GOVT. POLYTECHNIC BHUBANESWAR

LEARNING MATERIAL ON PHYSICAL, INORGANIC & ORGANIC CHEMISTRY

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ATOMIC STRUCTURE

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.

Atomic structure or the structure of an atom means, how the sub-atomic particles (electrons, protons, neutrons) are arranged inside an atom.

Fundamental Particles:

Protons

- Protons are positively charged subatomic particles. The charge of a proton is 1e, which corresponds to approximately 1.602×10^{-19} coulomb
- The mass of a proton is approximately 1.672×10^{-27}kg.

Neutrons

- The mass of a neutron is almost the same as that of a proton, i.e., 1.674×10^{-24} kg
- Neutrons are electrically neutral particles and carry no charge.

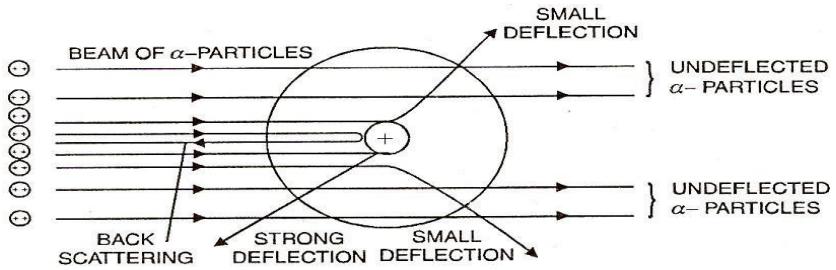
Electrons

- The charge of an electron is -1e, which approximates to -1.602×10^{-19} coulomb
- The mass of an electron is approximately 9.1×10^{-31}kg.

RUTHERFORD'S ATOMIC MODEL:

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

In 1911, Rutherford gave the first information about the almost-correct-picture of an atom. He bombarded a number of α-particles (He2+ ions) emitting from a radioactive material like Uranium on a very thin gold foil. A circular zinc sulphide (ZnS) screen was provided at the back side of the gold foil in order to register the impressions made by the α-particles.



Observations and Conclusions:

From the α- scattering experiment, Rutherford observed that:

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.

A few α-particles were found to be deflected strongly from their normal paths. This indicates the presence of a massive (heavy) positively charged body inside the atom. This massive positively charged body is called nucleus.

A very few (0.01%) α-particles were found to be retraced their original paths (deflected through almost 180º). This indicates that the size of nucleus is very small. The size of atomic nuclei is of the order of 10-13 cm.

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

An atom consists of two parts; they are (i) Nucleus and (ii) extra nuclear part.

Every atom consists of a very small but heavy positively charged body, called nucleus.

The whole mass of an atom is concentrated at the nucleus.

Electrons revolve around the nucleus with tremendous speed, like planets revolve around the Sun. Therefore, the electrons are also called as planetary electrons.

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.

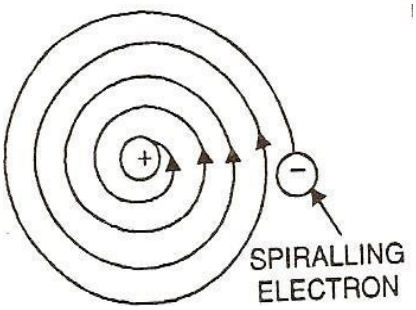
DRAWBACKS OR FAILURES OF RUTHERFORD'S ATOMIC MODEL:

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.

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

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

The theory fails to explain atomic spectra.



BOHR'S ATOMIC MODEL

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

Postulates of Bohr's atomic model:

- Electrons revolve around the nucleus in stable orbits without emission of radiant energy. Each orbit has a definite energy and is called an energy shell or energy level.
- An orbit or energy level is designated as K, L, M, N shells. When the electron is in the lowest energy level, it is said to be in the ground state.
- An electron emits or absorbs energy when it jumps from one orbit or energy level to another. When it jumps from a higher energy level to lower energy level it emits energy while it absorbs energy when it jumps from a lower energy level to a higher energy level.
- The energy absorbed or emitted is equal to the difference between the energies of the two energy levels (E_1, E_2) and is determined by Plank's equation.

$\Delta E = E_2 - E_1 = h\nu$

Where, ΔE = energy absorbed or emitted
h= Plank's constant
ν= frequency of electromagnetic radiation emitted or absorbed

- The angular momentum of an electron revolving in energy shells is given by:

$m_e vr = nh/2\pi$

Where,
n= number of corresponding energy shell; 1, 2, 3 ….
m_e= mass of the electron
v= velocity
r=radius
h= Plank's constant

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 $2n^2$ electrons, where n = number of the shell

Shell	Maximum number of electrons ($2n^2$)
K-Shell	n=1, $2 \times 1^2 = 2$
L-Shell	n=2, $2 \times 2^2 = 8$
M-Shell	n =3, $2 \times 3^2 = 18$
N-Shell	n=4, $2 \times 4^2 = 32$ and so on.

