

### Chemistry Part -1

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#### 9th STD Unit- 12- Periodic Classification of Elements

#### Introduction

• We live in the world of substances with great diversity. Substances are formed by the combination of various elements. All the elements are unique in their nature and property. To categorize these elements according to their properties, scientists started to look for a way. In 1800, there were only 31 known elements. By 1865, their number became 63. Now 118 elements have been discovered. As different elements were being discovered, scientists gathered more and more information about the properties of these elements. They found it difficult to organize all that was known about the elements. They started looking for some pattern in their properties, on the basis of which they could study such a large number of elements with ease. Let us discuss the concepts of classification of elements proposed by various scientists from early to modern period.

#### Early Concepts of Classification of Elements Dobereiner's Triads

- In 1817, Johann Wolfgang Dobereiner, a German chemist, suggested a method of grouping elements based on their relative atomic masses. He arranged the elements into groups containing three elements each. He called these groups as 'triads' (tri three).
- Dobereiner showed that when the three elements in a triad are arranged in the ascending order of their atomic masses, the atomic mass of the middle element is nearly the same as average of atomic masses of other two elements. This statement is called the Dobereiner's law of triads. Table 12.1 shows the law of triads proposed by Dobereiner.
- Example: In the triad group (1), arithmetic mean of atomic masses of 1st and 3rd elements, (6.9 + 39.1)/2 = 23. So the atomic mass of Na (middle element) is 23.

Triad Group (1)		Triad Group (2)		Triad Group (3)	
Element	Atomic	Element	Atomic	Element	Atomic
	Mass		Mass		Mass
Li	6.9	Cl	35.5	Ca	40.1
Na	23	Br	79.9	Sr	87.6
K	39.1	Ι	126.9	Ва	137.3



#### Limitations:

- Dobereiner could identify only three triads from the elements known at that time and all elements could not be classified in the form of triads.
- The law was not applicable to elements having very low and very high atomic mass.

#### Newlands' Law of Octaves

- In 1866, John Newlands arranged 56 known elements in the increasing order of their atomic mass. He observed that every eighth element had properties similar to those of the first element like the eighth note in an octave of music is similar to the first. This arrangement was known as 'law of octaves'.
- The octave of Indian music system is sa, re, ga, ma, pa, da, ni, sa. The first and last notes of this octave are same i.e. sa. Likewise, in the Newlands' table of octaves, the element 'F' is eighth from the element 'H', thus they have similar properties.

#### Limitations:

- There are instances of two elements being fitted into the same slot, e.g. cobalt and nickel.
- Some elements, totally dissimilar in their properties, were fitted into the same group. (Arrangement of Co, Ni, Pd, Pt and Ir in the row of halogens)
- The law of octaves was not valid for elements that had atomic masses higher than that of calcium.
- Newlands' table was restricted to only 56 elements and did not leave any room for new elements.
- Discovery of inert gases (Neon. Argon....) at later stage made the 9th element similar to the first one. Eg: Neon between Fluorine and Sodium.

#### Mendeleev's Periodic Table

• In 1869, Russian chemist, Dmitri Mendeleev observed that the elements of similar properties repeat at regular intervals when the elements are arranged in the order of their atomic masses. Based on this, he proposed the law of periodicity which states that "the physical and chemical properties of elements are the periodic functions of their atomic masses". He arranged 56 elements known at that time according to his law of periodicity. This was best known as the short form of periodic table.



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#### Features of Mendeleev's Periodic Table:

- It has eight vertical columns called 'groups' and seven horizontal rows called 'period'.
- Each group has two subgroups 'A' and 'B'. All the elements appearing in a group were found to have similar properties.
- For the first time, elements were comprehensively classified in such a way that elements of similar properties were placed in the same group
- It was noticed that certain elements could not be placed in their proper groups in this manner. The reason for this was wrongly determined atomic masses. Consequently those wrong atomic masses were corrected. Eg: The atomic mass of beryllium was known to be 14. Mendeleev reassessed it as 9 and assigned beryllium a proper place.
- Columns were left vacant for elements which were not known at that time and their properties also were predicted. This gave motivation to experiment in Chemistry. Eg: Mendeleev gave names EkaAluminium andEka Silicon to those elements which were to be placed below Aluminium and Silicon respectively in the periodic table and predicted their properties. The discovery of Germanium later on, during his life time, proved him correct.

	No.		No.		N	о.	No	D.	No.		No	).	No.		No.	
Н	1	Τ	F	8	Cl	15	Co & 1	Ni 22	Br	29	Pd	36	Ι	42	Pt & Ir	50
Li	2	Τ	Na	9	K	16	Cu	23	Rb	30	Ag	37	Cs	44	Os	51
G	3	T	Mg	10	Ca	17	Zn	24	Sr	31	Cd	38	Ba & V	45	Hg	52
Bo	4	T	Al	11	Cr	19	Y	25	Ce & La	33	U	40	Та	46	Ti	53
С	5	T	Si	12	Ti	18	In	26	Zr	32	Sn	39	W	47	Pb	54
Ν	6	T	Р	13	Mn	20	As	27	Di & Mo	34	Sb	41	Nb	48	Bi	55
0	7	T	S	14	Fe	21	Se	28	Ro & Ru	35	То	43	Au	49	Th	56

#### Limitations:

- Elements with large difference in properties were included in the same group. Eg: Hard metals like copper (Cu) and silver (Ag) were included along with soft metals like sodium (Na) and potassium (K).
- No proper position could be given to the element hydrogen. Non-metallic hydrogen was placed along with metals like lithium (Li), sodium (Na) and potassium (K).
- The increasing order of atomic mass was not strictly followed throughout. Eg. Co & Ni, Te& I.
- ✤ No place for isotopes in the periodic table.



#### **Properties of Germanium**

Property	Mendeleev's	Actual property
	prediction (1871)	(1886)
Atomic Mass	About 72	72.59
Specific Gravity	5.5	5.47
Colour	Dark grey	Dark grey
Formula of Oxide	EsO <sub>2</sub>	GeO <sub>2</sub>
Nature of Chloride	EsCl <sub>4</sub>	GeCl <sub>4</sub>

#### Modern Periodic Table

- In 1913, the English Physicist Henry Moseley, through his X-ray diffraction experiments, proved that the properties of elements depend on the atomic number and not on the atomic mass. Consequently, the modern periodic table was prepared by arranging elements in the increasing order of their atomic number.
- This modern periodic table is the extension of the original Mendeleev's periodic table and known as the long form of periodic table.

#### Modern Periodic Law

• Atomic number of an element (Z) indicates the number of protons (positive charge) or the number of electrons (negative charge). The physical and chemical properties of elements depend not only on the number of protons but also on the number of electrons and their arrangements (electronicconfiguration) in atoms. Hence, the modern periodic law can be stated as follows: "The chemical and physical properties of elements are periodic functions of their atomic numbers". Based on the modern periodic law, the modern periodic table is derived.

#### **Features of Modern Periodic Table**

- ◆ All the elements are arranged in the increasing order of their atomic number.
- ✤ The horizontal rows are called periods. There are seven periods in the periodic table.
- The elements are placed in periods based on the number of shells in their atoms.
- Vertical columns in the periodic table starting from top to bottom are called groups. There are 18 groups in the periodic table.
- Based on the physical and chemical properties of elements, they are grouped into various families.



Groups in modern periodic table

Group	Families
1	Alkali metals
2	Alkaline earth metals
3 to 12	Transition metals
13	Boron Family
14	Carbon Family
15	Nitrogen Family
16	Oxygen Family (or)
	Chalcogen Family
17	Halogens
18	Noble gases

#### **Classification of elements into blocks**

- We know that the electrons in an atom are accommodated in shells around the nucleus. Each shell consists of one or more subshells in which the electrons are distributed in certainmanner. These subshells are designated as s, p, d, and f. Based on the arrangement of electrons in subshells, the elements of periodic table are classified into four blocks namely s, p, d and f blocks.
- **s-Block Elements**: It includes group 1 (alkali metals) and group 2 (alkaline earth metals) elements. They are also called as representative elements. The elements of group 1 (except hydrogen) are metals. They react with water to form solutions that change the colour of a vegetable dye from red to blue. These solutions are said to be highly alkaline or basic. Hence they are called alkali metals.
- The elements of group 2 are also metals. They combine with oxygen to form oxides, formerly called 'earths', and these oxides produce alkaline solutions when they are dissolved in water. Hence, these elements are called alkaline earth metals.
- (2) p-Block Elements: These elements are in group 13 to 18 in the periodic table. They include boron, carbon, nitrogen, oxygen, fluorine families in addition to noble gases (Except helium). They are also called as representative elements. The p-block is home to the biggest variety of elements and is the only block that contains all three types of elements: metals, nonmetals, and metalloids.
- (3) **d-Block Elements:** It includes group 3 to group 12 elements. They are found in the centre of the periodic table. Their properties are intermediate to that of s block and p block elements and so they are called transition elements.



• **(4) f** – **Block Elements:** It includes 14 elements after (Lanthanum) La (57), called Lanthanoides and 14 elements after (Actinium) Ac (89), called Actinoides. They are placed at the bottom of the periodic table. They are also called as inner Transition elements.

#### Advantages of the Modern Periodic Table

- The table is based on a more fundamental property i.e., atomic number.
- It correlates the position of the element with its electronic configuration more clearly.
- The completion of each period is more logical. In a period, as the atomic number increases, the energy shells are gradually filled up until an inert gas configuration is reached.
- ✤ It is easy to remember and reproduce.
- Each group is an independent group and the idea of subgroups has been discarded.
- One position for all isotopes of an element is justified, since the isotopes have the same atomic number.
- The position of the eighth group (in Mendeleev's table) is also justified in this table. All transition elements have been brought in the middle as the properties of transition elements are intermediate between left portion and right portion elements of the periodic table.
- The table completely separates metals from nonmetals. The nonmetals are present in upper right corners of the periodic table.
- The positions of certain elements which were earlier misfit (interchanged) in the Mendeleev's periodic table are now justified because it is based on atomic number of the elements.
- Justification has been offered for placing lanthanides and actinides at the bottom of the periodic table.

#### Position of hydrogen in the periodic table

- Hydrogen is the lightest, smallest and first element of the periodic table. Its electronic configuration (1s1) is the simplest of all the elements. It occupies a unique position in the periodic table. It behaves like alkali metals as well as halogens in its properties.
- In the periodic table, it is placed at the top of the alkali metals.
- (1) Hydrogen can lose its only electron to form a hydrogen ion (H+) like alkali metals.
- (2) It can also gain one electron to form the hydride ion (H-) like halogens.
- (3) Alkali metals are solids while hydrogen is a gas.
- Hence the position of hydrogen in the modern periodic table is still under debate as the properties of hydrogen are unique.



#### **Position of Rare Gases**

• The elements Helium, Neon, Argon, Krypton, Xenon and Radon of group 18 in the periodic table are called as Noble gases or Rare gases. They are monoatomic gases and do not react with other substances easily, due to completely filled subshells. Hence they are called as inert gases. They are found in very small quantities and hence they are called as rare gases.

#### Metals, Non-Metals and Metalloids Metals

- Metals are typically hard, shiny, malleable (can be made as sheet), fusible and ductile (can be drawn into wire) with good electrical and thermal conductivity. Except mercury, most of the metals are solids at room temperature. Metals occupy larger area in the periodic table and are categorized as:
  - (1) Alkali metals. e.g. Lithium to Francium (top to bottom)
  - (2) Alkaline earth metals. e.g: Beryllium to Radium (top to bottom)

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- (3) Transition Metals. Group III B to II A
- (4) P-Block metals. e.g: Al, Ga, In, Tl, Sn, Pb and Bi.

#### Non-metals

• A non-metal is an element that does not have the characters like hardness, shiny, malleable, suitable and ductile. In other words, a non-metal is an element that does not have the properties of metal. e.g. All non metals are arranged in P-Block only. P-Block non metals: C, N O, P, S, Se, Halogen (F, Cl, Br and I) and inert gases (HeyoRn).

#### Metalloids

• Elements which have the properties of both metals and non-metals are called as metalloids. (eg) Boron, Arsenic.

#### Alloys

• During 3500 BC(BCE), people used an alloy named 'bronze'. The idea of making an alloy was quite old. The majority of the metallic substances used today are alloys. Alloys are mixtures of two or more metals and are formed by mixing molten metals thoroughly. Rarely nonmetals are also mixed with metals to produce alloys.



• It is generally found that alloying produces a metallic substance that has more useful properties than the original pure metals from which it is made. For example, the alloy brass is made from copper and zinc.

#### Advantages of alloys

- Alloys do not get corroded or get corroded to very less extent.
- They are harder and stronger than pure metals (Example: Gold is mixed with copper and it is harder than pure gold).
- They have less conductance than pure metals (Example: Copper is good conductor of heat and electricity whereas brass and bronze are not good conductors).
- Some alloys have lower melting point than pure metals (Example: Solder is an alloy of lead and tin which has lower melting point than each of the metals).
- When metal is alloyed with mercury, it is called amalgam.





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#### 8.PERIODIC CLASSIFICATION OF ELEMENTS

#### PERIODIC TRENDS IN PROPERTIES

- The electronic configurations of elements help us to explain the periodicrecurrence of physical and chemical properties. Anything which repeats itself after a regular interval is called periodic and this behaviour is called periodicity. Some of the atomic properties of the elements are periodic.
- Properties such as atomic radius, ionic radius, ionisation energy, electronegativity, electron affinity, show a regular periodicity and hence they are called periodic properties. The main significance of the modern periodic table is that it gives a clear understanding of the general properties and trends within a group or a period to predict with considerable accuracy, the properties of any element, even though that element may be unfamiliar to us. Let us discuss the periodic trend of some of the properties.

#### **Atomic Radius**

- Atomic radius of an atom is defined as the distance between the centreofits nucleus and the outermost shell containing the valence electron. Direct measurement of the radius of an isolated atom is not possible. Except for noble gases, usually the atomic radius is referred to as covalent radius or metallic radius depending on the nature of the bonding between the concerned atoms. Atomic radius in metal atoms is known as metallic radius. It is defined as half the distance between the nuclei of adjacent metal atoms.
- In non-metallic elements, their atomic radius is known as Covalentradius. It is defined as half the distance between the nuclei of two covalently bonded atoms of the same element in a molecule. For example, let us consider H2 molecule. The distance between the two hydrogen nuclei of the molecule is 0.74 Å. So its covalent radius is 0.74/2 = 0.37 Å.
- When you look at the variation of the atomic radii in the periodic table, there are two distinct trends. Along the period, from left to right, the atomic radius of the elements decreases whereas along the groups, from the top to bottom, the atomic radius increases. The increase, down a group, is due to the increase in the valence shell number down the group. As the shell number increases, the distance between the valence shell and the nucleus increases. In contrast, when you observe along the period, the shell number remains the same but the number of protons (i.e. atomic number) increases. More and more positive charges impose a



strong attraction over the electrons and thus the electron cloud shrinks towards the nucleus, which results in the decrease in the atomic size.

#### Ionic Radii

- It is defined as the distance from the centre of the nucleus of the ionupto the point where it exerts its influence on the electron cloud of the ion. You know that ions are formed when an atom lose or gain electrons. When a neutral atom loses an electron, it becomes a positively charged ion called cation, whereas the gain of an electron by a neutral atom forms a negatively charged ion called anion. The size of the ions is important to determine their behaviours in solutions and the structure of ionic solids. The size of a cation is always smaller than its corresponding neutral atom. But, the anion is larger than its neutral atom.
- For instance, lithium and sodium lose the single electron from theiroutermost energy level to form cations. The ions so formed are smaller because the remaining electrons are at a inner cells and attracted more strongly by the nucleus. Fluorine and chlorine become negative ions by gaining an electron. When electrons are added, the charge on the nucleus is not great enough to hold the increased number of electrons as closely as it holds the electrons in the neutral atom. So, as seen in atomic radius, ionic radii also decrease along the period from left to right and increase down the group.

#### **Ionisation Energy**

- Ionisation energy is the minimum energy required to remove anelectron from a gaseous atom in its ground state to form a cation. It is otherwise called ionisation enthalpy. It is measured in kJ/mol. Higher the ionisation energy, it is more difficult to remove the electron.
- As the atomic size decreases from left to right in a period, more energy is required to remove the electrons. So, the ionisation energy increases along the period. But, down the group, the atomic size increases and hence the valence electrons are loosely bound. They require relatively less energy for the removal. Thus, ionisation energy decreases down the group in the periodic table.

As the positive charge increases the size of the cation decreases As thenegative charge increases the size of the anion increases

#### **Electron Affinity**

• Electron affinity is the amount of energy released when a gaseous atomgains an electron to form its anion. It is also measured in kJ/mol and represented by the following equation:



 $A(g) + e^- \rightarrow A^{-(g)} + Energy$  $Cl(g) + e^- \rightarrow Cl^{-(g)} + energy$ 

• Like ionisation energy, electron affinity also increases from left to rightin a period and decreases from top to bottom in a group.

#### Electronegativity

- Electronegativity of an element is the measure of the tendency of itsatom to attract the shared pair of electrons towards itself in a covalent bond. Let us consider HCl molecule. Both the hydrogen and chlorine atoms share one electron each to form the covalent bond between them. chlorine atom has a higher electronegativity and hence it pulls the shared electrons towards itself more strongly than hydrogen. Thus, when the bond breaks, the bonding electrons are left with chlorine forming H+ and Cl- ions.
- Electronegativity is based on various experimental data such as bondenergy, ionization potential, electron affinity, etc.
- Pauling scale is the widely used scale to determine the electronegativity, which in turn predicts the nature of bonding (ionic or covalent) between the atoms in a molecule.

Electronegativity of some of the elements. F = 4.0, Cl = 3.0, Br = 2.8, I = 2.5, H = 2.1, Na = 1

- If the difference in electronegativity between two elements is 1.7, thebond has 50% ionic character and 50% covalent character.
- If the difference is less than 1.7, the bond is considered to be covalent.
- If the difference is greater than 1.7, the bond is considered to be ionic.
- Along the period, from left to right in the periodic table, theelectronegativity increases because of the increase in the nuclear charge which in turn attracts the electrons more strongly. On moving down a group, the electronegativity of the elements decreases because of the increased number of energy levels.

Periodic Property	In periods	In Groups
Atomic radius	Decreases	Increases
Ionic radius	Decreases	Increases
Ionisation energy	Increases	Decreases
Electron affinity	Increases	Decreases
Electronegativity	Increases	Decreases



#### METALLURGY

- Human life is associated with various metals. We use metals in our dayto day activities. It is the utmost need to have some metals like sodium, potassium, calcium, iron, etc. in the human body. Deficiency of these metals affects the metabolic activities thereby causing diseases. So, metals play a vital role in our life. In this section, let us discuss how metals are obtained from various sources by the process of metallurgy.
- Metallurgy is a science of extracting metals from their ores andmodifying the metals into alloys for various uses, based on their physical and chemical properties and their structural arrangement of atoms. A metallurgical process involve three main steps as follows:
- **Concentration or Separation of the ore:** It is the process of removal of impuries from the ore.
- **Production of the metal:** It is the convertion of the ore into metal.
- **Refining of the metal:** It is the process of purification of the metal

#### Terminology in metallurgy

- **Minerals:** A mineral may be a single compound or a complex mixture ofvarious compounds of metals found in the Earth.
- **Ore:** The mineral from which a metal can be readily and economicallyextracted on a large scale is said to be an ore.
- **For example:** Clay (Al2O3. 2 SiO2. 2 H2O) and bauxite (Al2O3.2 H2O) are the two minerals of aluminium, but aluminium can be profitably extracted only from bauxite. Hence, bauxite is an ore of aluminium and clay is its mineral.
- **Mining:** The process of extracting the ores from the Earth's crust iscalled mining.
- **Gangue or Matrix:** The rocky impurity associated with an ore is calledgangue or matrix.
- **Flux:** It is the substance added to the ore to reduce the fusiontemperature and to remove the impurities. E.g. Calcium oxide (basic), Silica (acidic). If the gangue is acidic, then basic flux is added and vice versa.
- **Slag:** It is the fusible product formed when a flux reacts with a gangueduring the extraction of metals.

Flux + Gangue  $\rightarrow$  Slag



• **Smelting:** Smelting is the process of reducing the roasted metallic oxidefrom the metal in its molten condition. In this process, impurities are removed as slag by the addition of flux.

#### Types of separation or concentration of an ore

• There are four major types of separation of ores based on the nature of the ore. The different kinds of ores of metals.

#### Hydraulic (Gravity Separation) method

- **Principle:** The difference in the densities or specific gravities of the oreand the gangue is the main principle behind this method. Oxide ores are purified by this method. e.g., Haematite<sub>Fe2O3</sub> the ore of iron.
- **Method:** The ore is poured over a sloping, vibrating corrugated tablewith grooves and a jet of water is allowed to flow over it. The denser ore particles settle down in the grooves and lighter gangue particles are washed down by water.

#### Magnetic separation method

- **Principle:** The magnetic properties of the ores form the basis ofseparation. When either the ore or the gangue is magnetic, this method is employed. e.g., Tinstone SnO<sub>2</sub>, the ore of tin.
- **Method:** The crushed ore is placed over a conveyer belt which rotatesaround two metal wheels, one of which is magnetic. The magnetic particles are attracted to the magnetic wheel and fall separately apart from the non-magnetic particles.

#### Froth floatation

- **Principle:** This process depends on the preferential wettability of the orewith oil (pine oil) and the gangue particles by water. Lighter ores, such as sulphide ores, are concentrated by this method. e.g., Zinc blende (ZnS).
- **Method:** The crushed ore is taken in a large tank containing oil andwater and agitated with a current of compressed air. The ore is wetted by the oil and gets separated from the gangue in the form of froth. Since the ore is lighter, it comes on the surface with the froth and the impurities are left behind. e.g., Zinc blende (ZnS).



#### Chemical method or Leaching

Oxide Ores	Carbonate Ores	Halide Ores	Sulphide ores
Bauxite	Marble (CaCO <sub>3</sub> )	Cryolite (Na <sub>3</sub> AIF <sub>6</sub> )	Galena (pbs)
(Al <sub>2</sub> O <sub>3.</sub> 2H <sub>2</sub> O)			
Cuprite (Cu <sub>2</sub> O)	Magnesite	Fluorspar (CaF <sub>2</sub> )	Iron Pyrite (FeS <sub>2</sub> )
	(MgCO <sub>3</sub> )		
Haematite (Fe <sub>2</sub> O <sub>3</sub> )	Siderite (FeCO <sub>3</sub> )	Rock Salt (NaCl)	Zinc Blende (Zns)

This method is employed when the ore is in a very pure form.

• The ore is treated with a suitable reagent such that the ore is soluble in itbut the impurities are not. The impurities are removed by filtration. The solution of the ore, ie., the filtrate is treated with a suitable reagent which precipitates the ore. E.g. Bauxite Al<sub>2</sub>O<sub>3</sub>.2H<sub>2</sub>O, the ore of aluminium.

#### OCCURRENCE OF ORES IN TAMIL NADU

- Lime stone: Coimbatore, Cuddalore, Dindugul
- ✤ Gypsum:Tiruchi and Coimbatore Distiricts
- \* Titanium minerals:Kanyakumari, Tirunelveli and Tuticorin.
- **Chromite:** Coimbatore and Salem district.
- \* Magnetite:.Dharmapuri, Erode, Salem, Thiruvannamalai.
- **Tungsten:** Madurai and Dindugal.

### PROPERTIES OF METALS

**Physical properties** 

- **Physical state:** All metals are solids at room temperature except mercury and gallium.
- Lustre: Metals possess a high lustre (called metallic lustre).
- **Hardness:** Most of the metals are hard and strong (exceptions: sodium and potassium can be cut with a knife)
- **Melting point and Boiling point:** Usually, metals possess high melting and boiling points and vaporize only at high temperatures (exceptions: gallium, mercury, sodium and potassium).
- **Density:** Metals have a high density (exceptions: sodium and potassium are less dense than water).
- **Ductility:** Metals are usually ductile. In other words, they can be drawn into thin wires without breaking.



- **Malleability:** Metals are usually malleable, i.e, they can be beaten into thin sheets without cracking (except zinc and mercury).
- **Conduction of heat and electricity:** Metals are good conductors of heat and electricity; silver and copper excel in this property (exception: tungsten)
- **Solubility:** Usually, metals do not dissolve in liquid solvents.

#### **Chemical Properties**

- Valence electrons: Atoms of metals usually have 1,2 or 3 electrons in their outermost shell.
- **Formation of ions:** Metals form Positive ions by the loss of electrons and hence they are electro positive.
- **Discharge of ions:** Metals are discharged at the cathode during the electrolysis of their compounds.
- Atomicity: Molecules of metals in their vapour state are usually monoatomic.
- Nature of oxides: Oxides of metals are usually basic.

# EXTRACTIVE METALLURGY OF ALUMINIUM

Aluminium is the metal found most abundantly in the Earth's crust.Since it is a reactive metal, it occurs in the combined state. The important ores of aluminium are as follows.

Ores of Aluminium	Formula
Bauxite	Al <sub>2</sub> O <sub>3</sub> .2H <sub>2</sub> O
Cryolite	Na <sub>3</sub> AlF <sub>6</sub>
Corundum	Al <sub>2</sub> O <sub>3</sub>

• Bauxite is the chief ore of aluminium. The extraction of aluminium from bauxite involves two steps:

#### **Conversion of bauxite into alumina – Baeyer's Process**

- The conversion of Bauxite into Alumina involves the following steps:
- Bauxite ore is finely ground and heated under pressure with a solution of concentrated caustic soda solution at 150° C to obtain sodium meta aluminate.



- On diluting sodium meta aluminate with water, a precipitate of aluminium hydroxide is formed.
- The precipitate is filtered, washed, dried and ignited at 1000°C to get alumina.

