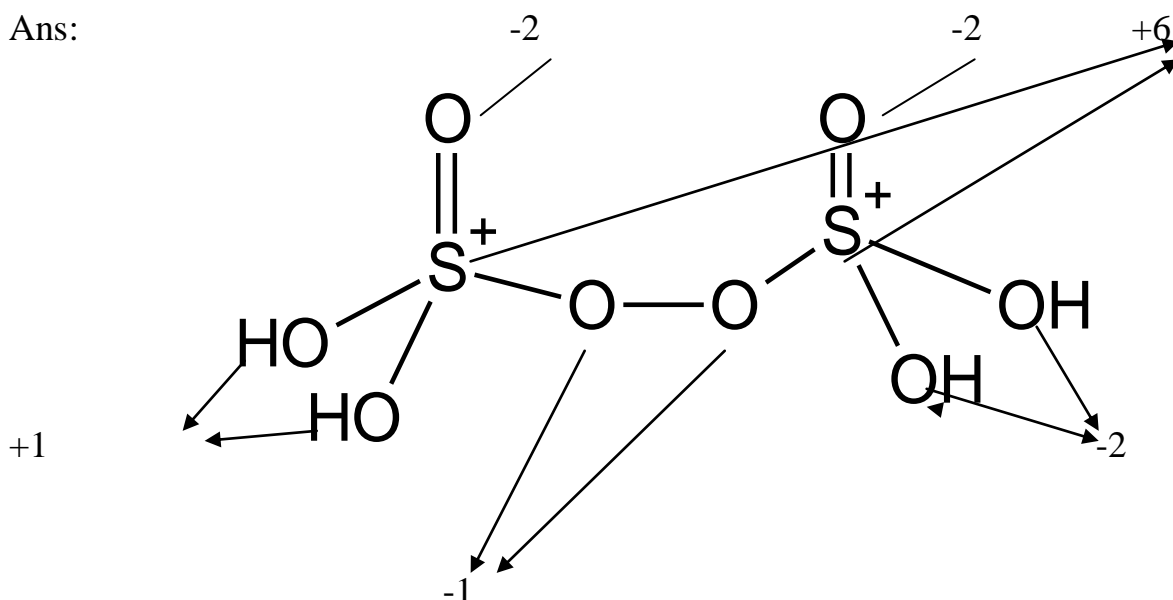
10.What is SHE? What is its use?

Ans :Standard Hydrogen Electrode (SHE) has beenselected to have zero standard potential at alltemperatures. It consists of a platinum foilcoated with platinum black (finely dividedplatinum) dipping partially into an aqueous solution in which the activity (approximateconcentration 1M) of hydrogen ion is unity andhydrogen gas is bubbled through the solutionat 1 bar pressure.The potential of the other half cell is measuredby constructing a cell in which reference electrode is standard hydrogen electrode. The potential of the other half cell is equal to thepotential of the cell.
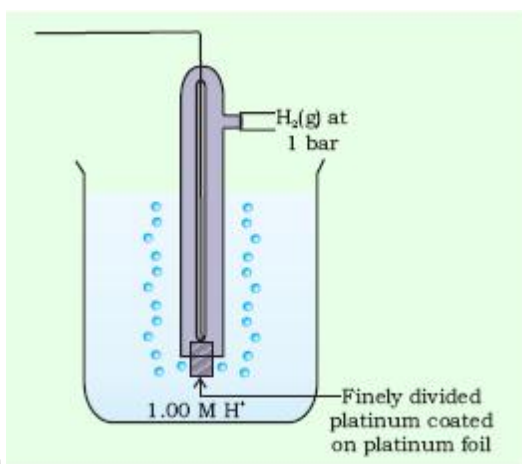
Fig: SHE

HOTS QUESTIONS

1. Is rusting of iron an electrochemical phenomenon? How ?explain.

Ans : Yes. Rusting of iron is an electrochemical phenomenon because this is possible due to formation of a small electrochemical cell over rough surface of iron and the following redox reaction takes place there in that cell-

Oxidation Fe(s) $\rightarrow$ Fe^{2+}(aq) + 2e$^-$

Reduction O$_2$+ 4H$^+$ 4e$^-$ $\rightarrow$ 2H$_2$O

e- + ½ O$_2$ + 2H$_2$O +2Fe^{2+}$\rightarrow$Fe$_2$O$_3$ + 4H$^+$
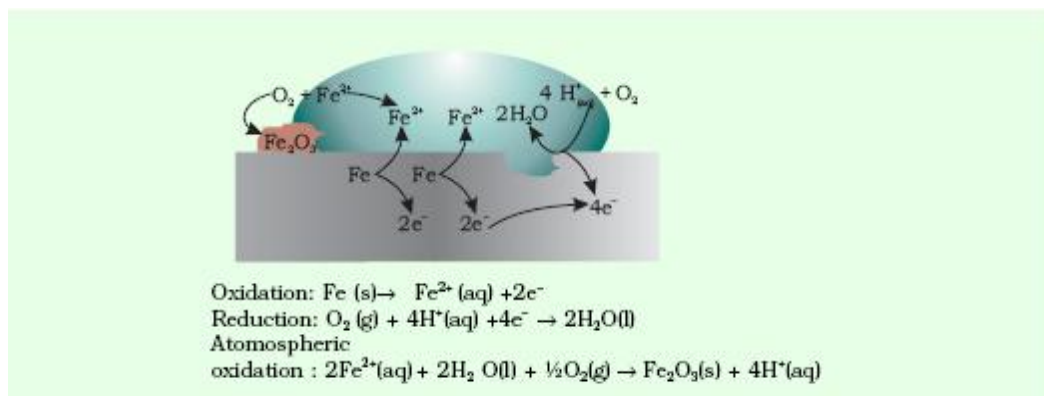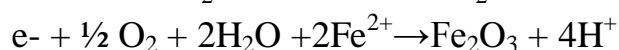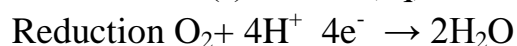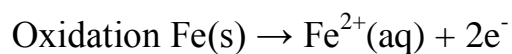
Fig. 5.14 *Corrosion of iron in atmosphere.*

2. We expand croreof Rupees and even thousands of lives every year due to corrosion. How can be preventing it. Explain.

Ans : (i) By Galvanization: Coating of a less reactive metal with a more reactive metal e.g.- coating of iron surface with Zn to prevent rusting of iron.

   (ii) By greasing /oiling (to keep away the object from the contact of air & moisture.)

   (iii)By painting (to keep away the object from the contact of air & moisture.)

CHAPTER 9
HYDROGEN

✪ **Position of Hydrogen in Periodic Table**
➢ Lightest element known having atomic number 1.
➢ Dihydrogen
➢ It resembles both alkali metals and halogens and therefore, its position is anomalous.
➢ In modern periodic table it is located separately

☆**Resemblance with alkali metals:-**

1. Electronic configuration
$_1H = 1s^1$ $_{11}Na = 1s^2, 2s^2, 2p^6, 3s^1$ $_{19}K = 1s^2, 2s^2, 2p^6, 3s^2 3p^6, 4s^1$
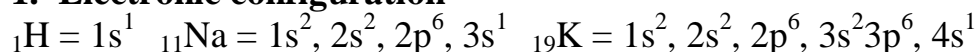
2. Electropositive character: H^+, Na^+, K^+ etc.

3. Oxidation state: +1

4. Combination with electronegative elements: form binary compounds with electronegative elements like alkali metals.

Halides: HClNaCl, KCletc

Sulphides: H_2S Na_2S, K_2S etc

☆**Resemblance with halogens:-**

1. Electronic configuration:
Both contain one electron less than the nearest noble gas configuration
$_1H = 1s^1$ (near to $_2He$)
$_9F = 1s^2, 2s^2, 2p^5$ (near to $_8Ne$)
     $_{17}K = 1s^2, 2s^2, 2p^6, 3s^2 3p^5$ (near to $_{18}Ar$)
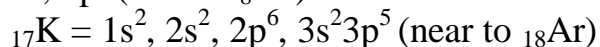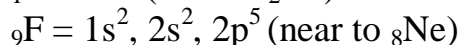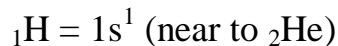
2. Non-metallic character: like halogens, hydrogen is non-metallic in nature.

3. Atomicity: Diatomic molecules.

4. Formation of similar types of compounds:
 i.   Halides: $CCl_4, SiCl_4, GeCl_4$
 ii.   Hydrides: CH_4, SiH_4, GeH_4

5. Oxidation state: −1
      $Na^{+1}H^{-1}$ $Na^{+1}Cl^{-1}$

☆**Difference from alkali metals:-**

1) **Ionization enthalpy: -** the ionization enthalpy of hydrogen is very high in comparison to alkali metals.
2) **Non- metallic character:** alkali metals are typical metals while hydrogen is non-metal
3) **Atomicity**: hydrogen is diatomic while alkali metals are monoatomic.
4) **Nature of compounds:** the compounds of hydrogen are predominantly covalent while those of alkali metals are ionic. For example: HCl is covalent while NaCl is ionic.
   The oxides of alkali metals are basic while hydrogen oxide is neutral.

✫Difference from halogens:-

1) **Less tendency for hydride formation:** Hydrogen has less tendency to take up electron to form hydride ion (H^-) as compared to the halogens which from halide ions (X^-) very easily.

2) **Absence of unshared pairs of electrons :**

3) **Nature of oxides:** The oxides of halogens are acidic while hydrogen oxide is neutral.

✪ Occurrence of Hydrogen:

➢ Hydrogen, the most abundant element in the universe and the third most abundant on the surface of the globe, is being visualised as the major future source of energy

✪Isotopes of hydrogen:-

S.N.	Property	Protium	Deuterium	Tritium
1	Relative abudance	99.985 %	0.015 %	10^{-15}%
2	Relative atomic mass	1.007825	2.014102	3.016
3	Radioactive stability	Non-radioactive	Non-radioactive	Radioactive $t_{1/2} = 12.334$ yrs

✪ Preparation:

✫Methods for commercial production of dihydrogen

1. Electrolysis of water

$$2H_2O(l) \xrightarrow[\text{traces of acid/base}]{\text{Elctrolysis}} O_2(g)$$
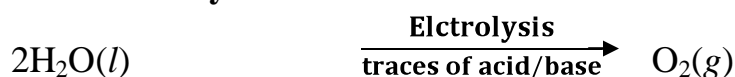
➢ The hydrogen prepared by this method is of very high purity. However, this method is not commonly used because it is very expensive. This method is can be used only at those places where the electricity is cheap.

2. By the reaction of steam on coke :-

$$C + H_2O(g) \qquad CO \xrightarrow{1270\,k}$$
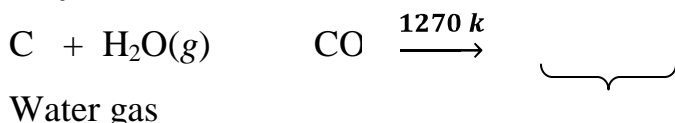
Water gas

➢ Since the mixture of CO and H_2 is used for the synthesis of methanol and a number of hydrocarbons, it is also called synthesis gas or syn gas.

➢ The process of producing syn gas from coal or coke is called coal gasification.

$$CO + H_2 + H_2O \xrightarrow[\text{770 k}]{\text{Fe2O3/Cr2O3}} CO_2 + 2H_2$$
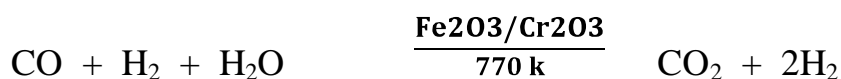
Water gas   steam

➢ This reaction is called water gas shift reaction.

✪Properties of Hydrogen:-

✪Physical Properties:-

1) It is slightly soluble in water (about 2 %)
2) It is highly combustible and therefore should be handled carefully.
3) It lightest substance. The weight of one litre hydrogen at NTP is only 0.0899 g.

✪Chemical properties:-Not very reactive due to high bond dissociation energy
(435.88 kJ mol^{-1} at 298.2 K)

(i)Combustion: - It burns with pale blue flame

$$2H_2\ (g) + O_2\ (g) \longrightarrow 2H_2O(l)$$
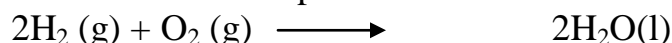
(ii) Reaction with metals:-Reactive metals like Na, K, Ca, Li and form hydrides.

$$Ca\ +\ H_2 \xrightarrow{525\ k} CaH_2$$

➢ Metals like Pt, Pd, Ni (elements of d block) form interstitial hydrides by absorbing large volume of hydrogen. Such hydrogen is called 'occluded hydrogen and this property of adsorption of a gas by a metal is called occlusion.

(iii) Reaction with metal oxides:-Hydrogen reduces oxides of less active metals to corresponding metal.

$$Fe_3O_4\ +\ 4H_2 \xrightarrow{Heat} 3Fe\ +\ 4H_2$$

$$CuO\ +\ H_2 \xrightarrow{Heat} Cu\ +\ H_2O$$
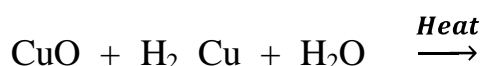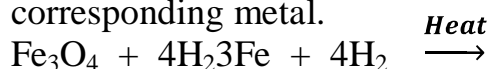
(iv) Reaction with non-metals:-

$$3H_2\ (g) + N_2\ (g) \xrightarrow[673k,\,200\ atm]{Fe,\ Mo} H_3(g) \quad \{\text{ Haber process}\}$$

$$\triangle H = -\ 92.6\ kj/mole$$

$$2H_2\ (g) +\ O_2\ (g) \xrightarrow{970\ k} 2H_2O \quad H = -\ 285.9\ kj/l \quad \triangle$$
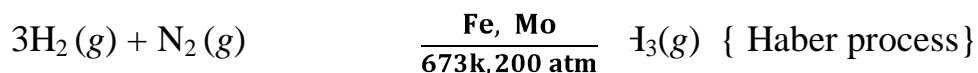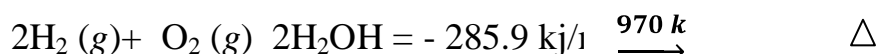
(v) Reaction with carbon monoxide:-

$$CO\ +\ H_2 \xrightarrow[700\ k,\,200\ atm]{ZnO,\ Cr2O3} H_3OH$$
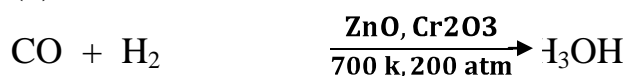
(vi) Reaction with unsaturated Hydrocarbons:-

(a) $H_2C = CH_2\ +\ H_2 \xrightarrow[473\ k,]{Ni,\ Pd\ or\ Pt} H_3C - CH_3$
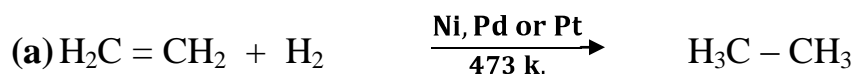
(b)Hydroformylation of olefins to aldehydes: Hydroformilation or Oxo process

$$RCH = CH_2\ +\ H_2\ +\ CO \xrightarrow[\text{high temp and pressure}]{[Co(CO)4]2} RCH_2CH_2CHO$$
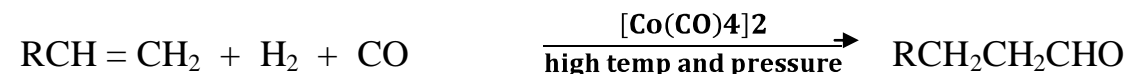
(c) Hydrogenation of oils:-Vegetable oils are polyun-saturated in nature. The C =C bonds in oils can easily undergo oxidation and the oil becomes rancid i.e.,

111

unpleasant in taste. Hydrogenation reduces the number of double bonds but completely.

Vegetable Oil + H$_2$ $\xrightarrow[\textbf{473 k,}]{\textbf{Ni}}$ *Solid*)

✪**Uses of Hydrogen:-**it itused ..
1. as a reducing agent.
2. In the manufacture of vanaspati fat, ammonia, metal hydrides, methanol, fertilizers such as urea etc.
3. In the manufacture of synthetic petrol.
4. In the atomic hydrogen torch and oxy hydrogen torches for cutting and welding. Dihydrogen is dissociated with the help of an electric arc and the hydrogen atoms produced are allowed to recombine on the surface to be welded. High temperature of about 4000 k is generated.
5. In the fuel cell for generating electrical energy.

✪**Ortho and parahydrogens:-**A molecules of dihydrogen …….**abc**
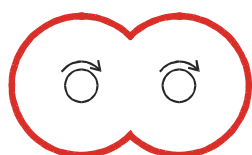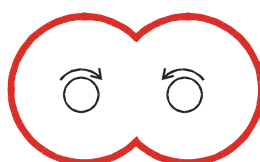
Ortho hydrogen   **Para hydrogen**

➢ They show different physical properties. For example :
(i)   The thermal conductivity of para hydrogen is about 50 % greater than that of ortho hydrogen.
(ii)   The melting point of para hydrogen is 0.15 k below that of hydrogen containing 75% ortho hydrogen.
➢ They show similar chemical properties.

✪**Atomic hydrogen:-**
➢ Because of high H—H bond enthalpy, atomic hydrogen is produced only at high temp in an electric arc or under ultraviolet radiation.

$$H_2\ (g) \xrightarrow{\textbf{3270 }k} \qquad 2H\ (g)\ \triangle \qquad H = +\ 435.9\ kj$$
(Atomic hydrogen)
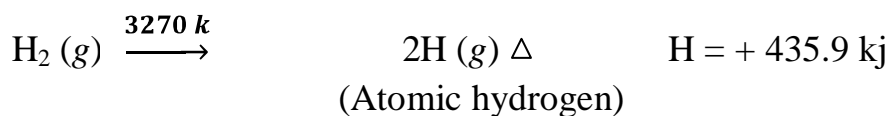
➢ Highly reactive.
➢ Half life period is 0.3 sec and therefore, it immediately gets converted into the molecular form liberating a large amount of energy which is used for cutting and welding purposes.

✪**Nascent hydrogen:-**The hydrogen produced in contact with the substance to be reduced is known as 'nascent hydrogen'. It is very reactive form of hydrogenBetter reducing agent than ordinary dihydrogen.

✪**Hydrides:-**Under certain conditions H_2 combines with almost all the elements ,except noble gases to form compounds called hydrides.

➢ There are three types of hydrides ,they are
    (i) Ionic or saline hydrides
    (ii) Covalent or molecular hydrides (iii) Metallic or non-stoichiometric hydrides**(i)**
Ionic or saline hydrides:-

➢ These are the compounds of H_2 formed with most of the s-block elements which are highly electro positive.

(ii) Covalent or molecular hydrides:-These are the compounds of hydrogen formed with most of the p-block elements

[a]Electron deficient:- The hydrides which do not have sufficient number of electrons to form normal covalent bonds is called electron deficient hydride. For example, hydride of group 13 (BH_3, AlH_3, etc.).They are known as <u>Lewis acids</u> i.e., electron acceptors. To make up their deficiency they generally exist in polymeric forms such as B_2H_6, Al_2H_6, etc.

[b] Electron precise:-The hydrides which have sufficient number of electrons required for forming covalent bonds is called electron precise hydride. For example, hydrides of group 14 (CH_4, SiH_4, GeH_4, SnH_4, PbH_4 etc.) they have tetrahedral geometry.

[c] Electron rich hydrides:-The hydrides which have excess electrons as required to form normal covalent bonds is called electron rich hydride. For example, hydrides of group 15 to 17 (NH_3, PH_3, H_2O, H_2S, H_2Se, H_2Te, HF etc.)

(iii) Metallic or non-stoichiometric hydrides:-

➢ *These are formed by many d-block and f-block elements*
➢ *These hydrides conducts heat and electricity though not efficient.*

✪**Water: -**Water! It is the major part of all living organisms.water is also known as the river of life.

➢ Human body has about 65%and some plants haveasmuch as 95%water.
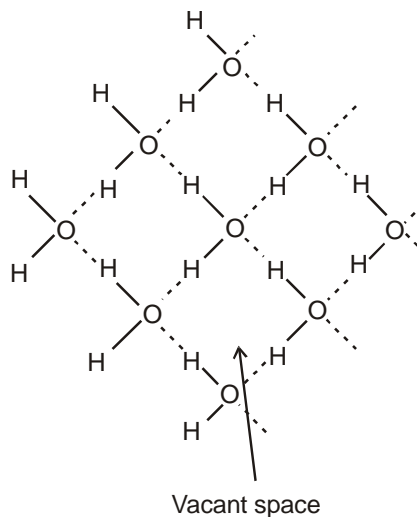
❖ **STRUCTURE OF WATER:-**

➢ In a gas phase water is bent molecule with a bond angle of 104.5 and O-H bond length of 95.7pm It is highly polar molecule.
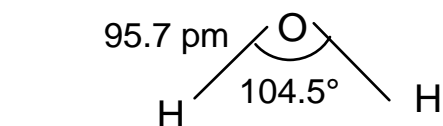
Solid state
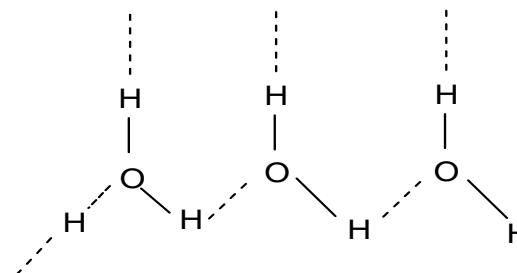
❖ **Structure of ice**:-Ice has a highly ordered 3D hydrogen bonded structure. Each oxygen atom is surrounded tetrahedrally by four other four other oxygen atoms at a distance of 276 pm
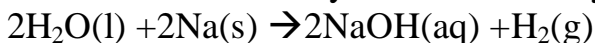
Vacant space

☆**Chemical Properties of water:-**

**[i] AMPHOTERIC NATURE:-**It has the ability .it acts as an acid with NH_3 and as a base with H_2S

$H_2O(l) + NH_3(aq) \rightarrow OH^-(aq) + NH_4^+ (aq)$

$H_2O(l) + H_2S(aq) \rightarrow H_3O^+(aq) + HS^- (aq)$

[ii] REDOX REACTIONS INVOLVING WATER:-

➤ Water can be easily reduced to H_2 by highly electropositive metals

$2H_2O(l) + 2Na(s) \rightarrow 2NaOH(aq) + H_2(g)$

[iii] HYDROLYSIS REACTION:-Due to high dielectric constant, it has a very strong hydrating tendency .it dissolves many ionic compounds

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$

$SiCl_4(l) + 2H_2O(l) \rightarrow SiO_2(s) + 4HCl(aq)$
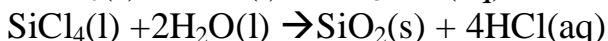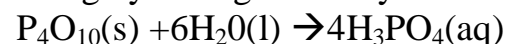
[iv] HYDRATES FORMATION:-From the aqueous solutions many salts can be crystallized as hydrated salts. It of different types.

(1) Coordinated water e.g., $[Cr(H_2O)_6]^{3+}$ $3Cl^-$

(2) Interstitial water e.g., $BaCl_2.2H_2O$

(3) hydrogen-bonded water e.g. $[Cu(H_2O)_4]^{2+}_4SO^{2-}.H_2O$ in $CuSO_4.5H_2O$
.

✪**Hard & Soft Water:-**

➤ The water which contains dissolved salts of bicarbonates, sulphates and chlorides of calcium and magnesium is called hard water. Hard water does not produce lather with soap solution.

➤ Soft water is free from bicarbonates, sulphates and chlorides of calcium and magnesium. It produces lather with soap solution easily. e.g., distilled water, rain water..

☆**Types of hardness:-**The hardness of water is of two types

(i)Temporary hardness

➤ Due to presence of soluble bicarbonates of calcium and magnesium.

➤ Can be removed by simple boiling.

(ii)Permanent hardness

➤ Due to presence of chlorides and sulphates of calcium and magnesium.

➤ Requires treatment of water to remove this type hardness.
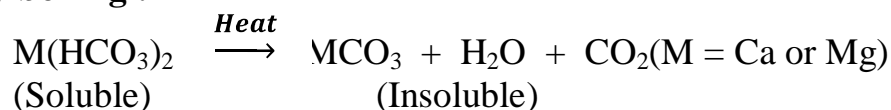
➤ *Do you know?*

Temporary hardness is also called carbonate hardness &
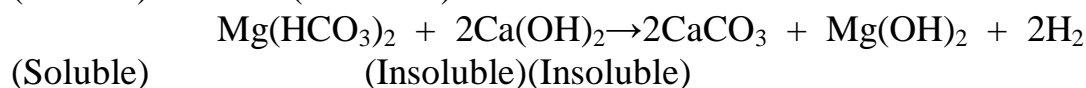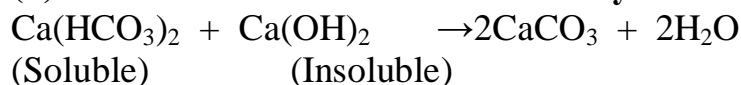
Permanent hardness is also called non-carbonate hardness

☆**Softening of water:-**The process of removal of Ca^{2+} and Mg^{2+} ions from water is called softening of water.

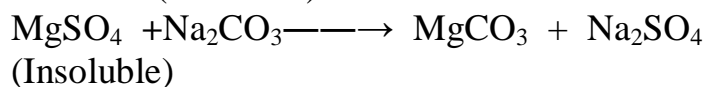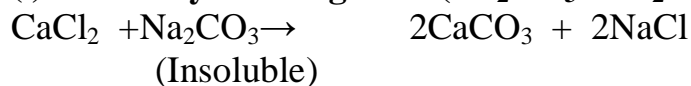❖ **Removal of temporary hardness:-**

(i)   By boiling :

$$M(HCO_3)_2 \xrightarrow{\text{Heat}} MCO_3 + H_2O + CO_2 (M = Ca\ or\ Mg)$$
(Soluble)   (Insoluble)

(ii)   Clark's method or calcium hydroxide method

$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$
(Soluble)   (Insoluble)

$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + 2H_2$
(Soluble)   (Insoluble)(Insoluble)

❖ **Removal of permanent hardness:-**

(i)   By washing soda (Na$_2$CO$_3$.10H$_2$O) treatment:

$CaCl_2 + Na_2CO_3 \rightarrow 2CaCO_3 + 2NaCl$
          (Insoluble)

$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3 + Na_2SO_4$
(Insoluble)

(ii)   By using inorganic cation exchanger (permutit method or Zeolite method):

$Na_2Al_2Si_2O_8 + CaCl_2 \rightarrow Ca(Al_2Si_2O_8)_2 + 2NaCl$
Zeolite   Settles at bottom
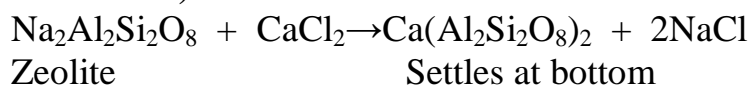
The zeolite can be regenerated by treatment with sodium chloride solution.

$Ca(Al_2Si_2O_8)_2 + 2NaCl \rightarrow Na_2Al_2Si_2O_8 + CaCl_2$

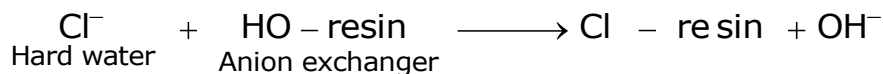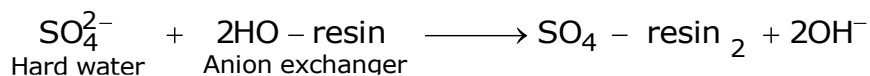**(iii)   By organic ion exchanger or synthetic resins (ion exchange resins):-**

➤ Synthetic resins are the insoluble polymeric solids having giant hydrocarbon network containing reactive acidic or basic groups. These are superior to Zeolitebecause they can remove all types of cations as well as anions present in water. This resulting water is known as demineralised or deionised water.

