# LEARNING MATERIAL OF CHEMISTRY (1<sup>ST</sup> & 2<sup>ND</sup> SEM)



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## CHAPTER - 1 ATOMIC STRUCTURE

#### Introduction:

According to *Dalton's Atomic theory* "Every matter is composed of very small particles called 'atoms' (Greek, a = cannot be; tom = cut) which cannot be further subdivided". But modern researches revealed that an atom is divisible and has a rather complex structure containing a large number of sub-atomic particles such as electrons, protons, neutrons, mesons, leptons, antiprotons, neutrinos, antineutrinos, positrons, quarks etc.

#### **Fundamental Particles:**

The sub-atomic particles 'electrons, protons and neutrons' are called fundamental particles of all matters.

**Electron:** Electron is a fundamental sub-atomic particle having negligible mass of 9.11 x 10  $^{-31}$  kg and carrying a charge of  $-1.602 \times 10^{-19}$  Coulomb.

**Proton:** Proton is a fundamental sub-atomic particle having mass of  $1.672 \times 10^{-27}$  kg and carrying a charge of +  $1.602 \times 10^{-19}$  Coulomb.

**Neutron:** Neutron is a fundamental sub-atomic particle having mass of 1.675x10<sup>-27</sup> Kg and carrying no charge.

Fundamental Particle	Mass	Charge	Relative Charge
Electron	9.11 x 10 <sup>-31</sup> Kg	- 1.602 x 10 <sup>-19</sup> Coulomb	- 1
Proton	1.672 X 10 <sup>-27</sup> Kg	+ 1.602 x 10 <sup>-19</sup> Coulomb	+1
Neutron	1.675 X 10 <sup>-27</sup> Kg	0	0

# <u>Rutherford's Gold-foil Experiment/Rutherford's α-scattering Experiment: (Discovery of Nucleus)</u>

In 1911, E. Rutherford gave the first information about the almost-correct-picture of an atom. He

bombarded a number of  $\alpha$ particles (*He*<sup>2+</sup> *ions*) emitting from a radioactive material like Uranium on a very thin gold foil. A circular zinc sulphide (**ZnS**) screen was provided at the back side of the gold foil in order to register the impressions made by the  $\alpha$ -particles (Fig. 1.1).



#### **Observations and Conclusions:**

From the *a*- scattering experiment, Rutherford observed that:

- 1. Most of the  $\alpha$ -particles went undeflected, i.e. they passed straight through the gold foil without any deviation. This clearly indicates that most of the parts of an atom are empty.
- **2.** A few α-particles were found to be deflected strongly from their normal paths. This indicates the presence of a heavy positively charged body inside the atom. This heavy positively charged body is called nucleus.
- **3.** A very few (0.01%)  $\alpha$ -particles were found to be retracted their original paths (deflected through almost 180<sup>°</sup>). This indicates that the size of nucleus is very small. The size of atomic nuclei is of the order of 10<sup>-13</sup> cm.

#### **RUTHER FORD'S ATOMIC MODEL:**

Based on the conclusions drawn from the  $\alpha$ -scattering experiment, Rutherford proposed an atomic model, as follows:

- 1. An atom consists of two parts; they are (i) Nucleus and (ii) extra nuclear part.
- 2. Every atom consists of a very small but heavy positively charged body, called nucleus.
- 3. The whole mass of an atom is concentrated at the nucleus.
- 3. Electrons revolve around the nucleus with tremendous speed, like planets revolve around the sun. Therefore, the electrons are also called as planetary electrons.
- 4. The electrostatic force of attraction (acting inward) between the nucleus and electrons is balanced by the centrifugal force (acting outward) arising due to the motion of electrons. That is why electrons do not fall into the nucleus.

#### DRAWBACKS OR FAILURES OF RUTHERFORD'S ATOMIC MODEL:

#### **1.** Stability of Atom:

The theory fails to explain the stability of atoms. According to the law of electrodynamics (by Clark Maxwell), whenever a charged particle revolves around another charged particle, the revolving charged particle emits (loses) energy continuously (Fig. 1.2).

As the energy of the revolving electron decreases, it should be attracted towards the nucleus, and should follow a spiral path and ultimately fall into the nucleus. However, this never happens.

**2.** The model is silent about the definite energy and velocity possessed by the revolving electrons.

3. The theory fails to explain *atomic spectra*.

**4**. It fails to explain the cause of chemical combinations.



#### BOHR'S ATOMIC MODEL (THEORY)

An almost correct picture of atomic model was provided by a **Dutch physicist** *Niels Bohr* in 1913. The Bohr's Atomic model is based on 'Planck's Quantum Theory' and 'quantization of energy'.

#### Postulates of Bohr's atomic model:

- 1. Every atom consists of a heavy positively charged body at the centre called 'nucleus' and electrons revolve around the nucleus in certain permitted definite circular paths called 'shells', 'orbits' or 'stationary states'.
- 2. The stationary states or shells are designated as K, L, M, N, O.....etc. for 1st, 2nd, 3rd, 4th.....shells respectively.
- **3.** Each shell is associated with a certain definite quantity of energy. Hence the shells are also called as **'Energy levels'**.
- 4. The energy contents of various shells are compared by the formula:

$$\mathsf{E}_{\mathsf{n}} = - \frac{2\pi^2 m e^4 z^2}{n^2 h^2}$$

where, m = mass of an electron

e = charge of electronz = Atomic number

n = No. of shell or principal quantum number (1,2,3.....)

 $h = Planck's constant = 6.625 \times 10^{-27} erg sec.$ 

$$E_n = -\frac{1312}{n^2} KJ / Mol,$$
 for Hydrogen atom

- **5.** The energy content increases on moving from lower to higher shells and become zero for the shell which is present at an infinite distance from the nucleus.
- 6. The energy levels are not equally spaced (Fig. 1.3).7. Through a large number of concentric circles are possible around the nucleus, only those circular paths are allowed for the electrons to revolve for which the angular momentum value (mvr) is a whole number

multiple of 
$$\frac{h}{2\pi}$$
, that is  
mvr = n  $\frac{h}{2\pi}$ , where n = 1, 2, 3,....

-145.78 KJ/mol -328 KJ/mol -1312 KJ/mol (Figure: 1.3 Decreasing energy gap)

Here, m = mass of the electron,

- v = tangential velocity of the revolving electron,
- r = radius of the orbit.
- h = Planck's constant,

**8.** When the electrons in an atom are in their normal energy state (ground state), they keep on revolving in their respective orbits without losing energy.

**9.** When external source of energy is supplied to an atom, the electrons jump from lower ground states to the higher excited states by absorbing energy. Electrons in the excited states are unstable and jump back to the lower ground states by releasing energy. The energy thus released appears in the form of light which is the origin of spectral lines (Fig. 1.4).



#### Failures of Bohr's Atomic Model:

- 1. According to Bohr's atomic model, the path followed by electrons is two-dimensional circular. But modern researches (Heisenberg's Uncertainty Principle) revealed that electrons revolve in three-dimensional paths called orbitals.
- 2. It fails to explain the spectra of multi-electron species.
- 3. It fails to explain the relative intensities of spectral lines.
- 4. It fails to explain the splitting up of spectral lines when exposed to electric field (Stark Effect) and magnetic field (Zeeman Effect).
- 5. It fails to explain the cause of chemical combinations.

#### **BOHR-BURY SCHEME:**

Bohr-Burry scheme deals with the arrangement of electrons in various shells. Various postulates of the scheme are:

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	Shell	n	Maximum No. of Electrons = $2n^2$			
	К	1	$2 \times 1^2 = 2$			
	L	2	$2 \times 2^2 = 8$			
	М	3	$2 \times 3^3 = 18$			
	N	4	2 X $4^4$ = 32, and so on.			

**1.** A shell can contain a maximum  $2n^2$  number of electrons. Where n = number of the shell.

- 2. The outer most shell (valence shell) of an element cannot hold more than '8' electrons.
- **3.** The penultimate shell (the shell just before the outer most shell) cannot hold more than '18' electrons.
- **4.** A higher orbit may start filling before the lower orbit is completely filled.

Arrangements of electrons in different orbits of some elements according to the Bohr-Bury scheme are given below:

Element	Electrons in					
	K- Shell	L-Shell	M-Shell	N-Shell		
₁H	1					
<sub>2</sub> He	2					

<sub>3</sub> Li	2	1		
<sub>4</sub> Be	2	2		
<sub>5</sub> B	2	3		
10Ne	2	8		
₁₁Na	2	8	1	
<sub>12</sub> Mg	2	8	2	
<sub>13</sub> AI	2	8	3	
<sub>18</sub> Ar	2	8	8	
<sub>19</sub> K	2	8	8	1
<sub>20</sub> Ca	2	8	8	2
<sub>21</sub> Sc	2	8	9	2

Atomic Number(Z): The total number of protons present in one atom of an element is called its atomic number.

Atomic Number = No. of Protons (p)

For Examples:

Element	No of Protons (p)	Atomic No. (Z)
Carbon (C)	6	6
Nitrogen (N)	7	7
Oxygen (O)	8	8

**Mass Number (A)**: The total number of protons and neutrons present in one atom of an element is called its mass number.

Mass Number (A) = No. of Protons (p) + No. of Neutrons (n)

Element	No of Protons (p)	No. of Neutrons (n)	Mass No. (A)
Carbon (C)	6	6	12
Nitrogen (N)	7	7	14
Sodium (Na)	11	12	23



#### Assignment:

Q. Find the no. of protons, electrons and neutrons in the following.

Atom/Molecule/Ion	Р	е	n
0			
Р			
N <sup>3 –</sup>			
Ca <sup>2+</sup>			
NH <sub>3</sub>			
H <sub>2</sub> O			
$NH_4^+$			
CO			
CO <sub>2</sub>			

**Isotopes:** Isotopes are the atoms of the same element having the same atomic number but different mass numbers.

Examples: Hydrogen has three isotopes: Protium  $\binom{1}{1}H$ , Deuterium  $\binom{2}{1}H$  and Tritium  $\binom{3}{1}H$ Similarly,  $\frac{35}{17}Cl$  and  $\frac{37}{17}Cl$ <u>Properties of Isotopes:</u>

- > These are atoms of the same element.
- > These have the same atomic no. but different mass number.
- > These have the same no. of protons and electrons.
- > These differ in their no. of neutrons.
- > These have similar chemical properties.
- > These have different physical properties such as m.pt., b.pt, density, viscosity, etc.

**Isobars:** Isobars are the atoms of different elements having the same mass number but different atomic numbers.

Examples:  ${}^{40}_{18}Ar$  and  ${}^{40}_{20}Ca$ 

#### Properties of Isobars:

- > These are atoms of different elements.
- > These have the different atomic no. but same mass number.
- > These have the different no. of protons and electrons.
- > These have different chemical properties.
- > These have different physical properties such as m.pt., b.pt, density, viscosity, etc.

**Isotones**: Isotones are the atoms of the elements having the same no of neutron.

Examples:  ${}^{23}_{11}Na \text{ and } {}^{24}_{12}Mg = {}^{27}_{13}Al \text{ and } {}^{28}_{14}Si = {}^{31}_{15}P \text{ and } {}^{32}_{16}S$ 

Note: The subatomic particles (protons and neutrons) present inside the nucleus are collectively called as nucleons.

#### Aufbau Principle:

The word "*Aufbau*" means "**building up**". This principle describes how the subs-hells are filled with electrons.

Aufbau principle may be stated as "electrons are filled in different sub-shells in order of their increasing energy content".

The sub-shell with lowest energy is filled with electron first and those with higher energies are filled with electrons later. The energy content of the various sub-shells can be compared by

(n+ /) rule.

#### The (n + / ) Rule:

i. The sub-shell having lower (n+ *l*) value possesses lower energy and is filled first.

ii. If the (n + *l*) value for two given sub-shells are equal, then the one with lower value of 'n' possesses lower energy and is filled first.

Following the (n+*I*) rule, let us compare the energy possessed by various sub-shells.

Sub- shell→	1s	2s	2р	3s	3р	3d	4s	4р	4d	4f	5s	5р
(n+/)	1+0	2+0	2+1	3+0	3+1	3+2	4+0	4+1	4+2	4+3	5+0	5+1
l	=1	=2	=3	=3	=4	=5	=4	=5	=6	=7	=5	=6

Hence the increasing order of energy content of sub-shells is

1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < ...



#### **ELECTRONIC CONFIGURATIONS: -**

Electronic configuration is the arrangement of electrons of an atom in different sub-shells/orbitals in the increasing order of their energy content. The electronic configurations of some elements are given below:

Elements	Electronic configurations	Elements	Electronic configurations
₁H	1s <sup>1</sup>	<sub>16</sub> S	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>4</sup>
₂He	1s <sup>2</sup>	17 <b>CI</b>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>5</sup>
<sub>3</sub> Li	1s <sup>2</sup> 2s <sup>1</sup>	<sub>18</sub> Ar	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup>
<sub>4</sub> Be	1s <sup>2</sup> 2s <sup>2</sup>	19 <b>K</b>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>1</sup>

₅B	$1s^2 2s^2 2p^1$	<sub>20</sub> Ca	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²
$O_{6}$	$1s^2 2s^2 2p^2$	<sub>21</sub> Sc	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>
<sub>7</sub> N	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>3</sup>	<sub>22</sub> Ti	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>2</sup>
O <sub>8</sub>	$1s^2 2s^2 2p^4$	<sub>23</sub> V	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>3</sup>
<sub>9</sub> F	$1s^2 2s^2 2p^5$	<sub>24</sub> Cr	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s¹3d <sup>5</sup>
10 <b>Ne</b>	$1s^2 2s^2 2p^6$	<sub>25</sub> Mn	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>5</sup>
11 <b>Na</b>	$1s^2 2s^2 2p^6 3s^1$	<sub>26</sub> Fe	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>6</sup>
<sub>12</sub> Mg	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup>	<sub>27</sub> Co	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>7</sup>
<sub>13</sub> AI	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>1</sup>	<sub>28</sub> Ni	1s² 2s²2p <sup>6</sup> 3s²3p <sup>6</sup> 4s²3d <sup>8</sup>
<sub>14</sub> Si	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>2</sup>	29 <b>Cu</b>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>6</sup> 4s <sup>1</sup> 3d <sup>10</sup>
15 <b>P</b>	1s <sup>2</sup> 2s <sup>2</sup> 2p <sup>6</sup> 3s <sup>2</sup> 3p <sup>3</sup>	<sub>30</sub> Zn	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>10</sup>

**Exceptional Electronic Configuration**: Some elements like 'Cr' and 'Cu' show exceptional electronic configurations.

The electronic configurations of 'Cr' & 'Cu' should be:

 $_{24}$ Cr = [Ar] $4s^23d^4$  &  $_{29}$ Cu = [Ar] $4s^23d^9$  respectively.