# 2Al(OH)31000°cAl2O3 + 3H2O

#### Electrolytic reduction of alumina - Hall's Process

- Aluminium is produced by the electrolytic reduction of fused alumina (Al<sub>2</sub>O<sub>3</sub>) in the electrolytic cell
- **Cathode**: Iron tank linked with graphite
- Anode: A bunch of graphite rods suspended in molten electrolyte.
- Electrolyte: Pure alumina+ molten cryolite + fluorspar (fluorspar lowers the fusion temperature of electrolyte)

#### **Temperature:** 900 - 950 °C Voltage used: 5-6 V **Overall reaction**: 2 Al2O3 $\rightarrow$ 4 Al +3 O2<sup>↑</sup>

Aluminium is deposited at the cathode and oxygen gas is liberated at the anode. Oxygen combines with graphite to form CO<sub>2</sub>. ENT

#### **Physical Properties of Aluminium**

- ✤ It is a silvery white metal
- ✤ It has low density (2.7) and it is light
- ✤ It is malleable and ductile
- ✤ It is a good conductor of heat and electricity.
- ✤ Its melting point is 660 °C.
- It can be polished to produce a shiny attractive appearance.

#### **Chemical Properties of Aluminium**

Reaction with air: It is not affected by dry air. On heating at 800 °C, aluminium burns very brightly forming it's oxide and nitride.

 $4 \text{ Al} + 3 \text{ O}_2 \rightarrow 2 \text{ Al}_2\text{O}_3$ (Aluminium oxide)  $2 \text{ Al} + \text{N}_2 \rightarrow 2 \text{ AlN}$  (Aluminium nitride)

Reaction with water: Water does not react with aluminium due to the layer of oxide on it. When steam is passed over red hot aluminium, hydrogen is produced.

 $2 \text{ Al} + 3 \text{ H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 3 \text{ H}_2\uparrow$ 



• Reaction with alkalis: It reacts with strong caustic alkalis forming aluminates.

 $2 \text{ Al} + 2 \text{ NaOH} + 2 \text{ H}_2\text{O} \rightarrow 2 \text{ NaAlO}_2 + 3 \text{ H}_2 \uparrow$ 

• **Reaction with acids:** With dilute and con. HCl it liberates H2 gas.

 $2 \text{ Al} + 6 \text{ HCl} \rightarrow 2 \text{ AlCl}_3 + 3 \text{ H}_2 \uparrow$ 

• Aluminium liberates hydrogen on reaction with dilute sulphuric acid. Sulphur dioxide is liberated with hot concentrated sulphuric acid

 $\begin{array}{l} 2 \text{ Al} + 3 \text{ } \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 3 \text{ } \text{H}_2 \\ 2 \text{ Al} + 6 \text{ } \text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 6 \text{ } \text{H}_2\text{O} + 3 \text{ } \text{SO}_2 \uparrow \end{array}$ 

**As reducing agent:** Aluminium is a powerful reducing agent. When a mixture of aluminium powder and iron oxide is ignited, the latter is reduced to metal. This process is known as **aluminothermic process**.

TR

 $Fe_2O_3 + 2 Al \rightarrow 2 Fe + Al_2O_3 + Heat.$ 

Uses

Aluminium is used in

- household utensils
- ✤ electrical cable industry
- making aeroplanes and other industrial mechine parts

## EXTRACTIVE METALLURGY OF COPPER

Occurrence:

• It was named as cuprum by the Romans because they got it from the Island of Cyprus. Copper is found in the native state as well as combined state.

Ores of copper	Formula
Copper pyrites	CuFeS2
Cuprite or ruby copper	Cu2O
Copper glance	Cu2S

- The chief ore of copper is copper pyrite. It yields nearly 76% of the world production of copper. Extraction of copper from copper pyrites involves the following steps
- **Concentration of ore:** The ore is crushed and the concentrated by froth floatation process.
- **Roasting:** The concentrated ore is roasted in excess of air. During the process of roasting, the moisture and volatile impurities are removed. Sulphur,



phosphorus, arsenic and antimony are removed as oxides. Copper pyrite is partly converted into sulphides of copper and iron.

 $2 \text{ CuFeS}_2 + \text{O}_2 \rightarrow \text{Cu2S} + 2 \text{ FeS} + \text{SO}_2 \uparrow$ 

- **Smelting:** The roasted ore is mixed with powdered coke and sand and is heated in a blast furnace to obtain matte (Cu2S + FeS) and slag. The slag is removed as waste.
- **Bessemerisation:** The molten matte is transferred to Bessemer converter in order to obtain blister copper. Ferrous sulphide from matte is oxidized to ferrous oxide, which is removed as slag using silica.

2 FeS + 3 O<sub>2</sub> 2 FeO + 2 SO<sub>2</sub> ↑ FeO + SiO<sub>2</sub> FeSiO<sub>3</sub> (slag) 2 Cu<sub>2</sub>S + 3O<sub>2</sub> 2 Cu<sub>2</sub>O + 2 SO<sub>2</sub> ↑ 2 Cu<sub>2</sub>O + Cu<sub>2</sub>S 6 Cu + SO<sub>2</sub>↑

- **Refining:** Blister copper contains 98% of pure copper and 2% of impurities and is purified by **electrolytic refining**. This method is used to get metal of a high degree of purity. For electrolytic refining of copper, we use:
- **Cathode**: A thin plate of pure copper metal.
- **Anode**: A block of impure copper metal.
- \* Electrolyte: Copper sulphate solution acidified with sulphuric acid
- When electric current is passed through the electrolytic solution, pure copper gets deposited at the cathode and the impurities settle at the bottom of the anode in the form of sludge called anode mud.

#### **Physical Properties of Copper**

• Copper is a reddish brown metal, with high lustre, high density and high melting point (1356°C).

#### **Chemical Properties of Copper**

• Action of Air and Moisture: Copper gets covered with a green layer of basic copper carbonate in the presence of CO2 and moisture.

 $2 \text{ Cu} + \text{O}_2 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{CuCO}_3.\text{Cu}(\text{OH})_2$ 

• Action of Heat: On heating at different temperatures in the presence of oxygen, copper forms two types of oxides CuO, Cu2O.

 $2 Cu + O_2 \underline{below 1370K} 2 CuO$ 



4 Cu + O2 above 1370K, 2 Cu<sub>2</sub>O

#### Action of Acids: With dilute HCl and dilute H2SO4:

• Dilute acids such as HCl and H2SO4 have no action on these metals in the absence of air. Copper dissolves in these acids in the presence of air.

 $2 Cu + 4 HCl + O_2 (air) 2 CuCl_2 + 2 H_2O$ 

#### With dil. HNO3:

• Copper reacts with dil. HNO3 with the liberation of Nitric Oxide gas.

 $3 \text{ Cu} + 8 \text{ HNO}_3 \rightarrow \text{Cu}(\text{NO}_3)_2 + 2 \text{ NO} \uparrow + 2\text{H}_2\text{O}$  $\text{Cu} + 2 \text{ H}_2\text{SO}_4 \rightarrow \text{Cu}\text{SO}_4 + \text{SO}_2 \uparrow + 2 \text{ H}_2\text{O}$ 

#### Action of Chlorine:

• Chlorine reacts with copper, resulting in the formation of copper(II) chloride.

GENTRE

Cu + Cl2 CuCl2

#### Action of Alkalis:

• Copper is not attacked by alkalis.

#### Uses of Copper:

- ✤ It is extensively used in manufacturing electric cables and other electric appliances.
- It is used for making utensils, containers, calorimeters and coins,
- ✤ t is used in electroplating.
- ◆ It is alloyed with gold and silver for making coins and jewels

# EXTRACTIVE METALLURGY OF IRON Occurrence:

• Iron is the second most abundant metal available next to aluminium. It occurs in nature as oxides, sulphides and carbonates. The ores of iron are as follows:

Ores of iron	Formula
Haematite	$Fe_2O_3$
Magnetite	Fe <sub>3</sub> O <sub>4</sub>
Iron pyrite	FeS <sub>2</sub>



• Iron is chiefly extracted from haematite ore (Fe<sub>2</sub>O<sub>3</sub>)

#### **Concentration by Gravity Separation:**

• The powdered ore is washed with a steam of water. As a result, the lighter sand particles and other impurities are washed away and the heavier ore particles settle down.

#### **Roasting and Calcination:**

• The concentrated ore is strongly heated in a limited supply of air in a reverberatory furnace. As a result, moisture is driven out and sulphur, arsenic and phosphorus impurities are oxidized off.

#### **Smelting (in a Blast Furnace):**

- The charge consisting of roasted ore, coke and limestone in the ratio 8:4:1 is smelted in a blast furnace by introducing it through the cup and cone arrangement at the top. There are three important regions in the furnace.
- The Lower Region (Combustion Zone)- The temperature is at 1500°C. In this region, coke burns with oxygen to form CO<sub>2</sub> when the charge comes in contact with a hot blast of air.

$$C + O_2 \xrightarrow{1500^{\circ}C} O_2 + Heat$$

- It is an exothermic reaction since heat is liberated.
- The Middle Region (Fusion Zone) The temperature prevails at 1000°C. In this region, CO2 is reduced to CO.

$$CO2 + C \xrightarrow{1000^{\circ}C} \Delta CO_2 + Heat$$

• Limestone decomposes to calcium oxide and CO<sub>2</sub>

$$CaCO3 \xrightarrow{\Delta} CO2 - Heat$$

• These two reactions are endothermic due to absorption of heat. Calcium oxide combines with silica to form calcium silicate slag.

$$CaO + SiO_2 \rightarrow CaSiO_3$$



The Upper Region (Reduction Zone)- The temperature prevails at 400°C. In this region carbon monoxide reduces ferric oxide to form a fairly pure spongy iron.

$$Fe_2O_3 + 3CO \xrightarrow{400^{\circ}C} 2Fe + 3CO_2$$

- The molten iron is collected at the bottom of the furnace after removing the slag.
- The iron thus formed is called pig iron. It is remelted and cast into different moulds. This iron is called cast iron.

#### **Physical properties:**

- ✤ It is a lustrous metal, greyish white in colour.
- ✤ It has high tensility, malleability and ductility.
- ✤ It can be magnetized

#### **Chemical properties:**

• Reaction with air or oxygen: Only on heating in air, iron forms magnetic oxide. EN

3 Fe + 2  $O_2 \rightarrow Fe_3O_4$  (black)

Reaction with moist air: When iron is exposed to moist air, it forms a layer of brown hydrated ferric oxide on its surface. This compound is known as rust and the phenomenon of formation of rust is known as rusting.

4 Fe+ 3 O<sub>2</sub> + x H<sub>2</sub>O  $\rightarrow$  2 Fe<sub>2</sub>O<sub>3</sub> .xH<sub>2</sub>O(rust)

**Reaction with steam:** When steam is passed over red hot iron, magnetic oxide is formed.

 $3 \text{ Fe} + 4 \text{ H}_2\text{O} \text{ (steam)} \rightarrow \text{Fe}_3\text{O}_4 + 4 \text{ H}_2 \uparrow$ 

Reaction with chlorine: Iron combines with chlorine to form ferric chloride.

 $2Fe + 3Cl_2 \rightarrow 2FeCl_3$  (ferric chloride)

**Reaction with acids:** With dilute HCl and dilute H<sub>2</sub>SO<sub>4</sub> it liberates H<sub>2</sub> gas.

Fe + 2HCl  $\rightarrow$  FeCl<sub>2</sub> + H<sub>2</sub>  $\uparrow$  $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \uparrow$ 



With dilute HNO3 in cold condition it gives ferrous nitrate.

4 Fe + 10 HNO<sub>3</sub>  $\rightarrow$  4 Fe(NO<sub>3</sub>)<sub>2</sub> + NH<sub>4</sub>NO<sub>3</sub> + 3 H<sub>2</sub>O

With con. H2SO4 it forms ferric sulphate.

 $2 \text{ Fe} + 6 \text{ H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + 3 \text{ SO}_2 + 6 \text{ H}_2\text{O}$ 

When iron is dipped in con. HNO3 it becomes chemically passive or inert due to the formation of a layer of iron oxide (Fe3O4) on its surface.

#### Uses of iron

- Pig iron (Iron with 2-4.5% of carbon): It is used in making pipes, stoves, radiators, railings, manhole covers and drain pipes.
- Steel (Iron with < 0.25% of carbon): It is used in the construction of buildings, machinery, transmission cables and T.V towers and in making alloys.
- Wrought iron (Iron with 0.25-2% of wraught carbon): It is used in making ENTR springs, anchors and electromagnets.

#### ALLOYS

- An alloy is a homogeneous mixture of two or more metals or of one or more metals with certain non-metallic elements.
- The properties of alloys are often different from those of its components. Pure • gold is too soft to be used. The addition of small percentage of copper enhances its strength and utility.

#### Amalgam

An amalgam is an alloy of mercury with another metal. These alloys are formed through metallic bonding with the electrostatic force of attraction between the electrons and the positively charged metal ions. Silver tin amalgam is used for dental filling.

#### **Reasons for alloying:**

- To modify appearance and colour
- ✤ To modify chemical activity.
- ✤ To lower the melting point.
- ✤ To increase hardness and tensile strength.
- ✤ To increase resistance to electricity.



#### Method of making alloys

- By fusing the metals together. E.g. Brass is made by melting zinc and copper.
- By compressing finely divided metals. E.g. Wood metal: an alloy of lead, tin, bismuth and cadmium powder is a fusible alloy.

#### Alloys as solid solutions:

- Alloys can be considered solid solutions in which the metal with high concentration is solvent and other metals are solute.
- For example, brass is a solid solution of zinc (solute) in copper (solvent). ٠

#### **Types of Alloys**

- Based on the presence or absence of Iron, alloys can be classified into:
- Ferrous alloys: Contain Iron as a major component. A few examples of ferrous alloys are Stainless Steel, Nickel Steel etc.
- Non-ferrous alloys: These alloys do not contain Iron as a major component. EENTR For example, Aluminium alloy, Copper alloy etc.

#### **Copper Alloys (Non- ferrous)**

Alloys	Uses
Brass (Cu, Zn)	Electrical fittings, medal, decorative items, hardware
Bronze (Cu, Sn)	Statues, coins, bells, gongs

#### Aluminium Alloys (Non-ferrous)

Alloys	Uses
Duralumin (Al, Mg,	Aircrafts, tools,
Mn, Cu)	pressure cookers
Magnalium (Al, Mg)	Aircraft, scientific
	instruments

#### Iron Alloys(Ferrous)

Alloys	Uses
Stainless steel (Fe,C,	Utensils, cutlery,
Ni,Cr)	automobile parts
Nickel steel	Cables , aircraftparts,
(Fe,C,Ni)	propeller



#### CORROSION

- It is the gradual destruction of metals by chemical or electrochemical reaction with the environment. It is a natural process which converts a metal into its oxide, hydroxide or sulphide so that it loses its metallic characteristics.
- Rust is chemically known as hydrated ferric oxide (it is formulated as Fe<sub>2</sub>O<sub>3</sub>.xH<sub>2</sub>O). Rusting results in the formation of scaling reddish brown hydrated ferric oxide on the surface of iron and iron containing materials.

#### **Types of Corrosion** Dry Corrosion or Chemical Corrosion:

The corrosive action in the absence of moisture is called dry corrosion. It is the process of a chemical attack on a metal by a corrosive liquids or gases such as O<sub>2</sub>, N<sub>2</sub>, SO<sub>2</sub>, H<sub>2</sub>S etc. It occurs at high temperature. Of all the gases mentioned above O<sub>2</sub> is the most reactive gas to impart the chemical attack.

#### Wet Corrosion or Electrochemical Corrosion:

The corrosive action in the presence of moisture is called wet corrosion. It occurs as a result of electrochemical reaction of metal with water or aqueous solution of salt or acids or bases. EN

#### Methods of preventing corrosion

- Alloying: The metals can be alloyed to prevent the process of corrosion. E.g. 1. Stainless Steel
- Surface Coating: It involves application of a protective coating over the 2. metal. It is of the following types:

#### Galvanization:

• It is the process of coating zinc on iron sheets by using electric current.

#### **Electroplating:**

• It is a method of coating one metal over another metal by passing electric current.

#### Anodizing:

It is an electrochemical process that converts the metal surface into a decorative, durable and corrosion resistant. Aluminium is widely used for anodizing process.



#### **Cathodic Protection:**

• It is the method of controlling corrosion of a metal surface protected is coated with the metal which is easily corrodible. The easily corrodible metal is called Sacrificial metal to act as anode ensuring cathodic protection

#### PAMBAN BRIDGE

It is a railway bridge which connects the town of Rameshwaram on Pamban Island to mainland India. Opened on 1914, it was India's first sea bridge in India until the opening of the BandraWorli Sea Link in 2010. We can control the corrosion and renovation of historical pamban bridge by a periodical protective coating which will be the strong example for applied chemistry to uphold our history.





#### 11<sup>th</sup> CHEMISTRY Vol. 1 Unit 1 - Basic Concept Of Chemistry

#### Classification of Matter Physical Classification of Matter :

Matter can be classified as solids, liquids and gases based on their physical state. The physical state of matter canbeconverted into one another by modifying the temperature and pressure suitably.

#### **Chemical Classification :**

Matter can be classified into mixtures and pure substances based on chemical compositions. Mixtures consist of more than one chemical entity present without any chemical interactions. Theycan be further classified as homogeneous or heterogeneous mixtures based on their physical appearance.

Pure substances are composed of simple atoms or molecules. They are further classified as elements and compounds.

#### Element :

An element consists of only onetype of atom. We know that an atom is thesmallest electrically neutral particle, beingmade up of fundamental particles, namelyelectrons, protons and neutrons.

Element can exist as monatomic orpolyatomic units.

#### Example :

Monatomic unit –Gold(Au), Copper (Cu); Polyatomic unit -Hydrogen (H<sub>2</sub>), Phosphorous (P<sub>4</sub>) andSulphur (S<sub>8</sub>)

#### Compound:

Compounds are made up ofmolecules which contain two or moreatoms of different elements.

#### Example :

Carbon dioxide (CO<sub>2</sub>), Glucose (C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>), HydrogenSulphide (H<sub>2</sub>S), Sodium Chloride (NaCl)

Properties of compounds are different from those of their constituent elements. For example, sodium is a shinymetal, and chlorine is an irritating gas. But the compound formed from these two elements, sodium chloride, shows different characteristics as it is a crystalline

solid, vital for biological functions.



#### **Evaluate Yourself**

1) By applying the knowledge of chemical classification, classifyeach of the following into elements, compounds or mixtures.

(i) Sugar
(ii) Sea water
(iii) Distilled water
(iv) Carbon dioxide
(v) Copper wire
(vi) Table salt
(vii) Silver plate
(viii) Naphthalene balls

#### **Atomic Masses**

The C-12 atom is considered asstandard by the IUPAC (InternationalUnion of Pure and Applied Chemistry), and its mass is fixed as 12 amu (or) u.Theamu (or) unified atomic mass unit is defined as one twelfth of the mass of aCarbon-12 atom in its ground state.

i.e. 1 amu (or)  $1u \approx 1.6605 \times 10^{-27}$  kg.

#### Molecular Mass

Similar to relative atomic mass, relative molecular mass is defined as the ratio of the mass of a molecule to the unified atomic mass unit. The relative molecular mass of any compound can be calculated by adding the relative atomic masses of its constituent atoms.

TRE

#### For example,

i) Relative molecular mass of hydrogenmolecule (H2)

- = 2 × (relative atomic mass of hydrogen atom)
- = 2 × 1.008 u
- = 2.016 u.

ii) Relative molecular mass of  $glucose(C_6H_{12}O_6)$ 

- $= (6 \times 12) + (12 \times 1.008) + (6 \times 16)$
- = 72+12.096+96
- = 180.096 u

#### Relative atomic masses of someelements

Element	Relativeatomicmass	Element	Relativeatomic
			mass
Н	1.008	Cl	35.45
С	12	K	39.10



			GHENNAT
Ν	14	Ca	40.08
0	16	Cr	51.99
Na	23	Mn	54.94
Mg	24.3	Fe	55.85
S	32.07	Cu	63.55

Evaluate Yourself

2) Calculate the relative molecular massof the following.

(i) Ethanol(C<sub>2</sub>H<sub>5</sub>OH)

- (ii) Potassium permanganate (KMnO<sub>4</sub>)
- (iii) Potassium dichromate (K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>)
- (iv) Sucrose (C12H22O11)

#### Mole Concept

To understand the mole concept,let us calculate the total number of atoms present in 12 g of carbon -12 isotopeor molecules in 158.03 g of potassiumpermanganate, 294.18 g of potassiumdichromate and 180 g of glucose.

#### Calculation of number of entities in one mole of substance.

S.No	Name of	Mass of the	Mass of single	No. of atoms or molecules
	substance	substance	atom	= Mass of substance $\div$
		taken	or molecule	Mass of
		(gram)	(gram)	Single atom or molecule
			= Atomic mass	
		UIL	or Molar mass /	
	67		Avovadro	
	D		Number	
	(1)	(2)	(3)	$(2) \div (3)$
1	Elemental	12	1.9926 x 10 <sup>-23</sup>	12 $-6.022 \times 10^{23}$
	Carbon (C-12)			$\frac{1.9926 \times 10^{-23}}{1.9926 \times 10^{-23}} = 0.022 \times 10^{-23}$
2	Glucose	180	29.89 x 10 <sup>-23</sup>	$\frac{180}{-6.022 \times 10^{23}}$
	(C6H12O6)			$\frac{1}{29.89 \times 10^{-23}} = 0.022 \times 10^{-23}$
3	Potassium	294.18	48.851 x 10 <sup>-23</sup>	$294.18 - 6.022 \times 10^{23}$
	dichromate			$48.851 \times 10^{-23} = 0.022 \times 10^{-23}$
	(K2Cr2O7)			
4	Potassium	158.03	$26.242  imes 10^{-23}$	$158.03 - 6.022 \times 10^{23}$
	permanganate			$\frac{1}{26.242 \times 10^{-23}} = 0.022 \times 10^{-23}$
	(KMnO4)			

One mole is the amount of substance of a system, which contains as manyelementary particles as there are atoms in 12 g of carbon-12 isotope. The elementaryparticles can be molecules, atoms, ions, electrons or any other specified particles.



#### Avogadro Number:

The total number of entities presentin one mole of any substance is equal to  $6.022 \times 1023$ . This number is called Avogadro number which is named after the Italian physicist Amedeo Avogadro who proposed that equal volume of all gases under the same conditions oftemperature and pressure contain equal number of molecules. Avogadro numberdoes not have any unit.

#### Molar Mass:

Molar mass is defined as the mass of one mole of a substance. The molar mass f a compound is equal to the sum of therelative atomic masses of its constituents expressed in g mol-1.

#### **Examples:**

• relative atomic mass of one hydrogenatom = 1.008 u

#### Molar Volume:

The volume occupied by one moleof any substance in the gaseous state at agiven temperature and pressure is calledmolar volume.

Conditions	Volume occupiedby one mole of any gaseous substances (inlitre)
273 K and 1 barpressure (STP)	22.71
273 K and 1 atm pressure	22.4
298 K and 1 atm pressure(Room	24.47
Temperature & pressure (SATP)	

#### Gram Equivalent Concept:

Gram equivalent mass is defined as the mass of an element (compound orion) that combines or displaces 1.008 ghydrogen or 8 g oxygen or 35.5 g chlorine.



#### 11<sup>th</sup>vol 1 Unit – 3 Periodic Classification of Elements

Lavoisier ta	ble
acid-making elements	gas-like elements
Sulphur	Light
Phosphorus	Caloric (heat)
Charcoal (carbon)	Oxygen
	Azote (nitrogen)
	Hydrogen

metallic elements	earthy elements
cobalt, mercury, tin	lime (calcium
	oxide)
copper, nickel, iron	magnesia
	(magnesium
	oxide)
gold, lead, silver, zinc	barytes (barium
	sulphate)
manganese, tungten	argilla (aluminium
	oxide)
platina (platinum)	silex (silicon dioxide)

#### Mendeleev's Classification

In 1868, Lothar Meyer had developed a table of the elements that closely resembles the modern periodic table. He plotted the physical properties such as atomic volume, melting point and boiling point against atomic weight and observed a periodical pattern.

During same period Dmitri Mendeleev independently proposed that "the properties of the elements are the periodic functions of their atomic weights" and this is called periodic law. Mendeleev listed the 70 known elements at that time in several vertical columns in order of increasing atomic weights. Thus, Mendeleev constructed the first periodic table based on the periodic law.

As shown in the periodic table, he left some blank spaces since there were no known elements with the appropriate properties at that time. He and others predicted the physical and chemical properties of the missing elements. Eventually these missing elements were discovered and found to have the predicted properties. For example, Gallium (Ga) of group III and germanium (Ge) of group IV were unknown at that time. But Mendeleev predicted their existence and properties. He referred the predicted elements as eka-aluminium and eka-silicon. After discovery of the actual



elements, their properties were found to match closely to those predicted by Mendeleev.

S. NO.	Property	Ekaaluminiu m	Gallium (Observed)	Ekasilicon (Predicted)	Germanium (Observed)
		(Predicted)	· · · · · ·	, , ,	, ,
1.	Atomic weight	68	70	72	72.59
2.	Density (g/cm3)	5.9	5.94	5.5	5.35
3.	Melting point	low	29.78°C	High	947°C
4.	Formula of oxide	$E_2O_3$	Ga <sub>2</sub> O <sub>3</sub>	EO <sub>2</sub>	GeO <sub>2</sub>
5.	Formula of chloride	ECl <sub>3</sub>	GaCl <sub>3</sub>	ECl <sub>4</sub>	GeCl <sub>4</sub>

#### Properties predicted for Eka-aluminium and Eka-silicon

#### Anomalies of Mendeleev's Periodic Table

Some elements with similar properties were placed in different groups and those with dissimilar properties were placed in same group.