2. The outer most shell of an element cannot hold more than '8'electrons.

3. The penultimate shell (the shell just before the outer most shell) cannot hold more than '18' electrons.

4. A higher orbit may start filling before the lower orbit is completely filled.

Aufbau's Principle

The word "aufbau" means "building up". The building up of orbitals means filling up of orbitals with electrons.

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

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.

The (n + l) Rule:

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

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

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

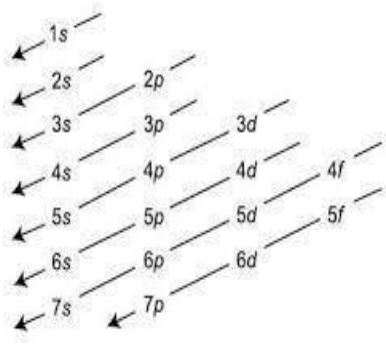
SUB-SHELL→	1s	2s	2p	3s	3p	3d	4s	4p	4d	4f	5s	5p
(n+1)	1+0 =1	2+0 =2	2+1 =3	3+0 =3	3+1 =4	3+2 =5	4+0 =4	4+1 =5	4+2 =6	4+3 =7	5+0 =5	5+1 =6

Thus, the increasing order of energy content of sub-shells is 1s < 2s < 2p < 3s < 3p <4s <3d <4p < ...

i. Arrange the sub-shell as given below.

ii. Draw parallel arrows as shown in the figure.

The sub-shell through which the arrow crossed first has lower energy.



ELECTRONIC CONFIGURATIONS

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

Elements	Electronic configurations
$_{1}H$	$1s^1$
$_{2}He$	$1s^2$
$_{8}O$	$1s^2\ 2s^2 2p^4$
$_{10}Ne$	$1s^2\ 2s^2 2p^6$
$_{11}Na$	$1s^2\ 2s^2 2p^6\ 3s^1$
$_{18}Ar$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6$
$_{20}Ca$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2$
$_{21}Sc$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^1$
$_{22}Ti$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^2$
$_{23}V$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^3$
$_{24}Cr$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^1 3d^5$
$_{25}Mn$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^5$
$_{26}Fe$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^6$
$_{27}Co$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^7$
$_{28}Ni$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^8$
$_{29}Cu$	**$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^1 3d^{10}$**
$_{30}Zn$	$1s^2\ 2s^2 2p^6\ 3s^2 3p^6 4s^2 3d^{10}$

Exceptional Electronic Configuration:

Exceptional Electronic Configuration: Some elements like ‘Cr’ and ‘Cu’ show exceptional electronic configurations. The exceptional electronic configuration is due to the fact that half- filled and completely filled orbitals are more stable due to the orbital symmetry and exchange energy.

The electronic configurations of ‘Cr’ & ‘Cu’ should be 24Cr = [Ar]4s23d 4 & 29Cu = [Ar]4s23d 9 respectively. But the actual electronic configurations are 24Cr = [Ar]4s13d 5 & 29Cu = [Ar]4s13d 10

CHEMICAL BONDING

Definition of Chemical Bond

Chemical bond is the force of attraction between the constituent atoms.

Types of Chemical Bond

- **Electrovalent / Ionic Bond**
- **Covalent bond**
- **Co-ordinate bond**

Electrovalent or ionic Bond

Definition: An electrovalent or ionic bond formed by complete transfer of electron orelectrons from one atom to the other.

Process of Formation of electrovalent bond

- The constituent atoms must be dissimilar in character, one with a tendency to loss electronsand the other having a tendency to gain electrons.
- The atom which loses electrons acquires positive charge and contracts. It is known as cation
- The atom which gains electrons acquires negative charge and increases in size. It is knownas anion.
- The cation and anion thus produced are held together by electrostatic lines of force andhence the linkage is called electrovalent bond.
- The compounds so produced are called electrovalent compounds.
- These are also called polar compounds since their molecules acquire polarity due to theformation of ions by electron transfer.

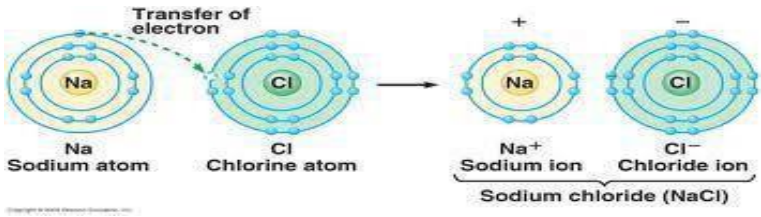
In the formation of the electrovalent bond, the electrons gained or lost are always from theoutermost shell and the ions occupied acquire the nearest inert gas configuration.