But the actual electronic configurations are

 $_{24}$ Cr = [Ar]4s<sup>1</sup>3d<sup>5</sup> &  $_{29}$ Cu = [Ar]4s<sup>1</sup>3d<sup>10</sup>

The exceptional electronic configuration is due to the fact that half-filled and ful-filled orbitals are more stable due to the orbital symmetry and exchange energy.

#### Assignment:

Q 1. Write down the electronic configurations of the following: O<sup>2-</sup>, Ca<sup>2+</sup>, P<sup>3-</sup>, Ti<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>.

Q 2. Arrange the following sub-shells in the increasing order of their energy content: 3d, 5p, 4s, 4p, 6s, 4d.

Q 3. What is (n+l) rule? Which out of 4s and 3d sub-shells has lower energy?

Q 4. What do you mean by 3d<sup>2</sup>?

#### Hund's Rule: -

Hund's rule may be stated as "**Pairing of electrons do not take place in the degenerate orbitals of** *p*, *d*, and *f*-sub shells until each degenerate orbital in the given sub-shell contains one electron."

The above is due to the reason that electrons being identical in charge repel each other when present in the same orbital. This repulsion can, however, be minimized if two electrons move as far apart as possible by occupying different degenerate orbitals.

Let us consider the electronic configurations of the following elements.

In case of boron the 5<sup>th</sup> electron is occupied by the  $2p_x$  orbital. In carbon the 6<sup>th</sup> electron will not be

paired with the electron of the  $2p_x$  orbital, rather it will be occupied by the  $2p_y$  orbital. Similarly, in case of SCTE&VT Learning Materials Engineering Chemistry Page **8** of 105



nitrogen all the 2p – electrons will remain unpaired. The rule is also called 'maximum multiplicity rule' because the total spin value of all the electrons of degenerate orbitals of a given sub-shell becomes maximum if they are arranged as per Hund's rule.

**<u>NOTE</u>** :- Degenerate orbitals are the orbitals having same or nearly same energy content. For example  $2p_x$ ,  $2p_y$ ,  $2p_z$  are degenerate orbitals.

#### Assignment

Q 1. How many vacant orbitals are there in C, O, P and Ti?

Q 2. How many unpaired electrons are there in N, F, Fe and Na<sup>+</sup>?

#### **Exercise**

#### (02 Marks Questions)

- 1. What are fundamental sub-atomic particle?
- 2. Write any two drawbacks of Rutherford's atomic model.
- 3. What are the results of Rutherford's gold foil experiment?
- 4. What do you mean by quantization of energy?
- 5. What do you mean by the stationary states of atoms?
- 6. How electronic transition occurs according to Bohr's atomic model?
- 7. What is the origin of spectral lines according to Bohr's atomic model?
- 8. Which circular orbits are allowed for the electrons to revolve?
- 9. Arrange the following in the increasing order of their energy content: 4f, 5p, 6s, 4p, 3d.
- 10. Write down the electronic configurations of Cr and Cu.
- 11. Write down the electronic configurations of Ca<sup>2+</sup> and O<sup>2-</sup>.
- 12. Write down the electronic configurations of  $Mg^{2+}$  and  $N^{3-}$ .
- 13. Write down the electronic configurations of  $Mn^{2+}$  and Cu.
- 14. Write down the electronic configurations of  $Cr^{3+}$  and  $Fe^{2+}$  ions.
- 15. Define mass number. How many protons, electrons and neutrons are present in an ion of N<sup>3-</sup>?
- 16. Define isotope with suitable example.
- 17. Define isotope. What are the isotopes of chlorine?
- 18. Define isobar with a suitable example.
- 19. Define isotone with a suitable example.

#### (05 Marks Questions)

- 1. Explain the Discovery of atomic nuclei.
- 2. Explain Rutherford's atomic model.
- 3. Explain the failures of Rutherford's atomic model.
- 4. Write down the postulates of Bohr-Bury Scheme.
- 5. Define and explain Aufbau principle. Write down the electronic configuration of manganese.
- 6. How did Bohr overcome Rutherford's atomic model?
- 7. Define and explain Hund's rule of maximum multiplicity.
- 8. Explain electronic transition according to Bohr's atomic theory.
- 9. Explain the origin of atomic spectral lines.

## CHAPTER - 2 CHEMICAL BONDING

**Definition of Chemical bonding**: The force of attraction which holds together the constituent atoms in a molecule or ion is called chemical bond.

#### Types of Chemical Bonding:

Depending upon the mode of bond formation (transfer or sharing of electrons), chemical bonding may be classified into the following types:

- 1. Ionic Bonding or Electrovalent bonding
- 2. Covalent bonding
- 3. Co-ordinate bonding or Dative Bonding
- 4. Hydrogen bonding
- 5. Metallic bonding

#### **IONIC OR ELECTROVALENT BONDING:**

"The chemical bond which is formed by the complete transfer of one or more valance electrons from one atom to another is called ionic or electrovalent bond and the compound formed is called ionic compound or electrovalent compound".

The number of electrons lost or gained by an atom during ionic bond formation is called its electrovalency.

Features of lonic bond: The formation of ionic bond involves:

- Formation of a positive ion by loss of electron/s from one kind of atom.
- Formation of a negative ion by gain of electron/s from another kind of atom.
- Electrostatic force of attraction between the oppositely charged ions.

#### Conditions for the formation of lonic bond:

- **1.** *Nature of element:* Atoms of different elements form ionic bonds. Atoms of the same element never form *ionic bond*.
- 2. Low lonization potential: Ionization potential of an element is the quantity of energy required to remove one valence electron from an isolated, neutral, gaseous atom. One of the combining atoms should have low IP. The elements of Gr 1 and Gr 2 of the modern periodic table have low ionization potentials; and hence they can form *ionic bonds*.
- 3. High Electron Affinity: It is the amount of energy released when an extra electron is added to an isolated, neutral, gaseous atom. Another participating atom should have high electron affinity. The elements of Gr 16 and Gr 17 of the modern periodic table have high electron affinities; and hence they can form *ionic bonds*.
- **4.** *High Lattice Energy:* The quantity of energy involved during the formation of or breaking of one mole of an ionic bond is called lattice energy. Higher is the lattice energy more is the stability of the ionic compound. Thus, the lattice energy of ionic compounds should be high.

#### Example: I: Formation of NaCI.

The electronic configurations of Na and Cl are given below:

11Na - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>1</sup> 17C/ - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>5</sup>

The electronic configurations indicate the presence of one and seven valence electrons in sodium and chlorine respectively. During the formation of NaC*I*, the sodium atom donates its valence electron completely to the chlorine atom (Fig. 2.1). Na becomes Na<sup>+</sup> with 8 electrons in valence shell and attains the nearest noble gas configuration of Ne; while C*I* atom becomes  $CI^-$  ion with '8' electrons in valence shell and attains the nearest noble gas configuration of Ar.





Now the electrostatic force of attraction between the oppositely charged ions Na<sup>+</sup> and Cl<sup>--</sup> results in the formation of **NaCl**.

#### Example :II : Formation of MgCl<sub>2</sub>

The electronic configurations of Mg and Cl are given below:

#### 17C/-1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>5</sup>

An atom magnesium and chlorine contain 2 and 7 valence electrons respectively. During the formation of  $MgCl_2$ , one of the valence electrons of Mg is completely transferred to one atom of chlorine

while the second valence electron is transferred to another atom (Fig. 2.2). Now Mg becomes  $Mg^{2+}$  with 8 valence electrons, with electronic configuration similar to that of Neon. On the other hand, each chlorine

atom after accepting an electron becomes C/ ion with 8 valence electrons, acquiring electronic configuration similar to that of Argon.



The electrostatic force of attraction between calcium and chloride ions results in the formation of MgC*I*<sub>2</sub>.

**Other examples of ionic compounds:** KCl, KBr, KI, CaF<sub>2</sub>, CaBr<sub>2</sub>, CaI<sub>2</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, CaO, MgO, Na<sub>2</sub>S, K<sub>2</sub>S etc.



Figure: 2.2

*Characteristics of ionic compounds:* Ionic compounds possess the following characteristic properties.

- **1.** These exist in solid states.
- 2. These are hard and rigid.
- **3.** These are crystalline in nature.
- 4. These have high melting and boiling point.
- 5. These have high densities.
- **6.** These are soluble in polar solvents like water, but are insoluble in non-polar solvents like  $CCl_4$ , ethers, benzene, toluene [ $C_6H_5 CH_3$ ], petrol, diesel, kerosene, etc.
- **7.** These are bad conductor of electricity in solid states, but are good conductor in molten, fused or solution state.
- 8. These do not show isomerism.
- 9. These are polar in nature.

#### COVALENT BOND:

# The chemical bond formed by the mutual (equal) sharing of valence electrons between two atoms is called covalent bond and the compound formed is called covalent compound.

The number of electrons shared by an atom during covalent bond formation is called **covalency**. A covalent may be formed between the atoms similar or dissimilar elements. When two, four and six electrons are shared between two atoms, then a single, double and a triple bond are formed respectively.

**Example : I** : Formation of  $H_2$  molecule.

The electronic configuration indicates the presence of 1



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valence electron in 'H' and requires one more electron to become duplet. Thus, each hydrogen atom shares its electron with each other to form a covalent bond (Fig. 2.3).

**Example : 2 :** Formation of Cl<sub>2</sub> molecule.

The electronic configuration of 'Cl' is

#### 17C/-1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>5</sup>

The electronic configuration indicates the presence of 7 valence electrons in 'Cl' and requires one more electron to become octet. Thus, each chlorine atom shares one of its valence electrons with each other to form a covalent bond (Fig. 2.4).





**Example :3 :** Formation of O<sub>2</sub> molecule.

The electronic configuration of 'O' is

## 80-1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>

The electronic configuration indicates the presence of 6 valence electrons in 'O' and requires two more electrons to become octet. Thus, each oxygen atom shares two of its valence electrons with each other to form a double covalent bond (Fig. 2.5).



 $\overbrace{\substack{\bullet \circ \\ \bullet \circ \\$ 

**Example : 4 :** Formation of N<sub>2</sub> molecule.

The electronic configuration of 'N' is

#### 7N-1s<sup>2</sup>2s<sup>2</sup>2p<sup>3</sup>

The electronic configuration indicates the presence of 5 valence electrons in 'N' and requires three more electrons to become octet. Thus, each nitrogen atom shares three of its valence electrons with each other to form a triple covalent bond (Fig. 2.6).



**Example : 5** : Formation of H<sub>2</sub>O molecule.

The electronic configuration of 'O' and 'H' are:

80-1s<sup>2</sup>2s<sup>2</sup>2p<sup>4</sup>

1<sup>H</sup> - 1s<sup>1</sup>

The electronic configurations indicate the presence of 6 and 1 valence electrons in 'O' and 'H' respectively. The central 'O' atom requires two more electrons to become octet while each hydrogen atom needs one electron to become duplet. Thus, each hydrogen atom shares its valence electron with the valence electrons of oxygen to form covalent bonds (Fig. 2.7). The shape of water molecule is bent shape or 'V' shape with bond angle 104.5<sup>o</sup>.



*Example: 6:* Formation of methane (CH<sub>4</sub>) molecule.

The electronic configuration of 'C' and 'H' are

The electronic configurations indicate the presence of 4 & 1 valence electrons in 'C' & 'H' respectively. Thus, the central carbon atom requires four more electrons to become octet and 'H' requires 1 more electron to become duplet.

Thus, each hydrogen atom shares its electron with one valence electron of carbon to form four single covalent bonds. By sharing an electron each hydrogen atom becomes duplet while carbon becomes octet. The shape of  $CH_4$  is tetrahedral with a bond angle of  $109^028$  (Fig. 2.8)<sup>'</sup>.



**Example:** 7: Formation of ammonia (NH<sub>3</sub>) molecule.

The electronic configuration of 'C' and 'H' are

<sub>7</sub>N - 1s<sup>2</sup>2s<sup>2</sup>2p<sup>3</sup> <sub>1</sub>H - 1s<sup>1</sup>

The electronic configurations indicate the presence of 5 & 1 valence electrons in 'N' & 'H' respectively. Thus, the central nitrogen atom requires three more electrons to become octet and each 'H' atom requires 1 more electron to become duplet.





Thus, each hydrogen atom shares its valence electron with one valence electron of nitrogen to form three single covalent bonds (Fig. 2.9). The shape of  $NH_3$  is pyramidal with a bond angle of  $107^0$ .

#### **Other examples of covalent compounds:** , F<sub>2</sub>, Br<sub>2</sub>, I<sub>2</sub>, BF<sub>3</sub>, AlCl<sub>3</sub>, HCl, HF, SiO<sub>2</sub>, etc.

#### Characteristics of Covalent Compounds:

- 1. These may exist in all the three states of matter i.e. solid, liquid and gaseous states.
- 2. These are generally soft.
- 3. These are non-crystalline in nature.
- **4.** These are generally insoluble in polar solvent like water, but are soluble in non-polar solvents such as CCl<sub>4</sub>, ethers, benzene, toluene, petrol, diesel, kerosene, etc.
- 5. These have low melting and boiling points.
- 6. These have low densities.
- 7. These are bad conductor of heat and electricity.
- 8. These compounds may show isomerism.
- 9. These are generally non-polar.

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#### CO-ORDINATE BOND:

The chemical bond formed by the partial donation and partial sharing of a lone pair of electrons between two atoms (or ions) is called a co-ordinate or dative bond.

#### Conditions for the formation of co-ordinate or Dative bond:

- i. One of the participating atoms should have at least one lone or unshared pair of electrons.
- ii. The other atom should be in short of a pair of electrons than the nearest inert gas element.

The lone pair of electrons present over one atom is partially shared by both the combining atoms. A co-ordinate bond is represented by an arrow ( $\rightarrow$ ) sign, the head of which points towards the acceptor atom, while the tail points towards the donor atom.