Example: Tellurium (127.6) was placed in VI group but Iodine (127.0) was placed in VII group.

Similarly elements with higher atomic weights were placed before lower atomic weights based on their properties in contradiction to his periodic law. Example 59Co27 was placed before <sup>58.7</sup>Ni<sub>28</sub>

#### Moseley's Work and Modern Periodic Law

In 1913, Henry Moseley studied the characteristic X-rays spectra of several elements by bombarding them with high energy electrons and observed a linear correlation between atomic number and the frequency of X-rays emitted which is given by the following expression.

$$\upsilon = a(Z - b)$$

Where, v is the frequency of the X-rays emitted by the element with atomic number 'Z'; a and b are constants and have same values for all the elements.

The plot of  $\sqrt{\nu}$  against Z gives a straight line. Using this relationship, we can determine the atomic number of an unknown (new) element from the frequency of X-ray emitted.



Based on his work, the modern periodic law was developed which states that, "the physical and chemical properties of the elements are periodic functions of their atomic numbers." Based on this law, the elements were arranged in order of their increasing atomic numbers. This mode of arrangement reveals an important truth that the elements with similar properties recur after regular intervals. The repetition of physical and chemical properties at regular intervals is called periodicity.

Series						Group	of Hements				
	0	-	Π	I	N	Λ	ΙΛ	ΝI		ШЛ	
1		Hydrogen									
	ł	H		Ì							
5	Heitum	Lithium I	Beryllium	Boron	Carbon	Nitrogen	Oxygen	Fluorine			
	9 Ge	ГI	Be	g	0	N	0	H			
	4.0	7.03	9.1	11.0	12.0	14.04	16.00	19.0			
m	Neon	Sodium	Magnesium	Aluminium	Silicon	Phosphorus	Sulphur	Chlorine			
	Ne.	Na	Mg	N	8	4	ŝ	0			
	19.9	23.5	24.3	27.0	28.04	31.0	32.06	35.45			
÷	Argon	Potassium	Calcium	Scandium	Thranium	Vanadum	Chromium	Manganese	Iron	Cobalt	Nide
	Ar	K	Q	Sc	μ	^	ð	Mn	Ŧ	ථ	ð N
	38	39.1	40.1	44.1	48.1	51.4	51.99	55.0	55.9	8	8
ŝ		Copper	Zind	Gallium	Germanium	Arsenic	Selenium	Bromine			
		ō	Zn	g	පී	As	8	Br			
		63.6	65.4	70.0	72.3	75	79	79.95			
	Krypton	Rubidium	Strontium	Yttrium	Zirconium	Niddum	Molybdenum	•	Ruthenium	Rhodium	Palladium
	Kr	Rb	Sr	Y	Z	Ê	Mo		Ru	Rh	V) Pd)
	81.8	85.4	87.6	89.0	90.6	94.0	96.0		1 01.7		106.5
2		Silver	Cadmium	Indium	ΠŢ	Antimony	Tellurium	Iodine			
		Ag	3	đ	Sn	8	đ	-			
		107.9	112.4	114.0	119.0	120.0	127.6	126.9			
90	Xenon	Caesium	Barium	Lanthanum	Cerium						
	Xe	ð	Ba	La	Ŭ						
	128	132.9	137.4	139	140						
9	•		Ì	•	ľ	Ì			•		
9				Ytterbium		Tantalum	Tungsten		Osmium	Iridium	Platinum
	Ì			χp	Ì	đ.	W		õ	FI.	Gr (Pr
				173		183	184		191	193	194.5
=			Gold	Mercury	Thallium	Lead	Bismuth	•			
			νn	Hg	Ħ	£	Bi				
			197.2	200.0	204.1	206.9	208				
12			Radium		Thorium		Uranium				
	Ì		Ra	•	ħ		D				
			224		232		239				
						Higher Saline (	Oxides				
	R	R20	R203		$RO_2$	$R_2O_5$	RO <sub>3</sub>	R2O,		RO.	
					Higher(	baseous Hydrog	en Compounds			Pow	
					RH4	RH3	RH2	RH			
1											

Mendeleev's periodic table



#### Modern Periodic Table

The physical and chemical properties of the elements are correlated to the arrangement of electrons in their outermost shell (valence shell). Different elements having similar outer shell electronic configuration possess similar properties. For example, elements having one electron in their valence shell s-orbital possess similar physical and chemical properties. These elements are grouped together in the modern periodic table as first group elements.

Elements	Atomic	Number of	Valence
in	number	electrons in	shell
Group 1		various shells	configuration
		in the order	
		KLMNP	
Li	3	2,1	2s <sup>1</sup>
Na	11	2,8,1	3s <sup>1</sup>
K	19	2,8,8,1	4s <sup>1</sup>
Rb	37	2,8,18,8,1	5s <sup>1</sup>
Cs	55	2,8,18,18,8,1	6s <sup>1</sup>
Fr	87	2,8,18,32,18,1	7s <sup>1</sup>

# Electronic configuration of alkali metals (ns1)

Similarly, all the elements are arranged in the modern periodic table which contains 18 vertical columns and 7 horizontal rows. The vertical columns are called groups and the horizontal rows are called periods. Groups are numbered 1 to 18 in accordance with the IUPAC recommendation which replaces the old numbering scheme IA to VIIA, IB to VIIB and VIII.

Each period starts with the element having general outer electronic configuration ns1 and ends with np6. Here 'n' corresponds to the period number (principal quantum number). The aufbau principle and the electronic configuration of atoms provide a theoretical foundation for the modern periodic table.

#### Nomenclature of Elements with Atomic Number Greater than 100

Usually, when a new element is discovered, the discoverer suggests a name following IUPAC guidelines which will be approved after a public opinion. In the meantime, the new element will be called by a temporary name coined using the following IUPAC rules, until the IUPAC recognises the new name.

1. The name was derived directly from the atomic number of the new element using the following numerical roots.



Digital	0	1	2	3	4	5	6	7	8	9
Root	Nil	Un	Bi	Tri	Quad	Pent	Hex	Sept	Oct	enn
Abbrevation	Ν	U	В	Т	Q	Р	Η	S	0	e

#### Notation for IUPAC Nomenclature of elements

- 2. The numerical roots corresponding to the atomic number are put together and 'ium' is added as suffix
- 3. The final 'n' of 'enn' is omitted when it is written before 'nil' (enn + nil = enil) similarly the final 'i' of 'bi' and 'tri' is omitted when it written before 'ium' (bi + ium = bium; tri + ium = trium)
- 4. The symbol of the new element is derived from the first letter of the numerical roots.

The following table illustrates these facts.

A				C 1 1
Atomic	Temp. Name	Temp.	Name of the	Symbol
number		Symbol	element	
101	Unnilunium	Unu	Mendelevium	Md
102	Unnilbium	Unb	Nobelium	No
103	Unniltrium	Unt	Lawrencium	Lr
104	Unnilquadium	Unq	Rutherfordium	Rf
105	Unnilpentium	Unp	Dubnium	Db
106	Unnilhexium	Unh	Seaborgium	Sg
107	Unnilseptium	Uns	Bohrium	Bh
108	Unniloctium	Uno	Hassium	Hs
109	Unnilennium	Une	Meitnerium	Mt
110	Ununnilium	Unn	Darmstadium	Ds
111	Ununnilium	Uuu	Roentgenium	Rg
112	Ununbium	Uub	Copernicium	Cn
113	Ununtrium	Uut	Nihonium	Nh
114	Ununquadium	Uup	Flerovium	Lv
115	Ununpentium	Uup	Moscovium	Ts
116	Ununhexium	Uuh	Livermorium	Lv
117	Ununseptium	Uus	Tennessine	Ts
118	Ununoctium	Uco	Oganesson	Og

Name of elements with atomic number above 100

#### **Grouping of Elements based on Electronic Configurations**

In the modern periodic table, the elements are organised in 7 periods and 18 groups based on the modern periodic law. The placement of element in the periodic table is closely related to its outer shell electronic configuration. Let us analyse the



change in the electronic configuration of elements along the periods and down the groups.

#### Variation of Electronic Configuration along the periods

We have already learnt that each period starts with the element having general outer electronic configuration ns1 and ends with ns2, np6 where n is the period number. The first period starts with the filling of valence electrons in 1s orbital, which can accommodate only two electrons. Hence, the first period has two elements, namely hydrogen and helium. The second period starts with the filling of valence electrons in 2s orbital followed by three 2p orbitals with eight elements from lithium to neon. The third period starts with filling of valence electrons in the 3s orbital followed by 3p orbitals. The fourth period starts with filling of valence electrons from 4s orbital followed by 3d and 4p orbitals in accordance with Aufbau principle. Similarly, we can explain the electronic configuration of elements in the subsequent periods.

Period number (n)	Filling of electrons in orbitals		Number of	Outer shell Electronic con- figuration	
	Starts from	Ends with	cientents	First element	Last element
1	1s	>1s	2	$H - 1s^1$	He – 1s <sup>2</sup>
2	2s	2p	8	$L1 - 2s^1$	Ar- 2s <sup>2</sup> 2p <sup>6</sup>
3	3s -	→ 3p	8	Na – 3s <sup>1</sup>	Ne – 3s²3p <sup>6</sup>
4	4s> 3d		18	$K - 4s^1$	Kr- 4s <sup>2</sup> 4p <sup>6</sup>
5	5s 4d		18	Rb – 5s <sup>1</sup>	Xe – 5s²5p <sup>6</sup>
6	6s → 4f →ð		32	Cs - 6s <sup>1</sup>	Rn – 6s <sup>2</sup> 6p <sup>6</sup>
7	7s → 5f → 6d	⇒7p	32	Fr - 7s <sup>1</sup>	Og – 7s²7p <sup>6</sup>

#### Table 3.10 Electronic configuration of elements in a period

In the fourth period the filling of 3d orbitals starts with scandium and ends with zinc. These 10 elements are called first transition series. Similarly 4d, 5d and 6d orbitals are filled in successive periods and the corresponding series of elements are called second, third and fourth transition series respectively.

In the sixth period the filling of valence electrons starts with 6s orbital followed by 4f, 5d and 6p orbitals. The filling up of 4f orbitals begins with Cerium (Z=58) and ends at Lutetium (Z=71). These 14 elements constitute the first inner-transition series called Lanthanides. Similarly, in the seventh period 5f orbitals are filled, and it's -14 elements constitute the second inner-transition series called Actinides. These two series are placed separately at the bottom of the modern periodic table.


## Variation of Electronic Configuration in the Groups:

Elements of a group have similar electronic configuration in the outer shell. The general outer electronic configurations for the 18 groups are listed in the Table 3.11. The groups can be combined as s, p, d and f block elements on the basis of the orbital in which the last valence electron enters.

The elements of group 1 and group 2 are called s-block elements, since the last valence electron enters the ns orbital. The group 1 elements are called alkali metals while the group 2 elements are called alkaline earth metals. These are soft metals and possess low melting and boiling points with low ionisation enthalpies. They are highly reactive and form ionic compounds. They are highly electropositive in nature and most of the elements imparts colour to the flame. We will study the properties of these group elements in detail in subsequent chapters.

The elements of groups 13 to 18 are called p-block elements or representative elements and have a general electronic configuration ns2, np1-6. The elements of the group 16 and 17 are called chalcogens and halogens respectively. The elements of 18<sup>th</sup> group contain completely filled valence shell electronic configuration (ns2, np6) and are called inert gases or nobles gases. The elements of p-block have high negative electron gain enthalpies. The ionisation energies are higher than that of s-block elements. They form mostly covalent compounds and shows more than one oxidation states in their compounds.

The elements of the groups 3 to 12 are called d-block elements or transition elements with general valence shell electronic configuration ns1-2, (n-1)d1-10. These elements also show more than one oxidation state and form ionic, covalent and co-ordination compounds. They can form interstitial compounds and alloys which can also act as catalysts. These elements have high melting points and are good conductors of heat and electricity.

The lanthanides (4f1-14, 5d0-1, 6s2) and the actinides (5f0-14, 6d0-, 7s2) are called f-block elements. These elements are metallic in nature and have high melting points. Their compounds are mostly coloured. These elements also show variable oxidation states.

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
ns <sup>1</sup>	ns <sup>2</sup>	$ns^2(n-1)d^1$	$ns^2 \left(n\text{-}1 \right) d^2$	$ns^2 (n-1)d^3$	ns <sup>1</sup> (n-1)d <sup>5</sup>	$ns^2(n\text{-}1)d^5$	$ns^2(n-1)d^6$	$ms^2(n-1)d^7$	$ms^2(n-1)d^8$	$ns^1 (n-1)d^{10}$	$ns^2 (n-1) d^{10}$	$ns^2 np^1$	$ns^2 np^2$	$ns^2 np^3$	$ns^2 np^4$	ns <sup>2</sup> np <sup>5</sup>	$\mathrm{ns}^2\mathrm{np}^6$
s E eler	llock nents		d-Block elements p-Block elements														
f blo	ock	+	Lan	Lanthanides 4f <sup>1-14</sup> 5d <sup>0-1</sup> 6s <sup>2</sup>													
eler	nents	L	Act	Actinides 5f <sup>0-14</sup> 6d <sup>0-2</sup> 7s <sup>2</sup>													

Table 3.11 General outer electronic configuration of elements in groups:



### **Periodic Trends in Properties**

As discussed earlier, the electronic configuration of the elements shows a periodic variation with increase in atomic numbers. Similarly a periodic trend is observed in physical and chemical behaviour of elements. In this section, we will study the periodic trends in the following properties of elements.

- 1. Atomic radius
- 2. Ionic radius
- 3. Ionisation enthalpy (energy)
- 4. Electron gain enthalpy (electron affinity)
- 5. Electronegativity

### **Atomic radius**

Atomic radius of an atom is defined as the distance between the centre of its nucleus and the outermost shell containing the valence electron.

It is not possible to measure the radius of an isolated atom directly. Except for noble gases, usually atomic radius is referred to as covalent radius or metallic radius depending upon the nature of bonding between the concerned atoms.

#### **Covalent radius**

It is one-half of the internuclear distance between two identical atoms linked together by a single covalent bond. Inter nuclear distance can be determined using x-ray diffraction studies.

## Example:

The experimental internuclear distance in  $Cl_2$  molecule is 1.98 Å. The covalent radius of chlorine is calculated as below.

$$d_{Cl-Cl} = r_{Cl+} r_{Cl}$$

$$\Rightarrow \quad d_{Cl-Cl} = 2r_{Cl}$$

$$\Rightarrow \quad r_{Cl} = \frac{d_{Cl-Cl}}{2}$$

$$= \frac{1.98}{2} = 0.99 \overset{\circ}{A}$$



The covalent radius of chlorine  $=\frac{198}{2}pm$  $= 99 \, pm$ 

The formation of covalent bond involves the overlapping of atomic orbitals and it reduces the expected internuclear distance. Therefore covalent radius is always shorter than the actual atomic radius.

The covalent radius of individual atom can also be calculated using the internuclear distance (d<sub>A-B</sub>) between two different atoms A and B. The simplest method proposed by Schomaker and Stevenson is as follows.

 $d_{A-B} = r_A + r_B - 0.09(\chi_A - \chi_B)$ 

where  $\chi_A$  and  $\chi_B$  are the electronegativities of A and B respectively in Pauling units. Here  $\chi_A > \chi_B$  and radius is in Å.

Let us calculate the covalent radius of hydrogen using the experimental dH-Cl value is 1.28 Å and the covalent radius of chlorine is 0.99 Å. In pauling scale the electronegativity of chlorine and hydrogen are 3 and 2.1 respectively. CENTRE

 $d_{\text{H-Cl}} = r_{\text{H}} + r_{\text{Cl}} - 0.09 (\chi_{cl} - \chi_{H})$  $1.28 = r_{\rm H} + 0.09 - 0.09 (3 - 2.1)$  $1.28 = r_{\rm H} + 0.09 - 0.09 (0.9)$  $1.28 = r_{\rm H} + 0.09 - 0.081$  $1.28 = r_{\rm H} + 0.909$  $\therefore r_{\rm H}$  = 1.28 - 0.909 = 0.317 Å

#### Metallic radius

It is defined as one-half of the distance between two adjacent metal atoms in the closely packed metallic crystal lattice.

For example, the distance between the adjacent copper atoms in solid copper is 2.56 Å and therefore the metallic radius of copper is

$$\frac{2.56}{2} = 1.28$$
Å

The metallic radius can be calculated using the unit cell length of the metallic crystal. You will study the detailed calculation procedure in XII standard solid state unit.



## **Periodic Trends in Atomic Radius** Variation in Periods

Atomic radius tends to decrease in a period. As we move from left to right along a period, the valence electrons are added to the same shell. The simultaneous addition of protons to the nucleus, increases the nuclear charge, as well as the electrostatic attractive force between the valence electrons and the nucleus. Therefore atomic radius decreases along a period.

### Effective nuclear charge

In addition to the electrostatic forces of attraction between the nucleus and the electrons, there exists repulsive forces among the electrons. The repulsive force between the inner shell electrons and the valence electrons leads to a decrease in the electrostatic attractive forces acting on the valence electrons by the nucleus. Thus, the inner shell electrons act as a shield between the nucleus and the valence electrons. This effect is called shielding effect.

The net nuclear charge experienced by valence electrons in the outermost shell is called the effective nuclear charge. It is approximated by the below mentioned equation.

 $Z_{\rm eff} = Z - S$ 

Where Z is the atomic number and 'S' is the screening constant which can be calculated using Slater's rules as described below.

#### Step 1:

Write the electronic configuration of the atom and rearrange it by grouping ns and np orbitals together and others separately in the following form. (1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p)...

#### Step 2:

Identify the group in which the electron of interest is present. The electron present right to this group does not contribute to the shielding effect.

Each of the electrons within the identified group (denoted by 'n') shields to an extent of 0.35 unit of nuclear charge. However, it is 0.30 unit for 1s electron.

#### Step 3:

Shielding of inner shell electrons. If the electron of interest belongs to either s or p orbital,

i) each electron within the (n-1) group shields to an extent of 0.85 unit of nuclear charge, and



ii) each electron within the (n-2) group (or) even lesser group (n-3, (n-4) etc... completely shields i.e. to an extent of 1.00 unit of nuclear charge. If the electron of interest belongs to d or f orbital, then each of electron left of the group of electron of interest shields to an extent of 1.00 unit of nuclear charge.

## Step 4:

Summation of the shielding effect of all the electrons gives the shielding constant  $\ensuremath{^{\rm S'}}$ 

**Example:** Let us explain the calculation of effective nuclear charge on 4s electron and 3d electron in scandium. The electronic configuration of scandium is 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>6</sup>, 3s<sup>2</sup>, 3p<sup>6</sup>, 4s<sup>2</sup>, 3d<sup>1</sup>. we can rearrange as below.

$(1s)^2$	(2s,2p) <sup>8</sup>	(3s,3p) <sup>8</sup> (3d) <sup>1</sup>	$(4s)^2$
	$\overline{}$		
(n-3)	(n-2)	(n-1)	n

Group	number of electron in the group	contribution of each electron to 'S'value	contribution of aparticular groupto electrons to 'S'value
(n)	1	0.35	0.35
(n-1)	9	0.85	7.65
(n-2) & others	10	1	10.00
	S value		18.00

 $Z_{eff} = Z - S i.e. = 21 - 18 \therefore Z_{eff} = 3$ 

Calculation of effective nuclear charge on 3d electron

$$\underbrace{(1s)^2}_{(n-3)} \underbrace{(2s,2p)^8}_{(n-2)} \underbrace{(3s,3p)^8}_{(n-1)} (3d)^1 \underbrace{(4s)^2}_{n-1}$$

Group	Group number of electron in the group		contribution of a particular group to electrons to 'S' value	
n	0	0.35	0	
(n-1) & others	18	1	18	
	18			

 $\therefore$  Z<sub>eff</sub> = Z - S i.e. =21 - 18  $\therefore$   $\therefore$  Z<sub>eff</sub> = 3



Electron Group	Electron of interest either	Electron of interest either		
	S or P	d or f		
n	0.35 (0.30 for	0.35		
	(S electron)			
(n-1)	0.85	1.00		
(n-2) and others	1.00	1.00		

Shielding effect from inner shell electrons (Slater's rules)

Elements	Effective nuclear charge	Covalent radius (pm)
Li <sup>3</sup>	1.30	167
Be <sup>4</sup>	1.95	112
C <sup>6</sup>	2.60	87
N <sup>7</sup>	3.25	67
O <sup>8</sup>	3.25	56
F9	4.55	48

5.85

Atomic radius (covalent radius) of second period elements.

## Variation in Group

Ne<sup>10</sup>

In the periodic table, the atomic radius of elements increases down the group. As we move down a group, new shells are opened to accommodate the newly added valence electrons. As a result, the distance between the centre of the nucleus and the outermost shell containing the valence electron increases. Hence, the atomic radius increases. The trend in the variation of the atomic radius of the alkali metals down the group os shown below.

Element	Outermost shell	Covalent
	containing valence	radius
	electron	(Å)
Li	L (n=2)	1.35
Na	M (n=3)	1.54
К	N (n=4)	1.96
Rb	O (n=5)	2.11
Cs	P(n=6)	2.25

## Variation of covalent radius of group 1 elements

## **Ionic radius**

It is defined as the distance from the centre of the nucleus of the ion up to which it exerts its influence on the electron cloud of the ion. Ionic radius of uniunivalent crystal can be calculated using Pauling's method from the inter ionic



distance between the nuclei of the cation and anion. Pauling assumed that ions present in a crystal lattice are perfect spheres, and they are in contact with each other therefore,

Where d is the distance between the centre of the nucleus of cation C+ and anion A- and rC +, rA - are the radius of the cation and anion respectively.

Pauling also assumed that the radius of the ion having noble gas electronic configuration (Na+ and Cl<sup>-</sup> having  $1s^2 2s^2$ ,  $2p^6$  configuration) is inversely proportional to the effective nuclear charge felt at the periphery of the ion.

Where  $Z_{eff}$  is the effective nuclear charge and  $Z_{eff} = Z - S$ 

Dividing the equation 1 by 3

$$\frac{r_{C^{+}}}{r_{A^{-}}} = \frac{\left(Z_{eff}\right)_{A^{-}}}{\left(Z_{eff}\right)_{C^{+}}}\dots\dots(4)$$

On solving equation (1) and (4) the values of  $r_C$  and  $r_A$  can be obtained

Let us explain this method by calculating the ionic radii of Na+ and F- in NaF crystal whose interionic distance is equal to 231 pm .

 $d = r_{Na^{-}} + r_{F}$ .....(5) *i.e.* $r_{Na^{+}} + r_{F^{-}} = 231 pm$ 

we know that



$$\frac{r_{Na^{+}}}{r_{F^{-}}} = \frac{\left(Z_{eff}\right)_{F^{-}}}{\left(Z_{eff}\right)_{Na^{+}}}$$

$$\left(Z_{eff}\right)_{F^{-}} = Z - S$$

$$= 9 - 4.15$$

$$= 4.85$$

$$\left(Z_{eff}\right)_{Na^{+}} = 11 - 4.15$$

$$= 6.85$$

$$\therefore \frac{r_{Na^{+}}}{r_{F^{-}}} = \frac{4.85}{6.85}$$

$$= 0.71$$

$$\Rightarrow r_{Na^{+}} = 0.71 \times r_{F^{-}}$$

Substitting (3) in (1)

 $(1) \Rightarrow 0.71r_{F^{-}} + r_{F^{-}} = 231pm$  $1.71r_{F^{-}} = 231pm$  $r_{F^{-}} = \frac{231}{1.71} = 135.1pm$ 

Substituting the value of  $r_{r^-}$  in equation (1)

1

$$r_{Na^+} + 135.1 = 23$$
  
 $r_{Na^+} = 95.9 \, pm$ 

## **Ionisation energy**

It is defined as the minimum amount of energy required to remove the most loosely bound electron from the valence shell of the isolated neutral gaseous atom in its ground state. It is expressed in kJ mol-1 or in electron volts (eV).

GENTR

 $M_{(g)} + IE_l \rightarrow M^+_{(g)} + 1e^-$ 

Where  $IE_1$  represents the first ionisation energy.



### **Successive Ionisation energies**

The minimum amount of energy required to remove an electron from a unipositivecation is called second ionisation energy. It is represented by the following equation.

$$M^{+}_{(g)} + IE_2 \rightarrow M^{2+}_{(g)} + 1e^{-1}$$

In this way we can define the successive ionisation energies such as third, fourth etc.

The total number of electrons are less in the cation than the neutral atom while the nuclear charge remains the same. Therefore the effective nuclear charge of the cation is higher than the corresponding neutral atom. Thus the successive ionisation energies, always increase in the following order

### IE<sub>1</sub>< IE<sub>2</sub>< IE<sub>3</sub>< .....

### **Periodic Trends in Ionisation Energy**

The ionisation energy usually increases along a period with few exceptions. As discussed earlier, when we move from left to right along a period, the valence electrons are added to the same shell, at the same time protons are added to the nucleus. This successive increase of nuclear charge increases the electrostatic attractive force on the valence electron and more energy is required to remove the valence electron resulting in high ionisation energy.

Let us consider the variation in ionisation energy of second periodelements. The plot of atomic number vs ionisation energy is given below.

In the following graph, there are two deviation in the trends of ionisiation energy. It is expected that boron has higher ionisation energy than beryllium since it has higher nuclear charge. However, the actual ionisation energies of beryllium and boron are 899 and 800 kJ mol<sup>-1</sup>respectively contrary to the expectation. It is due to the fact that beryllium with completely filled 2s orbital, is more stable than partially filled valence shell electronic configuration of boron.  $(2s^2, 2p^1)$ 

The electronic configuration of beryllium (Z=4) in its ground state is  $1s^2$ ,  $2s^2$  and that of boran (Z = 5)  $1s^2 2s^2 2p^1$ 

Similarly, nitrogen with 1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>3</sup> electronic configuration has higher ionisation energy (1402 kJ mol<sup>-1</sup>) than oxygen (1314 kJ mol<sup>-1</sup>). Since the half filled electronic configuration is more stable, it requires higher energy to remove an electron from 2p orbital of nitrogen. Whereas the removal one 2p electron from oxygen leads to a stable half filled configuration. This makes comparatively easier to remove 2p electron from oxygen.



