Session Outcome

- Determine the electronic structure of the given atom for the material used in industry.
- Calculate the quantum numbers for various energy levels of industrially applicable metals.
- Use theory of chemical bonding for identification of different properties material used in the industries.

ATOMIC STRUCTURE

The word “atom” was coined by ancient Greek philosopher. ‘Atom’ means indivisible unit.

Definition; **An atom is the smallest unit of matter that has the characteristic properties of a chemical element.**

Every atom is composed of a nucleus and surrounded by one or more electrons. The nucleus is made of one or more number of protons and typically a similar number of neutrons. More than 99.94% of an atom’s mass is in the nucleus. If the number of protons and electrons are equal, that atom is electrically neutral. If an atom has more or fewer electrons than protons, then it has an overall negative or positive charge, respectively, and it is called an **ion.** Protons and neutrons are called nucleons.

Important properties of the cathode rays:

1. Cathode rays contain the smallest unit of negative charge
2. Cathode rays come out at right angles to the surface of the cathode and move in straight lines.
3. Their path is independent on the position of the anode.
4. They produce phosphorescence on certain salts like ZnS and fluorescence on glass.
5. They blacken photographic plates.
6. The rays pass through thin sheet of metals. If the metal sheet is too thick to be penetrated the rays cast a shadow.
7. They produce X-ray when they strike a metal.
8. The rays ionize a gas through which they pass.
9. They heat a substance on which they fall.
10. They rotate a light wheel placed in their paths. This shows that cathode rays contain material particles having both mass and velocity.
11. The mass of a particle present in cathode rays is found to be 1/1837 of H-atom. This shows that the particle is of sub-atomic nature.
12. Cathode rays are deflected by a magnetic or an electric field showing the particle to be electrically charged, the direction of deflection shows that they are negatively charged.

DISCOVERY OF PROTON

Goldstein (1886) found that some rays passed through these holes in a direction opposite to that of the cathode rays. They seems to be coming from a perforated anode used in a discharge tube experiment so named as **anode rays**. Also known as Positive rays or Canal rays. These are made up of positively charged particles called **protons.**

Important properties of the Anode rays:

1. They are positively charged.
2. The positive charge is either equal to or whole number multiple of the charge on an electron.
3. When hydrogen gas was filled in the discharge tube the positive charge on the positive rays was equal to the negative charge on an electron, and the mass was less than the hydrogen atom.

4. Unlike cathode rays the properties of positive rays are characteristics of the gas in the tube.
5. The deflection of positive rays under the influence of an electric or magnetic field is smaller than that of the cathode rays for the same strength of field. This shows that the positive rays have a greater mass than that of electrons.
6. The mass of the positive rays depends on the atomic weights or molecular weights of the gases in the discharge tube. The charge/mass ratio also varies because the change in positive charge on the rays. It may be either equal to or integral multiple of the charge on an electron.
7. The lightest of all particles identified in positive rays from different elements was one with a mass very slightly less than that of hydrogen atom (or nearly equal to H-atom). The lightest positively charged particle is called a proton (P or P^+).

Table 2 - Comparison of properties of Cathode Rays and Positive (Canal) Rays

Properties	Cathode Rays	Canal Rays
Sign of Charge	Negative	Positive
Magnitude of Charge	Always –1	Mostly +1, but also +2, +3…
Mass	Definite value	Variable, depends on ions
e/m	Definite value	Variable, depends on ions

DISCOVERY OF NEUTRON

In 1932, Chadwick bombarded the element Beryllium with a-particles and noticed the emission of a radiation having the following characteristics.

1. The radiation was highly penetrating.
2. The radiation was unaffected by magnetic and electric fields which shows that it is electrically neutral.
3. It was found to have approximately the same mass as the protons.

Neutron is **"A sub-atomic particle, which is a fundamental constituent of matter having mass approximately equal to the hydrogen atom and which is electrically neutral, is called a neutron"**. It is denoted by n or ${}^{1}_{0}n$. Bombardment of beryllium by α-particles results in the formation of carbon and neutrons are emitted.Mass of a neutron is 1.008930 amu (1.6753×10^{-24}g or 1.6753×10^{-27} kg).

$$Be \rightarrow C + n^{1}_{0} \text{ (Bombarded by α-particles)}$$

At present there are a number of evidences which confirm that like electron, proton and neutron is also a fundamental constituent of atoms (a single exception is ${}^{1}_{1}H$ atom which does not contain any neutron)

SUBATOMIC PARTICLES

Subatomic particles are particles that are smaller than an atom. Important subatomic particles are five in numbers. They are **protons, neutrons, electrons, neutrinos, and positrons**. The first three particles were known to be the building blocks from which atoms are made. protons and neutrons in atomic nuclei and electrons in orbit around those nuclei.

