

Chemistry Class 11<sup>th</sup>





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#### Some Basic Concepts of Chemistry

Chemistry plays an important role in meeting human needs for food, health care products and other materials aimed at improving the quality of life.

### ✤ DEVELOPMENT OF CHEMISTRY

• Chemistry was not studied for its own sake, rather it came up as a result of search for two interesting things:

i. Philosopher's stone (Paras) which would convert all baser metals e.g., iron and copper into gold.

ii. 'Elexir of life' which would grant immortality.

- Chemistry developed mainly in the form of Alchemy and Iatrochemistry during 1300-1600 CE. Modern chemistry took shape in the 18th century Europe, after a few centuries of alchemical traditions which were introduced in Europe by the Arabs.
- Atharvaveda (1000 BCE) mentioned some dye stuff, the material used were turmeric, madder, sunflower, orpiment, cochineal and lac. Some other substances having tinting property were kamplcica, pattanga and jatuka.
- Recipes for hair dying were made from plants, like indigo and minerals like iron power, black iron or steel and acidic extracts of sour rice gruel.
- Excavations at Taxila indicate that ink was used in India from the fourth century. Colours of ink were made from chalk, red lead.
- Acharya Kanda, born in 600 BCE, originally known by the name Kashyap, was the first proponent of the 'atomic theory'.
- All substances are aggregated form of smaller units called atoms (Paramãnu), which are eternal, indestructible, spherical, suprasensible and in motion in the original state. He explained that this individual entity cannot be sensed through any human organ.
- Extreme reduction of particle size is termed as nanotechnology.
- Charaka Samhita describes the use of bhasma of metals in the treatment of ailments.

#### **IMPORTANCE OF CHEMISTRY**

- Many lifesaving drugs such as cisplatin and taxol, are effective in cancer therapy and AZT (Azidothymidine) used for helping AIDS victims, have been isolated from plant and animal sources or prepared by synthetic methods.
- Safer alternatives to environmentally hazardous refrigerants like CFCs (chlorofluorocarbons), responsible for ozone depletion in the stratosphere, have been successfully synthesised.

### **\*** NATURE OF MATTER

Anything which has mass and occupies space is called matter.

### States of Matter

- Matter can exist in three physical states viz. solid, liquid and gas.
- Solids have definite volume and definite shape.



- Liquids have definite volume but do not have definite shape. They take the shape of the container in which they are placed.
- Gases have neither definite volume nor definite shape. They completely occupy the space of the container in which they are placed.

# Classification of Matter:



- A mixture may be homogeneous or heterogeneous. In a homogeneous mixture, the components completely mix with each other, and its composition is uniform throughout. In heterogeneous mixtures, the composition is not uniform throughout and sometimes the different components can be observed.
- Pure substances have fixed composition, whereas mixtures may contain the components in any ratio. Constituents of pure substances cannot be separated by simple physical methods
- Hydrogen and oxygen are gases, whereas the compound formed by their combination i.e., water is a liquid. Hydrogen burns with a pop sound and oxygen is a supporter of combustion, but water is used as a fire extinguisher.

# > PROPERTIES OF MATTER AND THEIR MEASUREMENT

## Physical and chemical properties

- Physical properties can be measured or observed without changing the identity or the composition of the substance e.g., colour, odour, melting point, boiling point, density, etc.
- The measurement or observation of chemical properties requires a chemical change to occur like composition, combustibility, reactivity with acids and bases, etc.

# Measurement of physical properties

- Earlier, two different systems of measurement, English System and the Metric System were being used.
- Each modern industrialised country, including India, has a National Metrology Institute (NMI), which maintains standards of measurements. This responsibility has been given to the National Physical Laboratory (NPL), New Delhi. This



laboratory establishes experiments to realise the base units and derived units of measurement and maintains National Standards of Measurement.

### **\*** The International System of Units (SI)

- The International System of Units (in French Le Systeme International d'Unités abbreviated as SI) was established by the 11th General Conference on Weights and Measures (CGPM from Conference Generale des Poids et Measures).
- The SI system has seven base units. These units pertain to the seven fundamental scientific quantities.

Unit of length	metre	The metre, symbol m is the SI unit of length. It is defined by taking the fixed numerical value of the speed of light in vacuum c to be 299792458 when expressed in the unit ms <sup>-1</sup> , where the second is defined in terms of the caesium frequency $\Delta V_{cs}$ .
Unit of mass	kilogram	The <i>ktlogram</i> , symbol kg, is the SI unit of mass. It is defined by taking the fixed numerical value of the Planck constant <i>h</i> to be 6.62607015×10 <sup>-34</sup> when expressed in the unit Js, which is equal to kgm <sup>2</sup> s <sup>-1</sup> , where the metre and the second are defined in terms of c and $\Delta V_{Ce}$
Unit of time	second	The second symbol s, is the SI unit of time. It is defined by taking the fixed numerical value of the caesium frequency $\Delta V_{\rm GV}$ , the unperturbed ground-state hyperfine transition frequency of the caesium-133 atom, to be 9192631770 when expressed in the unit Hz, which is equal to s <sup>-1</sup> .
Unit of electric current	ampere	The <i>ampere</i> , symbol A, is the SI unit of electric current. It is defined by taking the fixed numerical value of the elementary charge <i>e</i> to be $1.602176634 \times 10^{19}$ when expressed in the unit C, which is equal to As, where the second is defined in terms of $\Delta V_{c_r}$ .
Unit of thermodynamic temperature	kelvin	The Kelvin, symbol k, is the SI unit of thermodynamic temperature. It is defined by taking the fixed numerical value of the Boltzmann constant k to be $1.380649 \times 10^{-23}$ when expressed in the unit JK <sup>1</sup> , which is equal to kgm <sup>2</sup> s <sup>-2</sup> k <sup>-1</sup> where the kilogram, metre and second are defined in terms of h, c and $\Delta V_{Ca}$ .
Unit of amount of substance	mole	The mole, symbol mol, is the SI unit of amount of substance. One mole contains exactly $6.02214076 \times 10^{22}$ elementary entities. This number is the fixed numerical value of the Avogadro constant, $N_A$ when expressed in the unit mol <sup>-1</sup> and is called the Avogadro number. The amount of substance, symbol <i>n</i> , of a system is a measure of the number of specified elementary entities. An elementary entity may be an atom, a molecule, an ion, an electron, any other particle or specified group of particles.
Unit of luminous Intensity	Candela	The candela, symbol cd is the SI unit of luminous intensity in a given direction. It is defined by taking the fixed numerical value of the luminous efficacy of monochromatic radiation of frequency 540×10 <sup>12</sup> Hz, $K_{\rm ref}$ to be 683 when expressed in the unit 1m-W <sup>-1</sup> , which is equal to cd-sr-W <sup>-1</sup> , or cd sr kg <sup>-1</sup> m <sup>-2</sup> s <sup>-3</sup> , where the kilogram, metre and second are defined in terms of <i>h</i> , <i>c</i> and $\Delta V_{\rm Cs}$ .

Definitions of SI Base Units



• The SI system allows the use of prefixes to indicate the multiples or submultiples of a unit.

Maltinia	Brefin	Gumbal
multiple	Prenx	Symbol
10.24	yocto	У.
10-44	zepto	z
10-29	atto	а
10 **	femto	ſ
10-22	pico	p
10-0	nano	n
10.*	mtero	μ
10-*	mtlii	m
10-2	centi	c
10-1	dect	d
10	deca	da
107	hecto	h
108	kilo	k
104	mega	М
10#	giga	G
10 <sup>m</sup>	tera	T
1078	peta	p
1018	exa	Е
1011	zeta	Z
1024	yotta	Y

# ✤ Mass and Weight

- 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.

#### Volume

- Volume is the amount of space occupied by a substance. It has the units of  $(length)^3$ . 1 L = 1000 mL, 1000 cm<sup>3</sup> = 1 dm<sup>3</sup>
- In the laboratory, the volume of liquids or solutions can be measured by graduated cylinder, burette, pipette, etc.
- A volumetric flask is used to prepare a known volume of a solution.



Some volume measuring devices



# Density

 $\circ$  Density of a substance is its amount of mass per unit volume. Its SI unit is kg m<sup>-3</sup>.

Density =  $\frac{\text{Mass}}{\text{Volume}}$ 

• Density of a substance tells us about how closely its particles are packed. If density is more, it means particles are more closely packed.

## ✤ Temperature

• There are three common scales to measure temperature — °C (degree celsius), °F (degree fahrenheit) and K (kelvin). Here, K is the SI unit.

$$^{\circ}F = \frac{9}{5} (^{\circ}C) + 32$$

$$K = C + 273$$

• Temperature below 0 °C (i.e., negative values) are possible in Celsius scale but in Kelvin scale, negative temperature is not possible.



## **\* UNCERTAINTY IN MEASUREMENT**

## Scientific Notation

- Problem of handling extremely large/small numbers is solved by using scientific notation for such numbers, i.e., exponential notation in which any number can be represented in the form  $N \times 10^n$ , where n is an exponent having positive or negative values and N is a number (called digit term) which varies between 1.000... and 9.999....
- While performing mathematical operations on numbers expressed in scientific notations, the following points are to be kept in mind:
- Multiplication and Division follow the same rules which are there for exponential numbers.



• For Addition and Subtraction, first the numbers are written in such a way that they have the same exponent. After that, the coefficients (digit terms) are added or subtracted as the case may be.

## ✤ Significant Figures

- Significant figures are meaningful digits which are known with certainty.
- o All non-zero digits are significant.
- Zeros preceding to first non-zero digit are not significant. Such zero indicates the position of decimal point.
- Zeros between two non-zero digits are significant.
- Zeros at the end or right of a number are significant provided they are on the right side of the decimal point.
- The terminal zeros are not significant if there is no decimal point
- In addition and subtraction of significant figures, the result cannot have more digits to the right of the decimal point than either of the original numbers.
- In multiplication and division of significant figures, the result must be reported with no more significant figures as are there in the measurement with the few significant figures.
- Precision refers to the closeness of various measurements for the same quantity. Accuracy is the agreement of a particular value to the true value of the result.

# **♦ LAWS OF CHEMICAL COMBINATIONS**

- Law of Conservation of Mass: It states that matter can neither be created nor destroyed. This law was given by Antoine Lavoisier in 1789.
- Law of Definite Proportions: This law was given by a French chemist, Joseph Proust. He stated that a given compound always contains exactly the same proportion of elements by weight. Proust worked with two samples of cupric carbonate — one of which was of natural origin and the other was synthetic. He found that the composition of elements present in it was same for both the samples.
- Law of Multiple Proportions: This law was proposed by Dalton in 1803. According to this law, 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.
- 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. Gay Lussac's discovery of integer ratio in volume relationship is actually the law of definite proportions by volume.
- Avogadro Law: Equal volumes of gases at the same temperature and pressure should contain equal number of molecules. Avogadro made a distinction between atoms and molecules.



# **\* DALTON'S ATOMIC THEORY**

Idea that matter is composed of small indivisible particles called 'atomio' (meaning, indivisible), dates back to the time of Democritus, a Greek Philosopher (460–370 BC). In 1808, Dalton published 'A New System of Chemical Philosophy', in which he proposed the following:

- Matter consists of indivisible atoms.
- All the atoms of a given element have identical properties including identical mass.
- Atoms of different elements differ in mass.
- Compounds are formed when atoms of different elements combine in a fixed ratio.
- Chemical reactions involve reorganization of atoms. These are neither created nor destroyed in a chemical reaction.
- Dalton's theory could not explain the laws of gaseous volumes.
- It could not provide the reason for combining of atoms.

#### **\* ATOMIC AND MOLECULAR MASSES**

#### Atomic mass

- One atomic mass unit is defined as a mass exactly equal to one twelfth the mass of one carbon 12 atom.
- $1 \text{ amu} = 1.66056 \times 10^{-24} \text{ g}$
- Mass of an atom of hydrogen = 1.0078 amu
- The mass of oxygen -16 = 15.995 amu.
- At present, 'amu' has been replaced by 'u', which is known as unified mass.

#### Average Atomic mass

- Many naturally occurring elements exist as more than one isotope. When we take into account the existence of these isotopes and their relative abundance (per cent occurrence), the average atomic mass of that element can be computed.
- In the periodic table of elements, the atomic masses mentioned for different elements represent their average atomic masses.

#### Molecular mass

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

#### Formula Mass

• For substance which exist as ions - the formula, such as NaCl, is used to calculate the formula mass instead of molecular mass as in the solid-state sodium chloride does not exist as a single entity.



# ✤ MOLE CONCEPT AND MOLAR MASSES

- One mole contains exactly  $6.02214076 \times 10^{23}$  elementary entities. This number is the fixed numerical value of the Avogadro constant, N<sub>A</sub>, when expressed in the unit mol<sup>-1</sup> and is called the Avogadro number.
- The mole of a substance always contains the same number of entities, no matter what the substance may be.
- One mole is the amount of a substance that contains as many particles or entities as there are atoms in exactly 12 g (or 0.012 kg) of the <sup>12</sup>C isotope.
- The mass of a carbon–12 atom was determined by a mass spectrometer and found to be equal to  $1.992648 \times 10^{-23}$  g.
- The mass of one mole of a substance in grams is called its molar mass. The molar mass in grams is numerically equal to atomic/molecular/ formula mass in u.

## **\* PERCENTAGE COMPOSITION**

• Mass % of an element =

mass of the element in compound  $\times 100$ 

molar mass of compound

• 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.

# **STOICHIOMETRY AND STOICHIOMETRIC CALCULATIONS**

- The word 'stoichiometry' is derived from two Greek words stoicheion (meaning, element) and metron (meaning, measure).
- All the reactants and the products which are gases in a reaction are indicated by letter (g) in the brackets next to its formula. Similarly, in case of solids and liquids, (s) and (l) are written respectively.
- A balanced equation is: CH<sub>4</sub>(g) + 2O<sub>2</sub>(g) → CO<sub>2</sub>(g) + 2H<sub>2</sub>O(g) According to the above chemical reaction –
  - One mole of CH<sub>4</sub>(g) reacts with two moles of O<sub>2</sub>(g) to give one mole of CO<sub>2</sub>(g) and two moles of H<sub>2</sub>O(g)
  - One molecule of CH<sub>4</sub>(g) reacts with 2 molecules of O<sub>2</sub>(g) to give one molecule of CO<sub>2</sub>(g) and 2 molecules of H<sub>2</sub>O(g)
  - o 22.7 L of CH<sub>4</sub>(g) reacts with 45.4 L of  $O_2(g)$  to give 22.7 L of  $CO_2(g)$  and 45.4 L of H<sub>2</sub>O(g)
  - 16 g of CH<sub>4</sub>(g) reacts with  $2 \times 32$  g of O<sub>2</sub>(g) to give 44 g of CO<sub>2</sub>(g) and  $2 \times 18$  g of H<sub>2</sub>O(g).

## Limiting Reagent

- The reactant, which gets consumed first, limits the amount of product formed and is, therefore, called the limiting reagent.
- Reactions in Solutions



- The concentration of a solution or the amount of substance present in its given volume can be expressed as
  - 1. Mass per cent or weight per cent (w/w%) =  $\frac{mass \ of \ solute}{mass \ of \ solution} \times 100$
  - 2. **Mole fraction:** It is the ratio of number of moles of a particular component to the total number of moles of the solution.

Mole fraction of A=  $\frac{\text{No. of moles of A}}{\text{No. of moles of solution}} = \frac{n_A}{n_A + n_B}$ 

3. **Molarity:** It is defined as the number of moles of the solute in 1 litre of the solution. It is denoted by M.

 $Molarity(M) = \frac{No. of moles of solute}{Volume of solution in litres}$ 

4. **Molality:** It is defined as the number of moles of solute present in 1 kg of solvent. It is denoted by m.

Molality(m) =  $\frac{\text{No. of moles of solute}}{\text{Mass of solvent in kg}}$ 



#### **Structure of Atom**

#### > Introduction:

- Atoms are the fundamental building blocks of matter.
- The word 'atom' has been derived from the Greek word 'a-tomio' which means 'uncuttable' or 'non-divisible'.

### > Dalton's atomic theory:

- In 1808 John Dalton proposed a theory, called Dalton's atomic theory, which explains the law of conservation of mass, law of constant composition and law of multiple proportions.
- However, it failed to explain the results of many experiments like why substances like glass or ebonite when rubbed with silk or fur generate electricity.
- In 1830, Michael Faraday's electrolysis experiment suggested the particulate nature of electricity.

#### > Discovery of Electron:

#### • Cathode ray discharge tube experiment:

(i) In the mid 1850s Faraday and other scientists began to study electrical discharge in partially evacuated tubes, known as cathode ray discharge tubes.



A cathode ray discharge tube

- (ii) A cathode ray tube is made of sealed glass containing electrodes.
- (iii) The electrical discharge through the gases was observed at very low pressures and at very high voltages, current started flowing through a stream of particles moving in the tube from the negative electrode(cathode) to the positive electrode (anode).
- (iv) These were called cathode rays or cathode ray particles.
- (v) The flow of current from cathode to anode was further checked by making a hole in the anode and coating the tube behind anode with phosphorescent material zinc sulphide.
- (vi) When these rays, after passing through anode, strike the zinc sulphide coating, a bright spot is developed on the coating.





A cathode ray discharge tube with perforated tube

- **\*** Results:
  - i. Cathode rays start from the cathode and move towards the anode.
  - ii. These rays themselves are not visible but their behaviour can be observed with the help of certain kinds of materials which glow when hit by them. (Television picture tubes are cathode ray tubes)
  - iii. In the absence of an electrical or magnetic field, these rays travel in straight lines.
  - iv. In the presence of an electrical or magnetic field, the behaviour of cathode rays are similar to that expected from negatively charged particles, suggesting that the cathode rays consist of negatively charged particles, called electrons.
  - v. The characteristics of cathode rays (electrons) do not depend upon the material of electrodes and the nature of the gas present in the cathode ray tube.

#### Conclusion:

Electrons are the basic constituent of all the atoms.

#### > e/m ratio of electron:

i. In 1897, British physicist J.J. Thomson measured the ratio of electrical charge (e) to the mass of electrons (m) by using a cathode ray tube and applying electrical and magnetic fields perpendicular to each other as well as to the path of electrons.



The apparatus to determine the charge to the mass ratio of electron

ii. When only electric field is applied, the electrons deviate from their path and hit the cathode ray tube at point A



- iii. Similarly when only a magnetic field is applied, an electron strikes the cathode ray tube at point C.
- iv. By carefully balancing the electrical and magnetic field strength, it is possible to bring back the electron to the path which is followed in the absence of electric or magnetic field and they hit the screen at point B.
- v. Deviation of the particles from their path in the presence of electrical or magnetic field depends upon:
  - (a) The magnitude of the negative charge on the particle. (greater the magnitude of the charge on the particle, greater is the interaction with the electric or magnetic field and thus greater is the deflection).
  - (b) The mass of the particle (lighter the particle, greater the deflection).
  - (c) The strength of the electrical or magnetic field. (the deflection of electrons from its original path increases with the increase in the voltage across the electrodes, or the strength of the magnetic field).
- vi.  $e/m = 1.758820 \times 10^{11} \text{ C kg}^{-1}$

where m is the mass of the electron in kg and

- e is the magnitude of the charge on the electron in coulomb (C).
- vii. Since electrons are negatively charged, the charge on electrons is -e.

#### Millikan's oil drop experiment:

- i. In 1914, R.A. Millikan devised a method known as oil drop experiment, to determine the charge on the electrons.
- ii. In this method, oil droplets in the form of mist, produced by the atomiser, were allowed to enter through a tiny hole in the upper plate of the electrical condenser.
- iii. The downward motion of these droplets was viewed through the telescope, equipped with a micrometer eyepiece.
- iv. By measuring the rate of fall of these droplets, Millikan was able to measure the mass of oil droplets.
- v. The air inside the chamber was ionized by passing a beam of X-rays through it.
- vi. The electrical charge on these oil droplets was acquired by collisions with gaseous ions.
- vii. The fall of these charged oil droplets can be retarded, accelerated or made stationary depending upon the charge on the droplets and the polarity and strength of the voltage applied to the plate.
- viii. By carefully measuring the effects of electrical field strength on the motion of oil droplets.

#### Conclusion:

i. The magnitude of electrical charge, q, on the droplets is always an integral multiple of the electrical charge, e, that is, q = n e, where n = 1, 2, 3...





The Millikan oil drop apparatus for measuring charge 'e'. In chamber, the forces acting on oil drop are: gravitational electrostatic due to electrical field and a viscous drag force when the oil drop is moving.

- ii. The charge on the electron was found to be  $-1.6 \times 10^{-19}$  C.
- iii. The mass of the electron was determined by combining these results with Thomson's value of e/m ratio. Mass of electron =  $9.1094 \times 10^{-31}$  kg.

#### Discovery of proton:

- Electrical discharge carried out in the modified cathode ray tube led to the discovery of canal rays carrying positively charged particles.
- The characteristics of these positively charged particles are listed below.
  - i. Mass of positively charged particles depends upon the nature of gas present in the cathode ray tube.
  - ii. The charge to mass ratio of the particles depends on the gas from which these originate.
  - iii. Some of the positively charged particles carry a multiple of the fundamental unit of electrical charge.
  - iv. The behaviour of these particles in the magnetic or electrical field is opposite to that observed for electrons.
- The smallest and lightest positive ion was obtained from hydrogen and was called proton.

#### > Discovery of neutron:

• Neutrons were discovered by Chadwick (1932) by bombarding a thin sheet of beryllium by  $\alpha$ -particles. Mass of a neutron is slightly greater than that of protons emitted.

Name	Symbol	Absolute charge/C	Relative charge	Mass/kg	Mass/u	Approz. mass/u
Electron	e	-1.6022×10 <sup>-19</sup>	-1	9.10939×10 <sup>-31</sup>	0.00054	0
Proton	р	+1.6022×10 <sup>-19</sup>	+1	1.67262×10 <sup>-27</sup>	1.00727	1
Neutron	п	0	0	1.67493×10 <sup>-27</sup>	1.00867	1

**Properties of Fundamental Particles** 



- Thomson Model of Atom/Plum Pudding/Raisin Pudding or Watermelon Model of an atom (proposed in 1898):
  - He 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



Thomson model of atom

• It explained the overall neutrality of the atom.

#### Radioactivity:

- In 1895 Wilhalm Röentgen showed that when electrons strike a material in the cathode ray tubes, they produce rays which can cause fluorescence in the fluorescent materials placed outside the cathode ray tubes, he named the radiation as X-rays.
- X-rays are not deflected by the electric and magnetic fields and have a very high penetrating power and are of very short wavelength.
- Henri Becqueral observed that there are certain elements which emit radiation on their own and named this phenomenon as radioactivity and the elements known as radioactive elements.
- It was observed that three kinds of rays i.e.,  $\alpha$ ,  $\beta$  and  $\gamma$ -rays are emitted.
- Rutherford found that α-rays consist of two units of positive charge and four units of atomic mass. (α- particles combine with two electrons to yield helium gas)
- Beta-rays are negatively charged particles similar to electrons.
- γ-rays are high energy radiations like X-rays, are neutral in nature and do not consist of particles.

**Order of penetrating power:**  $\alpha$ -particles <  $\beta$ -rays (100 times that of  $\alpha$ -particles) <  $\gamma$ -rays (1000 times of that  $\alpha$ -particles).

Rutherford's famous α-particle scattering experiment:





#### Rutherford's scattering experiment

- A stream of high energy α-particles from a radioactive source was directed at a thin foil (thickness ~ 100 nm) of gold metal.
- The thin gold foil had a circular fluorescent zinc sulphide screen around it.
- Whenever α-particles struck the screen, a tiny flash of light was produced at that point.

## Observations:

- i. Most of the  $\alpha$ -particles passed through the gold foil undeflected.
- ii. a small fraction of the  $\alpha$ -particles was deflected by small angles.
- iii. a very few  $\alpha$ -particles (~1 in 20,000) bounced back, that is, were deflected by nearly 180°.

## **Conclusion:**

- i. Most of the space in the atom is empty as most of the  $\alpha$ -particles passed through the foil undeflected.
- ii. A few positively charged  $\alpha$ -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  $\alpha$ -particles.
- iii. 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 the nucleus is  $10^{-15}$  m.



Schematic molecular view of the gold foil

#### > Rutherford's nuclear model of an atom:

- i. The positive charge and most of the mass of the atom was densely concentrated in an extremely small region. This very small portion of the atom was called the 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.



iii. Electrons and the nucleus are held together by electrostatic forces of attraction.

#### Atomic number, Mass number:

- The number of protons present in the nucleus is equal to atomic number (Z). Atomic number (Z) = number of protons in the nucleus of an atom = number of electrons in a neutral atom.
- 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)
- Elements can be represented as  $\overset{A}{z}X$ .

#### > Isotopes and Isobars:

• Atoms with identical atomic numbers but different atomic mass numbers are known as Isotopes.

For example:  ${}^{1}H$ ,  ${}^{2}H$ , and  ${}^{3}H$ .

- All the isotopes of a given element show the same chemical behaviour.
- Isobars are the atoms with the same mass number but different atomic numbers.

For example:  ${}^{14}_{6}C$  and  ${}^{14}_{7}N$ .

#### > Drawbacks of Rutherford Model:

• When a body is moving in an orbit, it undergoes acceleration even if it is moving with a constant speed in an orbit because of changing direction. So an electron in the nuclear model is under acceleration.

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.

Thus electrons in only  $10^{-8}$  s will spiral into the nucleus. But this does not happen. Thus, the Rutherford model cannot explain the stability of an atom.

• Another serious drawback of the Rutherford model is that it says nothing about distribution of the electrons around the nucleus and the energies of these electrons.

## > Bohr's Theory:

- Neils Bohr improved the model proposed by Rutherford and two developments played a major role in the formulation of Bohr's model of atom.
  - i. Dual character of the electromagnetic radiation which means that radiation possess both like and particle like properties, and
  - ii. Experimental results regarding atomic spectra.

#### > Wave Nature of Electromagnetic Radiation:



- James Maxwell (1870) suggested that when an electrically charged particle moves under acceleration, alternating electrical and magnetic fields are produced and transmitted. These fields are transmitted in the forms of waves called electromagnetic waves or electromagnetic radiation.
- In earlier days light was supposed to be made of particles (corpuscules).
- Maxwell was again the first to reveal that light waves are associated with oscillating electric and magnetic character



The electric and magnetic field components of an electromagnetic wave. These components have the same wavelength, frequency, speed and amplitude, but they vibrate in two mutually perpendicular planes.

#### Properties of electromagnetic waves:

- i. The oscillating electric and magnetic fields produced by oscillating charged particles are perpendicular to each other and both are perpendicular to the direction of propagation of the wave.
- ii. Unlike sound waves or waves produced in water, electromagnetic waves do not require medium and can move in vacuum.
- iii. There are many types of electromagnetic radiation, which differ from one another in wavelength (or frequency). These constitute electromagnetic spectrum



(a) The spectrum of electromagnetic radiation. (b) Visible spectrum. The visible region is only a small part of the entire spectrum .



## ✤ Characteristic of electromagnetic radiations:

- i. Frequency: It is defined as the number of waves that pass a given point in one Second. The SI unit for frequency (v) is hertz (Hz,  $s^{-1}$ ),
- ii. Wavelength: It is the distance between two adjacent crest or trough. SI unit of wavelength is meter (m)
- iii. Speed: In vacuum all types of electromagnetic radiations, regardless of wavelength, travel at the same speed, i.e.,  $3.0 \times 10^8$  m s<sup>-1</sup> (2.997925 × 10<sup>8</sup> m s<sup>-1</sup>, to be precise). This is called speed of light and is given the symbol 'c'.
- iv. The frequency (v ), wavelength ( $\lambda$ ) and velocity of light (c) are related by the equation.  $c = v \lambda$
- v. Wavenumber: It is defined as the number of wavelengths per unit length. Its units are reciprocal of the wavelength unit, i.e., m<sup>-1</sup>.
   However, the commonly used unit is cm<sup>-1</sup> (not SI unit).
- Electromagnetic radiation explains phenomenon such as diffraction(bending of wave around an obstacle) and interference (combination of two waves of the same or different frequencies) but fails to explain
  - i. The nature of emission of radiation from hot bodies (black -body radiation)
  - ii. Ejection of electrons from metal surface when radiation strikes it (photoelectric effect)
  - iii. variation of heat capacity of solids as a function of temperature
  - iv. Line spectra of atoms with special reference to hydrogen.

#### **Black Body Radiation**:

- Hot objects emit electromagnetic radiation over a wide range of wavelengths.
- At high temperatures, an appreciable proportion of radiation is in the visible region of the spectrum.
- As the temperature is raised, a higher proportion of short wavelength (blue light) is generated.

#### For example:

- When an iron rod is heated in a furnace, it first turns to dull red and then progressively becomes more and more red as the temperature increases.
- As this is heated further, the radiation emitted becomes white and then becomes blue as the temperature becomes very high. This means that red radiation is most intense at a particular temperature and the blue radiation is more intense at another temperature.
- This means intensities of radiations of different wavelengths emitted by the hot body depend upon its temperature.
- Objects made of different materials and kept at different temperatures emit different amounts of radiation.
- Also, when the surface of an object is irradiated with light (electromagnetic radiation), a part of radiant energy is generally reflected as such, a part is absorbed



and a part of it is transmitted. The reason for incomplete absorption is that ordinary objects are imperfect absorbers of radiation.

- An ideal body, which emits and absorbs radiations of all frequencies uniformly, is called a black body and the radiation emitted by such a body is called black body radiation. (No such body exists. Carbon black approximates fairly closely to black body) A good physical approximation to a black body is a cavity with a tiny hole, which has no other opening. Any ray entering the hole will be reflected by the cavity walls and will be eventually absorbed by the walls.
- A black body is also a perfect radiator of radiant energy.
- Furthermore, a black body is in thermal equilibrium with its surroundings. It radiates same amount of energy per unit area as it absorbs from its surrounding in any given time.
- The amount of light emitted (intensity of radiation) from a black body and its spectral distribution depends only on its temperature.



Also, as the temperature increases, the maxima of the curve shifts to short wavelength.

#### > Photoelectric Effect:

• In 1887, H. Hertz performed an 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 the Photoelectric effect.





Equipment for studying the photoelectric effect. Light of a particular frequency strikes a clean metal surface inside a vacuum chamber. Electrons are ejected from the metal and are counted by a detector that measures their kinetic energy.

- The results observed in this experiment were:
  - i. The electrons are ejected from the metal surface as soon as the beam of light strikes the surface, i.e. there is no time lag between the striking of a light beam and the ejection of electrons from the metal surface.
  - ii. The number of electrons ejected is proportional to the intensity or brightness of light.
  - iii. For each metal, there is a characteristic minimum frequency,  $v_0$  (also known as threshold frequency) below which photoelectric effect is not observed. At a frequency  $v > v_0$ , the ejected electrons come out with certain kinetic energy. The kinetic energies of these electrons increases with the increase of frequency of the light used. According to the latter, the energy content of the beam of light depends upon the brightness of the light. In other words, the number of electrons ejected and kinetic energy associated with them should depend on the brightness of light. It has been observed that though the number of electrons ejected does depend upon the brightness of light, the kinetic energy of the ejected electrons does not.
- Einstein (1905) was able to explain the photoelectric effect using Planck's quantum theory of electromagnetic radiation, when a photon of sufficient energy strikes an electron in the atom of the metal, it transfers its energy instantaneously to the electron during the collision and the electron is ejected without any time lag or delay. Greater the energy possessed by the photon, greater will be the transfer of energy to the electron and greater the kinetic energy of the ejected electron.

Since the striking photon has energy equal to hv and the minimum energy required to eject the electron is  $hv_0$  (also called work function,  $W_0$ ), then the difference in energy ( $hv - hv_0$ ) is transferred as the kinetic energy to the photoelectron.

Kinetic energy of the ejected electron =  $hv = hv_0 + \frac{1}{2} mv^2$ 

where m is the mass of the electron and v is the velocity associated with the ejected electron.

Lastly, a more intense beam of light consists of a larger number of photons, consequently the number of electrons ejected is also larger as compared to that in an experiment in which a beam of weaker intensity of light is employed.

## Planck's Quantum Theory:

- Planck assumed that radiation could be subdivided into discrete chunks of energy.
- He suggested that atoms and molecules could emit or absorb energy only in discrete quantities and not in a continuous manner.
- He gave the name quantum to the smallest quantity of energy that can be emitted or absorbed in the form of electromagnetic radiation.
- The energy (E) of a quantum of radiation is proportional to its frequency (v) and is expressed as E = hv

h = Planck's constant =  $6.626 \times 10^{-34}$  J s.



## > Dual Behaviour of Electromagnetic Radiation:

- The particle nature of light could explain the black body radiation and photoelectric effect satisfactorily and the wave behaviour of light could account for the phenomena of interference and diffraction.
- Thus light possesses both particle and wave-like properties, i.e., light has dual behaviour.
- Depending on the experiment, we find that light behaves either as a wave or as a stream of particles.
- Whenever radiation interacts with matter, it displays particle-like properties in contrast to the wavelike properties (interference and diffraction), which it exhibits when it propagates

#### > Atomic spectra:

- **Continuous spectrum:** When a ray of white light is passed through a prism, the wave with shorter wavelength bends more than the one with a longer wavelength. Since ordinary white light consists of waves with all the wavelengths in the visible range, a ray of white light is spread out into a series of coloured bands called spectrum. The light of red colour which has the longest wavelength is deviated the least while the violet light, which has the shortest wavelength is deviated the most. Such a spectrum is called a continuous spectrum. Continuous because violet merges into blue, blue into green and so on. (similar spectrum to rainbow).
- Emission spectrum: When electromagnetic radiation interacts with matter, it may absorb energy and reach a higher energy state. With higher energy, these are in an unstable state. For returning to their normal energy state, the atoms and molecules emit radiation in various regions of the electromagnetic spectrum. The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum. 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.
- Absorption spectrum: A continuum of radiation is passed through a sample which absorbs radiation of certain wavelengths. The missing wavelength which corresponds to the radiation absorbed by the matter, leaves dark spaces in the bright continuous spectrum.





(a) Atomic emission. The light emitted by a sample of excited hydrogen atoms (or any other element) can be passed through a prism and separated into certain discrete wavelengths. Thus an emission spectrum, which is a photographic recording of the separated wavelengths is called as line spectrum. Any sample of reasonable size contains an enormous number of atoms. Although a single atom can be in only one excited state at a time, the collection of atoms contains all possible excited states. The light emitted as these atoms fall to lower energy states is responsible for the spectrum. (b) Atomic absorption. When white light is passed through unexcited atomic hydrogen and then through a slit and prism, the transmitted light is lacking in intensity at the same wavelengths as are emitted in (a) The recorded absorption spectrum is also a line spectrum and the photographic negative of the emission spectrum.

#### Note:

The emission spectra of atoms in the gas phase do not show a continuous spread of wavelength from red to violet, rather they emit light only at specific wavelengths with dark spaces between them. Such spectra are called line spectra or atomic spectra. Each element has a unique line emission spectrum, which is used in chemical analysis to identify unknown atoms in the same way as fingerprints are used to identify people.

#### Line Spectrum of Hydrogen:

- When an electric discharge is passed through gaseous hydrogen, the H<sub>2</sub> 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.
- Lines of the hydrogen spectrum obey the following formula:

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

where  $n_1 = 1, 2, ..., n_1 = 1, 2, ..., n_2$ 

 $n_2 = n_1 + 1, n_1 + 2.....$ 

The value 109,677 cm<sup>-1</sup> is called the Rydberg constant for hydrogen The first five series of lines that correspond to  $n_1$ = 1, 2, 3,4, 5 are known as Lyman, Balmer, Paschen, Bracket and Pfund series respectively.

The Spectral Lines for Atomic Hydrogen





Transitions of the electron in the hydrogen atom (The diagram shows the Lyman, Balmer and Paschen series of transitions)

# > BOHR'S MODEL FOR HYDROGEN ATOM

- Bohr's model for hydrogen atom is based on the following postulates:
  - i. 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.
  - ii. 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 the required amount of energy is absorbed by the electron or energy is emitted



when the electron moves from higher stationary state to lower stationary state. The energy change does not take place in a continuous manner.

iii. The frequency of radiation absorbed or emitted when transition occurs between two stationary states that differ in energy by  $\Delta E$ , is given by

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

where  $E_1$  and  $E_2$  are the energies of the lower and higher allowed energy states respectively. This expression is commonly known as Bohr's frequency rule.

iv. The angular momentum of an electron in a given stationary state can be expressed as in equation

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

n = 1,2,3.....

Thus an electron can move only in those orbits for which its angular momentum is integral multiple of  $h/2\pi$  that is why only certain fixed orbits are allowed.

#### • According to Bohr's theory for hydrogen atom:

- a) The stationary states for electrons are numbered n = 1,2,3..... These integral numbers are known as Principal quantum numbers.
- b) The radii of the stationary states are expressed as:

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

where  $a_0 = 52.9$  pm. Thus the radius of the first stationary state, called the Bohr orbit, is 52.9 pm.

c) The most important property associated with the electron, is the energy of its stationary state. It is given by the expression

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

where  $R_H$  is called Rydberg constant and its value is  $2.18 \times 10^{-18}$  J.

When the electron is free from the influence of the nucleus, the energy is taken as zero, i.e.  $n = \infty$  and is called an ionized hydrogen atom. When the electron is attracted by the nucleus and is present in orbit n, the energy is emitted and its energy is lowered. That is the reason for the presence of negative sign in the energy equation.

- d) 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.
- e) It is also possible to calculate the velocities of electrons moving in these orbits.  $V_n = 2.165 \ x \ 10^6 \ (Z/n) \ m/s$



#### > Explanation of Line Spectrum of Hydrogen:

• Energy is absorbed if the electron moves from the orbit of smaller Principal quantum number to the orbit of higher Principal quantum number, whereas the Energy is emitted if the electron moves from higher orbit to lower orbit.

The energy gap between the two orbits is given as

$$\Delta E = E_t - E_t \qquad (2.16)$$
Combining equations (2.13) and (2.16)

Combining equations (2, 13) and (2, 16)

$$\Delta E = \left(-\frac{\mathbf{R}_{\mathrm{H}}}{n_{\mathrm{f}}^{2}}\right) - \left(-\frac{\mathbf{R}_{\mathrm{H}}}{n_{\mathrm{f}}^{2}}\right) \text{ (where } n_{\mathrm{f}} \text{ and } n_{\mathrm{f}}$$

stand for initial orbit and final orbits)

$$\Delta E = R_{\rm H} \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = 2.18 \times 10^{-18} \, J \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)$$
(2.17)

The frequency ( $\nu$ ) associated with the absorption and emission of the photon can be evaluated by using equation (2.18)

$$\nu = \frac{\Delta E}{h} = \frac{R_{\rm H}}{h} \left( \frac{1}{n_{\rm f}^2} - \frac{1}{n_{\rm f}^2} \right)$$

$$= \frac{2.18 \times 10^{-18} \,\mathrm{J}}{6.626 \times 10^{-34} \,\mathrm{Js}} \left( \frac{1}{n_{\rm f}^2} - \frac{1}{n_{\rm f}^2} \right) \qquad (2.18)$$

$$= 3.29 \times 10^{15} \left( \frac{1}{n_{\rm f}^2} - \frac{1}{n_{\rm f}^2} \right) Hz \qquad (2.19)$$

and in terms of wavenumbers (F)

$$\overline{\nu} = \frac{\nu}{c} = \frac{R_{\rm H}}{hc} \left( \frac{1}{n_{\rm t}^2} - \frac{1}{n_{\rm f}^2} \right)$$
(2.20)  
$$= \frac{3.29 \times 10^{15} \,{\rm s}^{-1}}{3 \times 10^8 {\rm m \ s}^{-n}} \left( \frac{1}{n_{\rm t}^2} - \frac{1}{n_{\rm f}^2} \right)$$
$$= 1.09677 \times 10^7 \left( \frac{1}{n_{\rm t}^2} - \frac{1}{n_{\rm f}^2} \right) {\rm m}^{-1}$$
(2.21)

#### 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.
- This model is also unable to explain the spectrum of atoms other than hydrogen,
- Bohr's theory was also unable to explain the splitting of spectral lines in the presence of a magnetic field (Zeeman effect) or an electric field (Stark effect).
- It could not explain the ability of atoms to form molecules by chemical bonds.

#### > Dual Behaviour of Matter:



- de Broglie in 1924 proposed that matter, like radiation, should also exhibit dual behaviour i.e., both particle and wavelike properties.
- This means that just as the photon has momentum as well as wavelength, electrons should also have momentum as well as wavelength.

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

where m is the mass of the particle, v its velocity and p its momentum.

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

## Heisenberg's Uncertainty Principle:

- Werner Heisenberg, a German physicist in 1927, stated the uncertainty principle which is the consequence of dual behaviour of matter and radiation.
- It states that it is impossible to determine simultaneously, the exact position and exact momentum (or velocity) of an electron.

$$\Delta \mathbf{x} \times \Delta p_{\mathbf{x}} \ge \frac{h}{4\pi}$$
  
or 
$$\Delta \mathbf{x} \times \Delta (m\mathbf{v}_{\mathbf{x}}) \ge \frac{1}{2\pi}$$

or 
$$\Delta \mathbf{x} \times \Delta \mathbf{v}_x \ge \frac{h}{4\pi m}$$

where  $\Delta x$  is the uncertainty in position and  $\Delta p_x$  (or  $\Delta v_x$ ) is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with a high degree of accuracy ( $\Delta x$  is small), then the velocity of the electron will be uncertain [ $\Delta(v_x)$  is large].

- On the other hand, if the velocity of the electron is known precisely ( $\Delta(v_x)$  is small), then the position of the electron will be uncertain ( $\Delta x$  will be large).
- One of the important implications of the Heisenberg Uncertainty Principle is that it rules out the existence of definite paths or trajectories of electrons and other similar particles.
- The effect of Heisenberg Uncertainty Principle is significant only for motion of microscopic objects and is negligible for that of macroscopic objects.
- In the case of a microscopic object like an electron on the other hand.  $\Delta v.\Delta x$  obtained is much larger and such uncertainties are of real consequence.
- It, therefore, means that the precise statements of the position and momentum of electrons have to be replaced by the statements of probability that the electron has at a given position and momentum. This is what happens in the quantum mechanical model of atom.



### > Reasons for the Failure of the Bohr Model:

- In the Bohr model, an electron is regarded as a charged particle moving in well defined circular orbits about the nucleus. The wave character of the electron is not considered in the Bohr model.
- Further, an orbit is a clearly defined path and this path can completely be defined only if both the position and the velocity of the electron are known exactly at the same time. This is not possible according to the Heisenberg uncertainty principle.

#### > QUANTUM MECHANICAL MODEL OF ATOM:

- The branch of science that takes into account the dual behaviour of matter is called quantum mechanics.
- Quantum mechanics is a theoretical science that deals with the study of the motions of microscopic objects that have both observable wave-like and particle-like properties.
- For a system (such as an atom or a molecule whose energy does not change with time) the Schrödinger equation is written as  $H \psi = E \psi$  where H is a mathematical operator called Hamiltonian.
- Solution of this equation gives E and  $\psi$ .
- When the Schrödinger equation is solved for a hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s) (ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number 1 and magnetic quantum number ml ) arise as a natural consequence in the solution of the Schrödinger equation.
- When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron. Such wave functions of hydrogen or hydrogen like species with one electron are called atomic orbitals. Such wave functions pertaining to one-electron species are called one-electron systems.
- The probability of finding an electron at a point within an atom is proportional to the  $|\psi|^2$  at that point.

#### > Orbitals and Quantum Numbers:

- Orbit and orbital are not synonymous.
- An orbit, as proposed by Bohr, is a circular path around the nucleus in which an electron moves.
- An atomic orbital, on the other hand, is a quantum mechanical concept and refers to the one electron wave function  $\psi$  in an atom. It is characterized by quantum numbers.

#### > Principal quantum number:

• The **principal quantum number** 'n' is a positive integer with value of n = 1, 2, 3..



- The principal quantum number determines the size and to large extent the energy of the orbital.
- The principal quantum number also identifies the shell.
- With the increase in the value of 'n', the number of allowed orbital increases and are given by n<sup>2</sup>.
- All the orbitals of a given value of 'n' constitute a single shell of atom.

## > Azimuthal quantum number:

- Azimuthal quantum number 'l' is also known as orbital angular momentum or subsidiary quantum number.
- It defines the three dimensional shape of the orbital.
- For a given value of n, 1 can have n values ranging from 0 to n 1.
- For a given value of n, the possible value of 1 are  $: 1 = 0, 1, 2, \dots, (n-1)$ .
- Each shell consists of one or more subshells or sub-levels. The number of subshells in a principal shell is equal to the value of n.

n	l	Subshell notation
1	0	15
2	0	25
2	1	2p
3	0	35
3	1	Зр
3	2	3d
4	0	4s
4	1	4p
4	2	4d
4	3	4 <i>f</i>

#### **Subshell Notations**

#### > Magnetic quantum number:

- Magnetic orbital quantum number 'm<sub>1</sub>' gives information about the spatial orientation of the orbital.
- $m_l = 2l+1$
- For l = 0, the only permitted value of ml = 0, [2(0)+1 = 1] i.e one s orbital.
- For l = 1,  $m_l$  can be -1, 0 and +1 [2(1)+1 = 3], three p orbitals.

## > Electron spin quantum number (ms):



- An electron spins around its own axis.
- Spin angular momentum of the electron is a vector quantity, and can have two orientations relative to the chosen axis.
- These two orientations are distinguished by the spin quantum numbers ms which can take the values of +½ or -½. These are called the two spin states of the electron and are normally represented by two arrows, ↑ (spin up) and ↓ (spin down). Two electrons that have different ms values (one +½ and the other -½)

#### > Shapes of Atomic Orbitals:

- The square of the wave function (i.e., $\psi^2$ ) at a point gives the probability density of the electron at that point.
- It may be noted that for 1s orbital the probability density is maximum at the nucleus and it decreases sharply as we move away from it.
- On the other hand, for 2s orbital the probability density first decreases sharply to zero and again starts increasing. After reaching a small maxima it decreases again and approaches zero as the value of r increases further.
- The region where this probability density function reduces to zero is called nodal surfaces or simply nodes.



The plots of (a) the orbital wave function  $\psi(\mathbf{r})$ ; (b) the variation of probability density  $\psi^2(\mathbf{r})$  as a function of distance r of the electron from the nucleus for 1s and 2s orbitals.