➤ These are two types:

(a)   Cation exchanger resins: they have acidic groups such as COOH or SO3H. they may be represented as **resin—H$^+$**

$$Mg^{2+} + 2H - resin \longrightarrow Mg\ (resin)_2 + 2H^+$$
In hard water   Cation exchanger

$$Ca^{2+} + 2H - resin \longrightarrow Ca\ (resin)_2 + 2H^+$$
Hard water   Cation exchanger

7/13
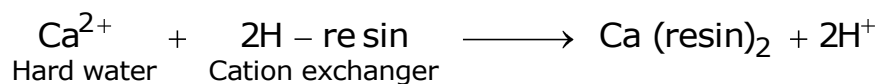
(b) **Anion exchanger resins:** they have basic groups such as –OH⁻ or –NH₂. they may be represented as **resin—OH⁻** or **resin—NH₃⁺OH⁻**

$$\underset{\text{Hard water}}{SO_4^{2-}} + \underset{\text{Anion exchanger}}{2HO-resin} \longrightarrow SO_4 - resin_2 + 2OH^-$$

$$\underset{\text{Hard water}}{Cl^-} + \underset{\text{Anion exchanger}}{HO-resin} \longrightarrow Cl - resin + OH^-$$

Regeneration of resiners:

$$\underset{\text{Exchausted resin}}{Cl-resin} + NaOH \longrightarrow \underset{\text{Re generated resin}}{HO-resin} + NaCl$$

❂**Hydrogen peroxide [H₂O₂]:-** discovered by French chemist J.L. Thenard

❖ **Methods of preparation**

1) **From sodium peroxide (Merck's process):-**
   $Na_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O_2$
   (20% ice cooled solution)   (30% solution)
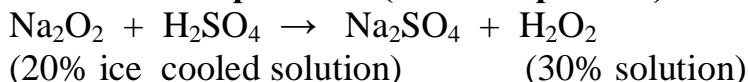
2. From Barium peroxide:-

➢ Hydrogen peroxide was first prepared by J. L. Thenard in 1818 by acidifying barium peroxide and removal of excess water by evaporation under reduced pressure.
   $BaO_2.8H_2O + H_2SO_4 \longrightarrow BaSO_4 + 8H_2O + H_2O_2$
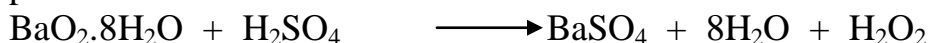
➢ Barium sulphate is filtered off leaving behind H₂O₂.

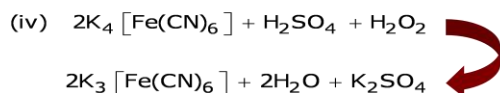**Store of Hydrogen peroxide:-**

a) Itmust be kept in wax lined coloured bottles because the rough glass surface causes its decomposition.

b) A small amount of phosphoric acid , glycerol or acetanilide is generally added which retard the decomposition of H_2O_2. These are also called negative catalysts.

❖ **Physical properties of Hydrogen peroxide:-**
   1. In the pure state H_2O_2 is an almost colourless(very pale blue) liquid.
   2. H_2O_2 is miscible with water in allproportions and forms a hydrate $H_2O_2.H_2O$ (mp 221K).
   3. A 30% solution of H_2O_2 is marketedas '100 volume' hydrogen peroxide. It means thatone millilitre of 30% H_2O_2 solution will give 100 Vof oxygen at STP. Commercially, it is marketedas 10 V, which means it contains 3% H_2O_2.

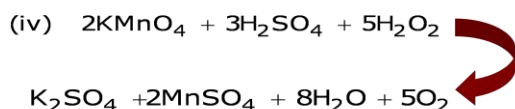**Chemical properties of Hydrogen peroxide:-**

(iv) $2K_4[Fe(CN)_6] + H_2SO_4 + H_2O_2$

$2K_3[Fe(CN)_6] + 2H_2O + K_2SO_4$

(v) $C_6H_6 + H_2O_2 \longrightarrow \underset{\text{Phenol}}{C_6H_5OH} + H_2$

(vii) $NaNO_2 + H_2O_2 \longrightarrow NaNO_3 + H_2O$

(viii) $K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \longrightarrow K_2SO_4 + CrO_5 + 5H_2O$

Reducing properties

(i) $H_2O_2 + O_3 \longrightarrow H_2O + O_2$

(ii) $Ag_2O_2 + H_2O_2 \longrightarrow 2Ag + H_2O + O_2$

(iii) $PbO_2 + 2HNO_3 + H_2O_2 \longrightarrow Pb(NO_3)_2 + 2H_2O + O_2$

Reducing properties

(iv) $2KMnO_4 + 3H_2SO_4 + 5H_2O_2$

$K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

(v) $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$

(vi) $6KAuCl_4 + 3H_2O_2 \longrightarrow 2Au + 2KCl + 6HCl + 3O_2$
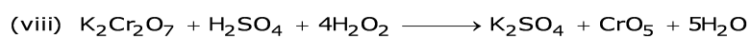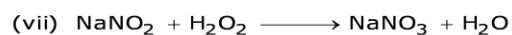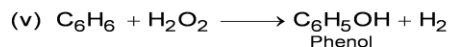
❖ Uses of hydrogen peroxide

1) For bleaching silk, wool, hair and leather
2) As rocket fuel

❖ Structure of hydrogen peroxide
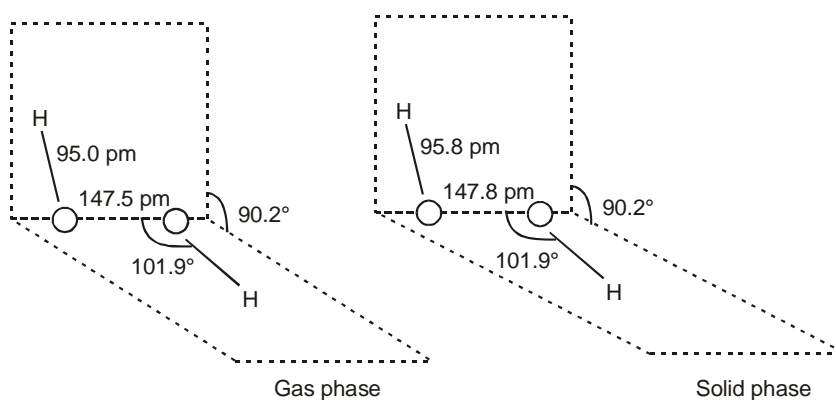
Structure of hydrogen peroxide

Hydrogen economy (Hydrogen as fuel)

☞ The electricity cannot be stored to run automobiles. It is not possible to store and transport nuclear energy. Hydrogen is an alternative source of energy and hence called as 'hydrogen economy'. Hydrogen has some advantages as fuel

☞ Available in abundance in combined form as water.

☞ On combustion produces H_2O. Hence pollution free.

☞ H_2-O_2 fuel cell give more power.

☞ Excellent reducing agent. Therefore can be used as substitute of carbon in reduction for processes in industry.

❖ **Obstacles in hydrogen economy**

☞ **Transportation:**

☞ Hydrogen gas is explosive and hence it is difficult to store and transport.

☞ Formation of hydrogen from H_2O:

☞ The cheaper production of the hydrogen is basic requirement of hydrogen economy which is not possible now.

☞ The main aim and advantage of hydrogen economy is to transmit energy in four of hydrogen.

One mark question:

1. What is meant by 10 volume hydrogen peroxide?
2. Why is dihydrogen gas not preferred in balloons?
3. Name the constituents of water gas.
4. Name one compound each in which hydrogen exists in (i) positive oxidation state, and (ii) Negative oxidation state.
5. What type of elements form interstitial hydrides?
6. How many hydrogen bonded water molecule(s) are present in $CuSO_4.5H_2O$?
7. What happens when heavy water is added to calcium carbonate?
8. Concentrated sulphuric acid cannot be used for drying H_2. Why?
9. Complete the following reactions?

   (i) $C_3H_8\ (g)\ +\ 3H_2O(g) \xrightarrow[\textbf{catalyst,}]{\textbf{heat}}$

   (ii) $Zn(s)\ +\ NaOH(aq) \xrightarrow{\textbf{heat}}$
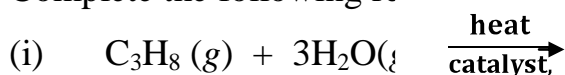
10. How heavy water is is obtained from ordinary water?

Solutions:

1. It means that 1 ml of H_2O_2 will give 10 ml of oxygen at N.T.P.
2. Dihydrogen gas is combustible in nature. Therefore, it may react with oxygen highly violently. Thus, it is not used in balloons.
3. Carbon monoxide and hydrogen.

4. (i) HCl (ii) NaH
5. Elements of d-and f-block.
6. In $CuSO_4.5H_2O$, there is one hydrogen bonded water molecule which is outside the coordination sphere. The other four molecules of water are coordinated.
7. Deutero acetylene is formed.
   $$CaC_2 + 2D_2O \longrightarrow Ca(OD)_2 + C_2D_2$$
8. Conc. H_2SO_4 on absorbing water from moist H_2 produces so much heat that H_2 catches fire.
9.

   (i) $C_3H_8\ (g) + 3H_2O_{(l)} \xrightarrow[\text{catalyst,}]{\text{heat}} 3CO + 7H_2(g)$

   (ii) $Zn(s) + NaOH(aq) \xrightarrow{\text{heat}} Na_2ZnO_2(aq) + H_2(g)$

10. Heavy water is obtained from ordinary water by repeated electrolysis in the presence of 3% NaOH.

Two mark question

1. Can we use concentrated sulphuric acid and pure zinc in the preparation of dihydrogen?
2. Write the chemical reactions to show the amphoteric nature of water.
3. Why is hydrogen peroxide stored in wax-lined plastic coloured bottles?
4. H_2O_2 acts as an oxidizing agent as well as reducing agent. Why?
5. What causes the temporary and permanent hardness of water?

Solutions:
1. (a) Conc. H_2SO_4 cannot be used because it acts as oxidizing agent also and gets reduced to SO_2.
   $$Zn + dil\ H_2SO_4 \longrightarrow ZnSO_4 + 2H_2O + SO_2$$
   (b) Pure Zn is not used because it is non-porous and reaction will be slow. The impurities in Zn help in constitute of electrochemical couple and speed up reaction.
2. Water is amphoteric in nature and it behaves both as an acid as well as a base. With acids stronger than itself (eg., H_2S) it behaves as a base and with bases stronger than itself (eg. NH3) it acts as an acid.
   (i) As a base: $H_2O(l) + H_2S(aq) \rightarrow H_3O^+(aq) + HS^-\ (aq)$
   (ii) As an acid: $H_2O(l) + NH_3(aq) \rightarrow OH^-(aq) + NH_4^+\ (aq)$
3. The decomposition of H_2O_2 occurs readily in the presence of rough surface (acting as catalyst). It is also decomposed by exposure of light. Therefore, wax-lined smooth surface and coloured bottles retard the decomposition of H_2O_2.

4. In H_2O_2, oxygen has -1 oxidation state which lies between maximum (0 or +2 in OF2) and minimum -2. Therefore, oxygen can be oxidized to O_2 (zero oxidation state) acting as reducing agent or can be reduced to H_2O or OH- (-2 oxidation state) acting as an oxidizing agent.
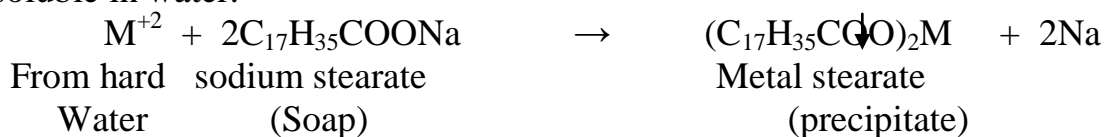
$$\overset{-1}{O_2} \rightarrow \overset{0}{O_2} + 2e-$$
(Reducing agent)

$$\overset{-1}{O_2} + 2e- \rightarrow \overset{-2}{2O}$$
(Oxidizing agent)
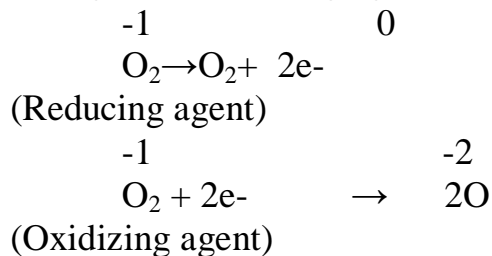
5. Temporary hardness is due to presence of soluble bicarbonates of calcium and magnesium. On the other hand, permanent hardness is due to presence of chlorides and sulphates of calcium and magnesium.

Three mark question:

1. Hard water is unsuitable for laundry, washing and dyeing. Explain.
2. What do you understand by (i) electron-deficient, (ii) electron-precise, and (iii) electron-rich compounds of hydrogen? Provide justification with suitable examples.
3. Compare the structures of H_2O and H_2O_2.
   Solutions:
1. Ans: - since we know that the soap are the sodium salts of higher fatty acids like stearic acid ($C_{17}H_{35}COOH$), oleic acid ($C_{17}H_{33}COOH$) or palmitic acid ($C_{17}H_{31}COOH$). When soap is added to hard water, the anions of soap combine with Ca^{+2} and Mg^{+2} ions to form calcium and magnesium salt which are insoluble in water.

   M^{+2} + $2C_{17}H_{35}COONa$ $\rightarrow$ $(C_{17}H_{35}COO)_2M$ + 2Na
   From hard sodium stearate   Metal stearate
   Water   (Soap)   (precipitate)

   Therefore, no lather is produce until all the calcium and magnesium ions are precipitated. This also results into wastage of lot of soap. So hard water is unsuitable for laundry, washing and dyeing.
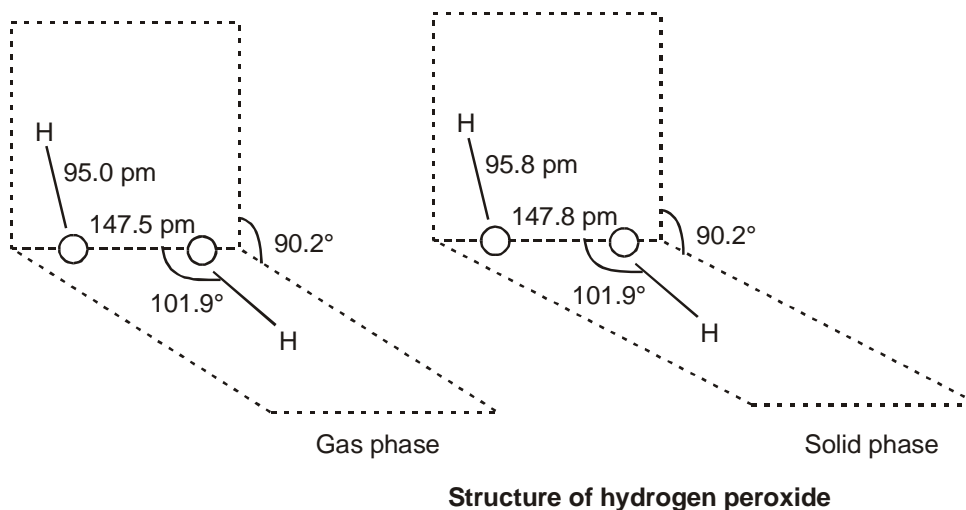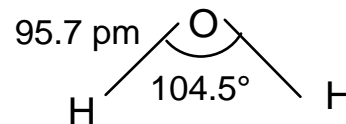2. **[a]Electron deficient**:- The hydrides which do not have sufficient number of electrons to form normal covalent bonds is called electron deficient hydride. For example, hydride of group 13 (BH_3, AlH_3, etc.).
   [b] Electron precise:-The hydrides which have sufficient number of electrons required for forming covalent bonds is called electron precise hydride. For

example, hydrides of group 14 (CH_4, SiH_4, GeH_4, SnH_4, PbH_4 etc.) they have tetrahedral geometry.

[c] Electron rich hydrides:-The hydrides which have excess electrons as required to form normal covalent bonds is called electron rich hydride. For example, hydrides of group 15 to 17 (NH_3, PH_3, H_2O, H_2S, H_2Se, H_2Te, HF etc.)

3. In water, O atom is sp^3 hybridised and there are two O—H bonds and two sp^3 hybrid orbitals occupy lone pairs of ele stronger lone pair-lone pair repulsions than bond pair-bond pair repulsions, the H-O-H bond decreases from 109.5 to 104.5^0. Therefore, water molecule is a bent or angular molecule. H_2O_2 has non-planar structure. In this structure, two O—O oxygen atoms are bonded to each other by a single covalent bond and each O atom is further bonded to a hydrogen atom by a single covalent bond. The two O—H bonds are in different planes in 111.50 in the gas phase.

95.7 pm   O   104.5°

H   H

H
95.0 pm
147.5 pm   90.2°
101.9°
H
Gas phase

H
95.8 pm
147.8 pm   90.2°
101.9°
H
Solid phase

Structure of hydrogen peroxide

Chapter 10
The s- Block Element

<u>Important points</u>

- Groups (1 & 2) belong to the s-block of the Periodic Table.
- Group 1 consists of : lithium, sodium, potassium, rubidium, caesium and francium and collectively known as the *alkali metals.*
- Group 2 include : beryllium, magnesium,calcium, strontium, barium and radium. Except Beryllium they are known as *alkaline*

❖ **Physical properties-**

a) **Large atomic radii:** The atomic radii of alkali metals are the largest in their respective periods. These increase as we travel down the group.

b) **Large ionic radii:** The ionic radii increase as we move down the group due to the addition of a new energy shell with each succeeding element.

c) **Low ionization enthalpy:** The ionization enthalpies decrease as we move down the group.The ionization enthalpies of the alkali metals are the lowest due to loosely held s- electron.

d) **Hydration enthalpy:** It decreases with the increase in ionic radii.The hydration enthalpy of Li ion is the maximum and the hydration enthalpy of Cs ion is the minimum.

e) **Oxidation state:** The alkali metals exhibit oxidation state of +1 in their compounds and are strongly electropositive in character. The electropositive character increases from Li to Cs.

f) **Metallic character:** The metallic character increases down the group.

g) **Melting point and boiling point::** The m p and b p of alkali metals are very low and decrease with increase in atomic number.

h) **Nature of bonds formed:** These metals form ionic bonds. The ionic character increases as we down the group.

i) **Flame colouration:** All the alkali metals impart a charactersistic colour to the flame.

j) **Photoelectric effect:** Alkali metals (except Li) exhibits photoelectric effect.

❖ **Chemical features of alkali metals:**

a) **Reducing character:** As the ionization enthalpies of the alkali metals decrease down the group their reducing character or reactivity in the gaseous state increases down the group. i.e., Li < Na < K < Rb < Cs .

b) **Reaction with dihydrogen:** Alkali metals react with dry hydrogen at about 673 K to form crystalline hydrides which are ionic in nature and have high melting points.

$$2\,M + H_2 \xrightarrow{\text{Heat}} 2M^+ H^-$$
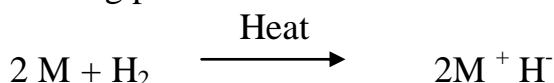
c) **Oxides and hydroxides:** Alkali metals when burnt in air form different compounds, for example the alkali metals on reaction with limited quantity of oxygen form normal oxides (M_2O) M= Li, Na, K, Rb, Cs

d) **Reaction with halogens:** The members of the family combine with halogen to form corresponding halides which are ionic crystalline solids.
Reactivity of alkali metls with particular halogen increases from Li to Cs.

e) **Reaction with water:** Alkali metals react with water and other compounds containing acidic hydrogen atoms such as hydrogen halides, acetylene etc. to liberate hydrogen gas.

f) **Solubility in liquid ammonia:** All alkali metals dissolve in liquid ammonia giving deep blue solutions which are conducting in nature.

g) **Reaction with sulphur and phosphorus:** Alkali metals react with sulphur and phosphorus on heating to form sulphides and phosphides respectively.

❖ **Diagonal relationship between Li and Al**

Li resembles Mg mainly due to similarity in sizes of their atoms and ions. The main points of similarity are:

i) Both are quite hard.
ii) Both LiOH and $Mg(OH)_2$ are weak bases.
iii) Carbonates of both on heating decompose to produce oxides and carbondioxide.
iv) Both react with nitrogen to give ionic nitrides.
v) Nitrates of both decompose on heating to give oxides.
vi) Both Li and Mg do not form solid bicarbonates.
vii) Because of covalent character LiCl and $MgCl_2$ are soluble in ethanol.
viii) The hydroxides, bicarbonates and fluorides of both Li and Mg are sparingly soluble in water.

❖ **Biological importance of Na and K**

i) Sodium ions participate in the transmission of nerve signals.
ii) Sodium ions also regulate flow of water across the cell membranes and in transport of sugars and amino acids into the cells.
iii) Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP.
iv) Potassium ions in combination with sodium ions are responsible for transmission of nerve signals.
v) The functional features of nerve cells depend upon the sodium potassium ion gradient that is established in the cell.

❖ **Group 2 elements: Alkaline earth metals**

(a) Atomic radii : The atomic radii of alkaline earth metals are fairly large though smaller than the corresponding alkali metals and they increase down the group. This is because on moving down the group, atomic radii increase primarily due to the addition of an extra shell of electrons in each succeeding element.

(b) Ionic radii: the atoms of these elements form divalent ions which show the same trend of increase in their size down the group.

(c) Ionization enthalpy: The alkaline earth metals have fairly low Ionizations enthalpies though greater than those of the corresponding elements of group 1 and this value decreases down the group.

(d) Hydration enthalpy: the Hydration enthalpies of alkaline earth metal ion decrease as the size of the metal ion increases down the Group

$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}$
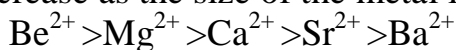
(e) Oxidation State: All the members of the family exhibit +2 oxidation state in their compounded and the form divalent cations (M^{2+})

(f) Electro negativity : The electro negativity values of alkaline earth metals are quite close to those of alkali metals, though slightly more.

(g) Metallic Character : Alkaline earth metals have stronger metallic bonds as compared to the alkali metals present in the same period.

(h) Melting and boiling point : The melting and Boiling points of these metals are higher than those of alkali metals present in the same period.

(i) Colouration to the flame : With the exceptio9n of beryllium and magnesium, the rest of the elements impart characters in colour to the same flame. For example,

Be	Mg	Ca	Sr	Ba	Ra
-	-	Brick Red	Crimson	Grassy Green	Crimson

J) Complex formation: Generally the members do not form complexes. However, smaller ions (Be & Mg Ions) form complexes with the electron donor species

k) **Formation of organo-metallic compounds:** Both beryllium and magnesium form a number of organo-metallic compounds containing M-C bond with certain organic compounds. For example, magnesium reacts with alkyl halide in the presence of dry ether to give Grignard reagent.

l) **Reducing character:** Alkaline earth metals are weak reducing agent than the corresponding alkali metals which have lower ionization enthalpies and comparatively bigger atomic sizes.

m) **Reaction with oxygen:** With the exception of Ba and Ra which form peroxides (MO_2) rest of the metals form normal oxides (MO) on heating with excess of oxygen.

n) **Reaction with halogen**s: The members of the family combine directly with halogen at appropriate temperature to form corresponding halides.

o) **Reaction with water:** The members of this group are less reactive towards water as compared to the corresponding alkali metals because these are less electropositive in nature.

p) **Reaction with hydrogen:** The members except Be combine with hydrogen directly upon heating to form metal hydrides.

Uses of some important compounds:-

(i) Caustic soda:

It is used: in soap, paper, textile, petroleum industry

ii) Sodium carbonate

It is used:
a) in glass and soap industry
b) in paper making and textile manufacturing
c) in paint and dye stuffs
d) in metal refining

e) in production of sodium compounds such as borax, caustic soda, sodium phosphate etc.

iii) **Quick lime:**

It is used:

    a. in the preparation of cement, glass and calcium carbide.

    b. In the purification of sugar

    c. In softening of hard water   d. As a flux in the extraction of metal

iv) Lime stone: It is used

  a) as building material

  b) in the manufacture of quick lime

  c) in Solvay process to prepare Na_2CO_3 as it is a source of CO_2

  d) in metallurgy for the extraction of iron

  e) in toothpaste and certain cosmetics

v) Cement: It is an important building material. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

vi)   Plaster of paris: It is used

  a) in making moulds for pottery and ceramics etc.

  b) in surgical bandages for setting broken bones of the body

  c) for making statues, models, decorative materials and black board chalk.

❖ **Biological importance of Ca and Mg**

    i)   Magnesium ions are concentrated in animal cells and Calcium ions are concentrated in body fluids, outside the cell.

    ii)   All enzymes that utilize ATP in phosphate transfer require magnesium ion as cofactor.

    iii)   In green plants magnesium is present in chlorophyll.

    iv)   Calcium and magnesium ions are also essential for the transmission of impulses along nerve fibres.

    v)   Calcium ions are important in blood clotting and are required to trigger the contraction of muscles.

    vi)   Calcium ions also regulate the beating of the heart.

One mark questions:

1. Why are halides of beryllium polymeric?

Ans:- the halides of Be are electron deficient as their octets are incomplete. Therefore, to complete their octets, the halides polymerize.

2. Name the groups which constitute s-block elements.

Ans:- group-1 and 2

3.Arrange the alkaline earth metal carbonates in the decreasing order of thermal stability.

    Ans:- $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3 > BeCO_3$

4.Write the general electronic configuration of s-block elements.

    Ans:- [Noble gas] ns^{1-2}

5.What is the chemical formula of Plaster of Paris?

    Ans:- $CuSO_4.1/2H_2O$

6.Name the compound which can be obtained by Solvay's process.

Ans:- Sodium carbonate

7.How does the basic character of hydroxides of alkali metals vary down the group?

Ans:- Increases down the group

8.Which out of $MgSO_4$ or $BaSO_4$ is more soluble in water?

Ans:- $MgSO_4$

9.Name radioactive elements of group 1 and 2.

Ans:- Francium and Radium.

10.Which elements of alkaline earth metals family do not give characteristic flame colouration?
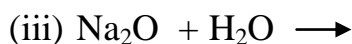
Ans:- Be and Mg
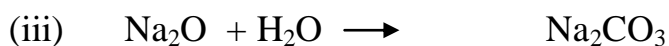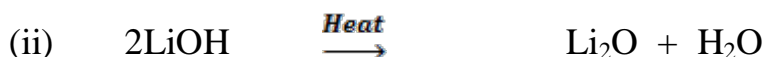
Two marks questions

1. Among the alkali metals which has
   (i) Highest melting point
   (ii) Most electropositive character
   (iii) Lowest size of ion
   (iv) Strongest reducing character.

Ans:- (i) Li (ii) Cs (iii) Li (iv) Li

2. **Complete the following reactions:**

   (i) $Mg(NO_3)_2 \xrightarrow{Heat}$

   (ii) $LiOH \xrightarrow{Heat}$

   (iii) $Na_2O + H_2O \longrightarrow$
   (iv) $Na + O_2 \longrightarrow$

Ans:-

(i) $2Mg(NO_3)_2 \xrightarrow{Heat} 2MgO + 4NO_2 + O_2$

(ii) $2LiOH \xrightarrow{Heat} Li_2O + H_2O$

(iii) $Na_2O + H_2O \longrightarrow Na_2CO_3$

(iv) $2Na + O_2 \longrightarrow Na_2O_2$

3. **Name the chief factors responsible for anomalous behaviour or lithium.**

Ans:- the anomalous behaviour of lithium is because of its:
   (i) Small size of atom and ion,
   (ii) High ionization enthalpy, and
   (iii) Absence of d-orbitals in its Valence shell.

4. **Which out of Li and Na has greater value for the following properties:**
   (i) Hydration enthalpy
   (ii) Stability of hydride
   (iii) Stability of carbonate
   (iv) Basic character of hydroxide
   Ans:- (i) Li (ii) Li (iii) Na (iv)Na

5. Why are alkali metals not found in nature?

Ans. Alkali metals are highly reactive in nature due to low ionization enthalpy and strong electropositive character. They do not occur in free state and are always combined with other elements. As a result alkali metals are not generally found in nature.

6. Why are lithium salts commonly hydrated and those of the other alkali ions usually anhydrous?

Ans. In the lithium salt, the Li^+ ion due to very small size gets readily hydrated on coming in contact with moisture (water). Therefore, lithium salts are commonly hydrated. But the other alkali metal ions are comparatively big in size. They have therefore, lesser tendency to get hydrated. These salts are usually anhydrous.

7. Beryllium and magnesium do not give colour to flame whereas other alkaline earth metals do so why?

Ans: Beryllium and magnesium atoms in comparison to other alkaline earth metals are comparatively smaller and their ionisation enthalpies are very high. Hence, the energy of the flame in not sufficient to excite their electrons to higher energy levels. These elements, therefore, do not give any colour in Bunsen flame.

7. Why are alkali metals soft and have low melting points?

Ans: Alkali metals have only one valence electron per metal atom. As a result, the binding energy of alkali metal ions in the close-packed metal lattices are weak. Therefore, these are soft and have low melting point.

8. Which out of the following and why can be used to store an alkali metal?
     H₂O, C₂H₅OH and Benzene

Ans:- Benzene can be used to store an alkali metal because other substance react with alkali metal as:

$$Na + H_2O \longrightarrow NaOH + 1/2H_2$$
$$Na + C_2H_5OH \longrightarrow C_2H_5ONa + 1/2H_2$$

9. Why are alkali metals not found free in nature?

Ans:- alkali metals are highly reactive and therefore, are not found free in nature, they are present in the combined state in the form of halides, oxides, silicates, nitrates, etc.

Three marks questions

1. When an alkali metal dissolves in liquid ammonia the solution can acquire different colours. Explain the reasons for this type of colour change.