## Periodic variation in group

The ionisation energy decreases down a group. As we move down a group, the valence electron occupies new shells, the distance between the nucleus and the valence electron increases. So, the nuclear forces of attraction on valence electron decreases and hence ionisation energy also decreases down a group.

#### Ionisation energy and shielding effect

As we move down a group, the number of inner shell electron increases which in turn increases the repulsive force exerted by them on the valence electrons, i.e. the increased shielding effect caused by the inner electrons decreases the attractive force acting on the valence electron by the nucleus. Therefore the ionisation energy decreases.

Let us understand this trend by considering the ionisation energy of alkali metals.

## **Electron affinity**

It is defined as the amount of energy released (required in the case noble gases) when an electron is added to the valence shell of an isolated neutral gaseous atom in its ground state to form its anion. It is expressed in kJ mol<sup>-1</sup>

 $A + 1e^- \rightarrow A^- + E_A$ 

## Variation of Electron Affinity in a period:

The variation of electron affinity is not as systematic as in the case of ionisation energy. As we move from alkali metals to halogens in a period, generally electron affinity increases, i.e. the amount of energy released will be more. This is due to an increase in the nuclear charge and decrease in size of the atoms. However, in case of elements such as beryllium (1s<sup>2</sup>, 2s<sup>2</sup>), nitrogen (1s<sup>2</sup>, 2s<sup>2</sup>, 2p<sup>3</sup>) the addition of extra electron will disturb their stable electronic configuration and they have almost zero electron affinity.

## Variation of electron affinity (electron gain energy) along I period

Noble gases have stable ns<sup>2</sup>, np<sup>6</sup> configuration, and the addition of further electron is unfavourable and requires energy. Halogens having the general electronic configuration of ns2, np5 readily accept an electron to get the stable noble gas electronic configuration (ns<sup>2</sup>, np<sup>6</sup>), and therefore in each period the halogen has high electron affinity. (high negative values)



## Variation of Electron affinity in a group:

As we move down a group, generally the electron affinity decreases. It is due to increase in atomic size and the shielding effect of inner shell electrons. However, oxygen and fluorine have lower affinity than sulphur and chlorine respectively. The sizes of oxygen and fluorine atoms are comparatively small and they have high electron density. Moreover, the extra electron added to oxygen and fluorine has to be accommodated in the 2p orbital which is relatively compact compared to the 3p orbital of sulphur and chlorine so, oxygen and fluorine have lower electron affinity than their respective group elements sulphur and chlorine.

## Electronegativity

It is defined as the relative tendency of an element present in a covalently bonded molecule, to attract the shared pair of electrons towards itself.

Electronegativity is not a measurable quantity. However, a number of scales are available to calculate its value. One such method was developed by Pauling, he assigned arbitrary value of electronegativities for hydrogen and fluorine as 2.2 and 4.0 respectively. Based on this the electronegativity values for other elements can be calculated using the following expression

$$(X_A - X_B) = 0.182\sqrt{E}_{AB} - (E_{AA} * E_{BB})^{1/2}$$

Where  $E_{AB}$ ,  $E_{AA}$  and  $E_{BB}$  are the bond dissociation energies of AB,  $A_2$  and  $B_2$  molecules respectively.

The electronegativity of any given element is not a constant and its value depends on the element to which it is covalently bound. The electronegativity values play an important role in predicting the nature of the bond.

## Variation of Electronegativity in a period:

The electronegativity generally increases across a period from left to right. As discussed earlier, the atomic radius decreases in a period, as the attraction between the valence electron and the nucleus increases. Hence the tendency to attract shared pair of electrons increases. Therefore, electronegativity also increases in a period.

## Variation of Electronegativity in a group:

The electronegativity generally decreases down a group. As we move down a group the atomic radius increases and the nuclear attractive force on the valence electron decreases. Hence, the electronegativity decreases.

Noble gases are assigned zero electronegativity. The electronegativity values of the elements of s-block show the expected decreasing order in a group. Except



13th and 14th group all other p-block elements follow the expected decreasing trend in electronegativity.

## **Periodic Trends in Chemical Properties:**

So far, we have studied the periodicity of the physical properties such as atomic radius, ionisation enthalpy, electron gain enthalpy and electronegativity. In addition, the chemical properties such as reactivity, valence, oxidation state etc... also show periodicity to certain extent.

In this section, we will discuss briefly about the periodicity in valence (oxidation state) and anomalous behaviour of second period elements (diagonal relationship).

## Valence or Oxidation States

The valence of an atom is the combining capacity relative to hydrogen atom. It is usually equal to the total number of electrons in the valence shell or equal to eight minus the number of valence electrons. It is more convenient to use oxidation state in the place of valence.

## **Periodicity of Valence or Oxidation States**

The valence of an atom primarily depends on the number of electrons in the valence shell. As the number of valence electrons remains same for the elements in same group, the maximum valence also remains the same. However, in a period the number of valence electrons increases, hence the valence also increases.

Alka	li Metals (Gro	up 1)	Group 15			
Element	No. of electrons in valence shell	Valence	Element	No. of electrons in valence shell	Valence	
Li	1	1	Ν	5	3,5	
Na	1	1	Р	5	3,5	
К	1	1	As	5	3,5	
Rb	1	1	Sb	5	3,5	
Cs	1	1	Bi	5	3,5	
Fr	1	1				

Variation of valence in groups

Variation of valence in period (1st period)

Element	Li	Be	В	C	N	0	F	Ne
No. of	1	2	3	4	5	6	7	8
electrons in								



							CHEN	NAI
valence shell								
Valence	1	2	3	4	5,3	6,2	7,1	8,0
(Combining								
capacity)								

In addition to that some elements have variable valence. For example, most of the elements of group 15 which have 5 valence electrons show two valences 3 and 5. Similarly transition metals and inner transition metals also show variable oxidation states.

#### Anomalous properties of second period elements:

As we know, the elements of the same group show similar physical and chemical properties. However, the first element of each group differs from other members of the group in certain properties. For example, lithium and beryllium form more covalent compounds, unlike the alkali and alkali earth metals which predominantly form ionic compounds. The elements of the second period have only four orbitals (2s & 2p) in the valence shell and have a maximum co-valence of 4, whereas the other members of the subsequent periods have more orbitals in their valence shell and shows higher valences. For example, boron forms BF4-and aluminium forms AlF6<sup>3-</sup> NTR

### **Diagonal Relationship**

On moving diagonally across the periodic table, the second and third period elements show certain similarities. Even though the similarity is not same as we see in a group, it is quite pronounced in the following pair of elements.

The similarity in properties existing between the diagonally placed elements is called 'diagonal relationship'.

#### **Periodic Trends and Chemical Reactivity:**

The physical and chemical properties of elements depend on the valence shell electronic configuration as discussed earlier. The elements on the left side of the periodic table have less ionisation energy and readily loose their valence electrons. On the other hand, the elements on right side of the periodic table have high electron affinity and readily accept electrons. As a consequence of this, elements of these extreme ends show high reactivity when compared to the elements present in the middle. The noble gases having completely filled electronic configuration neither accept nor lose their electron readily and hence they are chemically inert in nature.

The ionisation energy is directly related to the metallic character and the elements located in the lower left portion of the periodic table have less ionisation energy and therefore show metallic character. On the other hand the elements



located in the top right portion have very high ionisation energy and are nonmetallic in nature.

Let us analyse the nature of the compounds formed by elements from both sides of the periodic table. Consider the reaction of alkali metals and halogens with oxygen to give the corresponding oxides.

 $4 \text{ Na} + O_2 \rightarrow 2 \text{ Na}_2O$  $2 \text{ Cl}_2 + 7 \text{ O}_2 \rightarrow 2 \text{ Cl}_2O_7$ 

Since sodium oxide reacts withwater to give strong base sodiumhydroxide, it is a basic oxide. ConverselyCl<sub>2</sub>O<sub>7</sub> gives strong acid called perchloricacid upon reaction with water So, it is anacidic oxide.

 $\begin{array}{l} Na_2O + H_2O \rightarrow 2NaOH \\ Cl_2O_7 + H_2O \rightarrow 2 \; HClO_4 \end{array}$ 

Thus, the elements from the two extreme ends of the periodic table behave differently as expected.

As we move down the group, the ionisation energy decreases and the electropositive character of elements increases. Hence, the hydroxides of these elements become more basic. For example, let us consider the nature of the second group hydroxides:

 $Be(OH)_2$  amphoteric;  $Mg(OH)_2$  weakly basic;  $Ba(OH)_2$  strongly basic Beryllium hydroxide reacts with both acid and base as it is amphoteric in nature.

 $\begin{array}{l} Be(OH)_2 + HCl \rightarrow BeCl_2 + 2H_2O \\ Be(OH)_2 + 2 \ NaOH \rightarrow Na_2BeO_2 + 2H_2O \end{array}$ 



12<sup>th</sup> Chemistry 1<sup>st</sup> lesson

#### METALLURGY

#### Gravity separation or Hydraulic wash

In this method, the ore having high specific gravity is separated from the gangue that has low specific gravity by simply washing with running water. Ore is crushed to a finely powdered form and treated with rapidly flowing current of water. During this process the lighter gangue particles are washed away by the running water. This method is generally applied to concentrate the native ore such as gold and oxide ores such as haematite (Fe<sub>2</sub> O<sub>3</sub>), tin stone (SnO<sub>2</sub>) etc.

#### **Froth flotation**

This method is commonly used to concentrate sulphide ores such as galena (PbS), zinc blende (ZnS) etc... In this method, the metallic ore particles which are preferentially wetted by oil can be separated from gangue.

In this method, the crushed ore is suspended in water and mixed with frothing agent such as pine oil, eucalyptus oil etc. A small quantity of sodium ethyl xanthate which acts as a collector is also added. A froth is generated by blowing air through this mixture. The collector molecules attach to the ore particle and make them water repellent. As a result, ore particles, wetted by the oil, rise to the surface along with the froth. The froth is skimmed off and dried to recover the concentrated ore. The gangue particles that are preferentially wetted by water settle at the bottom.

When a sulphide ore of a metal of interest contains other metal sulphides as impurities, depressing agents such as sodium cyanide, sodium carbonate etc are used to selectively prevent other metal sulphides from coming to the froth. For example, when impurities such as ZnS is present in galena (PbS), sodium cyanide (NaCN) is added to depresses the flotation property of ZnS by forming a layer of zinc complex Na<sub>2</sub> [Zn(CN)<sub>4</sub>] on the surface of zinc sulphide.

#### Magnetic separation

This method is applicable to ferromagnetic ores and it is based on the difference in the magnetic properties of the ore and the impurities. For example tin stone can be separated from the wolframite impurities which is magnetic. Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non

magnetic siliceous impurities. The crushed ore is poured on to an electromagnetic separator consisting of a belt moving over two rollers of which one



is magnetic. The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it

## Conversion of ores into oxides Roasting

Roasting is the method, usually applied for the conversion of sulphide ores into their oxides. In this method, the concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.

$$2PbS + 3O_{2} \xrightarrow{\Delta} 2PbO + 2SO_{2} \uparrow$$
$$2Cu_{2}S + 3O_{2} \xrightarrow{\Delta} 2Cu_{2}O + 2SO_{2} \uparrow$$
$$2ZnS + 3O_{2} \xrightarrow{\Delta} 2ZnO + 2SO_{2} \uparrow$$

Roasting also removes impurities such as arsenic, sulphur, phosphorous by converting them into their volatile oxides. For example

$$4As + 3O_2 \longrightarrow 2As_2O_3 \uparrow$$
  

$$S_8 + 8O_2 \longrightarrow 8SO_2 \uparrow$$
  

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \uparrow$$

## Calcination

Calcination is the process in which the concentrated ore is strongly heated in the absence of air. During this process, the water of crystallisation present in the hydrated oxide escapes as moisture. Any organic matter (if present) also get expelled leaving behind a porous ore. This method can also be carried out with a limited supply of air.

ENTR

For examples,

During calcination of carbonate ore, carbon dioxide is expelled

 $PbCO_{2} \xrightarrow{\Delta} PbO + CO_{2} \uparrow$   $CaCO_{3} \longrightarrow CaO + CO_{2} \uparrow$   $ZnCO_{3} \xrightarrow{\Delta} ZnO + CO_{2} \uparrow$   $MgCO_{3}.CaCO_{3} \xrightarrow{\Delta} MgO + CaO + 2CO_{2} \uparrow$ 

During calcination of hydrated ore, the water of hydration is expelled as vapour

 $Fe_{2}O_{3}.3H_{2}O \xrightarrow{\Delta} Fe_{2}O_{3}(s) + 3H_{2}O(g) \uparrow$  $Al_{2}O_{3}.2H_{2}O \xrightarrow{\Delta} Al_{2}O_{3}(s) + 2H_{2}O(g) \uparrow$ 



## **Reduction of metal oxides**

Metal oxide can be reduced to crude metal by using a suitable reducing agent like carbon, carbon monoxide, hydrogen, aluminium and other reactive metals such as sodium etc...The choice of reducing agent depends on the nature of the metal. For example, carbon cannot be used as a reducing agent for the reactive metals such as sodium, potassium, aluminium etc...Similarly CO cannot be used to reduce oxides such as ZnO, Al<sub>2</sub>O<sub>3</sub>. Later in this, we study selection of suitable reducing agents by applying Ellingham diagram.

## Smelting

In this method, a flux (a chemical substance that forms an easily fusible slag with gangue) and a reducing agent such as carbon, carbon monoxide (or) aluminium is added to the concentrated ore and the mixture is melted by heating at an elevated temperature (above the melting point of the metal) in a smelting furnace. For example the oxide of iron can be reduced by carbon monoxide as follows.

 $Fe_2O_3(s)+3CO(g) \longrightarrow 2Fe(s)+3CO_2(g)$ 

In this extraction, a basic flux, quick lime (CaO) is used. Since the silica gangue present in the ore is acidic in nature, the quick lime combines with it to form calcium silicate (slag). NTRE

 $CaO(s) + SiO_2(s) \longrightarrow CaSio_3(s)$ Slag Flux Gangue

In the extraction of copper from copper pyrites, the concentrated ore is heated in a reverberatory furnace after mixing with silica, an acidic flux. The ferrous oxide formed due to melting is basic in nature and it combines with silica to form ferrous silicate (slag). The remaining metal sulphides Cu<sub>2</sub> S and FeS are mutually soluble and form a copper matte.

 $2\text{CuFeS}_2(s) + O_2(g) \longrightarrow 2FeS(1) + Cu_2S(1) + SO_2(g)$  $2\text{FeS}(l)+3O_2(g) \longrightarrow 2FeO(l)+2SO_2(g)$  $FeO(s) + SiO_2(s) \longrightarrow FeSiO_3(s)$ Gangue Flux Slag

The matte is separated from the slag and fed to the converting furnace. During conversion, the FeS present in the matte is first oxidised to FeO. This is removed by slag formation with silica. The remaining copper sulphide is further oxidised to its oxide which is subsequently converted to metallic copper as shown below.

 $2Cu_2S(l,s) + 3O_2(g) \rightarrow 2Cu_2O(l,s) + 2SO_2(g)$  $2Cu_2O(l) + Cu_2S(l) \rightarrow 6Cu(l) + SO_2(g)$ 



The metallic copper is solidified and it has blistered appearance due to evolution of SO<sub>2</sub> gas formed in this process. This copper is called blistered copper.

### **Reduction by carbon:**

In this method the oxide ore of the metal is mixed with coal (coke) and heated strongly in a furnace (usually in a blast furnace). This process can be applied to the metals which do not form carbides with carbon at the reduction temperature. Examples:

 $\begin{array}{l} ZnO\left(s\right) + C(s) \rightarrow Zn(s) + CO(g) \uparrow \\ Mn_{3}O_{4}(s) + 4C(s) \rightarrow 3Mn(s) + 4CO(g) \uparrow \\ Cr_{2}O_{3}\left(s\right) + 3C(s) \rightarrow 2Cr\left(s\right) + 3CO\left(g\right) \uparrow \end{array}$ 

### **Reduction by hydrogen:**

This method can be applied to the oxides of the metals (Fe, Pb, Cu) having less electropositive character than hydrogen.

 $\begin{array}{ll} Ag_2O(s) + H_2(g) & \rightarrow 2Ag(s) = H_2O \ (l) \\ Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(l) \end{array}$ 

Nickel oxide can be reduced to nickel by using a mixture of hydrogen and carbon monoxide (water gas)

 $2NiO(s) + CO(g) + H_2(g) \rightarrow 2Ni(s) + CO_2(g) + H_2O(l)$ 

## Reduction by metal:

Metallic oxides such as  $Cr_2O_3$  can be reduced by an aluminothermic process. In this process, the metal oxide is mixed with aluminium powder and placed in a fire clay crucible. To initiate the reduction process, an ignition mixture (usually magnesium and barium peroxide) is used.

 $BaO_2 + Mg \rightarrow BaO + MgO$ 

During the above reaction a large amount of heat is evolved (temperature up to 2400°C, is generated and the reaction enthalpy is : 852 kJ mol<sup>-1</sup>) which facilitates the reduction of  $Cr_2O_3$  by aluminium power.

 $Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$ 

Active metals such as sodium, potassium and calcium can also be used to reduce the metal oxide

 $\begin{array}{l} B_2O_3 + 6Na \longrightarrow 2B + 3Na_2O \\ Rb_2O_3 + 3Mg \longrightarrow 2Rb + 3MgO \\ TiO_2 + 2Mg \longrightarrow Ti + 2MgO \end{array}$ 



ThO<sub>2</sub> + 2Ca  $\xrightarrow{1250K}$  Th + 2CaO

## Auto-reduction:

Simple roasting of some of the ores give the crude metal. In such cases, the use of reducing agents is not necessary. For example, mercury is obtained by roasting of its ore cinnabar (HgS)

 $HgS(s) + O_2(g) \longrightarrow Hg(l) + SO_2\uparrow$ 

### Electrochemial extraction of aluminium - Hall-Heroult process:

In this method, electrolysis is carried out in an iron tank lined with carbon which acts as a cathode. The carbon blocks immersed in the electrolyte act as a anode. A 20% solution of alumina, obtained from the bauxite ore is mixed with molten cryolite and is taken in the electrolysis chamber. About 10% calcium chloride is also added to the solution. Here calcium chloride helps to lower the melting point of the mixture. The fused mixture is maintained at a temperature of above 1270 K. The chemical reactions involved in this process are as follows

Ionisation of alumina  $Al_2O_3 \rightarrow 2Al^{3+}+ 3O^{2-}$ Reaction at cathode  $2Al^{3+}$  (melt) + 6e<sup>-</sup> 2Al(l) Reaction at anode  $6O^{2-}$  (melt)  $\rightarrow 3O_2 + 12e^{-1}$ 

Since carbon acts as anode the following reaction also takes place on it.

 $\begin{array}{l} C(s) + O^{2\text{-}}(melt) \rightarrow CO + 2e^{\text{-}}\\ C(s) + 2O^{2\text{-}}(melt) \rightarrow CO_2 + 4e^{\text{-}} \end{array}$ 

Due to the above two reactions, anodes are slowly consumed during the electrolysis. The pure aluminium is formed at the cathode and settles at the bottom. The net electrolysis reaction can be written as follows.

 $4Al^{3+}$  (melt) +  $6O^{2-}$  (melt) +  $3C(s) \rightarrow 4Al(l) + 3CO_2(g)$ 

## **Electrolytic refining:**

The crude metal is refined by electrolysis. It is carried out in an electrolytic cell containing aqueous solution of the salts of the metal of interest. The rods of impure metal are used as anode and thin strips of pure metal are used as cathode. The metal of interest dissolves from the anode, pass into the solution while the same amount of metal ions from the solution will be deposited at the cathode. During electrolysis, the less electropositive impurities in the anode, settle down at the bottom and are removed as anode mud.

Let us understand this process by considering electrolytic refining of silver as an example.



Cathode : Pure silver

Anode : Impure silver rods

Electrolyte : Acidified aqueous solution of silver nitrate.

When a current is passed through the electrodes the following reactions will take place

Reaction anode	$Ag(s) \rightarrow Ag^+(aq) + Le^-$
Reaction at Cathode	$Ag^+(aq) + le^- \rightarrow Ag(s)$

During electrolysis, at the anode the silver atoms lose electrons and enter the solution. The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode. Other metals such as copper, zinc etc., can also be refined by this process in a similar manner.





## ACIDS AND BASES 8th term 3 Unit 5 ACIDS AND BASES

## Acids

The term acid is derived from the Latin word 'acidus' which means sour. Thus, the chemical compounds which have sour taste are called acids generally. All acids contain one or more replaceable hydrogen atoms in their molecules and when dissolved in water they release  $H^+$  ions. For example, Hydrochloric acid (HCl), Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) and Nitric acid (HNO<sub>3</sub>) release hydrogen ions (H<sup>+</sup>) when dissolved in water.

Hydrochloric + Water  $\rightarrow$  Hydrogen + Chloride

 $H_2SO_4 + H_2O \rightarrow 2H^+ + SO_4^{2-}$ 

Swedish chemist Svante Arrhenius proposed a theory on acids. According to him, an acid is a substance which furnishes H+ ions or  $H_3O^+$  ions in aqueous solution.

Thus, acids are defined as the chemical substances which release hydrogen ions when dissolved in water.

Acids can be classified into organic acids and inorganic acids depending on the sources. Some acids occur naturally in fruits and vegetables. These are called organic acids. Examples: Citric acid, tartaric acid etc.

Name of the AcidSourceCitric acidOranges, LemonLactic acidSour milkOxalic acidTomatoesAcetic acidVinegarMalic acidAppleTartaric acidTamarind

Organic acids and their sources

On the other hand, man produces acids artificially in industries. These acids are called mineral acids or inorganic acids. Examples: Hydrochloric acid (HCl), Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), Nitric acid (HNO<sub>3</sub>) etc., There are many more classifications of acids. You will study about them in your next class.]



## Properties of Acids Physical properties

- ✤ Acids are sour in taste.
- They are corrosive in nature. Strong acids can spoil substances like human skin, clothes and paper.
- Generally acids exist in liquid state but few acids exist in solid state too. E.g. Benzoic acid
- ✤ Acids are colourless.
- ✤ Acids change the colour of the indicators. Blue litmus paper turns red and methyl orange turns pink when treated with acids.
- ✤ They are soluble in water.
- Solutions of acids conduct electricity.

Wefeelhungryduetothecorrosive action of hydrochloric acid on the inner lining of the stomach. When the level of hydrochloric acid goes higher, it causes ulcer.

### Chemical properties Reaction with metals

Metals like zinc, magnesium, aluminum, iron etc., react with acids like hydrochloric acid, sulphuric acid to form metal salts and release hydrogen gas.

Metal + Dilute acids  $\rightarrow$  Metal salt + Hydrogen

Example:

Zinc + Hydrochloric  $\rightarrow$  Zinc chloride + Hydrogen

acid

 $Zn + 2HCl \rightarrow ZnCl_2 + H_2\uparrow$ 

Iron + Sulphuric acid  $\rightarrow$  Ferrous + Hydrogen sulphate

 $Fe + H_2SO_4 \rightarrow FeSO_4 + H_2 \uparrow$ 

Copper or brass cooking vessels are coated with tin metal (eyam). If it is not coated the organic acids present in the food materials will react with copper and make the food poisonous. The tin isolates the vessel from the action of acids and prevents food poisoning.



## Reaction with metal carbonates and bicarbonates

When carbonates and bicarbonates come into contact with dilute acids carbon dioxide is given out along with water. For example, limestone (calcium carbonate) reacts with dilute sulphuric acid to form calcium sulphate, carbon dioxide and water.

 $Calcium + dil Sulphuric \rightarrow Calcium + Carbon + Water carbonate acid sulphate dioxide$ 

 $CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$ 

## Reaction with metal oxide

Oxides of various metals react with dilute acids to form their metallic salts and water.

Metal oxides + dilute Acid  $\rightarrow$  Metal salts + Water

## Example:

Calcium + Hydrochloric  $\rightarrow$  Calcium + Water

oxideacid chloride

```
CaO + 2HCl \rightarrow CaCl_2 + H_2O
```

## Uses of Acids

- Hydrochloric acid present in our stomach helps in the digestion of foodstuff.
- Vinegar (acetic acid) is used to preserve food materials.
- Benzoic acid is also used to preserve food materials like pickles.
- Sodium or potassium salts of higher fatty acids are used to make washing and bathing soaps.
- Sulphuric acid is called the king of chemicals. It is an effective dehydrating agent. It is used in various industries to make detergents, paints, fertilizers and many more chemicals.
- Hydrochloric acid, Nitric acid and Sulphuric acid are important laboratory reagents.
- Cells of all living organisms contain the fundamental nuclear material called nucleic acids. Animals have deoxyribo nucleic acid (DNA) whereas plants contain ribo nucleic acid (RNA).

Pickles remain in good condition for long time because they contain vinegar (acetic acid) or benzoic acid.





#### Bases

Bases are chemical substances that are corrosive and bitter in taste. A lot of bleaches, soaps, detergents, kinds of toothpaste, etc., are bases. In contrast to acids which release hydrogen ions in water, bases release hydroxide ions in water.

Thus, the chemical substances that release hydroxide ions when dissolved in water are called as bases. Examples: Sodium hydroxide (NaOH) and Potassium hydroxide (KOH).