#### ➤ s-orbital:

- s-orbitals are spherical in shape.
- Probability of finding the electron at a given distance is equal in all directions.



• It is also observed that the size of the s orbital increases with increase in n i.e. 4s > 3s > 2s > 1s and the electron is located further away from the nucleus as the principal quantum number increases.



#### > p orbital:

- p orbital consists of two sections called lobes that are on either side of the plane that passes through the nucleus.
- The probability density function is zero on the plane where the two lobes touch each other.
- The size, shape and energy of the three orbitals are identical.
- They differ however, in the way the lobes are oriented. Since the lobes may be considered to lie along the x, y or z axis, they are given the designations 2px, 2py, and 2pz.



## > d orbital:

- The five d-orbitals are designated as  $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ,  $dx^2 y^2$  and  $dz^2$ .
- The shapes of the first four d-orbitals are similar to each other, whereas that of the fifth one, dz<sup>2</sup>, is different from others, but all five 3d orbitals are equivalent in energy.



• The orbitals having the same energy are called degenerate.



Boundary surface diagrams of the five 3d orbitals.

## > Energies of Orbitals:

- The energy of an electron in a H atom = 1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f
- In multi-electron atoms, electrons are filled as per (n + 1) rule.
- The lower the value of (n + 1) for an orbital, the lower is its energy. If two orbitals have the same value of (n + 1), the orbital with lower value of n will have the lower energy.

## > Aufbau Principle:

• In the ground state of the atoms, the orbitals are filled in order of their increasing energies.





## > Pauli Exclusion Principle:

- No two electrons in an atom can have the same set of four quantum numbers.
- Pauli exclusion principle can also be stated as : "Only two electrons may exist in the same orbital and these electrons must have opposite spin."
- The maximum number of electrons in the shell with principal quantum number n is equal to  $2n^2$ .

# > Hund's Rule of Maximum Multiplicity:

• Pairing of electrons in the orbitals belonging to the same subshell (p, d or f) does not take place until each orbital belonging to that subshell has got one electron each i.e., it is singly occupied.



# > Electronic Configuration of Atoms:

Elem	ent Z	15	25	2p	3s	3p	3d	<b>4</b> s	4p	4d	4 <i>f</i>	5s	5p	5d 5f	6s	6p	6đ	7s	
H He	1 2	1 2																	
Li Be B C N O F Ne	3 4 5 6 7 8 9 10	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	1 2 2 2 2 2 2 2 2 2 2	1 2 3 4 5 6															
Na Mg Al Si P S Cl Ar K Ca Sc I V Cr Mn Fe Co Ni Cu * Zn	11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	66666666666666666666666666666666666666	1 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	1 2 3 4 5 6 6 6 6 6 6 6 6 6 6 6 6 6	1 2 3 5 5 6 7 8 10 10	1222212221222122212221221222212222122											
Ga Ge As Se Br Kr Rb Sr Y Zr Nb* Mo* Tc Ru* Rh* Pd* Ag* Cd In Sn Sb Te I Xe	31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	666666666666666666666666666666666666666	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6 6	10 10 10 10 10 10 10 10 10 10 10 10 10 1	N N N N N N N N N N N N N N N N N N N	12345666666666666666666666666666666666666	1 2 4 3 5 5 7 8 10 10 10 10 10 10 10 10		1 2 2 2 1 1 2 1 1 2 2 2 2 2 2 2 2 2 2 2	1 2 3 4 5 6						



Elem	ent Z	15	2s	2p	35	3p	3d	<b>4</b> s	4p	4d	4 <i>f</i>	<b>5</b> s	5p	5d 5f	6s	6p	6d	7s
Cs	55	2	2	6	2	6	10	2	6	10		2	6		1			
Ва	56	2	2	6	2	6	10	2	6	10		2	6		2			
La*	57	2	2	6	2	6	10	2	6	10		2	6	1	2			
Ce*	58	2	2	6	2	6	10	2	6	10	2	2	6		2			
Pr	59	2	2	6	2	6	10	2	6	10	3	2	6		2			
Nd	60	2	2	6	2	6	10	2	6	10	4	2	6		2			
Pm	61	2	2	6	2	6	10	2	6	10	5	2	6		2			
Sm	62	2	2	6	2	6	10	2	6	10	6	2	6		2			
Eu	63	2	2	6	2	6	10	2	6	10	7	2	6		2			
Gd*	64	2	2	6	2	6	10	2	6	10	7	2	6	1	2			
Tb	65	2	2	6	2	6	10	2	6	10	9	2	6		2			
Dy	66	2	2	6	2	6	10	2	6	10	10	2	6		2			
Ho	67	2	2	6	2	6	10	2	6	10	11	2	6		2			
Er	68	2	2	6	2	6	10	2	6	10	12	2	6		2			
Tm	69	2	2	6	2	6	10	2	6	10	13	2	6		2			
Yb	70	2	2	6	2	6	10	2	6	10	14	2	6		2			
Lu	71	2	2	6	2	6	10	2	6	10	14	2	6	1	2			
Hi	72	2	2	6	2	6	10	2	6	10	14	2	6	2	2			
Ta	73	2	2	6	2	6	10	2	6	10	14	2	6	3	2			
W	74	2	2	0	2	6	10	2	6	10	14	2	0	4	2			
Re	75	2	2	6	2	6	10	2	6	10	14	2	6	5	2			
Us	70	2	2	6	2	0	10	2	0	10	14	2	6	0	2			
Ir D+*	11	2	2	0	2	0	10	2	0	10	14	2	6	1	2			
PU	10	4	2	0	4	0	10	2	0	10	14	2	0	9	1			
Au	79	2	2	0	2	6	10	2	C C	10	14	2	6	10	2			
rig Ti	81	2	2	G	2	6	10	2	6	10	14	2	6	10	2	5		
Db	80	2	2	6	2	6	10	2	6	10	14	2	G	10	0	0		
Ri	20	2	2	6	2	6	10	2	6	10	14	2	6	10	2	4		
Po	84	2	2	6	2	6	10	2	6	10	14	2	6	10	2	A		
At	85	2	2	6	2	6	10	2	6	10	14	2	6	10	2	5		
Rn	86	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		
Fr	87	2	2	6	2	6	10	2	6	10	14	2	6	10	2	6		1
Ra	88	2	2	6	2	6	10	2	0	10	14	2	6	10	2	0		2
AC	89	2	2	0	2	6	10	2	0	10	14	2	0	10	2	0	1	2
In Do	90	2	2	e e	2	6	10	2	6	10	14	2	C	10 2	2	6	4	2
ra	91	2	2	6	2	6	10	4	6	10	14	2	e e	10.2	4	6	1	2
Nn	02	2	2	6	2	G	10	2	6	10	14	2	6	10.4	2	6	1	2
Pu	94	2	2	6	2	6	10	2	6	10	14	2	6	10.6	2	6	100	2
Am	95	2	2	6	2	6	10	2	6	10	14	2	6	10.7	2	6		2
Cm	96	2	2	6	2	6	10	2	6	10	14	2	6	10.7	2	6	1	2
Bk	97	2	2	6	2	6	10	2	6	10	14	2	6	10.8	2	6	1	2
Cſ	98	2	2	6	2	6	10	2	6	10	14	2	6	10 10	2	6	323	2
Es	99	2	2	6	2	6	10	2	6	10	14	2	6	10 11	2	6		2
Fm	100	2	2	6	2	6	10	2	6	10	14	2	6	10 12	2	6		2
Md	101	2	2	6	2	6	10	2	6	10	14	2	6	10 13	2	6		2
No	102	2	2	6	2	6	10	2	6	10	14	2	6	10 14	2	6		2
Lr	103	2	2	6	2	6	10	2	6	10	14	2	6	10 14	2	6	1	2
Rf	104	2	2	6	2	6	10	2	6	10	14	2	6	10 10	2	6	2	2
Db	105	2	2	6	2	6	10	2	6	10	14	2	6	10 11	2	6	3	2
Sg	106	2	2	6	2	6	10	2	6	10	14	2	6	10 12	2	6	4	2
Bh	107	2	2	6	2	6	10	2	6	10	14	2	6	10 13	2	6	5	2
Hs	108	2	2	6	2	6	10	2	6	10	14	2	6	10 14	2	6	6	2
Mt	109	2	2	6	2	6	10	2	6	10	14	2	6	10 14	2	6	7	2
Ds	110	2	2	6	2	6	10	2	6	10	14	2	6	10 14	2	6	8	2
Rg**	111	2	2	6	2	6	10	2,	6	10	14	2	6	10 14	2	6	10	1

# > Stability of Completely Filled and Half Filled Subshells:

- In certain elements such as Cu, or Cr, where the two subshells (4s and 3d) differ slightly in their energies, an electron shifts from a subshell of lower energy (4s) to a subshell of higher energy (3d), provided such a shift results in all orbitals of the subshell of higher energy getting either completely filled or half filled.
- 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 associated with these electronic configurations.






# **Classification Of Elements and Periodicity in Properties**

### **Dobernier triads:**

- Classified elements into a group of three called triads.
- Arranged elements in triads in increasing order of atomic weight and the weight of the central element is equal to Arithmetic mean of other two elements.

Triad-1	Li (wt: 7)	Na (wt: 23)	K (wt: 39)
Traid-2	Ca (wt: 40)	Sr (wt: 88)	Ba (wt: 137)
Traid-3	Cl (wt: 35.5)	Br (wt: 80)	I (Wt: 127)

#### Law of octaves:

- Every 8th element had similar properties as that of the first element when all the elements were arranged in the increasing order of atomic weights.
- True only till Calcium.

Element	Li	Be	В	С	N	0	F
At. wt.	7	9	11	12	14	16	19
Element	Na	Mg	Al	Si	Р	s	CI
At. wt.	23	24	27	29	31	32	35.5
Element	K	Ca					
At. wt.	39	40					

## Lother Meyer curve:

• Plotted physical properties like volume, Melting point and boiling point against atomic weights and found a periodically repeating pattern.

#### Mendeleev's periodic table:

- Arranged elements in horizontal rows and vertical columns of the table in order of their increasing atomic weights in such a way that the elements with similar properties occupy the same vertical column.
- Relied on similarities in empirical formulas and properties of the compounds formed by the elements.
- Few elements did not fit in the classification if atomic weight was strictly followed so he ignored atomic weight order and placed elements based on similar properties. Eg: Iodine with lower weight than tellurium (Group VI) is placed in group VII.
- Gaps were left at few positions accounting to the fact that there are undiscovered elements.

#### Modern periodic table:

- Henry mosley plotted graphs and observed following points:
  - $\sqrt{v}$  Vs atomic mass : Non linear
  - $\sqrt{v}$  Vs atomic number : Linear/ straight line plot.



- Modern periodic law: The physical and chemical properties are periodic functions of their atomic numbers.
- Horizontal rows: Periods, Vertical columns: Groups
- Elements with similar outer electron configuration are arranged in the same group.
- Total : 7 periods, 18 groups (Numbered 1 to 18 as newer notation and IA, IIA ...VIIA, VIII, IB, IIB,...VIIB)
- 2,8,8,18,18,32 are the number of elements in each period from 1 to 6 respectively. The 7th is still incomplete.
- 14 elements of 6th and 7th period are placed below in separate rows.



• Classified into 4 blocks s,p,d,f based on the orbital which the last electron enters.

#### S-block:

- Group-1: Alkali metals, Group 2: Alkaline earth metals.
- Outermost electronic configuration: ns<sup>2</sup>
- Predominantly form ionic compounds except Li and Be
- Group-1: Easily form +1 ion, Group-2: Easily form +2 ions

#### **P-block:**

- From group:13-18
- Group-16: chalcogens, Group-17: Halogens, Group-18: Noble gases.
- s and p block together call as representative elements.
- Outermost electronic configuration: ns<sup>2</sup>np<sup>(1-6)</sup>

## d block elements (Transition elements):

- From group: 3-12
- Outer electronic configuration: (n-1)d<sup>1-10</sup> ns<sup>0-2</sup>
- Have variable valency, variable oxidation states, form coloured ions etc.
- Zn, Cd, Hg having  $(n-1)d^{10}ns^2$  do not show properties of transition elements.



• Form bridge between active s-block metals and less active 13,14 group elements and thus called as transition elements.

# f block elements (inner-transition elements):

- Group: 3
- The two rows placed in the bottom are called f-block elements.
- The first row (Ce-Lu) is called lanthanoids
- The second row (Th-Lr) is called actinoids
- Outermost electronic configuration: (n-2)f<sup>1-14</sup> (n-1)d<sup>0-1</sup> ns<sup>2</sup>.
- Radioactive in nature
- Elements after uranium are called transuranium metals



## **Determination of period and group number of elements:**

- Period number: Max principal quantum number
- Group: s block no. of valence electron p block - 10 + no. of valence electron d block - ns + no. of (n - 1) d electrons f block - III B

## Nomenclature of the elements with Z > 100:

• IUPAC nomenclature:

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

• Eg:

Z = 101 : Name - Unnilunium, Symbol - Unu

Z = 102: Name - Unnilbium, Symbol - Unb



Z = 110 : Name - Ununnilium, Symbol - Uun

# Atomic radius

- Determination of atomic radius is tough because the electronic cloud around the nucleus doesn't have a sharp boundary. Thus we approximately measure size by knowing the distance between atoms in a combined state.
- Types of atomic radius:
  - Covalent radius: Half the internuclear distance between covalently bonded atoms.
  - Metallic radius: Half the internuclear distance separating the metal cores in the metallic crystal
  - Vanderwaal radius: Half the internuclear distance between noble gas atoms bound together by vanderwaal force
  - Covalent radius < Metallic radius < Vanderwaal radius</p>
- General atomic trend:
  - Along group: Increases from T (top)  $\rightarrow$  B (bottom) as number of shells increase
  - Along period: Decreases form L → R as the last electron adds to same shell effective nuclear charge increases
- Exception:
  - ✤ d- block:
    - Along the period, show exceptions due to interplay between effective nuclear charge and interatomic repulsions.
    - Very low radius gap between 5th and 6th period elements due to poor shielding effect of f electrons.
  - Noble gases have exceptionally high radius due to van der waal radius
  - p-block: Due to poor shielding effect of d and f electrons there are exceptions along the group. Eg: In group-13 the size of Al is greater than Ga.

## **Ionic radius:**

- Order: Cation size < Atomic size < Anion size</li>
  Eg: Na<sup>+</sup> < Na, Cl<sup>-</sup> > Cl
- For isoelectronic species: If Z/e (Atomic number to electron) ratio increases size decreases

# Ionisation enthalpy (IE):

• The energy required to remove an electron from an isolated gaseous atom in its ground state.

 $X(g) \rightarrow X^+(g) + e^-$  IE1

 $X^+(g) \rightarrow X^{2+}(g) + e^-$  IE2

Equal to enthalpy change of the reaction. Always positive since its endothermic

- Variation of IE<sub>1</sub>:
  - Group: decreases from  $T \rightarrow B$  as the size increases



- ♦ Period: Increases from L → R as Z<sub>eff</sub> increases. But due to half filled and fully filled stability of few elements like Be, N etc they show higher IE than expected. Eg: Along period-2 : Li < Be > B < C < N > O < F < Ne</p>
- Exceptions: Based on the half filled stability, Z<sub>eff</sub>, shielding effect there are many exceptions throughout the periodic table.

# **Electron gain enthalpy:**

• The enthalpy change when an electron is added to a neutral gaseous atom.

 $X(g) + e^- \rightarrow X^-(g)$ 

- May be endothermic or exothermic based on element. Eg: Enthalpy change of halogens is negative whereas, for noble gases it highly positive
- More negative electron gain enthalpy => more energy released => more affinity to the electron (More electron affinity).
- Variation:
  - ◆ Group: Less negative from T → B i.e electron affinity decreases
  - Period: More negative from  $L \rightarrow R$  i.e electron affinity increases
- Exceptions: Less systematic than IE
  - Electron affinity of Cl > F, S > O due to very small size of F, O and higher repulsions when an electron is added.
- Cl is the element with highest electron affinity.

# **Electron**egativity (EN):

- Ability of an atom in a chemical compound to attract shared electrons to itself is called Electronegativity.
- 2 scales used to measure EN: Pauling scale (mostly used) and Mulliken scale.
  - Pauling scale: EN is a relative term and depends on the atoms attached. Fluorine is assigned with arbitrary highest value i.e 4.
  - ✤ Mulliken scale: Assumes EN is absolute.
- Variation:
  - Group: Decreases from  $T \rightarrow B$
  - Period: Increases from  $L \rightarrow R$
- Application:
  - Metallic elements => Low EN, Strong tendency to lose electrons.
  - ♦ Non-Metallic elements => High EN, Strong tendency to gain electrons.

# PERIODIC TRENDS IN CHEMICAL PROPERTIES:

## **Oxidation and reduction:**

- Oxidation: Loss of electrons, Reduction: Gain of electrons.
- Oxidising agent: Reduces itself and oxidises the other element, Reducing agent: Oxidises itself and reduces the other element.
- Trend:
  - Group: Reducing nature increases or tendency to get oxidised increases
  - Period: Oxidising nature increases or the tendency to get reduced increases.



• Strongest oxidising agent is F.

# PERIODIC TRENDS IN CHEMICAL REACTIVITY:

- High reactivity at the two extremes and low in between as the left extreme the metallic nature is high and at the right extreme nonmetallic behaviour is high.
- Metallic oxides (Extreme left) => Basic in nature ie in water they form base
- Non metallic oxides (Extreme right) => Acidic in nature ie in water they form acid
- Eg:
  - $Na_2O + H_2O \rightarrow 2NaOH$

 $Cl_2O_7 + H_2O \rightarrow 2HClO_4$ 

• Oxides in between are amphoteric (reacts with both acid and base) or neutral (do not react with acid or base).





# **Chemical Bonding and Molecular Structure**

### Chemical bonding and molecular structure

The attractive force which holds various constituents (atoms, ions, etc.) together in different chemical species is called a chemical bond.

# **KÖSSEL-LEWIS APPROACH TO CHEMICAL BONDING:**

- Lewis pictured the atom in terms of a positively charged 'Kernel' (the nucleus plus the inner electrons) and the outer shell that could accommodate a maximum of eight electrons.
- Lewis postulated that atoms achieve the stable octet when they are linked by chemical bonds.

## ➤ Lewis Symbol:

Only the outer shell electrons take part in chemical combination and they are known as valence electrons.

Li Be B C N O F

According to octet rule, the atoms can combine either by transfer of valence electrons from one atom to another (gaining or losing) or by sharing of valence electrons in order to have an octet in their valence shells.

The negative and positive ions are stabilized by electrostatic attraction. The bond formed was termed as the electrovalent bond.

Na<sup>+</sup> + Cl<sup>-</sup>  $\rightarrow$  NaCl or Na<sup>+</sup>Cl<sup>-</sup>

When two atoms share one electron pair they are said to be joined by a single covalent bond.



## Lewis Representation of Simple Molecules:

The Lewis dot structures provide a picture of bonding in molecules and ions in terms of the shared pairs of electrons and the octet rule.

The total number of electrons required for writing the structures are obtained by adding the valence electrons of the combining atoms.



	Dewis Representation
H : H*	H – H
:ö::ö:	:Ö=Ö:
Ö.	:0 <sup>0+</sup> 0:_
:F:N:F: :F:	$: \stackrel{\cdots}{\mathbf{E}} \stackrel{\cdots}{\overset{\cdots}{\mathbf{E}}} \stackrel{\cdots}{\mathbf{E}} :$
Ö:: N :Ö: H	$\ddot{\mathbf{Q}} = \mathbf{N} - \ddot{\mathbf{Q}} - \mathbf{H}$
	H: H <sup>*</sup> :O::O: O. :O :F: N:F: :F: :F: :O: C:O: O: C:O: O: H :O: H

\* Each H atom attains the configuration of helium (a duplet of electrons)

#### Formal Charge:

The formal charge of an atom in a polyatomic molecule or ion may be defined as the difference between the number of valence electrons of that atom in an isolated or free state and the number of electrons assigned to that atom in the Lewis structure.

=

Formal charge (F.C.) on an atom in a Lewis structure



## Limitations of the Octet Rule:

1. The incomplete octet of the central atom

Cl H:Be:H Cl:B:Cl

2. Odd-electron molecules

$$\ddot{N} = \ddot{O}$$
  $\ddot{O} = N^+ - \ddot{O}$ 

3. The expanded octet

Li:Cl

Let us consider the ozone molecule (O<sub>g</sub>). The Lewis structure of O<sub>g</sub> may be drawn as :



The atoms have been numbered as 1, 2 and 3. The formal charge on:

The central O atom marked 1

$$-6-2-\frac{1}{2}$$
 (6) = +1

$$= 6 - 4 - \frac{1}{2} (4) = 0$$

The end O atom marked 3

$$= 6 - 6 - \frac{1}{2}(2) = -1$$





- 4. The octet rule is based upon the chemical inertness of noble gases. However, some noble gases (for example xenon and krypton) also combine with oxygen and fluorine to form a number of compounds like XeF<sub>2</sub>, KrF<sub>2</sub>, XeOF<sub>2</sub> etc.,
- 5. This theory does not account for the shape of molecules.
- 6. It does not explain the relative stability of the molecules being totally silent about the energy of a molecule.

#### **IONIC OR ELECTROVALENT BOND:**

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. Ionic compounds in the crystalline state consist of orderly three-dimensional arrangements of cations and anions held together by coulombic interaction energies.

The crystal structure of sodium chloride, NaCl (rock salt), for example is shown below.



#### > Lattice Enthalpy:

The Lattice Enthalpy of an ionic solid is defined as the energy required to completely separate one mole of a solid ionic compound into gaseous constituent ions.

## **BOND PARAMETERS:**

#### • Bond Length:

Bond length is defined as the equilibrium distance between the nuclei of two bonded atoms in a molecule.

Covalent and van der Waals radii of chlorine are depicted below:





Covalent and van der Waals radii in a chlorine molecule. The inner circles correspond to the size of the chlorine atom ( $r_{vdw}$  and  $r_c$  are van der Waals and covalent radii respectively).

#### Bond Angle:

The angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.



### • 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.

$$\begin{split} \mathbf{O}_2 & (\mathrm{O}=\mathrm{O}) \; (\mathrm{g}) \to \mathrm{O}(\mathrm{g}) + \mathrm{O}(\mathrm{g}); \\ & \Delta_{\mathrm{a}} H^{\mathrm{\theta}} = 498 \; \mathrm{kJ} \; \mathrm{mol}^{-1} \\ \mathbf{N}_2 \; (\mathrm{N}\equiv\mathrm{N}) \; (\mathrm{g}) \to \mathrm{N}(\mathrm{g}) + \mathrm{N}(\mathrm{g}); \\ & \Delta_{\mathrm{a}} H^{\mathrm{\theta}} = 946.0 \; \mathrm{kJ} \; \mathrm{mol}^{-1} \end{split}$$

#### • Bond Order:

In the Lewis description of covalent bond, the Bond Order is given by the number of bonds between the two atoms in a molecule. Isoelectronic molecules and ions have identical bond orders; for example,  $F_2$  and  $O_2$ <sup>2–</sup> have bond order 1. N<sub>2</sub>, CO and NO<sup>+</sup> have bond order 3.





## **>** Resonance Structures:

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 non-bonding pairs of electrons are taken as the canonical structures of the hybrid which describes the molecule accurately.

#### > Polarity of Bonds:

In reality no bond or a compound is either completely covalent or ionic.

As a result of polarisation, the molecule possesses the dipole moment (depicted below) which can be defined as the product of the magnitude of the charge and the distance between the centres of positive and posetive charge

distance between the centres of positive and negative charge.



#### > Dipole moments of some molecules are shown in the Table below.

Type of Molecule	Example	Dipole Moment, µ(D)	Geometry
Molecule (AB)	HF	1.78	linear
	HCl	1.07	linear
	HBr	0.79	linear
	HI	0.38	linear
	H <sub>2</sub>	0	linear
Molecule (AB <sub>2</sub> )	H,O	1.85	bent
	H.S	0.95	bent
	CÔ <sub>2</sub>	0	linear
Molecule (AB <sub>3</sub> )	NHa	1.47	trigonal-pyramidal
	NFa	0.23	trigonal-pyramidal
	BF <sub>3</sub>	0	trigonal-planar
Molecule (AB <sub>4</sub> )	CH4	0	tetrahedral
	CHCI	1.04	tetrahedral
	CCI,	0	tetrahedral



# > VSEPR THEORY:

This theory provides a simple procedure to predict the shapes of covalent molecules.

- The main postulates of VSEPR theory are as follows:
  - 1. The shape of a molecule depends upon the number of valence shell electron pairs (bonded or nonbonded) around the central atom.
  - 2. Pairs of electrons in the valence shell repel one another since their electron clouds are negatively charged.
  - 3. These pairs of electrons tend to occupy such positions in space that minimise repulsion and thus maximise distance between them.
  - 4. The valence shell is taken as a sphere with the electron pairs localising on the spherical surface at maximum distance from one another.
  - 5. 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.
  - 6. 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)

These repulsion effects result in deviations from idealised shapes and alterations in bond angles in molecules.





Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electron pairs	Shape	Examples
AB <sub>2</sub> E	2	1	B B Trigonal planer	Bent	50 <sup>1</sup> 0,
AB <sub>2</sub> E	3	1	B B B B Tetrahedral	Trigonal pyramidal	NH3
AB <sub>s</sub> E <sub>s</sub>	2	2	B Tetrahedral	Bent	H,O
AB,E	4	1	B B B Trigonal bi-pyramidal	See saw	SF.
AB,E,	3	2	B B B B Trigonal bi-pyramidal	T-shape	CIFs
AB,E	5	1	B B A B Octahedral	Square pyramid	BrFs
AB <sub>e</sub> E <sub>s</sub>	4	2	B B B D Octahedral	Square planer	XeF,



Molecule type	No. of bonding pairs	No. of lone pairs	Arrangement of electrons	Shape	Reason for the shape acquired
AB <sub>2</sub> E	4	1	:0 <sup>3</sup> 119.5° 0; 0 <sup>5</sup>	Bent ≷o	Theoretically the shape should have been triangular planar but achually it is found to be bent or v-shaped. The reason being the lone pair- bond pair repulsion is much more as compared to the bond pair-bond pair repul- sion. So the angle is reduced to 119.5° from 120°.
AB <sub>3</sub> E	3	1	H 107 H	Trigonal pyramidal	Had there been a bp in place of lp the shape would have been tetrahedral but one lone pair is present and due to the repulsion between
			R N	8	ip-bp (which is more than bp-bp repulsion) the angle between bond pairs is reduced to 107° from 109.5°
AB <sub>2</sub> E <sub>2</sub>	2	2	H 104.5*	Bent Et	The shape should have beer tetrahedral if there were all bp but two lp are present so the shape is distorted tetrahedra or angular. The reason is lp-lp repulsion is more than lp-bp repulsion which is more than bp-bp repulsion. Thus the angle is reduced to 104,5° from 109,5°.
AB4E	4	1 (a		See- saw	In (a) the lp is present at axia position so there are three lp—bp repulsions at 90°. In(b) the lp is in an equatoria position, and there are two lp—bp repulsions. Hence arrangement (b) is more stable. The shape shown in (b) is described as a distorted tetrahedron, a folded square of





# > VALENCE BOND THEORY:

The valence bond theory is based on the knowledge of atomic orbitals, electronic configurations of elements, the overlap criteria of atomic orbitals, the hybridization of atomic orbitals and the principles of variation and superposition.

## • Orbital Overlap Concept:

The formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.

# • Overlapping of Atomic Orbitals:

When orbitals of two atoms come close to form bond, their overlap may be positive, negative or zero depending upon the sign (phase) and direction of orientation of amplitude of orbital wave function in space



s and p atomic orbitals

- Types of Overlapping and Nature of Covalent Bonds:
  - ✤ Sigma(*σ*) bond: formed by the end to end (head-on) overlap of bonding orbitals along the internuclear axis.







#### • $pi(\pi)$ bond:

Sidewise overlapping consists of two saucer type charged clouds above and below the plane of the participating atoms



# > HYBRIDISATION:

To explain the characteristic geometrical shapes of polyatomic molecules like CH<sub>4</sub>, NH<sub>3</sub> and H<sub>2</sub>O etc.,

The atomic orbitals combine to form a new set of equivalent orbitals known as hybrid orbitals. Unlike pure orbitals, the hybrid orbitals are used in bond formation. The phenomenon is known as hybridisation

## • Salient features of hybridisation:

- 1. The number of hybrid orbitals is equal to the number of the atomic orbitals that get hybridised.
- 2. The hybridised orbitals are always equivalent in energy and shape.
- 3. The hybrid orbitals are more effective in forming stable bonds than the pure atomic orbitals.
- 4. These hybrid orbitals are directed in space in some preferred direction to have minimum repulsion between electron pairs and thus a stable arrangement. Therefore, the type of hybridisation indicates the geometry of the molecules.

## • Types of Hybridisation:

There are various types of hybridisation involving s, p and d orbitals.

✤ sp hybridisation: Each sp hybrid orbitals has 50% s-character and 50% pcharacter.

E.g. BeCl<sub>2</sub> molecule.





(a) Formation of sp hybrids from s and p orbitals; (b) Formation of the linear BeCl, molecule

sp<sup>2</sup> hybridisation: 33.3 % s-character and 66.6 % p-character in each sp<sup>2</sup> hybrid orbital.



✤ sp<sup>3</sup> hybridisation:

25% s-character and 75% p-character in each sp<sup>3</sup> hybrid orbital. E.g. CH<sub>4</sub> molecule, H<sub>2</sub>O and NH<sub>3</sub>





Shape of molecules/ ions	Hybridisation type	Atomic orbitals	Examples
Square planar	dsp <sup>2</sup>	d+s+p(2)	$[N1(CN)_4]^{2-},$ $[Pt(Cl)_4]^{2-}$
Trigonal bipyramidal	sp³d	s+p(3)+d	PF <sub>5</sub> , PCl <sub>5</sub>
Square pyramidal	sp <sup>3</sup> d <sup>2</sup>	s+p(3)+d(2)	BrF <sub>5</sub>
Octahedral	sp <sup>3</sup> d <sup>2</sup> d <sup>2</sup> sp <sup>3</sup>	s+p(3)+d(2) d(2)+s+p(3)	$\begin{array}{c} {\rm SF}_{6^{*}} \; [{\rm CrF}_{6}]^{3} \\ [{\rm Co}({\rm NH}_{3})_{6}]^{3*} \end{array}$

## > MOLECULAR ORBITAL THEORY:

#### • Salient features:

- 1. The electrons in a molecule are present in the various molecular orbitals as the electrons of atoms are present in the various atomic orbitals.
- 2. The atomic orbitals of comparable energies and proper symmetry combine to form molecular orbitals.



- 3. While an electron in an atomic orbital is influenced by one nucleus, in a molecular orbital it is influenced by two or more nuclei depending upon the number of atoms in the molecule. Thus, an atomic orbital is monocentric while a molecular orbital is polycentric.
- 4. The number of molecular orbital forms is equal to the number of combining atomic orbitals. When two atomic orbitals combine, two molecular orbitals are formed. One is known as bonding molecular orbital while the other is called antibonding molecular orbital.
- 5. The bonding molecular orbital has lower energy and hence greater stability than the corresponding antibonding molecular orbital.
- 6. Just as the electron probability distribution around a nucleus in an atom is given by an atomic orbital, the electron probability distribution around a group of nuclei in a molecule is given by a molecular orbital.
- 7. The molecular orbitals like atomic orbitals are filled in accordance with the aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.
- Formation of Molecular Orbitals Linear Combination of Atomic Orbitals (LCAO):

The molecular orbital  $\sigma$  formed by the addition of atomic orbitals is called the bonding molecular orbital while the molecular orbital  $\sigma^*$  formed by the subtraction of atomic orbital is called antibonding molecular orbital.



Formation of bonding ( $\sigma$ ) and antibonding ( $\sigma$ \*) molecular orbitals by the linear combination of atomic orbitals  $\psi_A$ and  $\psi_B$  centered on two atoms A and B respectively.

## > Conditions for the Combination of Atomic Orbitals:

- 1. The combining atomic orbitals must have the same or nearly the same energy.
- 2. The combining atomic orbitals must have the same symmetry about the molecular axis.
- 3. The combining atomic orbitals must overlap to the maximum extent.
- Types of Molecular Orbitals:



Molecular orbitals of diatomic molecules are designated as  $\sigma$  (sigma),  $\pi$  (pi),  $\delta$  (delta), etc.

sigma( $\sigma$ ) molecular orbitals are symmetrical around the bond-axis while pi ( $\pi$ ) molecular orbitals are not symmetrical.



• Energy Level Diagram for Molecular Orbitals: For O<sub>2</sub> and F<sub>2</sub>

• The increasing order of energies of various molecular orbitals for O<sub>2</sub> and F<sub>2</sub> is given below:

```
\begin{split} \sigma ls < &\sigma^* \, ls < \sigma 2s < \sigma^* 2s < \sigma 2p_z < (\pi \ 2p_x = \pi \ 2p_y) \\ < &(\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z \end{split}
```

• The increasing order of energies of various molecular orbitals for Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, and N<sub>2</sub> is given below:

$$\begin{split} \sigma ls < &\sigma^* ls < \sigma 2s < \sigma^* 2s < (\pi \ 2p_x = \pi \ 2p_y) \\ < &\sigma 2p_z < (\pi^* 2p_x = \pi^* 2p_y) < \sigma^* 2p_z \end{split}$$



# > Electronic Configuration and Molecular Behaviour:

## • Bond order:

Bond order (b.o.) is defined as one half the difference between the number of electrons present in the bonding and the antibonding orbitals. Bond order (b.o.) =  $\frac{1}{2} (N_b - N_a)$ 

# • Magnetic nature:

If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one or more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field), e.g., O<sub>2</sub> molecule.

# > BONDING IN SOME HOMONUCLEAR DIATOMIC MOLECULES:

# H<sub>2</sub> molecule:

$\mathrm{H}_2:(\sigma Is)^2$	Bond order = $\frac{N_{b} - N_{s}}{2} = \frac{2 - 0}{2} = 1$
He <sub>2</sub> molecule:	$He_2: (\sigma Is)^2 (\sigma^* Is)^2$ Bond order of $He_2$ is $\frac{1}{2}(2-2) = 0$
Li <sub>2</sub> molecule: Bond order =1	Li <sub>2</sub> : $(\sigma 1 s)^2 (\sigma^* 1 s)^2 (\sigma 2 s)^2$
C <sub>2</sub> molecule:	$C_2: (\sigma ls)^3 (\sigma \cdot ls)^2 (\sigma \cdot 2s)^2 (\pi 2p_x^2 = \pi 2p_y^2)$ The bond order of $C_2$ is $\frac{1}{2}(8-4) = 2$
O <sub>2</sub> molecule:	$O_{2}: (\sigma l s)^{2} (\sigma^{*} l s)^{2} (\sigma^{*} 2 s)^{2} (\sigma^{*} 2 s)^{2} (\sigma 2 p_{z})^{2}  \left(\pi 2 p_{x}^{2} \equiv \pi 2 p_{y}^{2}\right) \left(\pi^{*} 2 p_{x}^{1} \equiv \pi^{*} 2 p_{y}^{1}\right)$

> MO occupancy and molecular properties for B<sub>2</sub> through Ne<sub>2</sub>. Bond order  $= \frac{1}{2}[N_b - N_a] = \frac{1}{2}[10 - 6] = 2$ 



MO occupancy and molecular properties for B<sub>2</sub> through Ne<sub>2</sub>.

# HYDROGEN BONDING:

Hydrogen bond can be defined as the attractive force which binds the hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule.

- There are two types of H-bonds
  - (i) Intermolecular hydrogen bond
  - (ii) Intramolecular hydrogen bond



Intramolecular hydrogen bonding in o-nitrophenol molecule



**States of Matter** 

- Bulk properties of matter are the properties associated with a collection of a large number of atoms, ions or molecules.
  - an individual molecule of a liquid does not boil but the bulk boils.
  - Collection of water molecules have wetting properties; individual molecules do not wet.
- Chemical properties of a substance do not change with the change of its physical state; but the rate of chemical reactions do depend upon the physical state.

# > INTERMOLECULAR FORCES

- Intermolecular forces are the forces of attraction and repulsion between interacting particles (atoms and molecules). It does not include the ionic and covalent bonds.
- Attractive intermolecular forces are known as van der Waals forces, in honour of Dutch scientist Johannes van der Waals (1837- 1923).
- Attractive forces between an ion and a dipole are known as ion-dipole forces and these are not van der Waals forces.

## 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.
- A dipole may develop momentarily even in such atoms and molecules.
- Instantaneous or transient dipoles distort the electron density of the other atom which is close to it and as a consequence a dipole is induced in that atom.
- The temporary dipoles attract each other.







- This force of attraction was first proposed by the German physicist Fritz London, and for this reason it is known as London force.
- Another name for this force is dispersion force.
- These forces are always attractive.
- Interaction energy is inversely proportional to the sixth power of the distance between two interacting particles (i.e., 1/r<sup>6</sup> where r is the distance between two particles)
- These forces are important only at short distances (~500 pm) and their magnitude depends on the polarisability of the particle.

## Dipole - Dipole Forces

- Dipole-dipole forces act between the molecules possessing permanent dipoles.
- Ends of the dipoles possess "partial charges" (shown by Greek letter delta ( $\delta$ )) which are always less than the unit electronic charge (1.6 × 10<sup>-19</sup> C)
- The polar molecules interact with neighbouring molecules.



- This interaction is stronger than the London forces but is weaker than ion-ion interaction because only partial charges are involved.
- The attractive force decreases with the increase of distance between the dipoles.
- The interaction energy is inversely proportional to distance between polar molecules.
  - $\circ$  Dipole-dipole interaction energy between stationary polar molecules (as in solids) is proportional to  $1/r^3$ .
  - Interaction energy between rotating polar molecules is proportional to  $1/r^6$ , where r is the distance between polar molecules.



• Besides dipole dipole interaction, polar molecules can interact by London forces also. Thus the cumulative effect is that the total of intermolecular forces in polar molecules increase.

# > 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 electron cloud.



- Interaction energy is proportional to  $1/r^6$  where r is the distance between two molecules.
- Induced dipole moment depends upon the dipole moment present in the permanent dipole and the polarisability of the electrically neutral molecule.
- Molecules of larger size can be easily polarized. High polarisability increases the strength of attractive interactions.
- Cumulative effects of dispersion forces and dipole-induced dipole interactions exists.

## Hydrogen bond

- This is a special case of dipole-dipole interaction.
- This is found in the molecules in which highly polar N–H, O–H or H–F bonds are present. However, species such as Cl<sup>-</sup> may also participate in hydrogen bonding
- Energy of the hydrogen bond varies between 10 to 100 kJ mol<sup>-1</sup>.
- Hydrogen bonds are a powerful force in determining the structure and properties of many compounds, for example proteins and nucleic acids.
- Strength of the hydrogen bond is determined by the coulombic interaction between the lone-pair electrons of the electronegative atom of one molecule and the hydrogen atom of another molecule.

# > Repulsive intermolecular forces

- Molecules also exert repulsive forces on one another.
- When two molecules are brought into close contact with each other, the repulsion between the electron clouds and that between the nuclei of two molecules comes into play.
- Magnitude of the repulsion rises very rapidly as the distance separating the molecules decreases.



• This is the reason that liquids and solids are hard to compress. In these states molecules are already in close contact; therefore they resist further compression; as that would result in the increase of repulsive interactions.

# > THERMAL ENERGY

- It is the energy of a body arising from motion of its atoms or molecules.
- Directly proportional to the temperature of the substance.
- It is the measure of average kinetic energy of the particles of the matter and is thus responsible for movement of particles. This movement of particles is called thermal motion.

## > INTERMOLECULAR FORCES vs THERMAL INTERACTIONS

- Intermolecular forces tend to keep the molecules together but thermal energy of the molecules tends to keep them apart.
- Three states of matter are the result of balance between intermolecular forces and the thermal energy of the molecules.
- When molecular interactions are very weak, molecules do not cling together to make liquid or solid unless thermal energy is reduced by lowering the temperature.
  - Gases do not liquify on compression only, although molecules come very close to each other and intermolecular forces operate to the maximum.
  - When thermal energy of molecules is reduced by lowering the temperature; the gases can be very easily liquified.



#### ➤ THE GASEOUS STATE

- This is the simplest state of matter.
- We spend our life in the lowermost layer of the atmosphere called the troposphere, which is held to the surface of the earth by gravitational force.
  - The thin layer of atmosphere is vital to our life.
  - It shields us from harmful radiations and contains substances like dioxygen, dinitrogen, carbon dioxide, water vapour, etc.
- Only eleven elements exist as gases under normal conditions.



Group number	1	3	15	16	17	18
	н					He
8	1	23	N	0	F	Ne
					CI	Ar
						Kr
						Xe
						Rn

## Physical properties of gases

- Gases are highly compressible.
- Gases exert pressure equally in all directions.
- Gases have much lower density than the solids and liquids.
- The volume and the shape of gases are not fixed. These assume the volume and shape of the container.
- Gases mix evenly and completely in all proportions without any mechanical aid.
- Simplicity of gases is due to the fact that the forces of interaction between their molecules are negligible.

#### > THE GAS LAWS

- The first reliable measurement on properties of gases was made by Anglo-Irish scientist Robert Boyle in 1662. The law which he formulated is known as Boyle's Law.
- Later on attempts to fly in air with the help of hot air balloons motivated Jaccques Charles and Joseph Lewis Gay Lussac to discover additional gas laws.
- Contribution from Avogadro and others provided a lot of information about the gaseous state.

## Boyle's 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 Boyle's law.
- Mathematically-

#### $\mathbf{p} \propto \mathbf{1/V} \Rightarrow \mathbf{p} = \mathbf{k}_1 (\mathbf{1/V})$

 $k_1$  is the proportionality constant whose value depends upon the amount of the gas, temperature of the gas and the units in which p and V are expressed.

• On rearranging, we obtain -

## $\mathbf{pV} = \mathbf{k}_1$

It means that at constant temperature, the product of pressure and volume of a fixed amount of gas is constant.

• If a fixed amount of gas at constant temperature T occupying volume V<sub>1</sub> at pressure p<sub>1</sub> undergoes expansion, so that volume becomes V<sub>2</sub> and pressure becomes p<sub>2</sub>, then according to Boyle's law:

#### $p_1V_1 = p_2V_2 = constant$



$$\Rightarrow \frac{p_1}{p_2} = \frac{V_2}{V_1}$$

• Two conventional ways of graphically presenting Boyle's law -



Graph of pressure, p vs. Volume, V of a gas at different temperatures.

- The value of k<sub>1</sub> for each curve is different because for a given mass of gas, it varies only with temperature.
- Each curve corresponds to a different constant temperature and is known as an isotherm (constant temperature plot).
- Higher curves correspond to higher temperatures.



Graph of pressure of a gas, p vs. (1/V)

- It is a straight line passing through the origin.
- However at high pressures, gases deviate from Boyle's law and under such conditions a straight line is not obtained in the graph.
- In a quantitative manner prove that gases are highly compressible because when a given mass of a gas is compressed, the same number of molecules occupy a smaller space. This means that gases become denser at high pressure.
- A relationship can be obtained between density and pressure of a gas by using Boyle's law:

$$d = \left(\frac{m}{\mathbf{k}_1}\right) p = \mathbf{k}' p$$



- This shows that at a constant temperature, pressure is directly proportional to the density of a fixed mass of the gas.
- > Charles' Law (Temperature Volume Relationship)
  - For a fixed mass of a gas at constant pressure, volume of a gas increases on increasing temperature and decreases on cooling.
  - For each degree rise in temperature, volume of a gas increases by (1/273.15) of the original volume of the gas at 0°C.

$$V_{\rm t} = V_0 \left(\frac{273.15 + t}{273.15}\right)$$

- New temperature scale called the **Kelvin temperature scale** or **Absolute temperature scale** is defined based on the above relationship.
  - t°C on new scale is given by T = 273.15 + t and 0°C will be given by  $T_0 = 273.15$
- Degree sign is not used while writing the temperature in absolute temperature scale, i.e., Kelvin scale.
- The Kelvin scale of temperature is also called Thermodynamic scale of temperature and is used in all scientific works.
- If the temperature is used in kelvin, we can write general expression of Charles' law as -

$$\frac{V_2}{V_1} = \frac{T_2}{T_1}$$
$$\Rightarrow \frac{V_1}{T_1} = \frac{V_2}{T_2}$$
$$\Rightarrow \frac{V}{T} = \text{constant} = \mathbf{k}_2$$
Thus  $V = \mathbf{k}_2 T$ 

- The value of constant k<sub>2</sub> is determined by the pressure of the gas, its amount and the units in which volume V is expressed.
- The mathematical expression for Charles' law states that pressure remaining constant, the volume of a fixed mass of a gas is directly proportional to its absolute temperature.
- For all gases, at any given pressure, the graph of volume vs temperature (in celsius) is a straight line and on extending to zero volume, each line intercepts the temperature axis at 273.15°C. Slopes of lines obtained at different pressure are different but at zero volume all the lines meet the temperature axis at 273.15°C.





- Each line of the volume vs temperature graph is called isobar.
- The volume of the gas at 273.15°C will be zero. This means that gas will not exist. In fact all the gases get liquified before this temperature is reached.
- The lowest hypothetical or imaginary temperature at which gases are supposed to occupy zero volume is called **Absolute zero**.
- All gases obey Charles' law at very low pressures and high temperatures.

# Gay Lussac's Law (Pressure-Temperature Relationship)

- The mathematical relationship between pressure and temperature was given by Joseph Gay Lussac and is known as Gay Lussac's law.
- At constant volume, pressure of a fixed amount of a gas varies directly with the temperature.
- Mathematically,

$$\Rightarrow \frac{p}{T} = \text{constant} = \mathbf{k}_3$$

• Pressure vs temperature (Kelvin) graph at constant molar volume is shown. Each line of this graph is called isochore.





