



Bhubanananda Orissa School of Engineering

Engineering Chemistry

LECTURE NOTES

Branches: 1 st/2nd semester

Prepared by: SUBHASMITA NAYAK

Lecturer (Chemistry)

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Syllabus

Th.2b. Engineering Chemistry(1st / 2nd Semester Common)

Theory: 4 Periods per Week

Total Periods: 60 Periods

Examination: 3 Hours

I.A: 20 Marks

Term End Exam: 80 Marks

TOTAL MARKS: 100 Marks

Objective:

Engineering Chemistry is concerned with the changes of matters with its environment and an ever growing subject. So, the aim of teaching Engineering Chemistry in Diploma Courses is to acquaint the students with the basic Chemistry of different materials used in industry and to equip the students with the basic principles of chemical changes taking place in different aspects connected to engineering fields. They also develop the right attitude to cope up with the continuous flow of new technology.

Topic wise distribution of periods

Sl. No	Topics/ Units	Periods
A	Physical Chemistry	22
B	Inorganic Chemistry	08
C	Organic Chemistry	10
D	Industrial Chemistry	20
	TOTAL	60

A. PHYSICAL CHEMISTRY

Chapter 1: Atomic structure: Fundamental particles (electron, proton & neutron Definition, mass and charge). Rutherford's Atomic model (postulates and failure), Atomic mass and mass number, Definition, examples and properties of Isotopes, isobars and isotones. Bohr's Atomic model (Postulates only), Bohr- Bury scheme, Aufbau's principle, Hund's rule, Electronic configuration (up to atomic no 30).

Chapter 2: Chemical Bonding: Definition, types (Electrovalent, Covalent and Coordinate bond with examples (formation of NaCl, MgCl₂, H₂, Cl₂, O₂, N₂, H₂O, CH₄, NH₃, NH₄⁺, SO₂).

Chapter 3: Acid base theory: Concept of Arrhenius, Lowry Bronsted and Lewis theory for acid and base with examples (Postulates and limitations only). Neutralization of acid & base. Definition of Salt, Types of salts (Normal, acidic, basic, double, complex and mixed salts, definitions with 2 examples from each).

Chapter 4: Solutions: Definitions of atomic weight, molecular weight, Equivalent weight. Determination of equivalent weight of Acid, Base and Salt. Modes of expression of the concentrations (Molarity, Normality &

Molality) with Simple Problems. pH of solution (definition with simple numerical) Importance of pH in industry (sugar, textile, paper industries only)

Chapter 5: Electrochemistry: Definition and types (Strong & weak) of Electrolytes with example. Electrolysis (Principle & process) with example of NaCl (fused and aqueous solution). Faraday's 1st and 2nd law of Electrolysis (Statement, mathematical expression and Simple numerical) Industrial application of Electrolysis- Electroplating (Zinc only).

Chapter 6: Corrosion: Definition of Corrosion, Types of Corrosion- Atmospheric Corrosion, Waterline corrosion. Mechanism of rusting of Iron only. Protection from Corrosion by (i) Alloying and (ii) Galvanization.

B. INORGANIC CHEMISTRY

Chapter 7: Metallurgy: Definition of Mineral, ores, gangue with example. Distinction between Ores and Minerals. General methods of extraction of metals,

- i) Ore Dressing
- ii) Concentration (Gravity separation, magnetic separation, Froth floatation & leaching)
- iii) Oxidation (Calcinations, Roasting)
- iv) Reduction (Smelting, Definition & examples of flux, slag)
- v) Refining of the metal (Electro refining, & Distillation only)

Chapter 8: Alloys: Definition of alloy. Types of alloys (Ferro, Non-Ferro & Amalgam) with example. Composition and uses of Brass, Bronze, Alnico, Duralumin

C. ORGANIC CHEMISTRY

Chapter 9: Hydrocarbons: Saturated and Unsaturated Hydrocarbons (Definition with example) Aliphatic and Aromatic Hydrocarbons (Huckle's rule only). Difference between Aliphatic and aromatic hydrocarbons. IUPAC system of nomenclature of Alkane, Alkene, Alkyne, alkyl halide and alcohol (up to 6 carbons) with bond line notation. Uses of some common aromatic compounds (Benzene, Toluene, BHC, Phenol, Naphthalene, Anthracene and Benzoic acid) in daily life.

D. INDUSTRIAL CHEMISTRY

Chapter 10: Water Treatment: Sources of water, Soft water, Hard water, hardness, types of Hardness (temporary or carbonate and permanent or non-carbonate), Removal of hardness by lime soda method (hot lime & cold lime— Principle, process & advantages), Advantages of Hot lime over cold lime process. Organic Ion exchange method (principle, process, and regeneration of exhausted resins)

Chapter 11: Lubricants: Definition of lubricant, Types (solid, liquid and semisolid with examples only) and specific uses of lubricants (Graphite, Oils, Grease), Purpose of lubrication

Chapter 12: Fuel: Definition and classification of fuel, Definition of calorific value of fuel, Choice of good fuel. Liquid: Diesel, Petrol, and Kerosene --- Composition and uses. Gaseous: Producer gas and Water gas (Composition and uses). Elementary idea about LPG, CNG and coal gas (Composition and uses only).

Chapter 13: Polymers: Definition of Monomer, Polymer, Homo-polymer, Co-polymer and Degree of polymerization. Difference between Thermosetting and Thermoplastic, Composition and uses of Polythene, & Poly-Vinyl Chloride and Bakelite. Definition of Elastomer (Rubber). Natural Rubber (its drawbacks). Vulcanisation of Rubber. Advantages of Vulcanised rubber over raw rubber.

Chapter 14: Chemicals in Agriculture: Pesticides: Insecticides, herbicides, fungicides Examples and uses. Bio Fertilizers: Definition, examples and uses.

Syllabus Coverage up to I.A

Chapter 1,2,3,4,5,6

Books Recommended

1. Textbook of Intermediate Chemistry Part-1 and Part-2 by Nanda, Das, Sharma, Kalyani Publishers
2. Engg. Chemistry by B.K. Sharma, Krishna Prakashan Media Pvt. Ltd
3. Engineering Chemistry by Y.R. Sharma and P. Mitra, Kalyani Publishers
4. Engineering Chemistry for Diploma – Dr. R K Mohapatra, PHI Publication, New Delhi.
5. Engineering Chemistry- Jain & Jain, Dhanpat Roy and Sons.

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 9.11×10^{-31} kg and carrying a charge of -1.602×10^{-19} Coulomb.

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

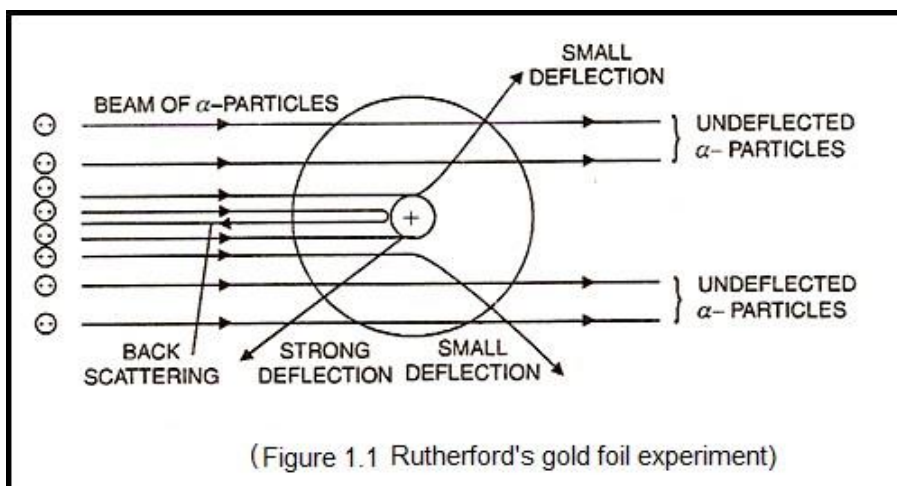
Neutron: Neutron is a fundamental sub-atomic particle having mass of 1.675×10^{-27} Kg and carrying no charge.

Fundamental Particle	Mass	Charge	Relative Charge
Electron	9.11×10^{-31} Kg	-1.602×10^{-19} Coulomb	-1
Proton	1.672×10^{-27} Kg	$+1.602 \times 10^{-19}$ Coulomb	+1
Neutron	1.675×10^{-27} Kg	0	0

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

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

particles (He^{2+} ions) emitting from a radioactive material like Uranium on a very thin gold foil. A circular zinc sulphide (ZnS) screen was provided at the backside of the gold foil in order to register the impressions made by the α -particles (Fig. 1.1).



Observations and Conclusions:

From the α -scattering experiment, Rutherford observed that:

1. Most of the α -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%) α -particles were found to be retraced their original paths (deflected through almost 180°). This indicates that the size of nucleus is very small. The size of atomic nuclei is of the order of 10^{-13} cm.

RUTHER FORD'S ATOMIC MODEL:

Based on the conclusions drawn from the α -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.

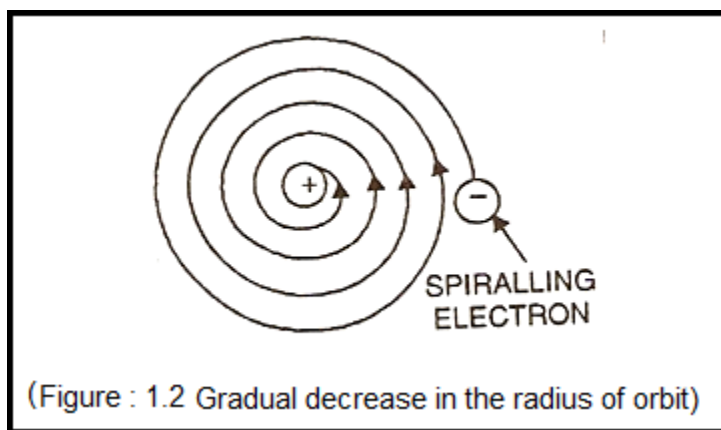
DRAWBACKS OR FAILURES OF RUTHERFORD'S ATOMIC MODEL:

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.