Sodium hydroxide  $\rightarrow$  Sodium ion + Hydroxide ion NaOH  $\rightarrow$  Na<sup>+</sup> + OH<sup>-</sup>

Potassium hydroxide  $\rightarrow$  Potassium ion + Hydroxide ion KOH  $\rightarrow$  K<sup>+</sup> + OH<sup>-</sup>

Water soluble bases are called Alkalis. Bases like sodium hydroxide, potassium hydroxide, calcium hydroxide and ammonium hydroxide are highly soluble in water and hence they are called alkalis. Certain chemical substances which do not release hydroxide ions when dissolved in water also behave as bases. Examples: Sodium carbonate, Sodium bicarbonate, Calcium carbonate etc.

Base	Formula	Products
Magnesium hydroxide	Mg(OH) <sub>2</sub>	Milk of magnesia
Sodium hydroxide	NaOH	Detergent
Ammonium hydroxide	NH4OH	Solution for cleaning windows
Calcium hydroxide	Ca(OH) <sub>2</sub>	Lime water
Potassium hydroxide	КОН	Soap

#### **Common bases in some products**



Sodium carbonate (Na2CO3) is commercially called washing soda. Similarly sodium bicarbonate (NaHCO3) is commercially called baking soda. Caustic soda is sodium hydroxide (NaOH) and caustic potash is potassium hydroxide (KOH).

## Properties of Bases Physical properties

- Bases generally exist in solid state but some bases exist in liquid state also.
   E.g. Ammonium hydroxide, calcium hydroxide
- Bases give soapy touch only in aqueous media not in dry nature.
- ✤ Bases are bitter in taste.
- Bases are corrosive in nature. When come in contact with the skin frequently they form painful blisters.
- ✤ Bases are generally colourless.
- Bases also change the colour of the indicators. Red litmus paper turns blue when treated with bases. Similarly, they turn methyl orange yellow and phenolphthalein pink.
- ✤ Bases also conduct electricity in aqueous solution.

### Chemical properties of bases Reaction with metals

Generally metals do not react with bases. Metals like Aluminium and Zinc react with bases like sodium hydroxide forming aluminates and release hydrogen.

Aluminum + Sodium hydroxide + Water  $\rightarrow$  Sodium aluminate + Hydrogen

 $2A1 + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2$ 

## Reaction with metal oxides

All bases react with non metallic oxides to form salt and water. For example sodium hydroxide reacts with carbon dioxide to form sodium carbonate.

Sodium hydroxide + Carbon dioxide  $\rightarrow$  Sodium carbonate + Water

 $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$ 

## Reaction with ammonium salts

Bases react with ammonium salts to form metal salts, ammonia gas and water.

Sodium hydroxide + Ammonium chloride – Sodium chloride + Ammonia + Water

 $NH_4Cl + NaOH \rightarrow NaCl + NH_3 + H_2O$ 



Though acids and bases have some unique properties there are certain similarities between them. Some of them are given below.

- ✤ They are corrosive in nature.
- ✤ They undergo ionization in aqueous solution.
- ✤ They conduct electricity in aqueous solution.
- They undergo neutralization reaction.

Some of the differences between acids and bases are given in Table.

## Difference between acids and bases

Acids	Bases	
They produce H+ ions in	They produce OH- ions in	
water.	water.	
They are sour in taste	They are bitter in taste.	
Few acids are in solid state.	Most of the bases are in solid	
	state.	
Acids turn blue litmus	Bases turn red litmus paper	
paper red.	blue.	
	I DE	
es	I.T.K.L	

### Uses of Bases

- 1. Potassium hydroxide is used to make bathing soaps.
- 2. Sodium hydroxide is used to make washing soaps.
- 3. Sodium hydroxide is also used in paper industries, textile industries and in the preparation of medicines.
- 4. Calcium hydroxide is used for white washing.
- 5. Aluminum hydroxide and magnesium hydroxides are used in antacids to cure acidity problems.
- 6. Ammonium hydroxide is used to manufacture fertilizers, nylon, plastics and rubber.

## **Neutralisation Reaction**

When neutrality is achieved between two different chemical substances with different chemical properties through a reaction then it is called neutralization in chemistry. Thus neutralization is a chemical reaction in whichan acid and a base react with each other to form salt and water. Neutralization reaction between an acid and a base can be written as:

Acid + Base  $\rightarrow$  Salt + Water



Similarly some other acids also produce their salts when they react with some bases. Some of the salts produced by neutralization reaction are given below in Table.

## Salts produced by neutralisation

Acid	Base	Salt
Hydrochloric acid	Sodium hydroxide	Sodium chloride
HC1	NaOH	NaCl
Sulphuric acid	Sodium hydroxide	Sodium sulphate
$H_2SO_4$	NaOH	Na <sub>2</sub> SO <sub>4</sub>
Nitric acid	Sodium hydroxide	Sodium nitrate
HNO <sub>3</sub>	NaOH	NaNO <sub>3</sub>
Acetic acid	Sodium hydroxide	Sodium acetate
CH <sub>3</sub> COOH	NaOH	CH <sub>3</sub> COONa

## Neutralisation reactions in our daily life

Balancing acids and bases is important for our health and for our environment. We come across various neutralization reactions in our daily life. Let us study about the importance of some of those reactions.

## Ant bite

Whenever bees or red ants bite they inject an acid called formic acid. These acids cause pain a suitable base in the form of calcium hydroxide (readily available at home) is applied so as to neutralise the formic acid.

## Wasp bite

When we are bitten by wasp, we feel the burning sensation and pain. It is due to an alkaline substance injected by the insect. To neutralise the alkalinity we use vinegar which is an acid.

## Tooth decay

Generally it is advised by the doctors that we should brush our teeth twice a day. This is because the bacteria present in our mouth decompose the food particles stuck in the gaps between our teeth thereby causing acid formation which leads to



tooth decay. To prevent this we have to neutralize the acid. When we brush with tooth powder or tooth paste containing weak bases, the acid gets neutralized. So our teeth will be strong and healthy.

#### Acidity

As we know, hydrochloric acid present in our stomach helps the digestion of food material along with the enzymes secreted by liver, gallbladder and pancreases. Sometimesdue to excessive production of hydrochloric acid in our stomach we feel burning sensation in food pipe and in chest area. If this happens again and again ulcer will be formed in stomach and food pipe, which further aggravates the conditions. In order to neutralize, antacids which are nothing but weak bases like aluminum and magnesium hydroxides are used. As a result the acidity is removed.

#### Agriculture

Acidic soil is not suitable for plant growth. So farmers add lime fertilisers such as powdered lime (CaO), limestone (CaCO<sub>3</sub>) or ashes of burnt wood to the soil to neutralise the acidity.

#### Industries

Effluents from the industries contain acids such as sulphuric acid. It is treated by adding lime to neutralise it before it is discharged into rivers and streams. Similarly, in power stations fossil fuels such as coal are burnt to produce electricity. Burning fossil feuls will liberate sulphur dioxide gas as an acidic pollutant in the air. Hence, power stations treat this acidicgas using powdered lime (CaO) or limestone (CaCO<sub>3</sub>) to neutralise it so that air pollutant can be prevented.

#### Indicators

An indicator or acid– base indicator is a chemical substance which indicates the acidic or basic nature of a solution by suitable colour change. These may be natural or synthetic.

## Natural indicators

Natural indicators are chemical substances which are obtained from the natural resources. Litmus, turmeric juice, China rose petals, red cabbage, grape juice and beetroot juice are the indicators obtained from natural resources.

#### **Turmeric indicator**

By adding small amount of water to turmeric powder a paste is prepared. This is applied on a blotting paper or filter paper and dried. These strips are used as indicators to find the nature of the solution. In acidic solution turmeric indicator



paper has no change in colour. That means it remains yellow. In basic solution the colour changes from yellow to red.

### Hibiscus flower indicator

Some hibiscus flowers soaked in warm water for about 5 to 10 minutes forms a solution. This solution can be used as indicator. In acidic solution, the colour will be changed to deep pink or deep red. In basic solution, the colour will be changed into a green.

#### Beet root juice indicator

Extracts of beet root are also used as an indicator for identifying the acidic or basic nature of a solution.

#### Litmus

Litmus is the most common indicatorz used in the laboratories. Litmus is a natural indicator which is extracted from lichens. It is available in the form of solution or in the form of strips prepared by absorbing litmus solution on filter paper. It is either red orblue in colour. Blue litmus paper turns red in acidic solution and red litmus paper turns blue in the basic solution.

#### Synthetic indicators

An indicator prepared from artificial substances is known as synthetic indicators. Phenolphthalein and methyl orange are the examples for synthetic indicators.

#### Phenolphthalein

Phenolphthalein is a colourless compound. Its alcoholic solution is used as an indicator. It is colourless in acidic solution but turns pink in basic solution.

#### Methyl orange

Solid methyl orange is dissolved in hot water and its filtrate is used as an indicator. It turns red in acidic solution and yellow in basic solution.

The following table gives the colour changes of different indicators in acidic and basic medium



# **Colour Changing Indicators**

Indicator	Acidic Solution	Basic Solution
Blue litmus	Red	No change in colour
Red litmus	No change in Colour	Blue
Phenolphthalein	Colourless	Pink
Methyl orange	Red	Yellow





## 9<sup>th</sup> book Unit – 14 – Acids, Bases and salts

## **Classification of Acids**

• Acids are classified in different ways as given below:

## (a) Based on their sources:

- **Organic Acids**: Acids present in plants and animals (living things) are organic acids. Example: HCOOH, CH<sub>3</sub>COOH
- **Inorganic Acids**: Acids prepared from rocks and minerals are inorganic acids or mineral acids. Example: HCl, HNO<sub>3</sub>, H2SO<sub>4</sub>

# (b) Based on their Basicity

• **Monobasic Acid**: Acid that contain only one replaceable hydrogen atom per molecule is called monobasic acid. It gives one hydrogen ion per molecule of the acid in solution. Example: HCl, HNO<sub>3</sub>

For acids, we use the term basicity that refers to the number of replaceable hydrogen atoms present in one molecule of an acid. For example, acetic acid (CH3COOH) has four hydrogen atoms but only one can be replaced. Hence it is monobasic.

- **Dibasic Acid:** An acid which gives two hydrogen ions per molecule of the acid in solution. Example: H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>CO<sub>3</sub>
- **Tribasic Acid**: An acid which gives three hydrogen ions per molecule of the acid in solution. Example: H3PO4

# (c) Based on Ionisation

- Acids get ionised in water (produce H+ ions) completely or partially. Based on the extent of ionisation acids are classified as below.
- **Strong Acids**: These are acids that ionise completely in water. Example: HCl
- Weak Acids: These are acids that ionise partially in water. Example: CH<sub>3</sub>COOH.

Ionisation is the condition of being dissociated into ions by heat or radiation or chemical reactions or electrical discharge.

## (d) Based on Concentration

• **Concentrated Acid:** It has relatively large amount of acid dissolved in a solvent.



• **Dilute Acid:** It has relatively smaller amount of acid dissolved in solvent.

## **Properties of Acids**

- a) They have sour taste.
- b) Their aqueous solutions conduct electricity since they contain ions.
- c) Acids turns blue litmus red.
- d) Acids react with active metals to give hydrogen gas.

 $\begin{array}{l} Mg + H_2SO_4 \rightarrow MgSO_4 + H_2 \uparrow \\ Zn + 2HCl \rightarrow ZnCl_2 + H_2 \uparrow \end{array}$ 

Few metals do not react with acid and liberate hydrogen gas. For example: Ag, Cu.

e) Acids react with metal carbonate and metal hydrogen carbonate to give carbon dioxide.

 $Na_{2}CO_{3} + 2HCl \rightarrow 2NaCl + H_{2}O + CO_{2} \uparrow$  $NaHCO_{3} + HCl \rightarrow NaCl + H_{2}O + CO_{2} \uparrow$ 

f) Acids react with metallic oxides to give salt and water. CaO + H2SO4  $\rightarrow$  CaSO4 + H2O g) Acids react with bases to give salt and water. HCl + NaOH  $\rightarrow$  NaCl + H2O

## Uses of Acids

- Sulphuric acid is called King of Chemicals because it is used in the preparation of many other compounds. It is used in car batteries also.
- Hydrochloric acid is used as a cleansing agent in toilets.
- Citric acid is used in the preparation of effervescent salts and as a food preservative.
- Nitric acid is used in the manufacture of fertilizers, dyes, paints and drugs.
- Oxalic acid is used to clean iron and manganese deposits from quartz crystals. It is also used as bleach for wood and removing black stains.
- Carbonic acid is used in aerated drinks.
- Tartaric acid is a constituent of baking powder.

## Role of water in acid solution

Acids show their properties only when dissolved in water. In water, they ionise to form H+ ions which determine the properties of acids. They do not ionise in organic solvents. For example, when HCl is dissolved in water it produces H+ ions and Cl\_ ions whereas in organic solvents like ethanol they do not ionise and remain as molecule.



# Aquaregia

We know that metals like gold and silver are not reactive with either HCl or HNO3. But the mixture of these two acids can dissolve gold. This mixture is called Aquaregia. It is a mixture of hydrochloric acid and nitric acid prepared optimally in a molar ratio of 3:1. It is a yellow-orange fuming liquid. It is a highly corrosive liquid, able to attack gold and other substances.

Chemical formula  $: 3 \text{ HCL} + \text{HNO}_3$ Solubility in water : Miscible in water : - 42°C (- 44°F, 231K) Melting point Boiling point : 108°C (226°F, 381K)

The **term**aquaregia is a Latin phrase meaning 'King's Water'. The name reflects the ability of aquaregia to dissolve the noble metals such as gold, platinum and palladium.

## **Uses of Aquaregia**

• It is used chiefly to dissolve metals such as gold and platinum. NTRE It is used for cleaning and refining gold.

## **Bases**

According to Arrhenius theory, bases are substances that ionise in water to form hydroxyl ions (OH-). There are some metal oxides which give salt and water on reaction with acids. These are also called bases. Bases that are soluble in water are called alkalis. A base reacts with an acid to give salt and water only.

Base + Acid  $\rightarrow$  Salt + Water

For example, zinc oxide (ZnO) reacts with HCl to give the salt zinc chloride and water.

 $ZnO_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl2_{(aq)} + H2O_{(l)}$ 

Similarly, sodium hydroxide ionises in water to give hydroxyl ions and thus get dissolved in water. So it is an alkali.

 $NaOH_{(aq)} \rightarrow Na^+(aq) + OH^-(aq)$ 

Bases contain one or more replaceable oxide or hydroxyl ions in solution. Table 14.3 enlists various bases and ions formed by them in water.

All alkalis are bases but not all bases are alkalis. For example: NaOH and KOH are



alkalis whereas Al(OH)3 and Zn(OH)2 are bases.

Base	Molecular Formula	Ions f	formed	No. of replaceable hydroxyl ion
Calcium oxide	CaO	Ca <sup>2+</sup>	O <sup>2-</sup>	1
Sodium oxide	Na <sub>2</sub> O	2Na+	O <sup>2-</sup>	1
Potassium	КОН	K+	OH-	1
hydroxide				
Calcium hydroxide	Ca(OH) <sub>2</sub>	Ca2+	OH-	2
Aluminium	Al(OH)3	Al <sup>3+</sup>	OH-	3
hydroxide				

### **Classification of Bases**

## (a) Based on their Acidity

- Monoacidic Base: It is a base that ionises in water to give one hydroxide ion per molecule. Example: NaOH, KOH
- Diacidic **Base**: It is a base that ionises in water to give two hydroxide ions per molecule. Example: Ca(OH)2. Mg(OH)2
- Triacidic **Base:** It is a base that ionises in water to give three hydroxide ions per molecule. Example: Al(OH)3, Fe(OH)3

## (b) Based on concentration

- Concentrated **Alkali**: It is an alkali having a relatively high percentage of alkali in its aqueous solution.
- Dilute **Alkali**: It is an alkali having a relatively low percentage of alkali in its aqueous solution.

## (c) Based on Ionisation

• Strong **Bases**: These are bases which ionise completely in aqueous solution.

Example:NaOH, KOH

• Weak **Bases**: These are bases that ionise partially in aqueous solution. **Example:** NH4OH, Ca(OH)2

The term acidity is used for base, which means the number of replaceable hydroxyl groups present in one molecule of a base.



## **Properties of Bases**

- a) They have bitter taste.
- b) Their aqueous solutions have soapy touch.
- c) They turn red litmus blue.
- d) Their aqueous solutions conduct electricity.
- e) Bases react with metals to form salt with the liberation of hydrogen gas.

 $Zn + 2 \ NaOH \rightarrow Na_2 ZnO_2 + H_2 \uparrow$ 

• f) Bases react with non-metallic oxides to produce salt and water. Since this is similar to the reaction between a baseand an acid, we can conclude that non-metallic oxides are acidic in nature.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

g) Bases react with acids to form salt and water.

$$KOH + HCl \rightarrow KCl + H2O$$

The above reaction between a base and an acid is known as Neutralisation reaction. h) On heating with ammonium salts, bases give ammonia gas.

$$NaOH + NH_4Cl \rightarrow NaCl + H_2O + NH_3 \uparrow$$

Few metals do not react with sodium hydroxide. Example: Cu, Ag, Cr

• In the above activity you can observe that the bulb will start glowing only in the case of acids. But, you will observe that glucose and alcohol solution do not conduct electricity. Glowing of the bulb indicates that there is a flow of electric current through the solution. The electric current is carried through the solution by ions. Repeat the same activity using alkalis such as sodium hydroxide and calcium hydroxide.

# Uses of Bases

- (i) Sodium hydroxide is used in the manufacture of soap.
- (ii) Calcium hydroxide is used in white washing of building.
- (iii) Magnesium hydroxide is used as a medicine for stomach disorder.
- (iv) Ammonium hydroxide is used to remove grease stains from cloths.

Tests for Acids and Bases a) Test with a litmus paper:

An acid turns blue litmus paper into red. A base turns red litmus paper into blue.
 b) Test with an indicator Phenolphthalein:



phenolphthalein is colourless. In In acid medium, basic medium, phenolphthalein is pink in colour.

## c) Test with an indicator Methyl orange:

In acid medium, methyl orange is pink in colour. In basic medium, methyl orange is yellow in colour.

Indicator	Colour in acid	Colour in acid	
Litmus	Blue to Red	Red to Blue	
Phenolphthalein	Colourless	Pink	
Methyl orange	Pink	Yellow	

## Strenght of Acidic or Basic solutions

## pH Scale

- A scale for measuring hydrogen ion concentration in a solution is called pH scale. The 'p' in pH stands for 'potenz' in German meaning power. pH scale is a set of numbers from 0 to 14 which is used to indicate whether a solution is acidic, basic or neutral.

  - Jases have pH greater than 7
    A neutral solution has pH equal to 7
    ts

## Salts

When you say salt, you may think of the common salt. Sea water contains many salts dissolved in it. Sodium chloride is separated from these salts. There are many other salts used in other fields. Salts are the products of the reaction between acids and bases. Salts produce positive ions and negative ions when dissolved in water.

## **Types of Salts**

Normal Salts: A normal salt is obtained by complete neutralization of an acid by a base.

## $NaOH + HCl \rightarrow NaCl + H2O$

Acid Salts: It is derived from the partial replacement of hydrogen ions of an acid by a metal. When a calculated amount of a base is added to a polybasic acid, acid salt is obtained.

## $NaOH + H2SO_4 \rightarrow NaHSO_4 + H_2O$


• **Basic Salts**: Basic salts are formed by the partial replacement of hydroxide ions of a diacidic or triacidic base with an acid radical.

# $Pb(OH)2 + HCl \rightarrow Pb(OH)Cl + H2O$

• Double **Salts**: Double salts are formed by the combination of the saturated solution of two simple salts in equimolar ratio followed by crystallization. For example, potash alum is a mixture of potassium sulphate and aluminium sulphate. KAl(SO<sub>4</sub>)<sub>2</sub>·12H2O

# **Properties of Salts**

- Salts are mostly solids which melt as well as boil at high temperature.
- Most of the salts are soluble in water. For example, chloride salts of potassium and sodium are soluble in water. But, silver chloride is insoluble in water
- They are odourless, mostly white, cubic crystals or crystalline powder with salty taste.
- Salt is hygroscopic in nature.

# Water of Crystallisation

- Many salts are found as crystals with water molecules. These water molecules are known as water of crystallisation. Salts that contain water of crystallisation are called hydrated salts. The number of molecules of water hydrated to a salt is indicated after a dot in its chemical formula. For example, copper sulphate crystal have five molecules of water for each molecule of copper sulphate. It is written as CuSO4.5H2O and named as copper sulphate pentahydrate. This water of crystallisation makes the copper sulphate blue. When it is heated, it loses its water molecules and becomes white.
- Salts that do not contain water of crystallisation are called anhydrous salt. They are generally found as powders. Fill in the blanks in the following table based on the concept of water of crystallisation.

## **Identification of Salts**

## (i) Physical examination of the salt.

• The physical examination of the unknown salt involves the study of colour, smell and density. This test is not much reliable.

# (ii) Dry heating Test.

• This test is performed by heating a small amount of salt in a dry test tube. After all the water get evaporated, the dissolved salts are sedimented in the container.



# (iii) Flame Test.

• Certain salts on reacting with concentrated hydrochloric acid (HCl) form their chlorides. The paste of the mixture with con. HCl is introduced into the flame with the help of platinum wire.

Colour of the flame	Inference
Brick red	Ca <sup>2+</sup>
Golden Yellow	Na <sup>2+</sup>
Pink Violet	K+
Green Fleshes	Zn <sup>2+</sup>

(iv) WhenHCl is added with a carbonate salt, it gives off CO2 gas with brisk effervescence.

## Uses of Salts

- Common Salt (Sodium Chloride NaCl)
- It is used in our daily food and used as a preservative.

## Washing Soda (Sodium Carbonate-Na2CO3)

- i. It is used in softening hard water.
- ii. It is used in glass, soap and paper industries.

## Baking Soda (Sodium bicarbonate -NaHCO3)

i. It is used in making of baking powder which is a mixture of baking soda and tartaric acid.

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ii. It is used in soda-acid fire extinguishers.

iii. Baking powder is used to make cakes and bread, soft and spongy.

iv. It neutralizes excess acid in the stomach and provides relief.

## Bleaching powder (Calcium Oxychloride - CaOCl2)

i. It is used as disinfectant.

ii. It is used in textile industry for bleaching cotton and linen.

## Plaster of Paris (Calcium Sulphate Hemihydrate - CaSO4 .1/2 H2O)

i. It is used for plastering bones.

ii. It is used for making casts for statues.



#### 10<sup>th</sup> STD Unit - 9 SOLUTIONS

#### SOLUTIONS IN DAY-TO-DAY LIFE

- One of the naturally existing solutions is sea water. We cannot imagine life on earth without sea water. It is a mixture of many dissolved salts. The another one is air. It is a mixture of gases like nitrogen, oxygen, carbon dioxide and other gases.
- All the life forms on the earth are associated with solutions. Plants take solutions of nutrients for their growth from the soil. Most of the liquids found in human body including blood, lymph and urine are solutions. Day to day human activities like washing, cooking, cleaning and few other activities involve the formation of solutions with water. Similarly, the drinks what we take, like fruit juice, aerated drinks, tea, coffee etc. are also solutions. Therefore, the ability of water to form solutions is responsible for sustenance of life. On the other hand, the same characteristic forms the basic cause of the addition of pollutants to water. However, the ability of water to form solutions influences the survival of man on the earth. In this lesson, let us learn the science of solutions.

#### COMPONENTS OF SOLUTIONS

- We know that, a **solution is a homogeneous mixture of two or more substances**. In a solution, the component which is present in lesser amount (by weight), is called **solute** and the component, which is present in a larger amount (by weight) is called **solvent**. The solute gets distributed uniformly throughout the solvent and thus forming the mixture homogeneous. So, the solvent acts as a dissolving medium in a solution. The process of uniform distribution of solute into solvent is called **dissolution**. Figure 9.2 shows the schematic representation of solution.
- A solution must at least be consisting of two components (a solute and a solvent). Such solutions which are made of one solute and one solvent (two components) are called **binary solutions**. e.g. On adding copper sulphate crystals to water, it dissolves in water forming a solution of copper sulphate as shown in Figure 9.3. It contains two components i.e. one solute- copper sulphate and one solvent-water. So it is a binary solution. Similarly, a solution may contain more than two components. For example if salt and sugar are added to water, both dissolve in water forming a solution. Here two solutes are dissolved in one solvent. Such kind of solutions which contain three components are called **ternary solutions**.

## Types of Solutions Based on the physical state of the solute and the solvent

• We know that substances normally exist in three physical states (phases) i.e., solid, liquid and gas. In binary solutions, both the solvent and solute may exist in



any of these physical states. But the solvent constitutes the major part of the solution. Its physical state is the primary factor which determine the characteristics of the solution. Therefore, there are different types of binary solutions as listed.

Solute	Solvent	Example	
Solid solution			
Solid	Solid	Copper dissolved in gold	
		(Alloys)	
Liquid	Solid	Mercury with sodium	
		(amalgam)	
Liquid solution			
Solid	Liquid	Sodium chloride dissolved	
		in water	
Liquid	Liquid	Ethyl alcohol dissolved in	
		water	
Gas	Liquid	carbon-di-oxide dissolved	
		in water (Soda water)	
Gaseous solution			
Liquid	Gas	Water vapour in air	
		(cloud)	
Gas	Gas	Mixture of Helium-	
		Oxygen gases,	
	EN		
Based on the type of solver	nt C. F.		

#### Based on the type of solvent

Most of the substances are soluble in water. That is why, water is called as 'Universal solvent". However some substances do not dissolve in water. Therefore, other solvents such as ethers, benzene, alcohols etc., are used to prepare a solution. On the basis of type of solvent, solutions are classified into two types. They are aqueous solutions and non-aqueous solutions.

## a) Aqueous solution:

The solution in which water acts as a solvent is called aqueous solution. In general, ionic compounds are soluble in water and form aqueous solutions more readily than covalent compounds. E.g. Common salt in water, Sugar in water, Copper sulphate in water etc.