Example-1

Formation of NaCl :-

$_{11}Na$- $1s^2, 2s^2, 2p^6, 3s^1$ ___

$_{17}Cl$- $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ _____

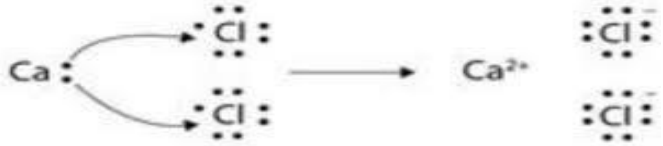


Example-2

Formation of $CaCl_2$

$_{20}Ca$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$ ___

$_{17}Cl$ $1s^2, 2s^2, 2p^6, 3s^2, 3p^5$ _____



Formation of Calcium chloride

Covalent Bond

Definition: A covalent bond is formed by mutual sharing of one or more electron pairs andthe atoms thus achieve their stability.

Process of formation of covalent Bond

- The electrons for pair formation are contributed equally by the two constituent atoms andbecome their common property.
- The covalent bond can connect similar atoms when both of them are short of a few electronsto achieve the stable electronic configuration of nearest inert gas.
- Depending upon whether the electron pairs are shared equally between the constituentatoms or not, a covalent bond may be non-polar or polar.

Covalent compounds are of two types

a. Homoatomic molecules

b. Heteroatomic molecules

Homoatomic molecules:-

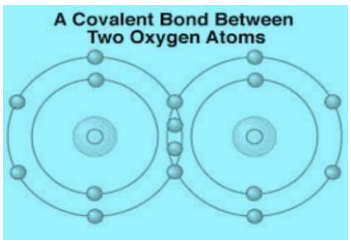
1) Formation of molecule having a single bond

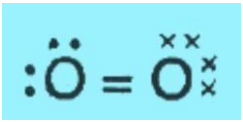
Ex- H_2 $_1H$ $1s^1$  = H - H

2) Formation of molecule having a double bond

Ex- O_2 $_8O$ $1s^2$ $2s^2$ $2p^4$

outermost electrons

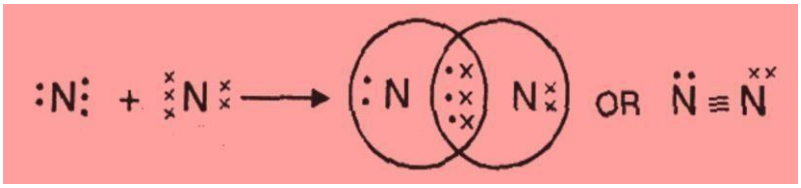




3) Formation of molecule having a triple bond Ex- N_2

$_7N$ $1s^2$ $2s^2$ $2p^3$

outermost electrons



Heteroatomic molecule:-

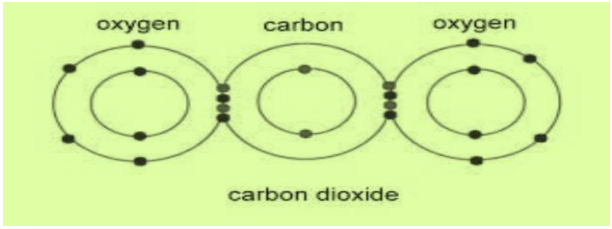
Formation of (CO_2) Carbon dioxide molecule

CO_2 $_6C$ $1s^2$ $2s^2$ $2p^2$

$_8O$ $1s^2$ $2s^2$ $2p^4$

Structure: Linear

O = C = O **Bond angle** = 180°



Co-ordinate Bond

Definition: A co-ordinate bond is formed, when an atom with complete octet (after natural sharing) donates its pair of electrons to the other atom. The donated pair is counted towardsthe stability of both the atoms.

Process of formation of co-ordinate bond

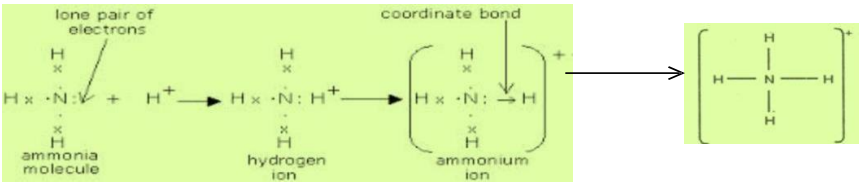
- This type of bond is formed by dissimilar atoms A and B
- Atom A has one or more lone pairs of electrons. Atom B is short of a pair of electrons thanthe nearest inert gas configuration.
- Atom A donates its lone pair of electrons to atom B. As a result, both the atoms get inert gasconfiguration.
- Atom A is called donor while atom B is called acceptor. The bond formed is called **dativeor directional bond.**

Formation of Ammonium ion

$_7N$ $1s^2$ $2s^2$ $2p^3$

outermost electrons

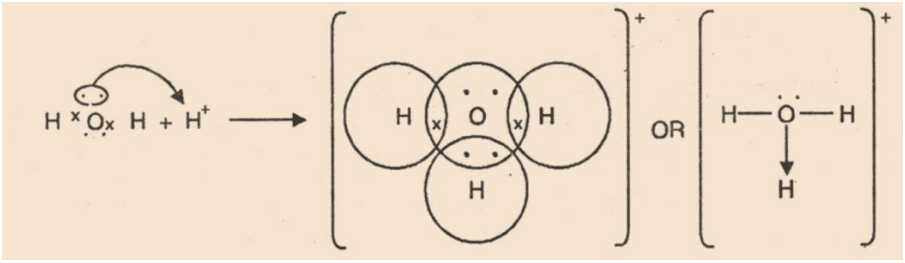
$_1H$ $1s$



Formation of Hydronium ion (H_3O^+)