Since co-ordinate bond has some polar character, it is also known as dative or semi-polar bond or coionic bond.



#### Example: 1: Formation of ammonium ion (NH<sub>4</sub><sup>+</sup>).

Ammonium ion  $(NH_4^+)$  is formed by the combination of  $NH_3$  and  $H^+$  ion.

 $NH_3 + H^+ \rightarrow NH_4^+$ 

Ammonia (NH<sub>3</sub>) contains a lone pair of electrons over 'N' while 'H<sup>+</sup>' ion contains no electron and requires two electrons to become duplet.

Thus, the unshared pair of electrons over nitrogen in  $NH_3$  is partially

shared with H<sup>+</sup> ion and a Co-ordinate bond is formed (Fig. 2.11).



#### Example: 2: Formation of Sulphur dioxide (SO<sub>2</sub>) molecule.

The electronic configurations of 'S' and 'O' are

The electronic configurations indicate the presence of 6 valence electrons in each of 'S' & 'O'. the central sulphur atom forms a double covalent by sharing two of its valence electrons with two valence electrons of one of the oxygen atoms. One of the lone pair of electrons of the central sulphur atom is partially shared with another oxygen atom to form a co-ordinate bond (Fig. 1.12).



#### **Characteristics of Coordinate Compound:**

- i. These bonds are rigid and directional.
- ii. Coordinate bonds do not ionise in a state of fusion of solution.
- iii. They are usually insoluble in water but dissolve in non-polar solvents.
- iv. Their melting and boiling points are higher than those of covalent compounds and lower than those of ionic compounds.
- v. These are semi-polar, that is more polar than covalent compounds and less polar than ionic compounds.
- vi. They show isomerism.

#### Lewis Structure:

A **Lewis Structure** is a simple representation of the valence shell electrons in a molecule. It is used to show how the electrons are arranged around individual atoms in a molecule. Electrons are shown as "dots" or for bonding electrons as a line between the two atoms. For examples:



#### <u>Assignment</u>

Q. Draw the Lewis structures of the following: MgCl<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, SO<sub>2</sub>, NH<sub>4</sub><sup>+</sup> and H<sub>3</sub>O<sup>+</sup>.

#### **Exercise**

#### (02 Marks Questions)

- 1. Define chemical bonding.
- 2. Define electrovalent bonding.
- 3. Define covalent bonding.
- 4. Define co-ordinate bonding.
- 5. What is Lattice energy? How is it related with the strength of an ionic bond?
- 6. Mention the conditions for formation of electrovalent bonding.
- 7. Mention the conditions for formation of co-ordinate bonding.
- 8. Define ionization potential. What should be the value of it for the metals to form ionic bond?
- 9. Define electron affinity. What should be the value of it for the metals to form ionic bond?
- 10. Which types of chemical bondings exist in  $MgCl_2$  and  $NH_3$ ?
- 11. Which types of chemical bondings exist in  $MgCl_2$  and  $H_2O$ ?

#### (05 Marks Questions)

- 1. Define and explain electrovalent bonding with a suitable example.
- 2. Define and explain covalent bonding with a suitable example.
- 3. Define and explain co-ordinate bonding with a suitable example.
- 4. Explain the formation of  $NH_3$  and  $NH_4^+$ .
- 5. Explain the conditions of formation of electrovalent bond.
- 6. Explain the conditions of formation of co-ordinate bond.
- 7. Define covalent bond. Explain the formation of  $CH_4$  molecule.
- 8. Define covalent bond. Explain the formation of  $H_2O$  molecule.
- 9. Define covalent bond. Explain the formation of  $O_2$  molecule.
- 10. Define covalent bond. Explain the formation of  $N_2$  molecule.
- 11. Define covalent bond. Explain the formation of  $NH_3$  molecule.
- 12. Define electrovalent bonding. Explain the formation of MgCl<sub>2</sub> molecule.
- 13. Define and explain co-ordinate bonding and explain the formation of  $NH_4^+$  ion.
- 14. Define and explain co-ordinate bonding and explain the formation of SO<sub>2</sub> molecule.
- 15. Write down at least ten properties of ionic compounds.
- 16. Write down at least ten properties of covalent compounds.

# <u>CHAPTER - 3</u> ACID – BASE THEORIES

#### Introduction:

There are many practical methods to identify a substance as an acid or a base. The practical methods include use of p<sup>H</sup> meter, indicator, litmus paper, chemical reactions, etc. However, theoretically it is now possible to know whether a substance is acid or a base. Accordingly, three theories have been proposed by different chemists. They are:

- 1. Arrhenius Theory
- 2. Lowery Bronsted Theory
- 3. Lewis Theory.

#### ARRHENIUS THEORY:

According to Arrhenius theory, "Acids are the substances which produce  $H^+$  ions (protons) in aqueous solution while bases are the substances which produce  $OH^-$  ions in aqueous solution."

*Example of Acid:* HCI  $\xrightarrow{water}$  H<sup>+</sup><sub>(aq)</sub> + Cl<sup>-</sup><sub>(aq)</sub> Other examples of acids are: HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, CH<sub>3</sub>COOH, etc.

Examples of Bases: NaOH<sub>(S)</sub>  $\xrightarrow{water}$  Na<sup>+</sup><sub>(aq)</sub> + OH<sup>-</sup><sub>(aq)</sub> Other examples of bases are: LiOH, KOH, NH<sub>4</sub>OH, Ca(OH)<sub>2</sub>, Al(OH)<sub>3</sub>, etc

#### Salient Features:

i. According to Arrhenius theory an acid reacts with a base to form salt and water and the reaction is called **<u>neutralization reaction</u>**.

HC/	+	NaOH	$\rightarrow$	NaC/	+	H <sub>2</sub> O
(Acio	1)	(Base)		(Salt)		(Water)

Neutralization reaction may be represented as:

H <sup>+</sup> (aq)	+	$OH^{(aq)} \rightarrow$	H <sub>2</sub> O <sub>(1)</sub>
(from acid)		(from base)	

**ii.** Higher is the degree of dissociation higher is the acidic or basic nature of the substance.

#### Limitations:

i.  $H^+$  ion does not exist in aqueous solution. It combines with  $H_2O$ , as soon as its formation to give hydronium ion ( $H_3O^+$ ).

 $H^+ + H_2O \rightarrow H_3O^+$ 

- ii. The theory fails to explain the acidic and basic nature of the substances in solvents other than water.
- iii. The theory fails to explain the acidic nature of the substances like SO<sub>2</sub>, CO<sub>2</sub>, SiO<sub>2</sub>, P<sub>2</sub>O<sub>5</sub>, BF<sub>3</sub>, AlCl<sub>3</sub>, etc. which cannot provide H<sup>+</sup> ions.

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- **iv.** The theory fails to explain the basic nature of the substances like NH<sub>3</sub>, PH<sub>3</sub>, Na<sub>2</sub>O, K<sub>2</sub>O, CaO etc. which can't provide OH<sup>-</sup>ions.
- **v.** The theory fails to explain neutralization reactions between some acidic and basic substances which do not produce water.  $HCI + NH_3 \rightarrow NH_4CI$

#### 2. BRONSTED - LOWRY THEORY:

According to Bronsted-Lowry theory "Acids are the substances (molecules/ions) which donate a proton ( $H^+$  ion) to any other substance, while bases are the substances (molecules/ions) which accept a proton ( $H^+$  ion) from any other substance".

In other words, acids are proton donors whereas a bases are proton acceptors. For example:



Since, HC/ has donated a proton (to  $NH_3$ ), it acts as an acid. On the other hand,  $NH_3$  has accepted a proton from HC/ and thus it acts as a base.

Other examples of Acids are:

- i. All Arrhenius acids are Bronsted-Lowry acids; (HCI, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, CH<sub>3</sub>COOH, H<sub>2</sub>CO<sub>3</sub> etc.), however the reverse is not true.
- ii. Ions having capacity to donate  $H^+$  ion: (HS<sup>-</sup>, HCO<sub>3</sub><sup>-</sup>, HPO<sub>4</sub><sup>2<sup>-</sup></sup>, HSO<sub>4</sub><sup>-</sup> etc.)

Examples of Bases:

i. Natural molecules such as: H<sub>2</sub>O, NH<sub>3</sub>, RNH<sub>2</sub>, PH<sub>3</sub>, AsH<sub>3</sub>, etc.

**ii.** Ions having capacity to accept  $H^+$  ion, like  $OH^-$ ,  $CN^-$ ,  $HCO_3^-$ , etc.

#### Salient Features:-

i. According to this theory an acid reacts with a base to form **another pair of acid and base**. For example:



The pair of acid and base which differ by a proton (H<sup>+</sup>ion) is called a conjugate acid-base pair.

Acid  $-H^+ \rightarrow$  Conjugate base

Base + H<sup>+</sup>  $\rightarrow$  Conjugate acid

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ii. The substances such as  $H_2O$ ,  $HS^-$ ,  $HCO^3^-$ ,  $HPO_4^2^-$ ,  $HSO_4^-$ , etc. which act as both acid (proton donor) as well as base (proton acceptor) are called amphoteric substances.

**iii.** Stronger is an acid weaker is its conjugate base and vice versa.

HCl + H<sub>2</sub>O  $\rightarrow$  H<sub>3</sub>O<sup>+</sup> + Cl<sup>-</sup>

[Strong acid]

[Weak base]

Limitations of the theory:

- i. It fails to explain the acidic nature of the substances, such as  $SiO_2$ ,  $CO_2$ ,  $SO_2$ ,  $BF_3$ , etc. which cannot donate H<sup>+</sup> ion.
- ii. It fails to explain the basic nature of the substances, such as Na<sub>2</sub>O, K<sub>2</sub>O, CaO etc. which cannot accept H<sup>+</sup> ion.
- iii. It fails to explain the reaction between some acids and bases which do not give another pair of acid and base. Example: HCl + NaOH  $\rightarrow$  NaCl + H<sub>2</sub>O.

Note: Some conjugate acid-base pairs are given below:

Acid	Conjugate- Base	Base	Conjugate- Acid
HCI	CI -	Br –	HBr
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> -	CN <sup>-</sup>	HCN
HS <sup>-</sup>	S <sup>2-</sup>	0 <sup>2</sup> -	ОН -
$NH_4^+$	$NH_3$	NH <sub>3</sub>	$NH_4^+$
H <sub>2</sub> O	OH-	H <sub>2</sub> O	H <sub>3</sub> O+

#### Assignment:

Q 1. What are the conjugate bases of the following acids?

HCN,  $H_2CO_3$ ,  $H_3PO_3$ ,  $CH_3COOH$ ,  $H_2O$ 

Q 2. What are the conjugate acids of the following bases?

 $CH_3NH_2$ ,  $(C_2H_5)_2NH$ ,  $NO_3^-$ ,  $NH_3$ 

#### 3. LEWIS THEORY: -

According to Lewis theory "Acids are the substances (molecules/ions) which can accept a pair of *electrons* from any other substance, while bases are the substances (molecules/ions) which can donate a pair of electrons to any other substance."

In other words, acids are electron acceptors while bases are electron donors.

#### Examples of acids: -

- i. Cations like:  $CH_3^+$ ,  $H^+$ , etc.
- Neutral molecules containing electron deficient atoms are Lewis acids. For example: BF<sub>3</sub>, AlCl<sub>3</sub>, FeCl<sub>3</sub>, ZnCl<sub>2</sub>, etc.
- **iii.** Neutral molecules containing vacant d-orbitals in the central atom for the accommodation of incoming electrons act as Lewis acids. For example: SiF<sub>4</sub>, SiCl<sub>4</sub>, etc.
- iv. The molecules having multiple bonding (= or  $\equiv$ ) between the atoms of different elements are acidic in nature. For example: CO<sub>2</sub> ( O = C = O ), SO<sub>2</sub>, etc.

#### Examples of Bases: -

- i. All anions are Lewis bases:  $F^{-}$ ,  $CI^{-}$ ,  $CO_{3}^{2-}$ , etc.
- ii. Neutral molecules containing, at least one lone pair of electrons are Lewis bases: Examples: NH<sub>3</sub>, PH<sub>3</sub>, H<sub>2</sub>O, etc.

#### Salient Features:

i. According to this theory, an acid reacts with a base to form a co-ordinate or dative bond. For example, the reaction between NH<sub>3</sub> (Lewis base) and H<sup>+</sup> (Lewis acid) results in the formation of a dative bond.



All Bronsted- Lowery bases are Lewis bases while the reverse is not always true.

#### Limitations:

- i. According to this theory, the reaction between an acid and base results in the formation of a dative bond. Formation of a coordinate bond is a slow process. While the reactions between the acids and the bases are instantaneous or fast.
- **ii.** The theory fails to explain the relative strengths of different acids and bases.
- iii. It fails to explain reaction between some acids and bases where no coordinate bond is formed.
- iv. It fails to explain the acidic nature of well-known acids like HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, etc. which cannot accept electrons.
- v. It fails to explain the basic nature of well-known bases like NaOH, KOH, etc. which cannot donate electrons.
- vi. It fails to explain acid-catalyzed reactions, where H<sup>+</sup> ion plays important role.

#### **Neutralization of Acids and Bases:**

According to Arrhenius Theory, acid react with bases to form salt and water. This type of reaction is called *neutralization reaction*. Neutralization reaction may take place as follows:

1. **Neutralization between a Strong Acid and a Strong Base:** A strong acid reacts with a strong base to form a simple or normal salt. Its aqueous solution has a p<sup>H</sup> of about 7 and is neutral.

Example: HCl + NaOH  $\rightarrow$  NaCl + H<sub>2</sub>O

2. Neutralization between a Strong Acid and a weak Base: A strong acid reacts with a weak base to form a acidic salt. Its aqueous solution has a  $p^{H} < 7$  and the solution is acidic.

Example: HCl + NH<sub>4</sub>OH  $\rightarrow$  NH<sub>4</sub>Cl + H<sub>2</sub>·O

 Neutralization between a Weak Acid and a Strong Base: A weak acid reacts with a strong base to form a basic salt. Its aqueous solution has a p<sup>H</sup> > 7 and is alkaline.

Example:  $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ 

4. Neutralization between a Weak Acid and a Weak Base: A weak acid reacts with a weak base to form a neutral salt. Its aqueous solution has a p<sup>H</sup> > 7 and is alkaline.