Ans. The dissolution of the metal in liquid ammonia is accompanied by their formation of ammoniated electrons that give rise to dark colour. This is because ammoniated electrons absorb energy corresponding to the red region of the visible light. However, if the concentration increases above 3M, the colour changes to copper-bronze and the solution acquires metallic luster due to the formation of metal ion clusters.

$$M+(x+y)NH_3 \rightarrow [M(NH_3)_3] + [e(NH_3)]$$

2. In what ways lithium shows similarities to magnesium in its chemical behaviour?

Ans. Li resembles Mg mainly due to similarity in sizes of their atoms and ions. The main points of similarity are:

Both are quite hard.

   1 Both LiOH and $Mg(OH)_2$ are weak bases.

    2 Carbonates of both on heating decompose to produce oxides and carbondioxide.

    3 Both react with nitrogen to give ionic nitrides.

3. Discuss the various reactions that occur in the Solvay process.

Ans. In Solvay ammonia process.

When carbon dioxide is passed through a concentrated solution of brine saturated with NH_3, $NaHCO_3$ gets precipitated. $NaHCO_3$ on subsequent heating gives Na_2CO_3.

$$NaCl + NH_3 + CO_2 + H_2O \rightarrow NaHCO_3 + NH_4Cl$$
$$2\ NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$
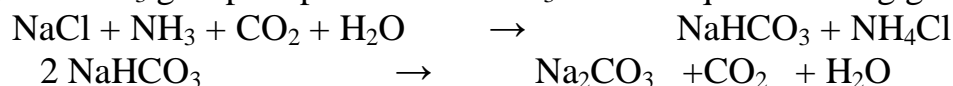
CO_2 needed for the reaction is prepared by heating calcium carbonate and the quick lime, CaO is dissolved in water to form slaked lime, $Ca(OH)_2$

$$CaCO_3 \rightarrow CaO + CO_2$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
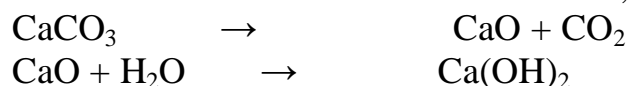
NH_3 needed for the purpose is prepared by heating NH_4Cl and $Ca(OH)_2$

$$2\ NH_4Cl + Ca(OH)_2 \rightarrow 2\ NH_3 + CaCl_2 + H_2O$$
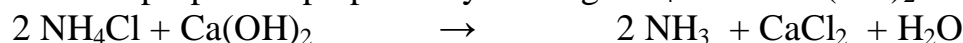
4. What happen when (i) magnesium is burnt in air (ii) quick lime is heated with silica (iii) chlorine reacts with slaked lime (iv) calcium nitrate is heated?

Ans. (i) A mixture of magnesium oxide and magnesium nitride is formed
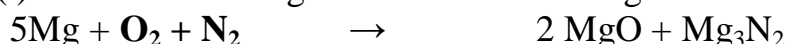
$$5Mg + O_2 + N_2 \rightarrow 2\ MgO + Mg_3N_2$$
$$\textbf{In air}$$

(ii) Calcium silicate is formed.

$$CaO + SiO_2 \rightarrow CaSiO_3$$
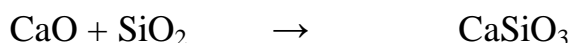
(iii) Calcium oxychloride (bleaching powder) is formed

$$Ca(OH)_2 + Cl_2 \rightarrow CaOCl_2 + H_2O$$
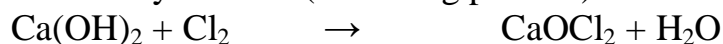
(iv) Nitrogen dioxide is evolved.

$$Ca(NO_3)_2 \xrightarrow{\textit{Heat}} CaO + 2\ NO_2 + O_2$$

5. Describe the importance of the following (i) limestone (ii) cement (iii) plaster of paris.

Ans. i) Lime stone: It is used

 f) as building material

 g) in the manufacture of quick lime

 h) in Solvay process to prepare Na_2CO_3 as it is a source of CO_2

 i) in metallurgy for the extraction of iron

 j) in toothpaste and certain cosmetics

ii) Cement: It is an important building material. It is used in concrete and reinforced concrete, in plastering and in the construction of bridges, dams and buildings.

iii) Plaster of paris: It is used
d) in making moulds for pottery and ceramics etc.
e) in surgical bandages for setting broken bones of the body
f) for making statues, models, decorative materials and black board chalk.
6. What happens when:
a) Sodium metal is dropped in water?
b) Sodium metal is heated in free supply of air?
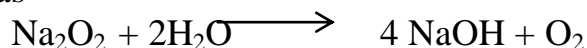**c) Sodium peroxide dissolves in water?**
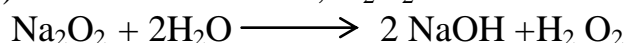**Ans.** a) Sodium metal catches fire and hydrogen gas is evolved

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2 + Heat$$

   b) Sodium peroxide is formed

$$2Na + O_2 \longrightarrow Na_2O_2$$
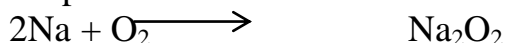
   c) (i) Sodium peroxide reacts with water at ordinary temperature to liberate oxygen gas

$$Na_2O_2 + 2H_2O \longrightarrow 4\ NaOH + O_2$$

   ii) With ice cold water, H_2O_2 is formed

$$Na_2O_2 + 2H_2O \longrightarrow 2\ NaOH + H_2\ O_2$$

7.   **State as to why**
a) a solution of Na_2CO_3 is alkaline?
b) alkali metals are prepared by electrolysis of their fused chlorides?
c) sodium is found to be more useful than potassium?
Ans. (a) Sodium carbonate being a salt of strong base (NaOH) and weak acid (H_2CO_3) forms alkaline solution upon hydrolysis

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3$$
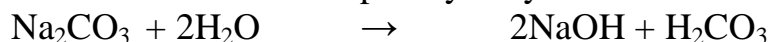
  (b) Since the discharge potential of alkali metals is much higher than that of hydrogen, therefore, when the aqueous solution of any alkali metal chloride is subjected to electrolysis, H_2 instead of the alkali metal is produced at the cathode. Therefore, to prepare alkali metals, electrolysis of their fused chlorides is carried out.
(c) Sodium is relatively more abundant than potassium. At the same time, it is also less reactive and its reactions with other substances can be better controlled.
8. Why are potassium and cesium, rather than lithium used in photoelectric cells?
Ans. The ionization enthalpy of lithium is quite high. The photons of light are not in a position to eject electrons from the surface of lithium metal. Therefore photoelectric effect is not noticed. However, both potassium and cesium have comparatively low ionization enthalpies. This means that the electrons can quite easily be ejected from the surface of these metals when photons of certain minimum frequency (threshold frequency) strike against their surface
9. Why is Li_2CO_3 decomposed at a lower temperature whereas Na_2CO_3 at higher temperature?
Ans. Li^+ ion is very small in size. It is stabilized more by smaller anions such as oxide ion rather than large anions such as carbonate. Therefore Li_2CO_3 decomposes into Li_2O on mild heating. On the other hand, Na^+ ion is larger in size. It is stabilized

more by carbonate ion than oxide ion. Hence, Na_2CO_3 does not undergo thermal decomposition easily.

10.Explain why can alkali and alkaline earth metals not be obtained by chemical reduction methods?

Ans. The metals belonging to both these families are very strong reducing agents. It is therefore not possible to reduce their oxides by reacting with common reducing agents like carbon (coke), zinc etc. These are normally isolated by carrying out the electrolysis of the salts of these metals in the molten state.

Five marks questions:

1. Compare the solubility and thermal stability of the following compounds of the alkali metals with those of the alkaline earth metals.(a) Nitrates (b) Carbonates (c) Sulphates.

Ans. Solubility:

In case of alkali metals: Nitrates, carbonates and sulphates of alkali metals are soluble in water. In alkali metals lattice energies decrease more rapidly than the hydration energies, therefore their solubility increases down the group.

In case of alkaline earth metals: Nitrates of all alkaline earth metals are soluble in water but their solubility decreases down the group because their hydration energies decrease more rapidly than their lattice energies.

Since the size of CO_3^{2-} and SO_4^{2-} anions is much larger than the cations, therefore lattice energies remain almost constant with in a particular group. Since, the hydration energies decrease as we move down the group, therefore the solubility of alkaline earth metal carbonates and sulphates decrease down the group. However, the hydration energy of Be^{2+} and Mg^{2+} ions overcome the lattice energy factor and therefore $BeSO_4$ and $MgSO_4$ are readily soluble in water while the solubility of other sulphates decreases down the group from $CaSO_4$ to $BaSO_4$.

Thermal Stability:

a) Nitrates: Nitrates of both alkali and alkaline earth metals decompose on heating. All alkaline earth metal nitrates decompose to form metal oxide, NO_2 and O_2.

$$2M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2$$
M= Be, Mg, Ca, Sr, or Ba

The nitrates of Na, K. Rb and Cs decompose to form metal nitrites and O_2.

$$2MNO_3 \longrightarrow 2MNO_2 + O_2$$

However, due to diagonal relationship between Li and Mg, lithium nitrate decomposes like $Mg(NO_3)_2$ to form metal oxide, NO_2 and O_2.

$$4LiNO_3 \xrightarrow{\textit{Heat}} 2LiO_2 + 4NO_2 + O_2$$
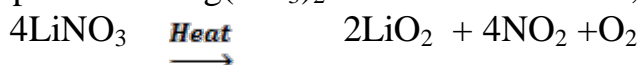
b) Carbonates: Carbonates of alkaline earth metals decompose on heating to form metal oxide and carbon di oxide.

$$2MCO_3 \longrightarrow 2MO + CO_2 \quad M= Be, Mg, Ca, Ba$$
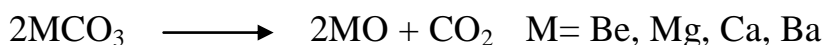
Further as the electropositive character of the metal increases down the group the stability of these metal carbonates increases or the temperature of their decomposition increases.

c) Sulphates: Sulphates of alkaline earth metals decompose on heating to form metal oxide and SO_3.

$$MSO_4 \xrightarrow{\text{Heat}} 2MO + SO_3 \quad M= Be, Mg, Ca, Ba$$
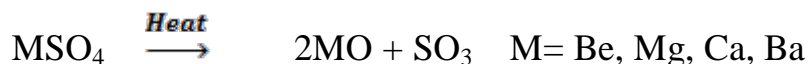
The temperature of decomposition of these sulphates increases as the electropositive character of the metal or the basicity of the metal hydroxide increases down the group.

Among the alkali metals due to diagonal relationship, Li_2SO_4 decomposes like $MgSO_4$ to form the corresponding metal oxide and SO_3.

$$Li_2SO_4 \xrightarrow{\text{Heat}} Li_2O + SO_3$$

$$MgSO_4 \xrightarrow{\text{Heat}} 2MgO + SO_3$$
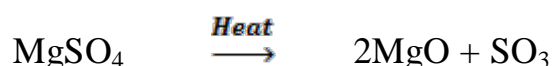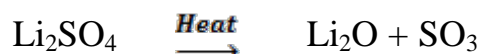
Other alkali metals are stable to heat and do not decompose easily.

2. Compare the alkali metals and alkaline earth metals with respect to (i) ionization enthalpy (ii) basicity of oxides and (iii) solubility of hydroxides..

Ans.

(i) Ionization enthalpy (I E): I E of alkaline earth metals are higher than those of alkali metals of group 1. This is because the atoms of alkaline earth metals have smaller size (due to higher nuclear charge) as compared to the alkali metals.

(ii) Basicity of oxides: The oxides of alkali and alkaline earth metals dissolve in water to form their respective hydroxides. These hydroxides are strong bases. The hydroxides of alkaline earth metals are less basic than of alkali metals of the corresponding periods. This is due to their (i) high ionization enthalpy (ii) small ionic size and (iii) dipositive charge on the ions.

As a result M-O bond in these hydroxides is relatively stronger than that of corresponding alkali metals and therefore does not break.

(iii) Solubility of hydroxides: Because of smaller size and higher ionic charge, the lattice enthalpies of alkaline earth metals are much higher than those of alkali metals and hence the solubility of alkali metal hydroxides is much higher than that of alkaline earth metals. However the solubility of the hydroxides of both alkali and alkaline earth metals increase down the group due to large decrease in their lattice enthalpies as compared to their hydration enthalpies.

3. Explain the significance of sodium, potassium, magnesium and calcium in biological fluids.

Ans. Significance of sodium and potassium:

(i) Sodium ions participate in the transmission of nerve signals.

(ii) Sodium ions also regulate flow of water across the cell membranes and in transport of sugars and amino acids into the cells.

(iii) Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in oxidation of glucose to produce ATP.

(iv) Potassium ions in combination with sodium ions are responsible for transmission of nerve signals.

(v) The functional features of nerve cells depend upon the sodium potassium ion gradient that is established in the cell.

Significance of Magnesium and Calcium:

1. Magnesium ions are concentrated in animal cells and Calcium ions are concentrated in body fluids, outside the cell.
2. All enzymes that utilize ATP in phosphate transfer require magnesium ion as cofactor.
3. In green plants magnesium is present in chlorophyll.
4. Calcium and magnesium ions are also essential for the transmission of impulses along nerve fibres.
5. Calcium ions are important in blood clotting and are required to trigger the contraction of muscles.
6. Calcium ions also regulate the beating of the heart.

HOTS QUESTIONS

1. Potassium carbonate cannot be prepared by Solvay process. Why?

Ans. This is due to the reason that potassium bicarbonate ($KHCO_3$) formed as an intermediate (when CO_2 gas is passed through ammoniated solution of potassium chloride) is highly soluble in water and cannot be separated by filtration.

2. The hydroxides and carbonates of sodium and potassium are easily soluble in water while the corresponding salts of magnesium and calcium are sparingly soluble in water. Explain.

Ans. All the compounds are crystalline solids and their solubility in water is guided by both lattice enthalpy and hydration enthalpy. In case of sodium and potassium compounds, the magnitude of lattice enthalpy is quite small as compared to hydration enthalpy since the cationic sizes are large. Therefore, the compounds of sodium and potassium that are mentioned, readily dissolve in water. However, in case of corresponding magnesium and calcium compounds, the cations have smaller sizes and more magnitude of positive charge. This means that their lattice enthalpies are more as compared to the compounds of sodium and potassium. Therefore, the hydroxides and carbonates of these metals are only sparingly soluble in water.

3. Why is LiF almost insoluble in water whereas LiCl soluble not only in water but also in acetone?

Ans. The low solubility of LiF in water is due to its very high lattice enthalpy (F^- ion is very small in size). On the other hand, in lithium chloride (LiCl) the lattice enthalpy is comparatively very small. This means that the magnitude of hydration enthalpy is quite large. Therefore lithium chloride dissolves in water. It is also soluble in acetone due to dipolar attraction. (Acetone is polar in nature)

CHAPTER 11

The p-block elements

Elements in which the last electron enters in the any one of the three p- orbital of their outermost shells – p-block elements

- Gen. electronic configuration of outer shell is ns^2np^{1-6}

The inner core of e-config.may differ which greatly influences their physical & to some extent chemical properties.

- The block of elements in the periodic table consisting of the main groups :

- Group 13   (B to Tl)

- Group14   (C to Pb)

- Group15   (N to Bi)

- Group 16   (O to Po)

- Group17   (F to At)

- Group18   (He to Rn)

(1)   Members at the top and on the right of the *p*-block are nonmetals (C, N,   P, O, F, S, Cl, Br, I, At).

(2) Those on the left and at the bottom are metals (Al, Ga, In,Tl, Sn, Pb, Sb Bi, Po).

(3)   Between the two, from the top left to bottom right, lie an ill-defined group of metalloid elements (B, Si, Ge, As, Te)

GROUP 13 : The boron group

- Outer Electronic Configuration:-ns^2np^1

- group members: boron (B), aluminum (Al), gallium (Ga), indium (In)& thallium (Tl) .   All, except boron, are metals.

- Boron show diagonal relationship with Silicon;   both are semiconductors metalloids & forms covalent compounds.

- Boron compounds are electron deficient, they are lack of an octet of electrons about the B atom .

- diborane B_2H_6, is simplest boron hydride

- Structure: three-center two-electron: the H atoms are simultaneously bonded to two B atoms the B-H bridging bond lengths are greater than B-H terminal.

- - Boron oxide is acidic (it reacts readily with water to form boric acid)

- aluminium compounds:aluminium oxide is amphoteric

- aluminum halides, e.g., $AlCl_3$ is dimer, an important catalyst in organic chemistry have anincomplete octet, acts as Lewic acid by accepting lone pairs from Lewic bases, forming adduct

- aluminum hydride, e.g., $LiAlH_4$, a reducing agent

- Atomic Properties - Electronic Configurations

Element	Symbol	Atomic No.	Electronic Configuration	Abundance in Earth's Crest (in ppm)
Boron	B	5	$[He]2s^2\,2p^1$	8
Aluminium	Al	13	$[Ne]3s^2\,3p^1$	81,300
Galium	Ga	31	$[Ar]3d^{10}4s^2\,4p^1$	15
Indium	In	49	$[Kr]\,4d^{10}5s^2\,5p^1$	1
Thallium	Tl	81	$[Xe]\,5d^{10}6s^2\,6p^1$	0.3

. Atomic and ionic radii

- The atomic and ionic radii of group 13 elements are compared to corresponding elements of group 2. From left to right in the period, the magnitude of nuclear charge increases but the electrons are added to, the same shell. These electrons do not screen each other, therefore, the electrons experience greater nuclear charge.

- In other words, effective nuclear charge increases and thus, size decreases. Therefore, the elements of this group have smaller size than the corresponding elements of second group.

- On moving down the group both atomic and ionic radii are expected to increase due to the addition of new shells. However, the observed atomic radius of Al (143 pm) is slightly more than that of Ga (l35 pm).

Ionization energies

The first ionization energies of group 13 elements are less than the corresponding members of the alkaline earths.

2/14

The sharp decrease in I.E. from B to Al is due to increase in size. In case of Ga, there are ten d-electrons in its inner electronic configuration.

The very high value of 3rd I. E. of thallium indicates that +3 O.N. state is not stable, rather +1 is more stable for thallium .

Electropositive (or metallic) character

the elements of group 13 are less electropositive as compared to elements of group 2. On moving down the group the electropositive (metallic) character increases because ionization energy decreases. For e.g., Boron is a non-metal white the other elements are typical metals.

Oxidation states

The common oxidation states of group 13 elements are +3 and + 1 .The stability of the + 1 oxidation state increases in the sequence Al <Ga< In <Tl, Due to Inert pair effect.

Element	B	Al	Ga	In	Tl
Oxidation state	+3	+3	+3, +1	+3, +1	+3, +1

Chemical reactivity of Gr.13 Elements

All elements in their compounds exhibit the oxidation state of + 3 and +1.
Hydrides
- None of the group 13 elements reacts directly with hydrogen. However, a no. of hydrides of these elements have been prepared by indirect methods. The boron hydrides are called boranes& classified in two series: (a) B_nH_{n+4} called nidoboranes   (b) B_nH_{n+6} called arachnoboranes

- INUDSTRIAL PREPERATION :-

  $2BF_3(g) + 6LiH(s) \rightarrow B_2H_6(g) + 6LiF(s)$
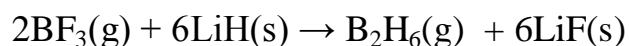
- Laboratory method:

  (i)   By the reaction of iodine with sodium borohydride in a high boiling solvent.
  $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$
  (ii)   By reduction of BCl_3 with $LiAlH_4$
  $4BCl_3 + 3LiAlH_4 \rightarrow 2 B_2H_6 + 3AlCl_3 + 3 LiCl$

Structure of Diborane, B_2H_6
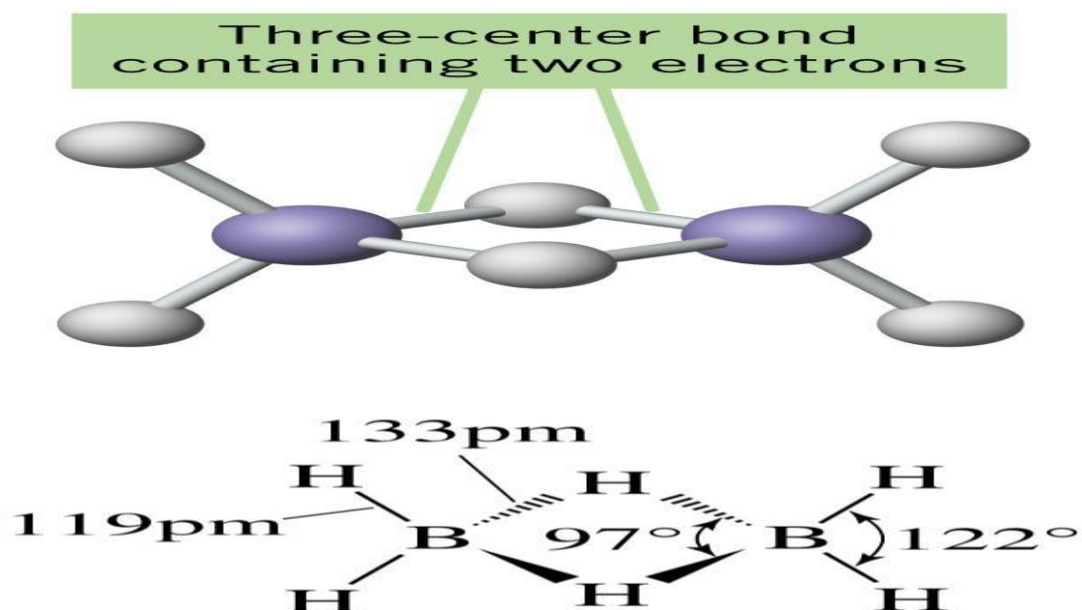
Some important characteristics of boranes:

 i) Lower boranes are colourless gases while higher boranes are volatile liquids or solids.

 ii) They undergo spontaneous combustion in air due to strong affinity of boron

   for oxygen.

  $B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O + Heat$

   iii) Boranes react with alkali metal hydrides in diethyl ether to form borohydride complexes.

  $B_2H_6 + 2MH \rightarrow 2M^+[BH_4]^-$ (M= Li or Na)

         Metal borohydride

- (iv) Diborane reacts with ammonia to give borazine at 450 K.

  $B_2H_6 + 6NH_3 \rightarrow 3B_3N_3H_6 + 12H_2$
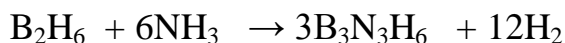
- Borazine has a cyclic structure similar to benzene and thus is called inorganic benzene

- The other elements of this group form only a few stable hydrides. The thermal stability decreases as we move down the group.

- AlH$_3$ is a colourless solid polymerized via Al - H - Al bridging units. These hydrides are weak Lewis acids and readily form adducts with strong Lewis base (B:) to give compounds of the type MH$_3$ (M = Al or Ga). They also form complex-tetrahydrido anions, [MH4]-. The most important tetrahydrido compound is Li[AlH$_4$]

$$4LiH + AlCl_3 \xrightarrow{\text{ether}} LiAlH_4 + 3LiCl$$
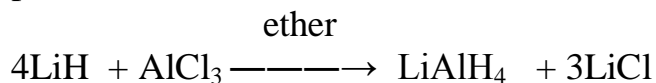
OXIDES & HYDROXIDES

- M$_2$O$_3$ & M(OH)$_3$

B(OH)$_3$ and B$_2$O$_3$	Al(OH)$_3$ and Al$_2$O$_3$	Ga(OH)$_3$ and Ga$_2$O$_3$	In(OH)$_3$ and In$_2$O$_3$	Tl(OH)$_3$ and Tl$_2$O$_3$
Acidic	Amphoteric	Amphoteric	Basic	Strong base

Basic Character Increases
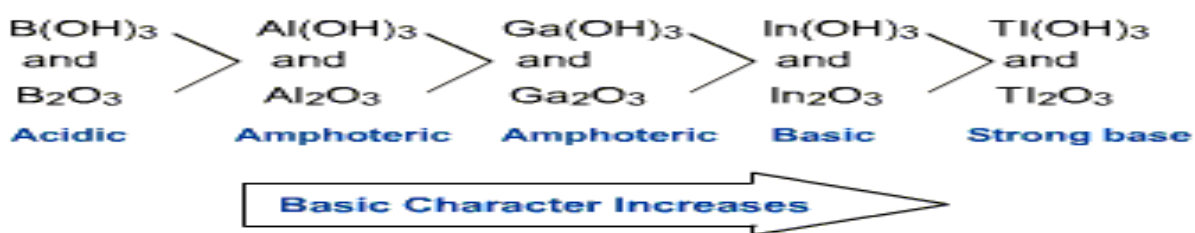
HALIDES: Structure of boron trihalides

X = F, Cl or Br
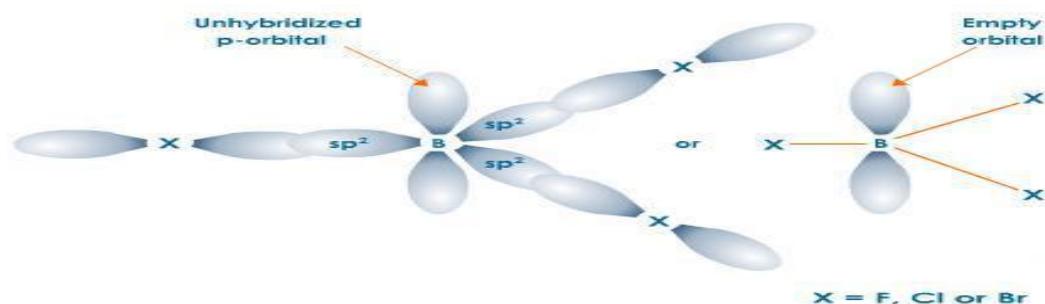
Dimeric structure of aluminium chloride

    – Boron halides do not form dimers because the size of boron is so small that it is unable to coordinate four large-sized halide ions.
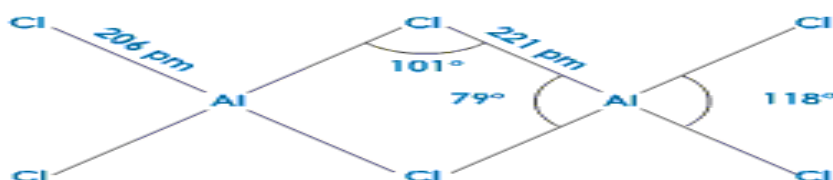
- Anomalous properties of boron

1. Boron is a non-metal & bad conductor of electricity whereas aluminium is a metal & good conductor. B is hard but Al is a soft metal.
2. Boron exists in two forms-crystalline and amorphous. But Al does not exist in different forms.

3. The melting and boiling point of boron are much higher than that of Al .

 4. Boron forms only covalent compounds whereas Al forms even some ionic compounds.

5. The hydroxides and oxides of boron are acidic in nature whereas those of aluminium are amphoteric.

 6. The trihalides of boron exist as monomers. On the other hand, aluminium halides exist as dimers .

7. The hydrides of boron are quite stable while those of aluminium are unstable

- Boron and silicon exhibit the typical properties of non-metals. These do not form cations. Both exist in amorphous as well as crystalline forms.

- Boron oxide (B_2O_3) and silica (SiO_2) both are acidic and dissolve in alkali solutions to form borates and silicates respectively.

  B_2O_3 + 6NaOH → $2Na_2BO_3$ + $3H_2O$

  SiO_2 + 2NaOH → Na_2SiO_3 + H_2O
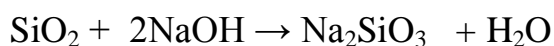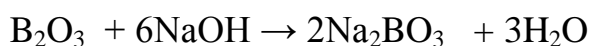
- The chlorides of both B and Si get hydrolyzed by water to boric acid and silicic acid respectively.

  BCl_3 + $3H_2O$ →H_3BO_3 + 3HCl $SiCl_4$ + $3H_2O$ → H_2SiO_3 + 4HCl

- The hydrides of Boron and Silicon are quite stable. Numerous volatile hydrides are also known which catch fire on exposure to air and are easily hydrolyzed.
- Both elements are semiconductors.

Behavior in Aqueous Solutions

1 Al, Ga, In and Tl exhibit a well-defined aqueous chemistry in their tripositive states. Species like [M(OH)4]-, [M(H2O)2(OH)4]-, [M(OH2)6]3+ for M = Al, Ga, In, exist in aqueous solution.

2. Al, Ga. In and T1 ions exist as octahedral aqua ions, [M(OH2)6]3+ in aqueous solution and many salts like halides, sulphates, nitrates and perchlorates exist as hydrates.

3. Aluminiumsulphate forms double salts - called alum, having the general formula

 M_2SO_4. $Al_2(SO_4)_3$.$12H_2O$, where M=Na+ or K+.