$_1H$ $1s^1$

$_8O$ $1s^2$ $2s^2$ $2p^4$



ACID, BASE AND SALT

THEORIES OF ACIDS AND BASES

1. ARRHENIUS THEORY:

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

Example of Acid: **HCl** $\xrightarrow{\text{water}}$ **H^+ (aq) + Cl^- (aq)**

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

Examples of Base: **NaOH (s)** $\xrightarrow{\text{water}}$ **Na^+ (aq) + Cl^- (aq)**

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

Salient Features:

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

HCl + NaOH → NaCl + H_2O

(Acid) (Base) (Salt) (Water)

Neutralisation reaction may be represented as:

H^+(aq) + OH^- (aq) → H_2O(l)

(from acid) (from base)

ii. Higher the degree of dissociation, higher is the acidic or basic nature of thesubstance.

Limitations:

i. H^+ ion does not exist freely in aqueous solution. It combines with H_2O, as soon as itforms 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 otherthan 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 neutralisation reactions between some acidic and basicsubstances which do not produce water. $HCl + NH_3 \rightarrow NH_4Cl$

2. LOWRY- BRONSTED THEORY

According to Lowry - Bronsted theory ***"Acids are the substances (molecules/ions) whichdonate 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.

Examples of acids are:

i. HCl, HNO_3, H_2SO_4, H_3PO_4, CH_3COOH, H_2CO_3 etc.

ii. Ions having capacity to donate H^+ ion*:* (HS^-, HCO_3^-, HPO^{2-}, HSO_4^- et4c.)

Examples of Bases:

i. Neutral 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.

All Arrhenius acids are Bronsted acids but all Bronsted bases are not Arrhenius bases.

Salient Features:-

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

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

Acid – H^+ → Conjugate baseBase + H^+ → Conjugate acid

iii. 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.

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

$HCl + H_2O \rightarrow H_3O^+ + Cl^-$

[Strong acid] [Weak base]

Limitations of the theory:

i. It fails to explain the acidic nature of the substances, such as SiO_2, CO_2, SO_2, BF_3, etc. which cannot donate H^+ ion.

ii. It fails to explain the basic nature of the substances, such as Na_2O, K_2O, CaO etc. which cannot accept H^+ ion.

iii. It fails to explain the reaction between some acids and bases which do not give another pair of acid and base. Example: $HCl + NaOH \rightarrow NaCl + H_2O$.

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^-	HCN
NH_4^+	NH_3	NH_2^-	NH_3
H_2O	OH^-	H_2O	H_3O^+

3. LEWIS THEORY

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

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

Examples of acids:-

i. All cations are Lewis acids: For example; Na^+, K^+, Ca^{2+}, Cu^{2+}, Al^{3+}, Fe^{3+} etc.

ii. Neutral molecules containing electron deficient atoms are Lewis acids. For example: BF_3, $AlCl_3$, $FeCl_3$, $ZnCl_2$ etc.

iii. Neutral molecules containing vacant d-orbitals in the central atom for the accommodation of incoming electrons act as Lewis acids. For example: SiF_4, $SiCl_4$, etc.

iv. The molecules having multiple bonding (= or ≡) between the atoms of different elements are acidic in nature. For example: CO_2 (O = C = O), SO_2, etc. **Examples of Bases:-**

i. All anions are Lewis bases: F^-, Cl^-, CO_3^{2-} etc

ii. Neutral molecules containing, at least one lone pair of electrons are Lewis bases

Salient Features:

i. According to this theory, an acid reacts with a base to form an acid- base complex which involves a co-ordinate or dative bond. For example, the reaction between H_2O(Lewis base) and H^+ (Lewis acid) results in the formation of a dative bond.

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

Limitations:

i. According to this theory, the reaction between an acid and base results in the formationof a dative bond. Formation of a coordinate bond is a slow process. While the reactions between the acids such as HCl, HNO_3, H_2SO_4 and the bases such as NaOH, KOH etc. are instantaneous or fast.

ii. Catalytic activity of Lewis acids cannot be explained because catalytic activity of manyacids is due to their tendency to furnish H^+ ion. Lewis acids are lacking this activity.

iii. The theory fails to explain the relative strengths of different acids and bases.