Example:  $CH_3COOH + NH_4OH \rightarrow CH_3COONH_4 + H_2O$ 

#### SALTS:

Def<sup>n</sup> (1) : Salts are regarded as ionic compounds made up of positive and negative ions. The positive part comes from a base while negative part from an acid.

Def<sup>n</sup> (2) : Salts are ionic compounds which produce cation other than  $H^+$  and anion other than  $OH^-$  in aqueous solution.

Def<sup>n</sup> (3) : Salts are the compounds formed by the neutralization reaction between acids and bases.

#### TYPE OF SALTS:

Salts may be classified into the following types:

**1. Normal salts:** The salt obtained by the complete replacement of all the replaceable hydrogen atoms of an acid by metal atoms is called a normal salt. These salts are obtained by the reaction between strong acids and strong bases. These salts are not hydrolyzed in aqueous solution.

Example:	<u>Acids</u>	Normal salts
	HCI	NaCl, KCl, CaCl <sub>2</sub> , MgCl <sub>2</sub> , etc
	HNO <sub>3</sub>	NaNO <sub>3</sub> , KNO <sub>3</sub> , Ca(NO <sub>3</sub> ) <sub>2</sub> , Mg(NO <sub>3</sub> ) <sub>2</sub> , etc.
	$H_2SO_4$	Na <sub>2</sub> SO <sub>4</sub> , K <sub>2</sub> SO <sub>4</sub> , CaSO <sub>4</sub> , MgSO <sub>4</sub> , etc.
	$H_3PO_4$	Na <sub>3</sub> PO <sub>4</sub> , K <sub>3</sub> PO <sub>4</sub> , Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> , etc.

2. Acidic salts: The salt obtained by the partial replacement of replaceable hydrogen atoms of an acid by metal atoms is called an acidic salt. These types of salts still contain one or more replaceable hydrogen atoms.

Example:	<u>Acids</u>	<u>Acidic salts</u>
	$H_2SO_4$	NaHSO <sub>4</sub> , KHSO <sub>4</sub> etc.
	$H_3PO_4$	NaH <sub>2</sub> PO <sub>4</sub> , KH <sub>2</sub> PO <sub>4</sub> ,
		Na <sub>2</sub> HPO <sub>4</sub> , K <sub>2</sub> HPO <sub>4</sub> etc.

Also, these are the salts obtained by the neutralization between strong acids and weak bases. For examples:  $NH_4CI$ ,  $NH_4NO_3$ ,  $(NH_4)_2SO_4$ , etc.

**3.** Basic salt: These are the salts obtained by the incomplete neutralization of poly acidic bases. Such salts contain one or more 'OH' groups. Example: Ca (OH)C/, Mg(OH)C/, Zn(OH)C/, Al(OH)<sub>2</sub>Cl etc.

Also, these are the salts obtained by the neutralization reaction between weak acids and strong bases.

For examples: CH<sub>3</sub>COONa, CH<sub>3</sub>COOK, Na<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, etc.

**4. Double salts:** These are the molecular addition compounds obtained from two simple salts, the ions of which retain their identity in aqueous solution. Such salts give the test of all the constituent ions when dissolved in water.

Example:  $K_2SO_4$ . $Al_2(SO_4)_3$ . $24H_2O \xrightarrow{water} 2K^+ + 2Al^{3+} + 3SO_4^{2-}$ 

(Potash Alum)

Other examples: Mohr's Salt [FeSO<sub>4</sub>.(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.6H<sub>2</sub>O], carnalite (KCI. MgC*l*<sub>2</sub>.6H<sub>2</sub>O), etc.

**5.** Complex Salts: These are the molecular addition compounds obtained by the combination of simple salts, the ions of which lose their identity in aqueous solution. Such salts do not give tests of all the constituent ions in aqueous solution.

Example:  $K_4[Fe(CN)_6] \xrightarrow{water} 4K^+ + [Fe(CN)_6]^{4-}$ 

Other examples:  $K_3[Fe(CN)_6]$ ,  $[Cu(NH_3)_4]SO_4$ , etc.

6. Mixed Salts: These are the salts which give either more than one cation or more than one anion in aqueous solution.

Examples: Bleaching powder Ca (OCI)CI; Sodium potassium sulphate NaKSO<sub>4</sub>, etc.

#### **Exercise**

#### (02 Marks Questions)

- 1. Define Arrhenius theory of acids and bases.
- 2. Define Bronsted-Lowery theory of acids and bases.
- 3. Define Lewis theory of acids and bases.
- 4. Justify that all Arrhenius acids are Bronsted-Lowery acids.
- 5. Explain how  $BF_3$  is a Lewis acid.
- 6. Explain how  $SiCl_4$  is a Lewis acid.
- 7. Explain how  $BF_3$  is a Lewis acid.
- 8. Explain how  $AICI_3$  is a Lewis acid.
- 9. Explain how  $SO_2$  is a Lewis acid.
- 10. Explain how  $NH_3$  is both a Bronsted-Lowery base and a Lewis base.
- 11. Write down the conjugate acids and conjugate bases of  $H_2O \& NH_3$ .
- 12. What do you mean by conjugate acid-base pair? Explain with a suitable example.
- 13. CH<sub>3</sub>COOH is a weak acid while CH<sub>3</sub>COO<sup>-</sup> is a strong base. Explain.
- 14. What is neutralization reaction? Give an example of it.
- 15. Define salt. How does an acidic salt form?
- 16. Define salt. How does a basic salt form?
- 17. What is double salt? Give an example.
- 18. What is co-ordination salt? Give an example.
- 19. What is mixed salt? Give an example.
- 20. Explain how bleaching powder is a mixed salt.
- 21. Explain how potash alum is a double salt.

#### (05 Marks questions)

- 1. Define and explain Arrhenius theory of acids and bases.
- 2. Define and explain Bronsted-Lowery theory of acids and bases.
- 3. Define and explain Lewis theory of acids and bases.
- 4. Explain the limitations of Arrhenius theory.
- 5. Explain the limitations of Bronsted-Lowery theory.
- 6. Explain the limitations of Lewis theory.
- 7. Justify that all Arrhenius acids are Bronsted-Lowery acids, but all Arrhenius bases are not Bronsted Lowery bases.
- 8. Explain how SiCl<sub>4</sub> and  $BF_3$  are acids.
- 9. Explain why SiCl<sub>4</sub> is an acid but  $CCl_4$  is not.
- 10. Define and explain conjugate acid-base pair with a suitable example.
- 11. Justify your answer that  $H_2O$  is amphoteric.
- 12. How many grams of KOH are required to get 2 lit of its solution having P<sup>H</sup> 10?
- 13. Explain how potash alum is a double salt while,  $K_3[Fe(CN)_6]$  is a complex salt.
- 14. 14.7 grams of  $H_2SO_4$  are present in 2 liters of its solution. Find morality and normality of the solution.
- 15. How many grams of calcium hydroxide are required to prepare 10<sup>-2</sup> M and 10<sup>-2</sup> N solutions?
- 16. How many grams of decahydrated sodium carbonate of 80% purity are required to prepare 2.5 lit. of its decinormal solution?

# <u>CHAPTER – 4</u> <u>SOLUTIONS</u>

#### Introduction:

A solution is a special type of homogeneous mixture composed of two or more substances. In such a mixture, a solute is a substance dissolved in another substance, known as a solvent. The mixing process of a solution happens at a scale where the effects of chemical polarity are involved, resulting in interactions that are specific to solvation. The solution usually has the state of the solvent when the solvent is the larger fraction of the mixture, as is commonly the case. One important parameter of a solution is the concentration, which is a measure of the amount of solute in a given amount of solution or solvent. The term "aqueous solution" is used when one of the solvents is water. Solutions may be of three basic types: solid solutions, liquid solutions and gaseous solutions. A binary solution is composed of two components, one is solute and the other is solvent.

#### Atomic weight/mass:

The atomic mass of an element may be defined as "the average relative mass of one atom of the element as compared to the mass of an atom of carbon  $(^{12}C)$  taken as 12".

Unit: amu (atomic mass unit) or simply 'u'.

For example:	Element	Atomic mass in amu
	Н	1.008 ≈ 1
	Ν	14
	0	16

#### Atomic masses of some elements are given below:

<u>Element</u>	Symbol	Atomic Weight in a.m.u
Hydrogen	Н	1
Helium	He	4
Lithium	Li	7
Berylium	Be	9
Boron	В	11
Carbon	С	12
Nitrogen	Ν	14
Oxygen	0	16
Fluorine	F	19
Neon	Ne	20
Sodium	Na	23
Magnesium	Mg	24
Aluminium	AI	27
Silicon	Si	28
Phosphorous	Р	31
Sulphur	S	32
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Chlorine	Cl	35.5
Argon	Ar	40
Potassium	K	39
Calcium	Ca	40
Chromium	Cr	52
Iron	Fe	56
Copper	Cu	63.5
Bromine	Br	80
Silver	Ag	108
Lead	Pb	207

#### **GRAM ATOMIC MASS:**

The gram atomic mass of an element is simply its atomic mass expressed in gram. For example: Element Gm.atomic mass

Н	1.008 gm
0	16 gm
Mg	24 gm

<u>Note:</u> When the mass is expressed in amu, it refers to the mass one atom of the element. But, when expressed in gm, it refers to the mass of 1 mole of atoms ( $6.023 \times 10^{23}$  atoms) of the element.

#### **MOLECULAR WEIGHT:**

The molecular weight of a substance may be defined as "the relative average weight of one molecule of the substance as compared to the weight of an atom of carbon  $(^{12}C)$  taken as 12".

Molecular weight of a substance is calculated by adding the atomic weights of the constituent atoms present in one molecule.

Unit: amu (atomic mass unit)

For example: The molecular wt. of sulphuric acid ( $H_2SO_4$ ) can be obtained as

H<sub>2</sub>SO<sub>4</sub> = [2 × At.wt.of H] + At.wt. of sulphur +[4 × At.wt of oxygen]

= 2 × 1+32+4×16 = **98 amu** 

Other examples:

<u>Compound</u>	Molecular weight
NaCl	23+35.5 = 58.5 amu
HNO3	1+14+48 = 63 amu
CaCO3	40+12+48 = 100 amu
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	2x27+3x32+12x16 = 342 amu

#### **Assignment**

Q 1. Find the molecular weights of the following: Na<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, CuSO<sub>4</sub>.5H<sub>2</sub>O

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#### Gram molecular weight: -

The gram molecular weight of a substance is simply its molecular weight expressed in gram. *For example*:

<u>Compound</u>	<u>Gm. mol. weight</u>
NaCl	58.5 gm
HNO3	63 gm

#### **EQUIVALENT WEIGHT:**

The equivalent weight of a substance may be defined as "the number of parts by mass of it, which combines with or displaces directly or indirectly 1.008 parts by mass of hydrogen, 8 parts by mass of oxygen or 35.5 parts by mass of chlorine."

Unit: Equivalent weight has no unit.

<u>Gram equivalent weight</u>: The gram equivalent weight of a substance is its equivalent weight expressed in gram.

*Example :1* The equivalent wt. of 'Ca' in CaCl<sub>2</sub> can be calculated as follows:

Ca C*l*<sub>2</sub> 40 parts 2×35.5 parts

2×35.5 parts by mass of chlorine combines with 'Ca' = 40 parts

or 35.5 parts by mass of chlorine combines with calcium =  $\frac{40}{2x35.5}x35.5 = 20$  parts

Thus, equivalent weight of 'Ca' in CaCl<sub>2</sub> is 20.

#### **Assignment**

Q 2. Find out the equivalent weights of the underlined elements in the followings.

MgCl<sub>2</sub>, CaH<sub>2</sub>, FeO, Fe<sub>2</sub>O<sub>3</sub>

Q 3. Find out the equivalent weight of 'Mg' from the following chemical equation.

 $Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$ 

#### Relationship between atomic weight, equivalent weight and valency :

Consider a metal M with atomic weight 'A' and valency 'V'. The metal combines with hydrogen to forms the compound " $MH_v$  ".

#### In MH<sub>v,</sub>

V X 1.008 parts by mass of hydrogen combines with metal 'M' = 'A' parts

Or, 1.008 parts by mass of hydrogen combines with M = 
$$\frac{A}{(V \ X \ 1.008)} X \ 1.008$$
 parts =  $\frac{A}{V}$ 

Hence, equivalent weight (E) =  $\frac{A}{V}$ 

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Or, Equivalent weight (E) =  $\frac{Atomic \ weight}{Valency}$ 

#### Variable equivalent weights:

Since equivalent weight is related with valency, the elements like *Cu, Fe, Sn, Pb,* Hg etc. having variable valencies have variable equivalent weights.

For example, the equivalent weight of iron in FeCl<sub>2</sub> and FeCl<sub>3</sub> are:

Eq. Wt. of 'Fe' in FeC/<sub>2</sub> = 
$$\frac{Atomic weight}{Valency} = \frac{56}{2} = 28$$

Eq. Wt. of 'Fe' in FeCl<sub>3</sub> =  $\frac{Atomic weight}{Valency}$  =  $\frac{56}{3}$  = 18.66

#### EQUIVALENT WEIGHTS OF ACIDS, BASES AND SALTS:

#### Equivalent weights of acids:

The equivalent weight of an acid is numerically equal to the molecular weight of the acid divided by the basicity.

$$\mathsf{E}_{\mathsf{Acid}} = \frac{Molecular \ weight}{Basicity}$$

Where 'basicity' is the number of replaceable hydrogen atoms present one molecule of the acid.