USES OF BORON & ALUMINIUM

- Aluminium is used extensively in industry and everyday life. It forms many useful alloys with Cu. Mn, Mg, Si and Zn. Hence, aluminium and its alloys find use in packaging, utensil making, construction, aerospace and other transportation industries. It is used as a conductor for transmission of electricity. Aluminium is alsoused in the alumino-thermite process for production of chromium and manganese from their ores.

Group 14 Elements:-The Carbon Family

Group 14 includes carbon (C), silicon (Si), germanium (Ge), tin (Sn) and lead (Pb).

General electronic configuration of carbon family is ns^2np^2.

Covalent radius:-Covalent radius expected to increase from Cto Si,

From Si to Pb small increase is found.

Ionization Enthalpy:-The first ionization enthalpies of group 14 elements are higher than those of the corresponding group 13 elements.

Electronegativity:-Group 14 elements are smaller in size as compared to group 13 elements that's why this group elements are slightly more electronegative than group 13

Chemical properties:-

Carbon and silicon mostly show +4 oxidation state. Germanium forms stable compounds in +4 state and only few compounds in +2 state.

Tin forms compounds in both oxidation states. Lead compounds in +2 state are stable and in +4 state are strong oxidizing agents.

Exception:-Pb_4 and SnF_4 are ionic in nature.

Except CCl_4 other tetrachlorides are easily hydrolysed by water.

Since carbon does not have d-orbitals and hence cannot expand its coordination number beyond 4

$$CCl_4 +H_2O \qquad No\ Reaction$$

$$SiCl_4+4H_2O \qquad Si(OH)_4+4HCl$$

$$Silicic\ acid$$
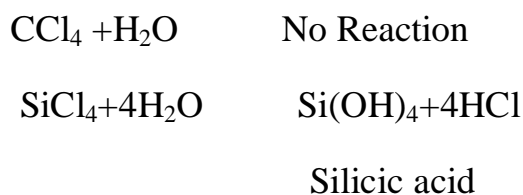
Allotropes of Carbon:-The three types of allotropes are –

1-Diamond   2-Graphite   3-Fullerence

Diamond:-In diamond each carbon atom undergas SP^3 hybridisation.

Each carbon is tetrahedrally linked to four other carbon atoms.

Graphite:-In graphite, carbon is SP^2-hyberdized graphite has a two-dimensional sheet like structure consisting of a number of hexagonal rings fused together.

Graphite conducts electricity along the sheet.It is very soft and Slippery

FullerenceFullerence was discovered collectively by three scientists namely R.E Smalley,R.F Curl and H.W Kroto

SOME Important Compounds Of Carbon and Silicon

Carbon monoxide:-It I prepared by direct oxdisation of C in limited supply of oxygen.

$$2C+O_2(g) \quad \rightarrow \quad 2CO(g)$$
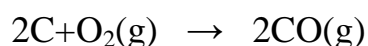
Commercially it is prepared by the passage of steam over hot coke

Carbon Dioxide:-It is prepared by complete combustion of carbon and carbon fuels in excess of air.

$$C(s) +O_2(g) \quad \rightarrow CO_2(g)$$
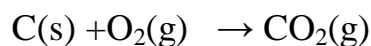
Laboratory method:-

In laboratory it is prepared by the treatment of dilHCl on $CaCO_3$

$$CaCO_3(s) +2HCl(aq) \quad \rightarrow \quad CaCl_2(aq) +CO_2(g)+H_2O(l)$$

Silicon dioxide:-Silicon dioxide is a COVALENT THREE DIMENSIONAL NETWORK SOLID.

Each silicon atom is covalently bonded in a tetrahedral manner to four oxygen atoms.

Silicones:-Silicones are the synthetic organo-siliconpolymers having general formulae $(R_2SiO)_n$ in which R = alkyl (methyl,ethyl or phenyl)

Silicates:-Silicates are exist in nature in the form of feldspar, zeolites,mica and asbestos etc.

The basic structure of silicates is SiO_4^{4-}

Zeolites:-Zeolites is aalumino-silicate of metal. Metal cations participating in formationof Zeolite are use usually Na^+, K^+, or Ca^{2+}.

Zeolites are used to remove permanent hardness of water.

ONE MARK QUESTIONS

1. Why is boron used in nuclear reactions?

Ans:-Because Boron can absorb neutrons.

2. By giving a balanced equation show how $B(OH)_3$ behaves as an acid in water.

Ans:-$B(OH)_3 + 2HOH \longrightarrow [B(OH)_4]^- + H_3O^+$
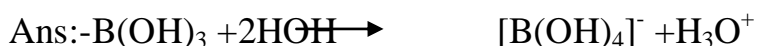
3.Name the element of group 14 which exhibits maximum tendency for catenation?

Ans:-Carbon

4. What is the basic building unit of all silicates?

Ans:-SiO_4^{4-} is the basic unit of all silicates.

5. What happens when $NaBH_4$ reacts with iodine?

Ans:-$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$.

6. What happens when boric acid is heated

Ans:-$4H_3BO_3 \longrightarrow 4HBO_2 \longrightarrow H_2B_4O_7$.

7. What is producer gas?

Ans:-Producer gas is a mixture of CO and N_2 in the ratio of 2:1.

8.Write the state of hybridization of 'B' in BF_3.

ANS:-Hybridisation of 'B' in BF_3 is Sp^2.

9.Mention the state of hybridization in B in BH_4^-.

Ans:-Sp^3.

10. Which oxide of carbon is regarded as anhydride of carbonic acid.

Ans:-CO_2 is regarded as a hydride of carbonic acid .

Because $H_2CO_3 \rightarrow H_2O + CO_2$

TWO MARKS QUESTIONS

1. Give the chemical reaction as an evidence for each of the following observations.

    (i) Tin (II) is a reducing agent where as lead (II) is not.

    (ii)Gallium (I) undergoes disproportionation reaction.

Ans:- (i) Due to inert pair effect pb^{2+} is more stable than Pb^{4+}. Whereas Sn^{4+} is more stable than Sn^{2+}.

    (ii) $3Ga^+ \rightarrow \quad 2Ga + Ga^{3+}$

    This is because Ga^{3+} is more stable than Ga^+.

2. What happens when
    (i) Quick lime is heated with coke?
    (ii) Carbon monoxide reacts with Cl_2

Ans:- (i) $Cao + 3C \quad \rightarrow \quad CaC_2 + CO$

    (iii) $CO + Cl_2 \rightarrow \quad COCl_2$

3.Give reason

    (i) C and Si are always tetravalent but Ge,Sn,Pb show divalency.

    (ii) Gallium has higher ionization enthalpy than Al. Explain.

Ans:-(i) Ge, Sn, Pb show divalency due to inert pair effect, Pb^{2+} is more stable than Pb^{4+}.

    (ii) Due to poor shielding effect of d-electrons in Ga effective nuclear charge increases as compared to Al thus the I.E is higher than Al.

4.Give reason why boron and aluminium tend to form covalent compounds.

Ans:-Sumof three ionization of both the element are very high. Thus they have no tendency to lose electrons to form ionic compound.Instead they form covalent compounds.

5.If B-Cl bond has a dipole moment, Explain why BCl_3 molecule has zero dipole moment.

Ans:- B-Cl bond has dipole moment because of polarity.In BCl_3 since the molecule is symmetrical thus the polarities cancel out.

6.Suggest a reason as to why CO is poisonous.

Ans:-CO reacts with haemoglobin to form carboxy-haemoglobin which can destroy the oxygen carrying capacity of haemoglobin and the man dies of suffocation.

7.What do you understand by-

   (a) Inert pair effect:-The pair of electron in the valence shell does not take part in bond formation it is called inert pair effect.

   (b) Allotropy:-It is the property of the element by which an element can exists in two forms which have same chemical properties but different physical properties due to their structures.

8.How is excessive content of CO_2 responsible for global warming?

Ans:-Excess of CO_2 absorbs heat radiated by the earth.Some of it dissipated into the atmosphere while the remaining part is radiated back to the earth.Temperature of the earth increases.

9.Describe two similarities and two dissimilarities between B and Al.

Ans:-Similarities:-

   (i)   Both have same number of valence electrons.
   (ii)   Both have similar electronic configuration.

   Dissimilarities:-

   (i)   Bis a non- metal where Al is a metal
   (ii)   B forms acidic oxide whereas Al forms atmospheric oxides.

10.What are fullerene? How they were prepared?

Ans:- Fullerene are the allotropes of carbon.Its structure is like a soccer ball.

   They are prepared by heating graphite in electric arc in presence of inert gases such as helium or argon.

THREE MARKS QUESTIONS

1.What happens when

  (a)Borax is heated strongly

(b)Boric acid is added to water

(c)Aluminium is treated with dilute NaOH

Ans:-(a) $Na_2B_4O_7 . 10H_2O \rightarrow Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3$

(b) $B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+$

(C) $2Al + 2NaOH + H_2O \rightarrow 2NaAlO_2 + 3H_2$
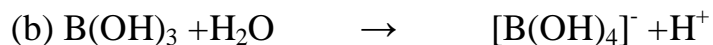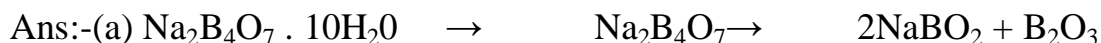
2.Explain the following reactions.

(a)Silicon is heated with methyl chloride at high temperature in the presence of copper.

(b)Silicon dioxide is treated with hydrogen fluoride.

(c) CO is heated with ZnO.

Ans:- (a) A mixture of mono-,di- and trimethylchlorosilianes along with a small amount of tetramethylsilane is formed.

$CH_3Cl + Si \rightarrow CH_3SiCl_3 + (CH_3)_2 SiCl_2 + (CH_3)_3SiCl + (CH_3)_4 Si$
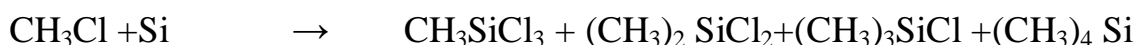
(b) The initially formed silicon tetrafluroide dissolves in HF to form hydrofluorosilicic acid

$SiO_2 + 2HF \rightarrow SiF_4 + 2H_2O$

$SiF_4 + 2HF \rightarrow H_2SiF_6$
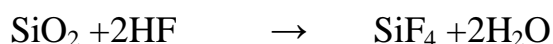
(c) ZnO is reduced to zinc metal

$ZnO + CO \rightarrow Zn + CO_2$
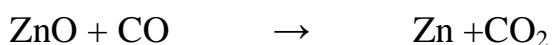
3.Give reasons:-

(a)Diamond is used as an abrasive.

(b) Aluminium alloys are used to make aircraft body.

(c) Aluminium utensils should not be kept in water overnight.

Ans:- (a) Diamond is used as an abrasive because it is an extremely hard substance.
(b)Alloys of alumimium likeduralium is used to make aircraft body due to
Someof its property .

(c)Generally aluminium metal does not react with water quickly but when it is kept overnight.It reacts slowly with water in presence of air.

$$2Al(s) + O_2(g) + H_2O(l) \rightarrow Al_2O_3(s) + H_2(g)$$
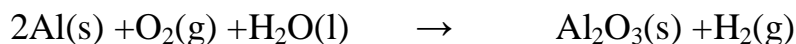
4.A certain salt X,gives the following results.

(i)Its aqueous solution is alkaline to litmus.

(ii)It swells up to a glassy material Y on strong heating.

(iii)when conc.H_2SO_4 is added to a hot solution of X,whitecrystalof an acid Z separates out.

Ans:- (i) $\quad Na_2B_4O_7 + 10H_2O \rightarrow 2NaOH + H_2B_4O_7 + 8H_2O$

(ii) $\quad Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3$

(iii)$Na_2B_4O_7.10H_2O + H_2SO_4 \rightarrow 4H_3BO_3 + Na_2SO_4 + 5H_2O$
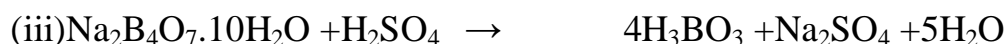
5. draw structure of diborane .

Ans.
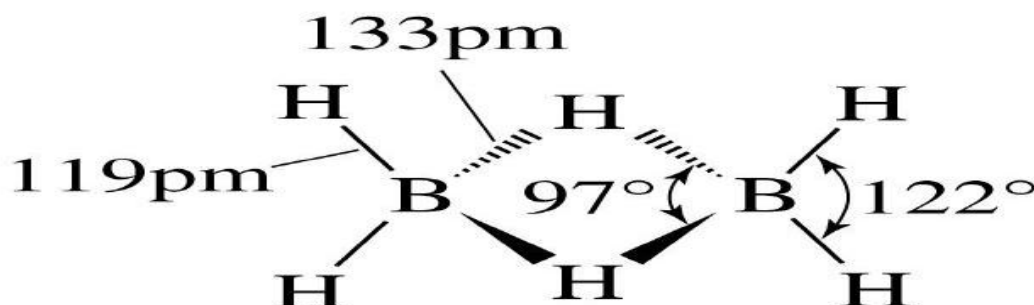
FIVE MARKS QUESTIONS

1 Explain the formation of (i) Water gas (ii) Producer gas. Give their uses. What happens when CO_2 is passed through lime water (i) for short duration (ii) folong duration.

Ans:-(i)$C(s) + H_2O(g) \rightarrow CO(g) + H_2(g)$
(Water gas)

(ii) $2C(s) + O_2 + 4N_2(g) \rightarrow 2CO(g) + 4N_2(g)$
(Producer gas)
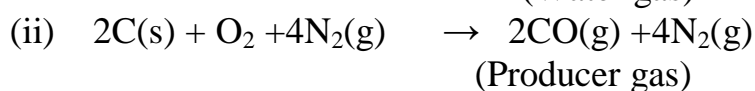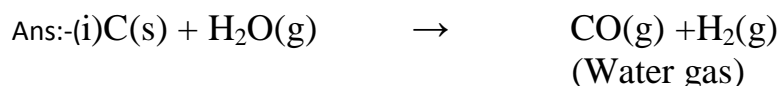
Water gas and Producer gas are used as fuel.

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

(White ppt.)

(i) $CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$

(Soluble)
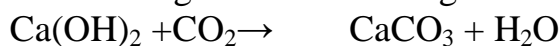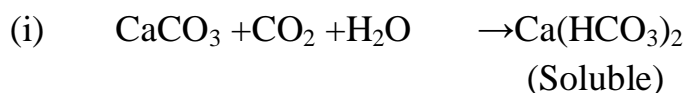
2 (a) Why do Boron halides from addition compound with NH_3 ?

(b) Assign appropriate reason for each of the following observations :-

(i)   Anhydrous $AlCl_3$ is used as a catalyst in many organic reactions.

(ii)   No form of elemental silicon is comparable to graphite.

Ans:- (a) It is because BX_3 is electron deficient whereas NH_3 is electron rich.

(b) (i) It is Lewis acid.

(ii) It cannot form $p\pi - p\pi$ bond due to large size.

3. (i) Give reason for the following observations:-

(a) The tendency for catenation decreases down the group in Group 14.

(b) The decreasing stability of +3 oxidations state with increasing atomic number in group 13.

(c) PbO_2 is a stronger oxidizing agent than SnO_2.

(d) Molten aluminium bromide is a poor conductor of electricity.

Ans:- (i)(a) It is due to decrease in bond dissociation energy which is due to increase in atomic size.

C-C > Si-Si >Ge-Ge>Sn-Sn>Pb-Pb.

(b) It is due to inert pair effect.

(c) PbO_2 is stronger oxidizing agent than SnO_2 because Pb^{2+} is more stable than Pb^{4+} whereas Sn^{4+} is more stable than Sn^{2+}.

(d) Molten $AlBr_3$ is poor conductor of electricity because it is covalent compound.

CHAPTER 12

Organic chemistry : Some Basic Principles and Techniques

Organic compounds are the hydrocarbons and their derivatives and organic chemistry is that branch of chemistry that deals with the study of these compounds

Tetravalency of carbon

The atomic number of Carbon is 6 and its electronic configuration is 2,4 i.e. it has 4 valence electrons. Thus carbon is always tetracovalent, i.e. it forms 4 covalent bonds with other atoms

$$-\overset{|}{\underset{|}{C}}-$$
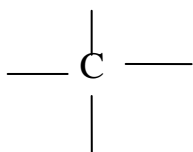
Due to tetravalency of carbon it has a tetrahedron shape.

Catenation- The self linking property of carbon is known as catenation. This is the main reason of existence of such large number of compounds

Classification of organic compounds
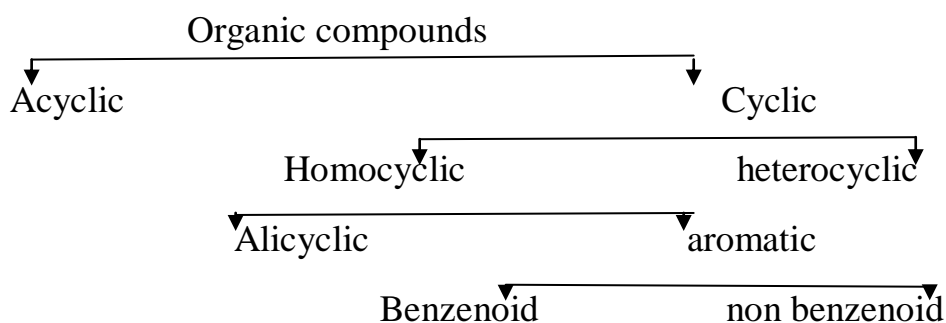
Functional groups:A functional group may be defined as an atom or a group of atoms present in a molecule which largely determines the chemical properties.

CLASS OF ORGANIC COMPOUNDS	NAME OF FUNCTIONAL GROUP	STRUCTURE
Alkenes	double bond	$=C=C=$
Alkynes	triple bond	$- C \equiv C -$
Halogens	halogen	$- X$ (F,Cl,Br,I)
Alcohols	hydroxyl	$-OH$
Aldehydes	aldehydic(formyl)	$-CHO$
Carboxylic acids	carboxyl	$-COOH$
Acid amides	amides	$-CONH_2$
Primary amines	amino	$- NH_2$

HOMOLOGOUS SERIES

Homologous series is defined as a family or group of structurally similar organic compounds all members of which contain the same functional group, show a gradation in physical and similarity in chemical properties and any two adjacent members of which differ by $-CH_2$ group. The individual members of this group are called homologues and the phenomenon is called homology.

NOMENCLATURE OF ORGANIC COMPOUNDS

Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming known as IUPAC system of nomenclature is adopted. The names are such that the listener can deduce the structure from it. The IUPAC name consists of three parts:

Prefix   Word root   Suffix

EX: 3 methlyoctane

NOMENCLATURE OF ALKANES

Straight chain alkanes:

The names of such compounds is based on their chain structure,and end with suffix '-ane' and carry a prefix indicating the number of carbon atoms present in the chain.

Branched chain hydrocarbons:

1.) The longest carbon chain in the molecule is identified.
2.) The numbering is done in such a way that the branched carbon atoms get the lowest possible value.
3.) The names of the alkyl groups attached as a branch are then prefixed to the name of the parent alkane and its position is indicated by numbers.
4.) The lower number is given to the first in alphabetical order.
5.) The carbon atom of the branch that attaches to the root alkane is numbered 1.

Organic compounds having Functional Groups:

The longest chain of carbon atoms containing the functional groups is numbered in such a way that the functional group attached to the carbon atom gets the lowest possible number in the chain.

When there are more functional groups then a priority order is followed as:

-COOH, -SO$_3$H, -COOR, COCl, -CONH$_2$, -CN, -HC=O, =C=O, -OH, -NH$_2$, =C=C=, -C≡ C-.

ISOMERISM
Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism.

Chain isomerism: When two or more compounds having same molecular formula but different carbon skeletons are referred to as chain isomers.
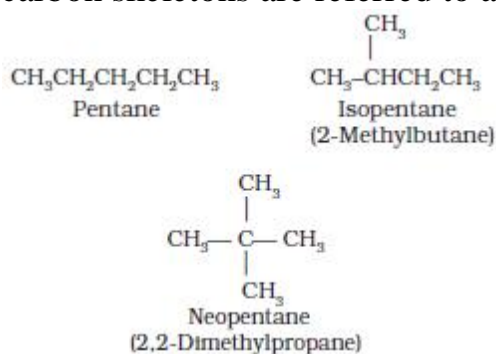
$$CH_3CH_2CH_2CH_2CH_3 \qquad \underset{\underset{\displaystyle CH_3}{|}}{CH_3-CH}CH_2CH_3$$

Pentane   Isopentane
(2-Methylbutane)

$$CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_3$$

Neopentane
(2,2-Dimethylpropane)

Position Isomerism : Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group are called position isomers and this phenomenon is called Position Isomerism. e g

$CH_3-CH_2-CH=CH_2$ $CH_3-CH = CH - CH_3$

Functional Isomerism : Compounds which have the same molecular formula but different functional group are called functional isomers and this phenomenon is called functional Isomerism. e g

$CH_3 - CH_2 - OH$ $CH_3 - O - CH_3$

Metamerism: It is due to the presence of different alkyl groups on either side of functional group in the molecule. Ex. $C_4H_{10}O$ represents $C_2H_5OC_2H_5$ and $CH_3OC_3H_7$.

FISSION OF COVALENT BOND

Heterolytic cleavage: In this cleavage the bond breaks in such a way that the shared pair of electron remains with one of the fragments.

$H_3C - Br \longrightarrow\ ^+CH_3\ + Br^-$

Homolytic Cleavage: In this cleavage the shared pair of electron goes with each of the bonded atom.

$R - X \longrightarrow \qquad R^. + X^.$

       Alkyl free radical

Nucleophiles : A reagent that brings an electron pair is called nucleophile ie nucleus seeking e g -OH , -CN

Electrophiles: A reagent that takes away electron pair is called electrophile I e electron seeking e g $> C= O$, $R_3C - X$

Inductive Effect: The displacement of the electron along the chain of the carbon atoms due to presence of an atom or group at the end of the chain.

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

Resonance Effect : The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom.

There are two types of resonance effect:

1) Positive resonance effect : In this effect the transfer of electrons is away from an atom or substituent group attached to the conjugated system.
   The atoms or groups which shows +R effect are halogens,-OH , -OR,-NH_2

2) Negative resonance effect : In this effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

   The atoms or groups which shows -R effect are –COOH , -CHO , -CN

METHODS OF PURIFICATION OF ORGANIC COMPOUNDS :

Sublimation : This method is used to separate the sublimable compounds from non sublimable compounds.

Crystallisation: This method is based on the difference in the solubilities of compound and impurities in a suitable solvent. The impure compound is dissolved in solvent at heated at higher temp .on cooling the hot and conc solution pure compounds crystallizes out.

Distillation: This method is used to separate volatile liquids from non volatile liquids and liquids having sufficient difference in their boiling points.

Fractional distillation: If the boiling points of two liquids is not much , they are separated by this method.

Distillation under reduced pressure : This method is used to purify liquids having high boiling points and decomposes at or below their boiling points.

Steam distillation : This method is used to separate substances which are steam volatile and are immiscible with water.

Differential Extraction: When an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is more soluble than in water. The aqueous solution is mixed with organic solvent in a separating funnel and shaken for sometimes and then allowed to stand for some time .when organic solvent and water form two separate layers the lower layer is run out by opening the tap of funnel and organic layer is separated. the process is repeated several times and pure organic compound is separated.

Chromatography : This technique is used to separate mixtures in to their components ,purify the compounds and test the purity of compounds.It is classified as

Adsorption Chromatography : It is based on the fact that different compounds are adsorbed on an adsorbent to different degrees. Silica jel or alumina is used as adsorbents.

Partition Chromatography : It is based on the continuous differential portioning of components of a mixture between stationary and mobile phase.

QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Detection of Carbon and Hydrogen: The Carbon and Hydrogen present in the Organic compound is detected by heating the compound with Copper II oxide in a hard glass tube when carbon present in the compound is oxidized to CO2 which can be tested with lime Water and Hydrogenis converted to water which can be tested with anhydrous copper sulphate which turns blue.

$C + CuO \longrightarrow 2Cu + CO_2$
$2 H + CuO \longrightarrow Cu + H2O$
$CO_2 + Ca (OH)_2 \longrightarrow CaCO_3 + H_2O$
$5H_2O + CuSO_4 \longrightarrow CuSO_4.5H_2O$
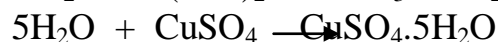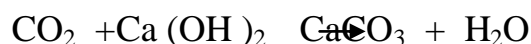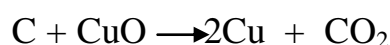
DETECTION OF OTHER ELEMENTS

Sodium Fusion Extract: A small piece of dry Sodium metal is heated with a organic compound in a fusion tube for 2 -3 minutes and the red hot tube is plunged in to distilled water contained in a china dish. The contained of the china dish is boiled ,cooled and filtered. The filtrate is known as Sodium fusion extract.

Test for Nitrogen : The sodium fusion extract is boiled with iron II sulphate and then acidified with Concsulphuric acid , the formation of Prussian blue colour confirms the presence of nitrogen.

$6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$

$3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3.xH_2O$
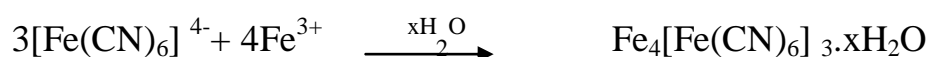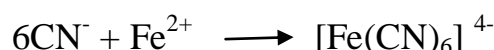
Test for Sulphur: the sodium fusion extract is acidified with acetic acid and lead acetate is added to it. A black precipitate of lead sulphide indicates the presence of sulphur. $S^{2-} + Pb^{2+} \longrightarrow PbS$

 Black

Test for halogens: The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate. A white precipitate, soluble in ammonium hydroxide shows the presence of chlorine, a yellowish ppt. sparingly soluble in ammonium hydroxide shows the presence of bromine, a yellowish ppt. insoluble in ammonium hydroxide shows the presence of iodine.

$X^- + Ag^+ \longrightarrow AgX$
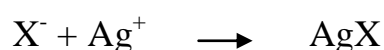
QUANTITIVE ANALYSIS(Carbon and Hydrogen)

Let the mass of organic compound be m g. Mass of water and carbon dioxide produced be m_1 and m_2 g respectively;

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

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

Nitrogen

DUMAS METHOD: A known mass of organic compound is heated with excess of CuO in an atmosphere of CO_2, when nitrogen of the organic compound is converted into N_2 gas. The volume of N_2 thus obtained is converted into STP and the percentage of nitrogen determined by applying the equation:

$$\text{Volume of Nitrogen at STP} = \frac{P_1 V_1 \times 273}{760 \times T_1}$$

$$\%N = \frac{28 \times \text{vol of } N_2 \text{ at STP} \times 100}{22400 \times \text{mass of the substance taken}}$$

KJELDAHL'S METHOD: A known mass of organic compound is heated with conc. H_2SO_4 in presence of K_2SO_4 and little $CuSO_4$ or Hg in a long necked flask called Kjeldahl's flask when nitrogen present in the organic compound is quantitatively converted into $(NH_4)_2SO_4$. $(NH_4)_2SO_4$ thus obtained is boiled with excess of NaOH solution to liberate NH_3 gas which is absorbed in a known excess of a standard acid such as H_2SO_4 or HCl.

The vol of acid unused is found by titration against a standard alkali solution. From the vol of the acid used, the percentage of nitrogen is determined by applying the equation,

$$\%N = \frac{1.4 \times \text{Molarity of the acid} \times \text{Basicity of the acid} \times \text{Vol of the acid used}}{\text{Mass of the substance taken}}$$

Halogens
Carius method:
A known mass of an organic compound is heated with fuming nitric acid in the presence of silver nitrate contained in a hard glass test tube known as carius tube in a furnace. Carbon and hydrogen present in the compound are oxidized to carbon dioxide and water. The halogen present forms the corresponding silver halide. It is filtered, dried, and weighed.

Let the mass of the organic compound taken = m g

Mass of AgX formed = m_1 g

1 mol of AgX contains 1 mol of of X

Mass of halogen in m_1 g of AgX

$$= \frac{\text{at mass of X} \times m_1}{\text{Molecular mass of AgX}} \text{ g}$$

% of halogen

$$= \frac{\text{at mass of X} \times m_1 \text{ g} \times 100}{\text{Molecular mass of AgX} \times m} \%$$

Sulphur

Let the mass of the organic compound taken = m g

Mass of $BaSO_4$ formed = m_1 g

$$\% \text{ of sulphur} = \frac{32 \times m_1 \times 100}{233 \times m} \%$$

Phosphorous

Let the mass of the organic compound taken = m g

Mass of ammonium phosphomolydate = m_1 g

$$\% \text{ of phosphorous} = \frac{31 \times m_1 \times 100}{1877 \times m} \%$$

Oxygen

Let the mass of the organic compound taken = m g

Mass of CO_2 = m_1 g

$$\% \text{ of oxygen} = \frac{32 \times m_1 \times 100}{44 \times m} \%$$

One Mark Questions

Q1 Suggest a method to purify a liquid which decomposes at its boiling point.