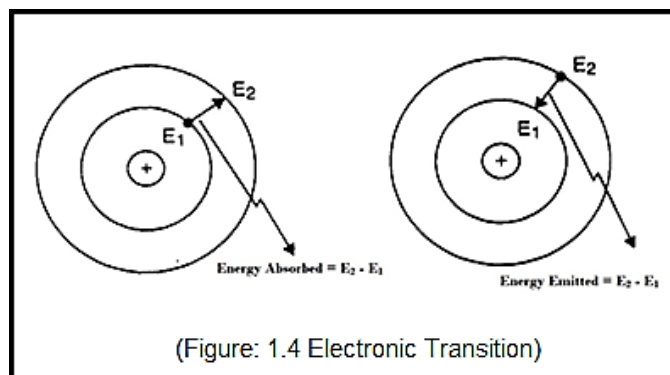


Bohr's Atomic Model:

1. Electrons revolve around the nucleus in a fixed circular path termed “orbits” or “shells” or “energy level.”
2. The orbits are termed as “stationary orbit.”
3. Every circular orbit will have a certain amount of fixed energy and these circular orbits were termed orbital shells. The electrons will not radiate energy as long as they continue to revolve around the nucleus in the fixed orbital shells.
4. The different energy levels are denoted by integers such as $n=1$ or $n=2$ or $n=3$ and so on. These are called quantum numbers. The range of quantum numbers may vary and begin from the lowest energy level (nucleus side $n=1$) to the highest energy level. Learn the concept of an Atomic number [here](#).
5. The different energy levels or orbits are represented in two ways such as 1, 2, 3, 4... or K, L, M, N..... shells. The lowest energy level of the electron is called the ground state. Learn the concept of Valency here in detail [here](#).
6. The change in energy occurs when the electrons jump from one energy level to other. In an atom, the electrons move from lower to higher energy level by acquiring the required energy. However, when an electron loses energy it moves from higher to lower energy level.

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:

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

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

- The outer most shell (valence shell) of an element cannot hold more than 8 electrons.
- The penultimate shell (the shell just before the outer most shell) cannot hold more than 18 electrons.
- 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-Buryscheme are given below:

Element	Electrons in			
	K- Shell	L-Shell	M-Shell	N-Shell
${}_1\text{H}$	1			
${}_2\text{He}$	2			
${}_3\text{Li}$	2	1		
${}_4\text{Be}$	2	2		
${}_5\text{B}$	2	3		
${}_{10}\text{Ne}$	2	8		
${}_{11}\text{Na}$	2	8	1	
${}_{12}\text{Mg}$	2	8	2	
${}_{13}\text{Al}$	2	8	3	
${}_{18}\text{Ar}$	2	8	8	
${}_{19}\text{K}$	2	8	8	1
${}_{20}\text{Ca}$	2	8	8	2
${}_{21}\text{Sc}$	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:

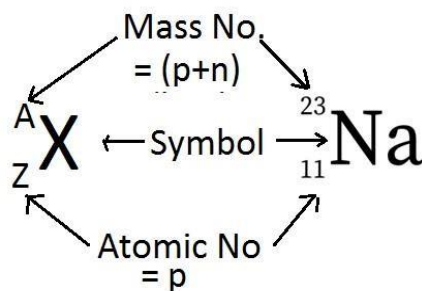
Element	No of Protons (p)	Atomic No. (Z)
Carbon (C)	6	6
Nitrogen (N)	7	7
Oxygen (O)	8	8

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)
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Carbon (C)	6	6	12
Nitrogen (N)	7	7	14
Sodium (Na)	11	12	23



Note: $A - ne^- \rightarrow A^{n+}$ Example: $Mg - 2e^- \rightarrow Mg^{2+}$

$A + ne^- \rightarrow A^{n-}$ Example: $N + 3e^- \rightarrow N^{3-}$

Assignment:

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

Atom/Molecule/ion	P	e	n
O			
P			
N^{3-}			
Ca^{2+}			
NH_3			
H_2O			
NH_4^+			
CO			
CO ₂			

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

Examples: Hydrogen has three isotopes: Protium (1H), Deuterium (2H) and Tritium (3H). Similarly, $^{35}_{17}Cl$ and $^{37}_{17}Cl$.

Properties of Isotopes:

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

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

Aufbau Principle:

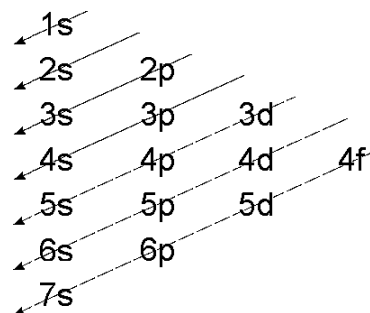
The word “*Aufbau*” means —**building up**. This principle describes how the sub-shells are filled with electrons.

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+l) rule.

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

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < \dots$$



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
${}_1\text{H}$	$1s^1$	${}_{16}\text{S}$	$1s^2 2s^2 2p^6 3s^2 3p^4$
${}_2\text{He}$	$1s^2$	${}_{17}\text{Cl}$	$1s^2 2s^2 2p^6 3s^2 3p^5$
${}_3\text{Li}$	$1s^2 2s^1$	${}_{18}\text{Ar}$	$1s^2 2s^2 2p^6 3s^2 3p^6$
${}_4\text{Be}$	$1s^2 2s^2$	${}_{19}\text{K}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$
${}_5\text{B}$	$1s^2 2s^2 2p^1$	${}_{20}\text{Ca}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
${}_6\text{C}$	$1s^2 2s^2 2p^2$	${}_{21}\text{Sc}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$
${}_7\text{N}$	$1s^2 2s^2 2p^3$	${}_{22}\text{Ti}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
${}_8\text{O}$	$1s^2 2s^2 2p^4$	${}_{23}\text{V}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
${}_9\text{F}$	$1s^2 2s^2 2p^5$	${}_{24}\text{Cr}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
${}_{10}\text{Ne}$	$1s^2 2s^2 2p^6$	${}_{25}\text{Mn}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
${}_{11}\text{Na}$	$1s^2 2s^2 2p^6 3s^1$	${}_{26}\text{Fe}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
${}_{12}\text{Mg}$	$1s^2 2s^2 2p^6 3s^2$	${}_{27}\text{Co}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
${}_{13}\text{Al}$	$1s^2 2s^2 2p^6 3s^2 3p^1$	${}_{28}\text{Ni}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
${}_{14}\text{Si}$	$1s^2 2s^2 2p^6 3s^2 3p^2$	${}_{29}\text{Cu}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
${}_{15}\text{P}$	$1s^2 2s^2 2p^6 3s^2 3p^3$	${}_{30}\text{Zn}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

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

The electronic configurations of Cr & Cu should be:

${}_{24}\text{Cr} = [\text{Ar}] 4s^2 3d^4$ & ${}_{29}\text{Cu} = [\text{Ar}] 4s^2 3d^9$ respectively. But

the actual electronic configurations are

${}_{24}\text{Cr} = [\text{Ar}] 4s^1 3d^5$ & ${}_{29}\text{Cu} = [\text{Ar}] 4s^1 3d^{10}$

The exceptional electronic configuration is due to the fact that half-filled and full-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^{2-} , Ca^{2+} , P^{3-} , Ti^{2+} , Cr^{3+} , Cu^{2+} .

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+1) rule? Which out of 4s and 3d sub-shells has lower energy?

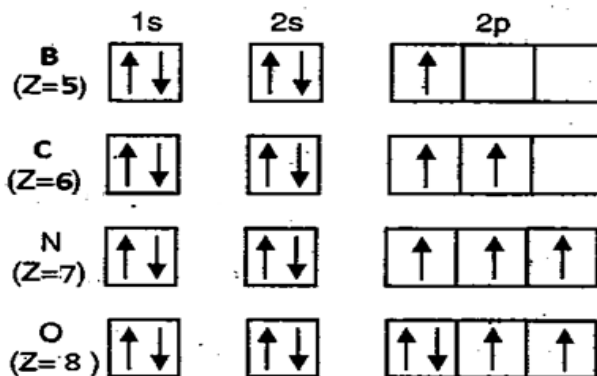
Q 4. What do you mean by $3d^2$?

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 5th electron is occupied by the $2p_x$ orbital. In carbon the 6th 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 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.

NOTE:- 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^+ ?

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^{2+} and O^{2-} .
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^{3-} ?
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 valence 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 Ionic bond: The formation of ionic bond involves:

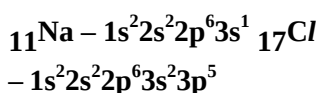
- ☞ Formation of a positive ion by loss of electron/s from one kind of atom.
- ☞ Formation of a negative ion by gain of electron/s from another kind of atom.
- ☞ Electrostatic force of attraction between the oppositely charged ions.