# > Avogadro Law (Volume - Amount Relationship)

- In 1811 Italian scientist Amedeo Avogadro tried to combine conclusions of Dalton's atomic theory and Gay Lussac's law of combining volumes which is now known as Avogadro law.
- Equal volumes of all gases under the same conditions of temperature and pressure contain equal numbers of molecules.
- As long as the temperature and pressure remain constant, the volume depends upon the number of molecules of the gas or in other words amount of the gas.
- Mathematically we can write
  V ∝ n (where n is the number of moles of the gas)
  ⇒ V = k<sub>4</sub> n
- Standard temperature and pressure (STP): 273.15 K (0°C) temperature and 1 bar (i.e., exactly 10<sup>5</sup> pascal) pressure. These values approximate freezing temperature of water and atmospheric pressure at sea level.
- One mole of each gas at standard temperature and pressure (STP) will have the same volume. At STP the molar volume of an ideal gas or a combination of ideal gases is 22.71098 L mol<sup>-1</sup>.
- Standard ambient temperature and pressure (SATP), conditions are also used in some scientific works. SATP conditions means 298.15 K and 1 bar (i.e., exactly 10<sup>5</sup> Pa).
- At SATP (1 bar and 298.15 K), the molar volume of an ideal gas is 24.789 L mol<sup>-1</sup>.
- On rearranging the avogadro's law we can also conclude The density of a gas is directly proportional to its molar mass.

$$\mathbf{M} = \mathbf{k}_4 \ \frac{m}{V} = \mathbf{k}_4 d$$

- A gas that follows Boyle's law, Charles' law and Avogadro law is called an ideal gas. Such a gas is hypothetical.
- It is assumed that intermolecular forces are not present between the molecules of an ideal gas.
- Real gases follow these laws only under certain specific conditions when forces of interaction are practically negligible. In all other situations these deviate from ideal behaviour.

# IDEAL GAS EQUATION

- The three laws (Boyle's, Charles', Avogadro's) can be combined together in a single equation which is known as the ideal gas equation.
  - $\mathbf{pV} = \mathbf{nRT}$
- R is called **gas constant**. It is the same for all gases. Therefore, it is also called **Universal Gas Constant**.
- This equation will be applicable to any gas, under those conditions when behaviour of the gas approaches ideal behaviour.
- The value of R depends upon units in which p, V and T are measured. Volume of one mole of an ideal gas under STP conditions (273.15 K and 1 bar pressure) is 22.710981 L mol<sup>-1</sup>. Value of R for one mole of an ideal gas can be calculated under these conditions.



# $R = 8.314 J K^{-1} mol^{-1}$

- According to the **previous definition of STP** temperature of 0°C (273.15 K), but a slightly higher pressure of 1 atm (101.325 kPa), One mole of any gas of a combination of gases occupies 22.413996 L of volume at STP.
- The value of R as per previous definition is 0.0820578 L atm K<sup>-1</sup> mol<sup>-1</sup>.
- Ideal gas equation is a relation between four variables and it describes the state of any gas, therefore, it is also called the equation of state.
- Combined gas law –

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

## > Density and Molar Mass of a Gaseous Substance

• On rearrangement of ideal gas equation, we get the relationship for calculating molar mass of a gas –

$$M = \frac{dRT}{p}$$

## Dalton's Law of Partial Pressures

- The law was formulated by John Dalton in 1801.
- The total pressure exerted by the mixture of non-reactive gases is equal to the sum of the partial pressures of individual gases.
- In a mixture of gases, the pressure exerted by the individual gas is called partial pressure.
- Mathematically, p<sub>Total</sub> = p<sub>1</sub> + p<sub>2</sub> + p<sub>3</sub> + ..... (at constant T, V) p<sub>Total</sub> is the total pressure exerted by the mixture of gases and p<sub>1</sub>, p<sub>2</sub>, p<sub>3</sub> etc. are partial pressures of gases.
- Gases are generally collected over water and therefore are moist. Pressure exerted by saturated water vapour is called aqueous tension. Aqueous tension of water at different temperatures is given in Table.

Temp./K	Pressure/bar	Temp./K	Pressure/bar
273.15	0.0060	295.15	0.0260
283.15	0.0121	297.15	0.0295
288.15	0.0168	299.15	0.0331
291.15	0.0204	301.15	0.0372
293.15	0.0230	303.15	0.0418

Pressure of dry gas can be calculated by subtracting vapour pressure of water from the total pressure of the moist gas which contains water vapours also.
 p<sub>Dry gas</sub> = p<sub>Total</sub> – Aqueous tension

## > Partial pressure in terms of mole fraction

Using a combination of ideal gas equation and Dalton's law of partial pressures, we get the relationship partial pressure of a gas = total pressure × mole fraction

 $\mathbf{p}_{i} = \mathbf{p}_{total} \boldsymbol{\chi}_{i}$ 



 $p_i$  and  $\chi_i$  are partial pressure and mole fraction of i<sup>th</sup> gas respectively.

## > KINETIC MOLECULAR THEORY OF GASES

- A theory is a model (i.e., a mental picture) that enables us to better understand our observations.
- The theory that attempts to elucidate the behaviour of gases is known as kinetic molecular theory.

#### > Assumptions or postulates of the kinetic molecular theory of gases

- Gases consist of a 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.
- 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 the total energy of molecules before and after the collision remains the same. There may be exchange of energy between colliding molecules, their individual energies may change, but the sum of their energies remains constant.
  - If there were loss of kinetic energy, the motion of molecules will stop and gases will settle down. This is contrary to what is actually observed.
- At any particular time, different particles in the gas have different speeds and hence different kinetic energies.
  - This assumption is reasonable because as the particles collide, we expect their speed to change. Even if initial speed of all the particles was same, the molecular collisions will disrupt this uniformity. Consequently, the particles must have different speeds, which go on changing constantly.
  - It is possible to show that though the individual speeds are changing, the distribution of speeds remains constant at a particular temperature.
- If a molecule has variable speed, then it must have a variable kinetic energy. Under these circumstances, we can talk only about average kinetic energy. In kinetic theory it is assumed that average kinetic energy of the gas molecules is directly proportional to the absolute temperature.
  - It is seen that on heating a gas at constant volume, the pressure increases. On heating the gas, kinetic energy of the particles increases and these strike the walls of the container more frequently thus exerting more pressure.



• Kinetic theory of gases allows us to derive theoretically, all the gas laws. Calculations and predictions based on kinetic theory of gases agree very well with the experimental observations and thus establish the correctness of this model.

#### > BEHAVIOUR OF REAL GASES: DEVIATION FROM IDEAL GAS BEHAVIOUR

• To test how far the relation pV = nRT reproduces the actual pressure - volume - temperature relationship of gases we plot pV vs p plot of gases -



a plot of pV vs p for real gas and ideal gas constructed from actual data for several gases at 273 K.

- Two types of curves are seen.
  - In the curves for dihydrogen and helium, as the pressure increases the value of pV also increases.
  - The second type of plot is seen in the case of other gases like carbon monoxide and methane. In these plots first there is a negative deviation from ideal behaviour, the pV value decreases with increase in pressure and reaches to a minimum value characteristic of a gas. After that pV value starts increasing. The curve then crosses the line for ideal gas and after that shows positive deviation continuously.
- We can conclude Real gases do not follow ideal gas equation perfectly under all conditions.
- Deviation from ideal behaviour also becomes apparent when pressure vs volume plot is drawn –





Plot of pressure vs volume for real gas and ideal gas

- At very high pressure the measured volume is more than the calculated volume. At low pressures, measured and calculated volumes approach each other.
- It is found that real gases do not follow Boyle's law, Charles law and Avogadro law perfectly under all conditions.
- We find that two assumptions of the kinetic theory do not hold good. These are -
  - There is no force of attraction between the molecules of a gas. If this assumption is correct, the gas will never liquify. However, we know that gases do liquify when cooled and compressed. Also, liquids formed are very difficult to compress. This means that forces of repulsion are powerful enough and prevent squashing of molecules in tiny volumes.
  - Volume of the molecules of a gas is negligibly small in comparison to the space occupied by the gas. If this assumption is correct, the pressure vs volume graph of experimental data (real gas) and that theoretically calculated from Boyle's law (ideal gas) should coincide.

## **Van der Waals equation**

- Real gases show deviations from ideal gas law because molecules interact with each other.
- At high pressures molecules of gases are very close to each other. Molecular interactions start operating. At high pressure, molecules do not strike the walls of the container with full impact because these are dragged back by other molecules due to molecular attractive forces. This affects the pressure exerted by the molecules on the walls of the container.
- Thus, the 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.


- Repulsive interactions are short-range interactions and are significant when molecules are almost in contact. This is the situation at high pressure. The repulsive forces cause the molecules to behave as small but impenetrable spheres.
- The volume occupied by the molecules also becomes significant because instead of moving in volume V, these are now restricted to volume (V–nb) where nb is approximately the total volume occupied by the molecules themselves. Here, b is a constant.
- Having taken into account the corrections for pressure and volume, we can rewrite ideal gas equation as -

$$\left(p + \frac{an^2}{V^2}\right)(V - n\mathbf{b}) = n\mathbf{R}T$$

- It is known as van der Waals equation.
- n is the number of moles of the gas.
- Constants a and b are called van der Waals constants and their value depends on the characteristic of a gas.
- At very low temperatures, intermolecular forces become significant. As the molecules travel with low average speed, these can be captured by one another due to attractive forces.
- Real gases show ideal behaviour when conditions of temperature and pressure are such that the intermolecular forces are practically negligible. The real gases show ideal behaviour when pressure approaches zero.

#### Compressibility factor

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

$$Z = \frac{pV}{n\,\mathrm{R}T}$$

- For ideal gas Z = 1 at all temperatures and pressures.
- For gases which deviate from ideality, the value of Z deviates from unity.



Variation of compressibility factor for some gases



- → At very low pressures all gases shown have  $Z \approx 1$  and behave as ideal gas.
- $\rightarrow$  At high pressure all the gases have Z > 1. These are more difficult to compress.
- → At intermediate pressures, most gases have Z < 1.
- Gases show ideal behaviour when the volume occupied is large so that the volume of the molecules can be neglected in comparison to it.
- The temperature at which a real gas obeys ideal gas law over an appreciable range of pressure is called Boyle temperature or Boyle point.
  - The Boyle point of a gas depends upon its nature.
  - Above their Boyle point, real gases show positive deviations from ideality and Z values are greater than one. The forces of attraction between the molecules are very feeble.
  - Below Boyle temperature real gases first show decrease in Z value with increasing pressure, which reaches a minimum value. On further increase in pressure, the value of Z increases continuously.
- Significance of Z -

$$Z = \frac{V_{\text{real}}}{V_{\text{ideal}}}$$

From this equation we can see that the compressibility factor is the ratio of actual molar volume of a gas to the molar volume of it, if it were an ideal gas at that temperature and pressure.

#### LIQUEFACTION OF GASES

- Liquids may be considered as continuation of the gas phase into a region of small volumes and very high molecular attraction.
- First complete data on pressure volume temperature relations of a substance in both gaseous and liquid state was obtained by Thomas Andrews on carbon dioxide.
- He plotted isotherms of carbon dioxide at various temperatures –



Isotherms of carbon dioxide at various temperatures



#### > Observations -

- At high temperatures isotherms look like that of an ideal gas and the gas cannot be liquified even at very high pressure.
- At 30.98°C carbon dioxide remains gas upto 73 atmospheric pressure. At 73 atmospheric pressure, liquid carbon dioxide appears for the first time. The temperature 30.98°C is called critical temperature (T<sub>C</sub>) of carbon dioxide.
  - $\circ$  Critical temperature (T<sub>C</sub>) is the highest temperature at which liquid state of substance is observed. Above this temperature it is gas.
  - $\circ$  Volume of one mole of the gas at critical temperature is called critical volume (V<sub>C</sub>) and pressure at this temperature is called critical pressure (p<sub>C</sub>).
  - $\circ$   $\,$  The critical temperature, pressure and volume are called critical constants.
- Further increase in pressure above 73 atm at 30.98°C simply compresses the liquid carbon dioxide and the curve represents the compressibility of the liquid. The steep line represents the isotherm of liquid. Even a slight compression results in a steep rise in pressure indicating very low compressibility of the liquid.
- Below 30.98 °C, the behaviour of the gas on compression is quite different -
  - At 21.5 °C, carbon dioxide remains as a gas only upto point B. At point B, liquid of a particular volume appears. Further compression does not change the pressure. Liquid and gaseous carbon dioxide coexist and further application of pressure results in the condensation of more gas until the point C is reached. At point C, all the gas has been condensed and further application of pressure merely compresses the liquid as shown by the steep line. A slight compression from volume V<sub>2</sub> to V<sub>3</sub> results in steep rise in pressure from p<sub>2</sub> to p<sub>3</sub>.
- A point under the dome-shaped area represents the existence of liquid and gaseous carbon dioxide in equilibrium.

#### Conclusions -

- Gases should be cooled below their critical temperature for liquefaction. Critical temperature of a gas is the highest temperature at which liquefaction of the gas first occurs.
- Liquefaction of permanent gases (i.e., gases which show continuous positive deviation in Z value) requires cooling as well as considerable compression.
  - Compression brings the molecules in close vicinity and cooling slows down the movement of molecules therefore, intermolecular interactions may hold the closely and slowly moving molecules together and the gas liquifies.
- There is continuity between the gaseous and liquid state. The term fluid is used for either a liquid or a gas to recognise this continuity.
- a liquid can be viewed as a very dense gas.
- Liquid and gas can be distinguished only when the fluid is below its critical temperature and its pressure and volume lie under the dome, since in that situation liquid and gas are in equilibrium and a surface separating the two phases is visible. In the absence of this surface there is no fundamental way of distinguishing between two states.
- At critical temperature, liquid passes into gaseous state imperceptibly and continuously; the surface separating two phases disappears.
- A gas below the critical temperature can be liquified by applying pressure, and is called vapour of the substance.



Substance	T <sub>e</sub> /K	p <sub>c</sub> /bar	V <sub>e</sub> /dm <sup>3</sup> mol <sup>-1</sup>
H <sub>2</sub>	33.2	12.97	0.0650
He	5.3	2.29	0.0577
N <sub>2</sub>	126.	33.9	0.0900
O <sub>2</sub>	154.3	50.4	0.0744
CO2	304.10	73.9	0.0956
H <sub>2</sub> O	647.1	220.6	0.0450
NH <sub>3</sub>	405.5	113.0	0.0723

• Critical constants for some common substances are given in Table

#### > LIQUID STATE

- Liquids have definite volume because molecules do not separate from each other.
- However, molecules of liquids can move past one another freely, therefore, liquids can flow, can be poured and can assume the shape of the container in which these are stored.

#### > Vapour Pressure

- If an evacuated container is partially filled with a liquid -
  - Initially the liquid evaporates and pressure exerted by vapours on the walls of the container (vapour pressure) increases.
  - After some time it becomes constant, an equilibrium is established between liquid phase and vapour phase.
- Vapour pressure at equilibrium stage is known as equilibrium vapour pressure or saturated vapour pressure.
- Process of vapourisation is temperature dependent; the temperature must be mentioned while reporting the vapour pressure of a liquid.
- The temperature at which vapour pressure of liquid is equal to the external pressure is called boiling temperature at that pressure.
- At 1 atm pressure boiling temperature is called normal boiling point. If pressure is 1 bar then the boiling point is called the standard boiling point of the liquid.
- Standard boiling point of the liquid is slightly lower than the normal boiling point because 1 bar pressure is slightly less than 1 atm pressure.
  - The normal boiling point of water is 100°C (373 K), its standard boiling point is 99.6°C (372.6 K)
- At high altitudes atmospheric pressure is low. Therefore liquids at high altitudes boil at lower temperatures in comparison to that at sea level. Since water boils at low temperature on hills, the pressure cooker is used for cooking food.
- In hospitals surgical instruments are sterilized in autoclaves in which boiling point of water is increased by increasing the pressure above the atmospheric pressure by using a weight covering the vent.
- Boiling does not occur when liquid is heated in a closed vessel. As the temperature increases more and more molecules go to the vapour phase and the density of vapours rises. At the same time liquid becomes less dense. It expands because molecules move apart.
- When the density of liquid and vapours becomes the same; the clear boundary between liquid and vapours disappears. This temperature is called critical temperature.



#### Surface Tension

- Observed phenomena -
  - $\circ$   $\,$  drops of mercury form spherical bead instead of spreading on the surface.
  - particles of soil at the bottom of the river remain separated but they stick together when taken out.
  - a liquid rises (or falls) in a thin capillary as soon as the capillary touches the surface of the liquid.
- A molecule in the bulk of liquid experiences equal intermolecular forces from all sides. The molecule, therefore, does not experience any net force.
- For the molecule on the surface of liquid, net attractive force is towards the interior of the liquid, due to the molecules below it. Since there are no molecules above it.



- Liquids tend to minimize their surface area. The molecules on the surface experience a net downward force and have more energy than the molecules in the bulk. Therefore, liquids tend to have a minimum number of molecules at their surface.
- If the surface of the liquid is increased by pulling a molecule from the bulk, attractive forces will have to be overcome. This will require expenditure of energy.
- The energy required to increase the surface area of the liquid by one unit is defined as surface energy. Its dimensions are J m<sup>-2</sup>.
- 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 the Greek letter  $\gamma$  (Gamma).
  - $\circ$  It has dimensions of kg s<sup>-2</sup> and in SI units it is expressed as N m<sup>-1</sup>.
- The lowest energy state of the liquid will be when surface area is minimum. Spherical shape satisfies this condition, that is why mercury drops are spherical in shape.
  - This is the reason that sharp glass edges are heated to make them smooth. On heating, the glass melts and the surface of the liquid tends to take the rounded shape at the edges, which makes the edges smooth. This is called fire polishing of glass.
- Liquids wet the things because they spread across their surfaces as thin film.
- Moist soil grains are pulled together because the surface area of the thin film of water is reduced.



- Surface tension gives stretching properties to the surface of a liquid. On a flat surface, droplets are slightly flattened by the effect of gravity; but in the gravity free environments drops are perfectly spherical.
- The magnitude of surface tension of a liquid depends on the attractive forces between the molecules.
  - When the attractive forces are large, the surface tension is large.
  - Increase in temperature increases the kinetic energy of the molecules and effectiveness of intermolecular attraction decreases, so surface tension decreases as the temperature is raised.

#### > Viscosity

- 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.
- When a liquid flows over a fixed surface, the layer of molecules in the immediate contact of the surface is stationary.
- The velocity of upper layers increases as the distance of layers from the fixed layer increases. This type of flow in which there is a regular gradation of velocity in passing from one layer to the next is called laminar flow.
- If we choose any layer in the flowing liquid, the layer above it accelerates its flow and the layer below this retards its flow.



- If the velocity of the layer at a distance dz is changed by a value du then velocity gradient is given by the amount (du/dz).
- A force is required to maintain the flow of layers. This force is proportional to the area of contact of layers and velocity gradient i.e.

$$F = \eta A \frac{\mathrm{du}}{\mathrm{dz}}$$

- ' $\eta$ ' is proportionality constant and is called coefficient of viscosity.
- (du/dz) is velocity gradient; the change in velocity with distance.
  - A is the area of contact.
- Viscosity coefficient is the force when velocity gradient is unity and the area of contact is unit area. Thus ' $\eta$ ' is a measure of viscosity.
- SI unit of viscosity coefficient is 1 newton second per square metre (N s  $m^{-2}$ ) = pascal second (Pa s = 1 kg  $m^{-1}s^{-1}$ ).
- In cgs system the unit of coefficient of viscosity is poise (named after great scientist Jean Louise Poiseuille).

1 poise = 1 g cm<sup>-1</sup>s<sup>-1</sup> =  $10^{-1}$  kg m<sup>-1</sup>s<sup>-1</sup>

- Greater the viscosity, the more slowly the liquid flows.
- Hydrogen bonding and van der Waals forces are strong enough to cause high viscosity.



- Glass is an extremely viscous liquid. It is so viscous that many of its properties resemble solids
  - The flow of glass can be experienced by measuring the thickness of window panes of old buildings. These become thicker at the bottom than at the top.
- 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.





### Thermodynamics

- Chemical energy stored by molecules is
  - Released as heat during chemical reactions when a fuel like methane, cooking gas or coal burns.
  - Used to do mechanical work when a fuel burns in an engine
  - Used to provide electrical energy through a galvanic cell
- > The study of these energy transformations forms the subject matter of thermodynamics.
- ➤ Laws of thermodynamics
  - Deal with energy changes of macroscopic systems involving a large number of molecules
  - Doesnt deal in how and the rate of energy transformations
  - Is based on initial and final states of a system undergoing the change
  - Apply only when a system is in equilibrium or moves from one equilibrium state to another equilibrium state.
- System is part of the universe in which observations are made.
- Remaining universe constitutes the surroundings.
- > The universe = The system + The surroundings.
- > Practically surroundings are that part which can interact with the system.



System and the surroundings

- The wall that separates the system from the surroundings is called boundary. It can be real or imaginary.
- > At boundary energy and matter exchange occurs.
- > Types of the System
  - The open System exchanges energy and matter both with the surrounding. The presence of reactants in an open beaker is an example of an open system.





(a) Open System

• Closed System exchanges only energy with the surroundings. The presence of reactants in a closed vessel made of conducting material e.g., copper or steel is an example of a closed system.



(b) Closed System

• In an isolated system, there is no exchange of energy or matter. The presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.



(c) Isolated System

- The state of a thermodynamic system is described by its measurable or macroscopic (bulk) properties.
- State variables or state functions depend only on the state of the system and not on how it is reached.
- > State of the surroundings can never be completely specified.
- To define the state all properties are not necessary only a certain number of properties can be varied independently and the number depends on the nature of the system.
- > Internal Energy represents the total energy of the system.
  - It may be chemical, electrical, mechanical or any other type of energy.



- ➤ Internal energy, U, may change, when
  - Heat passes into or out of the system,
  - Work is done on or by the system,
  - Matter enters or leaves the system.
- > Internal energy, U, of the system is a state function.

#### > Types of processes:

- **Isothermal process:** T = Constant dT = 0
  - $\Delta T = 0$
- Isochoric process: V = Constant dV = 0

$$\Delta V = 0$$

- Isobaric process: P = Constant dP = 0
  - $\Delta \mathbf{P} = \mathbf{0}$
- Adiabatic process: q = 0 Heat exchange with the surrounding = 0 (zero)



An adiabatic system which does not permit the transfer of heat through its boundary.

- ➤ J. P. Joule was able to show that a given amount of work done on the system, no matter how it was done (irrespective of path) produced the same change of state
- > Work is positive when work is done on the system.
- ▶ Work done by the system will be negative.
- > Exchange of energy, which is a result of temperature difference is called heat, q
  - q is positive, when heat is transferred from the surroundings to the system
  - q is negative when heat is transferred from system to the surroundings
- $\blacktriangleright \Delta U = q + w$  is mathematical statement of the first law of thermodynamics
  - It states that energy of an isolated system is constant.
  - Also known as the law of conservation of energy
- > Absolute value of thermodynamic property energy eg. U cannot be defined



- Only the changes in the internal energy,  $\Delta U$  of the system is defined
- > Thermodynamic work consider only mechanical work i.e., P-V work



• Work done when compressed by constant P<sub>ex</sub> (in single step) is equal to the shaded area w = force × distance = P<sub>ex</sub> . A .1

$$= P_{ex} \cdot (-\Delta V) = -P_{ex} \Delta V = -P_{ex} (V_f - V_i)$$

- The negative sign of this expression is required to obtain conventional sign for w
- If the pressure changes in number of finite steps work will be summed over all the steps i.e  $-\sum p V\Delta$



final volume, V<sub>f</sub>. Work done on the gas ts represented by the shaded area.



• If the pressure changes such that it is always infinitesimally greater than the pressure of the gas



pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume, Vi to final volume, Vf. Work done on the gas is represented by the shaded area.

- > 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.
  - If the process proceeds infinitely slowly by a series of equilibrium states.
  - System and the surroundings are always in near equilibrium with each other.
- > Processes other than reversible processes are known as irreversible processes.
- > We can relate work to internal pressure of the system under reversible conditions

$$W_{rev} = -\int_{V}^{V_f} p_{in} dV$$

 $\Rightarrow p = nRT/V$ 

At constant temperature,  $W_{rev} = -2.303 \text{ nRT} \log (V_f/V_i)$ 

- > Free expansion: Expansion of a gas in vacuum ( $p_{ex} = 0$ ) is called free expansion.
  - No work is done during free expansion of an ideal gas whether the process is reversible or irreversible.

► 
$$\Delta U = q - p_{ex} \Delta V$$

If  $(\Delta V = 0)$ , then,  $\Delta U = q_V$ 

subscript V in  $q_V$  denotes that heat is supplied at constant volume.

- > Isothermal and free expansion of an ideal gas
  - W = 0 as  $P_{ex} = 0$
  - q = 0 as joules calculated
  - ΔU=0



- ► Applying  $\Delta U = q + w$ 
  - Isothermal irreversible:  $\Delta U = 0$ ,  $q = -w = p_{ex} (V_f V_i)$
  - Isothermal reversible:  $\Delta U = 0$ , q = -w = -2.303 nRT log (V<sub>f</sub>/V<sub>i</sub>)
  - Adiabatic change: q = 0,  $\Delta U = W_{ad}$
- > Enthalpy (H, greek word meaning heat content)
  - When the system is under conditions of constant pressure, the energy of the system is called enthalpy.
  - H = U + pV
  - $\Delta H = \Delta U + P \Delta V$
  - $p \Delta V = \Delta n_g RT$  ( $\Delta n_g$  refers to the number of moles of gaseous products minus the number of moles of gaseous reactants)
  - $\Delta H = \Delta U + \Delta n_g RT$
  - $\Delta H = Q_p$ , heat exchanged at constant pressure
  - $\Delta H = -ve$  (exothermic reaction
  - $\Delta H = +ve$  (endothermic reaction)
- > Extensive property depends on the quantity or size of matter present in the system.
  - Example: m, V, U, H, heat capacity(C), etc.
- Properties which do not depend on quantity or size of matter are known as intensive properties.example temperature, density, pressure etc.



A gas at volume V and temperature T



Partition, each part having half the volume of the gas

- Molar property is an extensive property. examples: molar volume, V<sub>m</sub> and molar heat capacity, C<sub>m</sub>.
- Heat Capacity(C) is the quantity of heat needed to raise the temperature of system by one degree celsius.
  - $q = C \times \Delta T$
  - A large heat capacity means a lot of energy is needed to raise its temperature.
- > The molar heat capacity  $(C_m) = C/n$ 
  - Is the heat capacity for one mole of the substance .
  - Is the quantity of heat needed to raise the temperature of one mole by one degree celsius
  - $q = nC_m \Delta T$



- > Specific heat, also called specific heat capacity (S) = C/m
  - Is the quantity of heat required to raise temperature of unit mass of substance by one degree celsius
  - $q = mS\Delta T$
- $\succ$  C<sub>p</sub> C<sub>v</sub> = R (both are molar heat capacity)
- >  $\Delta$ H and  $\Delta$ U are measured in coffee cup calorimeter (constant pressure condition) and bomb calorimeter (constant volume condition) respectively.



- First law of thermodynamics is about the relationship between heat absorbed and work done on or by a system.
  - It puts no restrictions on the direction of heat flow
  - Flow of heat is unidirectional from higher T to lower T
  - All natural processes will proceed spontaneously in one direction only.
  - Example, a gas expanding to fill the available volume
  - Example, burning carbon in oxygen gives carbon dioxide.
- A spontaneous process is an irreversible process and may only be reversed by some external agency.
- Enthalpy as Criterion for Spontaneity
  - Phenomenon like flow of water downhill or fall of a stone on to the ground (both spontaneous process)
  - There is a net decrease in potential energy.
  - By analogy, we may state a chemical reaction is spontaneous in exothermic direction, because decrease in energy takes place.





Enthalpy diagram for exothermic reactions

> But endothermic reactions are also spontaneous



- Therefore decrease in enthalpy may be a contributory factor for spontaneity, but it is not true for all cases.
  - A case in which  $\Delta H = 0$ , but still the process is spontaneous
  - Example diffusion of two gases into each other in a closed isolated container



• In isolated systems, there is always a tendency for the system's energy to become more disordered or chaotic and this could be a criterion for spontaneous change!



- > Entropy denoted as S, is a measure of the degree of randomness or disorder in the system
  - Greater the disorder in an isolated system, the higher is the entropy
  - For chemical reaction, this entropy change is due to rearrangement of atoms or ions from one pattern (in the reactants) to another (in the products)
  - Decrease of regularity in structure would mean increase in entropy
  - The crystalline solid state is the state of lowest entropy (most ordered)
  - Gaseous state is state of highest entropy
  - Entropy is a state function and  $\Delta S$  is independent of path.
  - Heat (q) has randomising influence on the system as it increases molecular motions
  - $\Delta S$  is directly proportional to q
  - Distribution of heat also depends on the temperature at which heat is added to the system.
  - Heat added at lower temperature causes greater randomness than same quantity of heat added at higher temperature
  - $\Delta S$  is inversely proportional to the temperature
  - $\Delta S = q_{rev} / T$  (6.18)
- > The total entropy change ( $\Delta S_{total}$ ) for the system and surroundings of a spontaneous process is given by  $\Delta S_{tot} = \Delta S_{sys} + \Delta S_{surr} > 0$ .
- > For a system in equilibrium, the entropy is maximum, and the change in entropy,  $\Delta S = 0$ 
  - Entropy for spontaneous process increases till it reaches maximum
  - At equilibrium the change in entropy is zero
- > For reversible and irreversible expansion for an ideal gas, under isothermal conditions
  - $\Delta U = 0$
  - But  $\Delta S_{total}$  is not zero for irreversible processes.
  - $\Delta U$  does not discriminate between reversible and irreversible processes, whereas  $\Delta S$  does.
- Neither decrease in enthalpy nor increase in entropy alone can determine the direction of spontaneous change for systems.
  - Hence New thermodynamic function the Gibbs energy or Gibbs function, G, is defined.
- $\blacktriangleright$  G = H TS
  - Gibbs function, G is an extensive property and a state function
  - At constant temp(isothermal)  $\Delta G_{sys} = \Delta H_{sys} T\Delta S_{sys}$
  - $\Delta G_{sys} = -T\Delta S_{total}$
  - $\Delta G$  gives a criteria for spontaneity at constant pressure and temperature.
  - If  $\Delta G$  is negative (< 0), the process is spontaneous.
  - If  $\Delta G$  is positive (> 0), the process is non spontaneous.
- Second law of thermodynamics states that an increase in entropy of isolated systems is the natural direction of a spontaneous change.



- > The entropy of any pure crystalline substance approaches zero as the temperature approaches absolute zero. This is called the third law of thermodynamics.
  - Because there is perfect order in a crystal at absolute zero
  - Theoretical arguments and practical evidences have shown that entropy of solutions and supercooled liquids is not zero at 0 K
  - It permits the calculation of absolute values of entropy of pure substance from thermal data alone
  - Standard entropies can be used to calculate standard entropy changes by a Hess's law type of calculation
- > Free energy change ( $\Delta G$ ) of a chemical reaction allows:
  - i. Prediction of the spontaneity of the chemical reaction.
  - ii. Prediction of the useful work that could be extracted from it.
- ➤ The criterion for equilibrium

$$A + B \rightleftharpoons C + D;$$

is  $\Delta \mathbf{r} \mathbf{G} = 0$ 

 $\Delta r G^0 = - RT \ln K \text{ or } \Delta r G^0 = -2.303 RT \log K$ 

- For strongly endothermic reactions,
  - $\Delta_r H^0$  may be large and positive.
  - Value of K will be much smaller than 1
  - and the reaction is unlikely to form much product.
- In case of exothermic reactions,
  - $\Delta_{\rm r} {\rm H}^0$  is large and negative,
  - and  $\Delta_r G^0$  is likely to be large and negative too.
  - K will be much larger than 1
- Effect of Temperature on Spontaneity of Reactions

Effect of Temperature on Spontanelty of Reactions

$\Delta_r H^{\ominus}$	$\Delta_r S^{\ominus}$	$\Delta_r G^{\Theta}$	Description*
7.	+		Reaction spontaneous at all temperature
-	-	- (at low $T$ )	Reaction spontaneous at low temperature
-	-	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low $T$ )	Reaction nonspontaneous at low temperature
+	+	- (at high $T$ )	Reaction spontaneous at high temperature
+	=	+ (at all $T$ )	Reaction nonspontaneous at all temperatures



#### Equilibrium

- Equilibria involving O<sub>2</sub> molecules, and the protein hemoglobin play a crucial role in the transport and delivery of O<sub>2</sub> from our lungs to our muscles. Similar equilibria involving CO molecules and hemoglobin account for the toxicity of CO.
- Chemical equilibrium relates to such a state when the reactants, as well as products, will no longer undergo any further change. In such a case, the rate of forward and backward reaction remains the same.
- Types of chemical reactions based on extent to which it proceeds -
  - The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left.
  - The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.
  - The reactions in which the concentrations of the reactants and products are comparable when the system is in equilibrium.

#### Equilibrium in physical processes

- Sol<mark>id-Liquid Equilibriu</mark>m
  - Ice and water kept in a perfectly insulated thermos flask at 273 K and the atmospheric pressure are in equilibrium state.
  - The mass of ice and water do not change with time and the temperature remains constant.
  - Equilibrium is dynamic. The intense activity can be noticed at the boundary between ice and water.
  - Molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K.
  - For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance.
- Liquid-Vapour Equilibrium
  - The rate of evaporation is constant.
  - The rate of increase in vapour pressure decreases with time due to condensation of vapour into water.
  - The equilibrium is attained when rate of evaporation= rate of condensation.
  - At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the equilibrium vapour pressure of water (or just vapour pressure of water).
  - Vapour pressure of water increases with temperature.



- The liquid which has a higher vapour pressure is more volatile and has a lower boiling point.
- Time taken for complete evaporation of a volatile liquid depends on (i) the nature of the liquid, (ii) the amount of the liquid and (iii) the temperature.
- It is not possible to reach equilibrium in an open system.
- For any pure liquid at one atmospheric pressure (1.013 bar), the temperature at which the liquid and vapours are at equilibrium is called normal boiling point of the liquid.
- Boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place, at high altitude the boiling point decreases.
- Solid Vapour Equilibrium
  - Colour of solid iodine Violet. If we place solid iodine in a closed vessel, after some time the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained.
  - Solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine.
- Equilibrium Involving Dissolution of Solid in Liquids
  - If we make a thick sugar syrup solution by dissolving sugar at a higher temperature, sugar crystals separate out if we cool the syrup to the room temperature.
  - A saturated solution is when no more of solute can be dissolved in it at a given temperature.
  - The concentration of the solute in a saturated solution depends upon the temperature.
  - In a saturated solution, a dynamic equilibrium exits between the solute molecules in the solid state and in the solution.
  - If we drop some radioactive sugar into saturated solution of non-radioactive sugar, then after some time radioactivity is observed both in the solution and in the solid sugar. The ratio of the radioactive to non-radioactive molecules in the solution increases till it attains a constant value.
- Equilibrium Involving Dissolution of Gases in Liquids
  - Henry's law: 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.
  - Solubility of gas in liquid decreases with increasing temperature.
  - The soda water bottle is sealed under pressure of gas when its solubility in water is high. As soon as the bottle is opened, some of the dissolved carbon dioxide gas escapes to reach a new equilibrium condition required for the lower pressure, namely its partial pressure in the atmosphere. This is how the soda water in bottle when left open to the air for some time, turns 'flat'.
- General Characteristics of Equilibria Involving Physical Processes
  - Equilibrium is possible only in a closed system at a given temperature.
  - Both the opposing processes occur at the same rate and there is a dynamic but stable condition.



- All measurable properties of the system remain constant.
- When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature.

Some Features of Physical

Process	Conclusion
Liquid $\rightleftharpoons$ Vapour H <sub>2</sub> O (I) $\rightleftharpoons$ H <sub>2</sub> O (g)	$p_{\rm B_{2}0}$ constant at given temperature
Solid $\rightleftharpoons$ Liquid H <sub>2</sub> O (s) $\rightleftharpoons$ H <sub>2</sub> O (l)	Melting point is fixed at constant pressure
$Solute(s) \rightleftharpoons Solute$ (solution) $Sugar(s) \rightleftharpoons Sugar$ (solution)	Concentration of solute in solution is constant at a given temperature
$Gas(g) \rightleftharpoons Gas (aq)$ $CO_2(g) \rightleftharpoons CO_2(aq)$	[gas(aq)]/[gas(g)] is constant at a given temperature [CO <sub>2</sub> (aq)]/[CO <sub>1</sub> (g)] is constant at a given temperature

• The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

#### Equilibrium in Chemical Processes – Dynamic Equilibrium

• Reversible reaction - These reactions can occur both in forward and backward directions.

 $A + B \rightleftharpoons C + D$ 

• 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.



Depiction of equilibrium for the reaction  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ 



- Chemical reactions reach a state of dynamic equilibrium in which the rates of forward and reverse reactions are equal and there is no net change in composition.
- If we mix two separate mixture having two different equilibriums achieved - $N_2 + 3H_2 \rightleftharpoons 2NH_3$  and  $N_2 + 3D_2 \rightleftharpoons 2ND_3$ , we find that at equilibrium ammonia and all deuterium containing forms of ammonia (NH<sub>3</sub>, NH<sub>2</sub>D, NHD<sub>2</sub> and ND<sub>3</sub>) and dihydrogen and its deutrated forms (H<sub>2</sub>, HD and D<sub>2</sub>) are present. Thus proves the dynamic nature of chemical equilibrium.
- Equilibrium can be attained from both sides.



from either direction

- **Law of Chemical Equilibrium and Equilibrium Constant** 
  - Based on experimental studies of many reversible reactions, the Norwegian chemists Cato Maximillian Guldberg and Peter Waage proposed law of mass action in 1864.
  - In the early days of chemistry, concentration was called "active mass".
  - Equilibrium Law or Law of Chemical Equilibrium At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value.

The equilibrium constant for a general reaction,

 $a A + b B \rightleftharpoons c C + d D$  is expressed as,

 $K_c = [C]^c [D]^d / [A]^a [B]^b$ 

where [A], [B], [C] and [D] are the equilibrium concentrations of the reactants and products and  $K_c$  is the equilibrium constant. The subscript 'c' indicates that  $K_c$  is expressed in concentrations of mol L<sup>-1</sup>.

• Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.



 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ 

 $K_{c} = [HI]^{2} / [H_{2}][I_{2}]$ 

The equilibrium constant for the reverse reaction,

 $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ , at the same temperature is,

 $K^\prime{\,}{}_c = [H_2]~[I_2] \ / ~[HI]^2 \ Thus, K^\prime{}_c = 1/K_c$ 

• If we change the stoichiometric coefficients in a chemical equation by multiplying throughout by a factor, than equilibrium constant must be raised by the same power as the multiplying factor.

 $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$ 

The equilibrium constant for the above reaction is given by

$$K_{c}^{\prime\prime} = [\text{HI}] / [\text{H}_{2}]^{1/2} [\text{I}_{2}]^{1/2} = \{[\text{HI}]^{2} / [\text{H}_{2}][\text{I}_{2}]\}^{1/2} = K_{c}^{1/2}$$

Chemical equation	Equilibrium constant
$a A + b B \rightleftharpoons c C + dD$	K
$c C + d D \rightleftharpoons a A + b B$	$K_{c}^{'} = (1/K_{c})$
na A + nb B ≓ ncC + ndD	$K_c'' = (K_c^n)$

#### Homogeneous Equilibria

In a homogeneous system, all the reactants and products are in the same phase. Examples-

- $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
- $CH_3COOC_2H_5(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$

• 
$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)$$

- Equilibrium Constant in Gaseous Systems
  - For reactions involving gases, equilibrium constant is expressed in terms of partial pressure.
  - If concentration c, is in mol/L or mol/dm<sup>3</sup>, and p is in bar then p = cRT (R = 0.0831 bar-L/mol-K)
  - At constant temperature, the pressure of the gas is proportional to its concentration i.e., p ∝ [gas]
  - For a general reaction  $aA + bB \rightleftharpoons cC + dD$

$$K_{p} = \frac{\left(p_{C}^{c}\right)\left(p_{D}^{d}\right)}{\left(p_{A}^{a}\right)\left(p_{B}^{b}\right)} = \frac{\left[C\right]^{c}\left[D\right]^{d}\left(RT\right)^{(c+d)}}{\left[A\right]^{a}\left[B\right]^{b}\left(RT\right)^{(a+b)}}$$
$$= \frac{\left[C\right]^{c}\left[D\right]^{d}}{\left[A\right]^{a}\left[B\right]^{b}}\left(RT\right)^{(c+d)-(a+b)}$$
$$= \frac{\left[C\right]^{c}\left[D\right]^{d}}{\left[A\right]^{a}\left[B\right]^{b}}\left(RT\right)^{\Delta n} = K_{c}\left(RT\right)^{\Delta n}$$



where  $\Delta n = (number of moles of gaseous products) - (number of moles of gaseous reactants) in the balanced chemical equation.$ 

- It is necessary that while calculating the value of K<sub>p</sub>, pressure should be expressed in bar because standard state for pressure is 1 bar.
- 1 pascal,  $Pa=1 Nm^{-2}$ , and 1 bar =  $10^5 Pa$ .

rew Selected Reactions				
Reaction	Temperature/K	K <sub>p</sub>		
$N_2(g) + 3H_2(g) \Rightarrow 2NH_3$	298	$6.8 \times 10^{5}$		
	400	41		
	500	$3.6 \times 10^{-2}$		
$2SO_2(g) + O_2(g) \Rightarrow 2SO_3(g)$	298	$4.0 \times 10^{24}$		
	500	$2.5 \times 10^{10}$		
	700	$3.0 \times 10^4$		
$N_2O_4(g) \Rightarrow 2NO_2(g)$	298	0.98		
	400	47.9		
	500	1700		

# Equilibrium Constants, $K_p$ for a Few Selected Reactions

#### Heterogeneous Equilibria

- Equilibrium in a system having more than one phase is called heterogeneous equilibrium.
- Examples
  - The equilibrium between water vapour and liquid water in a closed container  $H_2O(l) \rightleftharpoons H_2O(g)$
  - o Equilibrium between a solid and its saturated solution –

$$Ca(OH)_2(s)+(aq) \rightleftharpoons Ca^{2+}(aq)+2OH^-(aq)$$

- The molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present).
- It must be remembered that for the existence of heterogeneous equilibrium pure solids or liquids must also be present (however small the amount may be) at equilibrium, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. For example – for the reaction  $Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$ , both Ni and CO must be present initially for

attainment of equilibrium, but Ni doesn't appear in equilibrium constant expression.

$$K_{c} = \frac{\left[Ni(CO)_{4}\right]}{\left[CO\right]}$$

#### > Summary of Features of Equilibrium constant

- Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at 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 a particular 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.

#### > Applications of Equilibrium Constants

- 1. Predict the extent of a reaction based on its magnitude -
  - An equilibrium constant does not give any information about the rate at which the equilibrium is reached.
  - A high value of K is suggestive of a high concentration of products and vice-versa.
  - If  $K_c > 10^3$ , products predominate over reactants, i.e., if  $K_c$  is very large, the reaction proceeds nearly to completion. Examples of such reactions –

$$\circ \quad 2H_2 + O_2 \xrightarrow{500K} 2H_2O$$

$$\circ \quad H_2 + Cl_2 \xrightarrow{300K} 2HCl$$

$$\circ$$
  $H_2 + Br_2 \xrightarrow{300K} 2HBr$ 

- If  $K_c < 10^{-3}$ , reactants predominate over products, i.e., if  $K_c$  is very small, the reaction proceeds rarely. Examples of such reactions
  - The decomposition of  $H_2O$  into  $H_2$  and  $O_2$  at 500 K.

$$\circ N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \text{ [At 298 K]}$$

• If K<sub>c</sub> is in the range of 10<sup>-3</sup> to 10<sup>3</sup>, appreciable concentrations of both reactants and products are present. Examples –

$$\circ H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \text{ [At 700 K]}$$

$$N_2 O_4(g) \rightleftharpoons 2NO_2(g) \text{ [At 298 K]}$$
Negligible K: Extremely



Dependence of extent of reaction on K<sub>c</sub>

#### 2. Predict the direction of the reaction

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

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



Where Q is the reaction quotient (Qc with molar concentrations and  $Q_P$  with partial pressures) is defined in the same way as the equilibrium constant Kc except that the concentrations in Qc are not necessarily equilibrium values.



Fig. 7.7 Predicting the direction of the reaction

- If Q<sub>c</sub> < K<sub>c</sub>, net reaction goes from left to right
- If  $Q_c > K_c$ , net reaction goes from right to left.
- If  $Q_c = K_c$ , no net reaction occurs.

#### 3. Calculate equilibrium concentrations

- In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following steps shall be followed:
  - Step 1. Write the balanced equation for the reaction.
  - **Step 2**. Under the balanced equation, make a table that lists for each substance involved in the reaction:
    - (a) the initial concentration
    - (b) the change in concentration on going to equilibrium, and
    - (c) the equilibrium concentration
  - **Step 3**. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x.
  - Step 4. Calculate the equilibrium concentrations from the calculated value of x.
  - Step 5. Check your results by substituting them into the equilibrium equation.

#### > RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT K, REACTION QUOTIENT Q AND GIBBS ENERGY G

- $\Delta G = \Delta G^{\circ} + RT \ln Q$
- At equilibrium  $\Delta G = 0$  and Q = Kc,  $\Delta G^{\circ} = -RT \ln K$  or  $K = e^{-RT}$
- If  $\Delta G^{\circ} < 0 \Longrightarrow K > 1 \Longrightarrow$  a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.

 $-\Delta G^{\circ}$ 

• If  $\Delta G^{\circ} > 0 \Longrightarrow K < 1 \Longrightarrow$  a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.



#### Factors Affecting Equilibria

- One of the principal goals of chemical synthesis is to maximise the conversion of the reactants to products while minimizing the expenditure of energy. This implies maximum yield of products at mild temperature and pressure conditions.
- Annual world production of ammonia is about hundred million tonnes, primarily for use as fertilizers.
- To decide what course the reaction adopts and make a qualitative prediction about the effect of a change in conditions on equilibrium we use Le Chatelier's principle.
- Le Chatelier's principle: It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.
- Le Chatelier's principle is applicable to all physical and chemical equilibria.

#### A. Effect of Concentration Change

- The concentration stress of an added reactant/product is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a removed reactant/product is relieved by net reaction in the direction that replenishes the removed substance.
- In the large-scale production of CaO (used as important building material) from CaCO<sub>3</sub>, constant removal of CO<sub>2</sub> from the kiln drives the reaction to completion.
- For the reaction  $Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons \left[Fe(SCN)\right]^{2+}(aq)$ <sub>Yellow</sub> Colourless
  - Oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), reacts with Fe<sup>3+</sup> ions to form the stable complex ion  $[Fe(C_2O_4)_3]^{3-}$ , thus decreasing the concentration of free Fe<sup>3+</sup>(aq). Intensity of red colour decreases.
  - Addition of aq. HgCl<sub>2</sub> also decreases red colour because Hg<sup>2+</sup> reacts with SCN<sup>-</sup> ions to form stable complex ion  $[Hg(SCN)_4]^{2-}$ . Equilibrium shifts right to left.
  - Addition of potassium thiocyanate increases the colour intensity of the solution as it shift the equilibrium to right.