ACID	<b>FORMULA</b>	MOL.Wt	<u>BASCIT</u>	<u> EQ.Wt.</u>
Nitric Acid	HNO <sub>3</sub>	63	1	63/1 = 63
Sulphuric Acid	H <sub>2</sub> SO <sub>4</sub>	98	2	98/2 = 49
Phosphoric Acid	H <sub>3</sub> PO <sub>4</sub>	98	3	98/3 = 32.66
Formic Acid	НСООН	46	1	46/1=46
Acetic Acid	CH3COOH	60	1	60/1 = 60
Oxalic Acid	соон			
	соон	90	2	90/2=45
Phosphorous Acid	H <sub>3</sub> PO <sub>3</sub>	82	2	82/2 = 41
Boric Acid	H <sub>3</sub> BO <sub>3</sub>	62	1	62/1 = 62
Note: HCOOH $\rightarrow$ HC	COO <sup>-</sup> + H <sup>+</sup>	I	$H_3PO_3 \rightarrow 2H^+ +$	- HPO3 <sup>2-</sup>
$CH_3COOH \rightarrow$	CH <sub>3</sub> COO <sup>-</sup> + H <sup>+</sup>	I	$H_3BO_3 \rightarrow H^+ + H_3BO_3 \rightarrow H^+ \rightarrow H^+ + H_3BO_3 \rightarrow H^+ \rightarrow H^+ + H^+ \rightarrow H^+ $	−1 <sub>2</sub> BO3 <sup>−</sup>

#### Equivalent weights of bases:

The equivalent weight of a base is numerically equal to the molecular weight of the base divided by the acidity.

 $E_{Base} = \frac{Molecular weight}{Acidity}$ , Where acidity is the number of replaceable OH groups present in one

molecule of the base.

Exaamples:-

Base	Mol.formula	Mol. wt.	acidity	Equivalent Wt.
Potassium hydroxide	KOH	56	1	56/1 = 56
Calcium hydroxide	Ca(OH) <sub>2</sub>	74	2	74/2 = 37
Aluminium hydroxide	AI(OH) <sub>3</sub>	78	3	78/3 = 26

#### **Equivalent Weights of Salts:**

The equivalent weight of a salt is numerically equal to the molecular weight of the salt divided by the total number of positive or negative charges.

$$\mathsf{E}_{\mathsf{Salt}} = \frac{Molecular \ weight}{Total \ no. \ of \ +ve \ or \ -ve \ ch \arg e}$$

Note: Total no of positive charge = No. of metal X valency.

Salt	Molecular formula	Mol. weight	Total +ve or – ve Charge	Eq. weight
Sodium chloride	NaCl	58.5	1x1 = 1	58.5
Potassium carbonate	K <sub>2</sub> CO <sub>3</sub>	138	1x2 = 2	69
Calcium Sulphate	CaSO <sub>4</sub>	136	1x2 = 2	68
Aluminium Suplhate	$AI_2(SO_4)_3$	342	2x3 = 6	57

#### <u>Assignment</u>

Q 4: Determine the equivalent weights of the following acids, bases and salts.

Acids:  $H_2CO_3$ ,  $HNO_3$ ,  $C_2H_5COOH$ Bases:  $Mg(OH)_2$ , LiOH Salts: KCI,  $Na_2CO_3$ 

#### **EQUIVALENT WEIGHTS OF METALS**

#### i. Oxidation method:

In this method metals like Na, K, Mg, Ca etc. are heated strongly to get the respective metal oxides. However, metals like Cu, Sn etc. are first treated with HNO<sub>3</sub> to get the respective metal nitrates. The metal nitrates so obtained are ignited strongly to get metal oxides. From the weights of metals and metal oxides, the equivalent weights of the metals are calculated as follows:

 $\begin{array}{rrrr} \mathsf{M} & + & \mathsf{O}_2 & \rightarrow & \mathsf{MO}_2 \\ \mathsf{x} \ \mathsf{gm} & (\mathsf{y}-\mathsf{x}) \ \mathsf{gm} & \mathsf{y} \ \mathsf{gm} \end{array}$ 

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Let the weight of metal = x gm

The weight of metal oxide = y gm

Hence, the weight of oxygen = (y - x) gm

(y - x) gm of oxygen is combined with metal = x gm

∴ 8 gm of oxygen is combined with metal = 
$$\frac{x}{(y-x)}X$$
 8

Hence, the equivalent weight of metal =  $\frac{x}{(y-x)}X = \frac{\text{weight of metal}}{\text{weight of oxygen}}X = \frac{x}{(y-x)}X = \frac{x}{(y-$ 

#### **Numerical Problems:**

**EXAMPLE I:** Find out the equivalent weights of the underlined elements in the following compounds.

(a)  $\underline{Fe}_2O_3$  (b)  $\underline{Cu}Cl_2$  (c)  $\underline{Al}_2O_3$ 

#### SOLUTION:

In  $Fe_2O_3$ 

3x16 parts by mass of 'O' combines with 'Fe' = 2x56 parts

 $\Rightarrow$  8 parts by mass of 'O' combines with 'Fe' =  $\frac{2 \times 56}{3 \times 16} \times 8 = 18.66$ 

In  $CuCl_2$ 

2x35.5 parts by mass of 'Cl' combines with 'Cu' = 63.5 parts

 $\Rightarrow$  35.5 parts by mass of Cl' combines with 'Cu' =  $\frac{63.5}{2 \times 35.5} \times 35.5 = 31.75$ 

**EXAMPLE II:** 1.201 g. of a metal dissolved in nitric acid. The nitrate was ignited when 1.497g. of the oxide was obtained. Calculate the equivalent weight of the metal.

#### SOLUTION:

Given Data: Weight of metal = 1.201 gm. Weight of metal oxide = 1.497 gm.  $\therefore$  Weight of oxygen = 1.497 - 1.201 = 0.296 gm Hence, equivalent weight of metal =  $\frac{weight of metal}{weight of oxygen} \times 8 = \frac{1.201}{0.296} \times 8 = 32.45$ 

**EXAMPLE III:** 0.723g. of copper displaced 2.455g. of silver from a solution of silver nitrate. Calculate equivalent weight of copper that of sliver being 107.88.

#### SOLUTION:

Weight of Copper  $W_{Cu} = 0.723$  gm Weight of Silver  $W_{Aa} = 2.455$  gm

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Equivalent weight of Silver  $E_{Ag} = 107.88$ Equivalent weight of Cu  $E_{Cu} = ?$ 

Applying Faraday's 2<sup>nd</sup> law of electrolysis:

 $\frac{W_{Cu}}{W_{Ag}} = \frac{E_{Cu}}{E_{Ag}} \implies E_{Cu} = \frac{W_{Cu}}{W_{Ag}} \times E_{Ag} \implies E_{Cu} = \frac{0.723}{2.455} \times 107.88 = 31.77$ 

#### EQUIVALENT WEIGHT OF IONS:

Equivalent weight of Ion ( $E_{Ion}$ ) =  $\frac{Ionic Mass}{Total Ch \arg e}$ 

For example,

$$E_{Ca^{2+}} = \frac{40}{2} = 20; \ E_{CO_3^{2-}} = \frac{12+48}{2} = 30$$

#### <u>Assignment</u>

Q 5. Find out the equivalent masses of the underlined atoms in the following. <u>Ca</u>C $l_2$ , <u>Fe</u>O, <u>Na</u>HCO<sub>3</sub>, <u>Fe</u>C $l_3$ .

Q 6. 1 gm. of a metal on heating produces 1.5 gm of its oxide. Find the equivalent mass of the metal.

Q 7. 4 gm of a divalent metal 'M' reacts with chlorine to form 11.1 gm of its chloride. Find the equivalent and atomic mass of the metal. Also write the formulae of metal chloride and metal sulphate.

Q 8. Certain mass of a metal is heated in oxygen. The mass is found to be increased by 10%. Find the equivalent mass of the metal.

#### MODES OF EXPRESSIONS OF CONCENTRATION

Concentration of a solution is the measure of the amount of solute in a given amount of solution or solvent. The concentration of a solution can be expressed in the following ways:

- > Molarity
- > Normality
- > Molality
- > Strength
- > Percentage
- Parts per million (ppm)
- Mole fraction, etc.

#### MOLARITY (M):

Molarity of a solution may be defined as "the number of gram mole of the solute present per liter of solution".

Unit = gram mole/liter or M.

Mathematically,

 $M = \frac{w \ x \ 1000}{Ms \ x \ Vml} \quad ; \qquad Where \ w = weight \ of \ the \ solute \ in \ gram$ 

Ms = Molecular weight of the solute.  $V_{ml}$  = Volume of solution in ml.

#### Molar solution:

The solution containing 1 gm mole of the solute per liter of solution is called a 'molar' solution.

For example: The solution containing 36.5 gm of HCl, 40 gm of NaOH, 58.5 gm of NaCl or 98 grams of  $H_2SO_4$  per liter of solution is called molar solution.

- **NOTE: 1.** Deci molar solution means (1/10) M solution, Semi-molar solution means (½) M solution, centi-molar solution means (1/100) M solution.
- 2. The solution whose strength is known is called *standard solution*.

#### **PROBLEMS FOR DISCUSSION:**

**QUESTION: 1.** 0.4 gm of caustic soda (NaOH) is present in 200 ml of its solution. Find out the molarity of the solution.

#### Solution : Given Data

weight of solute (w) = 0.4 gm

Volume of solution ( $V_{ml}$ ) = 200 ml.

Mol.wt. of solute (NaOH),  $M_s = 23.+16+1 = 40$  amu.

Thus, Molarity (M) = M = 
$$\frac{w \times 1000}{Ms \times Vml} = \frac{0.4 \times 1000}{40 \times 200} = 0.05 \text{ M}$$

Hence, the molarity of the solution is 0.05M.

**QUESTION:2.** How many grams of caustic potash (KOH) are required to prepare 1.5 lit. of a decimolar solution?

#### Solution : Given Data

Weight of solute (w) = ? Volume of the solution ( $V_{ml}$ ) = 1.5 lit = 1500 ml. Molecular weight of solute, Ms for KOH =39+16+1 =56 amu Molarity of the solution = 1/10 M = 0.1M

Thus,  $M = \frac{w \ x \ 1000}{Ms \ x \ Vml} \Rightarrow w = \frac{M \ x \ Ms \ x \ Vml}{1000} = \frac{0.1 \ x \ 56 \ x \ 1500}{1000} = 8.4 \text{ gram.}$ 

Thus, 8.4 gm of caustic potash is required to prepare 1.5 lit. of deci-molar solution.

#### NORMALITY (N):

Normality of a solution may be defined as "the number of gram equivalent of the solute present per litre of solution." It is represented by 'N'. Unit: - gram equivalent/liter or 'N'.

Mathematically,

 $N = \frac{w \ x \ 1000}{Es \ x \ Vml};$  Where,  $w = weight \ of \ solute \ in \ gm.$  $V_{ml} = volume \ of \ solution \ in \ ml.$  $E_{s} = Equivalent \ weight \ of \ solute$ 

**Normal Solution:** The solution containing 1 gm. equivalent of the solute per litre of solution or the solution having normality '1' is called a normal solution or 1N solution.

For example: The solution containing 36.5 gm of HCl, 49 gm of  $H_2SO_4$  or 40 gm of NaOH per liter of solution is called a **normal solution**.

#### **PROBELMS FOR DISCUSSION:**

**QUESTION:1.** 5.6 gm of caustic potash (KOH) is present in 800 ml of its solution. What is the normality of the solution?

#### Solution: Given Data

Weight of solute, w = 5.6 gm

Volume of solution,  $V_{ml} = 800$  ml.

Equivalent weight of solute, KOH (E<sub>s</sub>) =  $\frac{Molecular weight}{Acidity} = \frac{56}{1} = 56$ 

Normality 'N' =  $\frac{w \ x \ 1000}{Es \ x \ Vml} = \frac{5.6 \ x \ 1000}{56 \ x \ 800} = 0.125 \ N$ 

Hence, the normality of the solution is 0.125N.

**QUESTION:2.** 10 ml of sulphuric acid ( $H_2SO_4$ ) having density 1.2 gm/ml is present in 400 ml of its solution. Calculate the normality of the solution.

Soution : Given Data,

Wt. of solute, w = density × volume =  $1.2 \times 10 = 12$  gm Volume of solution, V<sub>ml</sub> = 400 ml

Equivalent weight of  $H_2SO_4 = \frac{Molecular \ weight}{Basicity} = 98/2 = 49$ 

Normality N = 
$$\frac{W \times 1000}{Es \times Vml} = \frac{12 \times 1000}{49 \times 400} = 0.612N$$

Hence, normality of the solution is 0.612N.

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#### MOLALITY (m):

*Molality of a solution may be defined as* "the number of gram mole of solute present per 1000gm (1kg) of solvent" and it is represented by the symbol '**m**'. Unit: - gram mole/kg.

Mathematically,

$$m = \frac{w \times 1000}{M_S \times W}$$

Where, w = weight of solute in gm

W = weight of solvent in gm  $M_S$  = Molecular weight of solute

#### Molal solution:

The solution containing 1 gm mole of solute per 1000gm of solvent is called molal solution. For example: 58.5 gm of NaCl, 40 gm of NaOH, 56 gm of KOH or 98gm of  $H_2SO_4$  per 1000 gm of water (solvent) is called molal solution.

#### **PROBLEMS FOR DISCUSSION:**

**QUESTION:1.** 5.85 gm of common salt (NaCl or table salt) is present in 200 gm of water. Calculate the molality of the solution.

#### Solution : Given Data

wt. of solute, w = 5.85 gm wt. of solvent, W = 200 gm, Mol. wt. of Solute, M<sub>S</sub> (NaCl) = 23+35.5 = 58.5 amu.  $m = \frac{w \times 1000}{M_S \times W}$  $= \frac{5.85 \ x \ 1000}{58.5 \ x \ 200} = 0.5m$ 

Hence, molality of the solution is 0.5m.

**QUESTION:2.** 5.6 gm of potassium hydroxide is present in 300 gm of its solution in water. Calculate the molality of the solution.

#### Solution : Given Data

wt. of solute, w = 5.6 gm
wt. of solution = 300 gm
wt. of solvent, W = wt. of solution - wt. of solute = 300 - 5.6 = 294.4 gm

Thus, molality

 $m = \frac{w \times 1000}{M_S \times W} = \frac{5.6 \times 1000}{56 \times 294.4} = 0.339 \text{ m.}$ 

Hence, molality of the solution is 0.339 m.

#### <u>Assignment</u>

Q 9. How many gm of Common salt is required to prepare 2 litres of a semi molar solution? Q 10.9.8 gm of  $H_2SO_4$  is present in 400ml of its solution. Calculate its molarity and normality.

Q 11.0.49 gm of  $H_2SO_4$  is present in 600ml of its solution having density 1.2 gm/ml. Find molarity, normality and molality of the solution.

### **P<sup>H</sup> of Solutions**

The  $p^{H}$  of a solution may be defined as "the negative logarithm of H<sup>+</sup> ion concentration in moles/liter or molarity."