ELECTROCHEMISTRY

Definition: The branch of chemistry which deals with the study of relationship between electrical energy, chemical energy and inter conversion of one form into another is called electrochemistry

Electrolysis

Definition: The process of chemical decomposition of an electrolyte in solution or in thefused state by passage of electric current is known as electrolysis

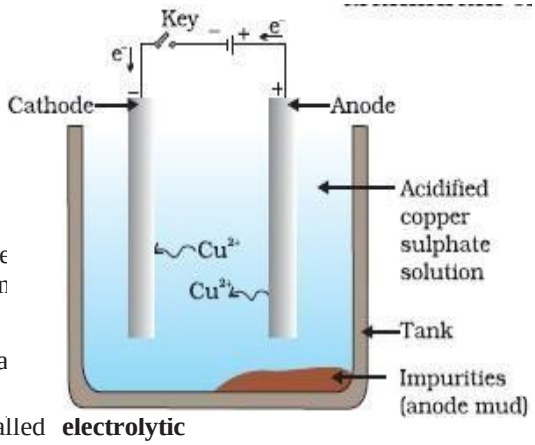
Electrolyte

Definition: The substances which conduct electricity in their fused or in aqueous solution arecalled electrolysis
Ex- NaCl, $CaCl_2$ etc

Electrolytic cell

Definition: Electrolytic cell is a device in which electrical energy is converted in to chemicalenergy.

Process of Electrolysis



- The process of electrolysis is carried out in a vessel knownas electrolytic tank
- It is made up of some insulating material such as glass,stone etc.
- Fused electrolyte or an aqueous solution of the electrolyte is taken in an electrolytic tank and two metallic plates aredipped in the electrolyte. These plates are known aselectrodes.
- The electrodes are connected to an external source of emf (battery).The ele positive end of the battery is called **anode** and the electrode which is conn **cathode**.
- When an electric current is passed through the solution, cations move towa move towards the anode.
- This movement of ions towards oppositely charged electrodes is called **electrolytic** conduction.

Example of electrolysis

By using copper sulphate solution (using Pt electrode)

- When copper sulphate is dissolved in water it ionises as:

$CuSO_4 \longrightarrow Cu^{2+} + SO_4^{2-}$

$H_2O \longrightarrow 2H^+ + O^{2-}$ (slightly ionised)

- When electric current is passed through copper sulphate solution using platinum (Pt)electrodes, Cu^{2+} and H^+ ions move towards the cathode. However, only Cu^{2+} ions are discharged more readily than H^+ ions because of their low discharge potentials.
- These Cu^{2+} ions gain electrons and change into neutral atoms and get deposited at cathode.At cathode: $Cu^{2+} + 2e^-$ $\longrightarrow$ Cu (deposited)

b) SO_4^{2-} and OH^- ions move towards anode. However, only OH^- ions are discharged more readily than SO_4^{2-} ions because of their low discharge potential. These OH^- ions lose electrons and change into neutral hydroxyl groups

At anode: $2OH^- + 2e^- \longrightarrow 2OH$ (neutral)

- The neutral hydroxyl groups being unstable react with other neutral OH groups to formwater and oxygen.

$2OH \longrightarrow H_2O + [O]$

$[O] + [O] \longrightarrow O_2$

Conclusion:

Hence during electrolysis of copper sulphate solution using platinum (unattackable)electrodes, copper and oxygen are liberated.

Faraday's 1st law of electrolysis

Definition: The mass of substance liberated at the electrode as a result of electrolysis isdirectly proportional to the quantity of electricity passed through the electrolyte.
If W is the mass of substance liberated at the electrode and Q is the quantity of electricity (incoulombs) passed through the electrolyte.

Then, $W \propto Q$

We know Q = C.t

Where c = current in amperest =
time in seconds

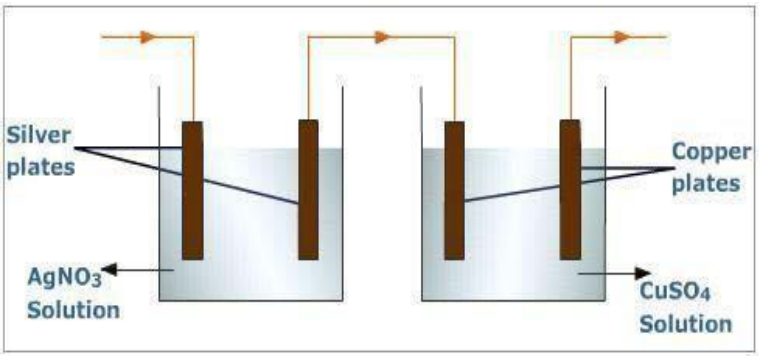
Thus $W \propto C.T$
OR

$$W = ZC.T$$

Where Z is a constant called Electro chemical Equivalent

In the above relationship, if c = 1 ampere and t = 1 secondthen $W = Z$

Definition of ECC Electrochemical equivalent of asubstance is defined as the mass ofsubstance liberated when oneampere of current is passed throughthe electrolyte for one second.