Conditions for the formation of Ionic bond:

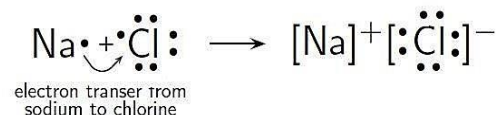
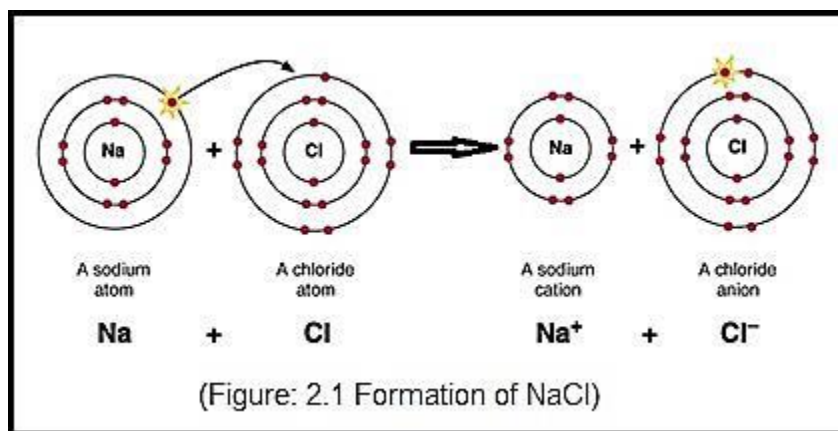
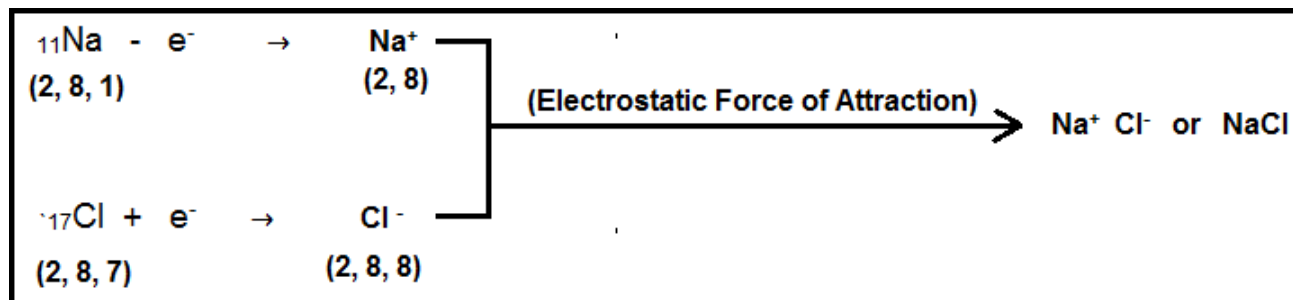
- 1. Nature of element:** Atoms of different elements form ionic bonds. Atoms of the same element never form *ionic bond*.
- 2. Low Ionization potential:** Ionization potential of an element is the quantity of energy required to remove one valence electron from an isolated, neutral, gaseous atom. One 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 NaCl.

The electronic configurations of Na and Cl are given below:



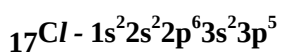
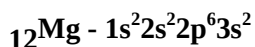
The electronic configurations indicate the presence of one and seven valence electrons in sodium and chlorine respectively. During the formation of NaCl , the sodium atom donates its valence electron completely to the chlorine atom (Fig. 2.1). Na becomes Na^+ with 8 electrons in valence shell and attains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



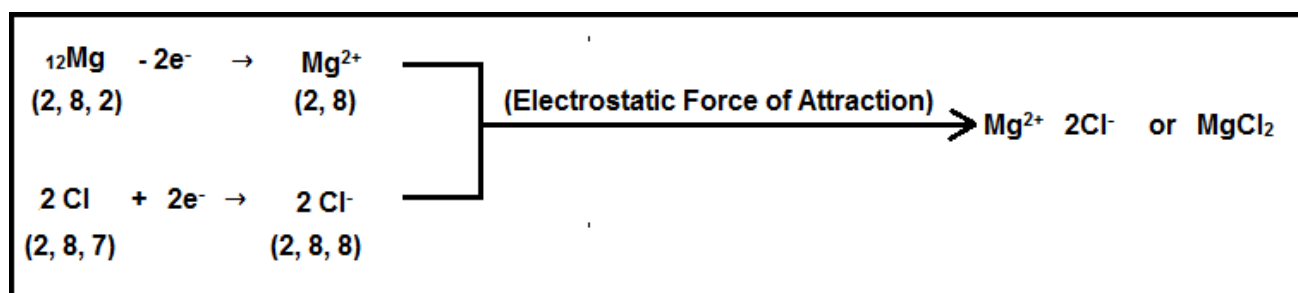
Now the electrostatic force of attraction between the oppositely charged ions Na^+ and Cl^- results in the formation of NaCl .

Example : II : **Formation of MgCl_2**

The electronic configurations of Mg and Cl are given below:



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 Cl^- 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 **MgCl₂**.

Other examples of ionic compounds: KCl, KBr, KI, CaF₂, CaBr₂, CaI₂, Na₂O, K₂O, CaO, MgO, Na₂S, K₂S etc.

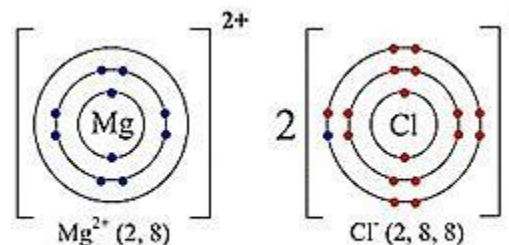


Figure: 2.2

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 CCl₄, ethers, benzene, toluene [C₆H₅ - CH₃], 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.

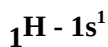
COVALENT BOND:

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 H₂ molecule.

The electronic configuration of H is



The electronic configuration indicates the presence of 1

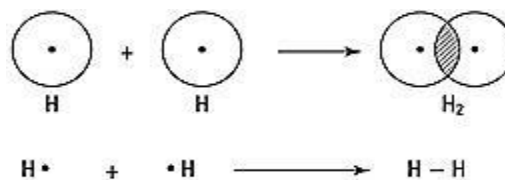
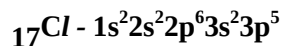


Figure: 2.3

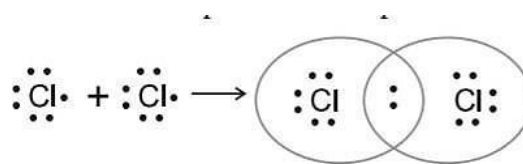
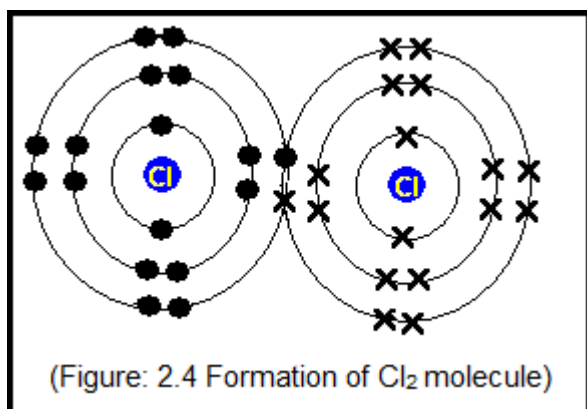
valence electron in $\text{H}^\bullet$ and requires one more electron to become duplet. Thus, each hydrogen atom shares its electron with each other to form a covalent bond (Fig. 2.3).

Example : 2 : Formation of Cl_2 molecule.

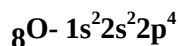
The electronic configuration of ' Cl ' is



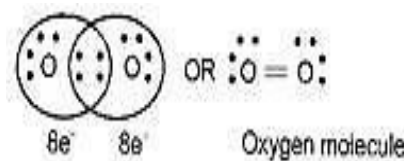
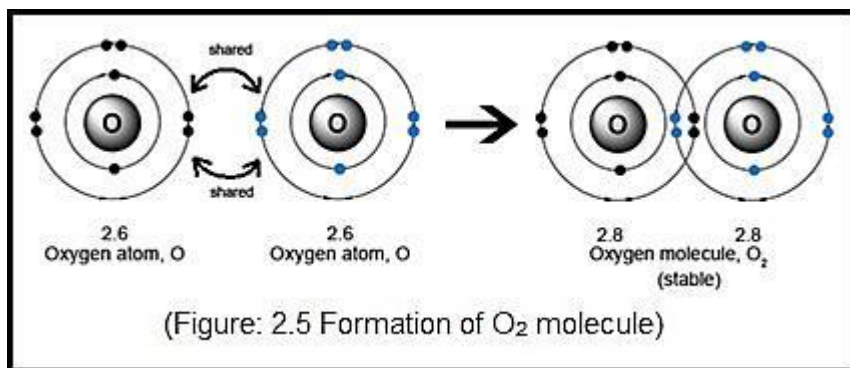
The electronic configuration indicates the presence of 7 valence electrons in $\text{Cl}^\bullet$ and requires one more electron to become octet. Thus, each chlorine atom shares one of its valence electrons with each other to form a covalent bond (Fig. 2.4).



Example-3 : Formation of O_2 molecule. The electronic configuration of ' O ' is

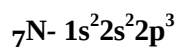


The electronic configuration indicates the presence of 6 valence electrons in $\text{O}^\bullet$ and requires two more electrons to become octet. Thus, each oxygen atom shares two of its valence electrons with each other to form a double covalent bond (Fig. 2.5).