A 1 The process Distillation Under reduced pressure is used to purify a liquid which decomposes at its boiling point.

Q 2 How will you separate a mixture of O-nitrophenol and p- nitrophenol ?

A 2 O-nitrophenol is steam volatile therefore it can be separated by Steam distillation.

Q 3 Lassaigne's test is not shown by diazonium Salt. Why?

A 3 On heating diazonium Salts loses Nitrogen and could not fuse with the Sodium metal therefore diazonium Salt do not show Positive Lassaigne's test for nitrogen.

Q 4 Alcohols are weaker acids than Water, Why ?

A 4 The alkyl group in alcohols has + I effect due to which electron density is increases on Oxygen atom which makes the release of hydrogen ion more difficult from alcohol. $R \rightarrow O \rightarrow H$

Q 5 Why is nitric acid is added to Sodium extract before adding Silver nitrate for testing halogens ?

A 5 Nitric acid is added to decompose NaCN and Na_2S

$NaCN + HNO_3 \rightarrow NaNO_3 + HCN$

$Na_2S + 2HNO_3 \rightarrow 2NaNO_3 + H_2S$
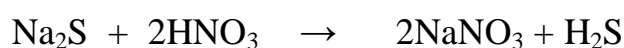
Q 6 which of the two $O_2NCH_2CH_2^-$ or $CH_3CH_2O^-$ is expected to be more stable and why ?

A 6 NO_2 group has –I effect and disperse the negative charge on Oxygen atom

$O_2N \leftarrow CH_2 \leftarrow CH_2O^-$
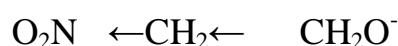
Q 7 Arrange the following in increasing Order of Stability ;

$(CH_3)_3C^+$, $CH_3CH_2CH_2C^+H_2$, $CH_3CH_2C^+HCH_3$, $CH_3C^+H_2$, $CH_3CH_2C^+H_2$

A 7 $CH_3C^+H_2 < CH_3CH_2C^+H_2 < CH_3CH_2CH_2C^+H_2 < CH_3CH_2C^+HCH_3 < (CH_3)_3C^+$

Q 8 Write the IUPAC name of the following

CH_3 CH CH CH_2 CH_3

CH_3CH_3
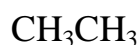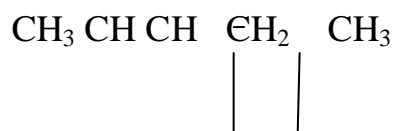
A 8   2,3Dimethylpentane

Q 9 Write the hybridized state of C atoms in the following

$CH_2 = CH - C \equiv N$

A 9 sp^2sp^2sp

$CH_2 = CH - C \equiv N$

Q 10 Give the IUPAC name of the following compound.
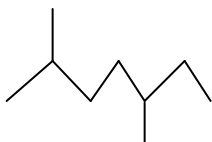
A 10   2,5Dimethylheptane

Two Marks Questions

Q 1 Draw the Structures of the following compounds.

A)   Hex-3-enoic acid   b) 2-chloro-2-methylbutan-1-ol

A 1 a)

$$CH_3\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}OH$$

b)

$$CH_3\text{ - }CH_2 - \underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle Cl}{|}}{C}} \text{ - }CH_2 - OH$$
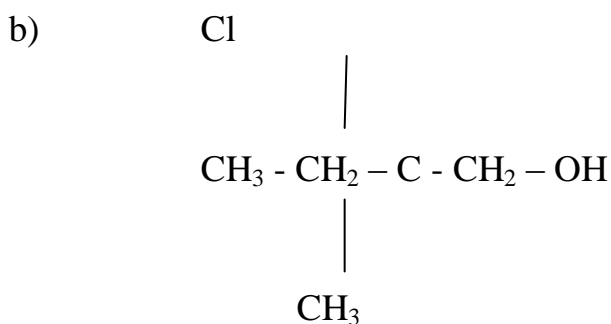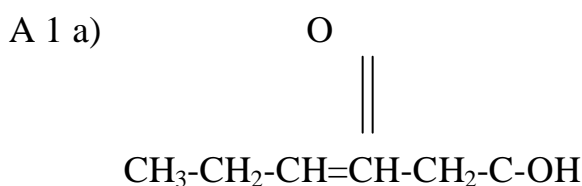
Q 2 Explain Inductive effect with example.

A 2 Inductive Effect: The displacement of the electron along the chain of the carbon atoms due to presence of an atom or group at the end of the chain.

$$\delta{+}{+}{+} \qquad \delta{+}{+} \qquad \delta{+}$$

$CH_3{\rightarrow} \quad C\,H_2 \ \rightarrow \ CH_2 \ {\rightarrow}Cl$
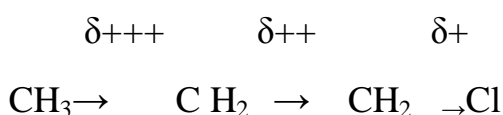
Q 3 Explain why $(CH_3)_3C^+$ is more stable than $CH_3C^+H_2$.

A 3 $(CH_3)_3C^+$ has nine alpha hydrogens and has nine hyperconjugation structures while $CH_3C^+H_2$ has three alpha hydrogens and has three hyperconjugation structures, therefore $(CH_3)_3C^+$ is more stable than $CH_3C^+H_2$

Q 4 Give the number of Sigma and pi bonds in the following molecules

a) CH_3NO_2 b)$HCONHCH_3$

A 4   a)   6 Sigma and 1 pi bond

b) 8 Sigma and 1 pi bond

Q 5 Write the condensed and bond line formula of 2,2,4-Trimethylpentane.

A 5

$CH_3—\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}—\ CH_2—\overset{}{\underset{\underset{\displaystyle CH_3}{|}}{CH}}—CH_3$
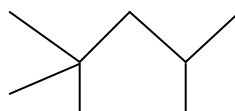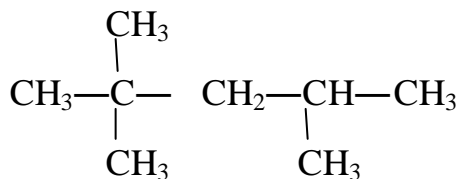
Q 6 How Sodium fusion extract is prepared ?

A 6 A small piece of dry Sodium metal is heated with a organic compound in a fusion tube for 2 -3 minutes and the red hot tube is plunged in to distilled water contained in a china dish. The contained of the china dish is boiled ,cooled and filtered. The filtrate is known as Sodium fusion extract.

Q 7 Explain the principle of paper chromatography.

A 7 Paper chromatography is based on the difference in the rates at which the components of a mixture are adsorbed. The material on which different components are adsorbed is called Stationary phase which is generally made up of alumina, silica jel or activated charcoal. The mixture to be separated is dissolved in a suitable medium and it is called moving phase. The moving phase is run on the Stationary phase , the different compounds are adsorbed on stationary phase at different rates.

Q 8 Why is an organic compound fused with Sodium for testing nitrogen,halogens and sulphur ?

A 8 On fusing with sodium metal the elements presents in an organic compounds are converted in to sodium salts which are water soluble which can be filtered and detected by the respective tests.

Q 9 It is not advisable to use sulphuric acid in place of acetic acidfor acidification while testing sulphur by lead acetate test. Give reason

A 9 Lead acetate on reacting with sulphuric acid will give a white ppt of lead sulphatewhih interfere in the detection of sulphur.

$$(CH_3COO\ )_2Pb\ +\ H_2SO_4 \longrightarrow PbSO_4 + 2\ CH_3COOH$$
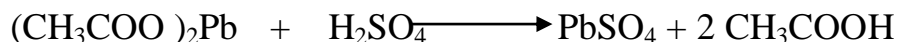
Q 10 Under what conditions can the process of steam distillation is used ?

A 10 Steam distillation is used to purify the liquids which are steam volatile and water and the liquid are not miscible with each other.

Three Marks Questions

Q 1 In an estimation of sulphur by carius method 0.468 g of an organic compound gave 0.668 g of barium sulphate. Find the percentage of sulphur in the compound.

A 1 Mass of the compound = 0.468 g

Mass of the barium sulphate = 0.668 g

% of sulphur = $\dfrac{32 \text{ X Mass of barium sulphate X } 100}{233 \text{ X Mass of the compound}}$

$= \dfrac{32 \text{ x } 0.668 \text{x} 100}{233 \text{ x} 0.468}$

= 19.60 %

Q 2 Which bond is more polar in the following pairs of molecules.

   a) H_3C-H, H_3C-Br   b) H_3C-NH_2, H_2C-OH   c) H_3C-OH, H_3C-SH

A 2 a) C-Br because Br is more electronegative than H

   b) C-O because O is more electronegative than N
   c) C-O because O is more electronegative than S

Q 3 Define Isomerism.Explain position Isomerism and Functional Isomerism with examples.

A 3 Two or more compounds having the same molecular formula but different physical and chemical properties are called isomers and this phenomenon is called isomerism.

Position Isomerism : Compounds which have the same structure of carbon chain but differ in position of double or triple bonds or functional group are called position isomers and this phenomenon is called Position Isomerism. e g

CH_3-CH_2-CH=CH_2 CH_3-CH = CH – CH_3

Functional Isomerism :Compounds which have the same molecular formula but different functional group are called functional isomers and this phenomenon is called functional Isomerism. e g

$CH_3 – CH_2 – OH$ $CH_3 – O – CH_3$

Q 4 write the IUPAC names of the following compounds.

$$\text{A. CH3 – CH2} \overset{\overset{\displaystyle O}{\|}}{-}\text{C – CH2} \overset{\overset{\displaystyle O}{\|}}{-} \text{C – CH3}$$

       B HC Ξ C – CH = CH – CH – CH_2

       C Cl $CH_2CH_2CH_2CH_2$Br
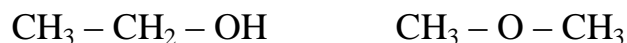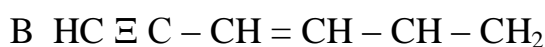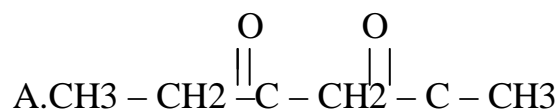
A 4   A   hexane 2,4dione

B hexa-1,3-dien-5-yne

C 1-bromo-4-chlorobutane

Q 5 Define Homologous series. Write the general formula of alkane, alkene and alkynes.

A 5 Homologous Series : It is defined as group of similar organic compounds which contains the similar functional groups and the two adjacent members of the series is differ by a $-CH_2$ group.

Alkanes C_nH_{2n+2}

Alkenes C_nH_{2n}

Alkynes C_nH_{2n-2}

Q 6 How many Sigma and pi bonds are present in the following molecules .

A $HC \equiv CCH = CHCH_3$

B $CH_2 = C = CHCH_3$

A 6 A Sigma bonds = 10 pi bonds = 3

  B Sigma bonds = 9 pi bonds = 2

Q 7 Define functional groups. Write the general formula of Carboxylic acids acid chlorides.

A 7 Functional Groups :It is an atom or group of atoms bonded together in a unique manner which is usually the site of chemical reactivity in an organic molecule. e g CH_3OH

General formula of Carboxylic acids : $C_nH_{2n+1}COOH$

General formula of acid chlorides :RCOCl

Q 8 Write a shirt note on differential extraction.

A 8 When an organic compound is present in an aqueous medium it is separated by shaking it with organic solvent in which it is more soluble than in water. The aqueous solution is mixed with organic solvent in a separating funnel and shaken for sometimes and then allowed to stand for some time .when organic solvent and water form two separate layers the lower layer is run out by opening the tap of funnel and organic layer is separated. the process is repeated several times and pure organic compound is separated.

Q 9 How carbon and Hydrogen is detected in a organic compounds.

A 9 The Carbon and Hydrogen present in the Organic compound is detected by heating the compound with Copper II oxide in a hard glass tube when carbon present

in the compound is oxidized to CO2 which can be tested with lime Water and Hydrogenis converted to water which can be tested with anhydrous copper sulphate which turns blue.

$C + CuO \rightarrow 2Cu + CO_2$

$2 H + CuO \rightarrow Cu + H_2O$

$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$

$5H_2O + CuSO_4 \rightarrow CuSO_4.5H_2O$
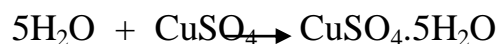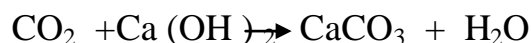
Q 10 Write a short note on Resonance effect .

Resonance Effect : The polarity produced in the molecule by the interaction of two pi bonds or between a pi bond and lone pair of electron present on an adjacent atom.

There are two types of resonance effect:

1. Positive resonance effect: In this effect the transfer of electrons is away from an atom or substituent group attached to the conjugated system.
   The atoms or groups which shows +R effect are halogens,-OH , -OR,-NH$_2$
2. Negative resonance effect: In this effect the transfer of electrons is towards the atom or substituent group attached to the conjugated system.

   The atoms or groups which shows -R effect are –COOH , -CHO , -CN

Five Marks Questions

Q 1 Differentiate between the principle of estimation of nitrogen in an organic compound by i) Dumas method   ii) Kjeldahl's method.

Ans: DUMAS METHOD: A known mass of organic compound is heated with excess of CuO in an atmosphere of CO_2, when nitrogen of the organic compound is converted into N_2 gas. The volume of N_2 thus obtained is converted into STP and the percentage of nitrogen determined by applying the equation:

$$\text{Volume of Nitrogen at STP} = \frac{P_1V_1 \times 273}{760 \times T_1}$$

$$\%N = \frac{28 \times \text{vol of } N_2 \text{ at STP} \times 100}{22400 \times \text{mass of the substance taken}}$$

KJELDAHL'S METHOD: A known mass of organic compound is heated with conc. H_2SO_4 in presence of K_2SO_4 and little $CuSO_4$ or Hg in a long necked flask called Kjeldahl's flask when nitrogen present in the organic compound is quantitatively converted into $(NH_4)_2SO_4$. $(NH_4)_2SO_4$ thus obtained is boiled with excess of

NaOHsolution to liberate NH_3 gas which is absorbed in a known excess of a standard acid such as H_2SO_4 or HCl.

The vol of acid unused is found by titration against a standard alkali solution. From the vol of the acid used, the percentage of nitrogen is determined by applying the equation,

%N= $\dfrac{1.4 \text{ x Molarity of the acid x Basicity of the acid x Vol of the acid used}}{\text{Mass of the substance taken}}$

Q 2 A sample of 0.50g of organic compound was treated according to Kjeldahl's method. The ammonia evolved was absorbed in 50mL of 0.5M H_2SO_4. The residual acid required 60mL of 0.5M solution of NaOH for neutralization. Find the percentage composition of nitrogen in the compound.

Ans: the vol ofH_2SO_4 used.

Vol of acid taken=50mL of 0.5M H_2SO_4= 25mL of 1M H_2SO_4

Vol of alkali used for neutralization of excess acid= 60 mL of 0.5m NaOH=30mL of 1M NaOH

Now 1 mole of H_2SO_4 neutralizes 2 moles of NaOH

(i.e. H_2SO_4 + 2 NaOH $\longrightarrow$ Na_2SO_4 + $2H_2O$)

… 30 mL of 1M NaOH = 15mL of 1M H_2SO_4

% of nitrogen.

1 mole of H_2SO_4 neutralizes 2 moles of NH_3 … 10mL of 1M H_2SO_4 = 20mL of 1M NH_3

But 1000mL of 1M NH_3 contain N=14g.

20 ml of 1M NH_3 will contain nitrogen = $\dfrac{14 \text{ x } 20}{1000}$

But this amount of nitrogen is present in 0.5 g of organic compound

$\therefore$ % of N = $\dfrac{14 \text{ x } 20 \text{ x } 100}{1000 \text{ x } 0.5}$ = 56.0

Q 3 You have a mixture of three liquids A, B , C. there is a large difference in the boiling point of A and the rest two liquids. Boiling points of liquids B and C are quite close. Liquid A boils at higher temperature than B and C and boiling point of B is lower than C. How will you separate the components of the mixture.

Ans Since the boiling point of liquid A is much higher than those of liquids B and C , therefore separate liquid A by simple distillation. Since boiling points of liquids B and C are quite close but much lower than liquid A therefore mixture of B and C will distil together leaving behind A. on further heating A will distil over.

Now place the mixture of liquids B and C in a flask fitted with fractionating column. Since the b.p. of liquid B is lower than that of C , on fractional distillation first liquid B will distil over and than liquid C.

HOTS QUESTIONS

Q 1 Explain hyperconjugation effect. How does hyperconjugationeffect explain the stability of alkenes?

Ans The relative stability of various classes of carbonium ions may be explained by the number of no-bond resonance structures that can be written for them. Such structures are obtained by shifting the bonding electrons from an adjacent C-H bond to the electron deficient carbon so the positive charge originally on carbon is dispersed to the hydrogen. This manner of electron release by assuming no bond character in the adjacent C-H bond is called Hyperconjugation. Greater the hyperconjugation greater will be the stability of alkenes.

$$CH_3 - CH = CH - CH_3 < CH_3 - \underset{\underset{CH_3}{|}}{C} = CH - CH_3 \qquad < CH_3 - \underset{\underset{CH_3}{|}}{C} = \underset{\underset{CH_3}{|}}{C} - CH_3$$
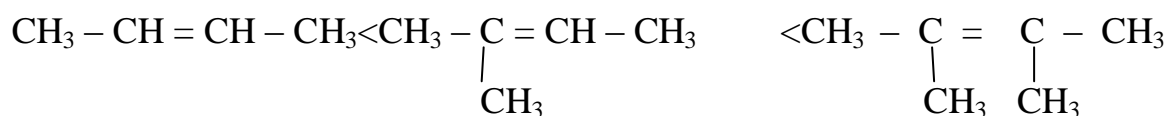
Q 2In DNA and RNA nitrogen is present in the ring system. Can kjeldahl method be used for the estimation of nitrogen present in these ?give reasons

AnsIn DNA and RNA nitrogen is present in hetrocyclicrings.Kjeldahl method can not be used to estimate nitrogen present in the ring because cannot be completely converted in to $(NH_4)_2SO_4$ during digestion. Therefore Kjeldahl method can not be used to estimate nitrogen present in DNA and RNA.

Q 3 1.216 g of an organic compound was Kjeldahlised and the ammonia evolved was absorbed in 100 mL 1N H_2SO_4. The remaining acid solution was made upto500ml by addition of water. 20ml of this dilute solution required 32mL of N/10 caustic soda solution for complete neutralization. Calculate the percentage of nitrogen in the organic compound.

Ans 20 ml of dil. Unreacted H_2SO_4 = 32mL of N/10 NaOH sol.

500ml of dilunreacted H_2SO_4 = $\dfrac{32 \times 500}{20}$ mL of $\dfrac{N}{10}$NaOH = $\dfrac{32 \times 500 \text{ ml of 1 N NaOH}}{20 \times 10}$

= 80ml 1 N NaOH

But   80ml 1 N NaOH= 80ml 1 N NaOH So, acid left unused = 80ml 1 N H_2SO_4

Acid used =(100 – 80) = 20ml 1 N H_2SO_4

%N= $\dfrac{1.4 \text{ x Normality of the acid x Vol of the acid used}}{\text{Mass of the substance taken}}$

$= \dfrac{1.4 \text{ x } 1 \text{ x } 20}{1.216}$ = 23.026

CHAPTER 13

HYDROCARBON

➢ Hydrocarbons are composed of Carbon and hydrogen.
➢ The important fuels like Petrol, kerosene, coal gas, CNG, LPG etc. are all hydrocarbons or their mixture.

Sources:

Petroleum and natural gas are the major sources of aliphatic hydrocarbon while coal is an important source of aromatic hydrocarbons. The oil trapped inside the rocks is known as petroleum. PETRA – ROCK, OLEUM – OIL. The oil in the petroleum field is covered with a gaseous mixture known as natural gas. The main constituents of the natural gas are methane, ethane, propane and butane.

CLASSIFICATION OF HYDROCARBONS:

HYDROCARBON

Acyclic or Aliphatic (Open chain)

Carbocyclic or Cyclic

Alkanes   Alkenes   Alkyne

Alicyclic   Aromatic

Cycloalkanes Cycloalkenes Cycloalkynes
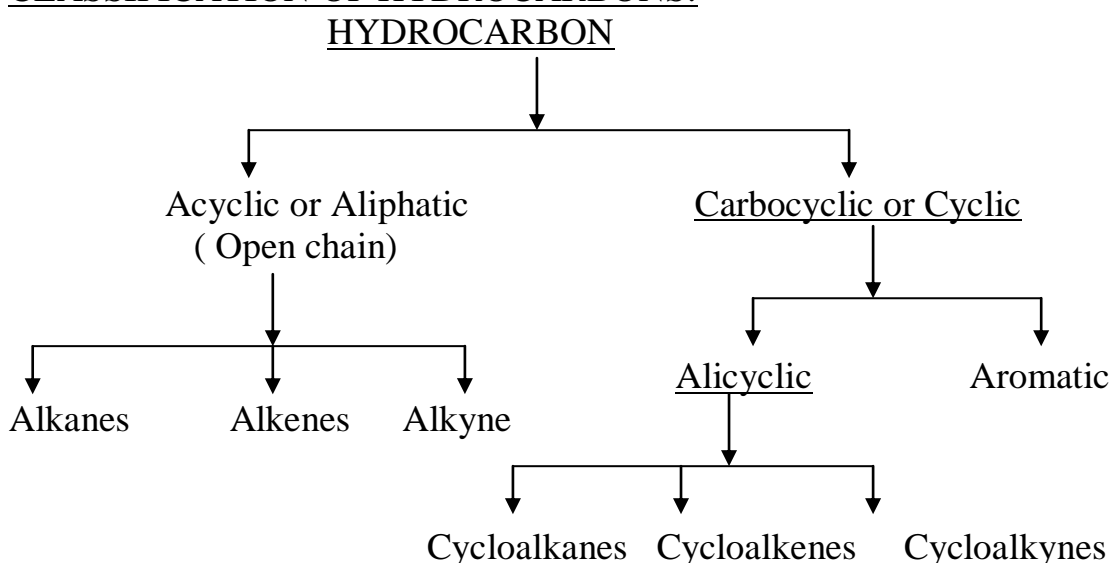
Alkanes:-
➢ Paraffins
➢ General formula C_nH_{2n+2}
➢ sp^3 hybridisation
➢ C–C bond length 1.15 4 A^0
➢ Chemically unreactive
➢ Show chain, position and optical isomerism.
➢ Heptane has 9 isomer, Octane 18 and Decane 75.

Nomenclature:

(c)

109.5°

109.5°

109.5°

109°

109.5°
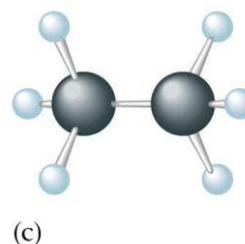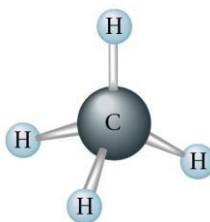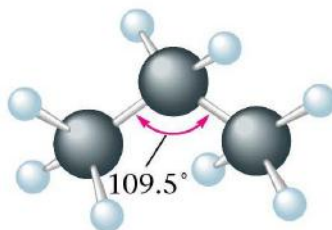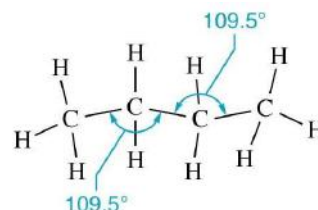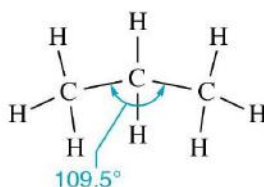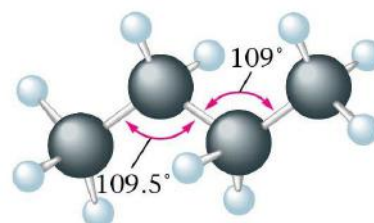
(a) Propane   (b) Butane

Preparation:-

❶ Wurtz reaction:-

$$2CH_3CH_2Br + 2Na \xrightarrow[\text{ether}]{\text{Dry}} CH_3CH_2CH_2CH_3 + 2NaBr$$
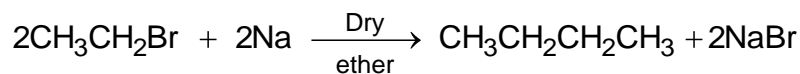
➢ Follow mainly free radical mechanism
➢ Useful in preparing an alkane containing even number of carbon atoms
➢ Stepping up reaction

Frankland reaction

$$RX + Zn + Rx \longrightarrow R-R + ZnX_2$$

❷ From Grignard reagent (RMgX)

$$RMgX + HOH \rightarrow RH + Mg(OH)X$$
$$RMgX + R'OH \rightarrow RH + Mg(OR')X$$
$$RMgX + R'NH_2 \rightarrow RH + Mg(NHR')X$$
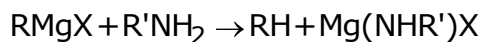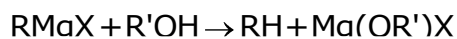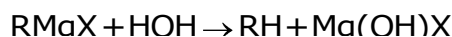
❸ From unsaturated hydrocarbons:-
Sabatier-Senderens reduction

$$R-CH=CH_2 + H_2 \xrightarrow{\text{Ni}/\Delta} R-CH_2-CH_3$$

$$R-C \equiv CH + H_2 \xrightarrow{\text{Ni}/\Delta} R-CH_2-CH_3$$
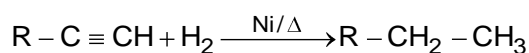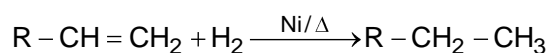
4. From carboxylic acids-
Decarboxylation.-

$$CH_3COO^-Na^+ + NaOH \xrightarrow[\Delta]{CaO} CH_4 + Na_2CO_3$$
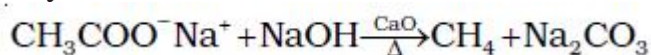
Sodium ethanoate

Kolbe's electrolytic method-

$$2CH_3COO^-Na^+ + 2H_2O$$
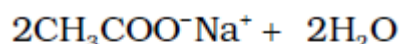
Sodium acetate

$$\downarrow \text{Electrolysis}$$

$$CH_3-CH_3 + 2CO_2 + H_2 + 2NaOH$$
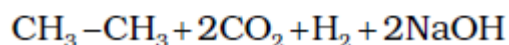
❖ **Physical Properties:-**
(1) Nature:- Non-Polar due to covalent nature of C—C bond and C—H bond. C—C bond enrgy = 83 kj/mole and C—H bond energy = 99 kj/mole.
C_1—C_4 = gases, C_5—C_{17} = colourless odourless liquid and $> C_{17}$ = Solid.
(2) Solubility:- Like dissolve like
Viz, Polar compounds dissolve in polar solvent and Non-Polar compound dissolve in non polar solvent.
(3) Boiling point:- Low boiling point due to non polar in nature.

The molecules are held together only by weak Van der Waalls' forces.
Since we known that the magnitude of Van der Waalls' forces is directly proportional to the molecular size. Therefore, the boiling point increases with increase the molecular size i.e. with increase in number of carbon atoms.

Noted:- the boiling points of the branched chain Alkanes are less than the straight chain isomers.

   This is due to the fact that branching of the chain makes the molecule more compact and thereby decreases the surface aria and consequently, the magnitudes of Van der Waalls' forces also decrease.