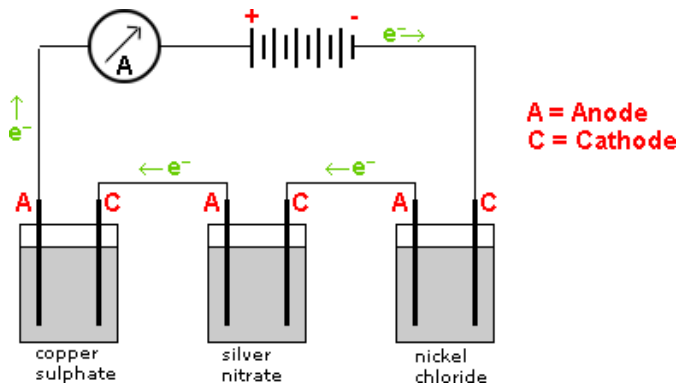
Unit of electricity - Coulomb

1 coulomb = 1 ampere x 1 second

1 Faraday = 96500 coulomb

Mass of substance liberated by passage of one faraday of electricity = 1 gm equivalent.

Faraday's 2nd law of electrolysis Definition: It states that when the samequantity of electricity is passed through different electrolytic solutions, the weights ofdifferent substances produced at the electrodesare proportional to their equivalent weights.



Explanation:

There are three electrolytic cells containing Copper Sulphate, Silver Nitrate and NickelChloride solutions respectively.

- They are connected in series as shown in the diagram above
- On passing the current through the three cells for some time, the three cells receivethe same amount of electricity.
- The weights of copper, silver and nickel liberated are in the ratio of their equivalentweights.

$$\frac{\text{Weight of Copper}}{\text{Weight of Silver}} = \frac{\text{Equivalent weight of Copper}}{\text{Equivalent weight of Silver}}$$

& $\frac{\text{Weight of Nickel}}{\text{Weight of Silver}} = \frac{\text{Equivalent weight of Nickel}}{\text{Equivalent weight of Silver}}$

CORRODION

Corrosion is a process which involves the conversion of metal into an undesirable compound(usually oxide) on exposure to atmospheric conditions i.e. moisture and oxygen.

Types of Corrosion

a) Atmospheric Corrosion

b) Waterline corrosion

Atmospheric Corrosion

Example:

Tarnishing of silver, development of a green coating on Copper and Bronze and rusting ofIron are some examples of corrosion.
Rust is a case of corrosion of iron. It is hydrated Ferric Oxide Fe_2O_3, nH_2O. It is non-stickingin nature and peels off exposing more of iron surface for further rusting.

Mechanism:

Atmospheric rusting can be explained by electro-chemical theory.

Commercial form of iron behaves like small electric cells in presence of water containingdissolved O_2, CO_2, or SO_2.

At anode

Oxidation reaction occurs as$2Fe \quad 2Fe^{2+} + 4e^-$

At cathode : $\rightarrow$

These electrons form hydroxyl ions

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

Fe^{2+} ions and OH^- ions then diffuse under the influence of dissolved oxygen and Fe^{2+} ions are oxidised to Fe^{3+} ions.

These Fe^{3+} ions, then combine with OH^- ion to form hydrated ferric oxide i.e. rust. $2Fe^{2+} + H_2O + [O]$

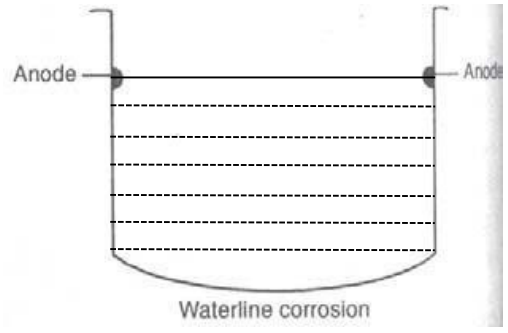
$2Fe^{3+} + 2OH^- \rightarrow$

$2Fe^{3+} + 6OH^- \rightarrow Fe_2O_3 \cdot 3H_2O$

Waterline Corrosion

Reason of waterline corrosion

- Waterline corrosion occurs due to differential oxygen concentration
- When water is stored in steel tank, considerable corrosion takes place along a line justbelow the level of water meniscus.
- The area above the water line is cathode as oxygen concentration is more in this area.
- The area just below the water line is anode, because hereoxygen concentration is less.



Occurrence:

This type of corrosion occurs in ships, water tanks, pipelines etc.

Mechanism:

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

$[O] + H_2O + 2e^- \rightarrow 2OH^-$

$2Fe(OH)_2 + [O] \longrightarrow Fe_2O_3.2H_2O$ (rust)

Protection of corrosion:

There are many methods to protect the metal from corrosion. But as per the syllabus, we will discuss the following methods.

a) Alloying:

By alloying of metals, we can protect those from corrosion. Alloys resist corrosion in twoways.

i) Homogeneity

ii) Oxide film

b) Galvanisation:

- Zinc is used to protect iron from rusting, because reduction potential of zinc is less than thatof iron. Zinc is more electropositive and protects iron from rusting.
- **The process of covering iron with zinc is called galvanisation.**
- Zinc loses electrons in preference to iron and is consumed in due course of time. As zincsacrifices itself and protect iron, it is known as sacrificing metal.