## b) Non - Aqueous solution:

The solution in which any liquid, other than water, acts as a solvent is called nonaqueous solution. Solvent other than water is referred to as non-aqueous solvent. Generally, alcohols, benzene, ethers, carbon disulphide, acetone, etc., are used as non-aqueous solvents. Examples for non-aqueous solutions: Sulphur dissolved in carbon disulphide, Iodine dissolved in carbon tetrachloride.



#### Based on the amount of solute

• The amount of the solute that can be dissolved in the given amount of solvent is limited under any given conditions. Based on the amount of solute, in the given amount of solvent, solutions are classified into the following types:

#### (i) Saturated solution (ii) Unsaturated solution (iii) Super saturated solution

(i) Saturated solution: A solution in which no more solute can be dissolved in a definite amount of the solvent at a given temperature is called saturated solution. e.g. 36 g of sodium chloride in 100 g of water at 25°C forms saturated solution.Further addition of sodium chloride, leave it undissolved.

(ii) Unsaturated solution: Unsaturated solution is one that contains less solute than that of the saturated solution at a given temperature. e.g. 10 g or 20 g or 30 g of Sodium chloride in 100 g of water at 25°C forms an unsaturated solution.

(iii) Super saturated solution: Supersaturated solution is one that contains more solute than the saturated solution at a given temperature. e.g. 40 g of sodium chloride in 100 g of water at 25°C forms super saturated solution. This state can be achieved by altering any other conditions liken temperature, pressure. Super saturated solutions are unstable, and the solute is reappearing as crystals when the solution is disturbed.

## Concentrated and dilute solutions

- It is another kind of classification of unsaturated solutions. It expresses the relative concentration of two solutions with respect to their solutes present in the given amount of the solvent. For example, you are given two cups of tea. When you taste them, you feel that one is sweeter than the other. What do you infer from it? The tea which sweet more contains higher amount of sugar than the other. How can you express your observation? You can say that the tea is stronger. But a chemist would say that it is 'concentrated'.
- When we compare two having same solute and solvent in a solutions, the one which contains higher amount of solute per the given amount of solvent is said to be 'concentrated solution' and the another is said to be 'dilute solution'. They are schematically represented by Figure 9.5.
- Differentiating solutions as dilute and concentrated is a qualitative representation. It does not imply the quantity of the solute. This difference is observed by means of some physical characteristics such as colour, density, etc.



# Solubility

Usually, there is a limit to the amount of solute that can be dissolved in a given amount of solvent at a given temperature. When this limit is reached, we have a saturated solution and any excess solute that is added, simply resides at the bottom of the solution. The extent of dissolution of a solute in a solvent can be better explained by its solubility. Solubility is measure of how much of a solute can be dissolved in a specified amount of a solvent.

# Solubility= $\frac{mass \ of \ the \ solve}{mass \ of \ the \ solvent} \times 100$

Name of	Formula of	Solubility	
the solute	the solute	g/100 g water	
Calcium carbonate	CaCO <sub>3</sub> (s)	0.0013	
Sodium chloride	NaCl (s)	36	
Ammonia	NH <sub>3</sub> (g)	48	
Sodium hydroxide	NaOH(s)	80	
Glucose	$C_6H_{12}O_6(s)$	91	
Sodium bromide	NaBr(s)	95	
Sodium iodide	NaI(s)	184	
Factors affecting solubility			

#### Solubility's of some common substances in water at 25°C

#### Factors affecting solubility

- There are three main factors which govern the solubility of a solute. They are:
- (i) Nature of the solute and solvent
- (ii) Temperature
- (iii) Pressure

#### (i) Nature of the solute and solvent

- The nature of the solute and solvent plays an important role in solubility. Although water dissolves an enormous variety of substances, both ionic and covalent, it does not dissolve everything. The phrase that scientists often use when predicting solubility is "like dissolves
- like." This expression means that dissolving occurs when similarities exist between the solvent and the solute. For example: Common salt is a polar compound and dissolves readily in polar solvent like water.
- Non-polar compounds are soluble in non-polar solvents. For example, Fat dissolved in ether. But non-polar compounds, do not dissolve in polar solvents; polar compounds do not dissolve in non-polar solvents.



## (ii) Effect of Temperature Solubility of Solids in Liquid:

- Generally, solubility of a solid solute in a liquid solvent increases with increase in temperature. For example, a greater amount of sugar will dissolve in warm water than in cold water.
- In endothermic process, solubility increases with increase in temperature.
- In exothermic process, solubility decreases with increase in temperature.

# Solubility of Gases in liquid

- Do you know why is it bubbling when water is boiled? Solubility of gases in liquid decrease with increase in temperature. Generally, water contains dissolved oxygen. When water is boiled, the solubility of oxygen in water decreases, so oxygen escapes in the form of bubbles.
- Aquatic animals live more in cold regions because, more amount of dissolved oxygen is present in the water of cold regions. This shows that the solubility of oxygen in water is more at low temperatures.

## (iii) Effect of Pressure

- Effectof pressure is observed only in the case of solubility of a gas in a liquid. When the pressure is increased, the solubility of a gas in liquid increases.
- The common examples for solubility of gases in liquids are carbonated beverages, i.e. soft drinks, household cleaners containingaqueous solution of ammonia, formalin-aqueous solution of formaldehyde, etc.

# Concentration of a Solution

• So far, we discussed what is a solution? what does it consist of and its types. Most of the chemical reactions take place in solutions form. So it is essential to quantify the solute in solvent to study the reactions. To quantify the solute in a solution, we can use the term "**concentration**".

# Concentration of a solution may be defined as the amount of solute present in a given amount of solution or solvent.

• Quantitatively, concentration of a solution may be expressed in different methods. But here, we shall discuss percentage by mass (% mass) and percentage by volume (% volume).

## Mass percentage

• Mass percentage of a solution is defined as the percentage by mass of the solute present in the solution. It is mostly used when solute is solid and solvent is liquid.



Mass percentage =  $\frac{mass of the solute}{mass of the solution} \times 100$ 

Mass percentage =  $\frac{mass \ of \ the \ solute}{mass \ of \ the \ solution +} \times 100$ mass of the solvent

For example: 5% sugar solution (by mass) means 5 g of sugar in 95 g of water. Hence it is made 100g of solution.

• Usually, mass percentage is expressed as w/w (weight / weight); mass percentage is independent of temperature.

## Volume percentage

• Volume percentage is defined as the percentage by volume of solute (in ml) present in the given volume of the solution.

Volume percentage =  $\frac{volume \ of \ the \ solute}{volume \ of \ the \ solution} \times 100$ 

Volume percentage =  $\frac{volume \ of \ the \ solute}{volume \ of \ the \ solution+} \times 100$ 

• For example, 10% by volume of the solution of ethanol in water, means 10 ml of ethanol in 100 ml of solution (or 90 ml of water)

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- Usually volume percentage is expressed as v/v (volume / volume). It is used when both the solute and solvent are liquids. Volume percentage decreases with increases in temperature, because of expansion of liquid.
- You can notice that in the commercial products that we come across in our daily life such as a solution of syrups, mouth wash, antiseptic solution, household disinfectants etc., the concentration of the ingredients is expressed as v/v. Similarly, in ointments, antacid, soaps, etc., the concentration of solutions are expressed as w/w.

## Hydrated salts and Water of Crystallization

• When ionic substances are dissolved in water to make their saturated aqueous solution, their ions attract water molecules which then attached chemically in certain ratio. This process is called hydration. These ionic substances crystallize out from their saturated aqueous solution with a definite number of molecules of water. The number of water molecules found in the crystalline substance is called **water of crystallization**. Such salts are called hydrated salts.



• On heating these hydrated crystalline salts, they lose their water of crystallization and become amorphous or lose their colour (if they are coloured). Table 9.3 shows some common hydrated salts:

Common	ILIPAC Name	Molecular
Nama	10171C I valie	Earmaula
Iname		Formula
Blue	Copper (II)	CuSO <sub>4</sub> .5H <sub>2</sub> O
Vitriol	sulphate	
	pentahydrate	
Epsom	Magnesium	MgSO <sub>4</sub> .7H <sub>2</sub> O
Salt	sulphate	
	heptahydrate	
Gypsum	Calcium sulphate	CaSO <sub>4</sub> .2H <sub>2</sub> O
	dihydrate	
Green	Iron (II) sulphate	FeSO <sub>4</sub> .7H <sub>2</sub> O
Vitriol	heptahydrate	
White	Zinc sulphate	$ZnSO_4.7H_2O$
Vitriol	heptahydrate	

## Copper sulphatepentahydrateCuSO4.5H2O (Blue vitriol)

• The number of water molecules in blue vitriol is five. So its water of crystallization is 5. When blue coloured copper sulphate crystals are gently heated, it loses its five watermolecules and becomes colourless anhydrous copper sulphate.

CHEO JELLO	Heating	
CusO <sub>4</sub> ·5H <sub>2</sub> O	Carlina	$CusO_4 + 5H_2O$
(Copper sulphate	Cooling	(Anhydrous copper
pentahydrate)		sulphate)

• If you add few drops of water or allow it to cool, the colourless anhydrous salt again turns back into blue coloured hydrated salt.

## Magnesium sulphateheptahydrateMgSO4.7H2O (Epsom salt)

• Its water of crystallization is 7. When magnesium sulphateheptahydrate crystals are gently heated, it loses seven water molecules, and becomes anhydrous magnesium sulphate.

$$MgSO_{4} \cdot 7H_{2}O \stackrel{Heating}{\approx} MgSO_{4} + 7H_{2}O$$

(Magnesium sulphate (Anhydrous Magnesium heptahydrate) sulphate)



• If you add few drops of water or allow it to cool, the colourless anhydrous salt again turns back into hydrated salt.

#### Hygroscopy

• Certain substances, when exposed to the atmospheric air at ordinary temperature, absorb moisture without changing their physical state. Such substances are called **hygroscopic substances** and this property is called hygroscopy.

Hygroscopic substances are used as drying agents.

## Example:

- 1. Conc.Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>).
- 2. Phosphorus Pentoxide ( $P_2O_5$ ).
- 3. Quick lime (CaO).
- 4. Silica gel (SiO<sub>2</sub>).
- 5. Anhydrous calcium chloride (CaCl<sub>2</sub>).

#### Deliquescence

- Certain substances which are so hygroscopic, when exposed to the atmosphericair at ordinary temperatures, absorb enough water and get completely dissolved. Such substances are called **deliquescent substances** and this property is called **deliquescence**.
- Deliquescent substances lose their crystalline shape and ultimately dissolve in the absorbed water forming a saturated solution. Deliquescence is maximum when:

The temperature is low
 The atmosphere is humid

**Examples:** Calcium chloride (CaCl<sub>2</sub>), Caustic soda (NaOH), Caustic potash (KOH) and Ferric chloride (FeCl<sub>3</sub>).



#### 10<sup>th</sup> book **Unit 10 - TYPES OF CHEMICAL REACTIONS**

#### What happens during a chemical reaction?

- In a chemical reaction, the atoms of the reacting molecules or elements are rearranged to form new molecules.
- Old chemical bonds between atoms are broken and new chemical bonds are formed.
- Bond breaking absorbs energy whereas bond formation releases energy

## **TYPES OF CHEMICAL REACTIONS** Classification based on the nature of rearrangements of atoms

• So far you studied about a chemical reaction and how it can be described as a chemical equation. A large number of chemical reactions are taking place around us every day. Are they taking place in a similar way? No. Each reaction involves different kinds of atoms and hence the way they react also differs. Thus, based on the manner by which the atoms of the reactants are rearranged, chemical reactions are classified as follows. EN

#### **Combination reactions**

• A combination reaction is a reaction in which two or more reactants combine to form a compound. It is otherwise called 'synthesis reaction' or 'composition reaction'. When a reactant 'A' combines with 'B', it forms the product 'AB'. The generalised scheme of a combination reaction is given below:



## **Example:**

• Hydrogen gas combines with chlorine gas to form hydrogen chloride gas.

$$H_{2(g)} + Cl_{2(g)} \rightarrow 2HC_{l(g)}$$

Depending on the chemical nature of the reactants, there are threeclassesof combination reactions:



#### Element + Element → Compound

• In this type of combination reaction, two elements react with one other to form a compound. The reaction may take place between a metal and a non-metal or two non-metals.

## Example 1:

• When solid sulphur reacts with oxygen, it produces sulphur dioxide. Here both the reactants are non-metals.



# Example 2:

• Sodium, a silvery-white metal, combines with chlorine, a pale yellow green gas, to form sodium chloride, an edible compound. Here one of the reactants is a metal (sodium) and the other (chlorine) is a non-metal.

$$2Na_{(s)} + Cl_{2(g)} \rightarrow 2NaCl_{(s)}$$

## **Test Yourself:**

• Identify the possible combination reactions between the metals and non-metals given in the following table and write their balanced chemical equations:

Metals	Non-metals	
Na, K, Cs, Ca, Mg	F, Cl, Br, I	

## Compound + Element $\rightarrow$ Compound

• In this case, a compound reacts with an element to form a new compound. For instance, phosphorous trichloride reacts with chlorine gas and forms phosphorous pentachloride.

 $PCl_{3(I)} + Cl_{2(g)} \rightarrow PCl_{5(s)}$ 

# $Compound + Compound \rightarrow Compound$



• It is a reaction between two compounds to form a new compound. In the following reaction, silicon dioxide reacts with calcium oxide to form calcium silicate.

$$SiO_{2(s)} + CaO_{(s)} \rightarrow CaSiO_{3(s)}$$

• Most of the combination reactions are exothermic in nature. Because, they involve the formation of new bonds, which releases a huge amount of energy in the form of heat.

#### **Decomposition reactions**

• In a decomposition reaction, a single compound splits into two or more simpler substances under suitable conditions. It is the opposite of the combination reaction. The generalised schemeof a decomposition reaction is given below:



• Breaking of bonds is the major phenomenon in a decomposition reaction and hence it requires energy to break the bonds, depending on the nature of the energy used in the decomposition reaction.

There are three main classes of decomposition reactions. They are

- Thermal Decomposition Reactions
- Electrolytic Decomposition Reactions
- Photo Decomposition Reactions

A solution of slaked lime is used for white washing walls. Calcium hydroxide reacts slowly with the carbon dioxide in air to form a thin layer of calcium carbonate on the walls. Calcium carbonate is formed aft er two to three days of white washing and gives a shiny finish to the walls. It is interesting to note that the chemical formula for marble is  $alsoCaCO_3$ 

 $Ca(OH)_{2(aq)} + CO_{2(g)} \rightarrow CaCO_{3(s)} + H_2O_{(I)}$ 

#### **Thermal Decomposition Reactions**

• In this type of reaction, the reactant is decomposed by applying heat. For example, on heating mercury (II) oxide is decomposed into mercury metal and oxygen gas. As the molecule is dissociated by the absorption of heat, it is otherwise called 'Thermolysis'.It is a class of compound to element/element decomposition. i.e. a compound (HgO) is decomposed into two elements (Hg and Oxygen).



$$2HgO_{(s)} \xrightarrow{Heat} 2Hg_{(l)} + O_{2(g)}$$

• Similarly, when calcium carbonate is heated, it breaks down in to calcium oxide and carbon dioxide. It is a type of compound to compound/compound decomposition.

 $CaCO_{3(s)} \xrightarrow{Heat} CaO_{(s)} + CO_{2(g)}$ 

• In thermal decomposition reaction, heat is supplied to break the bonds. Such reactions, in which heat is absorbed, are called 'Endothermic reactions'.

#### **Electrolytic Decomposition Reactions**

• In some of the decomposition reactions, electrical energy is used to bring about the reaction. For example, decomposition of sodium chloride occurs on passing electric current through its aqueous solution. Sodium chloride decomposes in to metallic sodium and chlorine gas. This process is termed as 'Electrolysis'.

 $2NaCl_{(aq)} \xrightarrow{Electricity} 2Na_{(s)} + Cl_{2(g)}$ 

• Here, a compound (NaCl) is converted into elements (Na and chlorine). So it is a type of compound to element/element decomposition.

#### **Photo Decomposition Reactions**

• Light is an another form of energy, which facilitates some of the decomposition reactions. For example, when silver bromide is exposed to light, it breaks down into silver metal and bromine gas. As the decomposition is caused by light, this kind of reaction is also called 'Photolysis'.

$$2AgBr_{(s)} \xrightarrow{\text{Ligh}} 2Ag_{(s)} + Br_{2(g)}$$

• The yellow coloured silver bromide turns into grey coloured silver metal. It is also a compound to element/element decomposition.

#### **Single Displacement Reactions**

• It is a reaction between an element and a compound. When they react, one of the elements of the compound-reactant is replaced by the element-reactant to form a new compound and an element. The general schematic representation of a single displacement reaction is given as:





• 'A' displaces element 'B' from the compound 'BC' and hence a single displacement reaction occurs. If zinc metal is placed in hydrochloric acid, hydrogen gas is evolved. Here, hydrogen is displaced by zinc metal and zinc chloride is formed.

 $Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$ 

 $Fe_{(s)} + CuSO_{4(aq)} \rightarrow FeSO_{4(aq)} + Cu_{(s)}$ 

- If an iron nail is placed in an aqueous solution of copper (II) sulphate as shown in Fig. 10.2, the iron displaces copper from its aqueous solution and the so formed copper deposits over the iron nail.
- It is easy to propose so many reactions of this kind with different combinations of reactants. Will they all occur in practice? No. This is most easily demonstrated with halogens. Let us consider the following two reactions:

$$\begin{split} &2NaCl_{(aq)}+F_{2(g)}\rightarrow 2NaF_{(aq)}+Cl_{2(g)}\\ &2NaF_{(aq)}+Cl_{2(g)}\rightarrow 2NaCl_{(aq)}+F_{2(g)} \end{split}$$

• The first reaction involves the displacement of chlorine from NaCl, by fluorine. In the second reaction, chlorine displaces fluorine from NaF. Out of these two, the second reaction will not occur. Because, fluorine is more active than chlorine and occupies the upper position in the periodic table. So, in displacement reactions, the activity of the elements and their relative position in the periodic table are the key factors to determine the feasibility of the reactions. More active elements readily displace less active elements from their aqueous solution.

The activity series of some elements is given below:



By referring the activity series, try to answer the following questions:



Which of the metals displaces hydrogen gas from hydrochloric acid? Silver or Zinc. Give the chemical equation of the reaction and Justify your answer

#### **Double Displacement Reactions**

When two compounds react, if their ions are interchanged, then the reaction is called double displacement reaction. The ion of one compound is replaced by the ion of the another compound. Ions of identical charges are only interchanged, i.e., a cation can be replaced by other cations. This reaction is also called 'Metathesis Reaction'. The schematic representation of a double displacement reaction is given below:



- For a double displacement reaction to take place, one of the products must be a precipitate or water. By this way, there are major classes of double displacement GENTR reactions. They are:
  - 1. Precipitation Reactions
  - 2. Neutralization Reactions

#### **Precipitation Reactions**

When aqueous solutions of two compounds are mixed, if they react to form an insoluble compound and a soluble compound, then it is called precipitation reaction. Because the insoluble compound, formed as one of the products, is a precipitate and hence the reaction is so called.

Differences between combination and decomposition reactions

	DECOMPOSITION REACTIONS
COMBINATION REACTIONS	
One or more reactants combine to form a	A single reactant is decomposed to form
single product	one or more products
Energy is released	Energy is absorbed
Elements or compounds may be the	Single compound is the reactant
reactants	

When the clear aqueous solutions of potassium iodide and lead (II) nitrate are mixed, a double displacement reaction takes place between them.



## $Pb(NO_3)_{2(aq)} + 2KI_{(aq)} \rightarrow PbI_{2(s)} \downarrow + 2KNO_{3(aq)}$

Potassium and lead displace or replace one other and form a yellow precipitate of lead.

## **Neutralization Reactions**

• In your lower classes, you have learned the reaction between an acid and a base. It isanother type of displacement reaction in which the acid reacts with the base to form a salt and water. It is called 'neutralization reaction' as both acid and base neutralize each other.



• Reaction of sodium hydroxide with hydrochloric acid is a typical neutralization reaction. Here, sodium replaces hydrogen from hydrochloric acid forming sodium chloride, a neutral soluble salt.

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

• Similarly, when ammonium hydroxide reacts with nitric acid, it forms ammonium nitrate and water.

 $HNO_{3(aq)} + NH_4OH_{(aq)} \rightarrow NH_4NO_{3(aq)} + H_2O_{(l)}$ 

## **Combustion Reactions**

• A combustion reaction is one in which the reactant rapidly combines with oxygen to form one or more oxides and energy (heat). So in combustion reactions, one of the reactants must be oxygen. Combustion reactions are majorly used as heat energy sources in many of our day to day activities. For instance, we use LPG gas for domestic cooking purposes. We get heat and flame from LPG gas by its combustion reaction of its constituent gases. LPG is a mixture of hydrocarbon gases like propane, butane, propylene, etc. All these hydrocarbons burn with oxygen to form carbon dioxide and water.

 $C_{3}H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_{2}O_{(g)} + Heat$ 

- Since heat is evolved, it is an exothermic reaction. As oxygen is added, it is also an oxidation. So, combustion may be called as an exothermic oxidation. If a flame is formed (as shown in Fig. 10.4), then it is called burning.
  - 1. Digestion of Food
  - 2. Rusting of iron



• Many thousands of reactions fall under these five categories and further you will learn in detail about these reactions in your higher classes.

#### Classification based on the direction of the reaction

• You know that innumerable changes occur every day around us. Are all they permanent? For example, liquid water freezes into ice, but then ice melts into liquid water. In other words, freezing is reversed. So, it is not a permanent change. Moreover, it is a physical change. Physical changes can be reversed easily. Can chemical changes be reversed? Can the products be converted into reactants? Let us consider the burning of a wood. The carbon compounds present in the wood are burnt into carbon dioxide gas and water. Can we get back the wood immediately from carbon dioxide and water? We cannot. So, it is a permanent change. In most of the cases, we cannot. But, some chemical reactions can be reversed. Our mobile phone gets energy from its lithium ion battery by chemical reactions. It is called discharging. On recharging the mobile, these chemical reactions. Hence, they aregrouped into two categories such as reversible and irreversible reactions.

#### **Reversible Reactions**

• A reversible reaction is a reaction that can be reversed, i.e., the products can be converted back to the reactants. A reversible reaction is represented by a double arrow with their heads in the direction opposite to each other. Thus, a reversible reaction can be represented by the following equation:



## **Explanation:**

• Here, the compound 'AB' undergoes decomposition to form the products 'A' and 'B'. It is the forward reaction. As soon as the products are formed, they combine together to form 'AB'. It is the backward reaction. So, the reaction takes place in both the directions. Do you think then that no products are formed in the aforesaid reaction? If you think so, you are wrong. Because, even though the reaction takes place in both the directions, at the initial stage the rates (speed) of these reactions are not equal. Consider the following decomposition reaction of phosphorous pentachloride into phosphorous trichloride and chlorine.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

• The forward reaction is the decomposition of PCl<sub>5</sub> and the backward reaction is the combination of PCl<sub>3</sub> and Cl<sub>2</sub>. Initially, the forward reaction proceeds faster



than the backward reaction. After sometimes, the speed of both the reactions become equal. So,  $PCl_5$  cannot be completely converted into the products as the reaction is reversed. It is a reversible reaction. The actual measurements of the given reaction show that the reaction is at equilibrium, but the amount of  $PCl_5$  is more than that of  $PCl_3$  and  $Cl_2$ .

• Thus, more amount of products can be obtained in a reversible reaction by the periodical removal of one of the products or the periodical addition of the reactants.

 $2H2O_{2(aq)} \rightleftharpoons 2H_2O_{(l)} + O_{2(g)}$ 

#### **Irreversible Reactions**

• The reaction that cannot be reversed is called irreversible reaction. The irreversible reactions are unidirectional, i.e., they take place only in the forward direction. Consider the combustion of coal into carbon dioxide and water.

 $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} + Heat$ 

• In this reaction, solid coal burns with oxygen and gets converted into carbon dioxide gas and water. As the product is a gas, as soon as it is formed it escapes out of the reaction container. It is extremely hard to decompose a gas into a solid. Thus, the backward reaction is not possible in this case. So, it is an irreversible reaction. Table 10.2 provides themain differences between a reversible and an irreversible reaction:

Differences between reversible and irreversible reactions

<b>REVERSIBLE REACTION</b>	<b>IRREVERSIBLE REACTION</b>
It can be reversed under suitable	It cannot be reversed.
conditions.	
Both forward and backward reactions	It is unidirectional. It proceeds only in
take place simultaneously.	forward direction.
It attains equilibrium	Equilibrium is not attained.
The reactants cannot be converted	The reactants can be completely
completely into products.	converted into products.
It is relatively slow.	It is fast.

## **RATE OF A CHEMICAL REACTION**

• "Rate of a reaction is the change in the amount or concentration of any one of the reactants or products per unit time".

Consider the following reaction



 $A \rightarrow B$ 

The rate of this reaction is given by

Rate = 
$$-\frac{d[A]}{dt} = +\frac{d[B]}{dt}$$

Where,

[A] – Concentration of A [B] – Concentration of B

- The negative sign indicates the decrease in the concentration of A with time.
- The postive sign indicates the increase in the concentration of B with time.

**Note:** '[]' represents the concentration, 'd' represents the infinitesimal change in the concentration.

## Why is reaction rate important?

• Faster the reaction, more will be the amount of the product in a specified time. So, the rate of a reaction is important for a chemist for designing a process to get a good yield of a product. Rate of reaction is also important for a food processor who hopes to slow down the reactions that cause food to spoil.