Thus,  $P^{H} = -\log[H^{+}]$ 

 $p^{H}$  is normally used to know whether a solution acidic, alkaline or neutral in nature.



The pH scale

- i. If  $P^{H} < 7$ ; the solution is Acidic,
- ii. If  $P^H > 7$ ; the solution is Alkaline,
- iii. If  $P^{H} = 7$ ; the solution is Neutral.

Note: Pure water has a  $P^{H}$  value of '7' at 25<sup>o</sup>C and is neutral. The P<sup>H</sup> value of water decreases with the increase in temperature.

#### Some important Formulae:

- i.  $P^{H} = -\log [H^{+}]$
- ii.  $P^{OH} = -\log [OH]$
- iii.  $P^H + P^{OH} = 14$
- iv.  $[H^+][OH^-] = 10^{-14}$
- **v.**  $[H^+] = 10^{-P^H}$
- **vi.**  $[OH^{-}] = 10^{-P^{OH}}$

#### **QUESTIONS FOR DISCUSSION:**

- **1.** Find out the  $p^H$  values of the following solutions.
  - i. 0.01M HCI solution
  - ii. 0.001 M HNO<sub>3</sub> solution
  - iii. 0.01M NaOH solution
  - iv.  $0.01M H_2SO_4$  solution

Solutions:i. HCI  $\rightarrow$  H<sup>+</sup> + Cl<sup>-</sup> 0.01M 0.01M  $[HCI] = [H^+] = 0.01M = 10^{-2}M$ Hence  $p^{H} = -\log[H^{+}] = -\log(10^{-2}) = -(-2)\log 10 = 2$  $HNO_3 \rightarrow H^+ + NO_3^$ ii. 0.001M 0.001M  $[HNO_3] = [H^+] = 0.001M = 10^{-3}M$ Hence,  $p^{H} = -\log[H^{+}] = -\log_{10}^{-3} = -(-3)\log_{10}^{-3} = -(-3)\log_$ iii. NaOH  $\rightarrow$  Na<sup>+</sup> + OH<sup>-</sup> 0.01M 0.01M  $[NaOH] = [OH^{-}] = 0.01M = 10^{-2}M$ We know  $[H^+][OH^-] = 10^{-14}$  $\Rightarrow [H^+] = \frac{10^{-14}}{[OH^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}$ Hence,  $P^{H} = -\log[H^{+}] = -\log(10^{-12}) = 12$  $H_2SO_4 \longrightarrow 2H^+$ + SO4<sup>2-</sup> iv. 0.01M (2 x 0.01)M  $[H^+] = 2 \times 0.01 = 2 \times 10^{-2} M$ 

Hence,  $p^{H} = -\log[H^{+}] = -\log(2 \times 10^{-2}) = 1.699$ .

#### **Assignment**

Q 12. Find out the pH values of the following solutions.(i) 1 M HNO3 solution (ii) 0.1 M Mg (OH)2 solution.[Ans: (i) 0, (ii) 12.301]Q 13. One liter of a solution contains 5.85 gm of HCI. Find the  $P^H$  value of the solution.[Ans: 1]

Q 14. 500 ml of an aqueous solution contains 1.6 gm of NaOH. Find  $P^H$  of the solution.

#### Importance of P<sup>H</sup> in Industries:

- **1.** In sugar Industry: The  $P^{H}$  value of the sugar cane juice should be nearly '7' i.e., it should be neural. If the  $P^{H}$  value of sugar cane juice becomes less than '7', the sucrose in the juice is hydrolyzed into glucose and fructose. On the other hand, if it exceeds '7', undesirable acids and coloured substances are produced.
- 2. In Paper Industries: Paper is used in a broad array of products essential for everyday life, from newspapers, books, magazines, printing, writing papers to cardboard boxes and bags, paper napkins, sanitary tissues etc. We are daily surrounded by paper products.

The most important use of paper is writing. The quality of paper used for printing or writing should be good and it depends on many parameters. One of the parameters is Cobb, which needs to be controlled. Cobb control is nothing but the control of quality and binding of pulp in such a fashion that whatever is written by any source such as ink, etc on paper it should not spread as well as leave its impression on back side of the paper. Cobb variation is minimized by maintaining pH of the pulp in the range of 5-6 pH. Before processing, the raw pulp has pH in the range of 7-8. This should be controlled and brought down to acidic range i.e., 5 to 6  $p^{H}$ .

Cobb control is done by addition of Alum (which is in the range of 2-3  $p^H$ ) and rosin to pulp. When alum and rosin are mixed with pulp after a certain distance pH of the mixture is measured and if it is not in the desired range the transmitter will control the Alum dosing via controller so that  $p^H$  of the pulp is maintained. Rosin on the other side has no such controlled action. It will be getting dosed to the pulp continuously in a specific quantity. It is the Alum whose dosing is controlled depending upon  $p^H$  variations.

**3.** In Textile Industries: In all textile processes in which aqueous solutions are used, balancing the pH of the solution is primary. pH control is critical for a number of reasons. The effectiveness of oxidizing and reducing agents is p<sup>H</sup> dependent. The amount of chemicals required for a given process is directly related to the p<sup>H</sup>. The solubility of substances, such as dyes and impurities, vary with p<sup>H</sup>. The corrosive and scaling potential of processing solutions is also heavily influenced by p<sup>H</sup>. All these issues affect quality and costs.

Along with surface tension, pH plays an important role in the wetting and saturating processes. For example, caustic solutions cause interfibrillar swelling in cotton cellulose and cannot be squeezed out as easily as water, which can reduce quality in subsequent processing.

The scouring of wool is a good example of a process where maintaining the pH value permits a better solubilization of certain impurities. For example, a  $p^{H}$  of 10 is considered optimum for the removal of wool wax.

In the instance of vat dyeing,  $p^{H}$  controls the solubilization of the dyes. Initially, the quantity of caustic soda present must be adequate to ensure the solubility of the leuco form. Once the dye has been exhausted, the  $p^{H}$  is adjusted such that the dye returns to its insoluble form and is mechanically trapped in the fibre.

Between the colour kitchen and processing, controlling the  $p^H$  improves the lab-to-bulk reproducibility of colour. Monitoring and controlling pH ensures consistency of colour from batch to batch, as well.

To effectively bleach cellulose (e.g., cotton) with a minimum amount of damage, the bleaching solution must be alkaline. This keeps the hypochlorite stable and also prevents the presence of reducing groups that cause an apparently well-bleached cloth to yellow with age. Additionally, an acidic solution will form toxic and corrosive chlorine gas. Bleaching liquor is therefore usually maintained at a  $p^{H}$  of 9. The permanence of the white obtained is thereby increased, and the bleaching is safe. Due to environmental concerns in recent times, hydrogen peroxide bleaching has become more prevalent. Its reaction products, oxygen and water, are relatively harmless. However, hydrogen peroxide is a weak acid. Thus, its conjugate base,  $HO_2^{-7}$ , is used to perform the actual bleaching. To ensure an adequate concentration of  $HO_2^{-7}$ , the solution  $p^{H}$  must be tightly controlled. Sodium hydroxide is used to maintain the  $p^{H}$  at a very alkaline level of 12-12.5.

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#### **Exercise**

#### (02 Marks Questions)

- 1. Define atomic weight.
- 2. Define molecular weight. What is the molecular weight of sulphuric acid?
- 3. Define equivalent weight. What is the equivalent weight of  $H_3PO_4$ ?
- 4. Find the molecular weights of  $AI_2(SO_4)_3$  and  $CuCO_3$ .
- 5. Find the equivalent weights of  $H_3PO_4$  and  $H_3PO_3$ .
- 6. Find the equivalent weights of  $Ca(HCO_3)_2$  and  $H_3BO_3$ .
- 7. Find the equivalent weights of acetic acid and calcium hydroxide.
- 8. Derive a relationship between atomic weight, equivalent weight and valency.
- 9. Define variable equivalent weights. Give suitable examples.
- 10. Why do the equivalent weights of FeO and  $Fe_2O_3$  vary?
- 11. 1 gm of a metal on heating with air produces 1.5 g of its oxide. Calculate the equivalent weight of the metal.
- 12. An oxide of metal contains 60% oxygen. Find the equivalent weight of the metal.
- 13. Find the equivalent weights of  $Ca(OH)_2$  and  $CH_3COOH$ .
- 14. Define molarity. Mention its unit.
- 15. How many grams of NaCl are required to prepare 2 liters of its solution having molarity 1M?

16. Define normality.

17. 4 grams of NaOH are present 2 lit of its solution. Find its normality.

18. Define molality.

- 19. 5.6 gram of KOH are present in 200 grams of water. Find molality of the solution.
- 20. Find the equivalent weights of calcium chloride and nitric acid.
- 21.8 grams of NaOH are present in 108 gram of its solution. Find molality of the solution.
- 22. Define normality. Mention its unit.
- 23. What do you mean by decimolar solution?
- 24. How many gms of Na<sub>2</sub>CO<sub>3</sub> are required to prepare one litre of its decimolar solution?
- 25. Obtain a relationship between molarity and normality.
- 26. Convert 0.01 M  $H_2SO_4$  in to normality.
- 27. Convert  $10^{-2}$  N H<sub>2</sub>SO<sub>4</sub> in to molarity.

28. Define  $P^H$  and  $P^{OH}$ .

- 29. The P<sup>H</sup> of a basic solution is 12. What is its hydroxyl ion concentration in moles/lit?
- 30. Define ionic product of water. What is its value at 25°C?
- 31. What is the importance of P<sup>H</sup> in sugar industry?
- 32. Write down the importance of  $P^{H}$  in textile industries.
- 33. Find the  $P^H$  value of 0.001 M HCl solution.
- 34. Find the  $P^H$  value of 0.01 M NaOH solution.
- 35. Find the  $P^H$  value of 0.01 M H<sub>2</sub>SO<sub>4</sub> solution.

# <u>CHAPTER – 5</u> ELECTROCHEMISTRY

#### Introduction:

Electrochemistry is the branch of chemistry which deals with the study of electricity relating to redox reactions. A redox reaction is that in which both oxidation as well as reduction reactions take place.

Depending upon electrical conductivity, substances can be classified into the following types:



#### Electrolyte:

The chemical substances which allow electricity to pass through their molten, fused or solution state are called electrolytes. Example: All acids, all alkalies and all salts.

#### Non-electrolyte:

The chemical substances which do not allow electricity to pass through their molten, fused or solution state are called non-electrolytes. Example: urea, sugar, glucose, fructose, maltose, lactose, etc.

#### **Classification of Electrolytes:**

Depending upon the strength, electrolytes may be classified into the following types:

- i. Strong electrolytes
- ii. Weak electrolytes

i. <u>Strong electrolytes</u>: These are the electrolytes which undergo almost complete ionization in aqueous solution.

Example: a) acids like HCI, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, etc.

- b) alkalies like NaOH, KOH, Ca (OH)<sub>2</sub>, Mg (OH)<sub>2</sub>, etc.
- c) salts like NaCl, KCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, etc.
- **ii.** <u>Weak electrolytes</u>: These are the electrolytes which undergo partial ionization in aqueous solution. Example: a) Organic acids like CH<sub>3</sub>COOH, HCOOH, (COOH)<sub>2</sub>, etc.

b) Inorganic acids like H<sub>2</sub>CO<sub>3</sub>, HCN, etc.

c) Base like NH<sub>4</sub>OH

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#### ELECTROLYSIS:

The process of chemical decomposition of an electrolyte by the passage of electricity through its molten fused or solution state is called *electrolysis*.

**Apparatus:** The apparatus used in the process of electrolysis is called electrolytic cell, which is made up of an insulating material like glass. An electrolytic solution is taken in the electrolytic cell. Two metallic electrodes are partially dipped in the solution. The electrodes are connected to the terminals of a battery. The electrode which is connected to the positive terminal of the battery is called **anode** and the electrode which is connected to the negative terminal of the battery is called **cathode** (Fig. 5.1).

#### Working Process:

Electrolytes exist in the ionic form in their molten, fused or solution state. When electricity is allowed to pass through the electrolytic solution, the ions migrate towards the oppositely charged electrodes. Cations migrate towards the cathode while anions migrate towards the anode. While reaching at the electrodes the ions get discharged at their respective electrodes to give neutral species (primary change). The neutral species may further undergo secondary change to give stable substances.



#### Example 1: Electrolysis of molten NaCI.

Molten NaC/ exists in the ionic form Na<sup>+</sup> and C/<sup>-</sup> During the process of electrolysis, Na<sup>+</sup> ions migrate towards the cathode while C/<sup>-</sup> ions migrate towards the anode. During electrolysis the following changes take place at different electrodes.

#### At Anode:

 $CI^- - e^- \rightarrow CI$  (Primary change)

 $CI + CI \rightarrow CI_2$  (Secondary change)

#### At Cathode:

#### $Na^+ + e^- \rightarrow Na$ (Primary change)

Thus, electrolysis of molten NaC/ liberates chlorine gas at the anode while metallic sodium at the cathode.

#### Example 2: Electrolysis of aqueous NaC/ solution.

In aqueous solution NaCl exists in ionic form. Also, water undergoes partial ionization to produce  $H^+$  and  $OH^-$  ions.

NaCl  $\rightarrow$  Na<sup>+</sup><sub>(aq)</sub> + Cl<sup>-</sup><sub>(aq)</sub>

 $H_2O \rightarrow H^+ + OH^-$ 

Out of Cl<sup>-</sup> and OH<sup>-</sup> ions, the former has lower discharge potential and hence preferably gets discharged at the anode.

 $2Cl^{-} \ - \ 2e^{-} \ \rightarrow \ Cl_2$ 

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On the other hand, out of H<sup>+</sup> and Na<sup>+</sup> ions, the former has lower discharge potential and hence preferably gets discharged at the cathode.

 $2H^+$  +  $2e^- \rightarrow H_2$ 

Thus electrolysis of aqueous NaC/ solution liberates chlorine gas at the anode and hydrogen gas at the cathode.

#### Faraday's 1<sup>st</sup> Law of Electrolysis:

The law may be stated as "during the process of electrolysis, the amount of substance (W) deposited or liberated at the electrode is directly proportional to the quantity of electricity (Q) passed through the electrolyte".