METALLURGY

Minerals-"The natural material in which the metal or their compounds occur in the earth is known asmineral". In other words the combined state occurrences of metals are called minerals.
For example: NaCl, $NaNO_3$, Na_2SO_4, etc. are the minerals of 'Na'. Similarly $Al_2O_3.2H_2O$(Bauxite), $Al_2O_3.2SiO_2.2H_2O$ (Kaolin) are the minerals of 'Al'.

Ores-

"Ores are the minerals from which the concerned metals can be extracted conveniently and economically."

For example: Both Bauxite (Al2O3. 2H2O) and Kaolin (Al2O3.2SiO2.2H2O) are the minerals of Al. However, 'Al' can be extracted easily and profitably from 'Bauxite'. Thus Bauxite is an ore of Al. On the other hand it is difficult and non-profitable to extract 'Al' from Kaolin, hence Kaolin is simply a mineral of Aluminium. All ores are minerals, however all minerals are not ores.

METALLURGICAL OPERATION:

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

The following steps are followed during the process of metallurgical operation:-

Step-I: Crushing and Grinding **Step-II**:

Concentration or Ore Dressing**Step-III**: Oxidation

Step-IV: Reduction

Step-V: Refining

STEP-I: CRUSHING AND GRINDING

The ores obtained from mines are in the form of huge lumps. These are first crushed into small pieces with the help of jaw crusher and then grinded in to their powder form with the help of stamp mill.

STEP-II: CONCENTRATION

The process of removal of maximum impurities (gangue or matrix) from the ore is called concentration or ore dressing. The method of concentration to be followed depends upon the nature of the impurities present.

METHODS OF CONCENTRATION

1. GRAVITY SEPARATION METHOD

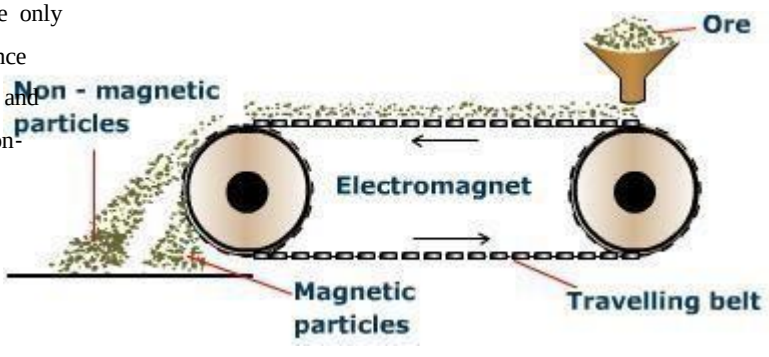
This method of concentration is adopted only when there is a gravity difference between the ore and impurities. Normally carbonate and oxide ores are heavier than the impurities associated with them and hence they are concentrated by this method. In this method the powdered or pulverized ores are kept in some containers over a specially designed table called **wilfly table.** The table contains a number of transverse grooves. The table is kept slightly inclined position and is provided with a rocking motion. When water is spread over the ore, lighter impurities are washed away while heavier ore particles get deposited in the grooves, which are finally carried out in to the main canal.

2. FROTH FLOATATION METHOD

This method is suitable for the concentration of **sulphide ores** only. In this method of concentration two interconnected tanks are used. In one of the tanks, a mixture of ore, oil (preferably pine oil), water and a little quantity of acid is agitated strongly by blowing air through it. Due to the preferential wetting of the sulphide ores by oil than by water, a layer of oil is covered over the surface of sulphide ores. These sulphide ores become lighter and float over the surface of the mixture, which are carried out in to the second container along withthe foam formed due to agitation.

3. MAGNETIC SEPARATION METHOD

This method of concentration is suitable only when there is a difference in magneticbehaviour between the ores and the impurities. Normally magnetic ores containing non-



magnetic impurities are concentrated by this method. In this method a belt is tied over two rollers of which one is made up of magnet. Pulverized ore is added over the belt through a hopper. The pulverized ore move towards the magnetic pulley along with the rotating belt. The non-magnetic impurities fall directly below the magnetic pulley while the magnetic ore form a separate heap due to the influence of the magnetic field.

STEP-III: OXIDATION (Conversion of ores into metal oxides)

In the third step of metallurgical operation the concentrated ores are converted into therespective metal oxides.
This is achieved by the following two methods:-

1. CALCINATION

The process of heating an ore strongly below its melting point in absence of or in a limitedsupply of air is called **calcination**. The various functions of calcination are:-

i) It removes moisture.

$Al_2O_3.2H_2O \rightarrow Al_2O_3 + 2H_2O$

ii) It removes volatile impurities like S, P, As, Sb, etc. $S + O_2 \rightarrow SO_2\uparrow$
$2P + 5O_2 \rightarrow 2P_2O_5\uparrow$

iii) It oxidizes oxidizable substances ('ous' to 'ic') $4FeO + O_2 \rightarrow 2Fe_2O_3$

iv) It decomposes carbonates of alkali and alkaline earth metals into oxides. $CaCO_3 \rightarrow CaO + CO_2\uparrow$

2. ROASTING

The process of heating an ore strongly below its melting point in a free but controlled supplyof air is called **roasting.** The various functions of roasting are:-

i) It removes moisture.