#### **B.** Effect of Pressure Change

- In applying Le Chatelier's principle to a heterogeneous equilibrium the effect of pressure changes on solids and liquids can be ignored because the volume (and concentration) of a solution/liquid is nearly independent of pressure.
- With increase in pressure the equilibrium shifts in a direction in which the number of moles of the gas or pressure decreases (we know pressure is proportional to moles of the gas) and vice versa.

#### C. Effect of Inert Gas Addition

- At constant volume: the equilibrium remains undisturbed.
- At constant pressure: the equilibrium will shift towards the direction in which there is increase in number of moles of gases.



#### **D.** Effect of Temperature Change

- When a change in temperature occurs, the value of equilibrium constant, K<sub>c</sub> is changed.
  - The equilibrium constant for an exothermic reaction (negative  $\Delta H$ ) decreases as the temperature increases.
  - The equilibrium constant for an endothermic reaction (positive  $\Delta H$ ) increases as the temperature increases.
- Exothermic reactions are favoured by low temperature whereas endothermic reactions are favoured by high temperature.
- In the reaction  $2NO_2 \rightleftharpoons N_2O_4$ ;  $\Delta H = -57.2$  kJ mol<sup>-1</sup>
  - At low temperatures, the forward reaction of formation of  $N_2O_4$  is preferred, as reaction is exothermic, and thus, intensity of brown colour due to  $NO_2$  decreases.
  - High temperature favours the reverse reaction of formation of NO<sub>2</sub> and thus, the brown colour intensifies.
- In the endothermic reaction -

$$\left[Co(H_2O)_6\right]^{3+}(aq) + 4Cl^{-}(aq) \rightleftharpoons \left[CoCl_4\right]^{2-}(aq) + 6H_2O(l)$$

• At room temperature, the equilibrium mixture is blue due to  $[CoCl_4]^{2-}$ . When cooled in a freezing mixture, the colour of the mixture turns pink due to  $[Co(H_2O)_6]^{3+}$ .

#### E. 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.
- German chemist, Fritz Haber discovered that iron can catalyse the reaction of formation of ammonia from nitrogen and hydrogen.
- Optimum conditions of temperature and pressure for the synthesis of NH<sub>3</sub> using catalyst are around 500°C and 200 atm.
- In manufacture of sulphuric acid by contact process, platinum or divanadium pentaoxide ( $V_2O_5$ ) is used as catalyst to increase the rate of the reaction.



#### **IONIC EQUILIBRIUM**

- Equilibrium involving ions in aqueous solution is called ionic equilibrium.
- Michael Faraday classified the substances into two categories based on their ability to conduct electricity.
  - One category of substances conducts electricity in their aqueous solutions and are called electrolytes.
  - The other do not and are thus, referred to as non-electrolytes.
- Faraday further classified electrolytes into strong and weak electrolytes.
  - Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated.
- In weak electrolytes, equilibrium is established between ions and the unionized molecules.

#### > Acids, Bases and Salts

- Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes.
- Acetic acid is known to be the main constituent of vinegar.
- Lemon and orange juices contain citric and ascorbic acid.
- Tartaric acid is found in tamarind paste.
- The word "acid" has been derived from a latin word "acidus" meaning sour.
- A common example of a base is washing soda used for washing purposes.
- When acids and bases are mixed in the right proportion, they react with each other to give salts.
- Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide.
- Sodium chloride exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species.
- The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent, possesses a very high dielectric constant of 80. Thus, when sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80 and this facilitates the ions to move freely in the solution. Also, they are well separated due to hydration with water molecules.
- The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced.
- Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution.



#### Arrhenius Concept of Acids and Bases

• Acids: substances that dissociates in water to give hydrogen ions H<sup>+</sup>

 $HX (aq) \rightarrow H^{+}(aq) + X^{-}(aq)$ or  $HX(aq) + H_{2}O(l) \rightarrow H_{2}O^{+}(aq) + X^{-}(aq)$ 

- Bases: substances that dissociates in water to give hydroxyl ions OH<sup>-</sup> MOH (aq) → M<sup>+</sup> (aq) + OH<sup>-</sup> (aq)
- Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.
- Hydronium and Hydroxyl Ions –
- Hydrogen ion by itself is a bare proton with very small size ( $\sim 10^{-15}$  m radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving H<sub>3</sub>O<sup>+</sup>. This species has been detected in many compounds (e.g., H<sub>3</sub>O<sup>+</sup>Cl<sup>-</sup>) in the solid state.
- In aqueous solution the hydronium ion is further hydrated to give species like  $H_5O_2^+$ ,  $H_7O_3^+$  and  $H_9O4^+$ .



- Similarly, the hydroxyl ion is hydrated to give several ionic species like H<sub>3</sub>O<sub>2</sub><sup>-</sup>, H<sub>5</sub>O<sub>3</sub><sup>-</sup> and H<sub>7</sub>O<sub>4</sub><sup>-</sup> etc.
- > The Brönsted-Lowry Acids and Bases (by Johannes Brönsted and Thomas M. Lowry)
  - Acids: substances that are capable of donating a hydrogen ion H<sup>+</sup>.
  - **Bases**: substances capable of accepting a hydrogen ion, H<sup>+</sup>.



- The acid-base pair that differs only by one proton is called a conjugate acid-base pair.
- If Brönsted acid is a strong acid then its conjugate base is a weak base and vice-versa.
- In case of reaction with HCl water acts as a base while in case of ammonia it acts as an acid by donating a proton.



#### Lewis Acids and Bases (by G.N. Lewis)

- Acids: species which accepts electron pair. Eg. BF<sub>3</sub>, AlCl<sub>3</sub>,  $Co^{3+}$ ,  $Mg^{2+}$ , etc.
- **Bases**: species which donates an electron pair. Eg. H<sub>2</sub>O, NH<sub>3</sub>, OH<sup>-</sup> etc.
- As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases.
- In Lewis concept many acids do not have proton.

#### Ionization of Acids And Bases

- According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions respectively in the medium.
- In terms of Brönsted-Lowry concept of acids and bases, a strong acid means a good proton donor and a strong base implies a good proton acceptor.
- The equilibrium moves in the direction of formation of weaker acid and weaker base because the stronger acid donates a proton to the stronger base.
- Strong acids have very weak conjugate bases. Similarly, a very strong base would give a very weak conjugate acid.
  - Strong acids like perchloric acid (HClO<sub>4</sub>), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO<sub>3</sub>) and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) will give conjugate base ions ClO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and HSO<sub>4</sub>, which are much weaker bases than H<sub>2</sub>O.
  - Examples of weak acids are nitrous acid (HNO<sub>2</sub>), hydrofluoric acid (HF) and acetic acid (CH<sub>3</sub>COOH). It should be noted that the weak acids have very strong conjugate bases. For example, NH<sub>2</sub><sup>-</sup>, O<sup>2-</sup> and H<sup>-</sup> are very good proton acceptors and thus, much stronger bases than H<sub>2</sub>O.
- Certain water-soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In<sup>-</sup>) forms.

 $HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$ 

Such compounds are useful as indicators in acid-base titrations and finding out H<sup>+</sup> ion concentration.

#### > The Ionization Constant of Water and its Ionic Product

• In pure water, one H<sub>2</sub>O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$
  
Dissociation constant: 
$$\frac{\left[H_3O^+\right]\left[OH^-\right]}{\left[H_2O\right]}$$

- Ionic product of water,  $Kw = \left[H^+\right]\left[OH^-\right]$
- The concentration of H<sup>+</sup> has been found out experimentally as  $1.0 \times 10^{-7}$  M at 298 K.
- The value of  $K_w$  at 298 K =  $10^{-14}$  M<sup>2</sup>.



• The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this the ratio of dissociated water to that of undissociated water can be given as  $10^{-7} = 1.8 \times 10^{-9}$ 

$$\frac{10}{55.5} = 1.8 \times 10^{-5}$$

 Acidic solution: [H<sub>3</sub>O<sup>+</sup>] > [OH<sup>-</sup>] Neutral solution: [H<sub>3</sub>O<sup>+</sup>] = [OH<sup>-</sup>] Basic solution: [H<sub>3</sub>O<sup>+</sup>] < [OH<sup>-</sup>]

#### > The pH Scale

- $pH = -\log_{10}(a_{H^+}) = -\log_{10}\frac{[H^+]}{\text{mol } L^{-1}}$
- In dilute solutions (< 0.01 M), activity of hydrogen ion (H<sup>+</sup>) is equal in magnitude to molarity represented by [H<sup>+</sup>].
- Activity has no units and is defined as:  $(a_{H^+}) = \frac{[H^+]}{\text{mol } L^{-1}}$
- At 25 °C
  - The pH of pure water is 7.
  - o Acidic solution has pH < 7
  - $\circ$  **Basic solution has p**H > 7
  - o Neutral solution has pH = 7
- $pK_w = pH + pOH = 14$
- Although K<sub>w</sub> may change with temperature the variations in pH with temperature are so small that we often ignore it.
- Change in pH by just one unit also means change in [H<sup>+</sup>] by a factor of 10.
- The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Now-a-days pH paper is available with four strips on it. The different strips have different colours at the same pH. The pH in the range of 1-14 can be determined with an accuracy of ~0.5 using pH paper.



have different colours at the same pH

• For greater accuracy pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within 0.001 precision.



Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of NaOH	~15	Black Coffee	5.0
0.1 M NaOH solution	13	Tomato juice	~4.2
Lime water	10.5	Soft drinks and vinegar	~3.0
Milk of magnesia	10	Lemon juice	~2.2
Egg white, sea water	7.8	Gastric juice	~1.2
Human blood	7.4	1M HCl solution	~0
Milk	6.8	Concentrated HCl	~-1.0
Human Saliva	6.4		

The pH of Some Common Substances

#### Ionization Constants of Weak Acids:

Consider a weak acid HX that is partially ionized in the aqueous solution.

$$HX(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + X^-(aq)$$
  
•  $K_a = \frac{\left[H_3O^+\right]\left[X^-\right]}{\left[HX\right]} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$ 

Ka = dissociation or ionization constant of acid HX

c = initial concentration of the undissociated acid, HX at time, t = 0.

 $\alpha$  = extent up to which HX is ionized into ions.

• At a given temperature T, K<sub>a</sub> is a measure of the strength of the acid HX i.e., larger the value of K<sub>a</sub>, the stronger is the acid.

The Ionization Constants of Some

Acid Ion	ization Constant K <sub>a</sub>
Hydrofluoric Acid (HF)	$3.5 \times 10^{-4}$
Nitrous Acid (HNO2)	$4.5 \times 10^{-4}$
Formic Acid (HCOOH)	$1.8 \times 10^{-4}$
Niacin (C <sub>g</sub> H <sub>4</sub> NCOOH)	$1.5 \times 10^{-5}$
Acetic Acid (CH3COOH)	$1.74 \times 10^{-5}$
Benzoic Acid (C <sub>6</sub> H <sub>5</sub> COOH)	$6.5 \times 10^{-5}$
Hypochlorous Acid (HCIO	$3.0 \times 10^{-8}$
Hydrocyanic Acid (HCN)	$4.9 \times 10^{-10}$
Phenol (C <sub>6</sub> H <sub>5</sub> OH)	$1.3 \times 10^{-10}$

- K<sub>a</sub> is a dimensionless quantity with the understanding that the standard state concentration of all species is 1 M.
- $pK_a = -\log(K_a)$



#### Ionization of Weak Bases

The ionization of base MOH can be represented by equation:

 $MOH(aq) \rightleftharpoons M^+(aq) + OH^-(aq)$ 

• 
$$K_b = \frac{\left[M^+\right]\left[OH^-\right]}{\left[MOH\right]} = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)}$$

Kb = base ionization constant.

c = initial concentration of base

 $\alpha$  = degree of ionization of base i.e. the extent to which the base ionizes.

The	Val	ues	of	t	he	Io	nizati	on
Const	tant	of	Som	e	W	eak	Bases	at
298 1	К							

Base	K	
Dimethylamine. (CH <sub>3</sub> J <sub>2</sub> NH	$5.4 \times 10^{-1}$	
Triethylamine, (C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> N	$6.45 \times 10^{-5}$	
Ammonia, NH <sub>a</sub> or NH <sub>4</sub> OH	$1.77 \times 10^{-5}$	
Quinine, (A plant product)	$1.10 \times 10^{-6}$	
Pyridine, C5H5N	$1.77 \times 10^{-9}$	
Aniline, C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub>	$4.27 \times 10^{-10}$	
Urea, CO (NH <sub>2</sub> l <sub>2</sub>	$1.3 \times 10^{-14}$	

- Many organic compounds like amines are weak bases. For example, methylamine, codeine, quinine and nicotine all behave as very weak bases due to their very small K<sub>b</sub>.
- $pK_b = -\log(K_b)$

#### **Relation between Ka and Kb**

• K<sub>a</sub> and K<sub>b</sub> represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced.

 $K_{w} = K_{a} \times K_{b}$ pKa + pKb = pKw = 14 (at 298 K)

#### > Di- and Polybasic Acids and Di- and Polyacidic Bases

- Some of the acids like oxalic acid, sulphuric acid and phosphoric acids have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids.
- The ionization reactions for example for a dibasic acid H2 X are represented by the equations:

 $H_2X(aq) \rightleftharpoons H^{+}(aq) + HX^{-}(aq)$  $HX^{-}(aq) \rightleftharpoons H^{+}(aq) + X^{2-}(aq)$ 

$$K_{a_1} = \frac{\left[H^+\right]\left[HX^-\right]}{\left[H_2X\right]} \text{ and } K_{a_2} = \frac{\left[H^+\right]\left[X^{2-}\right]}{\left[HX^-\right]}$$



Here,  $Ka_1$  and  $Ka_2$  are called the first and second ionization constants respectively of the acid  $H_2X$ .

• Higher order ionization constants (Ka<sub>2</sub>, Ka<sub>3</sub>) are smaller than the lower order ionization constant (Ka<sub>1</sub>) of a polyprotic acid. The reason for this is that it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces.

Acid	Ka1	Ka2	Ka3
Oxalic Acid	5.9 × 10 <sup>-2</sup>	6.4 × 10 <sup>-5</sup>	8
Ascorbic Acid	$7.4 \times 10^{-9}$	1.6 × 10 <sup>-12</sup>	
Sulphurous Acid	$1.7 \times 10^{-2}$	6.4 × 10 <sup>-4</sup>	
Sulphuric Acid	Very large	$1.2 \times 10^{-2}$	
Carbonic Acid	$4.3 \times 10^{-7}$	5.6 × 10 <sup>-11</sup>	
Citric Acid	$7.4 \times 10^{-4}$	$1.7 \times 10^{-5}$	$4.0 \times 10^{-7}$
Phosphoric Acid	$7.5 \times 10^{-3}$	6.2 × 10 <sup>-#</sup>	4.2 × 10 <sup>-13</sup>

#### The Ionization Constants of Some Common Polyprotic Acids (298K)

#### Factors Affecting Acid Strength

- The extent of dissociation of an acid depends on the strength and polarity of the H-A bond.
- When strength of H-A bond decreases, that is, the energy required to break the bond decreases, HA becomes a stronger acid.
- When the H-A bond becomes more polar, cleavage of the bond becomes easier thereby increasing the acidity.
- In the same group of the periodic table, H-A bond strength is a more important factor in determining acidity than its polar nature.



#### Similarly, H<sub>2</sub>S is stronger acid than H<sub>2</sub>O.

• When we discuss elements in the same row of the periodic table, H-A bond polarity becomes the deciding factor for determining the acid strength.

Electronegativity of A increases



> Common Ion Effect in the Ionization of Acids and Bases

• It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

#### > Hydrolysis of Salts and the pH of their Solutions

- Process of interaction between water and cations/anions or both of salts is called hydrolysis. The pH of the solution gets affected by this interaction.
- The cations (e.g., Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, etc.) of strong bases and anions (e.g., Cl<sup>-</sup>, Br<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup> etc.) of strong acids simply get hydrated but do not hydrolyse, and



therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7.

- Hydrolysis of the salts of weak acid and strong base (ex. CH<sub>3</sub>COO<sup>-</sup>Na<sup>+</sup>), anion undergoes hydrolysis in water to give weak acid and OH<sup>-</sup> ions. This results in increase of OH<sup>-</sup> ion concentration in solution making it alkaline. The pH of such a solution is more than 7.
- Hydrolysis of the salts of strong acid and weak base (ex. NH<sub>4</sub><sup>+</sup>Cl<sup>-</sup>), cation undergoes hydrolysis in water to give weak base and H<sup>+</sup> ions. This results in increase of H<sup>+</sup> ion concentration in solution making it acidic. The pH of such a solution is less than 7.
- Hydrolysis of the salts of weak acid and weak base (ex. CH<sub>3</sub>COO<sup>-</sup>NH<sub>4</sub><sup>+</sup>), both cation and anion undergoes hydrolysis in water. Degree of hydrolysis is independent of concentration of solution, and pH of such solutions is determined by their pK values:

$$pH = 7 + \frac{1}{2} \left( pK_a - pK_b \right)$$

#### **BUFFER SOLUTIONS**

- Blood or urine have definite pH and any deviation in their pH indicates malfunctioning of the body.
- The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.
- A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH 9.25.

#### > SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

- Calcium chloride is so soluble that it is hygroscopic in nature and even absorb water vapour from atmosphere.
- Lithium fluoride has so little solubility that it is termed as insoluble.
- The solubility depends on several factors important amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution.
  - For a salt to dissolve in a solvent the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions.
  - The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e., energy is released in the process of solvation.
  - The amount of solvation enthalpy depends on the nature of the solvent. In case of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent.
  - for a salt to be able to dissolve in a particular solvent its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by former.
- We classify salts based on their solubility in the following three categories –



Category I	Soluble	Solubility > 0.1M
Category II	Slightly Soluble	0.01M <solubility< 0.1m<="" td=""></solubility<>
Category III	Sparingly Soluble	Solubility < 0.01M

#### Solubility Product Constant

A solid salt of the general formula  $M_x^{p^+}X_y^{q^-}$  with molar solubility S in equilibrium with its saturated solution may be represented by the equation:

$$M_{x}X_{y}(s) \rightleftharpoons xM^{p+}(aq) + yX^{q-}(aq)$$
  
(where x × p<sup>+</sup> = y × q<sup>-</sup>)  
Here,  $K_{sp} = \left[M^{p+}\right]^{x} \left[X^{q-}\right]^{y} = x^{x}.y^{y}.S^{(x+y)}$ 

- K<sub>sp</sub> = Solubility product constant or solubility product
- S = Molar solubility of the salt
- If the concentration in  $K_{sp}$  expression is not at equilibrium, it is called  $Q_{sp}$ .

#### **Common Ion Effect on Solubility of Ionic Salts**

- If we increase the concentration of any one of the ions, it should combine with the ion of its opposite charge and some of the salt will be precipitated till once again  $K_{sp} = Q_{sp}$ .
- If the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again  $K_{sp} = Q_{sp}$ .
- If we take a saturated solution of sodium chloride and pass HCl gas through it, then sodium chloride is precipitated due to increased concentration (activity) of chloride ion available from the dissociation of HCl. Sodium chloride thus obtained is of very high purity and we can get rid of impurities like sodium and magnesium sulphates.
- The common ion effect is also used for almost complete precipitation of a particular ion as its sparingly soluble salt, with very low value of solubility product for gravimetric estimation. Thus, we can precipitate silver ion as silver chloride, ferric ion as its hydroxide (or hydrated ferric oxide) and barium ion as its sulphate for quantitative estimations.
- The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that  $K_{sp} = Q_{sp}$ .


## **Redox Reactions**

- Where there is oxidation, there is always reduction.
- Burning of different types of fuels for obtaining energy for domestic, transport and other commercial purposes, electrochemical processes for extraction of highly reactive metals and nonmetals, manufacturing of chemical compounds like caustic soda, operation of dry and wet batteries and corrosion of metals fall within the purview of redox processes.
- Environmental issues like Hydrogen Economy (use of liquid hydrogen as fuel) and development of 'Ozone Hole' have started figuring under the redox phenomenon.

### CLASSICAL IDEA OF REDOX REACTIONS – OXIDATION AND REDUCTION REACTIONS

- Originally, the term oxidation was used to describe the addition of oxygen to an element or a compound.
- The following reactions represent oxidation processes according to the limited definition of oxidation:
  - $\circ \quad 2Mg(s) + O_2(g) \rightarrow 2MgO(s)$
  - $\circ \quad \mathbf{S}(\mathbf{s}) + \mathbf{O}_2(\mathbf{g}) \to \mathbf{S}\mathbf{O}_2(\mathbf{g})$
  - $\circ \quad CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(1)$
- Removal of hydrogen can also be cited as an oxidation reaction.
  - $\circ \quad 2H_2S(g) + O_2(g) \rightarrow 2S(s) + 2H_2O(l)$
- Removal of electropositive elements can also be cited as oxidation.
  - $\circ 2K_4[Fe(CN)_6](aq) + H_2O_2(aq) \rightarrow 2K_3[Fe(CN)_6](aq) + 2KOH(aq)$
  - Removal of K from  $K_4[Fe(CN)_6]$  if considered its oxidation.
- The term reduction has been broadened these days to include removal of oxygen/electronegative elements from a substance or addition of hydrogen/ electropositive elements to a substance.
  - $\circ 2HgO(s) \rightarrow 2Hg(l) + O_2(g)$ (removal of oxygen from mercuric oxide)
  - $2\text{FeCl}_3(aq) + \text{H}_2(g) \rightarrow \text{FeCl}_2(aq) + 2\text{HCl}(aq)$ (removal of electronegative element, chlorine from ferric chloride)
  - $CH_2 = CH_2(g) + H_2(g) \rightarrow H_3C CH_3(g)$ (addition of hydrogen)
  - $2HgCl_2(aq) + SnCl_2(aq) \rightarrow Hg_2Cl_2(s) + SnCl_4(aq)$ (addition of mercury to mercuric chloride)
- Oxidation and reduction always occur simultaneously (as will be apparent by reexamining all the equations given above), hence, the word "redox" was coined for this class of chemical reactions.

## > REDOX REACTIONS IN TERMS OF ELECTRON TRANSFER REACTIONS

- Half reactions that involve loss of electrons are called oxidation reactions.
- The half reactions that involve gain of electrons are called reduction reactions.
- **Oxidation:** Loss of electron(s) by any species.
- **Reduction:** Gain of electron(s) by any species.
- **Oxidising agent:** Acceptor of electron(s).



• **Reducing agent:** Donor of electron(s).

### > Competitive Electron Transfer Reactions

- Place a strip of metallic zinc in an aqueous solution of copper nitrate, for about one hour. You may notice that the strip becomes coated with reddish metallic copper and the blue colour of the solution disappears.
  - Formation of  $Zn^{2+}$  ions among the products can easily be judged when the blue colour of the solution due to  $Cu^{2+}$  has disappeared.
  - $\circ$  If hydrogen sulphide gas is passed through the colourless solution containing  $Zn^{2+}$  ions, the appearance of white zinc sulphide, ZnS, can be seen in making the solution alkaline with ammonia.
  - The reaction between metallic zinc and the aqueous solution of copper nitrate is:  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$
- However on placing a strip of metallic copper in a zinc sulphate solution, no visible reaction is noticed.
  - Attempts to detect the presence of  $Cu^{2+}$  ions by passing H<sub>2</sub>S gas through the solution to produce the **black colour of cupric sulphide**, CuS, does not succeed.
  - Cupric sulphide has such a low solubility that this is an extremely sensitive test; yet the amount of  $Cu^{2+}$  formed cannot be detected.
- We thus conclude that the state of equilibrium for the reaction  $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$  greatly favours the products over the reactants.
- Similarly, on placing copper metal and silver nitrate solution in water, The solution develops blue colour due to the formation of Cu<sup>2+</sup> ions on account of the reaction: Cu(s) + 2Ag<sup>+</sup>(aq) → Cu<sup>2+</sup>(aq) + 2Ag(s)
- → Cu(s) is oxidised to Cu<sup>2+</sup>(aq) and Ag<sup>+</sup>(aq) is reduced to Ag(s). Equilibrium greatly favours the products Cu<sup>2+</sup>(aq) and Ag(s).
- When metallic cobalt placed in nickel sulphate solution -Co(s) + Ni<sup>2+</sup>(aq)  $\rightarrow$  Ni(s) + Co<sup>2+</sup>(aq)
- → At equilibrium, chemical tests reveal that both Ni<sup>2+</sup>(aq) and Co<sup>2+</sup>(aq) are present at moderate concentrations. In this case, neither the reactants [Co(s) and Ni<sup>2+</sup>(aq)] nor the products [Co<sup>2+</sup>(aq) and Ni (s)] are greatly favoured.
- By comparison we have come to know that zinc releases electrons to copper and copper releases electrons to silver and, therefore, the electron releasing tendency of the metals is in the order: Zn > Cu > Ag.
- We can develop a table in which metals and their ions are listed on the basis of their tendency to release electrons called activity series or electrochemical series.

## > OXIDATION NUMBER

- In a good number of reactions involving covalent compounds the charge transfer is only partial and is perhaps better described as an electron shift rather than a complete loss/gain of electrons.
- In order to keep track of electron shifts in chemical reactions involving formation of covalent compounds, a more practical method of using oxidation number has been developed.
  - In this method, it is always assumed that there is a complete transfer of electrons from a less electronegative atom to a more electronegative atom.



- Oxidation number denotes the oxidation state of an element in a compound ascertained according to a set of rules formulated on the basis that an electron pair in a covalent bond belongs entirely to a more electronegative element.
- If two or more than two atoms of an element are present in the molecule/ion such as Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>/Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, the oxidation number of the atom of that element will then be the average of the oxidation number of all the atoms of that element.
- The rules for the calculation of oxidation number:
  - In elements, in the free or the uncombined state, each atom bears an oxidation number of zero. Evidently each atom in H<sub>2</sub>, O<sub>2</sub>, Cl<sub>2</sub>, O<sub>3</sub>, P<sub>4</sub>, S<sub>8</sub>, Na, Mg, Al has the oxidation number zero.
  - For ions composed of only one atom, the oxidation number is equal to the charge on the ion.
    - In their compounds all alkali metals have oxidation number of +1
    - all alkaline earth metals have an oxidation number of +2
    - Aluminium is regarded to have an oxidation number of +3 in all its compounds
  - The oxidation number of oxygen in most compounds is -2. However, we come across two kinds of exceptions here.
    - While in peroxides (e.g., H<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>), each oxygen atom is assigned an oxidation number of -1, in superoxides (e.g., KO<sub>2</sub>, RbO<sub>2</sub>) each oxygen atom is assigned an oxidation number of -(<sup>1</sup>/<sub>2</sub>).
    - When oxygen is bonded to fluorine. In such compounds e.g., oxygen difluoride (OF<sub>2</sub>) and dioxygen difluoride (O<sub>2</sub>F<sub>2</sub>), the oxygen is assigned an oxidation number of +2 and +1, respectively.
  - The oxidation number of hydrogen is +1, except when it is bonded to metals in binary compounds (that is compounds containing two elements). For example, in LiH, NaH, and CaH<sub>2</sub>, its oxidation number is -1.
  - In all its compounds, fluorine has an oxidation number of -1.
    - Other halogens (Cl, Br, and I) also have an oxidation number of –1, when they occur as halide ions in their compounds
    - Chlorine, bromine and iodine when combined with oxygen, for example in oxoacids and oxoanions, have positive oxidation numbers.
  - The algebraic sum of the oxidation number of all the atoms in a compound must be zero.
    - In polyatomic ion, the algebraic sum of all the oxidation numbers of atoms of the ion must equal the charge on the ion.
- Metallic elements have positive oxidation numbers and nonmetallic elements have positive or negative oxidation numbers.
- The atoms of transition elements usually display several positive oxidation states.
- The highest oxidation number of a representative element is the group number for the first two groups and the group number minus 10 (following the long form of periodic table) for the other groups.
- The highest value of oxidation number exhibited by an atom of an element generally increases across the period in the periodic table.
  - In the third period, the highest value of the oxidation number changes from 1 to 7.
- The oxidation number denotes the oxidation state of an element in a compound.



- The oxidation number/state of a metal in a compound is sometimes presented according to the notation given by German chemist, Alfred Stock. It is popularly known as Stock notation.
  - The oxidation number is expressed by putting a Roman numeral representing the oxidation number in parenthesis after the symbol of the metal in the molecular formula. Examples -
    - aurous chloride Au(I)Cl
    - auric chloride Au(III)Cl<sub>3</sub>
    - stannous chloride Sn(II)Cl<sub>2</sub>
    - stannic chloride Sn(IV)Cl<sub>4</sub>
- This change in oxidation number implies change in oxidation state, which helps to identify whether the species is present in oxidised form or reduced form.
  - **Oxidation:** An increase in the oxidation number of the element in the given substance.
  - **Reduction:** A decrease in the oxidation number of the element in the given substance.
  - **Oxidising agent:** A reagent which can increase the oxidation number of an element in a given substance. These reagents are also called oxidants.
  - **Reducing agent:** A reagent which lowers the oxidation number of an element in a given substance. These reagents are also called reductants.
  - **Redox reactions:** Reactions which involve change in oxidation number of the interacting species.

### > Types of Redox Reactions

### • Combination reactions:

- denoted in the manner:  $A + B \rightarrow C$ .
- Either A and B or both A and B must be in the elemental form for such a reaction to be a redox reaction.
- All combustion reactions, which make use of elemental oxygen, as well as other reactions involving elements other than dioxygen, are redox reactions.
- Examples -
  - $C(s) + O_2(g) \rightarrow CO_2(g)$
  - $\blacksquare 3Mg(s) + N_2(g) \rightarrow Mg_3N_2(s)$
  - $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

### • Decomposition reactions:

- Decomposition reaction leads to the breakdown of a compound into two or more components, at least one of which must be in the elemental state.
- Examples -
  - $= 2H_2O(1) \rightarrow 2H_2(g) + O_2(g)$
  - $2NaH(s) \rightarrow 2Na(s) + H_2(g)$
  - $2KClO_3(s) \rightarrow 2KCl(s) + 3O_2(g)$
- $\circ~$  All decomposition reactions are not redox reactions. For example  $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$
- Displacement reactions:
  - In a displacement reaction, an ion (or an atom) in a compound is replaced by an ion (or an atom) of another element.



- It may be denoted as:  $X + YZ \rightarrow XZ + Y$
- **Metal displacement:** A metal in a compound can be displaced by another metal in the uncombined state. Examples -
  - $CuSO_4(aq) + Zn(s) \rightarrow Cu(s) + ZnSO_4(aq)$
  - $V_2O_5(s) + 5Ca(s) \rightarrow 2V(s) + 5CaO(s)$
  - $TiCl_4(l) + 2Mg(s) \rightarrow Ti(s) + 2MgCl_2(s)$
  - Cr<sub>2</sub>O<sub>3</sub>(s) + 2Al (s) → Al<sub>2</sub>O<sub>3</sub>(s) + 2Cr(s)
     The reducing metal is a better reducing agent than the one that is being reduced which evidently shows more capability to lose electrons as compared to the one that is reduced.
- **Non-metal displacement:** The non-metal displacement redox reactions include hydrogen displacement and a rarely occurring reaction involving oxygen displacement.
  - All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water.
    - $2Na(s) + 2H_2O(1) \rightarrow 2NaOH(aq) + H_2(g)$
    - $Ca(s) + 2H_2O(1) \rightarrow Ca(OH)_2(aq) + H_2(g)$
  - Less active metals such as magnesium and iron react with steam to produce dihydrogen gas.
    - $Mg(s) + 2H_2O(1) \rightarrow Mg(OH)_2(s) + H_2(g)$
    - $2Fe(s) + 3H_2O(1) \rightarrow Fe_2O_3(s) + 3H_2(g)$
  - Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. Cadmium and tin are examples of such metals.
  - Examples of displacement of hydrogen from acids -
    - $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$
    - Mg (s) + 2HCl (aq)  $\rightarrow$  MgCl<sub>2</sub>(aq) + H<sub>2</sub>(g)
    - $Fe(s) + 2HCl(aq) \rightarrow FeCl_2(aq) + H_2(g)$
  - The reactivity of metals is reflected in the rate of hydrogen gas evolution.
  - Very less active metals, which may occur in the native state such as silver (Ag), and gold (Au) do not react even with hydrochloric acid.
- Like metals, activity series also exist for the halogens.
  - The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table.
  - Fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water.

 $2H_2O(l) + 2F_2(g) \rightarrow 4HF(aq) + O_2(g)$ 

 Chlorine can displace bromide and iodide ions in an aqueous solution as shown below:

 $\begin{array}{l} Cl_2(g)+2Br^-(aq)\rightarrow 2Cl^-\left(aq\right)+Br_2(l)\\ Cl_2(g)+2I^-(aq)\rightarrow 2Cl^-\left(aq\right)+I_2(s) \end{array}$ 

As Br<sub>2</sub> and I<sub>2</sub> are coloured and dissolve in CCl<sub>4</sub>, can easily be identified from the colour of the solution. The above reactions form the basis of identifying Br<sup>-</sup> and I<sup>-</sup> in the laboratory through the test popularly known as 'Layer Test'.



■ There is no way to convert F<sup>-</sup> ions to F<sub>2</sub> by chemical means. The only way to achieve F<sub>2</sub> from F<sup>-</sup> is to oxidise electrolytically.

#### • Disproportionation reactions

- In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced.
- One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states
- The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction.
- Examples -
  - Decomposition of hydrogen peroxide  $2H_2O_2(aq) \rightarrow 2H_2O(1) + O_2(g)$
  - Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium –

 $P_4(s) + 3OH^{-}(aq) + 3H_2O(1) \rightarrow PH_3(g) + 3H_2PO_2^{-}$ 

 $S_8(s) + 12OH^-(aq) \rightarrow 4S^{2-}(aq) + 2S_2O_3^{2-}(aq) + 6H_2O(l)$ 

The formation of household bleaching agents – Cl<sub>2</sub>(g) + 2OH<sup>-</sup>(aq) → ClO<sup>-</sup>(aq) + Cl<sup>-</sup>(aq) + H<sub>2</sub>O(l) The hypochlorite ion (ClO<sup>-</sup>) formed in the reaction oxidises the colour-bearing stains of the substances to colourless compounds

#### The Paradox of Fractional Oxidation Number

- Fractional oxidation state is the average oxidation state of the element under examination.
- The structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states.
- Examples -
  - Carbon suboxide, C<sub>3</sub>O<sub>2</sub> [where oxidation number of carbon is (4/3)]

+2 0 +2  

$$O = C = C^* = C = O$$
  
Structure of  $C_3O_2$ 

• Tribromo Octaoxide, Br<sub>3</sub>O<sub>8</sub> [where oxidation number of bromine is (16/3)]



 $\circ$  tetrathionate ion, S<sub>4</sub>O<sub>6</sub><sup>2-</sup> (where oxidation number of sulphur is 2.5)





- Fe<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, Pb<sub>3</sub>O<sub>4</sub> are some of the other examples of the compounds, which are mixed oxides, where we come across fractional oxidation states of the metal atom.
- $\circ~$  The oxidation states may be in fraction as in  $O_2^+$  and  $O_2^-$  where it is +1/2 and -1/2 respectively.

### Balancing of Redox Reactions

### (a) Oxidation Number Method

- **Step 1:** Write the correct formula for each reactant and product.
- Step 2: Identify atoms which undergo change in oxidation number in the reaction by assigning the oxidation number to all elements in the reaction
- **Step 3:** Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal then multiply by a suitable number so that these become equal.
- Step 4: Ascertain the involvement of ions if the reaction is taking place in water, add H<sup>+</sup> or OH<sup>-</sup> ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. If the reaction is carried out in an acidic solution, use H<sup>+</sup> ions in the equation; if in the basic solution, use OH<sup>-</sup> ions.
- Step 5: Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H<sub>2</sub>O) molecules to the reactants or products. Now, also check the number of oxygen atoms. If there are the same number of oxygen atoms in the reactants and products, the equation then represents the balanced redox reaction.

### (b) Half Reaction Method

- **Step 1:** Produce unbalanced equation for the reaction in ionic form
- **Step 2:** Separate the equation into half-reactions
- **Step 3:** Balance the atoms other than O and H in each half reaction individually.
- **Step 4:** For reactions occurring in acidic medium, add H<sub>2</sub>O to balance O atoms and H<sup>+</sup> to balance H atoms.
- Step 5: Add electrons to one side of the half reaction to balance the charges. If need be, make the number of electrons equal in the two half reactions by multiplying one or both half reactions by appropriate numbers.
- Step 6: We add the two half reactions to achieve the overall reaction and cancel the electrons on each side. This gives the net ionic equation.
- Step 7: Verify that the equation contains the same type and number of atoms and the same charges on both sides of the equation. This last check reveals that the equation is fully balanced with respect to the number of atoms and the charges.
- Step 7: (optional) For the reaction in a basic medium, first balance the atoms as is done in acidic medium. Then for each H<sup>+</sup> ion, add an equal number of OH<sup>-</sup> ions to both sides of the equation. Where H<sup>+</sup> and OH<sup>-</sup> appear on the same side of the equation, combine these to give H<sub>2</sub>O.

### **>** Redox Reactions as the Basis for Titrations

- In redox systems, the titration method can be adopted to determine the strength of a reductant/oxidant using a redox sensitive indicator. For example -
  - **Type 1:** where the reagent itself is intensely coloured, e.g., permanganate ion,  $MnO_4^-$ . Here  $MnO_4^-$  acts as the self indicator. The visible end point in this case is



achieved after the last of the reductant ( $Fe^{2+}$  or  $C_2O_4^{2-}$ ) is oxidised and the first lasting tinge of pink colour appears at MnO<sub>4</sub><sup>-</sup> concentration as low as 10<sup>-6</sup> mol dm<sup>-</sup>  $^{3}$  (10<sup>-6</sup> mol L<sup>-1</sup>).

- Type 2: there are indicators which are oxidised immediately after the last bit of the 0 reactant is consumed, producing a dramatic colour change. The best example is afforded by  $Cr_2O_7^{2-}$ , which oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.
- **Type 3:** Its use is restricted to those reagents which are able to oxidise  $I^-$  ions, for 0 example -  $2Cu^{2+}(aq) + 4I^{-}(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$ 
  - $\rightarrow$  Iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulfate ions  $(S_2O_3^{2-})$ , which too is a redox reaction:  $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^{-}(aq) + S_4O_6^{2-}(aq)$
  - $\rightarrow$  I<sub>2</sub>, though insoluble in water, remains in solution containing KI as KI<sub>3</sub>.
  - $\rightarrow$  On addition of starch after the liberation of iodine from the reaction of Cu<sup>2+</sup> ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only.

### Limitations of Concept of Oxidation Number

In the recent past the oxidation process is visualised as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction.

### REDOX REACTIONS AND ELECTRODE PROCESSES

- A redox couple is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction.
  - This is represented by separating the oxidised form from the reduced form by a 0 vertical line or a slash representing an interface (e.g. solid/solution).
  - Oxidised form is put before the reduced form. Ex.  $Zn^{2+}/Zn$  and  $Cu^{2+}/Cu$ . 0
- Salt bridge: a U-tube containing a solution of potassium chloride or ammonium nitrate • usually solidified by boiling with agar agar and later cooling to a jelly like substance.
  - This provides an electric contact between the two solutions without allowing them to mix with each other.
- When two different redox couples in different beakers are connected externally through a metallic wire and a salt bridge, current flows through the wire and reactions take place in both the beakers. An example is Daniel cell-





- $\rightarrow$  The transfer of electrons now does not take place directly from Zn to Cu<sup>2+</sup> but through the metallic wire connecting the two rods.
- $\rightarrow$  Electrons produced at the anode due to oxidation of Zn travel through the external circuit to the cathode where these reduce the copper ions.
- $\rightarrow$  The circuit is completed inside the cell by the migration of ions through the salt bridge..
- $\rightarrow$  The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge.
- $\rightarrow$  The direction of current is opposite to the direction of electron flow.
- Flow of current is possible only if there is a potential difference between the copper and zinc rods known as electrodes here.
- The potential associated with each electrode is known as electrode potential.
- If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298 K, then the potential of each electrode is said to be the Standard Electrode Potential.
- By convention, the standard electrode potential (E°) of a hydrogen electrode is 0.00 volts.
- The electrode potential value for each electrode process is a measure of the relative tendency of the active species in the process to remain in the oxidised/reduced form.
  - A negative E° means that the redox couple is a stronger reducing agent than the  $H^+/H_2$  couple.
  - A positive  $E^{\circ}$  means that the redox couple is a weaker reducing agent than the 0  $H^+/H_2$  couple.



## Hydrogen

### > Position of hydrogen in the periodic table

- Placed separately in the periodic table (1st period, group not defined)
- Like alkali metals, hydrogen forms oxides, halides and sulphides
- Unlike alkali metals, it has a very high ionization enthalpy and does not possess metallic characteristics under normal conditions
- In terms of ionization enthalpy, hydrogen resembles more with halogens,
- Like halogens, it forms a diatomic molecule, combines with elements to form hydrides and a large number of covalent compounds

### **Dihydrogen - H**<sub>2</sub>

- Most abundant element in the universe & principal element in the solar atmosphere
- Due to its light nature, it is much less abundant (0.15% by mass) in the atmosphere
- In the combined form it constitutes 15.4% of the earth's crust and the oceans.

### Isotopes of Hydrogen

- Hydrogen has three isotopes: Protium,  ${}_{1}H^{1}$ ,  ${}_{1}H^{2}$  or D (Deuterium) and  ${}_{1}H^{3}$  or T (Tritium)
- The predominant form is protium. Terrestrial hydrogen contains 0.0156% of deuterium mostly in the form of HD
- The tritium concentration is about one atom per 1018 atoms of protium as it is radioactive
- They have almost the same chemical properties. The only difference is in their rates of reactions, mainly due to their different enthalpy of bond dissociation
- In physical properties these isotopes differ considerably due to their large mass differences.

### > **PREPARATION OF DIHYDROGEN**, H<sub>2</sub>

### Laboratory Preparation of Dihydrogen

- a) Usually prepared by the reaction of granulated zinc with dilute hydrochloric acid.  $Zn + 2H^* \rightarrow Zn^{2*} + H_{a}$
- b) Can also be prepared by the reaction of zinc with aqueous alkali.  $Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2$ Sodium zincate

### > Commercial Production of Dihydrogen

a) Electrolysis of acidified water using platinum electrodes

 $2H_2O(1) \xrightarrow{\text{Electrolysis}} 2H_2(g) + O_2(g)$ 

- b) High purity (>99.95%) di hydrogen is obtained by electrolysing warm aqueous barium hydroxide solution between nickel electrodes.
- c) Obtained as a byproduct in the manufacture of sodium hydroxide and chlorine by the electrolysis of brine solution. Reactions that take place are:



at anode:  $2Cl^{-}(aq) \rightarrow Cl_{2}(g) + 2e^{-}$ at cathode:  $2H_{2}O(l) + 2e^{-} \rightarrow H_{2}(g) + 2OH^{-}(aq)$ The overall reaction is  $2Na^{+}(aq) + 2Cl^{-}(aq) + 2H_{2}O(l)$  $\downarrow$  $Cl_{2}(g) + H_{2}(g) + 2Na^{+}(aq) + 2OH^{-}(aq)$ 

d) Reaction of steam on hydrocarbons at high temperatures in the presence of catalyst

 $\begin{array}{c} C_{n}H_{2n+2} + nH_{2}O \xrightarrow[Ni]{1270K} \\ \text{e.g.,} \end{array} \rightarrow nCO + (2n+1)H_{2} \\ CH_{4}\left(g\right) + H_{2}O\left(g\right) \xrightarrow[Ni]{1270K} \\ \hline \end{array} \rightarrow CO\left(g\right) + 3H_{2}\left(g\right) \end{array}$ 

- The mixture of CO and H<sub>2</sub> is called water gas
- As this mixture of CO and H<sub>2</sub> is used for the synthesis of methanol and a number of hydrocarbons, it is also called **synthesis gas** or **'syngas'**
- 'Syngas' is produced from sewage, saw-dust, scrap wood, newspapers etc. The process of producing 'syngas' from coal is called 'coal gasification'.
   C(s)+H<sub>2</sub>O(g) → CO(g)+H<sub>2</sub>(g)
- The production of dihydrogen can be increased by reacting carbon monoxide of syngas mixtures with steam in the presence of iron chromate as catalyst.

 $\operatorname{CO}(g) + \operatorname{H}_2\operatorname{O}(g) \xrightarrow{673\mathrm{K}} \operatorname{CO}_2(g) + \operatorname{H}_2(g)$ 

This is called water-gas shift reaction. Carbon dioxide is removed by scrubbing with sodium arsenite solution.

### PROPERTIES OF DIHYDROGEN

### Physical Properties

- Colourless, odourless, tasteless, combustible gas, lighter than air and insoluble in water.
- Chemical Properties
  - The H–H bond dissociation enthalpy is the highest for a single bond between two atoms
  - It is because of this factor that the dissociation of dihydrogen into its atoms is only ~0.081% around 2000K which increases to 95.5% at 5000K
  - ✤ It is relatively inert at room temperature.
  - Atomic H is produced at a high temperature in an electric arc or under ultraviolet radiations

### > Dihydrogen reactions:

a) Reaction with halogens:

 $H_2(g) + X_2(g) \rightarrow 2HX(g)$  (X = F, Cl, Br, I)

Gives hydrogen halides

While the reaction with fluorine occurs even in the dark, with iodine it requires a catalyst

b) Reaction with dioxygen: Forms water. The reaction is highly exothermic.



$$2H_2(g) + O_2(g) \xrightarrow{\text{catalyst or heating}} 2H_2O(l);$$
  
 $\Delta H^{\ominus} = -285.9 \text{ kJ mol}^{-1}$ 

c) Reaction with dinitrogen:

 $3H_{2}(g) + N_{2}(g) \xrightarrow{673K,200atm}{Fe} 2NH_{3}(g);$  $\Delta H^{\odot} = -92.6 \text{ kJ mol}^{-1}$ 

Forms ammonia

This is the method for the manufacture of ammonia by the Haber process.

d) Reactions with metals:

Combines at a high temperature to yield the corresponding hydrides  $H_2(g) + 2M(g) \rightarrow 2MH(s);$ 

where M is an alkali metal

e) Reactions with metal ions and metal oxides:

Reduces some metal ions in aqueous solution and oxides of metals (less active than iron) into corresponding metals.