## Factors influencing the rate of a reaction

- Can the rate of a reaction be changed? The rate of a reaction can be changed. Forexample, iron gets rusted faster in an acid than in water. Important factors that affect rate of a reaction are
  - 1. Nature of the reactants
  - 2. Concentration of the reactants
  - 3. Temperature
  - 4. Catalyst
  - 5. Pressure
  - 6. Surface area of the reactants

## Nature of the reactants

• The reaction of sodium with hydrochloric acid is faster than that with acetic acid. Do you know why? Hydrochloric acid is a stronger acid than acetic acid and thus more reactive. So, the nature of the reactants influence the reaction rate.

 $2Na_{(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_{2(g)}$  (fast)



#### $2Na_{(s)} + 2CH_3COOH_{(aq)} \rightarrow 2CH_3COONa_{(aq)} + H_{2(g)}(slow)$

#### **Concentration of the reactants**

• Changing the amount of the reactants also increases the reaction rate. The amount of the substance present in a certain volume of the solution is called 'concentration'. More the concentration, more particles per volume exist in it and hence faster the reaction. Granulated zinc reacts faster with 2M hydrochloric acid than 1M hydrochloric acid.

#### Temperature

• Most of the reactions go faster at higher temperature. Because adding heat to the reactants provides energy to break more bonds and thus speed up the reaction. Calcium carbonate reacts slowly with hydrochloric acid at room temperature. When the reaction mixture is heated the reaction rate increases.

Food kept at room temperature spoils faster than that kept in the refrigerator. In the refrigerator, the temperature is lower than the room temperature and hence the reaction rate is less.

#### Pressure

• If the reactants are gases, increasing their pressure increases the reaction rate. This is because, on increasing the pressure the reacting particles come closer and collide frequently.

## Catalyst

• A catalyst is a substance which increases the reaction rate without being consumed in the reaction. In certain reactions, adding a substance as catalyst speeds up the reaction. For example, on heating potassium chlorate, it decomposes into potassium chloride and oxygen gas, but at a slower rate. If manganese dioxide is added, it increases the reaction rate.

#### Surface area of the reactants

• When solid reactants are involve in a reaction, their powdered form reacts more readily. For example, powdered calcium carbonate reacts more readily with hydrochloric acid than marble chips. Because, powdering of the reactants increases the surface area and more energy is available on collision of the reactant particles. Thus, the reaction rate is increased.



#### STATE OF EQUILIBRIUM

• In a reversible reaction, both forward and backward reactions take place simultaneously. When the rate of the forward reaction becomes equal to the rate of backward reaction, then no more product is formed. This stage of the reaction is called 'equilibrium state'. After this stage, no net change in the reaction can occur and hence in the amount of the reactants and products. Since this equilibrium is attained in a chemical reaction, it is called 'Chemical Equilibrium'. Chemical Equilibrium: It is state of a reversible chemical reaction in which no change in the amount of the reactants and products takes place. At equilibrium,

Rate of forward reaction = Rate of backward reaction

## **Explanation:**

- Initially the rate of the forward reaction is greater than the rate of the backward reaction. However, during the course of reaction, the concentration of the reactants decreases and the concentration of the products increases. Since the rate of a reaction is directly proportional to the concentration, the rate of the forward reaction decreases with time, whereas the rate of the backward reaction increases.
- At a certain stage, both the rates become equal. From this point onwards, there will be no change in the concentrations of both the reactants and the products with time. This state is called as equilibrium state.
- Let us consider the decomposition of calcium carbonate into lime and carbon dioxide. It is a reversible reaction. The speed of each reaction can be determined by how quickly the reactant disappears. If the reaction is carried out in a closed vessel, it reaches a chemical equilibrium. At this stage,

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

- The rate of decomposition of CaCO<sub>3</sub>= The rate of combination of CaO and CO<sub>2</sub>.
- Not only chemical changes, physical changes also may attain equilibrium. When water kept in a closed vessel evaporates, it forms water vapour. No water vapour escapes out of the container as the process takes place in a closed vessel. So, it builds up the vapour pressure in the container. At one time, the water vapour condenses back into liquid water and when the rate of this condensation becomes equal to that of vapourisation, the process attains equilibrium.
- At this stage, the volume of the liquid and gaseous phases remain constant. Since it is a physical change, the equilibrium attained is called 'Physical Equilibrium'.



Physical equilibrium is a state of a physical change at which the volume of all the phases remain unchanged.

$$H2O(l) \xrightarrow{\text{Evaporation}} H_2O C \text{ (g)}$$

#### Characteristics of equilibrium .

- In a chemical equilibrium, the rates of the forward and backward reactions are equal.
- The observable properties such as pressure, concentration, colour, density, viscosity etc., of the system remain unchanged with time.
- The chemical equilibrium is a dynamic equilibrium, because both the forward and backward reactions continue to occur even though it appears static externally.
- In physical equilibrium, the volume of all the phases remain constant.

Aerated soft drinks contain dissolved carbon dioxide in a pop bottle (Soda). When the bottle is sealed, the dissolved carbon dioxide (in the form of carbonic acid) and gaseous CO2 are in equilibrium with each other. When you open the bottle, the gaseous CO2 can escape. So, the dissolved CO2 begins to undissolve back to the gas phase trying to replace the gas that was lost, when you opened the bottle. That's why if you leave it open long enough, it will goes 'flat'. All the CO2 will be gone, blown away in the

## IONIC PRODUCT OF WATER

 Although pure water is often considered as a non-conductor of electricity, precise measurements show that it conducts electricity to a little extent. This conductivity of water has resulted from the self-ionisation of water. Self-ionisation or auto ionisation is a reaction in which two like molecules react to give ions. In the process of ionisation of water, a proton from one water molecule is transferred to another water molecule leaving behind an OH – ion. The proton gets dissolved in water forming the hydronium ion as shown in the following equation:

 $H2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$ 



• The hydronium ion formed is a strong acid and the hydroxyl ion is a strong base. So as fast as they are formed, they react again to produce water. Thus, it is a reversible reaction and attains equilibrium very quickly. So, the extent of ionisation is very little and the concentration of the ions produced is also very less. The product of the concentration of the hydronium ion and the hydroxyl ion



is called 'ionic product of water'. It is denoted as 'Kw'. It is mathematically expressed as follows:

$$K_w = [H_3O^+][OH^-]$$

[H3O<sup>+</sup>] may be simply written as [H<sup>+</sup>]. Thus the ionic product of water may also be expressed as

$$K_w = [H^+] [OH^-]$$

Its unit is mol<sup>2</sup> dm<sup>-6</sup>. At 25° C, its value is  $1.00 \times 10^{-14}$ .

#### pHSCALE

- All the aqueous solutions may contain hydrogen and hydroxyl ions due to selfionisation of water. In addition to this ionisation, substances dissolved in water also may produce hydrogen ions or hydroxyl ions. The concentration of these ions decides whether the solution is acidic or basic. pH scale is a scale for measuring the hydrogen ion concentration in a solution. The 'p' in pH stands for 'Potenz' in German meaning 'power'. pH notation was devised by the Danish biochemist Sorensen in 1909. pH scale is a set of numbers from 0 to 14 which is used to indicate whether a solution is acidic, basic or neutral.
  - Acids have pH less than 7
  - Bases have pH greater than 7
  - A neutral solution has pH equal to 7

The pH is the negative logarithm of the hydrogen ion concentration

#### $pH = -log_{10}[H^+]$

Common Acids	<b>p</b> <sup>H</sup>	Common bases	р <sup>н</sup>
HCL(4%)	0	Blood plasma	7.4
Stomach acid	1	Egg white	8
Lemon juice	2	Sea water	9
Vinegar	3	Baking soda	10
Oranges	3.5	Antacids	10
Soda, Graps	4	Ammonia water	11
Sour milk	4.5	Lime water	12
Fresh Milk	5	Drain cleaner	13
Human saliva	6-8	Caustic soda 4% (NaOH)	14
Pure water	7	Milk of magnesia	10
Tomato juice	4.2	Coffee	5.6



How can we measure the pH of a given solution using pH Paper

- The pH of a solution can be determined by using a universal indicator. It contains a mixture of dyes. It comes in the form of a solution or a pH paper.
- A more common method of measuring pH in a school laboratory is by using the pH paper. A pH paper contains a mixture of indicators. It shows a specific colour at a given pH. A colour guide is provided with the bottle of the indicator or the strips of paper impregnated with it, which are called pH paper strips. The test solution is tested with a drop of the universal indicator, or a drop of the test solution is put on the pH paper. The colour of the solution on the pH paper is compared with the colour chart and the pH value is read from it. The pH values thus obtained are only approximate values.

## ROLE OF pH IN EVERYDAY LIFE Are plants and animals pH sensitive?

• Our body works within the pH range of 7.0 to 7.8. Living organisms can survive only in a narrow range of pH change. Different body fluids have different pH values. For example, pH of blood is ranging from 7.35 to 7.45. Any increase or decrease in this value leads to diseases. The ideal pH for blood is 7.4.

# pH in our digestive system

• It is very interesting to note that our stomach produces hydrochloric acid. It helps in the digestion of food without harming the stomach. During indigestion the stomach produces too much acid and this causes pain and irritation. pH of the stomach fluid is approximately 2.0.

## pH changes as the cause of tooth decay

• pH of the saliva normally ranges between 6.5 to 7.5. White enamel coating of our teeth is calcium phosphate, the hardest substance in our body. When the pH of the mouth saliva falls below 5.5, the enamel gets weathered. Toothpastes, which are generally basic are used for cleaning the teeth that can neutralise the excess acid and prevent tooth decay.

# pH of soil

• In agriculture, the pH of the soil is very important. Citrus fruits require slightly alkaline soil, while rice requires acidic soil and sugarcane requires neutral soil.

## pH of rain water

• The pH of rain water is approximately 7, which means that it is neutral and also represents its high purity. If the atmospheric air is polluted with oxide gases of



sulphur and nitrogen, they get dissolved in the rain water and make its pH less than 7. Thus, if the pH of rain water is less than 7, then it is called acid rain. When acid rain flows into the rivers it lowers the pH of the river water also.

## pH CALCULATION

The pH is the negative logarithm of the hydrogen ion concentration

 $pH = -log_{10} [H^+]$ 

## **Example:**

Calculate the pH of 0.01 M HNO<sub>3</sub>?

#### Solution:

 $\begin{array}{l} [\mathrm{H}^+] = 0.01 \\ \mathrm{pH} = -\mathrm{log}_{10} \; [\mathrm{H}^+] \\ \mathrm{pH} = -\mathrm{log}_{10} \; [0.01] \\ \mathrm{pH} = -\mathrm{log}_{10} \; [1 \times 10^{-2}] \\ \mathrm{pH} = -(\mathrm{log}_{10}1 - 2 \; \mathrm{log}_{10}10) \\ \mathrm{pH} = 0 + 2 \times \mathrm{log}_{10}10 \\ \mathrm{pH} = 0 + 2 \times 1 = 2 \\ \mathrm{pH} = 2 \end{array}$ 

# pOH:

• The pOH of an aqueous solution is realted to the pH. The pOH is the negative logarithm of the hydroxyl ion concentration

 $pOH = -log_{10}[OH^-]$ 

JENTR

## Example:

• The hydroxyl ion concentration of a solution is 1 × 10<sup>-9</sup>M. What is the pOH of the solution?

## Solution

 $pOH = -log_{10} [OH^{-}]$   $pOH = -log_{10} [1 \times 10^{-9}]$   $pOH = -(log_{10} 1.0 + log_{10} 10^{-9})$  $pOH = -(0-9 log_{10} 10)$ 



pOH = -(0 - 9)pOH = 9

Relationship between pH and pOH

- The pH and pOH of a water solution at 25oC are related by the following equation.
   pH + pOH = 14
- If either the pH or the pOH of a solution is known, the other value can be calculated.

**Example:** A solution has a pOH of 11.76. What is the pH of this solution?

pH = 14 - pOH pH = 14 - 11.76 = 2.24

#### PROBLEMS

#### Example 1:

Calculate the pH of 0.001 molar solution of HCl.

• Solution:

HCl is a strong acid and is completely dissociated in its solutions according to the process:

NTR

 $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$ 

From this process it is clear that one mole of HCl would give one mole of H<sup>+</sup> ions. Therefore, the concentration of H+ ions would be equal to that of HCl, i.e.,  $0.001 \text{ molar or } 1.0 \times 10^{-3} \text{mol litre}^{-1}$ .

Thus,  $[H^+] = 1 \times 10-3$  mol litre<sup>-1</sup>

 $pH = -log10[H^+] = -log1010^{-3} = -(-3 \times log_{10}) = -(3 \times 1) = 3$ 

Thus, pH = 3



# Example 2:

What would be the pH of an aqueous solution of sulphuric acid which is 5 × 10<sup>-5</sup>mol litre<sup>-1</sup> in concentration.

Solution:

Sulphuric acid dissociates in water as:

 $H2SO_{4(aq)} \rightarrow 2 H^{+}_{(aq)} + SO^{2-}_{4(aq)}$ 

Each mole of sulphuric acid gives two mole of H<sup>+</sup> ions in the solution. One litre of H<sub>2</sub>SO<sub>4</sub> solution contains  $5 \times 10^{-5}$  moles of H<sub>2</sub>SO<sub>4</sub> which would give  $2 \times 5 \times 10^{-5}$  $5 = 10 \times 10-5$  or  $1.0 \times 10^{-4}$  moles of H<sup>+</sup> ion in one litre of the solution.

Therefore,

 $[H+] = 1.0 \times 10^{-4} \text{mol litre}^{-1}$ 

 $pH = -log_{10}[H^+] = -log_{10}10^{-4} = -(-4 \times log_{10}10) = -(-4 \times 1) = 4$ 

Example 3:

Calculate the pH of 1 × 10-4 molar solution of NaOH.

Solution:

NaOH is a strong base and dissociates in its solution as:

 $NaOH_{(aq)} \rightarrow Na^+_{(aq)} + OH^-_{(aq)}$ 

One mole of NaOH would give one mole of OH- ions. Therefore,

 $[OH^{-}] = 1 \times 10^{-4} mol litre^{-1}$ £]  $= -(-4 \times \log_{10} 10) = -(-4) = 4$ Since, pH + pOH = 14pH = 14 - pOH = 14 - 4 = 10

$$pOH = -log_{10}[OH^{-}] = -log_{10} \times [10^{-4}]$$



## Example 4:

Calculate the pH of a solution in which the concentration of the hydrogen ions is  $1.0 \times 10^{-8}$ mol litre<sup>-1</sup>.

## • Solution:

Here, although the solution is extremely dilute, the concentration given is not of an acid or a base but that of H<sup>+</sup> ions. Hence, the pH can be calculated from the relation:

 $pH = -log10[H^+]$ given [H<sup>+</sup>] = 1.0 × 10<sup>-8</sup>mol litre<sup>-1</sup>  $pH = -log_{10}10^{-8} = -(-8 × log_{10}10)$ = -(-8 × 1) = 8

# Example 5:

If the pH of a solution is 4.5, what is its pOH?

# Solution:

pH + pOH = 14 pOH = 14 - 4.5 = 9.5 pOH = 9.5

## 12<sup>th</sup> vol -2 UNIT – 8. IONIC EQUILIBRIUM

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## **Arrhenius Concept**

One of the earliest theories about acids and bases was proposed by swedish chemist Svante Arrhenius. According to him, an acid is a substance that dissociates to give hydrogen ions in water. For example, HCl, H<sub>2</sub>SO<sub>4</sub> O etc., are acids. Their dissociation in aqueous solution is expressed as

#### H<sup>2</sup>O

$$HCl(g) \leftrightarrows H^+ (aq) + Cl^- (aq)$$

The H+ ion in aqueous solution is highly hydrated and usually represented as  $H_3O^+$ , the simplest hydrate of proton  $[H(H_2O)^+$ . We use both H<sup>+</sup> and  $H_3O^+$  to mean the same.

Similarly a base is a substance that dissociates to give hydroxyl ions in water. For example, substances like NaOH, Ca(OH)<sub>2</sub> etc., are bases.

 $H_2O$ 



## $Ca(OH)_2 \iff Ca^{2+}(aq)+2OH^{-}(aq)$

#### Limitations of Arrhenius concept

- i. Arrhenius theory does not explain the behaviour of acids and bases in non aqueous solvents such as acetone, Tetrahydrofuran etc...
- ii. This theory does not account for the basicity of the substances like ammonia (NH<sub>3</sub>) which do not possess hydroxyl group.

#### Lowry - Bronsted Theory (Proton Theory)

In 1923, Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton form other substance. In other words, an acid is a proton donor and a base is a proton acceptor.

When hydrogen chloride is dissolved in water, it donates a proton to the later. Thus, HCl behaves as an acid and  $H_2O$  is base. The proton transfer from the acid to base can be represented as

#### $HCl+H_2O \rightleftharpoons H_3O_++Cl^-$

When ammonia is dissolved in water, it accepts a proton from water. In this case, ammonia (NH3) acts as a base and H O2 is acid. The reaction is represented as H O2 3 +NH NH +4 OH  $\square$  + -

Let us consider the reverse reaction in the following equilibrium

HCl + H<sub>2</sub>O  $\rightleftharpoons$  H<sub>3</sub>O + Cl-Proton donar (acid) Proton acceptor (Base) proton donar (acid) Proton acceptor (Base)

 $H_3O^+$  donates a proton to Cl<sup>-</sup> to form HCl i.e., the products also behave as acid and base.

In general, Lowry – Bronsted (acid – base) reaction is represented as  $Acid_1 + Base_2$  $\Rightarrow Acid_2 + Base_1$ 

The species that remains after the donation of a proton is a base (Base<sub>1</sub>)and is called the conjugate base of the Bronsted acid ( $Acid_1$ ). In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.



Proton donar (acid) proton acceptor (Base) Proton acceptor (Base)



HCl and Cl<sup>-</sup>, H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> are two conjugate acid – base pairs. i.e., Cl<sup>-</sup> is the conjugate base of the acid HCl . (or) HCl is conjugate acid of Cl<sup>-</sup>. Similarly H<sub>3</sub>O<sup>+</sup> is the conjugate acid of H<sub>2</sub>O .

#### Limitations of Lowry - Bronsted theory

 $\succ$  Substances like BF<sub>3</sub> , AlCl<sub>3</sub> etc., that do not donate protons are known to behave as acids.

#### Lewis concept

In 1923, Gilbert . N. Lewis proposed a more generalised concept of acids and bases. He considered the electron pair to define a species as an acid (or) a base. According to him, an acid is a species that accepts an electron pair while base is a species that donates an electron pair. We call such species as Lewis acids and bases.

A lewis acid is a positive ion (or) an electron deficient molecule and a lewis base is a anion (or) neutral molecule with at least one lone pair of electrons.

Let us consider the reaction between Boron tri fluoride and ammonia Here, boron has a vacant 2p orbital to accept the lone pair of electrons donated by



ammonia to form a new coordinate covalent bond. We have already learnt that in coordination compounds, the Ligands act as a lewis base and the central metal atom or ion that accepts a pair of electrons from the ligand behaves as a lewis acid.

Lewis acids	Lewis bases
Electron deficient molecules such as BF <sub>3</sub> , AlCl <sub>3</sub> , BeF <sub>2</sub> etc	Molecules with one (or) more lone pairs of electrons. NH <sub>3</sub> ,H <sub>2</sub> O,R-O-H,R-O-R, R - NH <sub>2</sub>

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All metal ions (or) atoms Examples: Fe <sup>2+</sup>	All anions F <sup>-</sup> ,Cl <sup>-</sup> ,SCN <sup>-</sup> ,CN <sup>-</sup> ,SCN <sup>-</sup> ,SO <sub>4</sub> <sup>2-</sup>
,Fe <sup>3+</sup> ,Cr <sup>3+</sup> ,Cu <sup>2+</sup> etc	etc
Molecules that contain a polar double	Molecules that contain carbon - carbon
bond Examples : $SO_2$ , $CO_2$ , $SO_3$	multiple bond Examples: CH <sub>2</sub> =CH <sub>2</sub> ,CH
etc	≡ CH etc
Molecules in which the central atom can expand its octet due to the availability of empty d – orbitals Example: SiF <sub>4</sub> ,SF <sub>4</sub> ,FeCl <sub>3</sub> etc	All metal oxides CaO,MgO,Na2O etc
Carbonium ion (CH <sub>3</sub> )C <sub>3</sub> +	Carbanion CH <sub>3</sub> -

#### **Strength of Acids and Bases**

The strength of acids and bases can be determined by the concentration of  $H_3O^+$  (or) OH<sup>-</sup> produced per mole of the substance dissolved in  $H_2O$ . Generally we classify the acids / bases either as strong or weak. A strong acid is the one that is almost completely dissociated in water while a weak acid is only partially dissociated in water.

Let us quantitatively define the strength of an acid (HA) by considering the following general equilibrium.

 $\begin{array}{rcl} HA & + H_2O & \leftrightarrows & H_3O & + & A^-\\ Acid1 & base 2 & & acid 2 base 1 \end{array}$ 

The equilibrium constant for the above ionisation is given by the following expression

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

We can omit the concentration of H<sub>2</sub>O in the above expression since it is present in large excess and essentially unchanged.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$
.....(8.2)

Here,  $K_a$  is called the ionisation constant or dissociation constant of the acid. It measures the strength of an acid. Acids such as HCl,HNO<sub>3</sub> etc... are almost completely ionised and hence they have high  $K_a$  value ( $K_a$  for HCl at 25<sup>o</sup> C is 2×10<sup>6</sup>) Acids such as formic acid ( $K_a$ =1.8 X 10<sup>-4</sup> at 25<sup>o</sup>C), acetic acid (1.8X10<sup>-5</sup> at 25<sup>o</sup>C) etc..



are partially ionised in solution and in such cases, there is an equilibrium between the unionised acid molecules and their dissociated ions. Generally, acids with  $K_a$  value greater than ten are considered as strong acids and less than one are considered as weak acids.

Let us consider the dissociation of HCl in aqueous solution,

HC1	+ H - OH	- -	$H_3O^+$	+ Cl-
Acid1	hase 2		acid 2	hase 1

As discussed earlier, due to the complete dissociation, the equilibrium lies almost 100% to the right. i.e., the Cl<sup>-</sup> ion has only a negligible tendency to accept a proton form  $H_3O$  + . It means that the conjugate base of a strong acid is a weak base and vice versa.

## The following table illustrates the relative strength of conjugate acid – base pairs.



#### Ionisation of water

We have learnt that when an acidic or a basic substance is dissolved in water, depending upon its nature, it can either donate (or) accept a proton. In addition to that the pure water itself has a little tendency to dissociate. i.e, one water molecule donates a proton to an another water molecule. This is known as auto ionisation of water and it is represented as below.



Conjugate acid - base pairs



In the above ionisation, one water molecule acts as an acid while the another water molecule acts as a base.

The dissociation constant for the above ionisation is given by the following expression

$$K_{a} = \frac{[H_{3}O^{+}][OH^{-}]}{[H_{2}O]}$$
.....(8.3)

The concentration of pure liquid water is one. i.e,  $[H_2O]^2 = 1$  $K = [H_3O^+][OH]......(8.4)$ 

Here, Kw represents the ionic product (ionic product constant) of water

It was experimentally found that the concentration of  $H_3O^+$  in pure water is  $1X10^{-7}$  at  $25^{0}C$ . Since the dissociation of water produces equal number of  $H_3O^+$  and  $OH^-$ , the concentration of  $OH^-$  is also equal to  $1X10^{-7}$  at  $25^{0}C$ .

## Therefore, the ionic product of water o at 25°C is

$$K_{w} = [H_{3}O]^{+}[OH^{-}].....(8.4)$$
  

$$K_{w} = (1X10^{-7})(1X10^{-7})$$
  

$$= 1X10^{-14}.$$

Like all equilibrium constants,  $K_w$  is also a constant at a particular temperature. The dissociation of water is an endothermic reaction. With the increase in temperature, the concentration of H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> also increases, and hence the ionic product also increases.

Kw values at different temperatures are given in the following below

Temperature ( ° C )	Kw	
0	1.14 X 10 <sup>-15</sup>	
10	2.95 X 10 <sup>-15</sup>	
25	1.00 X 10 <sup>-14</sup>	
40	2.71 X 10 <sup>-14</sup>	
50	5.30 X 10 <sup>-14</sup>	

In neutral aqueous solution like NaCl solution, the concentration of  $H_3O^+$  is always equal to the concentration of OH- whereas in case of an aqueous solution of a



substance which may behave as an acid (or) a base, the concentration of  $[H_3O^+]$  will not be equal to  $[OH^-]$ .

We can understand this by considering the aqueous HCl as an example. In addition to the auto ionisation of water, the following equilibrium due to the dissociation of HCl can also exist.

 $HCl+H_2O \rightleftharpoons H_3O^++Cl^-$ 

In this case, in addition to the auto ionisation of water, HCl molecules also produces H3 O+ ion by donating a proton to water and hence  $[H_3O^+]>[OH^-]$ . It means that the aqueous HCl solution is acidic. Similarly, in basic solution such as aqueous NH<sub>3</sub> NaOH etc..... [OH-]>[H<sub>3</sub>O<sup>+</sup>].

#### Ostwald's dilution law

Ostwald's dilution law relates the dissociation constant of the weak acid (K) a with its degree of dissociation ( $\langle$ ) and the concentration (c). Degree of dissociation ( $\langle$ ) is the fraction of the total number of moles of a substance that dissociates at equilibrium.