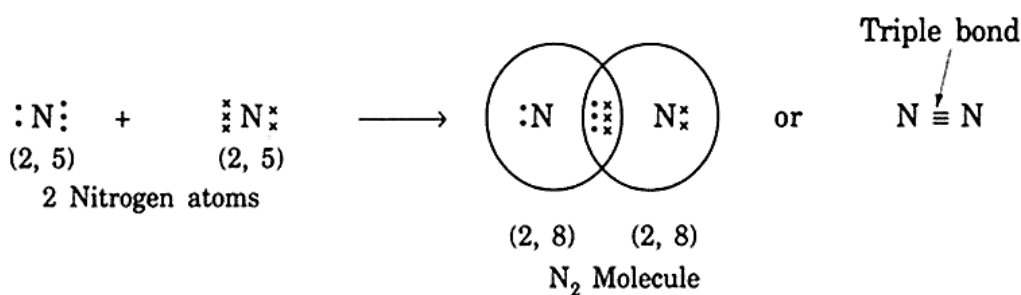
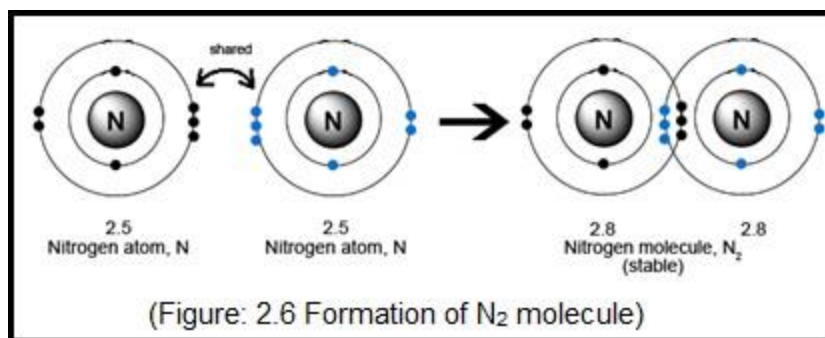


Example : 4 : Formation of N_2 molecule.

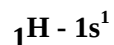
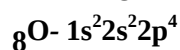
The electronic configuration of ' N ' is



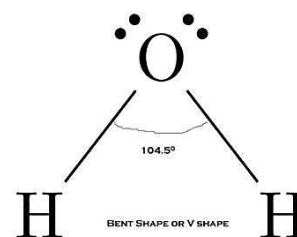
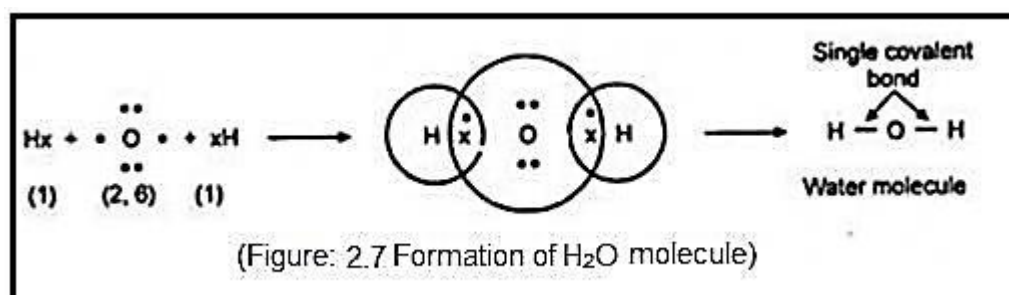
The electronic configuration indicates the presence of 5 valence electrons in $\text{N}^\bullet$ and requires three more electrons to become octet. Thus, each nitrogen atom shares three of its valence electrons with each other to form a triple covalent bond (Fig. 2.6).



Example : 5 : Formation of H₂O molecule. The electronic configuration of 'O' and 'H' are:

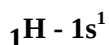
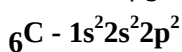


The electronic configurations indicate the presence of 6 and 1 valence electrons in O and H respectively. The central O atom requires two more electrons to become octet while each hydrogen atom needs one electron to become duplet. Thus, each hydrogen atom shares its valence electron with the valence 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°.



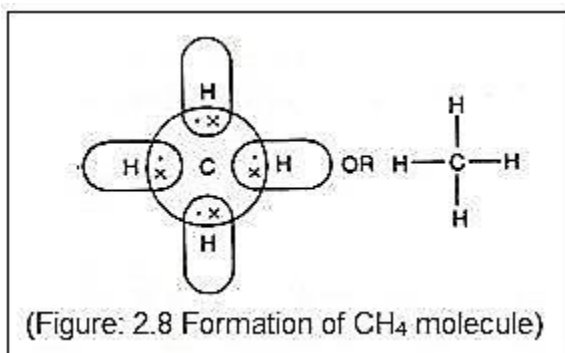
Example: 6: Formation of methane (CH₄) molecule.

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



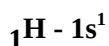
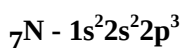
The electronic configurations indicate the presence of 4 & 1 valence electrons in C & H respectively. Thus, the central carbon atom requires four more electrons to become octet and H requires 1 more electron to become duplet.

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 CH₄ is tetrahedral with a bond angle of 109°28 (Fig. 2.8)

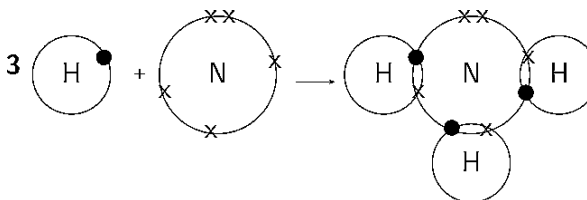
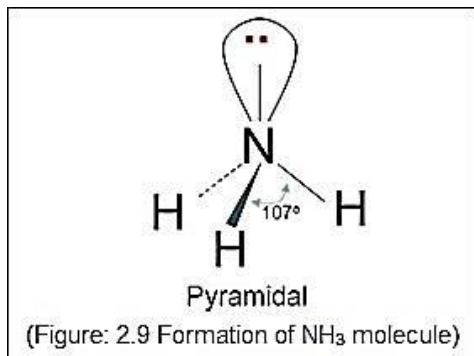


Example: 7: Formation of ammonia (NH₃) molecule.

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



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 NH₃ is pyramidal with a bond angle of 107°.

Other examples of covalent compounds: , F₂, Br₂, I₂, BF₃, AlCl₃, HCl, HF, SiO₂, 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 CCl₄, 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.

CO-ORDINATE BOND:

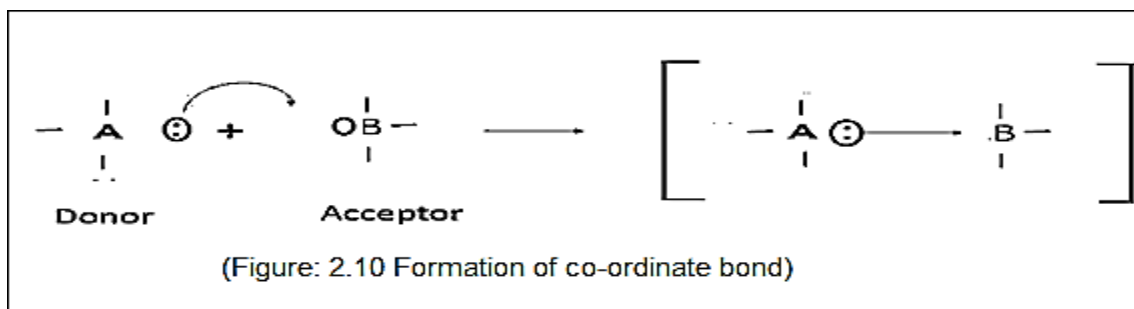
The chemical bond formed by the partial donation and partial sharing of a lone pair of electrons between two atoms (or ions) is called a co-ordinate or dative bond.

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

- One of the participating atoms should have at least one lone or unshared pair of electrons.
- 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 co-ionic bond.

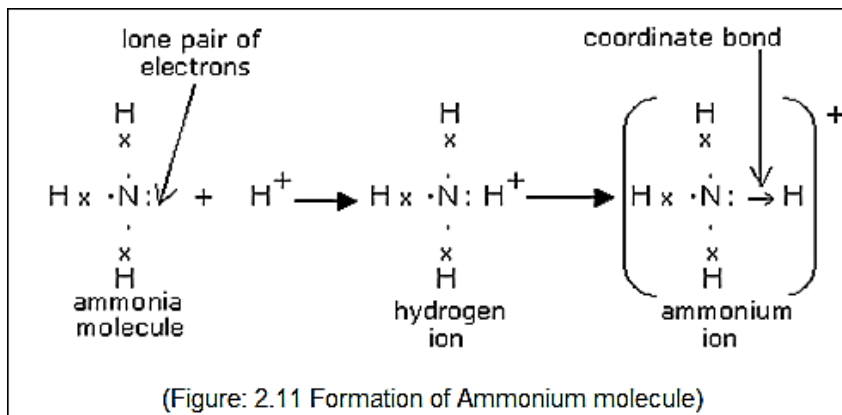


Example: 1: Formation of ammonium ion (NH_4^+).

Ammonium ion (NH_4^+) is formed by the combination of NH_3 and H^+ ion. $\text{NH}_3 + \text{H}^+ \rightarrow \text{NH}_4^+$

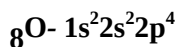
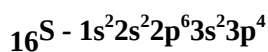
Ammonia (NH_3) contains a lone pair of electrons over N while H^+ ion contains no electron and requires two electrons to become duplet.

Thus, the unshared pair of electrons over nitrogen in NH_3 is partially shared with H^+ ion and a Co-ordinate bond is formed (Fig. 2.11).

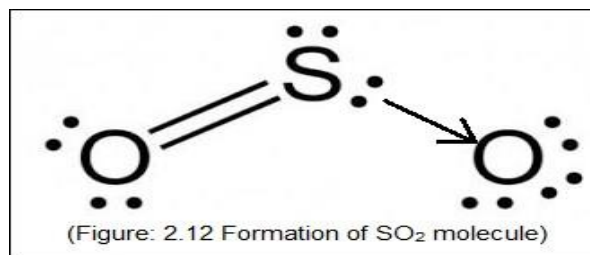


Example: 2: Formation of Sulphur dioxide (SO_2) molecule.

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).