$CH_3CH_2CH_2CH_2CH_3$

n-pentane
boiling point = 309 K

$H_3C — CH — CH_2CH_3$
              |
              CH_3
iso-pentane
boiling point = 301 K

CH_3
  |
$H_3C — C — CH_3$
  |
CH_3
neo-pentane
boiling point = 282.5 K

regular variation with i ... carbon atoms having higher melting point a ... immediately next lower and immediately next higher odd number of carbon atoms. ...en number of lkanes having

❖ Chemical properties

❶ Combustion:- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

$$\Delta H = -217.0 \text{ K cal/mole}$$

❷ Oxidation:-

$$CH_4 + O_2 \xrightarrow[573\ K]{Cu} 2CH_3OH$$

$$CH_4 + O_2 \xrightarrow{Mo_2O_3} \underset{\text{Methanal}}{HCHO} + H_2O$$
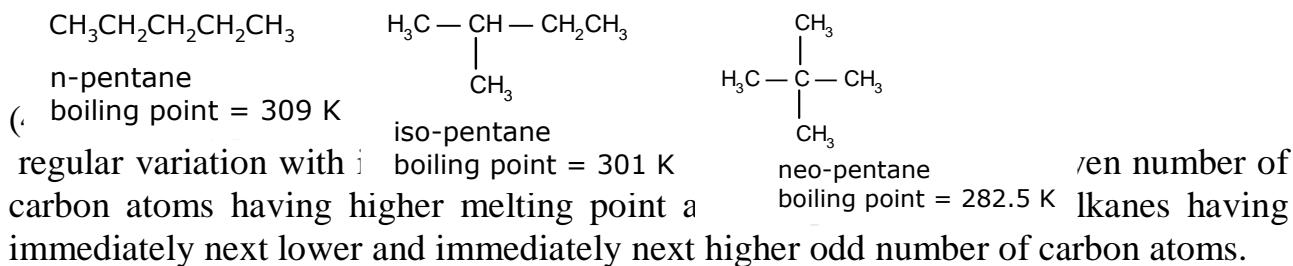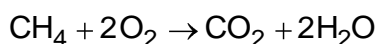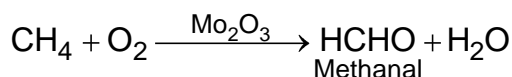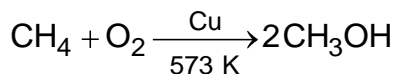
❸ Substitution:-
① Halogenation:-

$$CH_4 \ + \ Cl_2 \xrightarrow{\ UV\ } CH_3Cl \ + \ HCl$$

$$CH_3Cl \xrightarrow{UV} CH_2Cl_2 \xrightarrow{UV} CHCl_3 \xrightarrow{UV} CCl_4$$
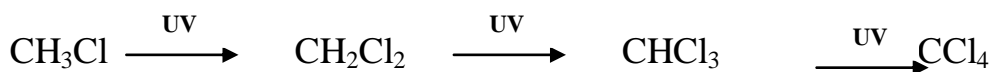
Noted:- Iodination is a reversible reaction. So it is carried out by heating alkane in the presence of some oxidizing agent like iodic acid (HIO_3) or nitric acid (HNO_3) or mercuric oxide (HgO) which oxidizes HI formed during the reaction.

$$CH_4 \ + \ I_2 \xrightarrow{\ Heat\ } CH_3I \ + \ HI$$

$$5HI \ + \ HIO_3 \longrightarrow 3H_2O \ + \ 3I_2$$

$$2HI \ + \ 2HNO_3 \longrightarrow 2H_2O \ + \ I_2 \ + \ 2NO_2$$
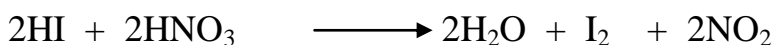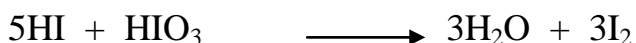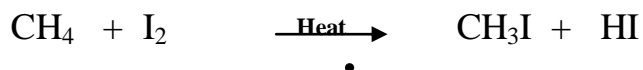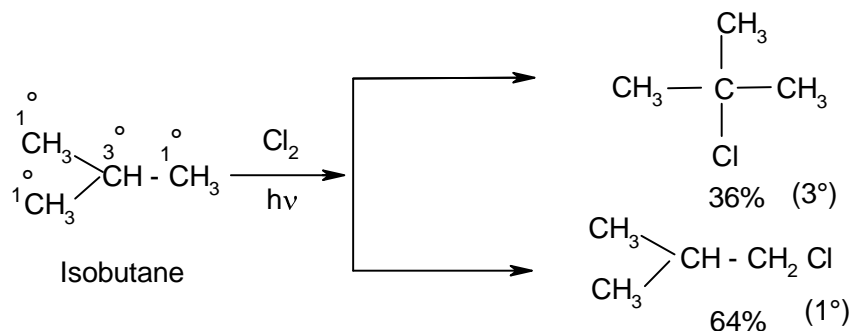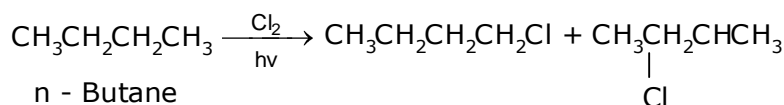
Noted:- Fluorination of alkane takes place explosively resulting even in the rupture of C—C bond in higher alkanes.

- Features of Halogenations:-
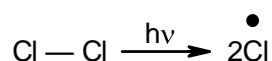 (i) The reactivity of Halogens:- $F_2 > Cl_2 > Br_2 > I_2$.
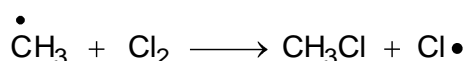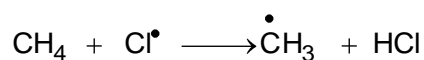 (ii) The rate of replacement of Hydrogens of alkanes is:
$$3° > 2° > 1°$$

$$CH_3CH_2CH_2CH_3 \xrightarrow[hv]{Cl_2} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHCH_3$$

n - Butane

Cl (on the second product)

Isobutane → (via Cl_2, hv)

product 1:

$$CH_3 - \underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_3$$

36%   (3°)

product 2:

$$CH_3{\diagdown}\atop{CH_3{\diagup}} CH - CH_2\ Cl$$

64%   (1°)

Mechanism:- halogenations reaction take place by free radical mechanism.   The reaction proceeds in the following steps:

Initiation

(i)   Chain initiation step:-

$$Cl - Cl \xrightarrow{hv} 2\overset{\bullet}{Cl}$$

(ii)   Chain Propagation step:-

$$CH_4 + Cl^\bullet \longrightarrow \overset{\bullet}{C}H_3 + HCl$$

$$\overset{\bullet}{C}H_3 + Cl_2 \longrightarrow CH_3Cl + Cl\bullet$$

(iii)   Chain Termination step:-

$$Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$$

$$\overset{\bullet}{C}H_3 + \overset{\bullet}{C}H_3 \longrightarrow CH_3 - CH_3$$

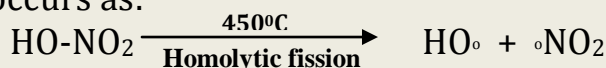$$\overset{\bullet}{C}H_3 + Cl^\bullet \longrightarrow CH_3Cl$$
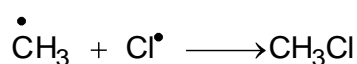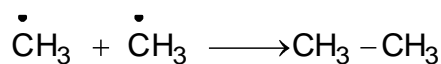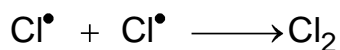
② Nitration:-
  ☞ The reaction takes places by free radicals mechanism at high temp (450^0C).
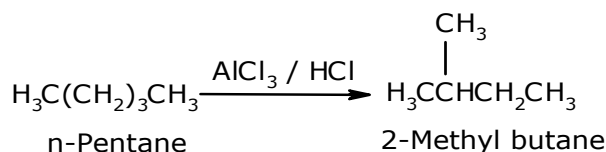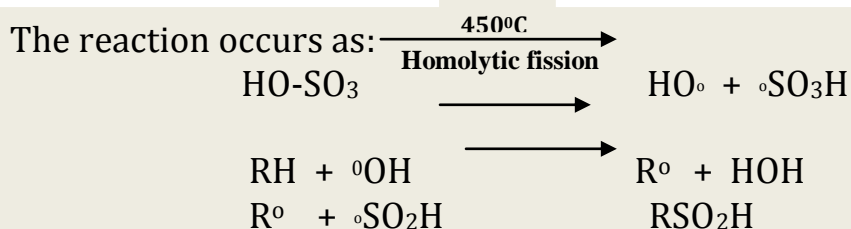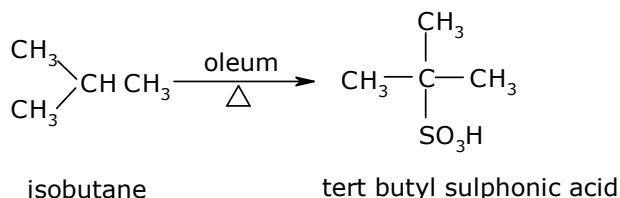 ☞ At high temp C—C bond is also broken so that mixture of nitroalkanes is obtained.
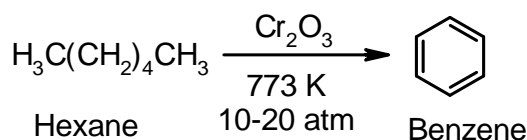
$$CH_3CH_2CH_3 \xrightarrow[Conc.\ HNO_3]{450°C} CH_3CH_2CH_2NO_2 + CH_3CHCH_3 + CH_3CH_2NO_2 + CH_3NO_2$$

NO₂ (on second product): NO_2

25%   40%   10%   25%

The reaction occurs as:

$$HO\text{-}NO_2 \xrightarrow[\textbf{Homolytic fission}]{\textbf{450}^\textbf{0}\textbf{C}} HO_\circ + {}_\circ NO_2$$

$$RH + {}^0OH \longrightarrow R^o + HOH$$
$$R^o + {}_\circ NO_2 \longrightarrow RNO_2$$
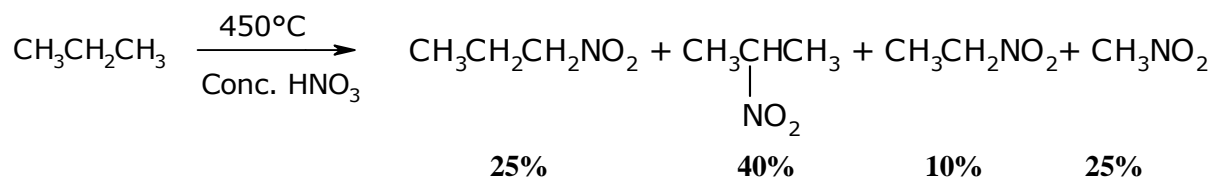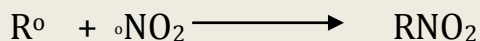
③ Sulphonation:- replacement of hydrogen atom of alkane by –SO$_3$H group.

      isobutane   tert butyl sulphonic acid

The reaction occurs as: $\xrightarrow[\textbf{Homolytic fission}]{\textbf{450}^\textbf{0}\textbf{C}}$

$$HO\text{-}SO_3 \longrightarrow HO_\circ + {}_\circ SO_3H$$

$$RH + {}^0OH \longrightarrow R^o + HOH$$
$$R^o + {}_\circ SO_2H \longrightarrow RSO_2H$$

$$H_3C(CH_2)_3CH_3 \xrightarrow{AlCl_3 / HCl} H_3CCHCH_2CH_3 \ (\overset{\overset{\textstyle CH_3}{|}}{})$$

     n-Pentane   2-Methyl butane

❺ Aromatization:-

$$H_3C(CH_2)_4CH_3 \xrightarrow[\substack{773 \text{ K} \\ 10\text{-}20 \text{ atm}}]{Cr_2O_3} \text{(Benzene ring)}$$

     Hexane   Benzene

This method is also called dehydrogenation or hydroforming
Similarly, heptane gives toluene, n-Octane give o-xylene and 2, methyl heptane give m-xylene.

❻ Thermal decomposition or Pyrolysis or cracking or Fragmentation: - when higher alkanes are heated at high temp (about 700-800k) in the presence of alumina or silica catalysts, the alkanes break down to lower alkanes and alkenes.
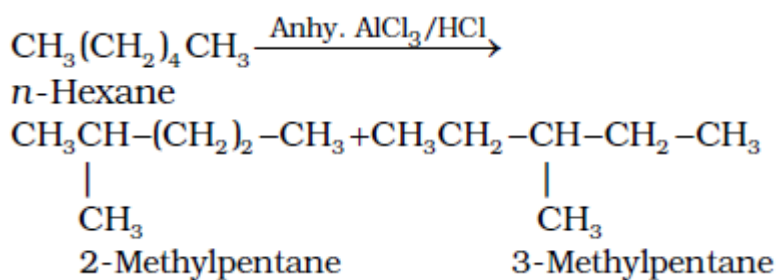
$$CH_3\text{-}CH_2\text{-}CH_3 \longrightarrow CH_3\text{-}CH\text{-}CH_2 + CH_3\text{-}CH_3 + C_2H_4 + CH_4$$
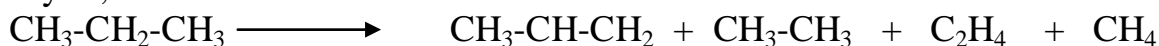
❼ Action of steam:- catalyst: nickel, alumina Al$_2$O$_3$

$$CH_4 + H_2O(\text{Steam}) \xrightarrow{1000\ ^0C} CO + 3H_2$$

This reaction is used for the industrial preparation of hydrogen from natural gas.

8. Isomerisation:-

$$CH_3(CH_2)_4 CH_3 \xrightarrow{\text{Anhy. AlCl}_3/\text{HCl}}$$
n-Hexane
$$CH_3CH-(CH_2)_2-CH_3 + CH_3CH_2-CH-CH_2-CH_3$$
$$\quad\quad | \quad\quad\quad\quad\quad\quad\quad\quad\quad |$$
$$\quad\quad CH_3 \quad\quad\quad\quad\quad\quad\quad\quad CH_3$$
2-Methylpentane   3-Methylpentane

❖ CONFORMATIONAL ISOMERISM:

The different molecular arrangements arising as a result of rotation around carbon carbon single bonds are called conformational isomers or rotational isomers and the phenomenon is called conformational isomerism.

Numerous possible arrangements of ethane are possible. Two extreme conformations are known. These are eclipsed conformation and staggered conformation.

SAWHORSE REPRESENTATION
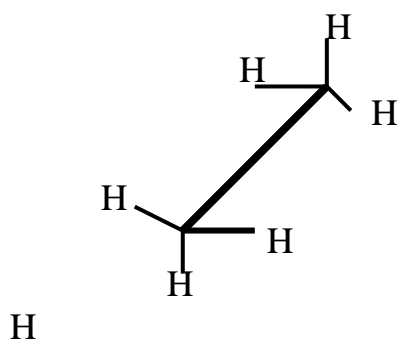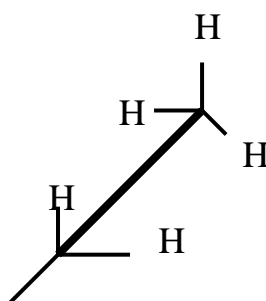
STAGGERED   ECLIPSED

NEWMAN PROJECTION
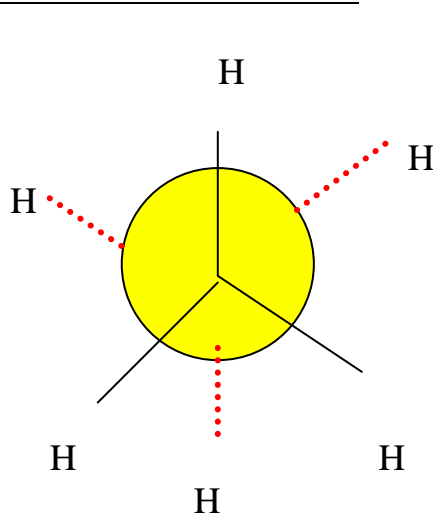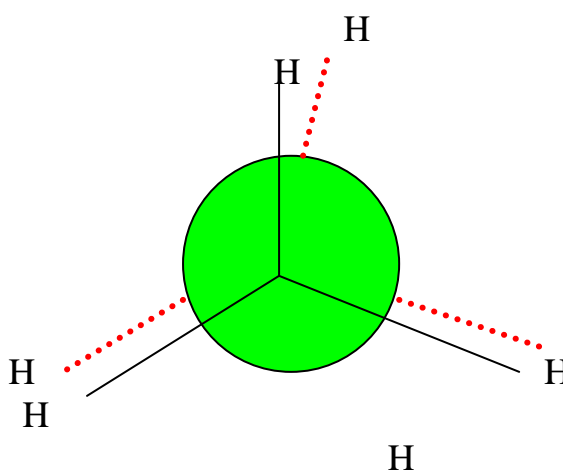
STAGGERED ➡ SKEW ⬅ ECLIPSED

Alkenes

☞ Unsaturated hydrocarbon which have double bond.
☞ General molecular formula C_nH_{2n}
☞ C–C bond hybridization 1.34 A^0
☞ sp^2 hybridization
☞ When we treated Alkene with chlorine, oily products are obtained. So Alkenes are also known as Olefins. (Greek olefiant meaning oil forming).
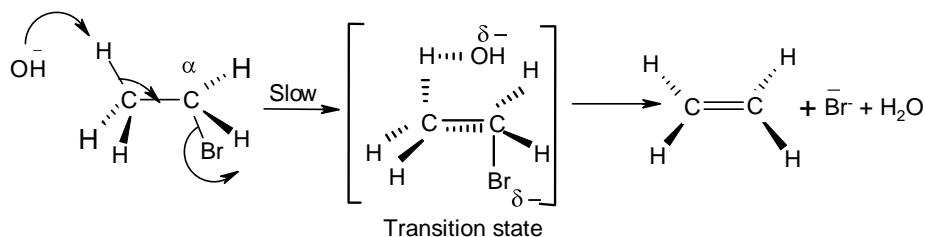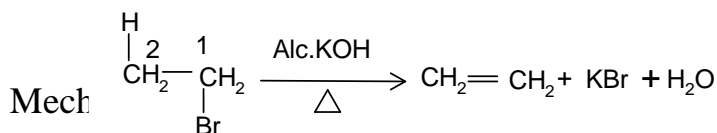☞ Show chain, positional and geometrical isomerism
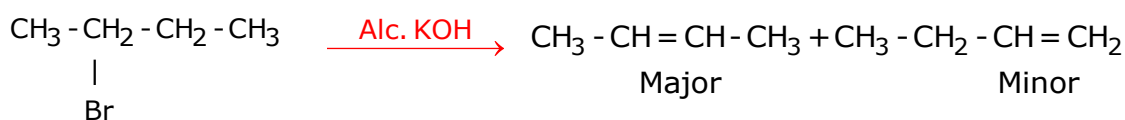❖ Structure of double bond:-

(a)   (b)   (c)
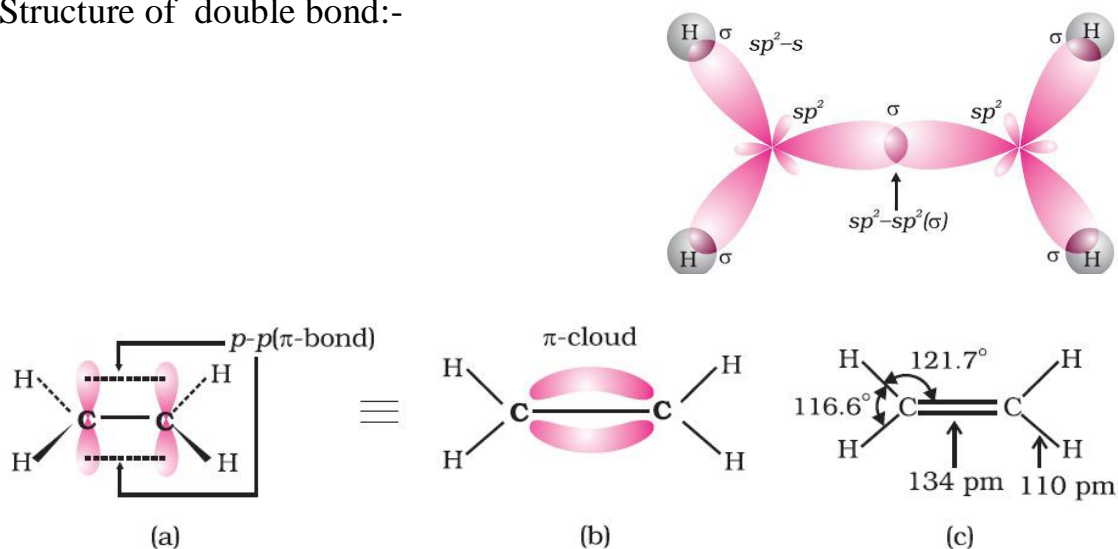
❖ **Preparation:-**

1. From Alkynes:- Alkynes on partial reduction with Partially deactivated palladised charcoal known as *Lindlar's catalyst* give alkynes.
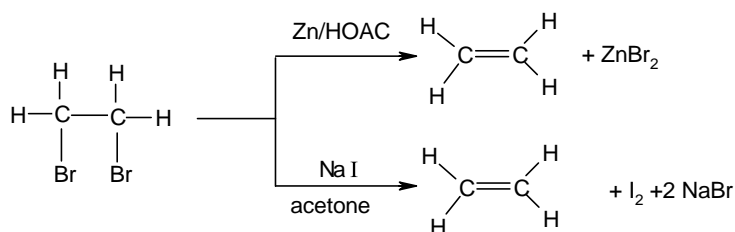
$$CH \equiv CH + H_2 \xrightarrow{Pd/C} CH_2 = CH_2$$
   Ethyne   Ethene
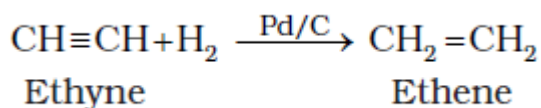
2. From Haloalkanes: - dehydrohalogenation
                    (E_2 or 1,2-elimination or Bita-elimination)

Mech

$$\underset{Br}{\underset{|}{CH_2}} - CH_2 \xrightarrow[\triangle]{Alc.KOH} CH_2 = CH_2 + KBr + H_2O$$
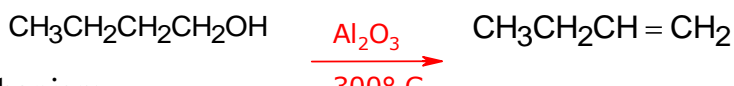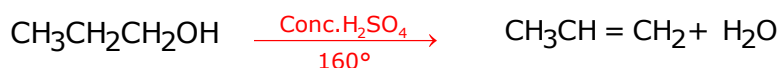

Transition state

➢ predominant formation of a substituted alkene is formed according to Saytzeff's rule

$$\underset{\underset{Br}{|}}{CH_3 - CH_2 - CH_2 - CH_3} \xrightarrow{Alc.\ KOH} CH_3 - CH = CH - CH_3 + CH_3 - CH_2 - CH = CH_2$$

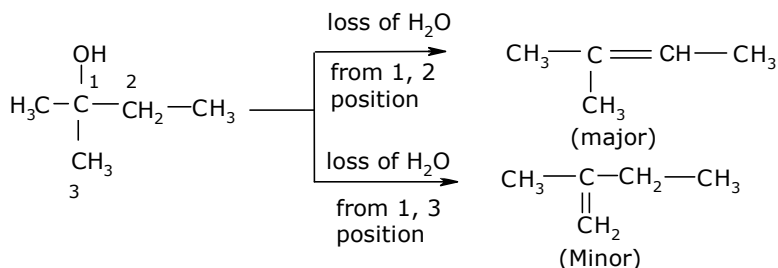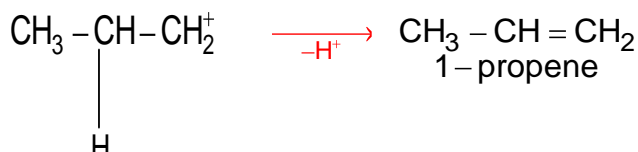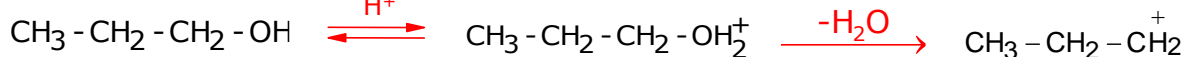   Major   Minor

3. From Dihaloalkanes: - dehalogenation
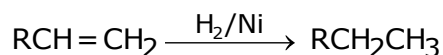

4. From Alcohols:- Dehydration
   (E1 - elimination)

$$CH_3CH_2CH_2OH \xrightarrow[160°]{Conc.H_2SO_4} CH_3CH = CH_2 + H_2O$$

$$CH_3CH_2CH_2CH_2OH \xrightarrow[300° C]{Al_2O_3} CH_3CH_2CH = CH_2$$

Mechanism

$$CH_3-CH_2-CH_2-OH \underset{H^+}{\overset{}{\rightleftharpoons}} CH_3-CH_2-CH_2-OH_2^+ \xrightarrow{-H_2O} CH_3-CH_2-\overset{+}{C}H_2$$

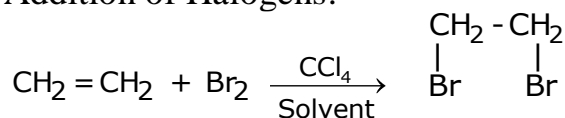$$CH_3-\overset{+}{C}H-CH_2^+ \xrightarrow[-H^+]{} CH_3-CH=CH_2$$
$$| \qquad\qquad 1-propene$$
$$H$$

❖ Chemical Properties:-
❶ Addition Reaction:- Alkene show electrophilic addition reaction.
   1. Addition of Hydrogen:-

   $$RCH = CH_2 \xrightarrow{H_2/Ni} RCH_2CH_3$$

   2. Addition of Halogens:-

   $$CH_2 = CH_2 + Br_2 \xrightarrow[Solvent]{CCl_4} \begin{array}{c} CH_2-CH_2 \\ | \qquad | \\ Br \qquad Br \end{array}$$

   $$CH_2 = CH_2 + Br_2 \xrightarrow[Solvent]{H_2O} Br-CH_2-CH_2-OH + HBr$$
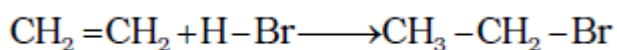
   (Brown colour)   (Colourless)
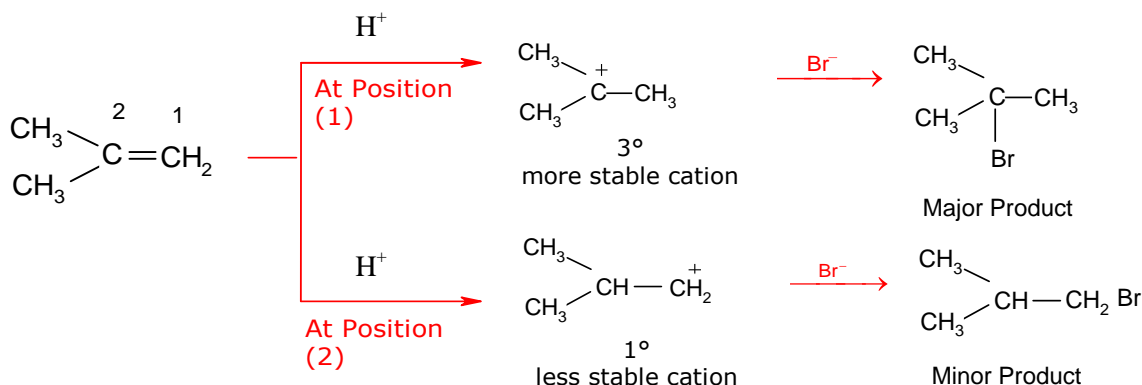
   3. Addition of hydrogen halides-
      Addition reaction of HBr to symmetrical alkenes

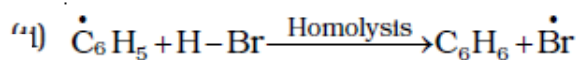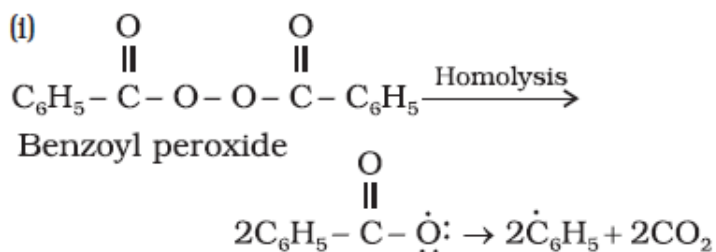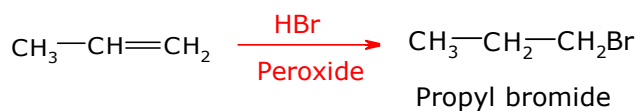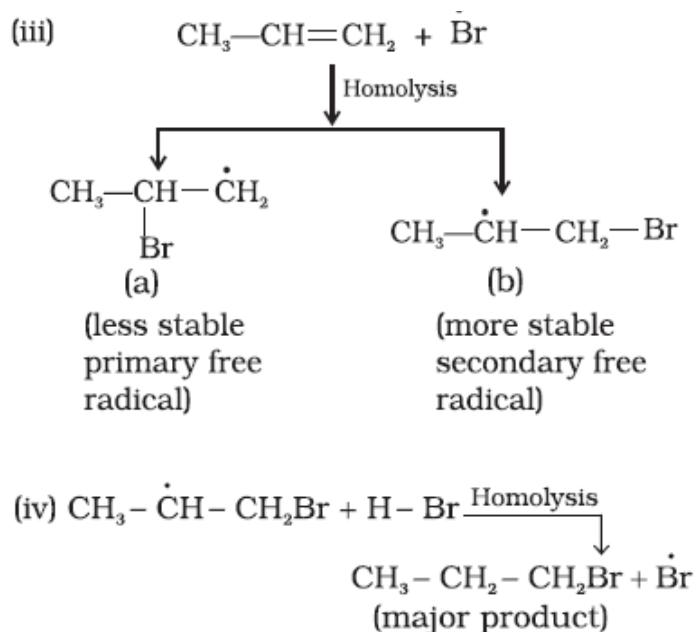$$CH_2 = CH_2 + H - Br \longrightarrow CH_3 - CH_2 - Br$$

Addition reaction of HBr to unsymmetrical alkenes takes place according to Markovnikov Rule

Markownikov rule:- negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses lesser number of hydrogen atoms. e g
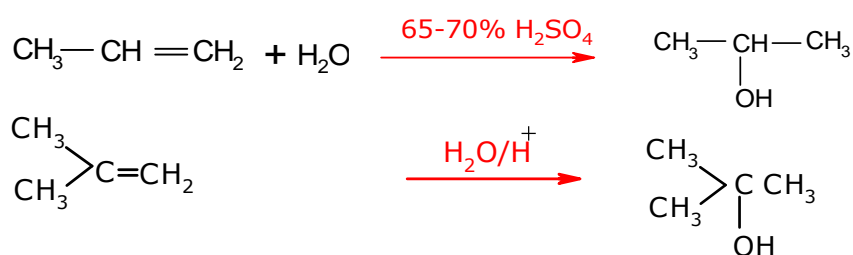

Peroxide effect or Kharasch (Anti Markownikoff's addition):- In 1933 Kharasch and Mayo observed that when HBr is added to an unsymmetrical double bond in the presence of organic peroxide, the reaction take places opposite to the Markovnikov rule.