Atomic number (Z) - The number of protons found in the nucleus of an atom.

Atomic Weight / Atomic mass (A) - The number of protons and neutrons combined give us the mass number of an atom.

Number of proton = Number of electron

Number of Neutron = A – Z

Isobars - Atoms with identical atomic weight but different in atomic numbers are known as Isobars.

Ex. Carbon (${}^{14}_{6}C$), Nitrogen (${}^{14}_{7}N$)

Isotopes – Atoms with identical atomic numbers but different in atomic weight are known as Isotopes. **Ex. Protium (${}^{1}_{1}H$), Deuterium (${}^{2}_{1}D$), Triton (${}^{3}_{1}T$)**

Problem 1

Calculate the number of protons, electrons and neutrons of ${}^{80}_{35}Br$

Solution – Given - Atomic mass (A) = 80, Atomic number (Z) = 35

Number of proton = Number of electron

$$Z = 35$$

Number of Neutrons = A – Z

$$80\text{-}35 = 45$$

THE RUTHERFORD MODEL

The Rutherford model is a model of the atom devised by Ernest Rutherford. Rutherford's new model for the atom, based on the experimental results. These are as below-

1. Positive charge and most of the charge of the atom are mainly concentrated in a small region called nucleus.
2. Electron revolves around the nucleus with very high speed in a circular path called orbits.
3. Electrons and nucleus held together in the atom with a strong electrostatic force of attraction.

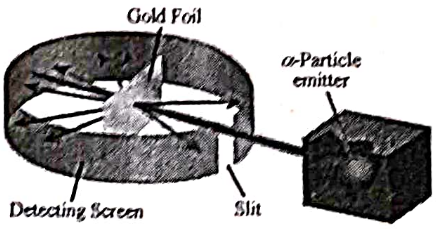


Figure 2 .–Rutherford scattering experiment

Limitations of Rutherford Model

Rutherford model of an atom failed because the comparison with the solar system is the main drawback.Rutherford proposed that the electrons revolve around the nucleus in fixed paths called orbits. According to Maxwell, accelerated charged particles emit electromagnetic radiations and hence an electron revolving around the nucleus should emit electromagnetic radiation. The energy radiated is continues till it eventually moves in a spiral path to collide with the nucleus. Rutherford model did not explain the stability of atoms

THE BOHR MODEL

- The electron in a hydrogen atom travels around the nucleus in a circular orbit.
- The energy of the electron in an orbit is proportional to its distance from thenucleus. The further the electron is from the nucleus, the more energy it has.
- Only a limited number of orbits with certain energies are allowed. In other words,the orbits are quantized.
- The only orbits that are allowed are momentum ofthe electron is an integra divided by 2π.

Facts in favor in Bohr's Model

a) The frequencies of spectral lines of experimentally are close to frequencie

b) 2. The emission and absorption sp explained nicely by Bohr's Theory.

c) There is a Good agreement of radii a hydrogen atoms as calculated on the

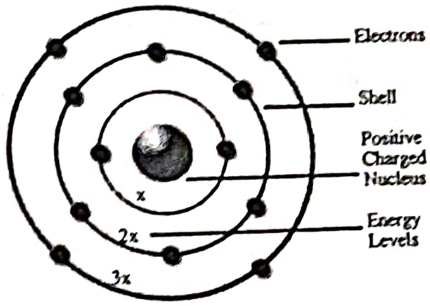


Figure 3 a. Bohr's atomic model

Limitation of Bohr's Theory

a) Bohr's Theory had explained the e spectrum, but it predicted only a

b) Bohr's Theory has success fully Hydrogen atom and hydrogen li lines of atoms or ions having lar

c) No explanation for Zeeman Effe

BOHR AND B

Important Rules. The o accommodate more than 8 elec accommodate more electrons. Thi called the Octet rule. The presenc makes the atom very stable.

HEISENBERG UNCERTAINTY PRINCIPLE

The the Heisenberg Uncertainty Principle also called uncertainty principle or Indeterminacy Principle articulated (1927) by the German physicist Werner Heisenberg" **it's impossible to know the position and the velocity (momentum) of an electron at the same time with absolute accuracy and certainty."**

Mathematically expressed as –

$$\Delta x \, X \, \Delta p \geq \frac{h}{4\pi}$$

Where,

Δx = Uncertainty in position

Δp = Uncertainty in momentum

$\frac{h}{4\pi}$ = Planck's Constant

QUANTUM NUMBERS

Each atom inside of an electron has its own 'address' that consists of four quantum numbers that communicate a great deal of information about that electron. We can say, Quantum numbers is a permanent address of finding electrons in any atom.

'Quantum numbers are a set of values that describes the state of an electron including its distance from the nucleus, the orientation and type of orbital where it is likely to be found, and its spin'.