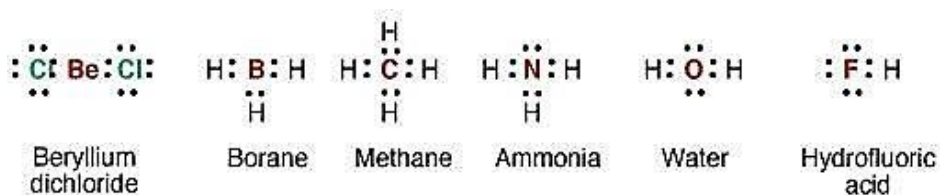


Characteristics of Coordinate Compound:

- i. These bonds are rigid and directional.
- ii. Coordinate bonds do not ionise in a state of fusion or 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:



Assignment

Q. Draw the Lewis structures of the following: MgCl₂, O₂, N₂, SO₂, NH₄⁺ and H₃O⁺.

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_2 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_2 molecule.
15. Write down at least ten properties of ionic compounds.
16. Write down at least ten properties of covalent compounds.

CHAPTER - 3

ACID – BASE THEORIES

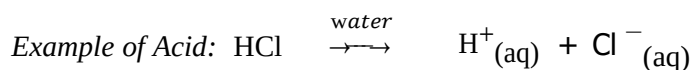
Introduction:

There are many practical methods to identify a substance as an acid or a base. The practical methods include use of p^H 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:

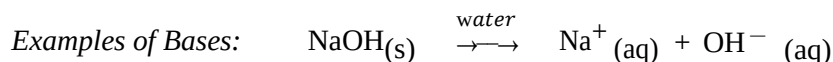
1. Arrhenius Theory
2. Lowery – Bronsted Theory
3. Lewis Theory.

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.¶



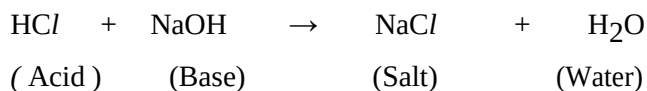
Other examples of acids are: HNO_3 , H_2SO_4 , CH_3COOH , etc.



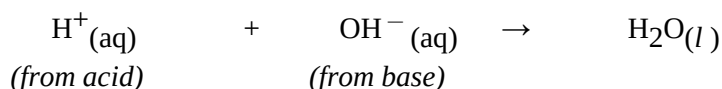
Other examples of bases are: $LiOH$, KOH , NH_4OH , $Ca(OH)_2$, $Al(OH)_3$, etc

Salient Features:

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



Neutralization reaction may be represented as:



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

Limitations:

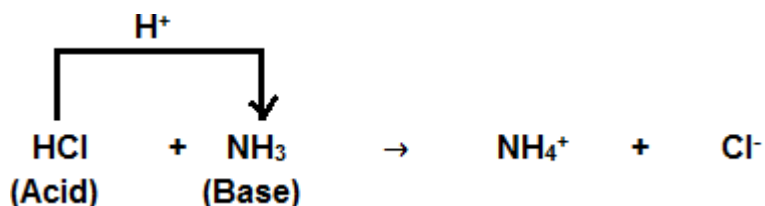
- i. H^+ ion does not exist in aqueous solution. It combines with H_2O , as soon as its formation to give hydronium ion (H_3O^+).
$$H^+ + H_2O \rightarrow H_3O^+$$
- ii. The theory fails to explain the acidic and basic nature of the substances in solvents other than water.
- iii. The theory fails to explain the acidic nature of the substances like SO_2 , CO_2 , SiO_2 , P_2O_5 , BF_3 , $AlCl_3$, etc. which cannot provide H^+ ions.

- iv. The theory fails to explain the basic nature of the substances like NH_3 , PH_3 , Na_2O , K_2O , CaO etc. which can't provide OH^- ions.
- v. The theory fails to explain neutralization reactions between some acidic and basic substances which do not produce water. $\text{HCl} + \text{NH}_3 \rightarrow \text{NH}_4\text{Cl}$

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 bases are proton acceptors. For example:



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

Other examples of Acids are:

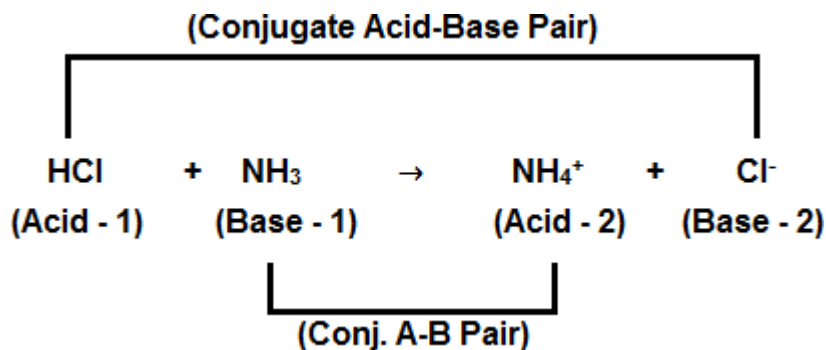
- i. All Arrhenius acids are Bronsted-Lowry acids; (HCl , HNO_3 , H_2SO_4 , H_3PO_4 , CH_3COOH , H_2CO_3 etc.), however the reverse is not true.
- ii. Ions having capacity to donate H^+ ion: (HS^- , HCO_3^- , HPO_4^{2-} , HSO_4^- etc.)

Examples of Bases:

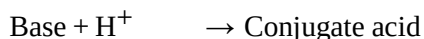
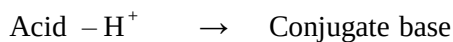
- i. Natural molecules such as: H_2O , NH_3 , RNH_2 , PH_3 , AsH_3 , etc.
- ii. Ions having capacity to accept H^+ ion, like OH^- , CN^- , HCO_3^- , etc.

Salient Features:-

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

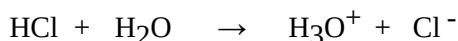


The pair of acid and base which differ by a proton (H^+ ion) is called a conjugate acid-base pair.



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.



[Strong acid]

[Weak base]

Limitations of the theory:

- 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^+ ion.
- It fails to explain the basic nature of the substances, such as Na_2O , K_2O , CaO etc. which cannot accept H^+ ion.
- It fails to explain the reaction between some acids and bases which do not give another pair of acid and base.
Example: $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$.

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

Acid	Conjugate- Base	Base	Conjugate- Acid
HCl	Cl^-	Br^-	HBr
H_2SO_4	HSO_4^-	CN^-	
	S^{2-}	O^{2-}	OH^-
NH_4^+	NH_3	NH_3	NH_4^+
H_2O	OH^-	H_2O	H_3O^+

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 , $(\text{C}_2\text{H}_5)_2\text{NH}$, 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: -

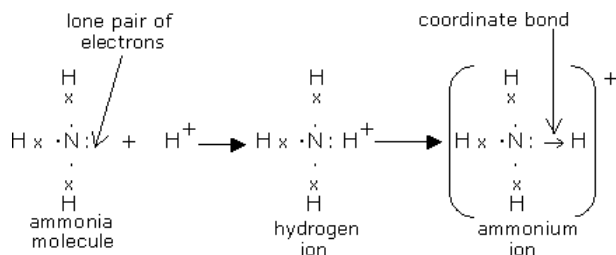
- Cations like: CH_3^+ , H^+ , etc.
- Neutral molecules containing electron deficient atoms are Lewis acids. For example: BF_3 , AlCl_3 , FeCl_3 , ZnCl_2 , etc.
- Neutral molecules containing vacant d-orbitals in the central atom for the accommodation of incoming electrons act as Lewis acids. For example: SiF_4 , SiCl_4 , etc.
- The molecules having multiple bonding ($=$ or $\equiv$) between the atoms of different elements are acidic in nature. For example: CO_2 ($\text{O}=\text{C}=\text{O}$), SO_2 , etc.

Examples of Bases: -

- All anions are Lewis bases: F^- , Cl^- , CO_3^{2-} , etc.
- Neutral molecules containing, at least one lone pair of electrons are Lewis bases: Examples: NH_3 , PH_3 , H_2O , etc.

Salient Features:

- According to this theory, an acid reacts with a base to form a co-ordinate or dative bond. For example, the reaction between NH_3 (Lewis base) and H^+ (Lewis acid) results in the formation of a dative bond.



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

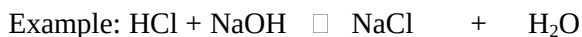
Limitations:

- 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.
- The theory fails to explain the relative strengths of different acids and bases.
- It fails to explain reaction between some acids and bases where no coordinate bond is formed.
- It fails to explain the acidic nature of well-known acids like HCl , HNO_3 , H_2SO_4 , etc. which cannot accept electrons.
- It fails to explain the basic nature of well-known bases like $NaOH$, KOH , etc. which cannot donate electrons.
- It fails to explain acid-catalyzed reactions, where H^+ 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:

- 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^H of about 7 and is neutral.



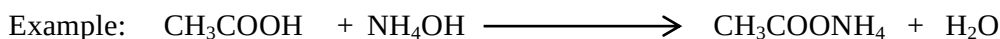
- Neutralization between a Strong Acid and a weak Base:** A strong acid reacts with a weak base to form an acidic salt. Its aqueous solution has a $p^H < 7$ and the solution is acidic.



3. **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 $p^H > 7$ and is alkaline.



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 $p^H > 7$ and is alkaline.



SALTS:

Defⁿ (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.

Defⁿ (2) : Salts are ionic compounds which produce cation other than H^+ and anion other than OH^- in aqueous solution.