Mathematically,

$$W \propto Q$$
  
But, Q = I X T

But, 
$$Q = I \lambda$$

 $\Rightarrow W \propto I \times T$ 

$$\Rightarrow W = Z \times I \times T$$

Where, W = Amount of substance in gram

Q = Quantity of electricity or Charge in coulomb

I = Current in ampere

t = time of flow of current in second.

Z = Electrochemical equivalent (ECE)

When, I = 1 ampere; t = 1 second,

W = Z

 $\Rightarrow$ 1

Thus, electrochemical equivalent is numerically equal to the amount of substance deposited or liberated at the electrode when 1 ampere of current is passed through an electrolyte for 1 second. Or it is the amount of substance deposited or liberated at the electrode when 1 coulomb of charge is made to flow through an electrolyte.

A bigger unit of charge is Faraday.

1 Faraday = 96500 coulomb

Experimentally it is observed that when 1 Faraday (96500 C) of charged is passed through an electrolyte 1 gram equivalent of the substance is deposited at the electrode.

96500 Coulomb of charge deposits 1 gram equivalent

coulomb of charge deposits 
$$\frac{1 \, gram \, equivalent}{96500 \, C}$$

Hence, Electrochemical Equivalent (Z) =  $\frac{1 gram \ equivalent}{96500 \ C} = \frac{A tomic \ mass \ / Valency}{96500}$ 96500

Unit of 'Z' is gram equivalent/coulomb.

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Note: 1 mole of electrons carries 1 Faraday or 96500 Coulomb of charge.

**Question 1**: How many grams of silver will be deposited at the cathode by the passage of 10 ampere of current through an aqueous solution of AgNO<sub>3</sub> for 1 hour?

#### Solution:

t = 1 hr = 3600 Sec.

$$Z = \frac{1 \, gram \, equivalent}{96500 \, C} = \frac{A tomic \, mass \, / Valency}{96500} = \frac{108 \, / 1}{96500} = -\frac{108}{96500} = 0.0011$$

Applying Faraday's 1<sup>st</sup> Law of electrolysis

W = ZIt = 0.0011 X 10 X 3600 = 39.6 gram.

Question 2: How many coulombs are required for the following changes?

- i. One mole  $Ca^{2+}$  into Ca.
- ii. Two moles of A/<sup>3+</sup> into A/.

#### Solution:

i.  $Ca^{2+} + 2e^- \rightarrow Ca$ 

1 mole of electrons carries 96500 coulombs.

 $\Rightarrow$  2 moles of electrons carry (2 x 96500) coulomb = 193000 Coulombs.

#### ii. $2AI^{3+} + 6e^- \rightarrow 2AI$

1 mole of electrons carries 96500 coulombs.

 $\Rightarrow$  6 moles of electrons carry (6 x 96500) coulomb = 579000 Coulombs.

**Question 3:** How many coulombs of charge are required to get 10 grams of calcium from molten CaC*l*<sub>2</sub>? **Solution:** 

W = 10 gm, Q =?  
W = Z Q  

$$= \frac{Eq.mass / Valency}{96500} \times Q$$

$$\Rightarrow 10 = \frac{40/2}{96500} \times Q \Rightarrow Q = 10 \times \frac{96500}{20} = 48250 Coulomb$$

#### **Assignment**

- Q 1. Find the ECE of Ca and Al.
- Q 2. How many coulombs of charges are required to reduce 10 gm of calcium ions into calcium?
- Q 3. How many coulombs of charge are required to get 3.6 grams of aluminium from molten alumina?
- Q 4. How many grams of copper will be deposited at the cathode by the passage of 20 ampere of current through an aqueous solution of CuSO<sub>4</sub> for half an hour?

# Faraday's 2<sup>nd</sup> Law of Electrolysis:

The law may be stated as "when the same quantity of electricity is passed through different electrolytes connected in series, the amounts (W) of substances deposited at various electrodes are directly proportional to their equivalent masses (E)".

Mathematically,

 $W \propto E$ 

Let us consider two electrolytic solutions  $AgNO_3$  and  $CuSO_4$  taken in two different electrolytic cells. Both the cells are connected in series and the same quantity of electricity is passed through the electrolytes.

Applying Faraday's 2<sup>nd</sup> law of electrolysis,

$$W_{Ag} \propto E_{Ag}$$
 -----(1)

 $W_{Cu} \propto E_{Cu}$  -----(2)



From equation (1) and (2), we have

$$\Rightarrow \frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}} \Rightarrow \frac{W_{Ag}}{W_{Cu}} = \frac{\frac{E_{Ag}}{96500}}{\frac{E_{Cu}}{96500}} = \frac{Z_{Ag}}{Z_{Cu}}$$
  
In general,  $\boxed{\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}}$  or  $W \propto E \propto Z$ 

**Question: 1.** The same quantity of electricity is passed simultaneously through acidulated water and copper sulphate solution. Weights of hydrogen and copper liberated are 0.0132 and 0.4164 gram respectively. Find out the equivalent weight of copper.

**Solution:** Weight of hydrogen  $W_{H_2} = 0.0132$  gm

Weight of copper  $W_{Cu} = 0.4164 \text{ gm}$ 

Equivalent weight of hydrogen  $E_{H_2}$  = 1.008

Equivalent weight of copper  $E_{Cu} = ?$ 

Applying Faraday's 2<sup>nd</sup> law of electrolysis,

$$\frac{W_{H_2}}{W_{Cu}} = \frac{E_{H_2}}{E_{Cu}} \implies E_{Cu} = E_{H_2} \times \frac{W_{Cu}}{W_{H_2}} = 1.008 \times \frac{0.4164}{0.0132} = 31.79$$

#### **Industrial Application of Electrolysis:**

1. Electroplating: The process of applying a coating of one metal over another by the process of electrolysis is called electroplating. Electroplating is used for three main purposes: a) Decoration, b) repairing and c) protection.

Zinc Platting: Normally iron gets rusted when exposed to moist air. Rusting of iron can be prevented by



applying a coating of zinc or chromium over it. The process of applying a coating of zinc over iron with a view to protect it from rusting is called **Galvanization.** 

During the process of galvanization, zinc plate is used as anode and iron article is used as cathode. Both the electrodes are connected to the terminals of a battery (Fig: 5.2). The electrodes are dipped in an aqueous solution of zinc sulphate. When electricity is passed, the anode, i.e., zinc plate dissolves in its aqueous salt solution to liberate zinc ion ( $Zn^{2+}$ ) which get discharged ad deposited over the cathode. In this way a coating of zinc is applied over the surface of the iron article.

#### **Exercise**

#### (02 Marks Questions)

- 1. Define electrolyte. Give an example of it.
- 2. Define strong and weak electrolytes with examples.
- 3. What are non-electrolytes? Give examples.
- 4. Define electrolysis. Which gas is evolved at the cathode during electrolysis of acidulated water?
- 5. Define Faraday's 1<sup>st</sup> law of electrolysis.
- 6. Define Faraday's 2<sup>nd</sup> law of electrolysis.
- 7. Define electrochemical equivalent. Mention its unit.
- 8. Find the electrochemical equivalent of calcium.
- 9. Find the electrochemical equivalent of aluminium.
- 10. How many coulombs of charge are required to get 10 grams of calcium from molten calcium chloride?
- 11. Define electroplating.
- 12. What is Galvanisation?
- 13. What is the relationship between the masses of the substances and their equivalent weights, when the same quantity of electricity is passed through different electrolytes?
- 14. What is the difference between electrolytes and non-electrolytes?

#### (05 Marks Questions)

- 1. Define electrolyte and electrolysis. What are strong and weak electrolytes? Give examples.
- 2. Define electrolysis. Explain the process of electrolysis of molten NaCl.
- 3. Define Faraday's 1<sup>st</sup> law of electrolysis. How many grams of calcium will be deposited at the cathode by passing 15 ampere of currents through molten CaCl<sub>2</sub> for 30 minutes?
- 4. Define electrochemical equivalent. Find the ECE of Ca and Al.
- 5. Define and explain Faraday's 2<sup>nd</sup> law of electrolysis.
- 6. Explain the process of applying a coating of zinc over an iron article by the process of electrolysis.
- 7. Explain the electro refining process of a crude copper bar.
- 8. Define and explain electrometallurgy.
- 9. Explain the electrolysis of acidulated water.
- 10. Define and explain Galvanisation.
- 11. Define Faraday's 1<sup>st</sup> law of electrolysis. How many coulombs of charges are required to get 36 grams of magnesium from molten magnesium chloride?

# <u>CHAPTER – 6</u> CORROSION

#### Introduction:

**Corrosion** is a natural process that converts a refined metal into a more chemically-stable form such as oxide, hydroxide, or sulphide. It is the gradual destruction of materials (usually a metal) by chemical and/or electrochemical reaction with their environment. Corrosion engineering is the field dedicated to controlling and preventing corrosion.

In the most common use of the word, this means electrochemical oxidation of metal in reaction with an oxidant such as oxygen or sulphates. Rusting, the formation of iron oxides is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal and results in a distinctive orange colouration. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term "degradation" is more common. Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases.

Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces. As a result, methods to reduce the activity of the exposed surface, such as passivation and chromate conversion, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

#### Corrosion:

The process of conversion of a metal into an undesirable compound on exposure to atmospheric conditions i.e., moisture (water) and air is called *corrosion*. It is also called weeping of metals.

Types of Corrosion: - Corrosion is of the following types:

- i. Atmospheric corrosion
- ii. Water line corrosion
- iii. Pitting corrosion
- iv. Stress corrosion
- i. **Atmospheric corrosion:** The process of development of undesirable substances usually oxide over the surface of a metal when exposed to atmosphere is called *atmospheric corrosion*. Example: (a) rusting of iron, (b) tarnishing of silver, (c) developing of green coating over copper and bronze.

#### Mechanism of Rusting of Iron:

Pure iron does not rust. However commercial form of iron behaves like a tiny electric cell in presence of water containing dissolved oxygen and acidic substances like  $CO_2$ ,  $SO_2$ , etc. The following changes stake place on the surface of iron during the process of corrosion (Fig. 6.1).

#### At Anode:

At anode iron gets oxidized in to ferrous ion.

$$2Fe \rightarrow 2Fe^{2+} + 4e^{-}$$

The electrons thus formed migrate towards the cathodic part of the piece of iron.

#### At Cathode:

At the cathodic part, the electrons combine with moisture and dissolved oxygen to form hydroxyl ions.

 $H_2O ~+~ O ~+~ 2e^- ~\rightarrow~ 2OH^-$ 



The  $Fe^{2+}$  ions and  $OH^{-}$  ions then diffuse under the influence of dissolved oxygen and  $Fe^{2+}$  ions are oxidized into  $Fe^{3+}$  ions. These ferric ions then combine with  $OH^{-}$  ions to form hydrated ferric oxide which is nothing but rust.

Note:

- Rust is nothing but hydrated ferric oxide (Fe<sub>2</sub>O<sub>3</sub>.nH<sub>2</sub>O)
- Presence of CO<sub>2</sub> in water or trace of Cu or Zn in iron accelerates the process of corrosion. Also, corrosion process is accelerated in saline water.
- Presence of alkalis in water or Cr, Ni in iron slows down the process of corrosion.
- ii. **Water line Corrosion:** This type of corrosion occurs due to differential oxygen concentration above and below the level of water. When water is stored in a steel tank, it is noticed that corrosion occurs along the line just below the level of water (Fig. 6.2).

The concentration of oxygen in the area above the water line is high and hence the area is called cathodic part. The area just below the water line is called anodic part as this part is deficient in oxygen. This type of corrosion is mostly seen in ships, water tanks, etc.



#### **Protection of Corrosion:**

- 1. Alloying: Corrosion can be prevented by alloying a metal. Alloying prevent corrosion in two ways.
  - **i. Homogeneity:** Alloying increases the homogeneity of the metal for which the rate of corrosion is reduced. Rusting of iron can be prevented by alloying it with chromium. It is important to note that only uniform alloy can prevent corrosion to a maximum extent.
  - **ii. Oxide film:** In some cases, the oxide film formed at the surface of the metal prevents corrosion. Duriron is a silica-iron alloy. It is resistant to acids as a layer of silicon oxide is formed at the surface of iron.
- 2. <u>Galvanization</u>: Normally iron gets rusted when exposed to moist air. Rusting of iron can be prevented by applying a coating of zinc or chromium over it. The process of applying a coating of zinc over iron with a view to protect it from rusting is called **Galvanization**.

During the process of galvanization of iron, zinc is used as anode and iron bar is used as cathode. Both the electrodes are connected to the terminals of a battery. The electrodes are dipped in an aqueous solution of zinc sulphate. When electricity is passed, the anode, i.e., zinc bar dissolves in its aqueous salt solution to liberate zinc ion  $(Zn^{2+})$  which get discharged ad deposited over the cathode. In this way a coating of zinc is applied over the surface of iron.

#### **Exercise**

#### (02 Marks Questions)

- 1. What do you mean by corrosion?
- 2. What is atmospheric corrosion?
- 3. What is water-line corrosion?
- 4. How is corrosion prevented by the alloy durriron?
- 5. How the rate of rusting of iron is accelerated in presence of CO<sub>2</sub> in moisture?

#### (05 Marks Questions)

- 1. Define and explain atmospheric corrosion.
- 2. Define corrosion. Explain waterline corrosion.
- 3. Explain the alloying process of protection of corrosion.

# <u>CHAPTER – 7</u> <u>METALLURGY</u>

**Mineral**: - The natural material in which the metal or their compounds occur in the earth's crust is known as mineral.

**Example**: Bauxite  $(Al_2O_3, 2H_2O)$  and Kaolin  $(Al_2O_3, 2SiO_2, 2H_2O)$  are the minerals of Aluminium.

**Ores**: - Ores are the minerals from which the concerned metals can be extracted conveniently and profitably.

**Example**: Both Bauxite and Kaolin are the minerals of 'AI'. However, 'AI' can be extracted easily and profitably from Bauxite. Thus, Bauxite is an ore of 'AI'. On the other hand, it is difficult and non-profitable to extract 'AI' from Kaolin, thus Kaolin is only a mineral of 'AI'.

All ores are minerals, but all minerals are not ores.