 $H_2(g) + Pd^{2+}(aq) \rightarrow Pd(s) + 2H^+(aq)$  $yH_2(g) + M_sO_s(s) \rightarrow xM(s) + yH_sO(1)$ 

- f) Reactions with organic compounds:
  - i. Hydrogenation of vegetable oils using nickel as catalyst gives edible fats (margarine and vanaspati ghee)
  - ii. Hydroformylation of olefins yields aldehydes which further undergo reduction to give alcohols.

 $H_2 + CO + RCH = CH_2 \rightarrow RCH_2CH_2CHO$ 

 $H_2 + RCH_2CH_2CHO \rightarrow RCH_2CH_2OH$ 

- > Uses
  - In synthesis of ammonia which is used to make nitric acid and nitrogenous fertilizers.
  - In preparation of hydrogen chloride, a highly useful chemical.
  - In metallurgical processes, it is used to reduce heavy metal oxides to metals.
  - Atomic hydrogen and oxy-hydrogen torches find use for cutting and welding purposes. Atomic hydrogen atoms (produced by dissociation of dihydrogen with the help of an electric arc) are allowed to recombine on the surface to be welded to generate the temperature of 4000 K.
  - Used as a rocket fuel in space research.
  - Used in fuel cells for generating electrical energy. It does not produce any pollution and releases greater energy per unit mass of fuel in comparison to gasoline and other fuels.

## > Hydrides

Dihydrogen, under certain reaction conditions, combines with almost all elements, except noble gases, to form binary compounds, called **hydrides**. If 'E' is the symbol of an element then hydride can be expressed as  $EH_x$  (e.g., MgH) or emhn (e.g.,  $B_2H_6$ ) The hydrides are classified into three estagories i

The hydrides are classified into three categories :

- (i) Ionic or saline or salt like hydrides
- (ii) Covalent or molecular hydrides



(iii) Metallic or non-stoichiometric hydrides

### > Ionic or saline or salt like hydrides

- Stoichiometric compounds of dihydrogen formed with most of the s-block elements which are highly electropositive in character
- Significant covalent character is found in the lighter metal hydrides such as lih, beh<sub>2</sub> and mgh<sub>2</sub>. In fact beh<sub>2</sub> and mgh<sub>2</sub> are polymeric in structure.
- Crystalline, non-volatile and non conductive in solid state
- Their melts conduct electricity and on electrolysis liberate dihydrogen gas at anode 2H<sup>-</sup> (melt) → H<sub>2</sub> (g) + 2e<sup>-</sup>
- Saline hydrides react violently with water producing dihydrogen gas.
   NaH(s) + H<sub>2</sub>O(aq) → NaOH(aq) + H<sub>2</sub>(g)
- Lithium hydride is rather unreactive at moderate temperatures with oxygen and chlorine. It is, therefore, used in the synthesis of other useful hydrides
   8LiH + Al<sub>2</sub>Cl<sub>6</sub> → 2LiAlH<sub>4</sub> + 6LiCl

 $2\text{LiH} + \text{B}_{2}\text{H}_{6} \rightarrow 2\text{LiBH}_{4}$ 

### Covalent or Molecular Hydride

- Hydrogen compounds of nonmetals have also been considered as hydrides.
- Being covalent, they are volatile compounds. Molecular hydrides are further classified according to the relative numbers of electrons
  - a) Electron-deficient hydride has too few electrons for writing its conventional Lewis structure. Ex B<sub>2</sub>H<sub>6</sub>
  - b) **Electron-precise compounds** have the required number of electrons to write their conventional Lewis structures. All elements of group 14 form such compounds
  - c) **Electron-rich hydrides** have excess electrons which are present as lone pairs. They will behave as Lewis bases i.e., electron donors

### > Metallic or Non-stoichiometric (or Interstitial ) Hydrides

- Are formed by d-block and f-block elements except 7,8,9 group and Cr from 6th group.
- Conduct heat and electricity though not as efficiently as their parent metals
- Earlier it was thought that in these hydrides, hydrogen occupies interstices in the metal lattice producing distortion without any change in its type. Consequently, they were termed as interstitial hydrides
- Recent studies have shown that except for hydrides of Ni, Pd, Ce and Ac, other hydrides of this class have a lattice different from that of the parent metal.
- Some of the metals (e.g., Pd, Pt) can accommodate a very large volume of hydrogen and, therefore, can be used as its storage media. This property has high potential for hydrogen storage and as a source of energy



## ≻ <u>Water</u>

### **Physical Properties of Water**

- Colourless and tasteless liquid
- The unusual properties of water in the condensed phase (liquid and solid states) are due to the presence of extensive hydrogen bonding between water molecules
- This leads to high freezing point, high boiling point, high heat of vaporisation and high heat of fusion in comparison to H<sub>2</sub>S and H<sub>2</sub>Se
- It has a higher specific heat, thermal conductivity, surface tension, dipole moment and dielectric constant, etc
- The high heat of vaporisation and heat capacity are responsible for moderation of the climate and body temperature of living beings

## Structure of Water

- In the gas phase water is a bent molecule with a bond angle of 104.5°, and H-O–H bond length of 95.7 pm
- At atmospheric pressure ice crystallises in the hexagonal form, but at very low temperatures it condenses to a cubic form.

## Structure of Ice

- Ice has a highly ordered three dimensional hydrogen bonded structure
- X-rays show that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms at a distance of 276 pm.
- Hydrogen bonding gives ice a rather open type structure with wide holes. These holes can hold some other molecules of appropriate size interstitially

## Chemical Properties of Water

## a) Amphoteric Nature

- Has the ability to act as an acid as well as a base
- In the Brönsted sense it acts as an acid with NH<sub>3</sub> and a base with H<sub>2</sub>S. H<sub>2</sub>O(l) + NH<sub>3</sub> (aq)  $\rightleftharpoons$  OH<sup>-</sup> (aq) + NH<sub>4</sub><sup>+</sup> (aq)

 $H_2O(1) + H_2S(aq) \rightleftharpoons H_3O^+(aq) + HS^-(aq)$ 

The auto protolysis (self ionization) of water takes place as follow -

 $\begin{array}{l} H_2O(1) + H_2O(1) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \\ acid-1 & base-2 & acid-2 & base-1 \\ (acid) & (base) & (conjugate & (conjugate & acid) & base) \end{array}$ 

## b) Redox Reactions Involving Water

• Can be easily reduced to dihydrogen by highly electropositive metals

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

Thus, This is a great source of dihydrogen. Water is oxidised to O<sub>2</sub> during photosynthesis.  $6CO_2(g) + 12H_2O(l) \rightarrow C_6H_{12}O_6(aq) + 6H_2O(l) + 6O_2(g)$ 

With fluorine also it oxidised to O<sub>2</sub>.  $2F_2(g) + 2H_2O(l) \rightarrow 4H^+ (aq) + 4F^-(aq) + O_2(g)$ 



### c) Hydrolysis Reaction:

• Due to high dielectric constant, it has a very strong hydrating tendency. It dissolves many ionic compounds. However, certain covalent and some ionic compounds are hydrolysed in water

$$P_4O_{10}(s) + 6H_2O(1) \rightarrow 4H_3PO_4(aq)$$

 $SiCl_4(1) + 2H_2O(1) \rightarrow SiO_2(s) + 4HCl(aq)$ 

### d) Hydrates Formation:

From aqueous solutions many salts can be crystallised as hydrated salts. Such an association of water is of different types viz.,

(i) coordinated water e.g.,

 $\left[\operatorname{Cr}(\operatorname{H}_{2}\operatorname{O})_{6}\right]^{3+}\operatorname{3Cl}^{-1}$ 

(ii) interstitial water e.g.,  $BaCl_2.2H_2O$ 

(iii) hydrogen-bonded water e.g.,

 $\left[Cu(H_2O)_4\right]^{2+}SO_4^{2-}.H_2O \text{ in } CuSO_4.5H_2O,$ 

## ➢ Hard and Soft Water

- Presence of calcium and magnesium salts in the form of hydrogen carbonate, chloride and sulphate in water makes water 'hard'
- Water free from soluble salts of calcium and magnesium is called Soft water.
- Hard water forms scum/precipitate with soap. Soap containing sodium stearate (c<sub>17h35</sub>coona) reacts with hard water to precipitate out Ca/Mg stearate.

 $2\mathrm{C_{17}H_{35}COONa}\,\mathrm{(aq)} + \mathrm{M^{2+}}\,\mathrm{(aq)} \rightarrow$ 

 $(C_{17}H_{35}COO)_{a} M \downarrow +2Na^{+}(aq); Mis Ca / Mg$ 

### Hardness of water is of two types:

(i) temporary hardness (ii) permanent hardness.

### Temporary Hardness

Presence of magnesium and calcium hydrogen carbonates is the reason of temporary hardness. These are the methods of removal -

### A) Boiling:

During boiling, the soluble  $Mg(HCO_3)_2$  is converted into insoluble  $Mg(OH)_2$  and  $Ca(HCO_3)_2$  is changed to insoluble caco<sub>3</sub>. It is because of high solubility product of  $Mg(OH)_2$  as compared to that of  $mgco_3$ , that  $Mg(OH)_2$  is precipitated. These precipitates can be removed by filtration.

 $Mg(HCO_3)_2 \xrightarrow{Hosting} \rightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow$ 

 $Ca(HCO_3)_2 \xrightarrow{Heating} CaCO_3 \downarrow +H_2O + CO_2 \uparrow$ 

## **B)** Clark's method:

Calculated amount of lime is added to hard water. It precipitates out calcium carbonate and magnesium hydroxide which can be filtered off

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

 $Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 \downarrow$  $+ Mg(OH)_2 \downarrow + 2H_2O$ 



### > Permanent Hardness

- Due to the presence of soluble salts of magnesium and calcium in the form of chlorides and sulphates in water
- Can not be removed by boiling.

### Methods to remove -

a) Treatment with washing soda (sodium carbonate):

Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

 $MCl_2 + Na_2CO_3 \rightarrow MCO_3 \downarrow + 2NaCl$ (M = Mg, Ca)

 $MSO_4 + Na_2CO_3 \rightarrow MCO_3 \downarrow + Na_2SO_4$ 

b) Calgon's method:

Sodium hexametaphosphate (Na<sub>6</sub>P<sub>6</sub>O<sub>18</sub>), commercially called 'calgon', when added to hard water, the following reactions take place.

 $\mathrm{Na}_{6}\mathrm{P}_{6}\mathrm{O}_{18}\rightarrow 2\mathrm{Na}^{+}+\mathrm{Na}_{4}\mathrm{P}_{6}\mathrm{O}_{18}^{2-}$ 

(M = Mg, Ca)

 $M^{2+} + Na_4P_6O_{18}^{2-} \rightarrow [Na_2MP_6O_{18}]^{2-} + 2Na^+$ 

c) Ion-exchange method / zeolite/permutit process Hydrated sodium aluminium silicate is zeolite/permutit. Sodium aluminium silicate (naalsio4) can be written as naz. It is added in hard water, exchange reaction happens  $2NaZ(s) + M^{2+}(aq) \rightarrow MZ_{2}(s) + 2Na^{+}(aq)$ 

$$(M = Mg, Ca)$$

Permutit/zeolite is said to be exhausted when all the sodium in it is used up. It is regenerated for further use by treating with an aqueous sodium chloride solution.  $MZ_2(s)+2NaCl(aq) \rightarrow 2NaZ(s)+MCl_2(aq)$ 

d) Synthetic resins method:

Nowadays hard water is softened by using synthetic cation exchangers. This method is more efficient than zeolite process. Cation exchange resins contain large organic molecule with - SO<sub>3</sub>H group and are water insoluble. Ion exchange resin (RSO<sub>3</sub>H) is changed to rna by treating it with nacl. The resin exchanges Na<sup>+</sup> ions with Ca<sup>2+</sup> and Mg<sup>2+</sup> ions present in hard water to make the water soft. Here R is resin anion.  $2RNa(s) + M^{2+}(aq) \rightarrow R_2M(s) + 2Na^+(aq)$ 

The resin can be regenerated by adding aqueous nacl solution. Pure demineralised (de-ionized) water free from all soluble mineral salts is obtained by passing water successively through a cation exchange (in the  $H^+$  form) and an anion exchange (in the  $OH^-$  form) resins:

 $2RH(s) + M^{2+}(aq) \rightleftharpoons MR_2(s) + 2H^+(aq)$ 

In this cation exchange process,  $H^+$  exchanges for Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and other cations present in water. This process results in proton release and thus makes the water acidic. In the anion exchange process:



 $RNH_{2}(s) + H_{2}O(l) \rightleftharpoons RNH_{3}^{*}.OH^{-}(s)$ 

$$RNH_{3}^{+}.OH^{-}(s) + X^{-}(aq) \rightleftharpoons RNH_{3}^{+}.X^{-}(s)$$

+ OH [ (aq)

 $OH^-$  exchanges for anions like  $Cl^-$ ,  $HCO_3^-$ ,  $SO_4^{2-}$  etc. Present in water.  $OH^-$  ions, thus, liberated neutralise the  $H^+$  ions set free in the cation exchange.

 $H^+(aq) + OH^-(aq) \rightarrow H_2O(1)$ 

The exhausted cation and anion exchange resin beds are regenerated by treatment with dilute acid and alkali solutions.

### **HYDROGEN PEROXIDE (H2O2)**

An important chemical used in pollution control treatment of domestic and industrial effluents.

### > Preparation Methods

a) By acidifying barium peroxide and removing excess water by evaporation under reduced pressure gives hydrogen peroxide.

 $BaO_2.8H_2O(s) + H_2SO_4(aq) \rightarrow BaSO_4(s) +$ 

 $H_2O_2(aq) + 8H_2O(l)$ 

b) Peroxodisulphate, obtained by electrolytic oxidation of acidified sulphate solutions at high current density, on hydrolysis yields hydrogen peroxide.

 $2HSO_{4}^{-}(aq) \xrightarrow{Electrolysis} HO_{3}SOOSO_{3}H(aq)$ 

 $Hydrolysis \rightarrow 2HSO_4^-(aq) + 2H^+(aq) + H_2O_2(aq)$ 

This method is now used for the laboratory preparation of  $D_2O_2$ .  $K_2S_2O_8(s)+2D_2O(l) \rightarrow 2KDSO_4(aq)+D_2O_2(l)$ 

c) Industrially it is prepared by the auto oxidation of 2-alkyl anthraquinone.

 $2 - ethylanthraquinol \xrightarrow{O_2(alr)} H_2O_2 +$ 

### (oxidised product)

In this case  $1\% H_2O_2$  is formed. It is extracted with water and concentrated to ~30% (by mass) by distillation under reduced pressure

• Can be further concentrated to  $\sim 85\%$  by careful distillation under low pressure. The remaining water can be frozen out to obtain pure H<sub>2</sub>O<sub>2</sub>

## > Physical Properties

- In pure state H<sub>2</sub>O<sub>2</sub> is an almost colourless (very pale blue) liquid.
- Miscible with water in all proportions and forms a hydrate H<sub>2</sub>O<sub>2</sub>.H<sub>2</sub>O (mp 221K).
- A 30% solution of H<sub>2</sub>O<sub>2</sub> is marketed as '100 volume' hydrogen peroxide. It means that one millilitre of 30% H<sub>2</sub>O<sub>2</sub> solution will give 100 ml of oxygen at STP. Commercially marketed sample is 10 V, which means that the sample contains 3% H<sub>2</sub>O<sub>2</sub>.



### Structure Hydrogen peroxide -

A non-planar structure. The molecular dimensions in the gas phase and solid phase are shown



(b) Solid phase (a) H<sub>2</sub>O<sub>2</sub> structure in gas phase, dihedral angle is 111.5°. (b) H2O2 structure in solid phase at 110K, dihedral angle is 90.2°.

#### Chemical Properties:

Acts as an oxidising as well as reducing agent in both acidic and alkaline media.

(a) Gas phase

(i) Oxidising action in acidic medium

 $2Fe^{2+}(aq) + 2H^{*}(aq) + H_2O_2(aq) \rightarrow$ 2Fe3+ (ag) + 2H,O(1)  $PbS(s) + 4H_2O_2(aq) \rightarrow PbSO_4(s) + 4H_2O(1)$ 

- (ii) Reducing action in acidic medium  $2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$  $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$
- (iii) Oxidising action in basic medium  $2Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + 2OH^{-}$  $Mn^{2+} + H_2O_2 \rightarrow Mn^{4+} + 2OH^{-}$
- (iv) Reducing action in basic medium  $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$  $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 +$

## $2H_{2}O + 2OH^{-}$

## > Storage

- H<sub>2</sub>O<sub>2</sub> decomposes slowly on exposure to light.  $2H_2O_2(1) \rightarrow 2H_2O(1) + O_2(g)$
- In the presence of metal surfaces or traces of alkali (present in glass containers), the above reaction is catalysed. It is, therefore, stored in wax-lined glass or plastic vessels in dark.
- Urea can be added as a stabiliser. It is kept away from dust because dust can induce explosive decomposition of the compound.
- > Uses:
  - Its wide scale use has led to tremendous increase in the industrial production of  $H_2O_2$ . Some of the uses are listed below:
    - (i) Used as a hair bleach and, mild disinfectant, antiseptic. It is sold in the market as perhydrol.



- (ii) Used to manufacture chemicals like sodium perborate and per -carbonate, which are used in high quality detergents.
- (iii) Used in the synthesis of hydroquinone, tartaric acid and certain food products and pharmaceuticals (cephalosporin) etc.
- (iv) Used in the industries as a bleaching agent for textiles, paper pulp, leather, oils, fats, etc.
- (v) Used in Environmental Chemistry. For example, in pollution control treatment of domestic and industrial effluents, oxidation of cyanides, restoration of aerobic conditions to sewage

### ➢ HEAVY WATER, D₂O

Extensively used as a moderator in nuclear reactors.

- In exchange reactions for the study of reaction mechanisms.
- Can be prepared by hard electrolysis of water or as a by-product in some fertilizer industries
- It is used for the preparation of other deuterium compounds, for example:

 $\operatorname{CaC}_2 + 2\operatorname{D}_2\operatorname{O} \rightarrow \operatorname{C}_2\operatorname{D}_2 + \operatorname{Ca}(\operatorname{OD})_2$ 

```
SO_3 + D_2O \rightarrow D_2SO_4
```

```
Al_4C_3 + 12D_2O \rightarrow 3CD_4 + 4Al(OD)_3
```

## **DIHYDROGEN AS A FUEL**

- Releases large quantities of heat on combustion as compared to other fuels
- The data on energy released by combustion of different fuels are compared in table 9.5.
- Pollutants in combustion of dihydrogen will be less than petrol. The only pollutants will be the oxides of dinitrogen (due to the presence of dinitrogen as impurity with dihydrogen). This, of course, can be minimised by injecting a small amount of water into the cylinder to lower the temperature so that the reaction between dinitrogen and dioxygen may not take place.
- A cylinder of compressed dihydrogen weighs about 30 times as much as a tank of petrol containing the same amount of energy. Mass of tank is a big issue.
- Dihydrogen gas is converted into liquid state by cooling to 20K. This would require expensive insulated tanks. Tanks of metal alloy like nanis, Ti-tih2, Mg-MgH2 etc.
- The basic principle of hydrogen economy is the transportation and storage of energy in the form of liquid or gaseous dihydrogen. Initially 5% dihydrogen has been mixed in CNG for use in four-wheeler vehicles. It is being increased to reach the optimum level.
- It is also used in fuel cells for generation of electric power. It is expected that economically viable and safe sources of dihydrogen will be identified in the years to come, for its usage as a common source of energy

Energy released on combustion in kJ state)	Dihydrogen (in gaseous state)	Dihydrogen (in liquid)	LPG	CH <sub>4</sub> gas	Octane (in liquid state)
per mole	286	285	2220	880	5511
per gram	143	142	50	53	47
per litre	12	9968	25590	35	34005

The Energy Released by Combustion of Various Fuels in Moles, Mass and Volume



## **The s-Block Elements**

#### ➤ General properties:

- Last electron enters outermost s-orbital
- Has two groups (1 & 2) as s-orbital can accommodate only 2 electrons.

#### **Group-1 elements**

#### ➢ General points:

- Also called as alkali metals because they form hydroxides on reaction with water, which are highly alkaline in nature.
- General valence shell electronic configuration: ns<sup>1</sup>.
- Readily looses electron to form monovalent ions and are most electropositive metals because the outermost s-electron is loosely held
- Elements and their electronic configuration:

Element	Symbol	Electronic configuration		
Lithium	Li	$1s^{2}2s^{1}$		
Sodium	Na	$1s^22s^22p^63s^1$		
Potassium	K	$1s^22s^22p^63s^23p^64s^1$		
Rubidium	Rb	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup> 5s <sup>1</sup>		
Caesium	Cs	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 3d <sup>16</sup> 4s <sup>2</sup>		
		4p <sup>6</sup> 4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup> 6s <sup>1</sup> or [Xe] 6s <sup>1</sup>		
Francium	Fr	[Rn]7s <sup>1</sup>		

- Abundance in lithosphere:
  - ✤ Abundant: Na, K
  - ✤ Less abundant: Li, Rb, Cs
- Fr is radioactive and has a half life of 21 minutes.

#### > Physical properties:

Property	Order	Points
Size	Li < Na < K < Rb < Cs	<ol> <li>Have larger sizes than other elements in their corresponding period</li> <li>Size of M<sup>+</sup> &lt; M</li> <li>From Na to K there is a greater increase in the size compared to others.</li> </ol>
At. weight	Li < Na < K < Rb < Cs	
Density	Li < K < Na < Rb < Cs	1. Low densities due to large size



		<ol> <li>Density (mass/volume) of K &lt; Na because the increase in size is greater than that of increase in mass.</li> </ol>
BP & MP	Li > Na > K > Rb > Cs	<ol> <li>Low MP &amp; BP due to weak metallic bonding (only one electron participates in Metallic bonding)</li> </ol>
IE	Li > Na > K > Rb > Cs	
HE (Hydratio n energy)	Li+ > Na+ > K+ > Rb+ > Cs+.	1. Li+ has a maximum degree of hydration. Eg: LiCl. 2H <sub>2</sub> O
Std oxidation potential and reducing nature	Li > Rb > Cs > K > Na	<ol> <li>Increases down the group, except for Li</li> <li>Std. potential measures the overall change in sublimation enthalpy, ionisation enthalpy and hydration enthalpy.</li> <li>Highest reducing power is shown by Li due to high hydration enthalpy and least is shown by Na</li> </ol>

### • Flam<mark>e test:</mark>

- Imparts characteristic color to an oxidising flame.
- Colour is imparted due to excitation and deexcitation of the electron in the ns orbital. Colours imparted by each metal is shown in the table below:
   Note that 'λ' corresponds to the highest intensity wavelength emitted during flame test

Metal	Li	Na	K	Rb	Cs
Colour	Crimson red	Yellow	Violet	Red violet	Blue
λ/nm	670.8	589.2	766.5	780.0	455.5

 Cs, K are used as electrodes in photochemical cells because simply by irradiating them with light they can loose electron.

## > Chemical properties:

- Reactivity towards air:
  - Tarnish in dry air due to formation of oxides.



- Li can form only oxide. Na can form oxide as well as peroxide. K, Rb, Cs form oxides, peroxide and superoxides. In all the cases the metals are in +1 oxidation state.
  - 4 Li  $+O_2 \rightarrow 2Li_2O$  (oxide)

 $2Na + O_2 \rightarrow Na_2O_2$  (peroxide)

- $M+O_2 \rightarrow MO_2$  (superoxide) (M = K, Rb, Cs)
- ♦ Li also forms LiN<sub>3</sub> (lithium nitride) by reacting directly with nitrogen
- Alkali metals are kept in kerosene due to their high reactivity towards air and water.

#### • Reactivity towards water:

- React to form hydroxides and H<sub>2</sub> gas.
- Order of reactivity: Li < Na < K < Rb < Cs
- Li is less reactive, Na reacts vigorously and other metals react explosively with water.
- Even though  $E^0$  (Li/Li+) >  $E^0$  (Na/ Na+), the reactivity of lithium is lower than that of sodium. This can be attributed to the small size and very high hydration energy of Li.
- They react with proton donors such as alcohols, alkynes and gaseous ammonia.

#### • Reactivity towards dihydrogen

- Form hydrides which are ionic solids having high melting points.
- $\bigstar 2M + H_2 \rightarrow 2M^+H^-$
- Reactivity towards halogens
  - Forms ionic halides of type M<sup>+</sup>X<sup>-</sup> except lithium halides which are covalent in nature due to high polarising power of Li+ ion and high polarisability of large anion X- (Using Fazan's rules).
  - Lithium iodide is the most covalent halide in nature compared to other lithium halides (Using Fazan's rules)
- Solutions in liquid ammonia
  - Dissolve in ammonia forming a conducting deep blue coloured solution. M+ (x + y) NH<sub>3</sub> → [M (NH<sub>3</sub>)<sub>x</sub>]<sup>+</sup> + [e(NH<sub>3</sub>)<sub>y</sub>]<sup>-</sup>
  - Colour is due to an ammoniated electron which absorbs energy from visible light region.
  - ♦ Solution on standing liberates hydrogen gas slowly.  $M^+(ammoniated) + e^- + NH_3 (l) \rightarrow MNH_2 (ammoniated) + \frac{1}{2} H_2(g)$
  - Solution is paramagnetic in nature. If concentrated then the blue colour changes to bronze and becomes diamagnetic.



### > General characteristics of the compounds of alkali metals

- Oxides and hydroxides
  - ♦ General formula: Oxides M<sub>2</sub>O, peroxides M<sub>2</sub>O<sub>2</sub>, superoxides MO<sub>2</sub>
  - Stability of the peroxide or superoxide increases, as the size of the metal ion increases, due to the stabilisation of large anions by larger cations through lattice energy.
  - Pure oxides, peroxides, superoxides can be formed under appropriate conditions.
  - Pure oxides, peroxides are colourless and pure superoxides are yellow or orange in colour because of their paramagnetic nature
  - Oxides on hydrolysis form hydroxides.  $M_2O + H_2O \rightarrow 2M^+ + 2OH^-$

 $M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2$ 

 $2 MO_3 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_3 + O_2$ 

All hydroxides are white crystalline solids and dissolve in water easily by liberating huge hydration energy.

## • Halides

- ✤ General formula: MX
- Properties: High MP, colourless, crystalline solids.
- ◆ Preparation: M<sub>2</sub>O/ MOH/ M<sub>2</sub>CO<sub>3</sub> with HX (hydrohalic acid)
- MP, BP: fluoride > chloride > bromide > iodide
- Solubility:
  - All halides are soluble in water
  - Lithium halides are also soluble in ethanol, acetone and ethyl acetate; LiCl is soluble in pyridine also.
  - LiF: low soluble in water due to high lattice enthalpy.
  - CsI: low soluble in water due to low hydration enthalpy
- $\Delta_{\rm f} H_0$  values:
  - Highly negative. Become less negative from fluorides to iodides
  - Fluorides: Less negative down the group
  - Chlorides/Bromides/Iodides: More negative down the group

### • Salts of oxoacids

- Oxoacid: Acidic proton on OH group along with an oxo group attached to the same atom. Eg: H<sub>2</sub>CO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>.
- ✤ Alkali metals form salts with oxoacids
- General properties: Soluble in water and thermally stable
- Carbonates and bicarbonates:
- Thermal stability: Increases down the group as the electropositive nature increases.Li<sub>2</sub>CO<sub>3</sub> is not stable to heat due to small size Li and decomposes to form Li<sub>2</sub>O and H<sub>2</sub>O. Its hydrogen carbonate does not exist as solid.



### > Anomalous behaviour of Lithium

- Due to small size and high polarising power, high covalent character in its compounds, it shows differences from other elements of the group.
- Difference between Li and other group-1 elements:
  - ♦ MP,BP: higher than others and is harder
  - ✤ Least reactive but has high reducing power
  - On reaction with air forms Li<sub>2</sub>O and Li<sub>3</sub>N
  - LiCl is deliquescent i.e forms hydrides LiCl. 2H<sub>2</sub>O. Other chlorides don't form hydrides
  - Lithium hydrogen carbonate is not in solid form while others form solid hydrogen carbonates.
  - Doesn't form ethynide on reaction with ethyne
  - Differ in the decomposition of the nitrates from others

 $4\text{LiNO}_3 \rightarrow 2\text{Li}_2\text{O} + 4\text{NO}_2 + \text{O}_2$ 

 $2 \text{ NaNO}_3 \rightarrow 2 \text{ NaNO}_2 + \text{O}_2$ 

- Oxides and fluorides are less soluble in water compared to others.
- Similarity with Magnesium (Diagonal relationship):
  - Similarity is due to similar sizes
  - Both are harder and lighter than other elements in the group and form nitrides on reaction with nitrogen.
  - Their oxides and hydroxides are less soluble and hydroxides decompose on heating
  - Carbonates decompose on heating and liberate CO<sub>2</sub>. Their hydrogen carbonates are not solids.
  - Their chlorides are deliquescent (LiCl.2H<sub>2</sub>O, MgCl<sub>2</sub>. 8H<sub>2</sub>O) and are soluble in ethanol.

#### Important compounds of group-1:

- Sodium carbonate (washing soda):
  - ✤ Formula: Na<sub>2</sub>CO<sub>3</sub>.10 H<sub>2</sub>O
  - Preparation: Solvay's process  $2NH_3 + H_2O + CO_2 \rightarrow (NH_4)_2 CO_3$   $(NH_4)_2 CO_3 + H_2O + CO_2 \rightarrow 2NH_4HCO_3$   $NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3$ Due to low solubility of NaHCO<sub>3</sub>, it is precipitated.  $2NaHCO_3 \xrightarrow{\Delta H} Na_2CO_3 + CO_2 + H_2O$   $NH_3 \text{ can be recycled using the following reaction:}$   $2NH_4Cl + Ca(OH)_2 \rightarrow 2NH_3 + CaCl_2 + H_2O$   $NOTE: Solvay's process cannot be used for K_2CO_3 due to high solubility of Package and Packa$

KHCO<sub>3</sub>.



- Properties:
  - White crystalline solid, decahydrate, readily soluble in water forming alkaline solution.
  - On heating it follows the below reactions:  $Na_2CO_3 \square OH_2O \xrightarrow{375K} Na_2CO_3 \square H_2O + 9H_2O$  $Na_2CO_3 \square H_2O \xrightarrow{>373K} Na_2CO_3 + H_2O$
- ♦ Uses:
  - Water softening, laundering and cleaning.
  - In the manufacture of glass, soap, borax and caustic soda.
  - In paper, paints and textile industries.
  - Important laboratory reagent both in qualitative and quantitative analysis

### • Sodium chloride:

- ✤ Formula: NaCl
- Preparation:
  - Crude NaCl is prepared by crystallization of brine solution (sea water).
     Impurities include sodium sulphate, calcium sulphate, calcium chloride and magnesium chloride.
  - Table salt is deliquescent due to presence of CaCl<sub>2</sub> and MgCl<sub>2</sub>
- Purification:
  - By dissolving crude salt in a small amount of water followed by filtration to remove insoluble impurities. The water is then passed through HCl to precipitate out the NaCl with MgCl<sub>2</sub> and CaCl<sub>2</sub> remaining dissolved in water.
- Properties:
  - MP: 1081K
  - Solubility in water: 36g/100ml of water at 273K. Also note that solubility doesn't increase appreciably with increase in temperature.
- ♦ Uses:
  - Table salt and preparation of Na<sub>2</sub>O<sub>2</sub>, NaOH, Na<sub>2</sub>CO<sub>3</sub>

## • Sodium hydroxide (Caustic soda):

- ✤ Formula: NaOH
- Preparation: Electrolysis of NaCl (In castner kellner cell)
  - Cathode: Mercury, Anode: Carbon, Brine solution
  - On electrolysis, sodium amalgam is produced at cathode and this is treated with water to form NaOH

```
Cathode: Na<sup>+</sup> + e<sup>-</sup> → Na - amalgam
```

Anode :  $Cl^- \rightarrow \frac{1}{2}Cl_2 + e^-$ 2Na-amalgam + 2H<sub>2</sub>O $\rightarrow$ 2NaOH+ 2Hg +H<sub>2</sub>

✤ Properties:



- White, translucent solid, MP: 591K, gives a strong alkaline solution with water.
- When exposed to air, reacts with CO<sub>2</sub> to form Na<sub>2</sub>CO<sub>3</sub>
- ♦ Uses:
  - Lab reagent and preparation of pure fats and oils
  - Manufacture of soap, paper, artificial silk
  - Petrol refining, Purification of bauxite.
  - In the textile industries for mercerising cotton fabrics
- Sodium Hydrogen carbonate (Baking soda):
  - ✤ Formula: NaHCO<sub>3</sub>
  - Preparation: By saturating the solution of sodium carbonate with CO<sub>2</sub> or by solvay's process.
    - $Na_2CO_3 + H_2O + CO_2 ---> NaHCO_3$
  - Properties:
    - White crystalline and less soluble comparatively (It is precipitated out during solvay's process due to its low solubility)
    - Decomposes on heating to generate bubbles of CO<sub>2</sub> (makes cakes fluffy and thus called baking soda).
  - ♦ Uses:
    - In baking, antiseptic for skin infections and in fire extinguishers.

➤ Uses:

- 'Li'
  - Li, Pb alloy 'white metal' bearings for motor engines
  - ✤ Li, Al alloy Aircrafts
  - Li, Mg alloy Armour plates
  - ✤ In thermonuclear reactions, electrochemical cells,
- 'Na'
  - ✤ In biological systems
  - Na,Pb alloy To make PbEt4, PbMe4 which are used as anti-knock additives to petrol, but nowadays vehicles use lead-free petrol.
  - Liquid sodium is used as a coolant in fast breeder nuclear reactors
- 'K'
  - ✤ In biological systems
  - Potassium chloride fertilizer
  - Potassium hydroxide manufacture of soft soap, absorbent of CO2
- 'Cs':
  - ✤ In photoelectric cells



### > Biological importance of sodium and potassium:

• Concentration of Na+ and K+

Ion	Intracellular.conc	Extracellular.conc	Points
K+	High (105 mmol/L in blood plasma)	Low (5 mmol/L in RBC)	<ol> <li>Found primarily inside the cell.</li> <li>Activate many enzymes inside cell, participate in the oxidation of glucose to produce ATP and, in transmission of nerve signals</li> </ol>
Na+	Low (10 mmol/L in RBC)	High (143 mmol/L in blood plasma)	<ol> <li>Found primarily outside the cell in blood plasma and interstitial fluid which surrounds cells</li> <li>Transmission of nerve signals, regulation of water flow across the membrane and in transport of sugars into cell etc</li> </ol>

The concentration gradient of K+ and Na+ across the cell is maintained by the mechanism of sodium-potassium pump across the cell membrane. It consumes more than one-third of the ATP used by a resting animal.

## <u>Group-2</u> elements

## General points:

- Group-2 elements except beryllium are also called alkaline earth metals because their hydroxides and oxides are highly alkaline and their oxides are found abundantly in the earth's crust.
- Beryllium slightly differs from others and shows similarities with aluminium (Diagonal relationship)
- General valence shell electronic configuration: ns<sup>2</sup>
- Compounds of them are predominantly ionic
- Elements and their electronic configuration:

Element	Symbol	Electronic configuration
Beryllium	Be	1s <sup>2</sup> 2s <sup>2</sup>
Magnesium	Mg	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup>
Calcium	Ca	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>2</sup>
Strontium	Sr	1s²2s²2p⁵3s²3p⁵3d¹⁰ 4s²4p⁵5s²
Barium	Ba	1 <i>s</i> <sup>2</sup> 2 <i>s</i> <sup>2</sup> 2 <i>p</i> <sup>6</sup> 3 <i>s</i> <sup>2</sup> 3 <i>p</i> <sup>6</sup> 3 <i>d</i> <sup>10</sup> 4 <i>s</i> <sup>2</sup> 4 <i>p</i> <sup>6</sup> 4 <i>d</i> <sup>10</sup> 5 <i>s</i> <sup>2</sup> 5 <i>p</i> <sup>6</sup> 6 <i>s</i> <sup>2</sup> or [Xe]6 <i>s</i> <sup>2</sup>
Radium	Ra	[Rn]7s <sup>2</sup>



## • Abundance:

- Beryllium is rare and radium is the rarest
- ♦ Ca, Mg rank 5th and 6th abundance in the earth crust
- Sr, Ba have low abundances

## > Physical properties:

Property	Order	Points
Size	Be< Mg < Ca < Sr < Ba	1. Increases down the group (both metallic and ionic radii)
At. weight	Be< Mg < Ca < Sr < Ba	
Density	Ca < Mg < Be < Sr < Ba	1. Density decreases from Be till Ca and them increases from Sr to Ba
BP & MP	Irregular	<ol> <li>Higher than alkali metals</li> <li>Irregular trends</li> <li>High MP: Be , Low MP: Mg</li> <li>High BP: Be , Low BP: Mg</li> </ol>
IE1	$\mathbf{Be} > \mathbf{Mg} > \mathbf{Ca} > \mathbf{Sr} > \mathbf{Ba}$	1. IE1 (group-1) < IE1 (group-2)
IE2	Be > Mg > Ca > Sr > Ba	1. IE2 (group-1) > IE2 (group-1)
HE (Hydration energy)	$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+}$ > $Ba^{2+}$	<ol> <li>Decreases down the group</li> <li>HE is greater for group-2 than group-1 elements, thus highly hydrated</li> <li>Eg: MgCl<sub>2</sub> and CaCl<sub>2</sub> exist as MgCl<sub>2</sub>.6H<sub>2</sub>O and CaCl<sub>2</sub>. 6H<sub>2</sub>O while NaCl and KCl do not form such hydrates</li> </ol>
Std oxidation potential and reducing nature	Be< Mg < Ca < Sr < Ba	<ol> <li>Increases down the group</li> <li>Std. potential measures the overall change in sublimation enthalpy, ionisation enthalpy and hydration enthalpy.</li> <li>The reducing power is less than their corresponding Alkali metals.</li> </ol>



<ol> <li>Be<sup>2+</sup> has large hydration enthalpy and high enthalpy of atomisation.</li> <li>Thus electropositive nature increases down the group</li> </ol>

- High thermal and electrical conductivities indicating they are metals
- Flame test:
  - Be, Mg doesnt show flame test becoz the energy is not sufficient to excite the electrons.

Ca	Brick red			
Sr	Crimson red			
Ba	Apple green			

Flame test for Ca, Sr and Ba is helpful in their detection in qualitative analysis and estimation by flame photometry

### Chemical properties:

- Reactivity towards air:
  - Be, Mg are rendered passive to oxygen and water due to formation of oxide film on the surface.
  - Be powder can easily form BeO and Be<sub>3</sub>N<sub>2</sub> on reaction with air. Similar behaviour is shown by Mg.
  - Unlike group-1, all the elements form oxides and nitrides on reaction with O<sub>2</sub> and N<sub>2</sub>.
  - On reaction with water forms hydroxides and the virgourosity increases down the group.
- Reactivity towards halogens:
  - React with halogens at elevated temperatures to form halides
  - ✤ BeF<sub>2</sub>, BeCl<sub>2</sub> are produced differently.
    - BeF<sub>2</sub> is prepared by thermal decomposition of (NH<sub>4</sub>)<sub>2</sub>BeF<sub>4</sub>.
    - BeCl<sub>2</sub> is formed from its oxide
       BeO + C + Cl<sub>2</sub> ----> BeCl<sub>2</sub> + CO

## • Reactivity towards hydrogen:

- ♦ All metals except Be form hydrides on heating with hydrogen.
- ♦ BeH<sub>2</sub> is formed using LiAlH<sub>4</sub>
   2BeCl<sub>2</sub> + LiAlH<sub>4</sub> → 2BeH<sub>2</sub> + LiCl + AlCl<sub>3</sub>
- Reactivity towards acids:
  - Liberate hydrogen on treatment with acids
     M + 2HCl → MCl<sub>2</sub> + H<sub>2</sub>



#### • Solution with ammonia:

✤ Form a deep blue ammoniated solution.

$$\mathbf{M} + (\mathbf{x} + \mathbf{y})\mathbf{N}\mathbf{H}_{3} \rightarrow \left[\mathbf{M}(\mathbf{N}\mathbf{H}_{3})_{\mathbf{X}}\right]^{2+} + 2\left[\mathbf{e}(\mathbf{N}\mathbf{H}_{3})_{\mathbf{Y}}\right]^{-1}$$

- Ammoniates  $[M(NH_3)_6]^{2+}$  can be recovered from the solution.
- > General characteristics of the compounds of alkaline earth metals

## • Oxides and hydroxides

- Alkaline earth metals burn in oxygen to form monoxide (MO) have rocksalt structure except for BeO.
- Enthalpy of formation of oxides are quite high and also they are stable to heat.
- All oxides Ionic and basic except BeO covalent and amphoteric.
- All oxides react with water to form sparingly soluble hydroxides.
- Solubility, thermal stability, basicity of hydroxides:
  - Increases down the group from Mg(OH)<sub>2</sub> to Ba(OH)<sub>2</sub>.
  - Less stable and lesser basic compared to alkali metals
  - Be(OH)<sub>2</sub> is amphoteric and reacts with both acid and base.

 $\begin{array}{rcl} \operatorname{Be(OH)}_2 + 2\operatorname{OH} & \rightarrow & [\operatorname{Be(OH)}_4]^{2^-} \\ & & & & \\ \operatorname{Beryllate \ ion} \\ \operatorname{Be(OH)}_2 + 2\operatorname{HCl} + 2\operatorname{H}_2\operatorname{O} & \rightarrow & [\operatorname{Be(OH)}_4]\operatorname{Cl}_2 \end{array}$ 

## • Halides

- Halides are ionic except beryllium halides which are covalent and soluble in organic solvents.
- Structure of BeCl<sub>2</sub>
  - Solid state: Chain structure



- Vapour phase: Dimer structure (Chloro bridged dimer) and forms liner monomer at high temperatures (Approx 1200K).
- Tendency to form hydrates decreases down the group.
   Eg: MgCl<sub>2</sub>·8H<sub>2</sub>O, CaCl<sub>2</sub>·6H<sub>2</sub>O, SrCl<sub>2</sub>·6H<sub>2</sub>O and BaCl<sub>2</sub>·2H<sub>2</sub>O
- On heating Ca, Sr, Ba halides get dehydrated whereas Be and Mg will suffer hydrolysis.
- Fluorides are less soluble than chlorides due to their high lattice energies.

## • Salts of oxoacids

### ✤ Carbonates

- Insoluble in water and can be precipitated easily by addition of sodium or ammonium carbonate to the solution of metal carbonate solution (due to common ion effect)
- Solubility decreases down the group
- Unstable to heat and decompose to form oxide and CO<sub>2</sub> on heating.



• Thermal stability increases down the group. BeCO<sub>3</sub> is unstable and can be kept only in the atmosphere of CO<sub>2</sub>.

### Suplates

- Properties: White solids
- Solubility decreases from CaSO4 to BaSO4. BeSO4 and MgSO4 are readily soluble (Due to high hydration enthalpy which overcomes lattice enthalpy).
- Stable to heat.

## Nitrates

- Preparation: Carbonates + dil. Nitric acid.
- Tendency to form hydrates decreases down the group due to decrease in hydration enthalpy.
- Eg: Mg(NO<sub>3</sub>)<sub>2</sub> crystallises with 6H<sub>2</sub>O, whereas Ba(NO<sub>3</sub>)<sub>2</sub> crystallises as the anhydrous salt.
- Decompose on heating similar to LiNO<sub>3</sub>.  $2M(NO_3)_2 \rightarrow 2MO + 4NO_2 + O_2$ (M = Be, Mg, Ca, Sr, Ba)

## Anomalous behaviour of Beryllium

- Different from the rest of its group elements and shows diagonal relationship with Aluminium.
- 'Be' compounds are highly covalent and get easily hydrolysed due to small size and high IE.
- Max coordination number of 'Be' is 4 while others show 6 due to availability of dorbitals.
- Oxides and hydroxides of Be are amphoteric unlike others which are basic.
- Similarities with Aluminium (Diagonal relationship)
  - Both have approx same ionic sizes and thus shows similarities with 'Al'
  - Both are rendered passive to acids due to formation of oxide film on the surface
  - ✤ Both the hydroxides dissolve in excess alkali forming beryllate ion ([Be(OH)4]<sup>2−</sup>) and aluminate ion ([Al(OH)4]<sup>−</sup>).
  - Both of their chlorides form Cl- bridged structure in vapour phase. Both chlorides are soluble in organic solvents, strong lewis acids and are used as friedel crafts catalysts.
  - Both have strong tendency to form complexes  $BeF_4^{2-}$ ,  $AlF_6^{3-}$

## > Important compounds of group-2:

- Calcium oxide (Quick lime)
  - Formula: CaO
  - Preparation:
    - Heating of limestone (CaCO<sub>3</sub>) in a rotary kiln at 1070-1270 K.
    - $CaCO_3 \rightarrow CaO + CO_2$
    - CO<sub>2</sub> is removed immediately to enable the reaction to the completion
  - Properties:



- White amorphous solid, MP: 2870K
- Absorbs moisture and CO<sub>2</sub> from atmosphere CaO+H<sub>2</sub>O → Ca(OH)<sub>2</sub>
- $CaO + CO_2 \rightarrow CaCO_3$
- Basic oxide and combines with acidic oxides at high temperature.
   CaO+StO<sub>2</sub> → CaStO<sub>3</sub>
- $6CaO + P_4O_{10} \rightarrow 2Ca_3(PO_4)_2$
- Slaking the lime: Adding a limited amount of water to the lump of lime.
- Soda lime: Slaking lime with soda to form soda lime.
- ♦ Uses:
  - Manufacturing of cement, sodium carbonate from caustic soda, dye stuffs.
  - In purification of sugar.