Defⁿ (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:	Acids	Normal salts
	HCl	NaCl, KCl, CaCl_2 , MgCl_2 , etc
	HNO_3	NaNO_3 , KNO_3 , $\text{Ca}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$, etc.
	H_2SO_4	Na_2SO_4 , K_2SO_4 , CaSO_4 , MgSO_4 , etc.
	H_3PO_4	Na_3PO_4 , K_3PO_4 , $\text{Ca}_3(\text{PO}_4)_2$, $\text{Mg}_3(\text{PO}_4)_2$, 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:	Acids	Acidic salts
	H_2SO_4	NaHSO_4 , KHSO_4 etc.
	H_3PO_4	NaH_2PO_4 , KH_2PO_4 , Na_2HPO_4 , K_2HPO_4 etc.

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

For examples: NH_4Cl , NH_4NO_3 , $(\text{NH}_4)_2\text{SO}_4$, 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: $\text{Ca}(\text{OH})\text{Cl}$, $\text{Mg}(\text{OH})\text{Cl}$, $\text{Zn}(\text{OH})\text{Cl}$, $\text{Al}(\text{OH})_2\text{Cl}$ etc.

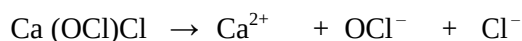
Also, these are the salts obtained by the neutralization reaction between weak acids and strong bases.

For examples: CH_3COONa , CH_3COOK , Na_2CO_3 , K_2CO_3 , 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. Other examples: Mohr's Salt $[\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}]$, carnalite $(\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O})$, etc.

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

Examples: Bleaching powder $\text{Ca}(\text{OCl})\text{Cl}$; Sodium potassium sulphate NaKSO_4 , etc.



Exercise

(02 Marks Questions)

1. Define Arrhenius theory of acids and bases.
2. Define Bronsted-Lowry theory of acids and bases.
3. Define Lewis theory of acids and bases.
4. Justify that all Arrhenius acids are Bronsted-Lowry 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 AlCl_3 is a Lewis acid.
9. Explain how SO_2 is a Lewis acid.
10. Explain how NH_3 is both a Bronsted-Lowry 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_3COOH is a weak acid while CH_3COO^- 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-Lowry 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-Lowry theory.
6. Explain the limitations of Lewis theory.
7. Justify that all Arrhenius acids are Bronsted-Lowry acids, but all Arrhenius bases are not Bronsted-Lowry bases.
8. Explain how SiCl_4 and BF_3 are acids.
9. Explain why SiCl_4 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^H 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^{-2} M and 10^{-2} N solutions?
16. How many grams of decahydrated sodium carbonate of 80% purity are required to prepare 2.5 lit. of its decinormal solution?

CHAPTER – 4

SOLUTIONS

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:

<i>Element</i>	<i>Atomic mass in amu</i>
<i>H</i>	<i>1.008 $\approx$ 1</i>
<i>N</i>	<i>14</i>
<i>O</i>	<i>16</i>

Atomic masses of some elements are given below:

Element	Symbol	Atomic Weight in a.m.u
Hydrogen	<i>H</i>	<i>1</i>
Helium	<i>He</i>	<i>4</i>
Lithium	<i>Li</i>	<i>7</i>
Beryllium	<i>Be</i>	<i>9</i>
Boron	<i>B</i>	<i>11</i>
Carbon	<i>C</i>	<i>12</i>
Nitrogen	<i>N</i>	<i>14</i>
Oxygen	<i>O</i>	<i>16</i>
Fluorine	<i>F</i>	<i>19</i>
Neon	<i>Ne</i>	<i>20</i>
Sodium	<i>Na</i>	<i>23</i>
Magnesium	<i>Mg</i>	<i>24</i>
Aluminium	<i>Al</i>	<i>27</i>
Silicon	<i>Si</i>	<i>28</i>
Phosphorous	<i>P</i>	<i>31</i>
Sulphur	<i>S</i>	<i>32</i>

GRAM ATOMIC MASS:

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

Element	Gm.atomic mass
H	1.008 gm
O	16 gm
Mg	24 gm

Note: 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 (6.023×10^{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

$$\begin{aligned}\text{H}_2\text{SO}_4 &= [2 \times \text{At.wt. of H}] + \text{At.wt. of sulphur} + [4 \times \text{At.wt. of oxygen}] \\ &= 2 \times 1 + 32 + 4 \times 16 = \mathbf{98 \text{ amu}}\end{aligned}$$

Other examples:

Compound	Molecular weight
NaCl	$23 + 35.5 = 58.5 \text{ amu}$
HNO_3	$1 + 14 + 48 = 63 \text{ amu}$
CaCO_3	$40 + 12 + 48 = 100 \text{ amu}$
$\text{Al}_2(\text{SO}_4)_3$	$2 \times 27 + 3 \times 32 + 12 \times 16 = 342 \text{ amu}$

Assignment

Q 1. Find the molecular weights of the following: Na_2SO_4 , $(\text{NH}_4)_2\text{CO}_3$, $(\text{NH}_4)_3\text{PO}_4$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

Gram molecular weight: -

The gram molecular weight of a substance is simply its molecular weight expressed in gram.

For example:

Compound	Gm. mol. weight
NaCl	58.5 gm
HNO_3	63 gm

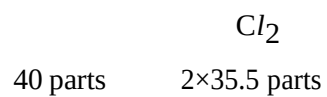
EQUIVALENT WEIGHT:

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.

Gram equivalent weight: The gram equivalent weight of a substance is its equivalent weight expressed in gram.

Example :1 The equivalent wt. of Ca in CaCl_2 can be calculated as follows: Ca



2×35.5 parts by mass of chlorine combines with $\text{Ca} = 40$ parts

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_2 and FeCl_3 are:

$$\text{Eq. Wt. of } \text{Fe}^+ \text{ in } \text{FeCl}_2 = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{56}{2} = 28$$

$$\text{Eq. Wt. of } \text{Fe}^+ \text{ in } \text{FeCl}_3 = \frac{\text{Atomic weight}}{\text{Valency}} = \frac{56}{3} = 18.66$$

EQUIVALENT WEIGHTS OF ACIDS, BASES AND SALTS:

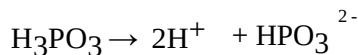
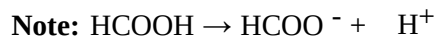
Equivalent weights of acids:

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

$$E_{\text{Acid}} = \frac{\text{Molecular weight}}{\text{Basicity}}$$

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

<u>ACID</u>	<u>FORMULA</u>	<u>MOL.Wt.</u>	<u>BASICITY</u>	<u>EQ.Wt.</u>
Nitric Acid	HNO_3	63	1	$63/1 = 63$
Sulphuric Acid	H_2SO_4	98	2	$98/2 = 49$
Phosphoric Acid	H_3PO_4	98	3	$98/3 = 32.66$
Formic Acid	HCOOH	46	1	$46/1 = 46$
Acetic Acid	CH_3COOH	60	1	$60/1 = 60$
Oxalic Acid	$\begin{array}{c} \text{COOH} \\ \\ \text{COOH} \end{array}$	90	2	$90/2 = 45$
Phosphorous Acid	H_3PO_3	82	2	$82/2 = 41$
Boric Acid	H_3BO_3	62	1	$62/1 = 62$



Equivalent weights of bases:

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

$E_{\text{Base}} = \frac{\text{Molecular weight}}{\text{Acidity}}$, 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) ₂	74	2	74/2 = 37
Aluminium hydroxide	Al(OH) ₃	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.

$$E_{\text{Salt}} = \frac{\text{Molecular weight}}{\text{Total no. of } \square \text{ ve or } \square \text{ ve charge}}$$

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 ₂ CO ₃	138	1x2 = 2	69
Calcium Sulphate	CaSO ₄	136	1x2 = 2	68
Aluminium Suplhate	Al ₂ (SO ₄) ₃	342	2x3 = 6	57

Assignment

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

Acids: H₂CO₃, HNO₃, C₂H₅COOH

Bases: Mg(OH)₂, LiOH

Salts: KCl, Na₂CO₃

Numerical Problems:

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

(a) Fe₂O₃ (b) CuCl₂ (c) Al₂O₃

SOLUTION:

In Fe₂O₃

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

□ 8 parts by mass of 'O' combines with 'Fe' =

In CuCl_2

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.

Weight of oxygen = $1.497 - 1.201 = 0.296$ gm

$$\text{Hence, equivalent weight of metal} = \frac{\text{weight of metal}}{\text{weight of oxygen}} \times 8 = \frac{1.201}{0.296} \times 8 = 32.45$$

Assignment

Q 5. Find out the equivalent masses of the underlined atoms in the following. $\underline{\text{Ca}}\text{Cl}_2$, $\underline{\text{Fe}}\text{O}$, $\underline{\text{Na}}\text{HCO}_3$, $\underline{\text{Fe}}\text{Cl}_3$.

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 $\underline{\text{M}}$ 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,

$$M = \frac{w \times 1000}{M_s \times V_{ml}} \quad ; \quad \text{Where } w = \text{weight of the solute in gram}$$

M_s = 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 ($\frac{1}{2}$) 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.