#### Difference between Minerals and Ores

	Minerals	Ores
1.	The combined state occurrences of metals	These are the minerals from which the
	are called Minerals and extraction of metals	concerned metals can be extracted easily
	from minerals is difficult and non-profitable.	and economically.
2.	Minerals contain low percentage of metals	Ores contain high percentage of metals but
	and high percentage of impurities.	low percentage of impurities.
3.	All minerals are not ores.	All ores are minerals.
	Example: Kaolin and Bauxite are the	Example: Bauxite is an ore of aluminium.
	minerals of aluminium.	

#### SOME IMPORTANT METALS AND THEIR MINERALS:

Metals	Minerals	Formula
Na	Rock Salt	NaCl
	Borax	$Na_2B_4O_7$
K	Carnallite	KCI.MgCl <sub>2</sub> .6H <sub>2</sub> O
	Niter	KNO₃
Mg	Magnesite	MgCO <sub>3</sub>
	Dolomite	MgCO <sub>3</sub> .CaCO <sub>3</sub>
	Epsom salt	MgSO <sub>4</sub> .7H <sub>2</sub> O
	Carnallite	KCI.MgCl <sub>2</sub> .6H <sub>2</sub> O
Ca	Limestone	CaCO <sub>3</sub>
	Dolomite	MgCO <sub>3</sub> .CaCO <sub>3</sub>
	Gypsum	CaSO <sub>4</sub> .2H <sub>2</sub> O
Cu	Copper pyrite	CuFeS <sub>2</sub>
	Copper glance	Cu <sub>2</sub> S
	Cuprite	Cu <sub>2</sub> O
Ag	Silver glance	Ag <sub>2</sub> S
	Horn silver	AgCl
Zn	Zinc blend	ZnS
	Zincite	ZnO
	Calamine	ZnCO <sub>3</sub>

Hg	Cinnabar	HgS
AI	Bauxite	Al <sub>2</sub> O <sub>3</sub> .2H <sub>2</sub> O
	Cryolite	Na <sub>3</sub> AIF <sub>6</sub>
Sn	Tin stone	SnO <sub>2</sub>
Pb	Galena	PbS
Cr	Chromite	FeO.Cr <sub>2</sub> O <sub>3</sub>
Fe	Haematite	Fe <sub>2</sub> O <sub>3</sub>
	Magnetite	Fe <sub>3</sub> O <sub>4</sub>
	Limonite	Fe <sub>2</sub> O <sub>3</sub> .3H <sub>2</sub> O

**METALLURGY**: - The art of extraction of metals from ores conveniently and economically is called metallurgy or metallurgical operation.

The following steps are followed during the process of metallurgical operation.

- 1. Crushing and Grinding.
- 2. Concentration or Ore dressing.
- 3. Oxidation.
- 4. Reduction.
- 5. Refining.
- 1. CRUSHING AND GRINDING: The ores obtained from mines are in the form of solid rocks. These are first crushed into small pieces with the help of jaw crusher and then grinded into their powder form with the help of stamp mill or ball mill. The powdered form of ore is called pulverized ore.
- 2. CONCENTRATION OR ORE DRESSING: The process of removal of maximum impurities (gangue or matrix) from the powdered ore is called ore concentration. The method of concentration to be followed depends upon the nature of the impurities present. Following are the different methods of concentration:

(i) Gravity Separation Method: - This method of concentration is adopted only when there is a gravity difference between the ore and impurities. Normally, Carbonate and oxide ores are heavier

than the impurities associated with them and hence they are concentrated by this method. In this method the powdered ores are kept in some containers over a specially designed table called Wilfley table (Fig. 7.1).

The table contains a number of horizontal grooves. The table is kept slightly inclined in position and is provided with a rocking motion. When water is spread over the ore, lighter impurities are washed away while heavier ore particles get deposited in the grooves, which are finally carried out into the main canal.



#### (ii) Froth Floatation Method: -

This method is suitable for the concentration of Sulphide Ores only. In this method, two



Sulphide Ores only. In this method, two interconnected tanks are used (Fig. 7.2). In one of the tanks, a mixture of ore, oil (pine oil), water and a little quantity of mineral acid is agitated strongly by blowing air through it. Due to the preferential wetting of the sulphide ores by oil than by water, a layer of oil gets covered over the surface of sulphide ores. These sulphide ores become lighter and float over the surface of the mixture, which are carried out into the second container along with the foam formed due to agitation.

#### (iii) Magnetic Separation method: -

This method of concentration is suitable only when there is a difference in the magnetic behavior

between the ores and the impurities. Normally, the magnetic ores containing non-magnetic impurities are concentrated by this method. In this method, a belt is tied over two rollers of which one is made of a magnet (Fig. 7.3). Powdered ore is added over the belt through a hopper. The magnetic part of the ore is attracted by the magnetic roller and forms a heap near it. Whereas the non-magnetic part of the ore forms a separate heap a little away from magnetic part.



#### (iv) Leaching: -

This is a chemical method in which the impure ore is treated with a suitable solvent which dissolves the ore leaving behind the impurities. The solution is filtered, impurities are removed, and the mother liquor is treated with another suitable chemical reagent to get the pure ore.

For example: Impure bauxite ore is treated with dil NaOH solution which dissolves Bauxite to form soluble sodium meta-aluminate.

$$Al_2O_3.2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2O$$

The solution is filtered to remove the impurities. The solution obtained is diluted with plenty of distilled water when a precipitate of  $Al(OH)_3$  is formed.

 $NaAlO_2 + 2H_2O \rightarrow Al(OH)_3 + NaOH$ 

The precipitate obtained is dried and heated strongly to get pure alumina from which aluminium is extracted.

$$2Al(OH)_3 \xrightarrow{\Delta} Al_2O_3 + 3H_2O_3$$

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**3. OXIDATION**: - In this step of metallurgical operation, the concentrated ores are converted into their respective metal oxides. This is achieved by the following two methods:

#### (i) Calcination:

- The process of heating an ore strongly below its melting point in the absence of air or in the limited supply of air is called Calcination.
- > This method is employed for carbonate ores and hydrated ores.
- > Carbon dioxide gas is produced along with metal oxides. Examples:

$$\begin{array}{l} ZnCO_3 \ \rightarrow ZnO \ + \ CO_2 \\ CuCO_3 \ \rightarrow CuO \ + \ CO_2 \end{array}$$

> During calcination following changes takes place:

Moisture is removed:  $Fe_2O_3$ .  $2H_2O \xrightarrow{\Delta} Fe_2O_3 + 2H_2O$ Volatile impurities are removed: S, P etc. are removed as vapours.

Carbonate ores get converted into oxides:  $FeCO_3 \rightarrow FeO + CO_2$ 

#### (ii) Roasting:

- The process of heating an ore strongly below its melting point in a free but controlled supply of air is called Roasting.
- > This method is employed for Sulphide ores.
- > Sulphur dioxide gas is produced along with metal oxides.

Examples: 
$$\begin{array}{ll} 2PbS+3O_2 \rightarrow 2PbO+2SO_2\\ 2Cu_2S+3O_2 \rightarrow 2Cu_2O+2SO_2\\ 2ZnS+3O_2 \rightarrow 2ZnO+2SO_2 \end{array}$$

> The changes taking place during roasting are:

Moisture is removed.

Volatile impurities are removed.

Impurities like sulphur, Arsenic, Phosphorous, etc. are removed in the form of their gaseous oxides:  $S + O_2 \rightarrow SO_2$ 

$$P_4 + 5O_2 \rightarrow 2P_2O_5 \quad , \quad 4As + 3O_2 \rightarrow 2As_2O_3$$

It makes the ore porous.

The process of roasting is carried out in a reverberatory furnace.

**4. REDUCTION**: - In this step of metallurgical operation, the roasted ores are reduced to convert the metal oxides into the respective metals. The various methods of reduction are:

(i) Smelting: - The process of heating a roasted ore strongly above its melting point with a suitable quantity of coke or charcoal is called smelting. During the process of smelting, metal oxides are reduced into their respective metals. For the reduction of the oxides of less electropositive metals such as Zn, Fe, Cu, Cr etc., the reducing agents like Co, Na, K,  $H_2O$  etc. are used.

$$Pb0 + C \rightarrow Pb + C0$$
$$Cu0 + C0 \rightarrow Cu + C0$$

During the process of smelting, an additional chemical substance called 'flux' is added which combines with the solid impurities to form fusible 'slag'.

#### Impurity + Flux $\rightarrow$ Slag

**Flux:** A substance added during the process of smelting to convert the solid gangue into fusible mass (slag) is called flux.

The nature of the flux to be added depends upon the nature of the impurity present. For acidic impurities basic flux are used and for basic impurities acidic flux are used.

Acidic Flux: It is used to remove basic impurities such as metallic oxides. Example:  $FeO + SiO_2 \rightarrow$ 

Example: FeSiO<sub>3</sub>(Slag)

Impurity flux (Basic) (Acidic)

**Basic flux:** It is used to remove acidic impurity such as sand.

 $Ca SiO_3$ (Slag)

Impurity

(Acidic) (Basic)

Flux

 $SiO_2 + CaO \rightarrow$ 

**Slag:** It is the fusible mass obtained during the process of smelting when flux combines with the solid impurities.

Example:  $SiO_2 + CaO \rightarrow CaSiO_3$ Smelting is carried out in a blast furnace (fig. 7.4) which is a tall cylindrical furnace made of steel



plates lined inside with fire bricks. Since the density of slag is lower, it floats over the molten metal. The molten metal is tapped out at the bottom of the furnace.

- **5. REFINING:** The metals obtained after reduction still contain some impurities. The process of removal of impurities from crude metal is called refining. The method of refining to be followed depends upon the nature of the metal and the impurity contaminated with it. The following are the methods of refining:
  - (i) **Distillation Method**: This method of refining is suitable for volatile metals like Hg, Zn, Pb contaminated with non-volatile impurities. The impure metal is heated in a distillation flask attached with a water condenser. During heating the volatile metal gets evaporated and condensed which is collected in a separate container while the non-volatile impurities are left at the bottom of the distillation flask.



(ii) Electro refining: - This method is employed to refine the less electropositive metals such as Zn, Pb, Cu, Al. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode (Fig. 7.5). Both the electrodes are dipped in a suitable aqueous salt solution of the concerned metal. During the process of electrolysis, the impure metal dissolves in its aqueous salt solution providing metal ions which get discharged and deposited at the cathode.

#### **ASSIGNMENT**

- 1. Define Minerals and Ores. Give examples.
- 2. Differentiate between Minerals and Ores.
- 3. Which method is employed for the concentration of Sulphide Ores and why? Explain the process.
- 4. Explain leaching.
- 5. Explain gravity separation method.
- 6. Explain magnetic separation method of concentration of ores.
- 7. Differentiate between Calcination and Roasting.
- 8. What is smelting?
- 9. Explain Electrolytic Refining.
- 10. Define Flux and Slag with examples.
- 11. Define gangue.

#### **Exercise**

#### (02 Marks Questions)

- 1. What do you mean by gangue?
- 2. Mention the basic steps involved in the metallurgical operation.
- 3. What do you mean by concentration of ore?
- 4. What happens during oxidation step of metallurgical operation?
- 5. What happens during reduction step of metallurgical operation?
- 6. Why only sulphide ores are concentrated by froth floatation method?
- 7. Which types of ores are concentrated by magnetic separation?
- 8. Which types of ores are concentrated by gravity separation method?
- 9. What is leaching?
- 10. What is the purpose of adding charcoal or coke during smelting?
- 11. What do you mean by smelting?
- 12. Define calcinations and roasting.
- 13. What is slag?
- 14. What is the principle of distillation method of refining of crude metals?
- 15. What is electrometallurgy?
- 16. What is the purpose of addition of flux during smelting?

#### (05 Marks questions)

- 1. Explain the gravity separation method of concentration of ores.
- 2. Explain the froth floatation method of concentration of ores.
- 3. Explain the magnetic separation method of concentration of ores.
- 4. Explain the gravity leaching process of concentration of ores.
- 5. Define calcinations. Write down its functions.
- 6. Define roasting. Write down its function.
- 7. Define and explain smelting.
- 8. Explain the electrolytic method of purification of impure copper.

# <u>CHAPTER – 8</u> <u>ALLOYS</u>

**Alloy:** The homogeneous material obtained by melting together metals or metals with non-metals or metals with metalloids is called an alloy.

Types of alloys:

- 1. **Ferro Alloys:** The alloy containing iron as the main constituent is called a ferro alloy. Example: Stainless Steel, Manganese Steel etc.
- 2. **Non-Ferro Alloy:** The alloy which does not contain iron as the main constituent is called as non-ferro alloy.

Example: Brass, Bronze, Gun metal etc.

 Amalgam: Alloys containing mercury as one of the constituents is called amalgam. Example: Silver Amalgam, Sodium amalgam, Copper amalgam is used for filling dental cavities; Tin amalgam is used for silvering cheap mirrors.

#### SI. No. Uses Allovs Composition 1. Cu: 60 - 90% It is used in making: Brass Zn: 10 – 40% Utensils, Jewellery, Musical instrument, Battery caps, Condenser Tubes, Name plates, etc. 2. Cu: 80 - 95% It is used in making: Bronze Sn: 5 – 20% Making imitation jewellery, Water fittings, Statues, Medals, Turbine blades, Pump Valves, Coins, etc. 3. Steel: 50% It is used in making: Alnico AI: 20% Permanent Magnet. Ni: 21% Co: 9% It is used in making: 4. Duralumin AI: 95% Cu: 4% Air ships, Light weight vehicular Mn: 0.5% parts, etc. Mg: 0.5%

#### COMPOSITION AND USES OF BRASS, BRONZE, ALNICO AND DURALUMIN

#### ASSIGNMENT

- 1. Define Alloy. Classify them as ferro and non-ferro alloys with examples.
- 2. What is amalgam? Give examples.
- 3. Give the composition and uses of Brass, Bronze, Alnico and Duralumin.

#### **Exercise**

#### (02 Marks Questions)

- 1. What is alloy? Give an example of non-ferrous alloy.
- 2. What is amalgam? How is it formed?
- 3. What is the composition and uses of Brass?
- 4. What is the composition and uses of Bronze?

#### (05 Marks Questions)

- 1. Define alloy. Write down the composition and uses of Brass and Bronze.
- 2. Define alloy. Classify alloys into different types with examples.
- 3. Define alloy. What do you mean by amalgam? Write the important uses of amalgams.