### • Calcium hydroxide (Slaked lime)

- ♦ Formula: Ca(OH)<sub>2</sub>
- Preparation: Adding quicklime (CaO) to water.
- Properties:
  - White amorphous powder and sparingly soluble in water
  - Milk of lime: Suspension of slaked lime in water. Milk of lime reacts with chlorine to form hypochlorite, a constituent of bleaching powder.

$$2Ca(OH)_{2} + 2Cl_{2} \rightarrow CaCl_{2} + Ca(OCl)_{2} + 2H_{2}O$$
Bleaching powder

- Lime water: Aqueous solution of calcium hydroxide. When CO<sub>2</sub> is passed through lime water it turns milky due to the formation of CaCO<sub>3</sub>. With excess CO<sub>2</sub>, the precipitate dissolves and forms calcium hydrogen carbonate.
- $Ca(OH)_{2} + CO_{2} \rightarrow CaCO_{3} + H_{2}O$  $CaCO_{3} + CO_{2} + H_{2}O \rightarrow Ca(HCO_{3})_{2}$
- ♦ Uses:

- Preparation of mortar (building material)
- White wash (as it is disinfectant in nature)
- Making of glass, in the tanning industry, preparation of bleaching powder and purification of sugar.

### • Calcium carbonate

- ✤ Formula: CaCO<sub>3</sub>.
- ♦ Occurrence: In the form of limestone, marble, chalk etc
- ♦ Preparation: 2 ways  $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

 $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$ 

Note: Avoid excess of CO2 as it leads to the formation of calcium hydrogen carbonate

- Properties:
  - White fluffy powder



- Insoluble in water.
- Other reactions:

 $CaCO_{3} \xrightarrow{1200K} CaO + CO_{2}$   $CaCO_{3} + 2HCl \rightarrow CaCl_{2} + H_{2}O + CO_{2}$   $CaCO_{3} + H_{2}SO_{4} \rightarrow CaSO_{4} + H_{2}O + CO_{2}$ 

- ♦ Uses:
  - Manufacture of quicklime , in building material as marble.
  - Along with MgCO<sub>3</sub> is used as flux in extraction of Iron and few other metals.
  - Manufacture of high quality paper.
  - Antacid, mild abrasive in toothpaste, in chewing gums and filler in cosmetics.

### • Calcium sulphate (Plaster of paris)

- ✤ Formula: CaSO<sub>4</sub>. <sup>1</sup>/<sub>2</sub> H<sub>2</sub>O
- Preparation: Heating gypsum

 $2(\text{CaSO}_4.2\text{H}_2\text{O}) \rightarrow 2(\text{CaSO}_4).\text{H}_2\text{O} + 3\text{H}_2\text{O}$ 

Note: Above 393K no water will be left forming CaSO<sub>4</sub> and is called dead burnt plaster.

- ✤ Properties:
  - Property of setting with water. It forms plastic mass which hardens to solid in 5 to 15 min when mixed with adequate water.
- ♦ Uses:
  - In the building industry and plasters for bone fracture or sprain.
  - In dentistry for ornamental work.
  - Casts for statues and busts

## • Cement

- Important building material. Also called portland cement as it resembles natural limestone quarried in the Isle of Portland.
- ✤ Preparation:
  - Raw materials are limestone and clay. Mixing material rich in line, CaO with clay containing silica along with oxides of Al, Mg, Fe.
  - Clay and limestone are strongly heated, fused and thus react and form 'cement clinker'. This clinker is mixed with 2-3% by weight of gypsum (CaSO4·2H<sub>2</sub>O) to form cement.
- Composition of portland cement:
  - CaO: 50- 60%, SiO<sub>2</sub>: 20-25%, Al<sub>2</sub>O<sub>3</sub>: 5-10%, MgO: 2- 3%, Fe<sub>2</sub>O<sub>3</sub>: 1-2% and SO<sub>3</sub>: 1-2%.
  - Important ingredients: dicalcium silicate (Ca<sub>2</sub>SiO<sub>4</sub>) 26%, tricalcium silicate (Ca<sub>3</sub>SiO<sub>5</sub>) 51% and tricalcium aluminate (Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub>) 11%.
- ✤ For a good quality cement:
  - The ratio of silica to alumina should be between 2.5 and 4



- The ratio of lime to the total of the oxides of silicon, aluminium and iron should be as close as possible to 2.
- Setting of cement:
  - With water form a hard mass due to hydration of molecules and their rearrangement.
  - Gypsum is added to slow down the process of setting so that it gets sufficiently hardened.
- ♦ Uses:
  - Most important next to iron and steel
  - Used in concrete and reinforced concrete, in construction of buildings, bridges and dams, in plastering etc
- ➤ Uses:
  - 'Be' :
    - ✤ Manufacture of alloys.
    - Cu-Be alloy High strength springs.
    - Metallic Be Windows of x ray tubes
  - 'Mg':
    - ♦ Mg forms alloys with Al, Zn, Mn, Sn
    - ◆ Mg-Al alloys Aircraft construction due to their lightweight properties.
    - Mg powder and ribbon in flash powders, bulb, incendiary bombs and signals.
    - Milk of magnesia (suspension of Mg(OH)<sub>2</sub> in water) Antacid
    - ✤ MgCO<sub>3</sub> in toothpaste
  - 'Ca'
    - Extraction of metal oxides which are difficult to reduce with 'C'
    - Ca (also Ba) used to remove air from vacuum tubes as they react with air to form oxides and nitrides.
  - 'Ra'
    - ✤ In radiotherapy

### Biological importance of Ca, Mg:

- Daily requirement: 25g Mg, 1200g Ca
- Magnesium:
  - Chlorophyll contains Mg.
  - ♦ All enzymes that utilize ATP require Mg as cofactor
- Calcium:
  - ♦ 99% of calcium in body is present in bones and teeth
  - Important role in neuromuscular function and interneuronal transmission, cell membrane integrity and blood coagulation.
  - Calcium concentration in plasma is regulated by calcitonin and parathyroid hormone.

Bone is regularly remodelled in the body i.e it is solubilised and redeposited everyday to an extent of 400mg in man per day. All the Calcium passes through the plasma.



## The p-Block Elements

### Group 13 and 14

### > P-block: General introduction

- What makes the heavier p-block elements chemistry interesting: the influence of d and f electrons in the inner core.
- Last electron  $\rightarrow$  outermost p orbital.
- Total groups in P-block- six groups, numbered from 13 to 18.
- Valence shell electronic configuration-  $ns^2 np^{1-6}$  (except for He).
- Maximum oxidation state- the total number of valence electrons (i.e., the sum of the sand p-electrons).
- The important oxidation states exhibited by p-block elements are shown in Table below.

Group	13	14	15	16	17	18
General electronic configuration	ns²np¹	ns <sup>2</sup> np <sup>2</sup>	ns²np³	ns <sup>2</sup> np <sup>4</sup>	ns²np⁵	ns²np <sup>6</sup> (1 s² for He)
First member of the group	в	с	N	0	F	Не
Group oxidation state	+3	+4	+5	+6	+7	+8
Other oxidation states	+1	+2 4	+3, - 3	+4, +2, -2	+5, + 3, +1, -1	+6, +4, +2

General Electronic Configuration and Oxidation States of p-Block Elements

- Occurrence of oxidation states two unit less than the group oxidation- 'inert pair effect'.
- Non-metals and metalloids exist only in- p-block.
- Non-metallic character- decreases down the group- best illustrated by the nature of oxides they form.
- Non-metal oxides- acidic or neutral || metal oxides- basic.
- Heaviest element in each p-block group is the most metallic in nature.
- Boron (second period elements of p-groups)-max covalency is 4 eg..BF4<sup>-</sup>
- Third period elements (3s<sup>2</sup>3p<sup>n</sup>) utilize the vacant 3d orbitals to expand their covalence above four. For example, aluminium gives [AlF<sub>6</sub>]<sup>3–</sup>ion.

## **Group 13- Boron family:**

- Boron- non-metal, Aluminium- metal but shows many chemical similarities to boron.
- Gallium, Indium, Thallium and nihonium- metallic in character.
- Boron (fairly rare element, poorly abundant) occurs as orthoboric acid, (H<sub>3</sub>BO<sub>3</sub>), borax, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O, and kernite, Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·4H<sub>2</sub>O.
- Two isotopic forms of boron- 10B (19%) and 11B (81%).



- Aluminium- third most abundant element in the earth's crust
- Important minerals of Aluminium- Bauxite, Al<sub>2</sub>O<sub>3</sub>. 2H<sub>2</sub>O and cryolite, Na<sub>3</sub>AlF<sub>6</sub>
- Half life of its most stable isotope of Nihonium (synthetically prepared radioactive element)- 20 seconds.
- Outer electronic configuration of B family- ns<sup>2</sup>np<sup>1</sup>.
- Refer to the following table for various physical properties of group 13 elements.

Atomic and	Physical	Properties	of Group	13	Element
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CONTRACTOR OF THE OWNER	Element				
Property	Boron B	Aluminium Al	Gallium Ga	Indium In	Thallium Tl
Atomic number	5	13	31	49	81
Atomic mass(g mol	10.81	26.98	69.72	114.82	204.38
Electronic Configuration	[He]2s22p1	[Ne]3s <sup>2</sup> 3p <sup>1</sup>	[Ar]3d104s24p1	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>1</sup>	[Xe]4f145d106s26p1
Atomic radius/pm <sup>a</sup>	(88)	143	135	167	170
Ionic radius M <sup>3</sup> */pm <sup>b</sup>	(27)	53.5	62.0	80.0	88.5
Ionic radius M*/pm			120	140	150
$\begin{array}{llllllllllllllllllllllllllllllllllll$	801 2427 3659	577 1816 2744	579 1979 2962	558 1820 2704	589 1971 2877
Electronegativity	2.0	1.5	1.6	1.7	1.8
Density /g cm <sup>-3</sup> at 298 K	2.35	2.70	5.90	7.31	11.85
Melting point / K	2453	933	303	430	576
Boiling point / K	3923	2740	2676	2353	1730
$E^{\Theta}/V$ for $(M^{3*}/M)$	1.00	-1.66	-0.56	-0.34	+1.26
$E^{\Theta} / V$ for $(M^+/M)$	1170	+0.55	-0.79(acid) -1.39(alkali)	-0.18	-0.34

<sup>a</sup>Metallic radius, <sup>b</sup> 6-coordination, <sup>c</sup> Pauling scale,

- Atomic radii order- B < Ga < Al < In < Tl.
- Boron- non-metal. Extremely hard and black coloured solid.
- Gallium- unusual low melting point (303K).
- B forms covalent bonds- Due to the small size of boron, the sum of its first three ionization enthalpies is very high. This prevents it to form +3 ions and forces it to form only covalent compounds.
- Relative stability of +1 oxidation state progressively- Al<Ga<In<Tl
- Boron in BF<sub>3</sub> has only six electrons- electron deficient molecule- Lewis acid. BCl<sub>3</sub> easily accepts a lone pair of electrons from ammonia to form BCl<sub>3</sub>NH<sub>3</sub>.




- The tendency to behave as Lewis acid decreases with the increase in the size down the group.
- AlCl<sub>3</sub> achieves stability by forming a dimer



- Tetrahedral
- Group 13 trichlorides on hydrolysis in water form tetrahedral M(OH)<sup>4-</sup> species where M is sp<sup>3</sup> hybridised.
- AlCl<sub>3</sub> in acidified aqueous solution forms octahedral [Al(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> ion. In this complex, 3d orbitals of Al are involved and the hybridisation state of Al is sp<sup>3</sup>d<sup>2</sup>.
- Boron is unreactive in crystalline form.
- Amorphous boron and aluminium metal on heating in air form B<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> respectively.
- B<sub>2</sub>O<sub>3</sub> is acidic and reacts with basic (metallic) oxides forming metal borates.
- Al2O3 and Ga2O3- amphoteric. In 2O3 and Tl2O3- basic.  $2E(s) + 3O_2(g) \xrightarrow{\Lambda} 2E_2O_3(s)$  $2E(s) + N_2(g) \xrightarrow{\Lambda} 2EN(s)$

(E = element)

- With dinitrogen at high temperature they form nitrides.
- Boron does not react with acids and alkalies even at moderate temperature.
- Aluminium shows amphoteric character. Aluminium dissolves in dilute HCl and liberates dihydrogen.

 $\begin{array}{l} \text{2Al(s)} + 6\text{HCl (aq)} \rightarrow 2\text{Al}^{3+} \text{ (aq)} + 6\text{Cl}^{-} \text{ (aq)} \\ &+ 3\text{H}_2 \text{ (g)} \end{array}$ 

- Al forms a protective oxide layer on the surface when reacted with conc. nitric acid
- Dihydrogen gas is released when Al reacts with alkali.

2Al (s) + 2NaOH(aq) + 
$$6H_2O(l)$$
  
 $\downarrow$   
2 Na<sup>+</sup>[Al(OH)<sub>4</sub>]<sup>-</sup>(aq) +  $3H_2(g)$   
Sodium

Group 13 elements react with halogens to form trihalides (except TII3).
 2E(s) + 3 X<sub>2</sub> (g) → 2EX<sub>3</sub> (s) (X = F, Cl, Br, I)



### > Borax:

White crystalline solid  $Na_2B_4O_7.10H_2O$ . contains the tetranuclear units  $[B_4O_5(OH)_4]2-$ Correct formula; therefore, is  $Na_2[B_4O_5(OH)_4].8H_2O$ .

• Borax dissolves in water to give an alkaline solution.  $Na_2B_4O_7 + 7H_2O \rightarrow 2NaOH + 4H_3BO_3$ 

Orthoboric acid

• Borax bead (glass like material) is obtained on heating borax.  $Na_2B_4O_7.10H_2O\_^{A} \rightarrow Na_2B_4O_7\_^{A} \rightarrow 2NaBO_2$ 

Sodium	$+ B_2O_3$
metaborate	Boric
	anhydride

- Borax bead test is performed to identify metaborates of many transition metals that have characteristic colours.
- Co(BO<sub>2</sub>)<sub>2</sub> bead is blue in color.
- Orthoboric acid:
- A weak monobasic acid.
- A protonic acid but acts as a Lewis acid
- H<sub>3</sub>BO<sub>3</sub> is a white crystalline sparingly soluble in water but highly soluble in hot water prepared by acidifying an aqueous solution of borax. Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub> + 2HCl + 5H<sub>2</sub>O → 2NaCl + 4B(OH)<sub>3</sub>
- It has layer structure in which planar BO3 units are joined by hydrogen bonds



Structure of boric acid; the dotted lines represent hydrogen bonds

• On heating, orthoboric acid above 370K forms metaboric acid, HBO2 which on further heating yields boric oxide, B<sub>2</sub>O<sub>3</sub>.

 $H_3BO_3 \xrightarrow{\Delta} HBO_2 \xrightarrow{\Delta} B_2O_3$ 



 Diborane B<sub>2</sub>H<sub>6</sub>: colourless, highly toxic gas with a b.p. of 180 K. catches fire in air. B<sub>2</sub>H<sub>6</sub>+3O<sub>2</sub>→B<sub>2</sub>O<sub>3</sub> + 3H<sub>2</sub>O;

 $\Delta_c H^{\ominus} = -1976 \text{ kJ mol}^{-1}$ 

- Prepared by treating BF<sub>3</sub> with LiAlH<sub>4</sub>  $4BF_3 + 3 LiAlH_4 \rightarrow 2B_2H_6 + 3LiF + 3AlF_3$
- laboratory method to prepare diborane:  $2NaBH_4 + I_2 \rightarrow B_2H_6 + 2NaI + H_2$
- Industry method to prepare diborane:  $2BF_3 + 6NaH \xrightarrow{450K} B_2H_6 + 6NaF$
- Boranes are readily hydrolysed by water  $B_2H_6(g) + 6H_2O(l) \rightarrow 2B(OH)_3(aq) + 6H_2(g)$
- Reaction of diborane with Lewis bases(L) to give borane adducts, BH3L.
   B<sub>2</sub>H<sub>6</sub> + 2 NMe<sub>3</sub> → 2BH<sub>3</sub>·NMe<sub>3</sub>
   B<sub>2</sub>H<sub>6</sub> + 2 CO → 2BH<sub>3</sub>·CO
- Reaction of diborane with ammonia to give borazine, B3N3H6 known as "inorganic benzene"

 $3B_{2}H_{6}+6NH_{3} \rightarrow 3[BH_{2}(NH_{3})_{2}]^{+}[BH_{4}]^{-}$  $\xrightarrow{Heat}{} 2B_{3}N_{3}H_{6}+12H_{2}$ 

Structure of B<sub>2</sub>H<sub>6</sub>:



Each B atom- sp<sup>3</sup> hybridised.

The terminal B-H bonds are normal 2-centre-2-electron bonds but the two bridge bonds are 3-centre-2-electron bonds (banana bonds).

• Boron forms a series of hydridoborates of several metals:  $2MH + B_2H_6 \rightarrow 2 M^+ [BH_4]^-$  (M = L1 or Na)

### > USES OF BORON AND ALUMINIUM AND THEIR COMPOUNDS:

- Boron fibres are used in making bullet-proof vest and light composite material for aircraft.
- Metal borides (10B isotope) are used in nuclear industry as protective shields and control rods.
- Industrial application of borax and boric acid- manufacture of heat resistant glasses (e.g., Pyrex), glass-wool and fibreglass.
- Borax: used as a flux for soldering metals, and as constituent of medicinal soaps.



- Orthoboric acid- aqueous solution is generally used as a mild antiseptic.
- Electrical conductivity of aluminium is twice that of copper.
- Aluminium and its alloys: pipe, tubes, rods, wires, plates or foils, construction, aeroplane and transportation industry.

#### Group 14: Carbon family

- Members: C, Si, Ge, Sn, Pb, Fl
- Carbon- most versatile element- available as coal, graphite and diamond. In combined state- metal carbonates, hydrocarbons and carbon dioxide gas (0.03%) in air.
- Carbon isotopes: 12C, 13C, and 14C.
- Silicon in nature- in the form of silica and silicates used in ceramics, glass and cement.
- Germanium exists only in traces. Tin occurs mainly as cassiterite, SnO<sub>2</sub> and lead as galena, PbS. Flerovium is a synthetically prepared radioactive element.
- Ultrapure form of germanium and silicon- used to make transistors and semiconductor devices.
- valence shell electronic configuration- ns2np2.
- Refer to the following table for various physical properties of group 14 elements

Atomic	and	Physical	Properties	of	Group	14	Elements
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		Element					
Property		Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb	
Atomic Nun	nber	6	14	32	50	82	
Atomic mas	s (g mol <sup>-1</sup> )	12.01	28.09	72.60	118.71	207.2	
Electronic configuratio	on	$[\text{He}]2s^22p^2$	$[Ne]3s^23p^2$	$[Ar]3d^{10}4s^24p^2$	$[Kr]4d^{10}5s^25p^2$	$[Xe]4f^{44}5d6s^{3}6p^{2}$	
Covalent ra	dius/pmª	77	118	122	140	146	
Ionic radius	M <sup>4</sup> */pm <sup>b</sup>	-	40	53	69	78	
Ionic radius	M <sup>2*</sup> /pm <sup>b</sup>	-	-	73	118	119	
Ionization	$\Delta H_1$	1086	786	761	708	715	
enthalpy/	$\Delta H_2$	2352	1577	1537	1411	1450	
kJ mol <sup>-1</sup>	$\Delta H_3$	4620	3228	3300	2942	3081	
	$\Delta_{i}H_{4}$	6220	4354	4409	3929	4082	
Electronega	tivity	2.5	1.8	1.8	1.8	1.9	
Density <sup>d</sup> /g	cm <sup>-3</sup>	3.51"	2.34	5.32	7.26	11.34	
Melting poin	nt/K	4373	1693	1218	505	600	
Boiling poir	nt/K	-	3550	3123	2896	2024	
Electrical r ohm cm (29	csistivity/ 3 K)	10 <sup>14</sup> -10 <sup>16</sup>	50	50	10-5	2 10 <sup>-5</sup>	

<sup>a</sup> for M<sup>N</sup> oxidation state; <sup>b</sup>6-coordination; <sup>c</sup>Pauling scale; <sup>d</sup>293 K; <sup>e</sup> for diamond; for graphite, density is 2.22; <sup>f</sup>β-form (stable at room temperature)

- All members of group14 are solids
- Carbon and silicon- non-metals
- Ge- metalloid.
- Tin and lead -soft metals with low melting points.
- The common oxidation states- +4 and +2.
- Group 14 (except carbon) halides undergo hydrolysis and have a tendency to form complexes by accepting electron pairs from donor species. For example, the species



like SiF $_{6}^{2-}$ , [GeCl $_{6}$ ]<sup>2-</sup>, [Sn(OH) $_{6}$ ]<sup>2-</sup> exist where the hybridisation of the central atom is  $sp^3d^2$ .

- Oxides: monoxide (MO) and dioxide (MO<sub>2</sub>)
- Oxides in higher oxidation states of elements are generally more acidic than those in lower oxidation states.
- CO<sub>2</sub>, SiO<sub>2</sub> and GeO<sub>2</sub> are acidic, whereas SnO<sub>2</sub> and PbO<sub>2</sub> are amphoteric in nature.
- CO is neutral, GeO is distinctly acidic whereas SnO and PbO are amphoteric.
- Tin decomposes steam to form dioxide and dihydrogen gas.

 $Sn + 2H_2O \xrightarrow{A} SnO_2 + 2H_2$ 

- These elements form covalent halides of formula MX2 and MX4 (where X = F, Cl, Br, • I).
- SnF<sub>4</sub> and PbF<sub>4</sub>, which are ionic in nature. PbI<sub>4</sub> does not exist.
- Ge to Pb are able to make halides of formula MX<sub>2</sub>.
- SiCl<sub>4</sub> undergoes hydrolysis leading to the formation of Si(OH)<sub>4</sub>



#### > IMPORTANT TRENDS AND ANOMALOUS BEHAVIOUR OF CARBON

- Carbon forms  $p\pi p\pi$  multiple bonds with itself (allotropic forms) and with other atoms of small size and high electrone gativity.
- Carbon atoms have the tendency to link with one another through covalent bonds to form chains and rings. This property is called catenation.
- The order of catenation is  $C >> Si > Ge \approx Sn$ .
- Allotropic forms of C: many (Diamond, graphite, and fullerenes). •

#### > Diamond:

- crystalline lattice
- Hybridisation of each C: sp<sup>3</sup>
- C–C bond length is 154 pm
- Diamond is the hardest substance on the earth.
- Uses: as an abrasive for sharpening hard tools, in making dyes and in the manufacture of tungsten filaments for electric light bulbs.





### > Graphite:

- layered structure
- Layers are held by van der Waals forces and distance between two layers is 340 pm.
- Each layer is composed of planar hexagonal rings of carbon atoms. C—C bond length within the layer is 141.5 pm.
- Hybridisation of each C: sp<sup>2</sup>. Fourth electron forms a bond.
- The electrons are delocalised over the whole sheet and hence conducts electricity.
- very soft and slippery
- Uses: as a dry lubricant
- Fullerenes: cage like molecules
- Made by heating graphite in an electric arc in the presence of inert gases such as helium or argon.
- Fullerenes are the only pure form of carbon because they have smooth structure without having 'dangling' bonds.

#### **Buckminsterfullerene: C60**

- Contains twenty six- membered rings and twelve fivemembered rings
- A six membered ring is fused with six or five membered rings but a five membered ring can only fuse with six membered rings.
- Hybridisation of each C: sp<sup>2</sup>.
- The fourth electron delocalise in molecular orbitals, which in turn give aromatic character to molecule.
- This spherical fullerenes are also called bucky balls in short. C60 has 60 vertices and each one is occupied by one carbon atom and it also contains both single and double bonds with C–C distances of 143.5 pm and 138.3 pm respectively.
- Graphite is thermodynamically most stable allotrope of carbon
- $\Delta_f H^\circ$  of graphite is taken as zero.  $\Delta_f H^\circ$  values of diamond and fullerene, C60 are 1.90 and 38.1 kJ mol-1, respectively. Other (impure) forms of elemental carbon like carbon black, coke, and charcoal.
- Uses of Carbon: embedded in plastic material form high strength, lightweight composites- tennis rackets, fishing rods, aircrafts
- graphite is used for electrodes in batteries
- activated charcoal is used in adsorbing poisonous gases
- Coke is used as a fuel and largely as a reducing agent in metallurgy. Diamond is used in jewellery.



The structure of graphite



The structure of  $C_{60}$ , Buckminsterfullerene : Note that molecule has the shape of a soccer ball (football).



### > SOME IMPORTANT COMPOUNDS OF CARBON AND SILICON

- Carbon Monoxide (CO): colourless,odourless and almost water insoluble gas.
- Produced by direct oxidation of C in limited supply of oxygen.  $2C(s) + O_2(g) \xrightarrow{\Delta} 2CO(g)$
- For small scale production: dehydration of formic acid with conc H<sub>2</sub>SO<sub>4</sub> at 373 K HCOOH → 373K conc.H<sub>2</sub>SO<sub>4</sub> → H<sub>2</sub>O + CO
- Commercial production: by the passage of steam over hot coke.  $C(s) + H_2O(g) \xrightarrow{473-1273K} CO(g) + H_2(g)$ Water gas
- The mixture of CO and H2 gas is known as water or synthesis gas.
- Producer gas is produced if coke is heated in air.  $2C(s) + O_2(g) + 4N_2(g) \xrightarrow{1273K} 2CO(g)$

 $+ 4N_2(g)$ 

### Producer gas

• CO is a powerful reducing agent.

$$\begin{array}{l} \operatorname{Fe}_{2}O_{3}\left(s\right) + 3\operatorname{CO}\left(g\right) \xrightarrow{\Delta} 2\operatorname{Fe}\left(s\right) + 3\operatorname{CO}_{2}\left(g\right) \\ \operatorname{ZnO}\left(s\right) + \operatorname{CO}\left(g\right) \xrightarrow{\Delta} \operatorname{Zn}\left(s\right) + \operatorname{CO}_{2}\left(g\right) \end{array}$$

- CO has one sigma and two  $\pi$ -bonds.
- Because of the presence of a lone pair on carbon, CO molecule acts as a donor.
- CO forms a complex with haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex.
- Carbon Dioxide (CO<sub>2</sub>): a colourless and odourless gas
- Prepared by complete combustion of carbon and carbon containing fuels in excess of air.

 $C(s) + O_2(g) \xrightarrow{\Delta} CO_2(g)$ 

$$CH_4(g) + 2O_2(g) \xrightarrow{\Delta} CO_2(g) + 2H_2O(g)$$

#### Laboratory method:

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

- On commercial scale, it is obtained by heating limestone.
- CO<sub>2</sub> react with water to form carbonic acid, H<sub>2</sub>CO<sub>3</sub> (a weak dibasic acid) H<sub>2</sub>CO<sub>3</sub>(aq) + H<sub>2</sub>O(l)  $\rightleftharpoons$  HCO<sub>3</sub><sup>-</sup>(aq) + H<sub>3</sub>O<sup>+</sup>(aq) HCO<sub>3</sub><sup>-</sup> (aq) + H<sub>2</sub>O(l)  $\rightleftharpoons$  CO<sub>3</sub><sup>2-</sup> (aq) + H<sub>3</sub>O<sup>+</sup>(aq)
- H<sub>2</sub>CO<sub>3</sub>/HCO<sub>3</sub>- buffer system helps to maintain pH of blood between 7.26 to 7.42.



#### > Photosynthesis:

$$6CO_2 + 12H_2O \xrightarrow{h\nu} C_6H_{12}O_6 + 6O_2 + 6H_2O$$

- CO<sub>2</sub> cause greenhouse effect
- Solid CO<sub>2</sub> is called dry ice
- C-O bond length is 115 pm on CO<sub>2</sub> due to resonance

$$\ddot{\circ}$$
  $\ddot{\circ}$   $-C \equiv 0$   $\leftrightarrow$   $\dot{\circ}$   $\ddot{\circ}$   $=C = \ddot{\circ}$   $\leftrightarrow$   $\dot{\circ}$   $c \equiv C = \ddot{\circ}$ 

#### Resonance structures of carbon dioxide

- Silicon Dioxide, SiO2: a covalent, threedimensional network solid.
- Each silicon atom is covalently bonded to four oxygen atoms.
- Each oxygen atom is covalently bonded to another silicon atoms
- eight membered rings are formed with alternate silicon and oxygen atoms



• SiO<sub>2</sub> can be attacked by HF and NaOH

$$\begin{split} &\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{Na}_2\text{SiO}_3 + \text{H}_2\text{O} \\ &\text{SiO}_2 + 4\text{HF} \rightarrow \text{SiF}_4 + 2\text{H}_2\text{O} \end{split}$$

• Quartz is extensively used as a piezoelectric material Kieselghur, an amorphous form of silica is used in filtration plants

$$\begin{array}{cccc} CH_{s} & CH_{s} & CH_{s} \\ HO - Si - OH & + HO - Si - OH & + HO - Si - OH \\ HO - Si - OH & + HO - Si - OH \\ CH_{s} & CH_{s} & CH_{s} \\ -H_{s}O & CH_{s} \\ -H_{s}O & CH_{s} \\ -H_{s}O & CH_{s} \\ -O & CH_{s} & CH_{s} \\ Silicone \\ \\ \end{array}$$



- Silicones: organosilicon polymers having R2SiO as a repeating unit
- Starting material of silicones:  $R_nSiCl_{(4-n)} R$  is alkyl or aryl group.
- Hydrolysis of dimethyldichlorosilane, (CH<sub>3</sub>)2SiCl<sub>2</sub> followed by condensation polymerisation yields straight chain polymers.
- The chain length of the polymer can be controlled by adding (CH3)3SiCl



- Silicates: examples are feldspar, zeolites, mica and asbestos
- The basic structural unit of silicates is SiO<sub>4</sub><sup>4–</sup>
- Silicate units links together to form chain, ring, sheet or three-dimensional structures
- Man made silicates: glass and cement.
- Zeolites: aluminosilicate
- Cations present in zeolites: Na<sup>+</sup>, K<sup>+</sup> or Ca<sup>2+</sup>
- Zeolites as a catalyst: e.g., ZSM-5 used to convert alcohols directly into gasoline.
- Hydrated zeolites are used as ion exchangers in softening of "hard" water.



<sup>(</sup>a) (b) (a) Tetrahedral structure of  $SiO_4^{4-}$ anion; (b) Representation of  $SiO_4^{4-}$  unit



### **Organic Chemistry – Some Basic Principles and Technique**

- Berzilius, a Swedish chemist proposed that a 'vital force' was responsible for the formation of organic compounds.
- 1828 F. Wohler synthesized an organic compound, urea from an inorganic compound, ammonium cyanate.

 $\begin{array}{ccc} \mathrm{NH}_4\mathrm{CNO} & \xrightarrow{\mathrm{Heat}} & \mathrm{NH}_2\mathrm{CONH}_2 \\ \mathrm{Ammonium\ cyanate} & \mathrm{Urea} \end{array}$ 

• Acetic acid synthesize by Kolbe (1845) and methane synthesize by Berthelot (1856)

### > The Shapes of Carbon Compounds

- Hybrid orbitals with more s character will be closer to the nucleus and have more electronegativity and form shorter and stronger bonds.
- sp hybrid orbital with 50% s character is more electronegative, have more bond energy, than sp<sup>2</sup> or sp<sup>3</sup> hybridised orbitals.

### **Some Characteristic Features of** $\pi$ **Bonds**

- In a  $\pi$  (pi) bond formation, parallel orientation of the two p orbitals on adjacent atoms is necessary for a proper sideways overlap.
- Thus, in the  $H_2C=CH_2$  molecule all the atoms must be in the same plane.
- $\pi$  bonds provide the most reactive centres in the molecules containing multiple bonds.

#### Structural Representations of organic compounds

#### Complete structural formulas

- A single dash represents a single bond, double dash is used for double bond and a triple dash represents triple bond.
- Lone-pairs of electrons on heteroatoms (e.g.,oxygen, nitrogen, sulphur, halogens etc.) may or may not be shown



#### Condensed structural formula:

Omitting some or all of the dashes representing covalent bonds and by indicating the number of identical groups attached to an atom by a subscript.

$CH_3CH_3$	$H_2C=CH_2$	HC=CH	CH <sub>3</sub> OH
Ethane	Ethene	Ethyne	Methanol

 $CH_3CH_2CH_2CH_2CH_2CH_2CH_3\ can \ be \ further \ condensed \ to \ CH_3(CH_2)_6CH_3$ 

### Sond-line structural

- Carbon and hydrogen atoms are not shown and the lines representing carbon-carbon bonds are drawn in a zig-zag fashion.
- The only atoms specifically written are oxygen, chlorine,nitrogen etc. The terminals denote methyl(–CH<sub>3</sub>) groups (unless indicated otherwise by a functional group),





while the line junctions denote carbon atoms bonded to the appropriate number of hydrogens required to satisfy the valency of the carbon atoms.

Classification of Organic Compounds





#### I. Acyclic or open chain compounds

These compounds are also called aliphatic compounds and consist of straight or branched chain compounds.



### II. Alicyclic or closed chain or ring compound

- Alicyclic (aliphatic cyclic) compounds contain carbon atoms joined in the • form of a ring (homocyclic).
- Heterocyclic: Atoms other than carbon (O, N, S) are present in the ring.



### Aromatic compounds

Aromatic compounds are special types of compounds Benzenoid aromatic compounds

Non-benzenoid compound









Benzene

Aniline

Heterocyclic aromatic compounds

Naphthalene

Tropolone





### Functional Group

- Atom or group of atoms joined in a specific manner which is responsible for the characteristic chemical properties of the organic compounds are called functional groups.
- For example hydroxyl group (–OH), aldehyde group (–CHO) etc.

### Homologous Series

- The successive members differ from each other in molecular formula by a –CH<sub>2</sub>– unit.
- Represented by general molecular formula.
- Ex. alkanes, alkenes, alkynes, haloalkanes, alkanols, alkanals, alkanoic acids, etc.

### > Nomenclature of Organic Compounds:

### **IUPAC** (International Union of Pure and Applied Chemistry

- Names which are traditional are considered as trivial or common names.
- Ex Citric acid is named so because it is found in citrus fruits and the acid found in red ant is named formic acid.
- Buckminsterfullerene is a common name given to the newly discovered C<sub>60</sub> cluster.

**Common or Trivial Names of Some Organic Compound** 

Compound	Common name
CH <sub>4</sub>	Methane
H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	n-Butane
(H <sub>3</sub> C) <sub>2</sub> CHCH <sub>3</sub>	Isobutane
(H <sub>3</sub> C) <sub>4</sub> C	Neopentane
H <sub>3</sub> CCH <sub>2</sub> CH <sub>2</sub> OH	n-Propyl alcohol
HCHO	Formaldehyde
(H <sub>3</sub> C) <sub>2</sub> CO	Acetone
CHCl <sub>3</sub>	Chloroform
CH <sub>3</sub> COOH	Acetic acid
$C_6H_6$	Benzene
C <sub>6</sub> H <sub>5</sub> OCH <sub>3</sub>	Anisole
$C_6H_5NH_2$	Aniline
$C_6H_5COCH_3$	Acetophenone
CH <sub>3</sub> OCH <sub>2</sub> CH <sub>3</sub>	Ethyl methyl ether

The IUPAC System of Nomenclature: A systematic name of an organic compound is generally derived by identifying the parent hydrocarbon and the functional group(s) attached to it.





### > IUPAC Nomenclature of Alkanes

- Straight chain hydrocarbons: The names of such compounds are based on their chain structure, and end with suffix '- ane -' and carry a prefix indicating the number of carbon atoms present in the chain (except from CH<sub>4</sub> to C<sub>4</sub>H<sub>10</sub>, where the prefixes are derived from trivial names.
- Paraffin (Latin: little affinity) was the earlier name given to alkanes IUPAC Names of Some Unbranched Saturated Hydrocarbons

Name	Molecular formula	Name	Molecular formula
Meth <mark>ane</mark>	CH <sub>4</sub>	Heptane	$C_7H_{16}$
Ethane	$C_2H_6$	Octane	$C_8H_{18}$
Propane	$C_3H_8$	Nonane	$C_9H_{20}$
Butane	$C_{4}H_{10}$	Decane	$C_{10}H_{22}$
Pentane	$C_5H_{12}$	Icosane	$C_{20}H_{42}$
Hexane	$C_6H_{14}$	Triacontane	$C_{30}H_{62}$

### • Branched chain hydrocarbons:

The small carbon chains (branches) are called alkyl groups which are named by substituting 'yl' for 'ane ' in the corresponding alkane.

Thus, CH<sub>4</sub> becomes -CH<sub>3</sub> and is called methyl group.

	Alkyl gi	roup
Name of alkane	Structural formula	Name of alkyl group
Methane	-CH <sub>3</sub>	Methyl
Ethane	-CH <sub>2</sub> CH <sub>3</sub>	Ethyl
Propane	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Propyl
Butane	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	Butyl
Decane	-CH <sub>2</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	Decyl
	Name of alkane Methane Ethane Propane Butane Decane	Alkyl gName of alkaneStructural formulaMethane-CH3Ethane-CH2CH3Propane-CH2CH2CH3Butane-CH2CH2CH2CH3Decane-CH2(CH2)8CH3

Abbreviations are used for some alkyl groups. For example, methyl is abbreviated as Me, ethyl as Et, propyl as Pr and butyl as Bu

Common branched groups have specific trivial names





#### The rules for naming

1. First of all, 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 numbers.

- **3.** If different alkyl groups are present, they are listed in alphabetical order.
- **4.** For identical substituents, prefixes such as di (for 2), tri (3), tetra (4), penta (5), hexa (6) etc. are used & these prefixes are not considered for alphabetical order.



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

6. In branched alkyl groups the carbon atom of the branch that attaches to the root alkane is numbered 1.

```
\begin{array}{cccccc} 4 & 3 & 2 & 1 \\ CH_{3}-CH-CH_{2}-CH- \\ & & | \\ & CH_{3} & CH_{3} \\ 1.3-Dimethylbutyl- \end{array}
```

- While writing the trivial names of substituents **in alphabetical order**, the prefixes iso- and neo- are considered to be the part of the fundamental name of alkyl group.
- The prefixes sec- and tert- are not considered to be part of the fundamental name.
- In multi-substituted compounds, the following rules may also be remembered:
  - If there happens to be two chains of equal size, then that chain is to be selected which contains more number of side chains.
  - After selection of the chain, numbering is to be done from the end closer to the substituent.





5-(2-Ethylbutyl)-3,3-dimethyldecane [and not 5-(2,2-Dimethylbutyl)-3-ethyldecane]

 $\begin{array}{c} CH(CH_3)_2 \\ 1 \quad 2 \quad 3 \quad 4 \middle| \quad 5 \quad 6 \quad 7 \quad 8 \quad 9 \quad 10 \\ CH_3 - CH_2 - CH_3 \end{array}$ 

CH3-CH-CH2-CH3

5-sec-Butyl-4-isopropyldecane



5-(2.2-Dimethylpropyl)nonane

### Cyclic Compounds:

Named by prefixing 'cyclo' to the corresponding straight chain alkane.



Cyclopentane 1-Methyl-3-propylcyclohexane



More branched carbon gets lower number

3-Ethyl-1,1-dimethylcyclohexane (not 1-ethyl-3,3-dimethylcyclohexane)

### **Solution** Nomenclature of Organic Compounds having Functional Group(s)

- The longest chain of carbon atoms containing the functional group is Numbered in such a way that the functional group is attached at the carbon atom possessing the lowest possible number in the chain.
- In polyfunctional compounds, one of the functional groups is chosen as the principal functional group and the compound is then named on that basis.
- The remaining functional groups are named as substitutes using the appropriate prefixes.
- The choice of principal functional group is made on the basis of preference order.



- Decreasing priority order for some functional groups is:
   -COOH, -SO<sub>3</sub>H, -COOR (R=alkyl group), COCl,-CONH<sub>2</sub>, -CN, -HC=O,
   >C=O, -OH, -NH<sub>2</sub>, >C=C<,-C=C-.</li>
- The –**R**, **C**<sub>6</sub>**H**<sub>5</sub>-, halogens (F, Cl, Br, I), –NO<sub>2</sub>, alkoxy (–OR) etc. are always prefix substituents.

Ex . HOCH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CH<sub>2</sub>COCH<sub>3</sub> will be named as 7-hydroxyheptan-2-one **BrCH<sub>2</sub>CH=CH<sub>2</sub>** is named as **3-bromoprop-1-ene** and not 1-bromoprop-2-en

- If more than one functional group of the same type is present, their number is indicated by adding di, tri, etc before the class suffix.
- The ending **ane** of the parent alkane is **dropped** in the case of compounds having more than one double or triple bond; for example, CH<sub>2</sub>=CH-CH=CH<sub>2</sub> is named as **buta–1,3–diene**.

Class of compounds	Functional group structure	IUPAC group prefix	IUPAC group suffix	Example
Alkanes	-	-	-ane	Butane, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>3</sub>
Alkenes	>C=C<	-	-ene	But-1-ene, CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>3</sub>
Alkynes	-C≡C-	-	-yne	But-1-yne, CH≡CCH <sub>2</sub> CH <sub>3</sub>
Arenes	-///	-	4	Benzene,
Halides	-X (X=F,Cl,Br,I)	halo-	-	1-Bromobutane, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub> Br
Alcohols	-OH	hydroxy-	-ol	Butan-2-ol,
Aldehydes	-СНО	formyl, or oxo	-al	Butanal, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CHO
Ketones	>C=O	oxo-	-one	Butan-2-one, CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub>
Nitriles	-C=N	cyano	nitrile	Pentanenitrile, CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CN
Ethers	-R-O-R-	alkoxy-	-	Ethoxyethane, CH <sub>3</sub> CH <sub>2</sub> OCH <sub>2</sub> CH <sub>3</sub>
Carboxylic acids	-COOH	carboxy	-oic acid	Butanoic acid, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H
Carboxylate ions	-COO-	-	-oate	Sodium butanoate, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> <sup>-</sup> Na <sup>+</sup>
Esters	-COOR	alkoxycarbonyl	-oate	Methyl propanoate, $CH_3CH_2COOCH_3$
Acyl halides	-COX (X=F,Cl,Br,I)	halocarbonyl	-oyl halide	Butanoyl chloride, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COCl

Some Functional Groups and Classes of Organic Compounds



Amines	-NH <sub>2</sub> , >NH,>N-	amino-	-amine	Butan -2-amine . CH <sub>3</sub> CHNH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>
Amides	-CONH <sub>2</sub> , -CONHR, -CONR <sub>2</sub>	-carbamoyl	-amide	Butanamide, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CONH <sub>2</sub>
Nitro compounds	-NO <sub>2</sub>	nitro	-	1-Nitrobutane, CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> NO <sub>2</sub>
Sulphonic acids	–SO <sub>3</sub> H	sulpho	sulphonic acid	Methylsulphonic acid CH <sub>3</sub> SO <sub>3</sub> H

#### Nomenclature of Substituted Benzene Compounds

• The substituent is placed as a prefix to the word benzene.



• If a benzene ring is disubstituted, the position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible.



- In the trivial system of nomenclature the terms ortho (o), meta (m) and para (p) are used as prefixes to indicate the relative positions 1,2-;1,3- and 1,4- respectively.
- In some cases, the common name of benzene derivatives is taken as the base compound.
- Substituent of the base compound is assigned number 1 and then the direction of numbering is chosen such that the next substituent gets the lowest number. The substituents appear in the name in alphabetical order.







1-Chloro-2,4-dinitrobenzene (not 4-chloro,1,3-dinitrobenzene)

2-Chloro-1-methyl-4-nitrobenzene (not 4-methyl-5-chloro-nitrobenzene)



2-Chloro-4-methylanisole 4-Ethyl-2-methylaniline



3.4-Dimethylphenol

• When a benzene ring is attached to an alkane with a functional group, it is considered as substituent, instead of a parent. and as **phenyl** (C<sub>6</sub>H<sub>5</sub>-, also abbreviated as **Ph**).

#### Isomerism

The phenomenon of existence of two or more compounds possessing the same molecular formula but different properties is known as **isomerism**. Such compounds are called **isomers**.



- **Structural Isomerism:** Compounds having the same molecular formula but different structures (manners in which atoms are linked) are classified as structural isomers.
- **I. Chain isomerism:** Same molecular formula but different carbon skeletons. For example, C<sub>5</sub>H<sub>12</sub> represents three compounds





**II. Position isomerism:** Differ in the position of substituent atom or functional group on the carbon skeleton. For example, C<sub>3</sub>H<sub>8</sub>O represents two alcohols:

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH CH<sub>3</sub>-CH-CH<sub>3</sub> Propan-1-ol Propan-2-ol

**III. Functional group isomerism:** same molecular formula but different functional groups. For example, C<sub>3</sub>H<sub>6</sub>O represents an aldehyde and a ketone

O H CH<sub>3</sub>-C-CH<sub>3</sub> CH<sub>3</sub>-CH<sub>2</sub>-C= O Propanone Propanal

**IV. Metamerism:** It arises due to different alkyl chains on either side of the functional group in the molecule.

For example, C<sub>4</sub>H<sub>10</sub>O represents methoxypropane (CH<sub>3</sub>OC<sub>3</sub>H<sub>7</sub>) and ethoxyethane (C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>).

Stereoisomerism

The compounds that have the same constitution and sequence of covalent bonds but differ in relative positions of their atoms or groups in space are called **stereoisomers.** This special type of isomerism is called stereoisomerism and can be classified as **geometrical** and **optical isomerism.** 

#### > Fundamental Concepts In Organic Reaction Mechanism:

The general reaction is depicted as follows

```
Attacking

Organic Reagent [Intermediate] Product(s)

molecule Byproducts
```

- **Substrate** is that reactant which supplies carbon to the new bond and the other reactant is called **reagent.** If both the reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called substrate.
- A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as **reaction mechanism.** 
  - Fission of a Covalent Bond



#### A covalent bond can get cleaved either by:

**I. Heterolytic cleavage:** The bond breaks in such a fashion that the shared pair of electrons remains with one of the fragments.

### > Carbocation:

 $H_{3C} \xrightarrow{f} Br \longrightarrow H_{3C} + Br$ 

- A species having a carbon atom possessing a sextet of electrons and a positive charge is called a **carbocation** (earlier called carbonium ion).
- Carbocation is classified as primary, secondary or tertiary.
- Carbocations are highly unstable and reactive species.
- Alkyl groups directly attached to the positively charged carbon stabilise the carbocations due to inductive and hyperconjugation effects, & order of stability is:

$$\overset{+}{C}H_{3} < CH_{3}\overset{+}{C}H_{2} < (CH_{3})_{2}\overset{+}{C}H < (CH_{3})_{3}\overset{+}{C}$$

• Carbocations have a trigonal planar shape with sp<sup>2</sup> hybridised.