Propyl bromide

(i)

$$\underset{\text{Benzoyl peroxide}}{C_6H_5 - \overset{O}{\underset{||}{C}} - O - O - \overset{O}{\underset{||}{C}} - C_6H_5} \xrightarrow{\text{Homolysis}}$$

$$2C_6H_5 - \overset{O}{\underset{||}{C}} - \overset{..}{\underset{..}{\dot{O}}}: \rightarrow 2\dot{C}_6H_5 + 2CO_2$$

(ii) $\dot{C}_6H_5 + H - Br \xrightarrow{\text{Homolysis}} C_6H_6 + \dot{B}r$

(iii) $CH_3-CH=CH_2 + \dot{Br}$

Homolysis

$CH_3-CH-\dot{C}H_2$
          |
          Br
(a)
(less stable
primary free
radical)

$CH_3-\dot{C}H-CH_2-Br$
(b)
(more stable
secondary free
radical)

(iv) $CH_3-\dot{C}H-CH_2Br + H-Br \xrightarrow{\text{Homolysis}}$

$CH_3-CH_2-CH_2Br + \dot{Br}$
(major product)

Noted:- peroxide effect is applicable only to HBr and not to HF, HCl and HI. Addition of HF, HCl and HI takes place according to Markovnikov's rule even in the presence of peroxide.
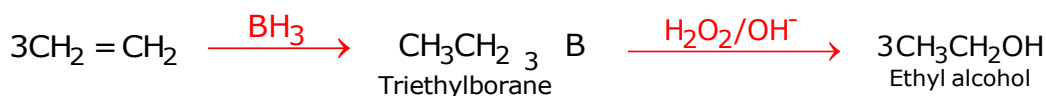
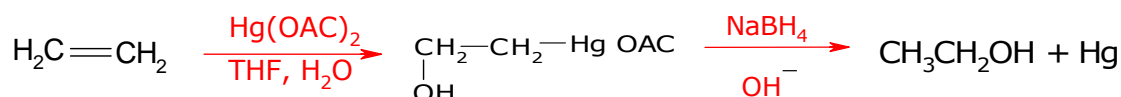4. **Addition of water (Hydration):-** Acid catalyzed addition of water

$CH_3-CH=CH_2 + H_2O \xrightarrow{\text{65-70\% } H_2SO_4}$ $CH_3-CH-CH_3$
                                                                    |
                                                                    OH

$\begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>C=CH_2 \xrightarrow{H_2O/H^+} \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!>\underset{\underset{OH}{|}}{C}\,CH_3$
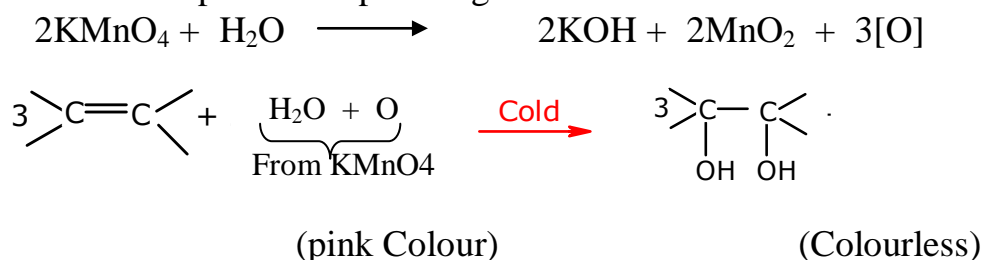
❷ Oxidation:-

① Combustion:- $CO_2 + H_2O$

② Hydroboration–oxidation:- Alkanes react with diborane to form trialkyl boranes which on oxidation with alkaline H_2O_2 give alcohols.

$3CH_2=CH_2 \xrightarrow{BH_3} (CH_3CH_2)_3 B \xrightarrow{H_2O_2/OH^-} 3CH_3CH_2OH$
                                Triethylborane   Ethyl alcohol

③ Oxymercuration–demercuration:-

$H_2C=CH_2 \xrightarrow[THF, H_2O]{Hg(OAC)_2} \underset{\underset{OH}{|}}{CH_2}-CH_2-Hg\,OAC \xrightarrow[OH^-]{NaBH_4} CH_3CH_2OH + Hg$

④ Oxidation with potassium permanganate:-

$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$

$3\!\!>\!C=C\!\!<\ + \underbrace{H_2O + O}_{\text{From KMnO4}} \xrightarrow{\text{Cold}} 3\!\!>\!\!\underset{\underset{OH}{|}}{C}-\underset{\underset{OH}{|}}{C}\!\!<\ .$

(pink Colour)   (Colourless)

> This reaction is also called *Hydroxylation*
> *Cis product I.e. cis*-diol is obtained.

Noted:- The alkaline potassium permanganate solution is known as Baeyer's reagent. It has bright pink colour. It oxidizes alkenes to glycols which is colourless. This reaction is used as a test for the presence of double bond in a molecule. This is also known as Baeyer test.

$$CH_3-CH=CH_2 \xrightarrow[\text{(ii) } H^+ \Delta]{\text{(i) Alk.KMnO}_4} CH_3COOH + CO_2 + H_2O$$
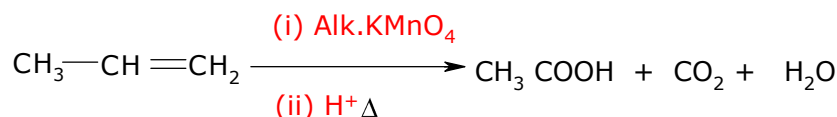
☺ Oxidation with Ozone:- Ozonolysis – give carbonyls compounds

Ozonide
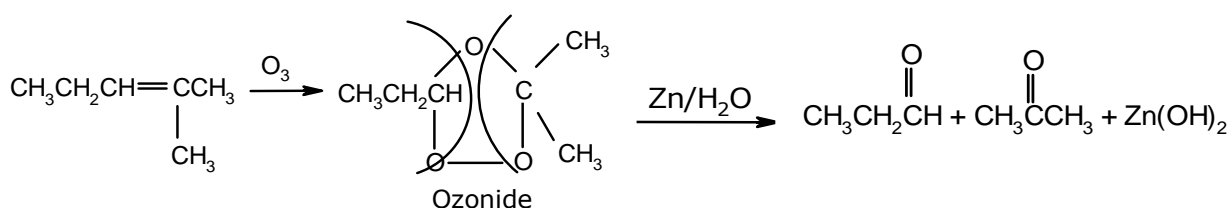
Noted:- Bromine water test and Baeyer's test are used to detect the presence of double bond while ozonolysis is used to detect the position of double bond.

Alkynes
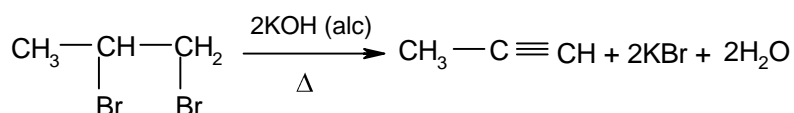
☞ Unsaturated hydrocarbon which have triple bond.
☞ General molecular formula C_nH_{2n-2}
☞ sp hybridization
☞ Shows chain, positional and functional isomerism

❖ Preparation:-

From vicinal dihalides: - dehalogenation

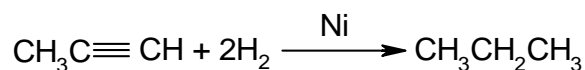By the action of water on calcium carbide:-

$$CaC_2 + H_2O \rightarrow HC \equiv CH + Ca(OH)_2$$

❖ Chemical Properties:-

❶ Addition Reaction:- Alkyne show electrophilic addition reaction.

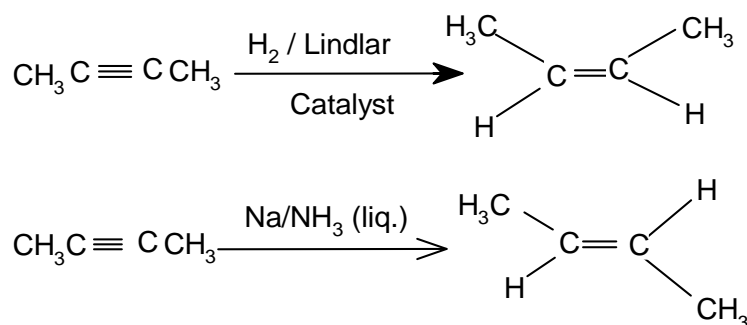① Addition of Hydrogen:- Hydrogenation.

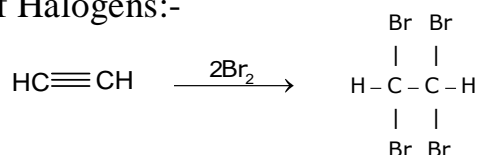$$CH_3C \equiv CH + 2H_2 \xrightarrow{Ni} CH_3CH_2CH_3$$

Propyne

Noted:- It may be noted that the hydrogenation can be controlled at the alkene stage only. This is possible by using a *Lindlar's catalysts* or *sodium in liquid NH₃* at 200k temp..
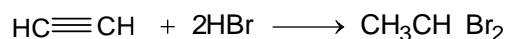
Noted:- It may be again noted that the catalytic reduction of alkynes in the presence of Lindlar's catalyst gives cis-alkenes while in the presence of sodium in liquid NH_3 (Birch reduction) gives trans-alkenes.
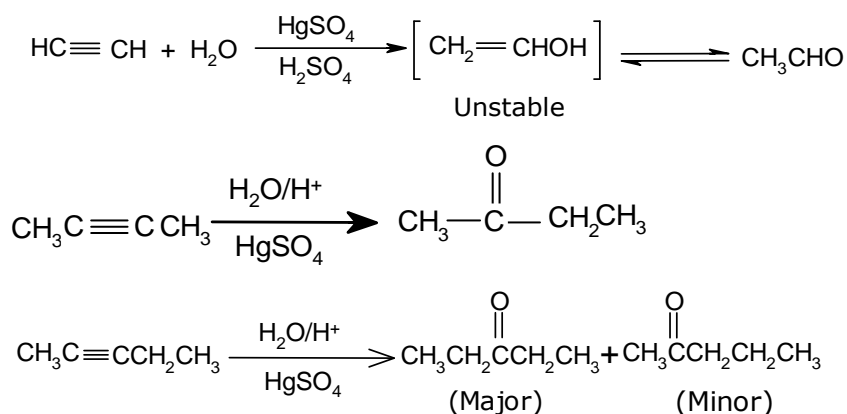
$$CH_3C \equiv C\,CH_3 \xrightarrow[\text{Catalyst}]{H_2 / \text{Lindlar}}$$

$$\underset{H}{\overset{H_3C}{>}}C=C\underset{H}{\overset{CH_3}{<}}$$

$$CH_3C \equiv C\,CH_3 \xrightarrow{\text{Na/NH}_3 \text{ (liq.)}}$$

$$\underset{H}{\overset{H_3C}{>}}C=C\underset{CH_3}{\overset{H}{<}}$$

② Addition of Halogens:-

$$HC \equiv CH \xrightarrow{2Br_2}$$

$$\begin{array}{c} Br\ \ Br \\ |\ \ | \\ H-C-C-H \\ |\ \ | \\ Br\ \ Br \end{array}$$

③ Addition of hydrogen halides:-

$$HC \equiv CH \ + \ 2HBr \longrightarrow CH_3CH\ Br_2$$

④ Addition of water (Hydration):- Acid catalyzed addition of water

$$HC \equiv CH + H_2O \xrightarrow[\text{H}_2\text{SO}_4]{\text{HgSO}_4} \left[CH_2 = CHOH \right] \rightleftharpoons CH_3CHO$$

Unstable

$$CH_3C \equiv C\,CH_3 \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{O/H}^+} CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2CH_3$$

$$CH_3C \equiv CCH_2CH_3 \xrightarrow[\text{HgSO}_4]{\text{H}_2\text{O/H}^+} CH_3CH_2\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_3 + CH_3\overset{\overset{\displaystyle O}{\|}}{C}CH_2CH_2CH_3$$
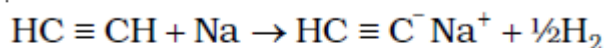
(Major)   (Minor)
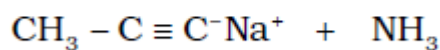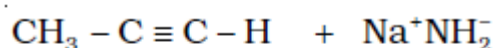
5. Polymerisation-
    a. ***Linear polymerisation***: of ethyne gives polyacetylene or polyethyne which is a high molecular weight polyene containing repeating units of $(CH = CH – CH = CH)$ and can be represented as —$(CH = CH – CH = CH)n$ —
    b. Cyclic polymerization- results in the formation of aromatic compound.
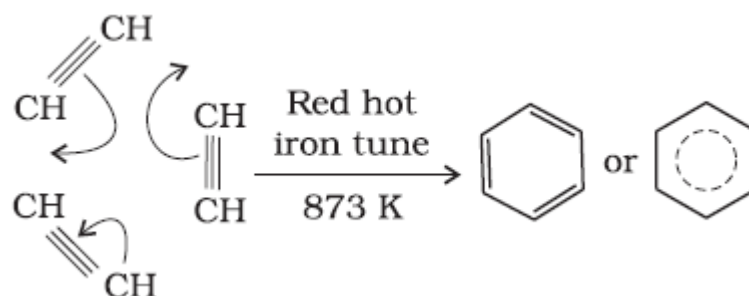
Acidity of Alkynes- Terminal alkynes are acidic in nature.

$$HC \equiv CH + Na \rightarrow HC \equiv C^- Na^+ + \frac{1}{2}H_2$$

Monosodium
ethynide

$$CH_3 - C \equiv C - H \quad + \quad Na^+NH_2^-$$
$$\downarrow$$
$$CH_3 - C \equiv C^- Na^+ \quad + \quad NH_3$$

Sodium propynide

Alkanes, alkenes and alkynes follow the following trend in their acidic behaviour :

i) $HC \equiv CH > H_2C = CH_2 > CH_3 - CH_3$

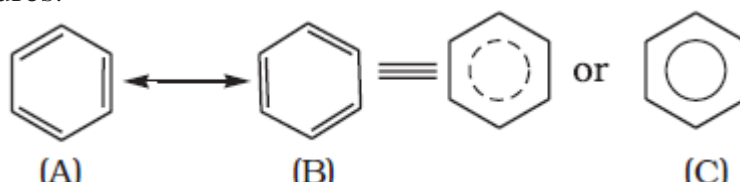ii) $HC \equiv CH > CH_3 - C \equiv CH >> CH_3 - C \equiv C - CH_3$

AROMATIC HYDROCARBON

Aromatic compounds containing benzene ring are known as **benzenoids** and those not containing a benzene ring are known as **non-benzenoids**.
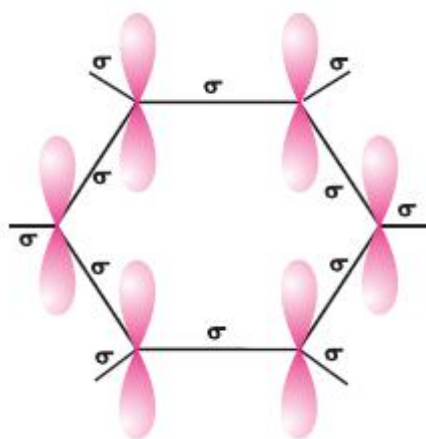
Structure of Benzene-   Kekulé structure
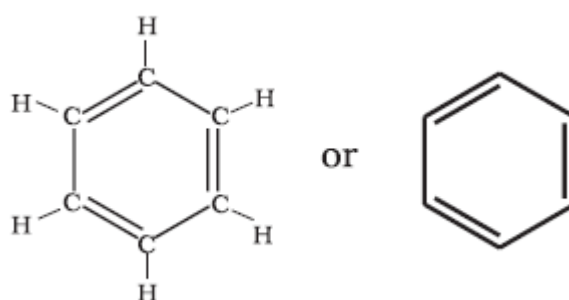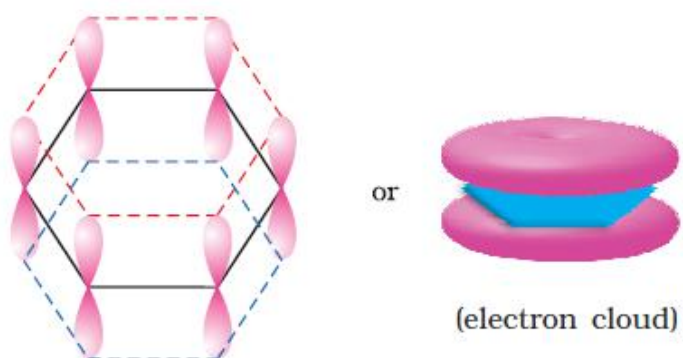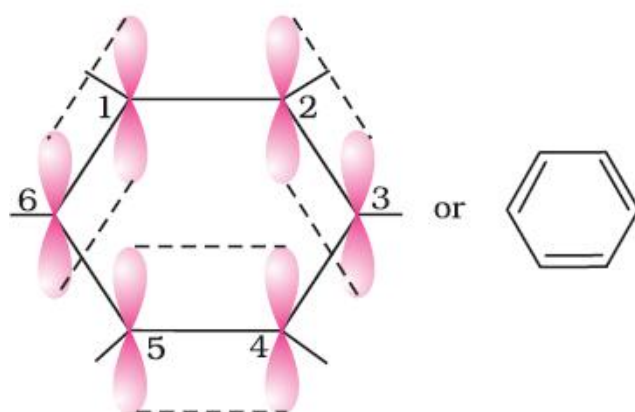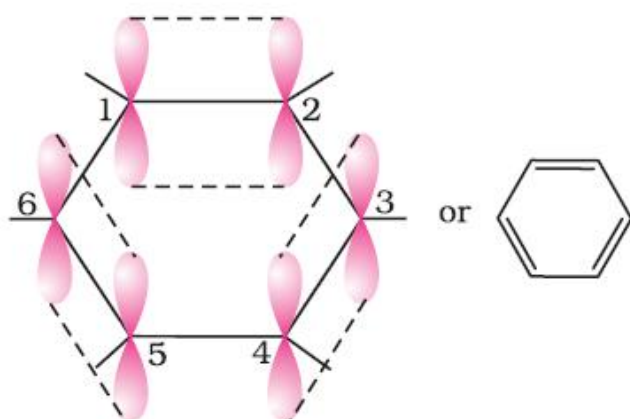

Resonance and stability of benzene-Benzene is a hybrid of various resonating structures.

The orbital overlapping picture benzene- All the six carbon atoms in benzene are sp^2 hybridized and these hybrid orbitals form sigma bonds.

The unhybridised p orbital of carbon atoms are close enough to form a π bond by lateral overlap.


(electron cloud)

The six π electrons are thus delocalised and can move freely about the six carbon nuclei. The delocalised π electron cloud is attracted more strongly by the nuclei of the carbon atoms than the electron cloud localized between two carbon atoms. Therefore, presence of delocalised π electrons in benzene makes it more stable .

Aromaticity:- The compounds that follow the following features are to be considered aromatic.
   (i) Planarity
     (ii) Complete delocalisation of the π electrons in the ring
     (iii) Presence of $(4n + 2)$ π electrons in the ring where n is an integer ($n = 0, 1, 2, \ldots$). This is often referred to as **Hückel Rule**.

Preparation of Benzene:
  (i) Cyclic polymerisation of ethyne:
  (ii) Decarboxylation of aromatic acids:
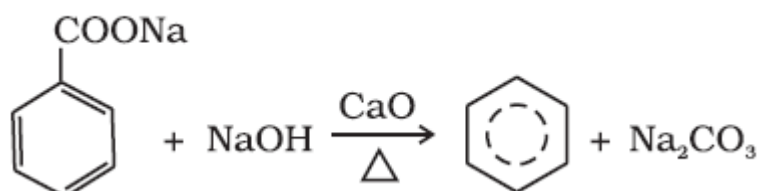
 (iii) *Reduction of phenol:* Phenol is reduced to benzene by passing its vapours over heated zinc dust
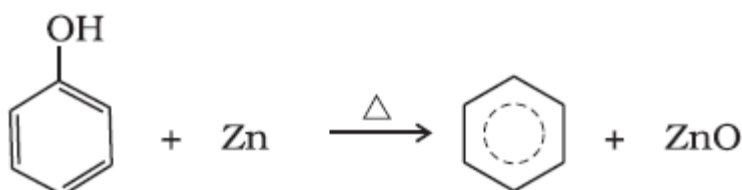
Physical properties:
1. Aromatic hydrocarbons are non- polar molecules and are usually colourless liquids or solids with a characteristic aroma.
2. Aromatic hydrocarbons are immiscible with water but are readily miscible with organic solvents.
3. They burn with sooty flame.

Chemical properties
Arenes are characterised by electrophilic substitution reactions proceed via the following three steps:
(a) Generation of the eletrophile
(b) Formation of carbocation intermediate
(c) Removal of proton from the carbocation intermediate

Nitration

Conc.HNO_3+Conc.H_2SO_4

Nitrobenzene

Halogenation

+Cl_2

Anhyd. $AlCl_3$

Chloro benzene

Sulphonation

Fuming sulphuric acid
$H_2SO_4(SO_3)$

Benzene
sulphonic acid

Friedel-Crafts alkylation

+C_2H_5Cl
Anhyd. $AlCl_3$

Ethyl benzene

Friedel-Crafts acylation

+CH_3COCl
Anhyd. $AlCl_3$

acetphenone
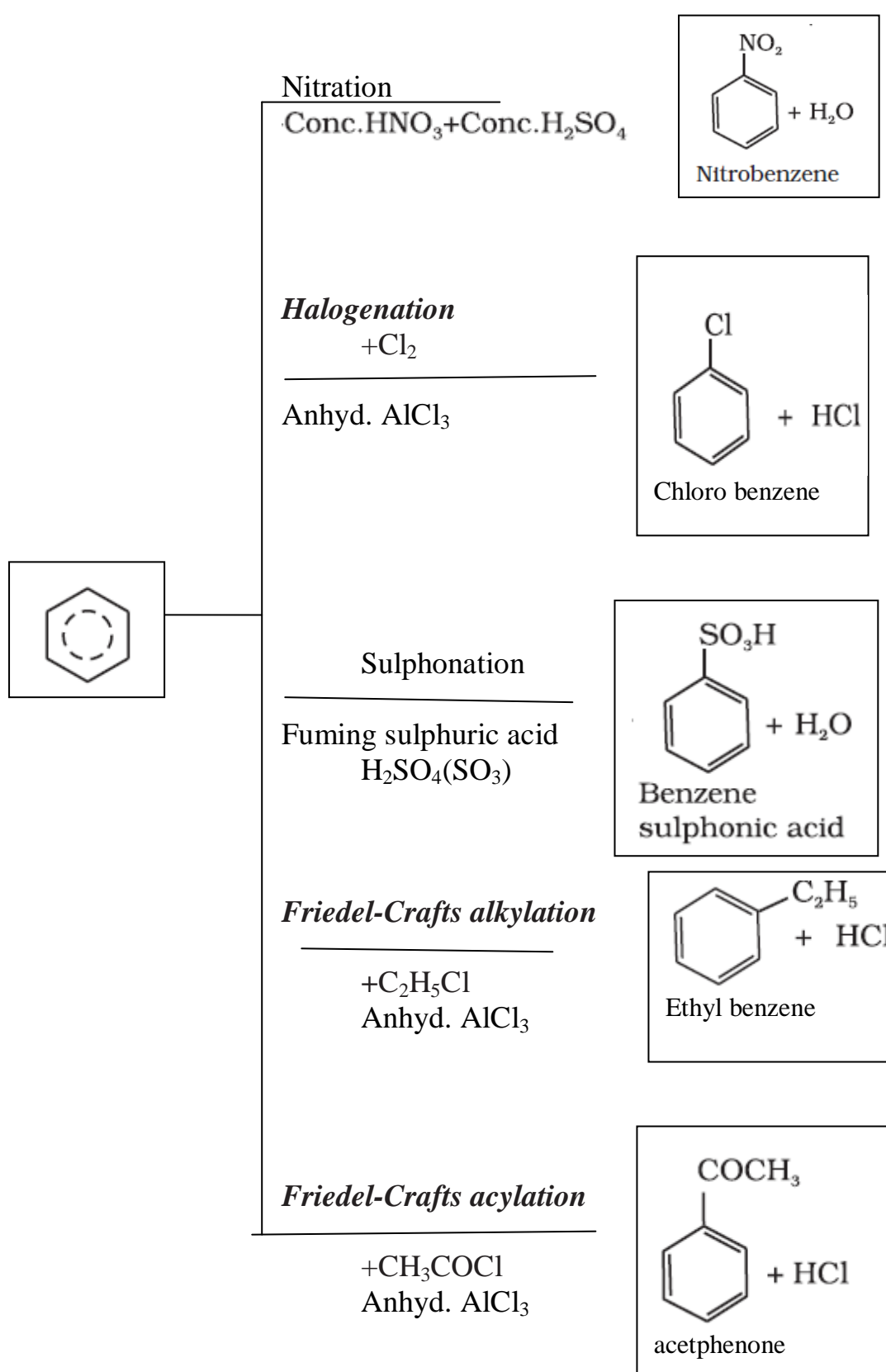
benzene ontreatment with excess of chlorine in the presence of anhydrous AlCl3 in dark yields hexachlorobenzene (C_6Cl_6)

Hexachlorobenzene
(C₆Cl₆)
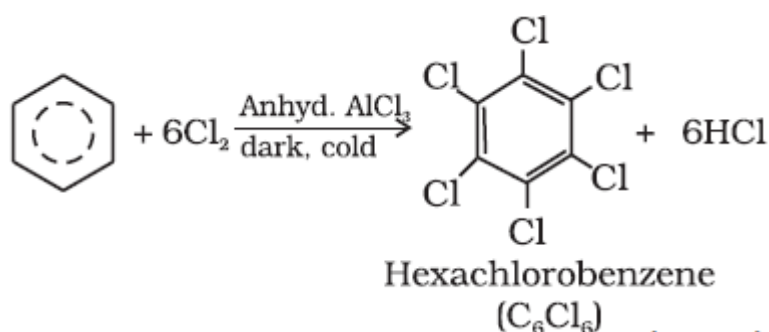
Addition reactions of benzene-

Cyclohexane

Benzene hexachloride,
(BHC)
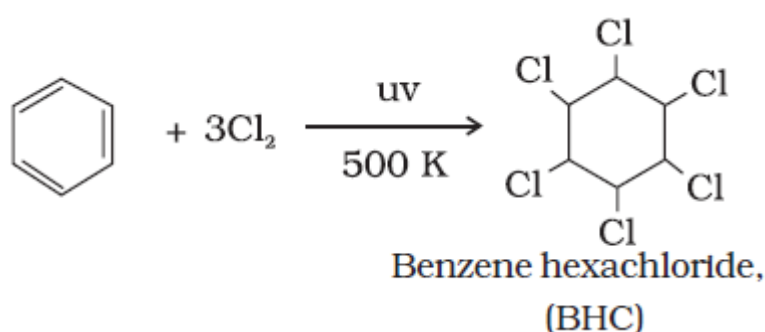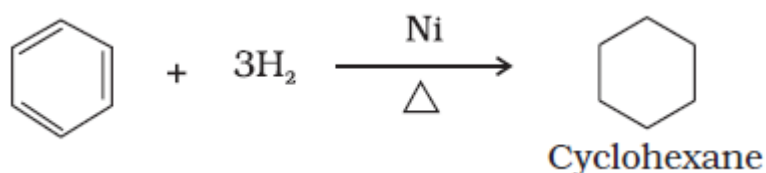
Directive influence of a functional group in monosubstituted benzene:-

1. Ortho and para directing groups and activating- –OH, –NH₂, –NHR, – NHCOCH₃, –OCH₃, –CH₃, –C₂H₅, etc.

   I   II   III   IV   V
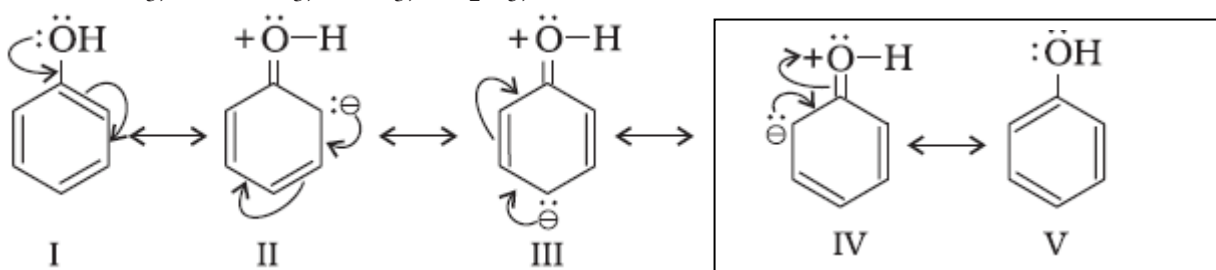
2. *Meta directing group and deactivating:*–NO₂, –CN, –CHO, –COR, –COOH, – COOR, –SO₃H, etc.