$Al_2O_3.2H_2O \rightarrow Al_2O_3 + 2H_2O\uparrow$

ii) It removes volatile impurities like S, P, As, Sb, etc.

$S + O_2 \rightarrow SO_2\uparrow$

iii) It oxidizes oxidizable substances ('ous' to 'ic') $4FeO + O_2 \rightarrow Fe_2O_3$

iv) It decomposes carbonates into oxides.

$CaCO_3 \rightarrow CaO + CO_2\uparrow$

v) It makes the ore porous.

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

STEP- IV: REDUCTION (Conversion of metal oxides into metals)

In this step of metallurgical operation the roasted ores are reduced to convert the metal oxidesinto the respective metals. The various methods of reduction are:-

1. SMELTING

The process of heating a roasted ore strongly above its melting point with a suitable quantity of coke or charcoal is called smelting. During the process of smelting, metal oxides are reduced into their respective metals. For the reduction of the oxides of less electro positive metals such as Zn, Fe, Cu, Cr, W etc. the reducing agents like H_2O, CO, Na, K etc are used.

$PbO + C \rightarrow Pb + CO$

$CuO + CO \rightarrow Cu + CO2\uparrow$

During the process of smelting, an additional substance called **flux** is added which combineswith the impurities to form fusible **slag.**

Impurity + flux → slag

Thus, **"a substance added during the process of smelting to convert the gangue ormatrix into fusible mass (slag) is called flux**.

"Slag is the fusible mass obtained during the process of smelting when flux combineswith impurities".

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

SiO_2	+	CaO	→	$CaSiO_3$
(Acidic impurity)		(Basic flux)		(fusible slag)

Smelting is carried out in a blast furnace which is a tall cylindrical furnace made up of steel plates lined inside with fire bricks. Since the density of slag is lower it floats over the molten metal. The molten metal is tapped out at the bottom of the furnace.

2. ELECTROLYTIC REDUCTION

This method of reduction is employed for the reduction of chlorides or oxides of highly electro positive metals such as Na, K, Ca, Mg, Al etc., because these can't be reduced with carbon as they would form the respective metal carbides. The molten oxides or chlorides of these metals are taken in an electrolytic cell and electricity is passed through the molten mass with the help of two electrodes. The metal ions get discharged and deposited at the cathode.

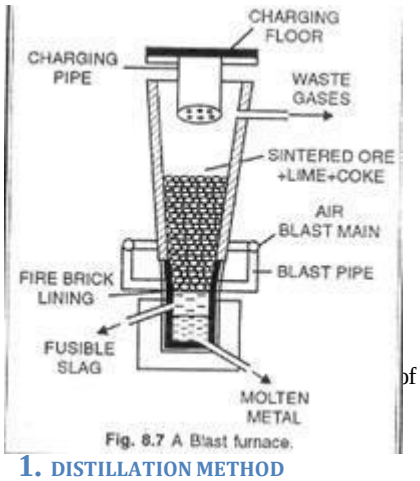


Fig. 8.7 A Blast furnace.

STEP-V: REFINING

The metals obtained after reduction still contain some impurities. The process of removal of impurities from crude

of refining to be followed depends upon the nature of the metal and the impurity

1. DISTILLATION METHOD

This method of refining is suitable for volatile metals like Hg, Zn, Pb etc. contaminated with non-volatile impurities. The impure metal is heated in a distillation flask attached with a water condenser. During heating the volatile metal get evaporated and condensed which is collected in a separate container while the non- volatile impurities left at the bottom of the distillation flask.

2. LIQUATION METHOD

This method is suitable for refining the easily fusible metals containing non-fusible impurities. Normally metals such as Sn, Pb etc. are refined by this method. In this method of refining the impure metal is taken in a sloping hearth and is heated from the bottom. The metal liquefies and flows down the sloping hearth leaving the impurities on the hearth.

3. ELECTRO REFINING

This method is employed to refine the less electro positive metals such as Zn, Pb, Al, Cu etc. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode. Both the electrodes are dipped in a suitable aqueous salt solution of the concerned metal. During the process of electrolysis, the impure metal dissolves in its aqueous salt solution providing metal ions which get discharge deposited over the cathode.

Mechanism:

$Fe \longrightarrow Fe^{2+} + 2e^-$

$[O] + H_2O + 2e^- \rightarrow 2OH^-$

$2Fe(OH)_2 + [O] \rightarrow Fe_2O_3.2H_2O$ (rust)

Protection of corrosion:

There are many methods to protect the metal from corrosion. But as per the syllabus, we will discuss the following methods.

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By alloying of metals, we can protect those from corrosion. Alloys resist corrosion in twoways.

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