Shape of methyl cation

#### > Carbanion:

$$CH_1 \longrightarrow H_1C_2^+ + Z^+$$

- Negative charge on a carbon atom is called **carbanion**.
- The organic reactions which proceed through heterolytic bond cleavage are called ionic or heteropolar or just polar.
- Carbanions are also unstable and reactive species.
  - **II. Homolytic cleavage**: One of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms.
  - Neutral species (atom or group) which contains an unpaired electron are called **free** radicals.

$$\overbrace{R \longrightarrow X}^{\text{Heat or Light}} \stackrel{\dot{R}}{\longrightarrow} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{+}{\stackrel{\dot{X}}{\stackrel{\dot{X}}{\longrightarrow}}} \stackrel{\dot{R}}{\stackrel{\text{Heat or Light}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{+}{\stackrel{\dot{X}}{\longrightarrow}} \stackrel{\dot{X}}{\stackrel{\text{Alkyl}}{\stackrel{\text{free radical}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{+}{\stackrel{\dot{X}}{\longrightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{+}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{+}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{+}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{+}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\longrightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\stackrel{\dot{R}}{\rightarrow}} \stackrel{\dot{R}}{\rightarrow} \stackrel{\dot{R}} \stackrel{\dot{R}}{\rightarrow}$$

• Alkyl radicals are classified as primary, secondary, or tertiary. & stability order

• Organic reactions, which proceed by homolytic fission are called free radical or homopolar or nonpolar reactions



#### > Nucleophiles and Electrophiles:

• A reagent that brings an electron pair is called a **nucleophile** (Nu:) i.e., nucleus seeking and the reaction is then called **nucleophilic**.

**Ex. Negatively charged** ions  $HO^-$ ,  $NC^-$  and carbanions (R<sub>3</sub>C:<sup>-</sup>).

Neutral molecules H<sub>2</sub>Ö:, R<sub>3</sub>N:, R<sub>3</sub>NH etc.,

• A reagent that takes away an electron pair is called **electrophile** (E<sup>+</sup>) i.e., electron seeking and the reaction is called **electrophilic.** 

Ex carbocations (<sup>+</sup>CH<sub>3</sub>) and carbonyl group (>C=O) or alkyl halides (R<sub>3</sub>C-X, where X is a halogen atom).

#### Electron Movement in Organic Reactions:

To show the change in position of a pair of electrons, a curved arrow starts from the point from where an electron pair is shifted and it ends at a location to which the pair of electrons may move.

Presentation of shifting of electron pair is given below:

(i) 
$$\stackrel{\checkmark}{=} Y \stackrel{\checkmark}{=} \stackrel{\leftarrow}{\longrightarrow} -Y = \text{ from } \pi \text{ bond to} \\ \text{adjacent bond position} \\ (ii) \stackrel{\frown}{=} \stackrel{\lor}{Y} - \stackrel{\leftarrow}{\longleftrightarrow} - \stackrel{\lor}{Y} - \begin{array}{c} \text{from } \pi \text{ bond to} \\ \text{adjacent atom} \end{array}$$

(iii)  $\underline{-} \stackrel{\frown}{\underline{\forall}} \underbrace{\longleftrightarrow}_{\underline{\neg}} -\underline{\gamma} =$ from atom to adjacent bond position

Movement of single electron is indicated by a single barbed 'fish hooks

$$\begin{array}{c} H \overset{\frown}{\text{O}} : + \overset{\frown}{\text{C}} H_{3} - \overset{\frown}{\text{B}} r : \longrightarrow C H_{3} O H + : \overset{\frown}{\text{B}} r : \\ C \overset{\frown}{\text{H}_{3}} - \overset{\frown}{\text{Cl}} \longrightarrow \overset{\leftarrow}{\text{C}} H_{3} + \overset{\leftarrow}{\text{Cl}} \end{array}$$

#### > Electron Displacement Effects in Covalent Bonds

#### Inductive Effect

- The electron density is more towards the more electronegative atom of the bond and it results in a polar C Cl bond.
- Carbon-1 gains some positive charge (δ<sup>+</sup>) and the chlorine gains some negative charge (δ<sup>-</sup>).

- Such polarisation of  $\sigma$ -bond caused by the polarisation of adjacent  $\sigma$ -bond is referred to as the inductive effect.
- This effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds.
- Substituents can be classified as **electron-withdrawing** (-**I**) or **electron donating groups**(+**I**) relative to hydrogen.

**Electron-withdrawing groups**: Halogens, nitro (-NO<sub>2</sub>), cyano (-CN), carboxy (-COOH), ester (-COOR), aryloxy (-OAr, e.g. – OC<sub>6</sub>H<sub>5</sub>), etc.



**Electron donating groups:** Alkyl groups like methyl (–CH<sub>3</sub>) and ethyl (–CH<sub>2</sub>– CH<sub>3</sub>).

#### Resonance Structure



- Actual structure of benzene cannot be adequately represented by any of these structures, rather it is a hybrid of the two structures (I and II) called **resonance structures**
- The resonance structures (canonical structures or contributing structures) are hypothetical and individually do not represent any real molecule.
- They contribute to the actual structure in proportion to their stability.
- The energy of the actual structure of the molecule (the resonance hybrid) is lower than that of any of the canonical structures.
- The difference in energy between the actual structure and the lowest energy resonance structure is called the **resonance energy**.
- The more the number of contributing structures, the more is the resonance energy.

#### **Rules for writing resonance structures:**

- The resonance structures have
  - (i) The same positions of nuclei.
  - (ii) The same number of unpaired electrons.
- Among the resonance structures, more stable is one which has
  - I. more number of covalent bonds.
  - II. All the atoms with octet of electrons (except hydrogen which has a duplet).
  - III. Less separation of opposite charges.
  - IV. A negative charge if any on more electronegative atoms and a positive charge if any on more electropositive atoms.
  - V. More dispersal of charge.

#### > Resonance Effect.

- The resonance effect is defined as 'the polarity produced in the molecule by the interaction of two  $\pi$ -bonds or between a  $\pi$ -bond and lone pair of electrons present on an adjacent atom'.
- The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system. and the  $\pi$ -electrons are delocalized and the system develops polarity
- The examples are 1,3- butadiene, aniline and nitrobenzene etc.
  - I. Positive Resonance Effect (+R effect)

When the transfer of electrons is away from an atom or substituent group attached to the conjugated system.





+R effect substituent groups: – halogen, –OH, –OR, –OCOR, –NH<sub>2</sub>, –NHR, – NR<sub>2</sub>, –NHCOR.

#### **II.** Negative Resonance Effect (-R effect)

When the transfer of electrons is towards the atom or substituent group attached to the conjugated system



-R effect substituent groups: - COOH, -CHO, >C=O, -CN, -NO2

### Electromeric Effect (E effect)

- It is a temporary effect.
- The organic compounds having a multiple bond (a double or triple bond) show this effect in the presence of an attacking reagent only.
- Defined as the complete transfer of a shared pair of  $\pi$ -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.
- I. Positive Electromeric Effect (+E effect) :  $\pi$ -electrons of the multiple bond are transferred to that atom to which the reagent gets attached.

$$>C = C < + H^+ \longrightarrow > C - C <$$
  
(attacking  
reagent) H

**II.** Negative Electromeric Effect (-E effect) :  $\pi$  - electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached.

$$>C = C < + CN \longrightarrow >C - C <$$
  
(attacking reagent)

**Note**: When inductive and electromeric effects operate in opposite directions, the electromeric effect predominates.

#### > Hyperconjugation

- Delocalization of  $\sigma$  electrons of C—H bond of an alkyl group directly attached to an atom of unsaturated system or to an atom with an unshared p orbital.
- Hyperconjugation is a permanent effect, also regarded as no bond resonance.
- Electrons of the C-H bonds of the methyl group can align in the plane of empty p orbital of positively charged carbon atom and get delocalized into the empty p orbital as depicted in below figure





- This type of overlap stabilises the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge.
- Greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyperconjugation interaction and stabilisation of the cation.
- Relative stability order of carbocations:

$$CH_{a} - CH_{a} + CH_{a}CH_{$$

• Hyperconjugation is also possible in alkenes and alkylarenes



Orbital diagram showing hyperconjugation in propene

#### > Types of Organic Reactions and Mechanisms

Organic reactions can be classified into the following categories:

- (i) Substitution reactions
- (ii) Addition reactions
- (iii) Elimination reactions



(iv) Rearrangement reactions

#### > Methods of Purification of Organic Compounds

### The common techniques used for purification are as follows :

(i) Sublimation (ii) Crystallisation (iii) Distillation

(iv) Differential extraction (v) Chromatography

### I. Sublimation:

Used to separate sublimable compounds from non-sublimable impurities

### II. Crystallisation

- Crystallisation is one of the most commonly used techniques for the purification of solid organic compounds.
- It is based on the difference in the solubilities of the compound and the impurities in a suitable solvent.
- The impure compound is dissolved in solvent and heated at higher temp. on cooling the hot and conc. solution pure compounds crystallizes out.
- If the compound is highly soluble in one solvent and very little soluble in another solvent, crystallisation can be satisfactorily carried out in a mixture of these solvents
- Impurities, which impart colour to the solution are removed by adsorbing over activated charcoal.

### III. Distillation

### Simple Distillation

- Used to separate
  - (i) Volatile liquids from nonvolatile impurities.
  - (ii) The liquids have sufficient difference in their boiling points.
- Ex Chloroform (b.p 334 K) and aniline (b.p. 457)
- On boiling, the vapours of the lower boiling component are formed first. The vapours are condensed by using a condenser and the liquid is collected in a receiver.
- The vapours of higher boiling components form later and the liquid can be collected separately.





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

#### Fractional Distillation:

- Used when the difference in boiling points of two liquids is not much.
- A fractionating column provides many surfaces for heat exchange, some of the condensing liquid in the fractionating column obtains heat from the ascending vapours and revaporises.
- The vapours thus become richer in low boiling components & ascend to the top of the column.
- On reaching the top, the vapours become pure in a low boiling component and pass through the condenser and the pure liquid is collected in a receiver.
- After a series of successive distillations, the remaining liquid in the distillation flask gets enriched in a high boiling component.
- Each successive condensation and vaporisation unit in the fractionating column is called a **theoretical plate**.
- It is used to separate different fractions of crude oil in petroleum industry





#### > Distillation under reduced pressure

- Used to purify liquids having very high boiling points and those, which decompose at or below their boiling points.
- Liquids are made to boil at a temperature lower than their normal boiling points by reducing the pressure on their surface with help of water pump or vacuum pump
- Ex. Glycerol can be separated from spent-lye in soap industry





Distillation under reduced pressure. A liquid boils at a temperature below its vapour pressure by reducing the pressure.

#### > Steam Distillation

- Used to separate substances which are steam volatile and are immiscible with water.
- The mixture of steam and the volatile organic compound is condensed and collected.
- The compound is later separated from water using a separating funnel.
- Aniline is separated by this technique from aniline water mixture.



Steam distillation. Steam volatile component volatilizes, the vapours condense in the condenser and the liquid collects in conical flask.

#### **III. Differential Extraction**

• Used to separate organic compounds present in an aqueous medium, by shaking it with an organic solvent in which it is more soluble than in water.



- The organic solvent and the aqueous solution should be immiscible with each other so that they form two distinct layers which can be separated by a separatory funnel.
- The organic solvent is later removed by distillation or by evaporation to get back the compound.
- If the organic compound is less soluble in the organic solvent, then, technique of **continuous extraction is employed** in which the same solvent is repeatedly used.



#### **IV.** Chromatography

- In this technique, the mixture of substances is applied onto a stationary phase, which may be a solid or a liquid. A pure solvent, a mixture of solvents, or a gas is allowed to move slowly over the **stationary phase**.
- The components of the mixture get gradually separated from one another. The moving phase is called the **mobile phase**.



Based on the principle involved, chromatography is classified into different categories. (a) Adsorption chromatography, and (b) Partition chromatography.

#### (a) Adsorption Chromatography:

- Based on the fact that different compounds are adsorbed on an adsorbent to different degrees.
- Commonly used adsorbents are silica gel and alumina.
- Two main types of chromatographic techniques

(i) Column chromatography, and (ii) Thin layer chromatography

#### I. Column Chromatography:

- It involves separation of a mixture over a column of adsorbent (stationary phase) packed in a glass tube.
- The mixture is placed on the top of the adsorbent column
- An appropriate eluant which is a liquid or a mixture of liquids is allowed to flow down the column slowly.
- The most readily adsorbed substances are retained near the top and others come down to various distances in the column.

### **II.** Thin Layer Chromatography:

- It involves separation of substances of a mixture over a thin layer (about 0.2mm thick) of an adsorbent coated on a glass tube.
- The plate is known as thin layer chromatography plate or Chroma plate.
- The solution of the mixture to be separated is applied as a small spot about 2 cm above one end of the TLC plate.
- As the eluant rises up the plate, the components of the mixture move up along with the eluant to different distances depending on their degree of adsorption and separation takes place.
- The relative adsorption of each component of the mixture is expressed in terms of its retardation factor i.e. R f value
  - $R_{f} = \frac{\text{Distance moved by the substance from base line (x)}}{\text{Distance moved by the solvent from base line (y)}}$
- The spots of colourless compounds, which are invisible to the eye, can be detected by putting the plate under ultraviolet light.
- Another detection technique is to place the plate in a covered jar containing a few crystals of iodine. Spots of compounds, which adsorb iodine, will show up as brown spots.
- Sometimes an appropriate reagent may also be sprayed on the plate. For example, amino acids may be detected by spraying the plate with ninhydrin solution









(b) **Partition Chromatography:** based on continuous differential partitioning of components of a mixture between stationary and mobile phases.



- Paper chromatography is a type of partition chromatography.
- In paper chromatography, a special quality paper known as **chromatography paper is** used. which contains water trapped in it, which acts as the stationary phase.
- A strip of chromatography paper spotted at the base with the solution of the mixture is suspended in a suitable solvent or a mixture of solvents.
- This solvent acts as the mobile phase & rises up the paper by capillary action and flows over the spot.
- The paper selectively retains different components according to their differing partition in the two phases.
- The paper strip so developed is known as a chromatogram.
- The spots of the separated coloured compounds are visible at different heights from the position of initial spot on the chromatogram.

### > Qualitative Analysis of Organic Compounds

### **Detection of Carbon and Hydrogen:**

- Presence of carbon and hydrogen is detected by heating the compound with copper (II) oxide.
- Carbon present in the compound is oxidised to carbon dioxide (tested with limewater, which develops turbidity) and hydrogen to water (tested with anhydrous copper sulphate, which turns blue).

 $\begin{array}{cccc} C + 2CuO & \underline{\quad} & \underline{\quad} & 2Cu + CO_2 \\ 2H + CuO & \underline{\quad} & \underline{\quad} & Cu + H_2O \\ CO_2 + Ca(OH)_2 & \longrightarrow & CaCO_3 \downarrow + H_2O \\ 5H_2O + CuSO_4 & \underbrace{\quad} & \underline{\quad} & CuSO_4.5H_2O \\ & & White & & Blue \end{array}$ 

#### Detection of Other Elements

- Nitrogen, sulphur, halogens and phosphorus present in an organic compound are detected by "Lassaigne's test".
- The elements present in the compound are converted from covalent form into the ionic form by fusing the compound with sodium metal.

```
\begin{array}{cccc} Na + C + N & \underline{ \land} & NaCN \\ 2Na + S & \underline{ \land} & Na_2S \\ Na + X & \underline{ \land} & Na X \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & &
```

• Cyanide, sulphide and halide of sodium so formed on sodium fusion are extracted from the fused mass by boiling it with distilled water. This extract is known as **sodium fusion extract.** 

#### (A) Test for Nitrogen

- The sodium fusion extract is boiled with iron (II) sulphate and then acidified with concentrated sulphuric acid. The formation of Prussian blue colour confirms the presence of nitrogen.
- On heating with concentrated sulphuric acid some iron (II) ions are oxidised to iron (III) ions.



$$6CN^{-} + Fe^{2+} \rightarrow [Fe(CN)_6]^{4-}$$
  
 $3[Fe(CN)_6]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} Fe_4[Fe(CN)_6]_3.xH_2O$   
Prussian blue

#### (B) Test for Sulphur

(a) 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.

 $S_2^- + Pb^{2+} \rightarrow PbS$  (Black)

(b) On treating sodium fusion extract with sodium nitroprusside, appearance of a violet colour further indicates the presence of sulphur

 $S^{2-}$  + [Fe(CN)<sub>5</sub>NO]<sup>2-</sup>  $\longrightarrow$  [Fe(CN)<sub>5</sub>NOS]<sup>4-</sup> Violet

If nitrogen and sulphur both are present in an organic compound, sodium thiocyanate is formed. It gives blood red colour and no Prussian blue since there are no free cyanide ions.

 $Na + C + N + S \longrightarrow NaSCN$   $Fe^{3+} +SCN^{-} \longrightarrow [Fe(SCN)]^{2+}$ Blood red

If sodium fusion is carried out with excess of sodium, the thiocyanate decomposes to yield cyanide and sulphide. These ions give their usual tests.

 $NaSCN + 2Na \rightarrow NaCN + Na_2S$ 

#### (C) Test for Halogens:

- The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.
- White precipitate, soluble in ammonium hydroxide shows the presence of chlorine.
- Yellowish precipitate, sparingly soluble in ammonium hydroxide shows the presence of bromine.
- Yellow precipitate, insoluble in ammonium hydroxide shows the presence of iodine.

```
X^- + Ag^+ \longrightarrow AgX
X represents a halogen – Cl, Br or I.
```

• If nitrogen or sulphur is also present in the compound, the sodium fusion extract is first boiled with concentrated nitric acid to decompose cyanide or sulphide of sodium formed during Lassaigne's test. These ions would otherwise interfere with silver nitrate test for halogens

#### (D) Test for Phosphorus

- The compound is heated with an oxidising agent (sodium peroxide). The phosphorus present in the compound is oxidised to phosphate.
- The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

 $Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$ 

 $\begin{array}{rl} \mathrm{H_3PO_4} &+& 12(\mathrm{NH_4})_2\mathrm{MoO_4} &+& 21\mathrm{HNO_3} \longrightarrow (\mathrm{NH_4})_3\mathrm{PO_4}.12\mathrm{MoO_3} + 21\mathrm{NH_4NO_3} + 12\mathrm{H_2O} \\ & \mathrm{Ammonium} \\ & & \mathrm{molybdate} \end{array}$ 

Quantitative Analysis



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

#### Carbon and Hydrogen

• A known mass of an organic compound is burnt in the presence of excess oxygen and copper (II) oxide.

 $CxHy + (x + y/4) O_2 \rightarrow x CO_2 + (y/2) H_2O$ 

- The mass of water produced is determined by passing the mixture through a weighed U-tube containing anhydrous calcium chloride.
- Carbon dioxide is absorbed in another U-tube containing a concentrated solution of potassium hydroxide.



Estimation of carbon and hydrogen. Water and carbon diaxide formed on oxidation of substance are absorbed in anhydrous calcium chloride and potassium hydroxide solutions respectively contained in U tubes.

• Let the mass of organic compound be m g, mass of water and carbon dioxide produced be m<sub>1</sub> and m<sub>2</sub> g respectively

Percentage of carbon =  $\frac{12 \times m_2 \times 100}{44 \times m}$ Percentage of hydrogen =  $\frac{2 \times m_1 \times 100}{18 \times m}$ 

#### Nitrogen

- There are two methods for estimation of nitrogen:
- (i) Dumas's method
- (ii) Kjeldahl's Method.
- (i) Dumas's method:

 $CxHyNz + (2x + y/2) CuO \rightarrow x CO_2 + y/2 H_2O + z/2 N_2 + (2x + y/2) Cu$ 





Dumas method. The organic compound yields nitrogen gas on heating it with copper(II) oxide in the presence of  $CO_2$  gas. The mixture of gases is collected over potassium hydroxide solution in which  $CO_2$  is absorbed and volume of nitrogen gas is determined.

let the mass of organic compound = m g Volume of nitrogen collected =  $V_1$  mL Room temperature =  $T_1$  K

Volume of nitrogen at STP =  $\frac{p_1 V_1 \times 273}{760 \times T_1}$ (Let it be V mL)

Where  $p_1$  and  $V_1$  are the pressure and volume of nitrogen.

The value of  $p_1$  is obtained by the relation;  $p_1$ = Atmospheric pressure – Aqueous tension

22400 mL N<sub>2</sub> at STP weighs 28 g.

V mL N<sub>2</sub> at STP weighs =  $\frac{28 \times V}{22400}$ g

Percentage of nitrogen =  $\frac{28 \times V \times 100}{22400 \times m}$ 

#### (ii) Kjeldahl's method

 $Organic \ compound + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O_4 \xrightarrow{2NaOH} Na_2SO_4 \xrightarrow{2NaOH} \xrightarrow{2NaOH} Na_2SO_4 \xrightarrow{2NaOH} \xrightarrow{2NaOH} Na_2SO_4 \xrightarrow{2NaOH} \xrightarrow{$ 

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

Let the mass of organic compound taken = m g

Volume of  $H_2SO_4$  of molarity, M,taken = V mL

Volume of NaOH of molarity, M, used for titration of excess of  $H_2SO_4 = V_1 mL$ 

 $V_1$ mL of NaOH of molarity M=  $V_1$  /2 mL of H<sub>2</sub>SO<sub>4</sub> of molarity M

Volume of  $H_2SO_4$  of molarity M unused= (V - V<sub>1</sub>/2) mL (V - V<sub>1</sub>/2) mL of  $H_2SO_4$  of molarity M = 2(V - V<sub>1</sub>/2) mL of NH<sub>3</sub> solution of molarity M.




Kjeldahl method. Nitrogen-containing compound is treated with concentrated  $H_2SO_4$  to get ammonium sulphate which liberates ammonia on treating with NaOH; ammonia is absorbed in known volume of standard acid.

**Note:** Kjeldahl method is not applicable to compounds containing nitrogen in nitro and azo groups and nitrogen present in the ring (e.g. pyridine) as nitrogen of these compounds does not change to ammonium sulphate under these conditions.

### > 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 tube known as Carius tube.
- The halogen present forms the corresponding silver halide (AgX).
- Let the mass of organic compound taken = m g Mass of AgX formed = m1 g 1 mol of AgX contains 1 mol of X

Mass of halogen in  $m_1 g$  of  $AgX = \frac{\text{atomic mass of } X \times m_1 g}{\text{molecular mass of } AgX}$ 

Percentage of halogen =  $\frac{\text{atomic mass of } X \times m_1 \times 100}{\text{molecular mass of } AgX \times m}$ 





Carius method. Halogen containing organic compound is heated with furning nitric acid in the presence of silver nitrate.

#### > Sulphur

- A known mass of an organic compound is heated in a Carius tube with sodium peroxide or fuming nitric acid.
- Sulphur present in the compound is oxidised to sulphuric acid. It is precipitated as barium sulphate by adding excess barium chloride solution in water.
- The percentage of sulphur can be calculated from the mass of barium sulphate. Let the mass of organic compound taken = m g and the mass of barium sulphate formed = m1g

1 mol of BaSO<sub>4</sub> = 233 g BaSO<sub>4</sub> = 32 g sulphur  
$$32 \times m_1$$

$$m_1 g BaSO_4 contains \frac{32 \times m_1}{233} g sulphur$$

Percentage of sulphur= $\frac{32 \times m_1 \times 100}{233 \times m}$ 

#### > Phosphorus

- A known mass of an organic compound is heated with fuming nitric acid where phosphorus oxidised to phosphoric acid.
- It is precipitated as ammonium phosphomolybdate, (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub>, by adding ammonia and ammonium molybdate, or maybe precipitated as MgNH<sub>4</sub>PO<sub>4</sub> by adding magnesia mixture which on ignition yields Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>.
- Let the mass of organic compound taken= m g mass of ammonium phosphomolybdate (Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) = m<sub>1</sub>g Molar mass of (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>.12MoO<sub>3</sub> = 1877 g



Percentage of phosphorus =  $\frac{31 \times m_1 \times 100}{1877 \times m}$ % If phosphorus is estimated as Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, Percentage of phosphorus =  $\frac{62 \times m_1 \times 100}{222 \times m}$ %

where, 222 u is the molar mass of Mg<sub>2</sub>P<sub>2</sub>O<sub>7</sub>

#### > Oxygen:

- The percentage of oxygen in an organic compound is usually found by the difference between the total percentage composition (100) and the sum of the percentages of all other elements.
- Oxygen can also be estimated directly as follows Compound  $\xrightarrow{\text{heat}} O_2$  + other gaseous products

 $2C + O_2 \xrightarrow{1373K} 2CO] \times 5$ (A)  $I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2] \times 2$ (B)

• On making the amount of CO produced in equation (A) equal to the amount of CO used in equation (B), we find that each mole of oxygen liberated from the compound will produce two moles of carbon dioxide; Thus 88 g carbon dioxide is obtained if 32 g oxygen is liberated.

Let the mass of organic compound taken be m g

Mass of carbon dioxide produced be m<sub>1</sub> g

 $\therefore$  m<sub>1</sub> g carbon dioxide is obtained from

$$\frac{32 \times m_1}{88} gO_2$$

 $\therefore \text{ Percentage of oxygen} = \frac{32 \times m_1 \times 100}{88 \times m} \%$ 



# Hydrocarbons

### Compounds of carbon and hydrogen

- > Classification
  - Classified as (i) saturated (ii) unsaturated (iii) aromatic hydrocarbons.
  - Saturated hydrocarbons contain carbon-carbon single bonds
  - Unsaturated hydrocarbons contain carbon-carbon multiple bonds double bonds, triple bonds or both.
  - Aromatic hydrocarbons are a special type of cyclic compounds

### > <u>Alkanes</u>

- Alkanes are saturated open chain hydrocarbons & general formula is  $C_nH_{2n+2}$
- Alkanes are inert under normal conditions as they do not react with acids, bases and other reagents. they were earlier known as **paraffins** (latin : parum, little; affinis, affinity)
- First member of alkane is Methane (CH<sub>4</sub>) & it is gas found in coal mines and marshy places & have a tetrahedral structure



• In alkanes, tetrahedra are joined together in which C-C and C-H bond lengths are 154 pm and 112 pm

### Nomenclature and Isomerism

- First three alkanes methane, ethane and propane have only one structure but higher alkanes can have more than one structure.
- Structures for C<sub>4</sub>H<sub>10</sub>
- Structures for C<sub>5</sub>H<sub>12</sub>







- Difference in properties due to difference in the structures of compound with the same molecular formula, they are known as **structural isomers**.
- Structural isomers which differ in chain of carbon atoms are known as chain isomers
- $C_6H_{14}$  has five isomers,  $C_7H_{16}$  has nine and  $C_{10}H_{22}$  has 75 isomers
- Carbon atom is classified as: Primary (1°): Carbon atom attached to no other carbon atom Secondary (2°): Carbon atom attached to two carbon atoms Tertiary (3°): Carbon atom attached to three carbon atoms Quaternary (4°): Carbon atom attached to four carbon atoms

Str	ucture and IUPAC Name	Remarks
(a)	$\begin{array}{ccc} CH_{3} & CH_{2}-CH_{3} \\ I & I \\ {}^{1}CH_{3}-{}^{2}CH - {}^{3}CH_{2} - {}^{4}CH - {}^{5}CH_{2} - {}^{6}CH_{3} \\ (4 - Ethyl - 2 - methylhexane) \end{array}$	Lowest sum and alphabetical arrangement
(b)	$CH_2 - CH_3$ $^8CH_3 - ^7CH_2 - ^6CH_2 - ^5CH - ^4CH - \ ^3C - ^2CH_2 - ^1CH_3$ I I CH $CH_2 - CH_3$ I $CH_2 - CH_3$ $CH_2 - CH_3 - ^1CH_3$ $CH_3 - ^2CH_2 - ^1CH_3$	Lowest sum and alphabetical arrangement
	(3,3-Diethyl-5-isopropyl-4-methyloctane)	
(c)	CH(CH <sub>3</sub> ) <sub>2</sub> I $^{1}CH_{3}^{-2}CH_{2}^{-3}CH_{2}^{-4}CH^{-6}CH^{-6}CH_{2}^{-7}CH_{2}^{-6}CH_{2}^{-9}CH_{2}^{-10}CH_{3}$ I $H_{3}C^{-}CH^{-}CH_{2}^{-}CH_{3}$ 5-sec- Butyl-4-isopropyldecane	sec is not considered while arranging alphabetically: isopropyl is taken as one word
(d)	<sup>1</sup> CH <sub>3</sub> - <sup>2</sup> CH <sub>2</sub> - <sup>3</sup> CH <sub>2</sub> - <sup>4</sup> CH <sub>2</sub> - <sup>5</sup> CH- <sup>6</sup> CH <sub>2</sub> - <sup>7</sup> CH <sub>2</sub> - <sup>8</sup> CH <sub>2</sub> - <sup>3</sup> CH <sub>3</sub>   CH <sub>2</sub>   CH <sub>3</sub> - <sup>2</sup> C-CH <sub>3</sub>   <sup>3</sup> CH <sub>2</sub>	Further numbering to the substituents of the side chain
(e)	5-(2, 2- Dimethylpropyl)nonane ${}^{1}CH_{3} - {}^{2}CH_{2} - {}^{3}CH - {}^{4}CH_{2} - {}^{5}CH - {}^{6}CH_{2} - {}^{7}CH_{3}$ I I $CH_{2} - CH_{3} CH_{3}$ 3-Ethyl-5-methylheptane	Alphabetical priority order

# • Writing structure from the given IUPAC name

**Ex**. 3-ethyl-2, 2–dimethylpentane in the following steps i) Draw the chain of five carbon atoms: C - C - C - C - Cii) Give number to carbon atoms:  $C^1 - C^2 - C^3 - C^4 - C^5$ 



iii) Attach ethyl group at carbon 3 and two methyl groups at carbon 2

$$CH_3$$
  
 $I$   
 $C^1 - {}^2C - {}^3C - {}^4C - {}^5C$   
 $I$   
 $CH_3$   
 $C_2H_5$ 

iv) Satisfy the valence of each carbon atom by putting requisite number of hydrogen atoms

$$\begin{array}{c} \operatorname{CH}_{3}\\ \operatorname{CH}_{3} & - \operatorname{C} & - \operatorname{CH} - \operatorname{CH}_{2} - \operatorname{CH}_{3}\\ \operatorname{I}_{3} & \operatorname{I}_{2} \operatorname{H}_{5} \end{array}$$

> Preparation.

- 1. From unsaturated hydrocarbons
- Hydrogenation: Addition of H<sub>2</sub> gas to alkenes and alkynes

```
\begin{array}{c} CH_{2}-CH_{2}+H_{2} \xrightarrow{-Pt/Pd/Ni} \rightarrow CH_{3}-CH_{5} \\ Ethene \\ \end{array} \begin{array}{c} CH_{3}-CH=CH_{1}+H_{2} \xrightarrow{-Pt/Pd/Ni} \rightarrow CH_{3}-CH_{2}-CH_{3} \\ Propene \\ \end{array} \begin{array}{c} Propene \\ Propane \end{array}
```

```
CH_3 - C = C - H + 2H_1 \xrightarrow{Pt/Pd/Nt} CH_3 - CH_2 - CH_3
Propyne Propane
```

2. From alkyl halides : (i) Reduction of alkyl halide (except fluorides)

 $CH_3 - Cl + H_2 \xrightarrow{Zn, H^*} CH_4 + HCl$ Chloromethane Methane

(ii) Wurtz reaction: on treatment with sodium metal in dry ethereal (free from moisture) solution give higher alkanes. (Containing even number of carbon atoms)

CH<sub>3</sub>Br+2Na+BrCH<sub>3</sub> → CH<sub>3</sub>-CH<sub>3</sub>+2NaBr Bromomethane Ethane

(13.7)

 $C_2H_5Br+2Na+BrC_2H_5 \xrightarrow{dry ether} C_2H_5 - C_2H_5$ Bromoethane n-Butane

# 3. From carboxylic acids

i) Decarboxylation: The process of elimination of carbon dioxide from a carboxylic acid

This method gives alkanes containing one carbon atom less than the carboxylic acid.

 $CH_{3}COO^{-}Na^{+} + NaOH \xrightarrow{CaO} CH_{4} + Na_{2}CO_{3}$ 

Sodium ethanoate

# ii) Kolbe's electrolytic method:

- On electrolysis we get alkane containing an even number of carbon atoms at the anode.
- Methane cannot be prepared by this method.



 $\begin{array}{rll} 2CH_{3}COO^{-}Na^{+}+&2H_{2}O\\ Sodium \ acetate\\ & \downarrow \ Electrolysts\\ CH_{3}-CH_{3}+2CO_{2}+H_{2}+2NaOH \end{array}$ 

- The reaction is supposed to follow the following path:
  - 1)  $2CH_{3}COO^{-}Na^{+} \rightleftharpoons 2CH_{3}-C-O^{-}+2Na^{+}$ 1) At anode:  $O O O O^{-}DO^{$
- > Properties
  - Physical properties
    - Alkanes are colourless & odourless, almost non-polar molecules, soluble in non-polar solvent.
    - They possess weak van der Waals forces which increase with increase of the molecular size or the surface area of the molecule. That's why C<sub>1</sub> to C<sub>4</sub> are gases, C<sub>5</sub> to C<sub>17</sub> are liquids and C<sub>18</sub> & higher members are solids at 298 K.
    - Boiling point increases with increase in molecular mass
    - Boiling point decreases with increase in number of branched chains, as the molecule attains the shape of a sphere which has lower surface area.

Molecular formula	Name	Molecular mass/u	b.p./(K)	m.p./(K)
CH4	Methane	16	111.0	90.5
C <sub>2</sub> H <sub>6</sub>	Ethane	30	184.4	101.0
C <sub>s</sub> H <sub>s</sub>	Propane	44	230,9	85.3
C <sub>4</sub> H <sub>10</sub>	Butane	58	272.4	134.6
C4H10	2-Methylpropane	58	261.0	114.7
C.H.,	Pentane	72	309.1	143.3
C <sub>5</sub> H <sub>19</sub>	2-Methylbutane	72	300.9	113.1
C <sub>c</sub> H <sub>in</sub>	2,2-Dimethylpropane	72	282.5	256.4
C.H.	Hexane	86	341.9	178.5
C,H <sub>te</sub>	Heptane	100	371.4	182.4
C <sub>s</sub> H <sub>1s</sub>	Octane	114	398.7	216.2
C <sub>0</sub> H <sub>20</sub>	Nonane	128	423.8	222.0
C.,,H.,,	Decane	142	447.1	243.3
C <sub>20</sub> H <sub>42</sub>	Eicosane	282	615.0	236.2

- Chemical properties
  - **1.** Substitution reactions



One or more hydrogen atoms of alkanes can be replaced by halogens, nitro group and sulphonic acid group

Lower alkanes do not undergo nitration and sulphonation reactions.

**Halogenation:** One or more hydrogen atoms of alkanes can be replaced by halogens. Halogenation takes place either at higher temperature (573-773 K) or in the presence of diffused sunlight or ultraviolet light

- Rate of reaction of alkanes with halogens is  $F_2 > Cl_2 > Br_2 > I_2$
- Rate of alkanes is:  $3^\circ > 2^\circ > 1^\circ$ .
- Fluorination is too violent to be controlled and Iodination is very slow and a reversible reaction. It can be carried out in the presence of oxidizing agents like HIO<sub>3</sub> or HNO<sub>3</sub>.

```
CH<sub>4</sub>+L<sub>2</sub> ⇒CH<sub>3</sub>I+HI
```

HIO<sub>3</sub>+5HI→ 3I<sub>2</sub>+3H<sub>2</sub>O

#### Halogenation Mechanism: free radical chain mechanism

I. Initiation: initiated by homolysis of chlorine molecules in the presence of light or heat.

```
\begin{array}{ccc} Cl-Cl & \stackrel{h\nu}{\longrightarrow} & Cl & + & Cl\\ \hline Chlorine free radicals \end{array}
```

II. Propagation:

(b)  $\dot{C}H_3 + Cl - Cl \longrightarrow CH_3 - Cl + Cl$ 

Many other propagation steps are possible which gives more highly halogenated products

$$CH_3Cl + Cl \rightarrow CH_2Cl + HCl$$

 $\dot{C}H_2Cl + Cl - Cl \rightarrow CH_2Cl_2 + \dot{C}l$ 

**III. Termination:** The reaction stops after some time due to consumption of reactants and or due to the side reactions:

The possible chain terminating steps are:

(a)  $\dot{C}I + \dot{C}I \rightarrow CI-CI$  (b)  $H_a\dot{C} + \dot{C}H_a \rightarrow H_aC-CH_a$  (c)  $H_a\dot{C} + \dot{C}I \rightarrow H_aC-CI$ 

2. Combustion:

 $CH_4(g)+2O_2(g) \rightarrow CO_2(g)+2H_2O(l); \Delta_H^{\odot} = -890 \text{ kJ mol}^{-1}$ 

 $C_4H_{10}(g)+13/2 O_2(g) \rightarrow 4CO_2(g)+5H_2O(l): \Delta_c H^{\odot} = -2875.84 \text{ kJ mol}^{-1}$ 

The general combustion equation for any alkane is



$$\mathbf{C}_{n}\mathbf{H}_{2n\times2} + \left(\frac{3n+1}{2}\right)\mathbf{O}_{2} \ \ \rightarrow \ \ \mathbf{n}\mathbf{C}\mathbf{O}_{2} + \ (n+1)\ \mathbf{H}_{2}\mathbf{O}$$

• During incomplete combustion with insufficient amount of air or dioxygen, carbon black is formed which is used in the manufacture of ink, printer ink, black pigments and as filters.

```
CH_4(g)+O_2(g) \xrightarrow{\text{Incomplete}} C(s)+2H_2O(l)
```

**3.** Controlled oxidation: On heating with a regulated supply of dioxygen or air at high pressure and in the presence of suitable catalysts give a variety of oxidation products.

(i) 
$$2CH_4 + O_2 \xrightarrow{Cu/523K/100atm} 2CH_3OH$$
  
Methanol  
(ii)  $CH_4 + O_2 \xrightarrow{Mo_2O_3} HCHO + H_2O$   
Methanal  
(iii)  $2CH_3CH_3 + 3O_2 \xrightarrow{(CH_3COO)_2Mn} 2CH_3COOH + 2H_2O$   
Ethanoic acid

**IV.** Ordinarily alkanes resist oxidation but alkanes having tertiary H atom can be oxidized to corresponding alcohols by potassium permanganate.

```
(CH_3)_3 CH \xrightarrow{KMnO_4} (CH_3)_3 COH
2-Methylpropane 2-Methylpropan-2-ol
```

4. Isomerization

$$\begin{array}{c} \operatorname{CH}_{3}(\operatorname{CH}_{2})_{4}\operatorname{CH}_{3} \xrightarrow{\operatorname{Anby, AlCl}_{3}/\operatorname{HCl}} \\ n\operatorname{-Hexane} \\ \operatorname{CH}_{3}\operatorname{CH}_{-}(\operatorname{CH}_{2})_{2}\operatorname{-CH}_{3}\operatorname{+CH}_{3}\operatorname{CH}_{2}\operatorname{-CH}_{-}\operatorname{CH}_{2}\operatorname{-CH}_{3} \\ | & | \\ \operatorname{CH}_{3} & | \\ 2\operatorname{-Methylpentane} & \operatorname{CH}_{3} \\ \end{array}$$

5. Aromatization: n-Alkanes having six or more carbon atoms get dehydrogenated and cyclised to benzene and its homologues. This reaction is known as aromatization or reforming.

$$\begin{array}{c} \overset{CH_3}{\underset{l}{\overset{l}{\underset{l}{\underset{cH_2}{\overset{l}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\underset{cH_2}{\overset{cH_2}{\underset{cH_2}{\atopcH_2}{\underset{cH_2}{\atop{cH_2}{\atopcH_2}{\underset{cH_2}{\underset{cH_2}{\atopcH_2}{\underset{cH_2}{\underset{cH_2}{\underset{cH_2}{\atopcH_2}{\underset{cH_2}{\atopcH_2}{\underset{cH_2}{\atopcH$$

**6. Reaction with steam;** this method is used for industrial preparation of dihydrogen gas.

 $CH_4 + H_2O \xrightarrow{NI} CO + 3H_2$ 

7. Pyrolysis: Decomposition of higher alkanes into smaller fragments by the application of heat is called **pyrolysis or cracking.** 



$$C_{g}H_{14} \xrightarrow{773K} C_{g}H_{12} + H_{2}$$
  
 $C_{4}H_{8} + C_{2}H_{6}$   
 $\rightarrow C_{3}H_{6} + C_{2}H_{4} + CH_{4}$ 

- Pyrolysis is a free radical reaction.
- Pyrolysis of dodecane, a constituent of kerosene oil.

 $C_{12}H_{26} \xrightarrow{Pt/Pd/NI} C_7H_{16} + C_5H_{10} + other products$ Dodecane Heptane Pentene

# > Conformations:

- Spatial arrangements of atoms which can be converted into one another by rotation around a C-C single bond are called **conformations or conformers or rotamers.**
- Rotation around a C-C single bond is hindered by a small energy barrier of 1-20 kJ mol<sup>-1</sup> due to weak repulsive interaction between the adjacent bonds. Such a type of repulsive interaction is called torsional strain

# **Conformations** of ethane:

- Rotation results in an infinite number of spatial arrangements of hydrogen atoms attached to one carbon atom with respect to the hydrogen atoms attached to the other carbon atom. These are called **conformational isomers.**
- Conformation in which hydrogen atoms attached to two carbons are as closed together as possible is called eclipsed conformation and the other in which hydrogens are as far apart as possible is known as the staggered conformation. Any other intermediate conformation is called a skew conformation.
- In all the conformations, the bond angles and the bond lengths remain the same.
- Eclipsed and the staggered conformations can be represented by Sawhorse and Newman projections

### 1. Sawhorse projections

- The molecule is viewed along the molecular axis.
- Central C C bond represented by a longer straight line.
- The front carbon is shown at the lower end & rear carbon is shown at the upper end.
- Each carbon has three lines inclined at an angle of 120° to each other.



Sawhorse projections of ethane





### 2. Newman projections

- The molecule is viewed at the C–C bond head on.
- The carbon atom nearer to the eye is represented by a point. Three hydrogen atoms attached to the front carbon atom are shown by three lines drawn at an angle of 120° to each other.
- The rear carbon atom (the carbon atom away from the eye) is represented by a circle and the three hydrogen atoms are shown attached to it by the shorter lines drawn at an angle of 120° to each other.

### Relative stability of conformations:

- Staggered forms have minimum repulsive forces, minimum energy and maximum stability & eclipsed forms have minimum repulsive forces, more energy and thus have lesser stability.
- Magnitude of torsional strain depends upon the angle of rotation about the C–C bond. This angle is also called dihedral **angle or torsional angle**.
- In ethane, the staggered form has the least torsional strain and the eclipsed form, the maximum torsional strain
- The energy difference between the two extreme forms is of the order of  $12.5 \text{ kJ mol}^{-1}$
- It has not been possible to separate and isolate different conformational isomers of ethane.

### > <u>Alkenes</u>

- Alkenes are unsaturated hydrocarbons containing at least one double bond & also known as **olefins (oil forming).**
- General formula is C<sub>n</sub>H<sub>2n</sub>
- Structure of Double Bond
  - Alkenes consists of one strong sigma ( $\sigma$ ) bond (bond enthalpy about 397 kJ mol<sup>-1</sup>) due to head-on overlapping of sp<sup>2</sup> hybridised orbitals and one weak pi ( $\pi$ ) bond (bond enthalpy about 284 kJ).
  - Alkenes are easily attacked by reagents or compounds which are in search of electrons due to weak pi bonds. Such reagents are called **electrophilic reagents**





Orbital picture of ethene showing formation of (a)  $\pi$ -bond, (b)  $\pi$ -cloud and (c) bond angles and bond lengths

#### Nomenclature:

- Numbering of the chain is done from the end which is nearer to the double bond.
- The suffix 'ene' replaces 'ane' of alkanes.
- First member of the alkene series is (:CH<sub>2</sub>) known as **methene** but has a very short life.
- First stable member of alkene series is C<sub>2</sub>H<sub>4</sub> known as **ethylene** (common) or **ethene** (IUPAC)

```
StructureIUPAC nameCH_3 - CH = CH_2PropeneCH_3 - CH_2 - CH = CH_2But - 1 - eneCH_3 - CH = CH - CH_3But - 2 - eneCH_2 = CH - CH = CH_2Buta - 1,3 - dieneCH_2 = C - CH_32 - Methylprop - 1 - eneCH_3CH_3CH_2 = CH - CH - CH_33 - Methylbut - 1 - ene
```

- Isomerism
  - Alkenes show both structural isomerism and geometrical isomerism.

#### Structural isomerism

• Alkenes higher than propene have different structures

#### Structure of C<sub>4</sub>H<sub>8</sub>:

III. 1 1. 1 2 3 4 II. 1 2 3 4 2 3  $CH_2 = CH - CH_2 - CH_3$  $= C - CH_{n}$ CH, - CH = CH - CH, CH. But-1-ene But-2-ene CH<sub>1</sub> (C4H8)  $(C_4H_8)$ 2-Methyprop-1-ene (C,H.)

• Structures I and III, and II and III are the examples of **chain isomerism** whereas structures I and II are **position isomers**.



### **\*** Geometrical isomerism:

- Restricted rotation of atoms or groups around the doubly bonded carbon atoms gives rise to different geometries of such compounds. The stereoisomers of this type are called **geometrical isomers.**
- The isomer in which two identical atoms or groups lie on the same side of the double bond is called **cis-isomer &** if lie on the opposite sides of the double bond is called **trans isomer.**
- These isomers differ in their properties like melting point, boiling point, dipole moment, solubility etc.
- Geometrical or cis-trans isomers of but-2-ene are represented below



- Cis form of alkene is found to be more polar than the trans.
- Trans isomer has higher melting point than the cis form.
- Geometrical or cis-trans isomerism is also shown by alkenes of the types XYC = CXZ and XYC = CZW

#### Preparation

- 1. From alkynes:
- Partial reduction of alkynes by Partially deactivated palladised charcoal is known as Lindlar's catalyst, gives cis alkene.
- Reduction with sodium in liquid ammonia forms trans alkenes.