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

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, M_s for KOH = $39 + 16 + 1 = 56$ amu

Molarity of the solution = $1/10 \text{ M} = 0.1 \text{ M}$

$$\text{Thus, } M = \frac{w \times 1000}{M_s \times V_{ml}} \quad \square \quad w = \frac{M \times M_s \times V_{ml}}{1000} = \frac{0.1 \times 56 \times 1500}{1000} = 8.4 \text{ gram.}$$

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,

$$N = \frac{w \times 1000}{E_s \times V_{ml}} ; \quad \text{Where, } w = \text{weight of solute in gm.}$$

$$V_{ml} = \text{volume of solution in ml. } E_s \\ = \text{Equivalent weight of solute}$$

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, $w = 5.6 \text{ gm}$

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

$$\text{Equivalent weight of solute, KOH } (E_s) = \frac{\text{Molecular weight}}{\text{Acidity}} = \frac{56}{1} = 56$$

$$\text{Normality } \text{N}^\circ = \frac{w \times 1000}{E_s \times V_{ml}} = \frac{5.6 \times 1000}{56 \times 800} = 0.125 \text{ N}$$

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, $w = \text{density} \times \text{volume} = 1.2 \times 10 = 12 \text{ gm}$

Volume of solution, $V_{ml} = 400 \text{ ml}$

$$\text{Equivalent weight of } \text{H}_2\text{SO}_4 = \frac{\text{Molecular weight}}{\text{Basicity}} = 98/2 = 49$$

$$\text{Normality } N = \frac{w \times 1000}{E_s \times V_{ml}} = \frac{12 \times 1000}{49 \times 400} = 0.612 \text{ N}$$

Hence, normality of the solution is 0.612N.

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 gmwt.

of solvent, W = 200 gm,

Mol. wt. of Solute, M_s (NaCl) = $23+35.5 = 58.5$ amu.

$$\begin{aligned} m &= \frac{w \times 1000}{M_s \times W} \\ &= \frac{5.85 \times 1000}{58.5 \times 200} = 0.5m \end{aligned}$$

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 gmwt.

of solution = 300 gm

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

$$\text{Thus, molality } m = \frac{w \times 1000}{M_s \times W} = \frac{5.6 \times 1000}{56 \times 294.4} = 0.339 \text{ m.}$$

Hence, molality of the solution is 0.339 m.

Assignment

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.

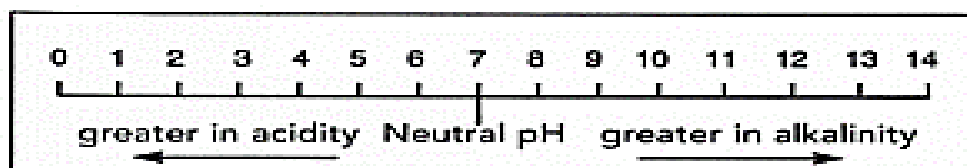
Q 11.0.49 gm of H_2SO_4 is present in 600ml of its solution having density 1.2 gm/ml. Find molarity, normality and molality of the solution.

P^H of Solutions

The p^H of a solution may be defined as -the negative logarithm of H^+ ion concentration in moles/liter or molarity. ||

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

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.

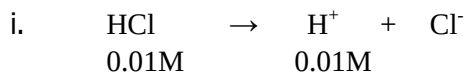
Note: Pure water has a P^H value of 7 at 25°C and is neutral. The P^H value of water decreases with the increase in temperature.

Some important Formulae:

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

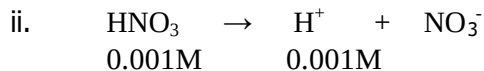
QUESTIONS FOR DISCUSSION:

1. Find out the p^H values of the following solutions.
 - i. 0.01M HCl solution
 - ii. 0.001 M HNO_3 solution
 - iii. 0.01M NaOH solution
 - iv. 0.01M H_2SO_4 solution

Solutions:-

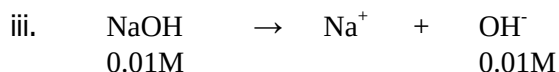
$$[\text{HCl}] = [\text{H}^+] = 0.01\text{M} = 10^{-2}\text{M}$$

$$\text{Hence } p^H = -\log[\text{H}^+] = -\log(10^{-2}) = -(-2)\log 10 = 2$$



$$[\text{HNO}_3] = [\text{H}^+] = 0.001\text{M} = 10^{-3}\text{M}$$

$$\text{Hence, } p^H = -\log[\text{H}^+] = -\log 10^{-3} = -(-3)\log 10 = 3.$$

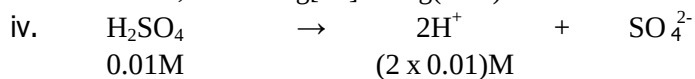


$$[\text{NaOH}] = [\text{OH}^-] = 0.01\text{M} = 10^{-2}\text{M}$$

$$\text{We know } [\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} = \frac{10^{-14}}{10^{-2}} = 10^{-12}$$

$$\text{Hence, } p^H = -\log[\text{H}^+] = -\log(10^{-12}) = 12$$



$$[\text{H}^+] = 2 \times 0.01 = 2 \times 10^{-2}\text{M}$$

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

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 HCl. 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^H in Industries:

1. **In sugar Industry:** - The P^H value of the sugar cane juice should be nearly 7 i.e., it should be neutral. 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 pH.

Cobb control is done by addition of Alum (which is in the range of 2-3 pH) 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 pH 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 pH 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 pH dependent. The amount of chemicals required for a given process is directly related to the pH. The solubility of substances, such as dyes and impurities, vary with pH. The corrosive and scaling potential of processing solutions is also heavily influenced by pH. 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 pH of 10 is considered optimum for the removal of wool wax.

In the instance of vat dyeing, pH 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 pH 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 pH improves the lab-to-bulk reproducibility of colour. Monitoring and controlling pH ensures consistency of colour from batch to batch, as well.

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 $\text{Al}_2(\text{SO}_4)_3$ and CuCO_3 .
5. Find the equivalent weights of H_3PO_4 and H_3PO_3 .
6. Find the equivalent weights of $\text{Ca}(\text{HCO}_3)_2$ 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 $\text{Ca}(\text{OH})_2$ 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 in 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_2CO_3 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_2SO_4 in to molarity.
28. Define P^{H} and P^{OH} .
29. The P^{H} 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^{H} 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_2SO_4 solution.

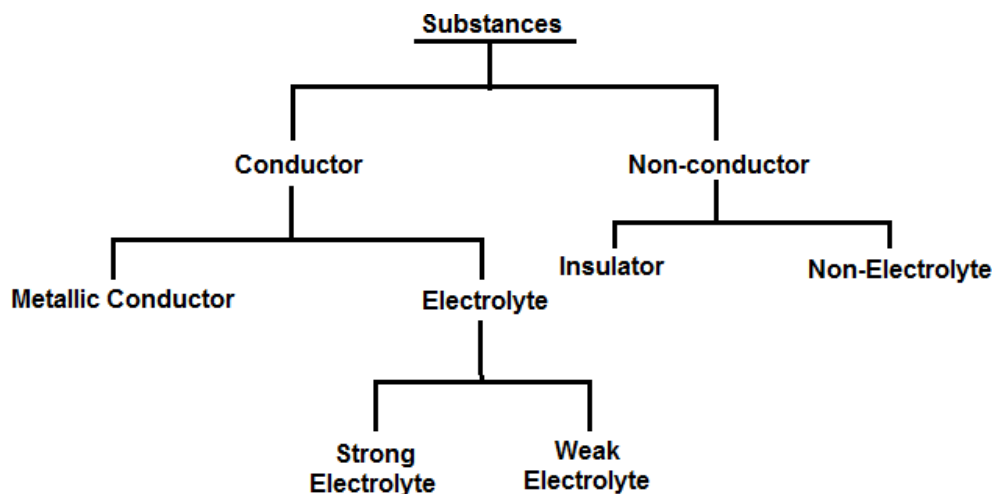
CHAPTER – 5

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. Strong electrolytes:** These are the electrolytes which undergo almost complete ionization in aqueous solution. Example:
- a) acids like HCl , HNO_3 , H_2SO_4 , etc.
 - b) alkalies like NaOH , KOH , $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, etc.
 - c) salts like NaCl , KCl , CaCl_2 , MgCl_2 , etc.
- ii. Weak electrolytes:** These are the electrolytes which undergo partial ionization in aqueous solution. Example:
- a) Organic acids like CH_3COOH , HCOOH , $(\text{COOH})_2$, etc.
 - b) Inorganic acids like H_2CO_3 , HCN , etc.
 - c) Base like NH_4OH

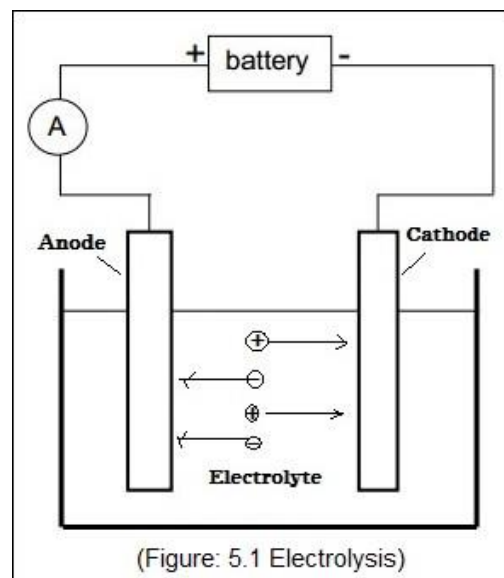
ELECTROLYSIS:

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:

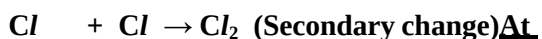
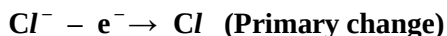
Electrolytes exist in the ionic form in their molten, fused or solution state. When electricity is allowed to pass through the electrolytic solution, the ions migrate towards the oppositely charged electrodes. Cations migrate towards the cathode while anions migrate towards the anode. While reaching 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.



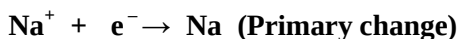
Example 1: Electrolysis of molten NaCl.

Molten NaCl exists in the ionic form Na^+ and Cl^- . During the process of electrolysis, Na^+ ions migrate towards the cathode while Cl^- ions migrate towards the anode. During electrolysis the following changes take place at different electrodes.