Number of moles dissociated

total number of moles

We shall derive an expression for ostwald's law by considering a weak acid, i.e. acetic  $acid(CH_3 COOH)$ . The dissociation of acetic acid can be represented as

 $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$ 

The dissociation constant of acetic acid is,

 $\alpha = -$ 

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$$

	CH <sub>3</sub> COOH	$\mathrm{H}^{+}$	CH <sup>3</sup> COO <sup>−</sup>
Initial number of			
moles	1	-	-
Degree of			
dissociation of	α	_	-
CH COOH			
Number of moles			
at	$1-\alpha$	$\alpha$	$\alpha$
equilibrium			
Equilibrium			
concentration	$(1-\alpha)C$	$\alpha$ C	$\alpha$ C

Substituting the equilibrium concentration in equation (8.13)

$$(\alpha C) (\alpha C)$$



$$K_{a} = \underbrace{(1-\alpha) C}_{K_{a}} = \underbrace{\alpha^{2}C}_{1-\alpha} \ldots (8.14)$$

We know that weak acid dissociates only to a very small extent compared to one, a is so small and hence in the denominator  $(1 - a) \approx 1$ . The above expression (8.14) now becomes,

$$K_{a} = \alpha^{2}C$$

$$\alpha^{\frac{K_{a}}{2}}$$

$$\alpha = \underbrace{\frac{C}{\sqrt{K_{a}}}}_{C}$$
(8.15)

Let us consider an acid with Ka value 4 · 10-4 and calculate the degree of dissociation of that acid at two different concentration 1.10-2M and  $1 \cdot 10$ -4M using the above expression (8.15) GENTRE

For 
$$1 \times 10^{-2} M$$
,  
 $\alpha = \sqrt{4 \times 10^{-2}}$   
 $= \sqrt{4 \times 10^{-2}}$   
 $= 2 \times 10^{-1}$   
 $= 0.2$   
 $1 \times 10^{-4} M$  acid,  
 $\alpha = \sqrt{-4 \times 10^{-4}}$   
 $= 2$ 

For

i.e, When the dilution increases by 100 times, (Concentration

decreases from  $1X10^{-2}$  to  $1X10^{-4}$ M), the dissociation increases by 10 times.

Thus, we can conclude that, when dilution increases, the degree of dissociation of weak electrolyte also increases. This statement is known as Ostwald's dilution Law.

The concentration of  $H^+(H_30^+)$  can be calculated using the Ka value as

below.  $[H+] = \alpha C$ (Refer table)

Equilibrium molar concentration of [H<sup>+</sup>] is equal to -C
#### **Common Ion Effect**

When a salt of a weak acid is added to the acid itself, the dissociation of the weak acid issuppressed further. For example, the addition of sodium acetate to acetic acid solution leads to the suppression in the dissociation of acetic acid which is already weakly dissociated. In this case,  $CH_3COOH$  and  $CH_3COONa$  have the common ion,  $CH_3COO^-$ 

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[ : equation (8.15)]

Let us analyse why this happens. Acetic acid is a weak acid. It is not completely dissociated in aqueous solution and hence the following equilibrium exists.

 $CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$ 

However, the added salt, sodium acetate, completely dissociates to produce  $Na^+$  and  $CH_3COO^-$  ion.

 $CH_3COONa(aq) \rightarrow Na^+ (aq) + CH_3COO^- (aq)$ 

Hence, the overall concentration of  $CH_3COO^-$  is increased, and the acid dissociation equilibrium is disturbed. We know from Le chatelier's principle that when a stress is applied to a system at equilibrium, the system adjusts itself to nullify the effect produced by that stress. So, inorder to maintain the equilibrium, the excess  $CH_3COO^-$  ions combines with H<sup>+</sup>ions toproduce much more unionized  $CH_3COOH$  i.e, the equilibrium will shift towards the left. Inother words, the dissociation of  $CH_3COOH$  is suppressed. Thus, the dissociation of a weak acid (CH3COOH) is suppressed in the presence of a salt (CH3COONa) containing an ioncommon to the weak electrolyte. It is called the common ion effect.

#### **Buffer Solution**

Do you know that our blood maintains a constant pH, irrespective of a number of cellularacid – base reactions. Is it possible to maintain a constant



hydronium ion concentration insuch reactions? Yes, it is possible due to buffer action.

Buffer is a solution which consists of a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid. This buffer solution resists drastic changes in its pH upon addition of a small quantities of acids (or) bases, and this ability is called buffer action. The buffer containing carbonic acid (H<sub>2</sub>CO 3) and its conjugate base  $H_3CO^-$  is present in our blood. There are two types of buffer solutions.

1. Acidic buffer solution : a solution containing a weak acid and its salt.

Example : solution containing acetic acid and sodium acetate

2. Basic buffer solution : a solution containing a weak base and its salt.

Example : Solution containing NH4OH and NH4Cl

## **Buffer action**

To resist changes in its pH on the addition of an acid (or) a base, the buffer solution should contain both acidic as well as basic components so as to neutralize the effect of added acid (or) base and at the same time, these components should not consume each other.

Let us explain the buffer action in a solution containing  $\rm CH_3COOH~$  and  $\rm CH_3COONa$ 

The dissociation of the buffer components occurs as below.

CH3COOH (aq)  $\Rightarrow$  CH3 - COO(aq) + H3O+(aq) H<sub>2</sub>O(1) CH3COONa(s)  $\longrightarrow$  CH3 - COO<sup>-</sup>(aq) + Na<sup>+</sup>(aq)

If an acid is added to this mixture, it will be consumed by the conjugate base CH<sub>3</sub>COO<sup>-</sup> to form the undissociated weak acid i.e, the increase in the concentration of H<sup>+</sup> does not reduce the pH significantly.

 $CH3COO^{-}(aq) + H^{+}(aq) - CH3GOOH(aq)$ 

If a base is added, it will be neutralized by H3O<sup>+</sup>, and the acetic acid is dissociated to maintain the equilibrium. Hence the pH is not significantly altered.

 $\begin{array}{c} OH^{-}(aq) + H_{3}O^{+}(aq) & \longrightarrow 2O(1) \\ H_{2}O(1) \\ CH3COOH(aq) & \leftrightarrows CH3 - COO^{-}(aq + H_{3}O^{+}(aq)) \end{array}$ 

OH<sup>-</sup>(aq) + CH<sub>3</sub>COOH( aq) → CH<sub>3</sub>COO<sup>-</sup>(aq) + H2O (1)



These neutralization reactions are identical to those reactions that we have already discussed in common ion effect.

Let us analyse the effect of the addition of 0.01 mol of solid sodium hydroxide to one litre of a buffer solution containing 0.8 M CH<sub>3</sub>COOH and 0.8 M CH<sub>3</sub>COONa. Assume that the volume change due to the addition of NaOH is negligible. (Given: Ka for CH<sub>3</sub>COOH is  $1.8 \times 10^{-5}$ ).

 $H_20$ CH<sub>3</sub>-COOH(aq)  $- H_3COO^{-}(aq) + H^{+}(aq)$ -0.8α α α  $H_2O$  $CH_3COONa(aq)$  $+CH_3COO^-(aq)+Na^+(aq)$ 0.80.8 0.8 The dissociation constant for CH<sub>3</sub>COOH is given by [CH<sub>3</sub>COO<sup>-</sup>][H+]  $K \equiv$ [CH<sub>3</sub>COOH] [CH<sub>3</sub>COOH]  $H^+=K_a =$  $[CH_3COO^-]$ 

The above expression shows that the concentration of H<sup>+</sup> is directly ENTR proportional to

[CH<sub>3</sub>COOH]

 $[CH_3COO^-]$ Let the degree of dissociation of CH3COOH  $\alpha$  be  $\Box$  then,  $[CH_{3}COOH] = 0.8 - \alpha \text{ and } [CH_{3}COO^{-}] = \alpha + 0.8$  $[0.8 - \alpha]$  $\therefore$  H<sup>+</sup>= K<sub>a</sub>  $[0.8 + \alpha]$  $0.8-\alpha = 0.8$  and  $0.8+\alpha = 0.8$  $\alpha \ll 0.8$ ,  $K_{a}(0.8)$  $[H^+] = ----- \Box$  $H^+ = K_a$ (0.8)Given that  $K_a$  for  $CH_3COOH$  is 1.8 X  $10^{-5}$  $\therefore$  [H+]=1.8 X 10<sup>-5</sup>; - log(1.8 X 10<sup>-5</sup>)

= 5 - log 1.8 = 5 - 0.26 Ph = 4.74

Calculation of pH after adding 0.01 mol NaOH to 1 litre of buffer.

 $CH_3$  -COOH(aq)  $\Leftrightarrow$   $CH_3COO^{-}(aq)+H^{+}(aq)$ 



0.8α α α CH<sub>3</sub>COONa(aq)  $-----GH_3COO^-(aq)+Na^+(aq)$ 0.8 0.8 0.8 CH<sub>3</sub>COOH + OH<sup>-</sup>(aq**)** ►  $CH_3COO^-(aq) + H_2O$  (1) :  $[CH_3COOH] = 0.8 - \alpha - 0.01 = 0.79 - \alpha$  $[CH_3COO^-] = \alpha + 0.8 + 0.01 = 0.81 + \alpha$  $\alpha << 0.8;$  $0.79 - \alpha = 0.79$  and  $0.81 + \alpha = 0.81$ 0.79  $\therefore$  [H<sup>+</sup>] = (1.8 X 10<sup>-5</sup>) X -----0.81  $[H+] = 1.76 \text{ X } 10^{-5}$  $\therefore$  pH = -LOG (1.76 x 10<sup>-5</sup>) = 5 - LOG 1.76 = 5 - 0.25 pH = 4.75

The addition of a strong base (0.01 M NaOH) increased the pH only slightly ie., from 4.74 to 4.75. So, the buffer action is verified.





# Oxidation And Reduction 9<sup>th</sup> std Chemical bonding

## **Oxidation, Reduction and Redox reactions**

When an apple is cut and left for sometimes, its surface turns brown. Similarly, iron bolts and nuts in metallic structures get rusted. Do you know why these are happening? It is because of a reaction called oxidation.

**Oxidation**: The chemical reaction which involves addition of oxygen or removal of hydrogen or loss of electrons is called oxidation.

2 Mg +  $O_2 \rightarrow 2$  MgO (addition of oxygen) CaH<sub>2</sub> $\rightarrow$  C<sub>a</sub> + H<sub>2</sub> (removal of hydrogen) Fe<sub>2</sub>+ $\rightarrow$ Fe<sub>3</sub>+ + e<sup>-</sup> (loss of electron)

**Reduction**: The chemical reaction which involves addition of hydrogen or removal of oxygen or gain of electrons is called reduction.  $2 \text{ Na} + \text{H}_2 \rightarrow 2 \text{ NaH}$  (addition of hydrogen)

2 Na + H<sub>2</sub> $\rightarrow$  2 NaH (addition of hydrogen) CuO + H<sub>2</sub> $\rightarrow$  Cu + H<sub>2</sub>O (removal of oxygen) Fe<sub>3</sub>++ e $\rightarrow$ Fe<sub>2</sub>+ (gain of electron)

**Redox reactions**: Generally, the oxidation and reduction occurs in the same reaction (simultaneously). If one reactant gets oxidised, the other gets reduced. Such reactions are called oxidation-reduction reactions or Redox reactions.

 $2 PbO + C \rightarrow 2 Pb + CO_2$ Zn + CuSO<sub>4</sub> $\rightarrow$  Cu + ZnSO<sub>4</sub>

	Addition of oxygen	
Oxidation	Removal of hydrogen	
	Loss of electron	
	Removal of oxygen	
Reduction	Addition of hydrogen	
	Gain of electron	

#### **Oxidising agents and Reducing agents**

Substances which have the ability to oxidise other substances are called oxidising agents.



These are also called as electron acceptors because they remove electrons from other substances.

Example: H<sub>2</sub>O<sub>2</sub>, MnO<sub>4</sub>-, CrO<sub>3</sub>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>

Substances which have the ability to reduce other substances are called Reducing agents. These are also called as electron donors because they donate electrons to other substances.

Example: NaBH<sub>4</sub>, LiAlH<sub>4</sub> and metals like Palladium, Platinum.

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## **Oxidation reactions in daily life:**

In nature, the oxygen present in atmospheric air oxidises many things, starting from metals to living tissues.

• The shining surface of metals tarnishes due to the formation of respective metal oxides on their surfaces. This is called corrosion.

• The freshly cut surfaces of vegetables and fruits turns brown after some time because of the oxidation of organic compounds present in them.

• The oxidation reaction in food materials that were left open for a long period is responsible for spoiling of food. This is called Rancidity.



## 11<sup>th</sup> chemistry vol -1

# Unit - 1 Basic Concepts of Chemistry

When an apple is cut, it turns brownafter sometime. Do you know the reasonbehind this colour change? It is because of a chemical reaction called oxidation. Wecome across oxidation reactions in ourdaily life.

## For example

 burning of LPGgas
 rusting of iron
 Oxidation of carbohydrates, lipids, etc.into CO2 and H2O to produce energyin the living organisms.

All oxidation reactions areaccompanied by reduction reactions and vice versa. Such reactions are calledredox reactions. As per the classical concept, addition of oxygen (or) removalof hydrogen is called oxidation and thereverse is called reduction

Consider the following two reactions.

Reaction 1 : 4 Fe +  $3O_2 \rightarrow 2 Fe_2O_3$ 

Reaction 2 :  $H_2S + Cl_2 \rightarrow 2 HCl + S$ 

Both these reactions are oxidationreactions as per the classical concept.

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In the first reaction which is responsible for the rusting of iron, the oxygen adds on to the metal, iron. In these cond reaction, hydrogen is removed from Hydrogen sulphide (H2S). Identity which species gets reduced.

Consider the following tworeactions in which the removal ofoxygen and addition of hydrogen takeplace respectively. These reactions arecalled reduction reactions as per theclassical concept.

 $CuO + C \rightarrow Cu + CO$  (Removal of oxygenfrom cupric oxide)

S +  $H_2 \rightarrow H_2S$  (Addition of hydrogen tosulphur).

Oxidation-reduction reactions i.e.redox reactions are not always associated with oxygen or hydrogen. In such cases, the process can be explained on the basis of electrons. The reaction involving loss of electron is termed oxidation and gain of electron is termed reduction.

## For example,



 $Fe^{2+} \rightarrow Fe^{3+} + e^{-}$  (loss of electron-oxidation).

 $Cu^{2+}$  2e- $\rightarrow$  Cu (gain of electron-reduction)Redox reactions can be better explainedusing oxidation numbers.

## **Oxidation Number:**

It is defined as the imaginary chargeleft on the atom when all other atoms of the compound have been removed in their usual oxidation states that are assigned according to set of rules. A term that isoften used interchangeably with oxidationnumber is oxidation state

1) The oxidation state of a free element(i.e. in its uncombined state) is zero.

## Example :

each atom in H<sub>2</sub>, Cl<sub>2</sub>, Na, S<sub>8</sub> have the oxidation number of zero.

2) For a monatomic ion, the oxidationstate is equal to the net charge on the ion. NTR

## Example :

The oxidation number of sodiumin Na<sup>+</sup> is +1. The oxidation number of chlorine in Cl- is -1.

3) The algebric sum of oxidation states of all atoms in a molecule is equal to zero, while in ions, it is equal to thenet charge on the ion.

## **Example:**

In  $H_2SO_4$ ; 2 × (oxidation number of hydrogen) + (oxidation number of S) + 4 (oxidation number of oxygen) = 0.

In SO<sub>4</sub><sup>2–</sup>; (oxidation number of S) + 4(oxidation number of oxygen) = -2.

4) Hydrogen has an oxidation number of +1 in all its compounds except in metal hydrides where it has -1 value.

## **Example:**

Oxidation number of hydrogen in hydrogen chloride (HCl) is + 1. Oxidation number of hydrogen in sodium hydride (NaH) is -1.

5) Fluorine has an oxidation state of – 1 in all its compounds.



6) The oxidation state of oxygen in most compounds is -2. Exceptions are peroxides, super oxides and compounds with fluorine.

#### Example :

Oxidation number of oxygen,

i) in water (H<sub>2</sub>O) is –2. ii) in hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) is –1.

 $2 (+1) + 2x = 0; \qquad \Rightarrow 2x = -2; \Rightarrow x = -1$ iii) in super oxides such as KO2 is  $-\frac{1}{2}$ +1 + 2x = 0; 2x = -1;  $x = -\frac{1}{2}$ 

iv) in oxygen difluoride (OF2) is + 2. x + 2(-1) = 0; x = + 2

7) Alkali metals have an oxidation state of + 1 and alkaline earth metals have anoxidation state of + 2 in all their compounds.

Sl.No	Oxidation umber of the element	In the compound	Calculation
1	С	CO <sub>2</sub>	x + 2(-2) = 0 x = +4
2	S	H <sub>2</sub> SO <sub>4</sub>	2 (+1) + x + 4 (-2) = 0 2 + x - 8 = 0 x = +6
3	Cr ST	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	2x+7(-2) = -2 2x-14 = -2 x = +6
4	С	CH <sub>2</sub> F <sub>2</sub>	x+2(+1)+2(-1) = 0 x = 0
5	S	SO <sub>2</sub>	x+2(-2) = 0 x = +4

#### Redox reactions in terms of oxidation numbers

During redox reactions, the oxidation number of elements changes. A reaction inwhich oxidation number of the element increases is called oxidation. A reaction in whichit decreases is called reduction.

Consider the following reaction

oxidation number increases - oxidation



+7 +2

+2 +3

2 KMnO4 + 10FeSO4 + 8H2SO4 +8H2O K2SO4 + MnSO4 + 5 Fe2(SO4)3

oxidation number decreases reduction

In this reaction, manganese in potassium permanganate (KMnO<sub>4</sub>) favours theoxidation of ferrous sulphate (FeSO<sub>4</sub>) into ferric sulphate (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> by gaining electronsand thereby gets reduced. Such reagents are called oxidising agents or oxidants. Similarly, the reagents which facilitate reduction by releasing electrons and get oxidised are called

reducing agents.

#### **Types of Redox Reactions**

Redox reactions are classified into the following types.

#### 1. Combination reactions:

Redox reactions in which two substances combine to form a single compoundare called combination reaction.

#### **Example:**

oxidation



## 2. Decomposition reactions:

Redox reactions in which a compound breaks down into two or more componentsare called decomposition reactions. These reactions are opposite to combination reactions. In these reactions, the oxidation number of the different elements in the same substance is changed.



# Example: oxidation



## 3. Displacement reactions:

Redox reactions in which an ion (oran atom) in a compound is replaced by anion (or atom) of another element are calleddisplacement reactions. They are further classified into (i) metal displacement reactions (ii) non-metal displacement reactions.

(i) Metal displacement reactions:

Place a zinc metal strip in anaqueous copper sulphate solution taken in a beaker. Observe the solution, theintensity of blue colour of the solution slowly reduced and finally disappeared.

The zinc metal strip became coated with brownish metallic copper. This isdue to the following metal displacement reaction.

oxidation

+2 0 0 +2  
CuSO4 (aq) + Zn(s) 
$$Cu(s) + Zn \xrightarrow{SO4}(aq)$$

TUD

Reduction

ii) Non-metal displacement

oxidation



4. Disproportionation reaction (Auto redox reactions)



In some redox reactions, the samecompound can undergo both oxidation and reduction. In such reactions, the oxidation state of one and the same element is bothincreased and decreased. These reactions are called disproportionation reactions.

Examples oxidation  $\begin{array}{cccc}
-1 & -2 & 0 & & & \\
2H_2O_22H_2O + O_2 & 2 & & & & \\
Reduction & & & & & & \\
oxidation & & & & & & \\
0 & 3 Cl_2 + 6KOH 5KCl + KCl & 3 + 3H_2O & & & & & \\
Reduction & & & & & & & & \\
\end{array}$ 

## 5. Competitive electron transfer reaction

In metal displacement reactions,we learnt that zinc replaces copper from copper sulphate solution. Let us examine whether the reverse reaction takes place ornot. As discussed earlier, place a metallic copper strip in zinc sulphate solution. If copper replaces zinc from zinc sulphatesolution, Cu<sup>2+</sup> ions would be released into the solution and the colour of the solution would change to blue. But no such change observed. Therefore, we conclude that among zinc and copper, zinc has more tendency to release electrons and copperto accept the electrons.

Let us extend the reaction to coppermetal and silver nitrate solution. Place astrip of metallic copper in sliver nitratesolution taken in a beaker. After sometime, the solution slowly turns blue. This is due to the formation of Cu<sup>2+</sup> ions, i.e.copper replaces silver from silver nitrate. The reaction is,

Cu(s) + 2AgNO3 (aq) Cu(NO3)2 (aq) + 2Ag (s)

oxidation

0 +1+2

0



# Reduction

It indicates that between copper andsilver, copper has the tendency to releaseelectrons and silver to accept electrons.

From the above experimental observations, we can conclude that among the three metals, namely, zinc, copper and silver, the electron releasing tendency is in the following order.

Zinc > Copper > Silver

This kind of competition forelectrons among various metals helps us to design (galvanic) cells. In XII standardwe will study the galvanic cell in detail.

## **Balancing (the Equation) of Redox Reactions**

The two methods for balancing theequation of redox reactions are as follows.

i) The oxidation number method

ii) Ion-electron method / half reactionmethod.

Both are based on the same principle:In oxidation - reduction reactions thetotal number of electrons donated by thereducing agent is equal to the total number electrons gained by the oxidising agent.

## Oxidation number method

In this method, the number of electrons lost or gained in the reaction is calculated from the oxidation numbers of elements before and after the reaction.Let us consider the oxidation of ferroussulphate by potassium permanganate inacid medium. The unbalanced chemical equation is,

 $FeSO_4 + KMnO_4 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + MnSO_4 + K_2SO_4 + H_2O$ 

## Step 1

Using oxidation number concept, identify the reactants (atom) which undergo oxidation and reduction.

oxidation





+  $MnSO_4$ +  $K_2SO_4$ + $H_2O$ 

## Reduction

a) The oxidation number of Mn in KMnO<sub>4</sub> changes from +7 to +2 by gaining five electrons.

b) The oxidation number of Fe in FeSO<sub>4</sub>changes from +2 to +3 by loosingone electron.

## Step 2

Since, the total number of electronslost is equal to the total number of electrons gained, equate, the number of electrons, by cross multiplication of therespective formula with suitable integers n reactant side as below. Here, the productFe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> contains 2 moles of iron, So, theCoefficients 1e-& 5e<sup>-</sup> are multiplied by thenumber

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+2 +7 +3  
FeSO<sub>4</sub> + KMnO<sub>4</sub>+H<sub>2</sub>SO<sub>4</sub>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> 
$$\rightarrow$$
  
+ MInSQ<sub>4</sub>  
1e<sup>-</sup> × 2 5e<sup>-</sup> × 2+ K<sub>2</sub>SO<sub>4</sub>+H<sub>2</sub>O  
2 , 10

10 FeSO<sub>4</sub>+2 KMnO<sub>4</sub>+H<sub>2</sub>SO<sub>4</sub>→Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> +MnSO<sub>4</sub> + K<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O

## Step 3

Balance the reactant / Product -Oxidised / reduced

Now, based on the reactant side, balance the products (ie oxidised and reduced). The above equation becomes

 $10FeSO_4 + 2KMnO_4 + H_2SO_4 \rightarrow 5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4 + H_2O_3 + 2MnSO_4 + 2M$ 

## Step 4

Balance the other elements exceptH and O atoms. In this case, we have tobalance K and S atoms but K is balancedautomatically.

Reactant Side : 10 'S' atoms (10 FeSO<sub>4</sub>)



Product Side : 18 'S' atoms

 $5Fe_2(SO_4)_3 + 2MnSO_4 + K_2SO_4$ 15S + 2S + 1S = 18S

Therefore the difference 8-S atoms in reactant side, has to be balanced by multiplying  $H_2SO_4$  by '8' The equation now becomes,

## Step 5

Balancing 'H' and 'O' atoms Reactant side '16'-H atoms ( $8H_2SO_4$  i.e.  $8x \ 2H = 16$  'H') Product side '2' - H atoms ( $H_2O$  i.e.  $1 \ x \ 2H = 2$  'H') Therefore, multiply  $H_2O$  molecules in the product side by '8'  $10 \ FeSO_4 + 2 \ KMnO_4 + 8 \ H_2SO_4 \rightarrow 5 \ Fe_2(SO_4)_3 + 2 \ MnSO_4 + K_2SO_4 + 8H_2O$ 

The oxygen atom is automaticallybalanced. This is the balanced equation.

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# Ion - Electron method

This method is used for ionic redoxreactions.

## Step 1

Using oxidation number concept, find out the reactants which undergo oxidation and reduction.

## Step 2

Write two separate half equations for oxidation and reduction reaction, Let us consider the same example which we have already discussed in oxidationnumber method.

$$\label{eq:KMnO4} \begin{split} KMnO_4 + FeSO_4 + H_2SO_4 &\rightarrow MnSO_4 + Fe_2(SO_4)3 + K_2SO_4 + H_2O \\ The ionic form of this reaction is, \end{split}$$

oxidation

```
+7
MnO<sub>4</sub>-+ Fe<sup>2+</sup> + H+Mn<sup>2+</sup> + He<sup>3+</sup> + H<sub>2</sub>\bigcirc
Reduction
```

The two half reactions are,



Balance the atoms and charges on bothsides of the half reactions. Equation (1) $\Rightarrow$  No changes i.e.,

 $Fe^{2+} \rightarrow Fe^{3+} + 1e^{-}$ ----- (1)

Equation (2)  $\Rightarrow$  4'O' on the reactant side, therefore add 4H<sub>2</sub>O on the product side, to balance 'H' - add, 8H+ in the reactantside  $MnO_{4}^{-}+5e^{-}+8H^{+}\rightarrow Mn^{2+}+4H_{2}O$ ----- (3)

CHENNAI

Step 3

Equate both half reactions such that the number of electrons lost is equal to number of electrons gained.

Addition of two half reactions gives he balanced equation represented byequation (6).

 $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^{-}$  (4) (1) x 5  $\Rightarrow$ 

 $MnO_{4}^{-}+ 5e^{-} + 8H^{+} \rightarrow Mn^{2+} + 4H_{2}O$  -----(5)  $\begin{array}{l} (3) \ge 1 \Rightarrow \\ (4) + (5) \end{array}$ 