- 2. From alkyl halides:
- Alkyl halides (R-X) on heating with alcoholic potash eliminate one molecule of halogen acid to form alkenes. This reaction is known as **dehydrohalogenation i.e.**, **removal of halogen acid.**
- This is example of  $\beta$ -elimination reaction, since hydrogen atom is eliminated from the  $\beta$  carbon atom



$$\begin{array}{c} H & H \\ H - C - C - C - H & \xrightarrow{\text{alc. KOH}} & H \\ I & I \\ H & X \end{array} \xrightarrow{H} C = C \\ H & H \end{array}$$

- Rate of reaction for halogens is: **Iodine > Bromine > Chlorine**
- Rate of reaction alkyl groups is: tert > secondary > primary

### 3. From vicinal dihalides (dehalogenation)

• Dihalides in which two halogen atoms are attached to two adjacent carbon atoms are known as **vicinal dihalides.** 

$$CH_2Br-CH_2Br+Zn\longrightarrow CH_2=CH_2+ZnBr_2$$
  
 $CH_3CHBr-CH_2Br+Zn\longrightarrow CH_3CH=CH_2+ZnBr_2$ 

### 4. From alcohols by acidic dehydration:

 Water molecule is eliminated from the alcohol molecule in the presence of an acid, this reaction is known as acidic dehydration of alcohols (β-elimination reaction).

$$\begin{array}{ccc} H & H \\ H - C & - C \\ I & I \\ H & OH \\ E thanol \end{array} \xrightarrow{\text{Conc. } H_2 SO_4} CH_2 = CH_2 + H_2O \\ CH_2 = CH_2$$

#### > Properties

- Physical properties
  - The first three members are gases, the next fourteen are liquids & the higher ones are solids.
  - Ethene is a colourless gas with a faint sweet smell. All Other alkenes are colourless and odourless, insoluble in water but fairly soluble in non-polar solvents like benzene, petroleum ether.
  - They show a regular increase in boiling point with increase in size i.e., every CH<sub>2</sub> Group added increases boiling point by 20–30 K.
  - Straight chain alkenes have higher boiling point than isomeric branched chain compounds.

### Chemical properties

- Addition of dihydrogen: Alkenes add up one molecule of dihydrogen gas in the presence of finely divided nickel, palladium or platinum to form alkanes.
- Addition of halogens:
  - Halogens like bromine or chlorine add up to alkene to form vicinal dihalides. Iodine does not show addition reaction under normal conditions.
  - Reddish orange colour of bromine solution in carbon tetrachloride is discharged when bromine adds up to an unsaturation site. This reaction is used as a test for unsaturation.
  - It is an electrophilic addition reaction involving cyclic halonium ion formation.



- 3. Addition of hydrogen halides: It is an electrophilic addition reaction.
  - Hydrogen halides (HCl, HBr, HI) add up to alkenes to form alkyl halides.
  - Order of reactivity of the hydrogen halides is HI > HBr > HCl.
    - ✤ Addition reaction of HBr to symmetrical alkenes

$$CH_2 = CH_2 + H - Br \longrightarrow CH_3 - CH_2 - Br$$

$$\begin{array}{c} \mathrm{CH}_3 - \mathrm{CH} = \mathrm{CH} - \mathrm{CH}_3 + \mathrm{HBr} \longrightarrow \mathrm{CH}_3 - \mathrm{CH}_2 - \mathrm{CH}\mathrm{CH}_3 \\ & | \\ \mathrm{Br} \end{array}$$

• Addition reaction of HBr to unsymmetrical alkenes (Markovnikov Rule)

$$CH_{3}-CH=CH_{2}+H-Br \longrightarrow I \qquad \begin{array}{c} CH_{3}-CH-CH_{3} \\ Br \\ 2-Bromopropane \\ II \\ -CH_{3}-CH_{2}-CH_{2}-Br \\ 1-Bromopropane \end{array}$$

**Markovnikov rule:** The negative part of the addendum (adding molecule) gets attached to that carbon atom which possesses a lesser number of hydrogen atoms. According to rule, product I i.e., 2-bromopropane is major

**Mechanism:** Hydrogen bromide provides an electrophile, H<sup>+</sup>, which attacks the double bond to form carbocation as shown below:

$$H_{3}C - CH = CH_{2} + H - Br$$

$$\downarrow H^{+}$$

$$\downarrow H^{+}$$

$$\downarrow H^{-}$$

$$\downarrow$$

- I. The secondary carbocation (b) is more stable than the primary carbocation (a), therefore, the former predominates because it is formed at a faster rate.
- II. The carbocation (b) is attacked by Br<sup>-</sup> ionto form the product as follows:

$$\overrightarrow{Br} \downarrow$$
  
 $H_3C-CH-CH_3 \longrightarrow H_3C-CH-CH_3$   
 $Br$   
2-Bromopropane  
(major product)

- Anti Markovnikov addition or peroxide effect or Kharash effect
- In the presence of peroxide, addition of HBr to unsymmetrical alkenes like propene takes place contrary to the Markovnikov rule. This reaction is known as **peroxide or Kharash effect** or addition reaction **anti to Markovnikov rule.**



$$CH_3 - CH = CH_2 + HBr \xrightarrow{(C_6H_5CO)_2O_2} CH_3 - CH_2$$
  
|  
 $CH_2Br$   
1-Bromopropane

> Mechanism: Peroxide effect proceeds via free radical chain mechanism as given below:

(i)  $O O C C_{6}H_{5} - C - O - O - C - C_{6}H_{5} \xrightarrow{\text{Homolysis}} 2C_{6}H_{5} - C - O \xrightarrow{O} 2C_{6}H_{5} + 2CO_{2}$ Benzoyl peroxide (ii)  $\dot{C}_{6}H_{5} + H - Br \xrightarrow{\text{Homolysis}} C_{6}H_{6} + \dot{B}r$ (iii)  $CH_{3} - CH = CH_{2} + \dot{B}r$ (a)  $CH_{3} - \dot{C}H - \dot{C}H_{2}$ (less stable primary free radical) (more stable secondary free radical) (iv)  $CH_{3} - \dot{C}H - CH_{2}Br + H - Br \xrightarrow{\text{Homolysis}} CH_{3} - CH_{2} - CH_{2}Br + \dot{B}r$ (major product)

- Peroxide effect happens only with HBr but not with HCl and Hl, because the H–Cl bond being stronger than H–Br bond, is not cleaved by the free radical, whereas the H–I bond is weaker and iodine free radicals combine to form iodine molecules instead of adding to the double bond.
- **4.** Addition of sulphuric acid: Cold concentrated sulphuric acid adds to alkenes in accordance with Markovnikov rule to form alkyl hydrogen sulphate by the electrophilic addition reaction

$$CH_{2} = CH_{2} + H - O - \bigcup_{O}^{O} O - H \longrightarrow CH_{3} - CH_{2} - O SO_{2} - OH \text{ or } C_{2}H_{5}HSO_{4}$$
  
Ethyl hydrogen sulphate  
$$CH_{3} - CH = CH_{2} + HOSO_{2}OH \longrightarrow CH_{3} - CH - CH_{3}$$
  
$$I OSO_{2}OH (Propyl hydrogen sulphate)$$

5. Addition of water: Follow the Markovnikov rule.

$$\begin{array}{ccc} CH_{3} & C = CH_{2} + H_{2}O & \xrightarrow{H'} & C - CH_{3} \\ & & & CH_{3} & CH_{3} \\ & & & CH_{3} & OH \\ \hline & & & & CH_{3} & OH \\ \hline & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & & CH_{3} & OH \\ \hline & & & & & CH_{3} & OH \\$$

- 6. Oxidation:
  - (a) Alkenes on reaction with cold, dilute, aqueous solution of potassium permanganate **(Baeyer's reagent)** produce vicinal glycols.
  - Decolourisation of KMnO<sub>4</sub> solution is used as a **test for unsaturation**.



(b) Acidic potassium permanganate or acidic potassium dichromate oxidises alkenes to ketones and/or acids depending upon the nature of the alkene and the experimental conditions.

 $(CH_3)_2C=CH_2 \xrightarrow{KMnO_3/H'} (CH_3)_2C=O + CO_2+H_2O$ 2-Methlypropene Propan-2-one

CH<sub>3</sub>−CH=CH−CH<sub>3</sub> KMnO<sub>4</sub>/H<sup>+</sup>→2CH<sub>3</sub>COOH But-2-ene Ethanoic acid

#### 7. Ozonolysis:

This reaction is highly useful in detecting the position of the double bond in alkenes or other unsaturated compounds.



#### 8. Polymerisation:

Polythene is obtained by the combination of a large number of ethene molecules at high temperature, high pressure and in the presence of a catalyst. The large molecules thus obtained are called **polymers**. This reaction is known as **polymerisation**. The simple compounds from which polymer are made are called **monomers** 

$$n(CH_{2}=CH_{2}) \xrightarrow{\text{High temp./pressure}}_{Catalyst} \xrightarrow{-(CH_{2}-CH_{2})_{n}}_{Polythene}$$

$$n(CH_{3}-CH=CH_{2}) \xrightarrow{\text{High temp./pressure}}_{Catalyst} \xrightarrow{-(CH-CH_{2})_{n}}_{|}$$

$$CH_{3}$$

$$Polypropene$$

#### > <u>Alkynes</u>

- Containing at least one triple bond between two carbon atoms. General formula is  $C_nH_{2n-2}$ .
- First stable alkyne is ethyne which is popularly known as acetylene.
- Acetylene is used for arc welding purposes in the form of oxyacetylene flame obtained by mixing acetylene with oxygen gas.

#### Nomenclature and Isomerism

• In IUPAC system, replacing ' ane ' by the suffix ' yne '



Value of n	Formula	Structure	Common name	IUPAC name
2	C <sub>2</sub> H <sub>2</sub>	H-C=CH	Acetylene	Ethyne
3	C <sub>3</sub> H <sub>4</sub>	CH <sub>3</sub> -C=CH	Methylacetylene	Propyne
4	C,H,	CH, CH, -C=CH	Ethylacetylene	But-1-yne
4	C <sub>4</sub> H <sub>6</sub>	CH3-C=C-CH3	Dimethylacetylene	But-2-yne

- Two possible structures for butyne (i) but-1-yne and (ii) but-2-yne. This are position isomers
- Possible Structure for alkyne  $C_5H_8$ Structure IUPAC name I.  $H_C^1 \equiv \stackrel{2}{C} \stackrel{3}{-} \stackrel{4}{-} \stackrel{5}{-} CH_2 \stackrel{-}{-} CH_2 \stackrel{-}{-} CH_3$  Pent-1-yne II.  $H_3^1 \stackrel{2}{-} \stackrel{3}{-} \stackrel{4}{-} \stackrel{5}{-} CH_3$  Pent-2-yne III.  $H_3^1 \stackrel{2}{-} \stackrel{-}{-} CH_2 \stackrel{-}{-} CH_3$  Pent-2-yne III.  $H_3^1 \stackrel{-}{-} CH_3 \stackrel{-}{-} CH_3 \stackrel{-}{-} CH_3$  Pent-2-yne III.  $H_3^1 \stackrel{-}{-} CH_3 \stackrel{-}{-} CH_3 \stackrel{-}{-} CH_3$  Pent-2-yne
- Structures I and II are position isomers and structures I and III or II and III are chain isomers.
- Structure of Triple Bond
  - Strength of  $C \equiv C$  bond (bond enthalpy 823 kJ mol<sup>-1</sup>) is more than those of C=C bond (bond enthalpy 681 kJ mol<sup>-1</sup>) and C - C bond (bond enthalpy 348 kJ mol<sup>-1</sup>)
  - The C = C bond length is shorter (120 pm) than those of C = C (133 pm) and C-C (154 pm)



Orbital picture of ethyne showing (a) sigma overlaps (b) pi overlaps.

#### **♦** Preparation

1. From calcium carbide:

 $\begin{array}{cccccccc} CaCO_3 & \stackrel{\Delta}{\longrightarrow} & CaO & + & CO_2 \\ CaO + 3C & \longrightarrow & CaC_2 & + & CO \\ Calcium & carbide \\ CaC_2 + & 2H_2O & \longrightarrow & Ca(OH)_2 + & C_2H_2 \end{array}$ 

2. From vicinal dihalides:



### Properties

#### **Physical properties:**

- All alkynes are colourless. Ethyene has a characteristic odour. Other members are odourless.
- Alkynes are weakly polar in nature. They are lighter than water and immiscible with water but soluble in organic solvents like ethers, carbon tetrachloride and benzene.
- Their melting point, boiling point and density increase with increase in molar mass.

#### Chemical properties:

#### A. Acidic character of alkyne:

- Due to the maximum percentage of s character (50%), the sp hybridised orbitals have highest electronegativity; hence, these attract the shared electron pair of the C-H bond & hydrogen atoms can be liberated as protons.
- Hence hydrogen atoms of ethyne attached to triply bonded carbon atoms are acidic in nature.

$$\begin{split} HC &= CH + Na \rightarrow HC \equiv C^{-}Na^{+} + \frac{1}{2}H_{2} \\ & Monosodium \\ ethynide \\ HC &= C^{-}Na^{+} + Na \rightarrow Na^{+}C^{-} \equiv C^{-}Na^{+} + \frac{1}{2}H_{2} \\ & Disodium \ ethynide \\ CH_{3} - C &\equiv C - H + Na^{+}NH_{2}^{-} \rightarrow CH_{3} - C \equiv C^{-}Na^{+} + NH_{3} \\ & Sodium \ propynide \end{split}$$

- Trend in their acidic behaviour
  - i)  $HC \equiv CH > H_2C = CH_2 > CH_3 CH_3$
  - ii)  $HC = CH > CH_3 C = CH >> CH_3 C = C CH_3$

#### **B.** Addition reactions:

• Formation of the addition product takes place according to the following steps.

$$-C = C - + H - Z \xrightarrow{H^+} -C = C - + :\overline{Z} \longrightarrow -C = C - + :\overline{Z} \longrightarrow -C = C - + :\overline{Z} \longrightarrow -C = C - -C - -C = C - -C =$$

#### Vinylic cation

- The addition product formed depends upon the stability of vinylic cation.
- Addition in unsymmetrical alkynes takes place according to Markovnikov rule.
- i. Addition of dihydrogen:

$$HC = CH + H_2 - \frac{Pt/Pd/Ni}{H_2C} = CH_2 - \frac{H_2}{CH_3} - CH_3$$

ii. Addition of halogens:



$$\begin{array}{c} \operatorname{CH}_3-\operatorname{C}=\operatorname{CH}+\operatorname{Br}-\operatorname{Br}\longrightarrow [\operatorname{CH}_3\operatorname{CBr}=\operatorname{CHBr}]\\ 1.2\text{-Dibromopropene}\end{array} \xrightarrow{\begin{array}{c} \operatorname{Br}_2\\ \longrightarrow\\ \end{array}} \begin{array}{c} \operatorname{Br}_2\\ \longrightarrow\\ \operatorname{CH}_3-\operatorname{C}-\operatorname{CH}\\ & 1\\ & 1\\ \end{array}$$

1,1,2,2-Tetrabromopropane

#### iii. Addition of hydrogen halides:

Two molecules of hydrogen halides (HCl, HBr,HI) add to alkynes to form **gem dihalides** (in which two halogens are attached to the same carbon atom)

$$CH_3 - C = CH + H - Br \longrightarrow [CH_3 - C = CH_2] + H - Br \longrightarrow CH_3 - C - CH_3$$
  
Br Br Br 2-Bromopropene 2,2-Dibromopropane

#### iv. Addition of water:

- Like alkanes and alkenes, alkynes are also immiscible and do not react with water.
- However, one molecule of water adds to alkynes on warming with mercuric sulphate and dilute sulphuric acid at 333 K to form carbonyl compounds

$$\begin{array}{c} CH_{3}-C=CH+H-OH \xrightarrow{Hg^{a^{*}}/H^{*}} CH_{3}-C=CH_{2}\\ Propyne & O-H\\ Isomerisation \\ CH_{3}-C-CH_{3}\\ \parallel \end{array}$$

#### v. Polymerization

#### (a) Linear polymerisation:

linear polymerisation of ethyne produce polyacetylene or polyethyne containing repeating units of (CH = CH – CH = CH) and can be represented as —(CH = CH – CH = CH)n—

O Propanone

• Under special conditions, this polymer conducts electricity. Thin film of polyacetylene can be used as electrodes in batteries.

#### (b) Cyclic polymerisation:

• This is the best route for entering from aliphatic to aromatic compounds.



#### > <u>Aromatic Hydrocarbon</u>

- These hydrocarbons are also known as 'arenes'.
- Since most of them possess pleasant odour (Greek; aroma meaning pleasant smelling), the class of compounds was named as ' **aromatic compounds'.**



• Aromatic compounds containing benzene ring are known as **benzenoids and** those not containing a benzene ring are known as **non-benzenoids** 



#### > Nomenclature and Isomerism

Three different position isomers 1, 2 or 1, 6 are known as the ortho (o -), the 1, 3 or 1, 5 as meta (m -) and the 1, 4 as para (p -) disubstituted compounds.



### Structure of Benzene:

• Kekulé in 1865 proposed a structure for benzene & suggested the concept of oscillating nature of double bonds in benzene as given below.



- All the six carbon atoms are  $sp^2$  hybridized & contain one unhybridized p orbital perpendicular to the plane of the ring to form a  $\pi$  bond by lateral overlap
- There are two equal possibilities of forming three π bonds by overlap of p orbitals of C1-C2, C3-C4, C5-C6 or C2-C3, C4-C5, C6-C1 respectively



Resonance and stability of benzene
 Aromaticity: Benzene was considered as the parent 'aromatic' compound.
 Characteristics for a compound to be aromatic.
 i. Planarity



ii. Complete delocalisation of the  $\pi$  electrons in the ring

iii. Presence of  $(4n + 2) \pi$  electrons in the ring where n is an integer (n = 0, 1, 2,...). This is often referred to as Huckel Rule.





Properties
 Physical properties



- These are non- polar molecules & have characteristic aroma. Ex naphthalene balls are used in toilets and for preservation of clothes because of the unique smell of the compound and the moth repellent property.
- These are immiscible with water but are readily miscible with organic solvents.
- They burn with sooty flame.

### > Chemical properties

- Electrophilic substitution reactions:
  - I. Nitration:



V. Friedel-Crafts acylation reaction:





# Mechanism of electrophilic substitution reactions (a) Generation of electrophile E<sup>⊕</sup>

Anhydrous AlCl<sub>3</sub>, being a Lewis acid helps in generation of the electrophile  $Cl^{\oplus}$ ,  $R^{\oplus}$ ,  $RC^{\oplus}O$  by combining with the attacking reagent.

In nitration, electrophile, NO<sub>2</sub><sup>+</sup> is produced by gaining proton (from sulphuric acid) sulphuric acid serves as an acid and nitric acid as a base.



(b) Formation of Carbocation (arenium ion): Attack of electrophile results in the formation of  $\sigma$ -complex or arenium ion in which one of the carbon is sp<sup>3</sup> hybridised.



sigma complex (arenium ion)

The arenium ion gets stabilised by resonance:



The Sigma complex loses its aromaticity because delocalisation of electrons stops at sp<sup>3</sup> carbon.

(c) Removal of proton: To restore the aromatic character, σ -complex releases proton from sp<sup>3</sup> hybridised carbon on attack by [AlCl<sub>4</sub>]<sup>-</sup> (in case of halogenation, alkylation and acylation) and [HSO<sub>4</sub>]<sup>-</sup> (in case of nitration).







Addition reactions



• **Combustion:** When heated in air, benzene burns with sooty flame producing CO<sub>2</sub> and H<sub>2</sub>O.

 $C_6H_6+\frac{15}{2}O_2\rightarrow 6CO_2+3H_2O$ 

General combustion reaction for any hydrocarbon may be given by

 $C_x H_y + (x + \frac{y}{4}) O_2 \rightarrow x CO_2 + \frac{y}{2} H_2O$ 

- > Directive influence of a functional group in monosubstituted benzene
  - Ortho and para directing groups:
  - Phenol is resonance hybrid of following structures:



- electron density is more on o- and p- positions. Hence, the substitution takes place mainly at these positions.
- -I effect of -OH group also operates due to which the electron density is slightly reduced, but the overall electron density increases due to resonance.
- -OH, -NH<sub>2</sub>, -NHR, -NHCOCH<sub>3</sub>, -OCH<sub>3</sub>, -CH<sub>3</sub>, -C<sub>2</sub>H<sub>5</sub>, etc group activates the benzene ring for the attack by an electrophile.
- In aryl halides, halogens are moderately deactivating, because of their strong –I effect, overall electron density on benzene ring decreases. It makes further substitution difficult. 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.
- > Meta directing group:



- The groups direct the incoming group to meta position.
- Meta directing groups are -NO<sub>2</sub>, -CN, -CHO, -COR, -COOH, -COOR, -SO<sub>3</sub>H, etc.
- Nitro group reduces the electron density in the benzene ring due to its strong –I effect.



- The overall electron density on the benzene ring decreases making further substitution difficult, therefore these groups are also called 'deactivating groups'.
- The electron density on o and p position is comparatively less than that at meta position. Hence electrophile attacks on comparatively electron rich meta position resulting in meta substitution.

#### Carcinogenicity and Toxicity

- Benzene and polynuclear hydrocarbons containing more than two benzene rings fused together are toxic and said to possess cancer producing (carcinogenic) properties.
- These are formed on incomplete combustion of organic materials like tobacco, coal and petroleum.
- They enter into the human body and undergo various biochemical reactions and finally damage DNA and cause cancer. Some of the carcinogenic hydrocarbons are given below (see box).



1.2-Benzanthracene



1,2-Benzpyrene

1.2.5.6-Dibenzanthracene

3-Methylcholanthrene





# **Environmental Chemistry**

- Elements of environment: Atmosphere, Lithosphere, Hydrosphere (Non-Living components), Biosphere
- Environmental pollution: Air, land and water pollution
- A substance responsible for pollution, is called as pollutant

### > Atmosphere

- Height of atmosphere: 500 km
- Approx. mass of atmosphere:  $4.5-5 \times 10^{15}$  tons
- Composition of dry air at sea level:
  - ✤ Major components: Nitrogen, oxygen, water vapour
  - Minor components: Argon, Carbon dioxide
  - ✤ Trace components: Neon, Helium, methane etc.

Region	Height (km)	<b>Temperature</b> ( <sup>0</sup> C)	Main constituents
Troposphere	0-11	15 to -56	O <sub>2</sub> , N <sub>2</sub> , CO <sub>2</sub> , H <sub>2</sub> O
Stratosphere	11-50	-56 to -2	<b>O</b> <sub>3</sub>
Mesosphere	50-90	-2 to -92	$O_2^+, NO^+$
Thermosphere	90-500	-92 to 1200	$O_2^+, O^+, NO^+$

• Major regions of the atmosphere:

### > Types of pollutants

- Primary and secondary pollutants:
  - Primary pollutants: Those which after their formation enter the environment and remain as such. Ex.: NO, NO<sub>2</sub>, SO<sub>2</sub>
  - Secondary pollutants: The harmful material which are formed by chemical reaction between primary pollutants in the atm. Ex.: Hydrocarbon + Oxide of nitrogen compound
- Bio degradable and Non bio degradable pollutants:
  - Bio degradable pollutants: Materials (eg. cow dungs) which are easily decomposed but in excess in environment, they do not undergo degradation completely and thus become pollutant.
  - Non bio degradable pollutants:- Materials (eg. Hg, Al, DDT) which do not undergo degradation (or degrade very slowly) but even in very small amount in the environment is very harmful. They may react with other compounds present in the environment and produce more toxic compound.

# > Tropospheric gaseous air pollutants

### **Oxides of carbon:**

### **Carbon Monoxide**

- Colorless, odourless, tasteless, non-irritating gas, sparingly soluble in water
- Fatal above 100 ppm (silent killer)
- Major sources: incomplete combustion of fossil fuels, cigarette smoke, coal gas (5-10%), water gas (30-40%), forest fire, volcanic eruptions, marine algae, marine siphmophone



# > Poisoning:

- $Hb + 4O_2 \rightleftharpoons HbO_8$  oxy-haemoglobin (formed when oxygen combines with blood)
- HbO<sub>8</sub> + CO ≓ HbCO+4O<sub>2</sub> carboxy-haemoglobin (when O in oxy-haemoglobin is replaced with CO)
- Oxygen carrying capacity of blood is decreased, leading to anoxia (oxygen starvation).
- Effects of anoxia: headache, dizziness, cardiac and pulmonary complications, improper growth of foetus in pregnant women.
- HbCO is 300 times more stable than HbO<sub>8</sub>.
- Poisoning cured by exposing the victim to oxygen under 2-2.5 atm. HbCO+4O<sub>2</sub>  $\rightleftharpoons$  HbO<sub>8</sub>+CO

# Carbon dioxide

- Colorless, odourless, 1.5 times heavier than air, non-poisonous (death in high CO<sub>2</sub> atmosphere caused by lack of oxygen leading to suffocation), does not support life.
- small amount of CO<sub>2</sub> is not harmful so not considered a pollutant.
- High amount of CO<sub>2</sub> causes global warming (it is a green house gas) and hence is a pollutant in large amount.
- Major sources: burning of fossil fuels, cultivation of soil, industrial manufacturing processes, decay of dead organisms, forest fire, volcanic eruptions, etc.
- Plants absorb CO<sub>2</sub> through photosynthesis and converts it into carbohydrates.
- Algae in oceans also absorb CO<sub>2</sub>
- Effect of CO<sub>2</sub>: Global warming (green house effect), maintaining pH of rain water at 5.6

# Oxides of sulphur.

# Sulph<mark>ur dioxide</mark>

- Colorless, suffocating smell (like that of burning sulphur), irritates the respiratory system and damages lungs
- Major sources: Burning fossil fuels, volcanic eruptions, H<sub>2</sub>S released in atmosphere is oxidised to SO<sub>2</sub>, roasting of sulphide ores.
- Effects of SO<sub>2</sub>:
- Poisonous to both plant and animal
- Small amount causes bronchitis, asthama, emphysema, irritation to the eyes,
- Discoloration of leaves on prolonged exposure (hampers formation of chlorophyll)
- Discoloration of fabrics, leather, paper etc.
- Reactions for acid rain

$$SO_{2} + \frac{1}{2}O_{2} \xrightarrow{hv} SO_{3}$$
$$SO_{2} + O_{3} \xrightarrow{hv} SO_{3} + O_{2}$$
$$SO_{3} + H_{2}O \rightarrow H_{2}SO_{4}$$

- > Oxides of nitrogen
  - Nitrogen combines with oxygen to form N<sub>2</sub>O (nitrous oxide), NO (nitric oxide), NO<sub>2</sub> (nitrogen dioxide), N<sub>2</sub>O<sub>3</sub> (dinitrogen trioxide), N<sub>2</sub>O<sub>4</sub> (dinitrogen tetraoxide), N<sub>2</sub>O<sub>5</sub> (dinitrogen pentoxide)
  - Major sources:



- ♦  $N_2 + O_2 \xrightarrow{\text{discharge}} NO$ . Theses reactions take place during thunderstorms and  $2NO + O_2 \rightarrow NO_2$ 
  - lightening
- Combustion of fuel at high temperature, N<sub>2</sub>O is produced by action of aerobic and anaerobic bacteria on nitrogenous fertilizers, bacterial decay of organic matter, NO<sub>2</sub> is released as by-product during manufacture of TNT.
- Effects : •
  - $\diamond$  NO, NO<sub>2</sub> destroy O<sub>3</sub> layer.
  - NO<sub>2</sub> causes extensive leaf-dropping in plants, higher concentration retards rate of photosynthesis
  - ◆ Inhalation of NO<sub>2</sub> for about 2 hours causes damage to lungs, liver and kidney
  - ✤ They react with hydrocarbons and sunlight to form photochemical smog

### > Hydrocarbons

- Produced due to incomplete combustion of fuel
- Carcinogenic in nature
- Harm plants by causing ageing, shading of leaves, flowers and twigs

#### Particulates in Atmospheric Pollution

- Particulates are the tiny solid or liquid particles suspended in air. These particles are usually individually invisible to the naked eye. Collectively, however, small particles often form a haze that restricts visibility.
- Particulates in the atmosphere may be viable or non-viable.
- Viable particulates: minute living organisms that are dispersed in atmosphere (bacteria, fungi, moulds, algae etc). Human beings are allergic to some of the fungi found in air. Fungi can also cause plant diseases.
- Non-viable particulates (particle size (0.001-100µm): formed either by the breakdown of larger materials or by the condensation of minute particles and droplets.
- Four types of non-viable particulates in the atmosphere: mists, smoke, fumes and dust.
  - ♦ Mists: particles of spray liquids (herbicides and insecticides) and the condensation of vapours in air.
  - Smoke: very small soot(carbon) particles produced by burning and combustion of organic matter. Oil smoke, tobacco smoke and carbon smoke are typical examples.
  - Fumes are condensed vapours: fumes of metals, metallurgical fumes and alkali fumes.
  - Dust: Particles produced during crushing, grinding and attribution of solid materials, ground limestone, sand tailings from floatation, pulverised coal, cement, fly ash and silica dust.
- Effects: •
  - ✤ Affects foetus by damaging the DNA.
  - ✤ Visibility decreases as the atmospheric particulate concentrations increase.
  - ♦ Mercury causes headache, nervousness, fatigue, breakdown of CNS (central nervous system)
  - ✤ Lead damages liver, kidneys, intestines, CNS. Prolonged exposure leads to accumulation in tissues causing anaemia



- Cadmium pollution from extraction of Zn and Cu causes lung irritation, vomiting and hypertension
- ✤ Major role in formation of photochemical smog
- coarser particles of size greater than 5 microns are likely to lodge in the nasal passages
- smaller ones are more likely to penetrate the lungs the rate of penetration being inversely proportional to the size of particles. A number of these fine particulates are carcinogens.
- Inhalation of small particles irritates the lungs and prolonged exposure causes 'scarring' or 'fibrosis' of the lung lining known as 'Pneumoconiosis'.
- Suspended particulate matter in the atmosphere effectively reduces the number of light rays reaching the surface of the earth and thus lowers the temperature of the earth. By blocking the sunlight, they contribute to a drop in the earth's temperature and by providing condensation nuclei; they contribute to increased fog and rain in cities.

### **Green House Effect:**

- Warming of earth due to remission of sun's energy absorbed by the earth. The remission of earth's energy is absorbed by CO<sub>2</sub> molecules and H<sub>2</sub>O vapour present near the earth's surface and then its radiation back to the earth, is called as green house effect. So the temp. of the earth is increased is called as global warming.
- Height of O<sub>3</sub> layer: 15-60 km from the surface (thickest layer of O<sub>3</sub> at 23 km)
- Height of CO<sub>2</sub> layer: 15 km from the surface
- Major green house gases and their sources:

Gas	Sources
Carbon dioxide (CO <sub>2</sub> )	1. Fossil fuel combustion (coal, oil,
	natural gas)
	2. Deforestation and land use changes
Methane (CH <sub>4</sub> )	1. Enteric fermentation in cattle and
	insects
	2. Biomass burning and garbage land fills.
	3. Leakage of gases from coal mines and
	natural gas.
	4. Rice paddies
	5. Swamps and tundra
Chloro fluoro carbon	1. plastic foams
	2. Refrigeration and air-conditioning
	3. Aerosols (spray propellants) CFC'
	4. Industrial solvents
Nitrous oxide (N <sub>2</sub> O)	1. Fertilizer use
	2. Fossil fuel combustion
	3. Biomass burning
	4. Changing land use



# Acid Rain:

- The rain containing H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> (and small amount of HCl) which are formed from the oxide of S and N<sub>2</sub> present in the air is called as acid rain. The pH of acid rain is 4-5. (pH of pure rain 5.6 due to dissolved CO<sub>2</sub> present as H<sub>2</sub>CO<sub>3</sub>)
- Formation of acid rain:
  - $N_2 + O_2 \xrightarrow{electrical \\ discharge} NO$
  - a.  $2NO + O_2 \rightarrow NO_2$  $NO_2 + H_2O \rightarrow HNO_3 + NO$

HNO<sub>3</sub> comes down with rain to earth.

b. 
$$SO_2 + \frac{1}{2}O_2 \xrightarrow{U.V} SO_3$$

 $SO_3 + H_2O \rightarrow H_2SO_4$ 

- c. Presence of H<sub>2</sub>S and Cl<sub>2</sub> in atmosphere
- Composition:  $H_2SO_4 = 60-70\%$ ,  $HNO_3 = 30-40\%$ , HCl = Very small amount.
- Aerosol particles of oxides or ammonium salts in rain drops result in wet deposition. SO<sub>2</sub> is absorbed directly on solid/liquid surfaces and is thus deposited by dry deposition
- Harmful effect of acid-rain:
  - ◆ It affects human nervous, respiratory and digestive system
  - It damages building and statues which contain marble, lime stone, state, mortar etc.

 $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$ 

- ✤ It damages iron and steel structure.
- It corrodes water pipe, so heavy metal (like Fe,Pb, Cu) get mixed with water which have toxic effect.
- ✤ The acid rain increases the acidity of the lake which is harmful to fishes.
- ✤ It damages the trees, plants and retards the growth of the plant.
- ✤ It increases the acidity of soil

# Smogs (Smoke + fog)

# **Classical smog:**

- Occurs in cool humid climate and present in the lower atmosphere
- Formed due to condensation of H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> on particulate matter from fuel combustion
- Decreases visibility, causes diseases like bronchitis, asthama, irritation to eyes, nose and throat
- When smog formed is from smoke of burning coal it is called reducing smog

# Photochemical smog:

- Occurs in warm, dry and sunny climate, in those cities which have very large populations and high vehicular density.
- Results from the action of sunlight on the nitrogen oxides and hydrocarbons produced by automobiles and factories along with smoke, dust and fog.
- Photochemical smog is an oxidising smog having a high concentration of oxidising agents whereas classical smog is chemically reducing smog with high concentrations of SO<sub>2</sub>.
- Formation of photochemical smog



Reactivehydrocarbons

$$\begin{array}{c} 0_{2} \text{ or atomic } 0 \\ RCH_{2}^{-} & \underbrace{O_{2}^{-}}_{RCH_{2}O_{2}^{-}} & \underbrace{NO}_{RCH_{2}O^{-}} + NO_{2} \\ (i) & (ii) & (iii) \\ \hline \\ RCH_{3}^{-} & HO^{-} & \underbrace{NO}_{HO_{2}^{-}} + RCHO \\ & & & & \\ NO_{2}^{-} & (iv) \\ \hline \\ RCHO & \underbrace{HO}_{Acyl}^{-} & \underbrace{RCO}_{2}^{-} & \underbrace{NO}_{2} \\ Redical & radical \\ \end{array}$$

- chemicals such as formaldehyde, acrolein and peroxyacetyl nitrate (PAN) that cause the eyes to water and burn and are harmful to the respiratory system.
- The brownish haze of photochemical smog is largely attributed to the brown colour or NO<sub>2</sub>.
- Effects of Photochemical Smog:
  - Pungent smelling, smog-produced by ozone is known to be toxic, causes coughing, wheezing, bronchial constriction
  - Peroxyacetyl nitrates (PAN) and aldehydes found in smog are eye irritants, has the highest toxicity to plants, attacking younger leaves and causing 'bronzing' and 'glazing' of their surfaces
  - Rubber has a high affinity for ozone and is cracked and aged by it, corrodes metals, building materials and painted surfaces
  - Smog also affects to cause damage to vegetation and reduction in plant growth and crop productivity.
- Control of Photochemical Smog:
  - ✤ Installation of efficient catalytic converters in the automobiles
  - Photochemical smog can also be suppressed by certain compounds, which act as free radical traps. When these compounds are sprayed in the atmosphere, they generate free radicals which readily combine with free radical precursors of photochemical smog.
  - Using reformed gasoline which contains about 10% fuel oxygenates (methyl tert. Butyl ether) which makes the fuel burn more efficiently.
  - Plants like Juniparus, Quercus, Pyrus, Vitis and Pinus metabolise nitrogen oxide

### Stratospheric Pollution

### Formation of ozone layer

In the stratosphere (11-50 km), the  $O_2$  is partially converted into  $O_3$ . Now at an altitude of 25-30 km, we have a layer in which the conc. of  $O_3$  is 10 ppm. It absorbs all radiation having wavelength less than 0.4 micron

step (I):  $O_2 \xrightarrow{hv} O^{\bullet} + O^{\bullet}$ 

step (II):  $O_2 + O^{\bullet} \xrightarrow{hv} O_3$ . Heat is also given out from this reaction which warm up stratosphere.

 $O_3 \xrightarrow{UV} O_2 + O^{\bullet}$  In this way the O<sub>3</sub> cycle is completed in this region.



### Depletion of ozone layer

NO and CFC are responsible for depletion of O3 layer.

a) NO (Nitric oxide) : NO +  $O_3 \rightarrow NO_2 + O_2$ 

$$NO_2 + O \rightarrow NO + O_2$$

Thus, no NO is consumed but O3 gets depleted.

b) Chlorofluoro carbons (CFC) or freons:

```
CF_2CI_2 \xrightarrow{hv} CF_2CI^{\bullet} + CI^{\bullet}CFCI_3 \xrightarrow{hv} CFCI_2^{\bullet} + CI^{\bullet}
```

The reactive chlorine atoms then destroy the ozone layer through the following sequence of reaction. Which are repeated because chlorine atom are regenerated in the second reaction.

Reaction.  $Cl^{\bullet} + O_3 \rightarrow ClO^{\bullet} + O_2$ 

 $CIO^{\circ} + O^{\circ} \rightarrow CI^{\circ} + O_{2}$ 

one molecule of CFC can destroy more than  $100,00 \text{ O}_3$  molecules in the stratosphere. Ozone concentration is measured in Dobson units, each corresponding to  $2.69 \times 10^{16}$  ozone molecules per cm<sup>2</sup>

### **Effect** of depletion of O<sub>3</sub> layer

- damage the cornea and lens of the eyes.
- affect the plant proteins so reduce the generation of chlorophyll.
- Upset the heat balance of the earth.
- Degradation of immune system
- Various forms of skin cancer
- Affects growth of phytoplankton Replace usual CFCs with HCFC-123 (CHCl<sub>2</sub>CF<sub>3</sub>) and HFC-134 (CH<sub>2</sub>FCF<sub>3</sub>)

### > Ozone hole

In summer

 $\text{CIO}^{\bullet}_{(g)} + \text{NO}_{2(g)} \rightarrow \text{CIONO}_{2(g)}$  &  $\text{CI}^{\bullet}_{(g)} + \text{CH}_{4}(g) \rightarrow \text{CH}_{3}^{\bullet}_{(g)} + \text{HCl}_{(g)}$ 

In winter, on polar stratospheric clouds

 $\mathsf{CIONO}_{2(g)} + \mathsf{H}_2\mathsf{O}_{(g)} \rightarrow \mathsf{HOCl}_{(g)} + \mathsf{HNO}_{3(g)} \qquad \& \qquad \mathsf{CIONO}_{2(g)} + \mathsf{HCl}_{(g)} \rightarrow \mathsf{Cl}_{2(g)} + \mathsf{HNO}_{3(g)}$ 

In spring

 $HOCl_{(g)} \xrightarrow{UV} OH^{\bullet}_{(g)} + Cl^{\bullet}_{(g)}$  &  $Cl_{2(g)} \xrightarrow{UV} Cl^{\bullet}_{(g)}$  The chlorine radical formed initiates

the chain reaction for  $O_3$  depletion.

### > Water Pollution

Pollutant	Source	
Microorganisms	Domestic sewage	
Organic wastes	Domestic sewage, animal waste,	
	decaying animals and plants and	
	discharge from food processing factories	
Plant nutrients	Chemical fertilizers	
Toxic heavy metals	Discharge from Factories	
Sediments	Erosion of soil	



Pesticides	Farming
Radioactive substances	Mining of radioactive minerals
Heat	Cooling water used by industries

In addition, industrial wastes also contaminate water.

- Heavy Metals: Cadmium and mercury can cause kidneys, liver brain and central nervous system. These metals are cumulative poisons, the body does not excrete them and their concentration builds up.
- Detergents and Fertilizers: The addition of phosphorus to water, in the form of the phosphate anion PO<sub>4</sub><sup>3–</sup>, encourages the formation of algae, which reduces the dissolved oxygen concentration of water. The process, known as eutrophication, impedes the development of higher life forms, such as fish.
- Acid-polluted water (pH < 3): This is deadly to most forms of aquatic life. Acid mine water principally contain subphuric acid produced by the oxidation of iron pyrites (FeS<sub>2</sub>).
- Polychlorinated biphenyls (PCBs): Having high stabilities, PCBs are used as fluids in transformer, capacitors. PCBs are resistant to oxidation and their release into the environment causes skin disorders in humans (carcinogens).

International standards for drinking water must be obeyed if water is to be used for drinking purposes. These are :

- Fluo<mark>ride:</mark>
  - Soluble fluoride is added to drinking water up to a conc. of 1 ppm to protect against tooth delay.F<sup>-</sup> ion makes the enamel harder by converting hydroxyapatite [3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.Ca(OH)<sub>2</sub>] into much harder [3Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>.CaF<sub>2</sub>]
  - Conc. above 2 ppm causes brown mottling of teeth.
  - High concentrations of fluoride are harmful to bone and teeth at levels over 10 ppm.
- Lead:
  - The limit for the concentration of lead ions in drinking water is 50 ppb.
  - If water is acidic and lead pipes are used, then the water is liable to get contaminated with lead.
- pH:
  - The pH of drinking water should be between 5.5 and 9.5. A decrease in the pH of the water increases the solubility of metal ions.
- Sulphate:
  - excessive sulphate (> 500 ppm) is thought to have a laxative effect.
- Nitrate:
  - Excess nitrate in drinking water can lead to methemoglobinemia (blue-baby syndrome), stomach cancer. A maximum limit of 50 ppm for the nitrate ion in drinking water has been set.
- Other Metals:

Metal	Max. concentration (ppm)
Zn	5
Fe	0.2
Mn	0.05
Cu	3
Cd	0.005
Al	0.2



### > Importance of dissolved Oxygen in water :

- The fish growth is inhibited if the dissolve concentration of oxygen in water is below 6 ppm.
- The lower the concentration of dissolved oxygen, the more polluted is the water sample.
- The dissolved oxygen in water is consumed rapidly by microorganisms to oxidise organic matter of sewage, bio-oxidation of nitrogenous material, chemical or biochemical oxidation of chemical reducing agents

#### Biochemical Oxygen Demand (BOD)

- Biochemical oxygen demand (BOD) is a measure of the dissolved oxygen that would be needed by the microorganisms to oxidise organic and inorganic pollutants.
- BOD, therefore, is a measure of the contamination caused by the totality of those compounds which can be oxidised in the presence of microorganisms.
- 'clean water' would have a BOD value of less than 5 ppm whereas highly polluted river water could have a BOD value of 17 ppm or more.

#### Chemical Oxygen Demand (COD):

- In COD (Chemical Oxygen Demand) determination, the water sample is treated with a known quantity of an oxidising agent, usually potassium dichromate K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in acidic medium.
- The remaining K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> is determined by back titration with a suitable reducing agent like Mohr's salt.
- From the concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> consumed, the amount of oxygen used in the oxidation may be calculated using the following chemical equation
   K<sub>2</sub>Cr<sub>2</sub>O<sub>7(aq)</sub> + 4H<sub>2</sub>SO<sub>4(aq)</sub> → K<sub>2</sub>SO<sub>4(aq)</sub> + Cr<sub>2</sub>(SO<sub>4)3(aq)</sub> + 4H<sub>2</sub>O<sub>(l)</sub> + 3O<sub>(aq)</sub>
- The results are expressed in terms of amount of oxygen, in ppm, that would be required to oxidise the contaminants.

#### Land Pollution

Most of the land pollution is caused by pesticides and other chemicals which are added to the soil grow better crops. Solid wastes are another cause of land pollution.

**Pesticides :** Pesticides are substances that are used to kill or block the reproductive processes of unwanted organisms.

**Insecticides** : Control of insects by insecticides helps to cure disease (for example malaria and yellow fever) and protect crops. The best known organochlorine compound is DDT (dichlorodiphenyltrichloroethane) Organochlorines are stable in the environment, toxic to insects in small amounts, but much less so to humans; and because they are organic compounds, not very soluble in water. These insecticides by accumulating in the environment affect many non-target organisms, not just the target pests.

**Herbicides:** Herbicides are used to kill weeds. Sodium chlorate, NaClO<sub>3</sub> and sodium arsenite Na<sub>3</sub>AsO<sub>3</sub> were commonly used as weed killers in the first half of the last century, but inorganic arsenic compounds in particular are toxic to mammals. Organic herbicides are, therefore, now used. They are much more toxic to certain types of plants than to others.



**Fungicides:** Fungicides are used to check the growth of fungi. Organic compounds of mercury have been used as fungicides. These compounds break down in solid and thus has had disastrous consequences

#### > Strategy for control of environmental pollution

**The management of waste:** The production and improper disposal of waste are causes for a great deal of environmental pollution.

**Recycling:** When materials are recycled, there are several benefits, apart from saving on the cost of raw materials, waste disposal costs are reduced.

Sewage treatment: The main stages in the treatment of sewage are as follows:

- The removal of large solids that get into the system of filtering the waste water through screens.
- Settlement in tanks to allow the removal of solids that settle out (called sludge). This process also allows removal of grease which floats to the surface and can be skimmed off.
- The degradation of the organic content of waste water by microbial oxidation.
- Application of various physical and chemical processes for improving the quality of waste water. The processes include chemical removal of phosphate, coagulation, filtration and disinfection using chlorine.

The safe disposal of the sludge produced during water treatment is a problem. The sludge is dried and then many be incinerated, digested or dumped.

**Incineration:** Incineration converts organic materials to  $CO_2$  and  $H_2O$ . It may serve to destroy household waste, chemical waste and biological waste (e.g. from hospitals). A high temperature is required usually in excess of 1000°C, and a plentiful supply of oxygen. Exhaust gases must be filtered. The process greatly reduced the volume of waste (around 90%) -an inorganic ash is left behind, which is disposed of as landfill. The chief disadvantage of incineration is that it leads to air pollution.

**Digestion:** Anaerobic digestion occurs when microganisms degrade wastes in the absence of oxygen. It may be used to treat sewage sludge, but the process can also be used to degrade a variety of toxic organic wastes. Carbon dioxide and methane, which may be used as a fuel, are the products.

**Dumping**: Ocean dumping of sewage sludge has been widely practiced in the seas around the worked. Urban areas produce sludge with high toxic metal content, so the amount of such sludge dumped in this way must be carefully controlled.

#### **Green** Chemistry

An ideal chemical reaction should have a number of attributes: safety, simplicity, selectivity, high yield, energy efficiency, use of renewable or recyclable materials, minimizing by-product formation.

Concept of green chemistry introduced by Paul Anastas in 1994

% atom economy = Formula mass of product/ sum of formula mass of all the reactants.