At Anode:



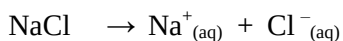
Cathode:



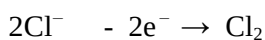
Thus, electrolysis of molten NaCl liberates chlorine gas at the anode while metallic sodium at the cathode.

Example 2: Electrolysis of aqueous NaCl solution.

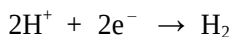
In aqueous solution NaCl exists in ionic form. Also, water undergoes partial ionization to produce H^+ and OH^- ions.



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



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



Thus electrolysis of aqueous $NaCl$ solution liberates chlorine gas at the anode and hydrogen gas at the cathode.

Faraday's 1st 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,

$$W \propto Q$$

$$\text{But, } Q = I \times T$$

$$\Rightarrow W \propto I \times T$$

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

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 =

$$Z$$

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 charge is passed through an electrolyte 1 gram equivalent of the substance is deposited at the electrode.

96500 Coulomb of charge deposits 1 gram equivalent

$$\square \quad 1 \text{ coulomb of charge deposits } \frac{1 \text{ gram equivalent}}{96500 C}$$

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

Unit of Z is gram equivalent/coulomb.

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_3 for 1 hour?

Solution:

Given Data: $I = 10$ Ampere

$t = 1 \text{ hr} = 3600 \text{ Sec.}$

$$Z = \frac{1 \text{ gram equivalent}}{96500 \text{ C}} = \frac{\text{Atomic mass / Valency}}{96500} = \frac{108 / 1}{96500} = 0.0011$$

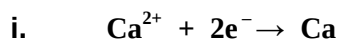
Applying Faraday's 1st Law of electrolysis

$$W = ZIt = 0.0011 \times 10 \times 3600 = 39.6 \text{ gram.}$$

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

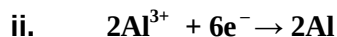
- i. One mole Ca^{2+} into Ca .
- ii. Two moles of Al^{3+} into Al .

Solution:



1 mole of electrons carries 96500 coulombs.

2 moles of electrons carry (2×96500) coulomb = 193000 Coulombs.



1 mole of electrons carries 96500 coulombs.

6 moles of electrons carry (6×96500) coulomb = 579000 Coulombs.

Question 3: How many coulombs of charge are required to get 10 grams of calcium from molten CaCl_2 ?

Solution:

$$W = 10 \text{ gm, } Q = ?$$

$$W = ZQ$$

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

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

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_4 for half an hour?

Faraday's 2nd 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 2nd law of electrolysis,

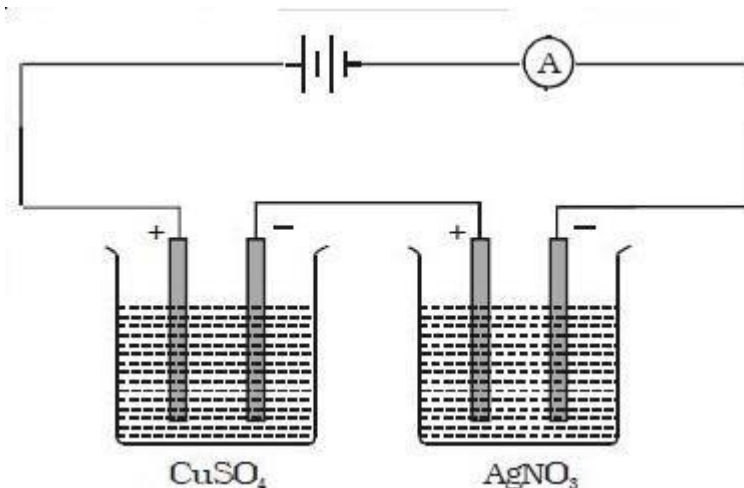
$$W_{\text{Ag}} \propto E_{\text{Ag}} \text{----- (1)}$$

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

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

$$\frac{W_{\text{Ag}}}{W_{\text{Cu}}} = \frac{E_{\text{Ag}}}{E_{\text{Cu}}} = \frac{W_{\text{Ag}}}{W_{\text{Cu}}} \cdot \frac{96500}{96500} = \frac{Z_{\text{Ag}}}{Z_{\text{Cu}}}$$

In general,
$$\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2} \quad \text{or} \quad W \propto E \propto Z$$



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 $W_{\text{H}_2} = 0.0132$ gm Weight of

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

Equivalent weight of hydrogen $E_{\text{H}_2} = 1.008$

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

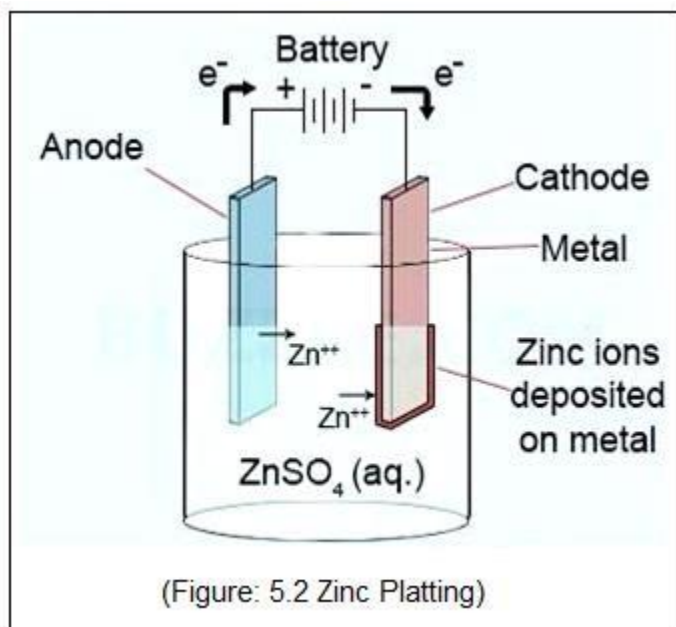
Applying Faraday's 2nd law of electrolysis,

$$\frac{W_{\text{H}_2}}{W_{\text{Cu}}} = \frac{E_{\text{H}_2}}{E_{\text{Cu}}} \Rightarrow \frac{0.0132}{0.4164} = \frac{1.008}{E_{\text{Cu}}} \Rightarrow E_{\text{Cu}} = \frac{1.008 \times 0.4164}{0.0132} = 31.79$$

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 Plating: 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 and 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 1st law of electrolysis.
6. Define Faraday's 2nd 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 1st law of electrolysis. How many grams of calcium will be deposited at the cathode by passing 15 ampere of currents through molten CaCl_2 for 30 minutes?
4. Define electrochemical equivalent. Find the ECE of Ca and Al.
5. Define and explain Faraday's 2nd 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 1st law of electrolysis. How many coulombs of charges are required to get 36 grams of magnesium from molten magnesium chloride?

CHAPTER – 6

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:

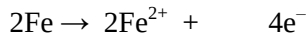
- i. Atmospheric corrosion
 - ii. Water line corrosion
 - iii. Pitting corrosion
 - iv. Stress corrosion
- i. **Atmospheric corrosion:** The process of development of undesirable substances usually oxide over the surface of a metal when exposed to atmosphere is called *atmospheric corrosion*. Example: (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 take place on the surface of iron during the process of corrosion (Fig. 6.1).

At Anode:

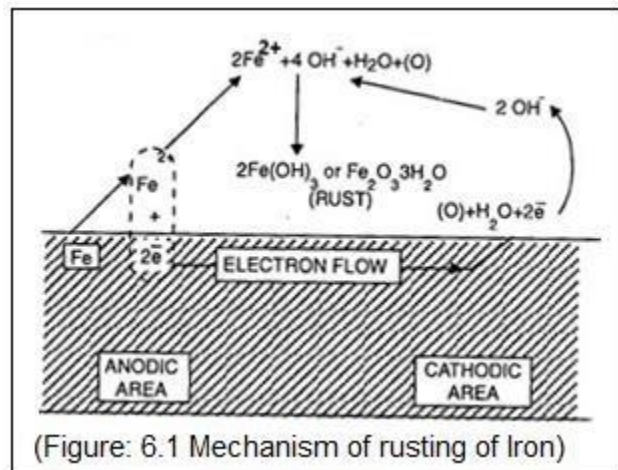
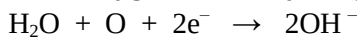
At anode iron gets oxidized into ferrous ion.



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

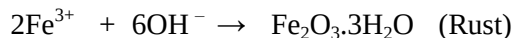
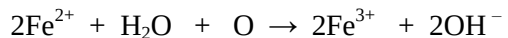
At Cathode:

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



(Figure: 6.1 Mechanism of rusting of Iron)

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.

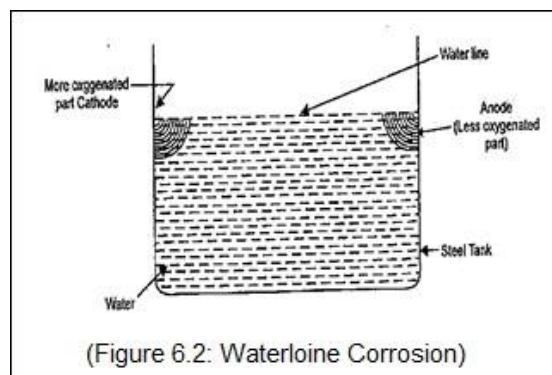


Note:

- ☞ Rust is nothing but hydrated ferric oxide ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$)
- ☞ Presence of CO_2 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.



(Figure 6.2: Waterline Corrosion)

Protection of Corrosion:

1. **Alloying:** Corrosion can be prevented by alloying a metal. Alloying prevents 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. Duralumin is a silica-iron alloy. It is resistant to acids as a layer of silicon oxide is formed at the surface of iron.
2. **Galvanization:** 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 and 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_2 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.