   I   II   III   IV   V
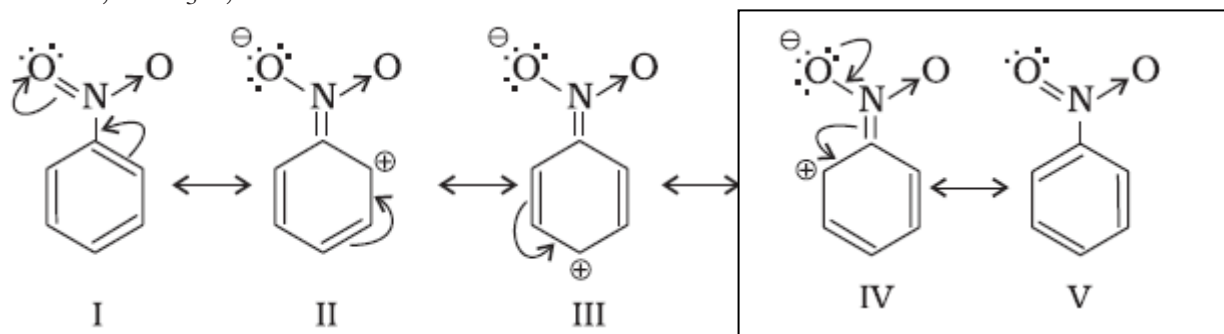
3. Ortho and para directing groups and deactivating- Halogens because of their strong – I effect, overall electron density on benzene ring decreases. However,

due to resonance the electron density on *o–* and *p–* positions is greater than that at the *m*-position. Hence, they are also *o–* and *p–* directing groups.

CARCINOGENICITY AND TOXICITY-Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) property.

ONE MARK QUESTIONS

1. What are hydrocarbons?
   Ans. Compounds of hydrogen and carbon.
2. What is the general formula of alkanes?
   Ans. C_nH_{2n+2}
3. Write the general formula of alkenes.
   Ans. C_nH_{2n}
4. What is the general formula of alkynes?
   Ans. C_nH_{2n-2}
5. Give the IUPAC name of lowest molecular weight alkane that contains a quaternary carbon.
   Ans. 2,2dimethylpropane.
6. Arrange the following in the increasing order of C-C bond length-
   C_2H_6 C_2H_4 C_2H_2
   Ans. C_2H_2 $< C_2H_4 < C_2H_6$
7. Out of ethylene and acetylene which is more acidic and why?
   Ans. Acetylene, due to greater electonegativity of the sp hybrid carbon.
8. Name two reagents which can be used to distinguish between ethene and ethyne.
   Ans.Tollen's reagent and ammonical CuCl solution.
9. Arrange the following in order of decreasing reactivity towards alkanes.
   HCl, HBr, HI, HF
   Ans.HI> HBr> HCl >HF
10. How will you detect the presence of unsaturation in an organic compound?
    Ans. Generally Unsaturated organic compound decolourise Bayer's reagent and Bromine water.
11. What is Grignard reagent?
    Ans. Alkyl magnesium halides

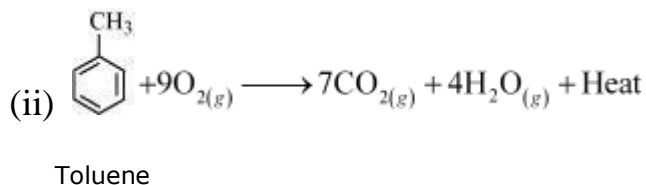## TWO MARKS QUESTIONS

1. Write the IUPAC names of the following-

   a. $CH_2=CH-C\equiv C-CH_3$

   b.
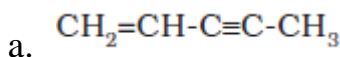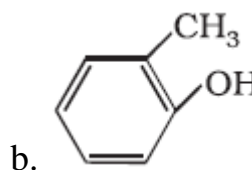
   Ans. a .Pent-en-3-yne   b. 2-methylphenol

2. Write chemical equations for combustion reaction of (i) Butane (ii) Toluene
Ans.

(i) $2C_4H_{10(g)} + 13O_{2(g)} \longrightarrow 8CO_{2(g)} + 10H_2O_{(g)} + \text{Heat}$

.   Butane

(ii)

Toluene

$+9O_{2(g)} \longrightarrow 7CO_{2(g)} + 4H_2O_{(g)} + \text{Heat}$
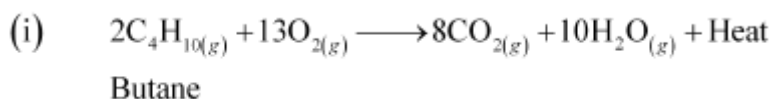
3. What are the necessary conditions for any system to be aromatic?
   Ans. A compound is said to be aromatic if it satisfies the following three conditions: **(i)** It should have a planar structure.
   (ii) The π–electrons of the compound are completely delocalized in the ring.
   (iii)The total number of π–electrons present in the ring should be equal to
   (4n + 2), where n = 0, 1, 2 … etc. This is known as Huckel's rule.

4. What effect does branching of an alkane chain has on its boiling point?
   Ans. As branching increases, the surface area of the molecule decreases which results in a small area of contact. As a result, the Van der Waals force also decreases which can be overcome at a relatively lower temperature. Hence, the boiling point of an alkane chain decreases with an increase in branching.

5. How would you convert the following compounds into benzene?
   (i)   Ethyne (ii) Ethene

Ans. **(i)** Benzene from Ethyne:
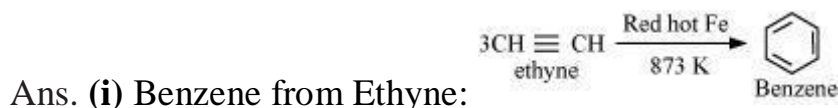
(ii) Benzene from Ethene:
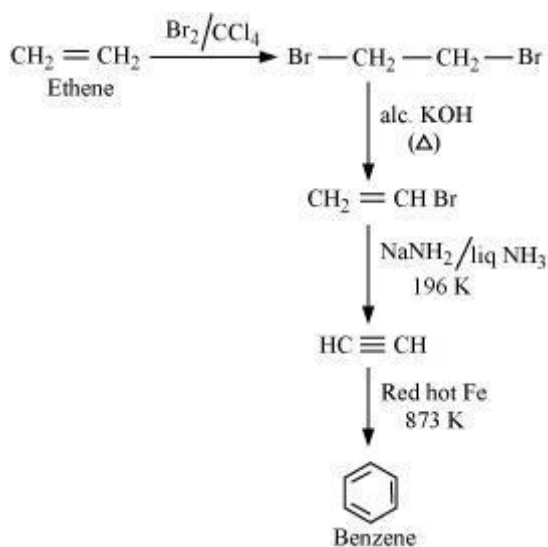
6. Suggest the name of Lewis acids other than anhydrous aluminium chloride which can be used during ethylation of benzene.

   Ans. anhydrous $FeCl_3$, $SnCl_4$, BF_3 etc.

7. Write the name of all the possible isomers of C2H2Cl2 and indicate which of them is non-polar.

   Ans.(i) cis-1,2-dichloroethene   (ii) trans-1,2-dichloroethene   (iii) 1,1-dichloroethene. trans-1,2-dichloroethene is non-polar.

8. Although benzene is highly unsaturated, it does not undergo addition reactions, why?

   Ans. Because of extra stability due to delocalization of π-electrons.

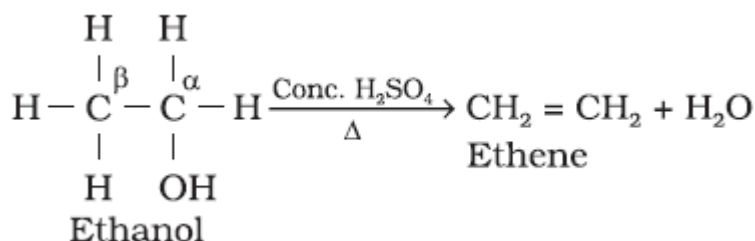9. What are alkanes? Why are they called paraffins?

   Ans. Those hydrocarbons which contain single bond between carbon- carbon are called alkanes. They are called paraffins because they are very less reactive (Latin- Parum= little, affins = affinity)

10. How can ethene be prepared from (i) ethanol (ii) ethyl bromide?

    Ans. (i) Ethene from ethanol- by acidic dehydration of alcohols

$$H-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}{}^{\beta}-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}{}^{\alpha}-H \xrightarrow[\Delta]{\text{Conc. } H_2SO_4} CH_2 = CH_2 + H_2O$$

<div style="text-align:center">Ethanol   Ethene</div>

   (ii)   Ethene from ethyl bromide- by dehydrohalogenation of ethyl bromide

   $CH_3CH_2Br + KOH (alc) \rightarrow H_2C = CH_2 + KBr + H_2O$

THREE MARKS QUESTIONS

1. What is Wurtz reaction? How can it be used to prepare butane?

   Ans- When alkyl halides is treated with metallic Na in presence of dry ether, alkanes are formed. This reaction is called Wurtz reaction.

   Butane is prepared by the reaction of bromoethane with metallic Na in presence of dry ether

   $$C_2H_5Br + 2Na + BrC_2H_5 \xrightarrow{\text{dry ether}} C_2H_5 - C_2H_5$$

   Bromoethane   n-Butane

2. An alkene 'A' contains three C – C, eight C – H σ bonds and one C – C π bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Deduce IUPAC name of 'A'.

   Ans.. The formation of two moles of an aldehyde indicates the presence of identical structural units on both sides of the double bond containing carbon atoms. Hence, the structure of 'A' can be represented as:

           XC = CX

   There are eight C–H σ bonds. Hence, there are 8 hydrogen atoms in 'A'. Also, there are three C–C bonds. Hence, there are four carbon atoms present in the structure of 'A'.

Combining the inferences, the structure of 'A' can be represented as:

(A)
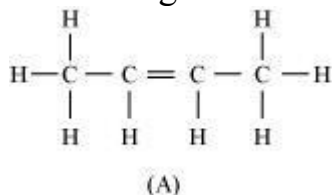
the IUPAC name of 'A' is But-2-ene.
Ozonolysis of 'A' takes place as:

2CH₃CHO
Ethanal
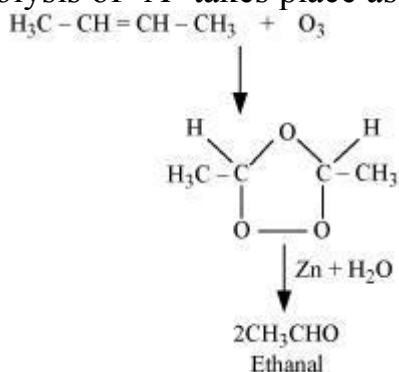
The final product is ethanal with molecular mass

$$= \left[(2 \times 12) + (4 \times 1) + (1 \times 16)\right]$$

$$= 44 \text{ u}$$

3. In the alkane H3C – CH2 – C(CH3)2 – CH2 – CH(CH3)2, identify 1°,2°,3° carbon atoms and give the number of H atoms bonded to each one of these.
Ans.
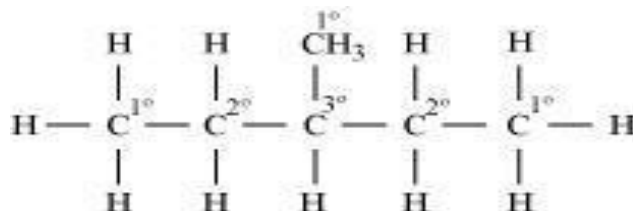
The given structure has five 1° carbon atoms and fifteen hydrogen atoms attached to it.
The given structure has two 2° carbon atoms and four hydrogen atoms attached to it.
The given structure has one 3° carbon atom and only one hydrogen atom is attached to it

<u>FIVE MARKS QUESTIONS</u>

4. Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism

Ans. Addition of HBr to propene is an example of an electrophilic substitution reaction.

Hydrogen bromide provides an electrophile, H^+. This electrophile attacks the double bond to form 1° and 2° carbocations as shown:

$$H_3\overset{3}{C} - \overset{2}{CH} = \overset{1}{CH_2} + H-Br$$

$$\downarrow H^+$$

$$H_3C - CH_2 - \overset{+}{CH_2} + Br^- \qquad H_3C - \overset{+}{CH} - CH_3 + Br^-$$

(Less stable)   (More stable)
primary carbocation   secondary carbocation

Secondary carbocations are more stable than primary carbocations. Hence, the former predominates since it will form at a faster rate. Thus, in the next step, Br^- attacks the carbocation to form 2 − bromopropane as the major product.

$$H_3C - \overset{+}{CH} - CH_3 + Br^- \longrightarrow CH_3 - \underset{\underset{Br}{|}}{CH} - CH_3$$
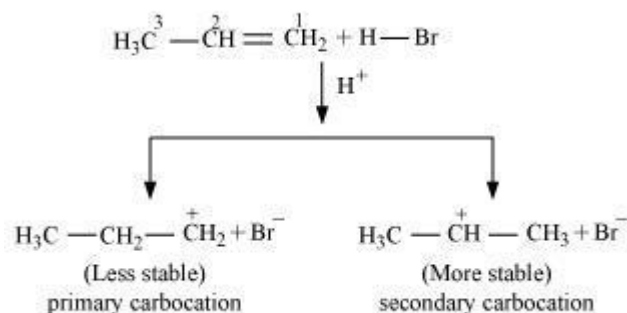
2 − Bromopropane
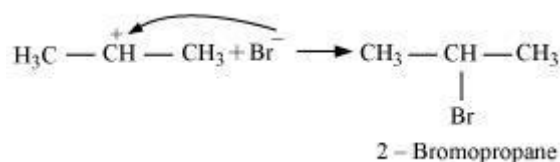
This reaction follows Markovnikov's rule

In the presence of benzoyl peroxide, an addition reaction takes place anti to Markovnikov's rule. The reaction follows a free radical chain mechanism as:

$$C_6H_5 - \underset{\underset{O}{\|}}{C} - O - O - \underset{\underset{O}{\|}}{C} - C_6H_5$$

$$\downarrow \text{Homolysis}$$

$$2C_6H_5 - \underset{\underset{O}{\|}}{C} - \ddot{\underset{..}{O}}: \longrightarrow 2\dot{C}_6H_5 + 2CO_2$$

$$\dot{C}_6H_5 + H - Br \xrightarrow{\text{Homolysis}} C_6H_5 + \dot{Br}$$

$$CH_3 - CH = CH_2 + \dot{Br}$$

$$\downarrow \text{Homolysis}$$

$$CH_3 - \underset{\underset{Br}{|}}{CH} - \dot{CH_2} \qquad\qquad CH_3 - \dot{CH} - CH_2 - Br$$

(Less stable   (More stable
primary free radical)   secondary free radical)
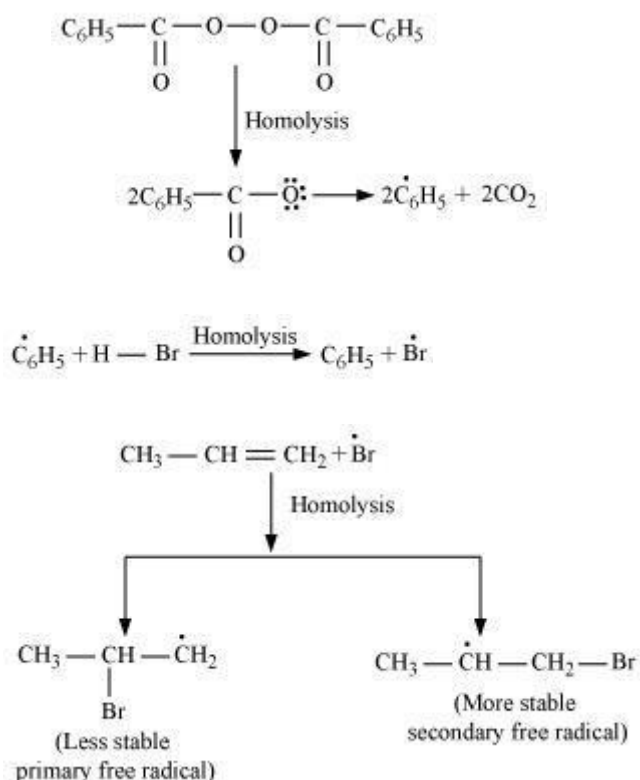
Secondary free radicals are more stable than primary radicals. Hence, the former predominates since it forms at a faster rate. Thus, 1 – bromopropane is obtained as the major product.

$$CH_3 - \overset{\bullet}{CH} - CH_2Br + H - Br$$

$$\xrightarrow{\text{Homolysis}} CH_3 - CH_2 - CH_2Br + \overset{\bullet}{Br}$$

1 – Bromopropane
major product
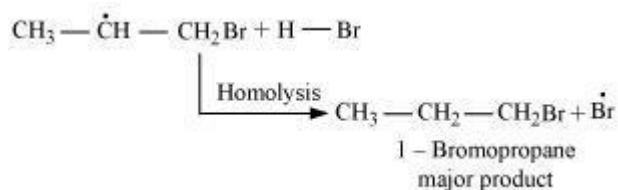
HOTS QUESTIONS

1. How will you demonstrate that double bonds of benzene are somewhat different from that of olefins?
   Ans. The double bonds of olefins decolourize bromine water and discharge the pink colour of Bayer's reagent while those of benzene not
2. How will you separate propene from propyne?
   Ans. By passing the mixture through ammonical silver nitrate solution when propyne reacts while propene passes over.
3. Write is the structure of the alkene which on reductive ozonolysis gives butanone and ethanol,
   Ans.-$CH_3CH_2C(CH_3)=CHCH_3$

CHAPTER 14

ENVIRONMENTAL CHEMISTRY

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

- ENVIRONMENTAL POLLUTION:-Environmental pollution is the effect of undesirable changes in our surroundings that have harmful effects on plants, animals and human beings.A substance which causes pollution is called a pollutant.they can be solid,liquid or in the gaseous state.

- ATMOSPHERIC POLLUTION:-The atmosphere that surrounds the earth is not of the same thickness at different heights.Atmospheric pollution is generally studied as tropospheric and stratospheric pollution.The ozone layer prevents about 99.5% of the sun's UV rays.

- TROPOSPHERIC POLLUTION:-Tropospheric pollution occurs due to the presence of undesirable solid or gaseous particles in the air. The following are the major gaseous and particulate pollutants present in the troposphere;

  - Gaseous air pollutants:These are oxides of sulphur, nitrogen and carbon, hydrogen sulphide, hydrocarbons, ozone and other oxidants.
  - Particulate pollutants; these are dust, mist, fumes, smoke, smog etc

- GLOBAL WARMING AND GREENHOUSE EFFECT:-About 75% of the solar energy reaching the earth is absorbed by the earth's surface,which increases it's temperature.The rest of the heat radiates back to the atmosphere.Some of the heat is trapped by the gases such as carbon dioxide,methane,ozone,CFCS and Water vapour.they add to the heating of the atmosphere causing Global warming

  In a greenhouse,visible light passes through the transparent glass and heats up the soil and the plants.The warm soil and plants emit infrared rays,it partly reflects and partly absorbs these radiations,this mechanism keeps the energy of the sun trapped in the greenhouse.

- ACID RAIN:When the pH of the rain water drops below5.6, it is called acid rain.Acid rain is harmful for agriculture, trees and plants as it dissolves and washes away nutrients needed for their growth. It causes respiratory ailments

in human beings and animals. When acid rain falls and flows as ground water to reach rivers, lakes etc. it affects plants and animal life in aquatic ecosystem

- SMOG:The word smog is derived from smoke and fog.There are two types of smog:classical and photochemical smog. Classical smog occurs in cool humid climate. It is a mixture of smoke, fog and sulphur dioxide. It is also called reducing smog. Whereas photochemical smog occurs in warm and dry sunny climate. It has high concentration of oxidizing agents and therefore ,it is also called as oxidizing smog

- OZONE HOLE:Depletion of ozone layer is known as ozone hole.

- EFFECTS OF DEPLETION OF THE OZONE LAYER: With the depletion of ozone layer, more UV radiation filters into troposphere. UV radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplanktons, damage to fish productivity etc
- WATER POLLUTION:-contamination of water by foreign substances which make it harmful for health of animals or plants or aquatic life and make it unfit for domestic, industrial and agriculture use.

- SOURCES/ CAUSES OF WATER POLLUTION-
  - Sewage and domestic wastes
  - Industrial effluents
  - Agriculture effluents
  - Siltation-mixing of soil or rock into water
  - Thermal pollutants
  - Radioactive discharge
- EUTROPHICATION:The process in which nutrientenriched water bodies support a dense plantpopulation, which kills animal life by deprivingit of oxygen and results in subsequent loss ofbiodiversity is known asEutrophication

- BOD: The amount of oxygen required by bacteria to break down the organic matter present in a certain volume of a sample of water, is called Biochemical Oxygen Demand (BOD)

- SOIL POLLUTION:Insecticides, pesticides and herbicides cause soil pollution.

● GREEN CHEMISTRY:Green chemistry us a way of thinking and is about utilizing the existing knowledge and principles of chemistry and other sciences to reduce the adverse impact on environment.Green chemistry is a production process that would bring out minimum pollution or deterioration to the environment..Utilization of existing knowledge base for reducing the chemical hazards along with the development of activities is the foundation of green chemistry.

ONE MARK QUESTION

1. What is the name of the compound formed when CO combines with blood?
   Ans:-Carboxyhaemoglobin.
2. Which zone is known as ozonosphere?
   Ans:-Stratosphere.
3. Which main gas esis responsible for damage in ozone layer?
   Ans:-NO and CFCs(freons).
4. What is the nature of classical smog?
   Ans:-Reducing
5. Name the acids which are responsible for acid rain?
   Ans:-H_2SO_4,HNO_3 and HCl.
6. List out the gasses which are considered as major source of air pollution?
   Ans:-Carbon monoxide(CO),sulphur dioxide(SO_2)and oxides of nitrogen(NO_2).
7. What is PAN stands for?
   Ans:-It is peroxyacetyl nitrate.
8. Give the examples of insecticides?
   Ans:-DDT,BHC.
9. Which gas is mainly responsible for BHOPAL gas tragedy?
   Ans:-Methyl isocyanate.
10. What should be the tolerable limit of F^- ions in drinking water?
    Ans:-1ppm or 1mg dm^{-3}.

TWO MARKs QUESTION

1. What is 'acid rain'? How is it harmful to the environment?
   Ans:-Acid rain is the rain water mixed with small amount of sulphuric acid, nitric acid along with hydrochloric acid which are formed from the oxides of sulphur and nitrogen present in air as pollutants.It has a pH of 4-5.
   Harmful effects of acid rain:-
   It is toxic to vegetation and aquatic life.
   It damages buildings and status

2. What do youmean byGreen house effect ?What is the role of CO_2 in the greenhouse effect.
   Ans:-It is the phenomenon in which earth's atmosphere traps the heat from the sun and prevents it from escaping in outer space. Gases such as CO_2 ,methane,ozone,CFCs are believed to be responsible for this effect.
   Heat from the sun after being absorbed by the earth absorbed by CO_2 and then radiated back to the earth.Thus making the environment of the earth warm.

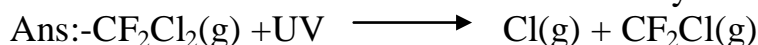3. Which gases are responsible for greenhouse effect?List some of them.
   Ans:-CO_2 is mainly responsible for greenhouse effect.Other greenhouse gases are methane nitrous oxide, water vapours.

4. What is smog?How is classical smogdifferent from photochemical smog?
   Ans:-The word smog is a combination of smoke andfog.It is a type of air pollution that occurs in many cities throughoutthe world.Classical smog occurs in cool humid climate.It is also called reducing smog.
   Whereas photochemical smog occurs in warm and dry sunny climate. It has high concentrationof oxidizing agents and therefore ,it is also called as oxidizing smog.

5. What are the reactions involved for ozone layer depletion in the stratosphere?
   Ans:-$CF_2Cl_2(g)$ +UV $\longrightarrow$ $Cl(g)$ + $CF_2Cl(g)$
   $Cl(g)$ +$O_3(g)$ $\longrightarrow$ $ClO(g)$ +$O_2(g)$
   $ClO(g)$ +$O(g)$ $\longrightarrow$ Cl+$O_2(g)$

6. What is the full form of BOD and COD?
   Ans:-BOD stands for Biochemical Oxygen Demand whereas COD stands for Chemical Oxygen Demand.

7. What are viable and non-viable particulates?
   Ans:-Viable particulates:-They are minute living organisms that are dispersed in the atmosphere including bacteria,fungi,moulds,algae etc.
   Non-viable particulates:-They are formed by the breakdownof larger materials or by the condensation of minute particles and droplets.

8. What is B.H.C?Give its IUPAC name?
   Ans:-B.H.C is BENZENE HEXACHLORIDE Its IUPAC name is 1,2,3,4,5,6-hexa chlorocyclohexane.

9. What is meant by PCBs?
   Ans:-PCBs arepolychlorinated biphenyls.They are contaminates of water. They are used as fluids in transformers and capacitors.

10. What is the compound formed when COcombines with blood?
    Ans:-When CO combines with blood, the following reaction occurs forming carboxyhaemoglobin:-
    HB +CO $\longrightarrow$ (HBCO) Carboxyhaemoglobin

THREE MARKS QUESTION

1. What do you understand by- (i) Mist (ii) Smoke (iii) Fumes

   Ans(i) Mists:-Mists are produced by particles of spray liquids and the condensation of vapours in air.

   (ii)Smoke:- They are very small soot particles produced by burning of organic matter.

   (iii)Fumes:- These are condensed vapours;fumes of metals are well known particulates of this type.

2. Define the term pesticides? What are three categories of pesticides?

   Ans:-Pesticides are substances which are used to kill or block the reproductive process of unwanted organisms.

   The three main categories of pesticides are:-

   (i)Insecticides:-These are used to control insects and curb diseasesand protect crops.

(ii)Herbicides:-These are used to kill weeds .Example- sodium chlorate $(NaClO_3)$, sodium arsinite(Na_3AsO_3)

(iii)Fungicides:- These are used to check the growth of fungi. Example-methyl, mercury.

3. What do you mean by ozone hole? What are its consequences?

   Ans:-Depletion of ozone hole creates some sort of holes in the blanket of ozone which surround as. This is known as ozone hole.

   (i)With the depletion of the ozone layer UV radiation filters into the troposphere which leads to aging of skin,cataract,sunburn etc.

   (ii)By killing many of the phytoplanktons it can damage the fish productivity.

4. What are harmful effects of photochemical smog and how can they becontrolled?

   Ans:- (i)Photochemical smog causes eye irritation.

   (ii)It damages plants (the leaves develop a metallic sheen)

   (iii)Rubber on exposure to photochemical smog loses its elasticity and becomes inflexible and brittle.

    Usually catalyticconverters are used in the automobiles, whichprevent the release of nitrogen oxide andhydrocarbons to the atmosphere. Certainplants e.g., Pinus, Juniparus, Quercus, Pyrusand Vitis can metabolise nitrogen oxide andtherefore, their plantation could help in thismatter.

5. Give three examples in which green chemistry has been applied.

   Ans:-

   (i) In dry cleaning ,use of liquefied CO_2 in place of tetrachloroethene$(Cl_2C=CCl_2)$

   (ii)In bleaching of paper using H_2O_2 in place of chlorine.

   (iii)In the manufacture of chemicals like ethanal using environment-friendly chemicals and conditions.