Each electron in an atom is described by four different quantum numbers. The first three (n, l, m) specify the particular orbital of interest, and the fourth (s) specifies how many electrons can occupy that orbital. These are –

1. Principal Quantum Number(n): $n = 1, 2, 3, \ldots, \infty$

The first quantum number that describes an electron is called the principal quantum number. It is often symbolized by the letter **'n'** and can have any whole number, like as **1, 2, 3, 4....** This number tells us the energy level or size of an orbital. The higher the number, the larger the region is.The principal quantum number also identifies the **shell.**

$$n = 1, 2, 3, 4 \ldots,$$

Shell = K, L, M, N.....

Example - For a Hydrogen atom with n=1, the electron is in its ground state; if the electron is in the n=2 orbital, it is in an excited state.

The total number of orbitals for a given n value is $\mathbf{n^2}$.

2. Angular Momentum (Secondary, Azimuthal) Quantum Number (l): $l = 0, ..., n-1$.

Specifies the **shape** of an orbital with a particular principal quantum number. The secondary quantum number divides the shells into smaller groups of orbitals called **subshells (sublevels)**. Usually, a letter code is used to identify l to avoid confusion with n:

Values for l	=	0	1	2	3	4	5	...
Notation for Sub shell	=	*s*	*p*	*d*	*f*	*g*	*h*	...

The subshell with n=2 and l=1 is the 2*p* subshell; if n=3 and l=0, it is the 3*s* subshell, and so on. The value of l also has a slight effect on the energy of the subshell; the energy of the subshell increases with l ($s < p < d < f$).

3. Magnetic Quantum Number (m_l): $m_l = -l, ..., 0, ..., +l$.

Specifies the **orientation in space** of an orbital of a given energy (n) and shape (l). This number divides the subshell into individual **orbitals** which hold the electrons; there are **($2l$+1)** orbitals in each subshell. Thus the *s* subshell has only one orbital, the *p* subshell has three orbitals, and so on.

Values of *l*	0	1	2	3	4
Notation Sub shell	s	p	d	f	g
Number of orbitals	1	3	5	7	9

4. Spin Quantum Number (m_s): $m_s = +½$ or $-½$.

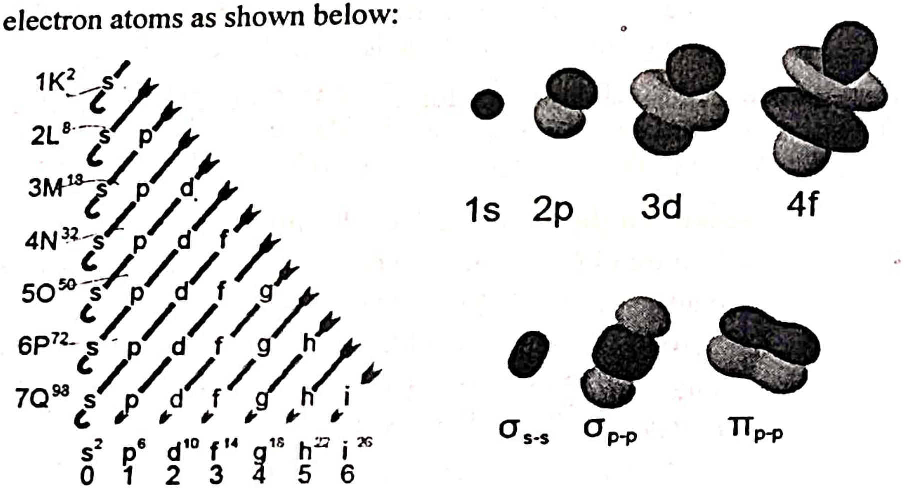
Specifies the **orientation of the spin axis** of an electron. An electron can spin in only one of two directions (sometimes called *up* and *down*).These two direction of orientations are distinguished by the spin quantum numbers. Which can take the values +½ or -½. These are called two spin states of electrons and represented by arrows. (‘!) Spin up and (“!) spin down.

THE AUFBAU PRINCIPLE

The Aufbau procedure (filling order of atomic orbitals) is used to work out the electron confiturations of all atoms. However, modification should be made by applying Hund's rule to be discussed in the next section. The principle states: **In the ground state of the atoms, the orbitals are filled in order of their increasing energy.** The orbitals are filled in following order –

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 4f, 5d, 6p, 7s....

The Aufbau procedure is based on a rough energy levels diagram of many-electron atoms as shown below:



$1s^2_2 2s^2_4 2p^6_{10} 3s^2_{12} 3p^6_{18} 4s^2_{20} 3d^{10}_{30} 4p^6_{36} 5s^2_{38} 4d^{10}_{48} 5p^6_{54} 6s^2_{56} 4f^{14}_{70} 5d^{10}_{80} 6p^6_{86} 7s^2_{88} 5f^{14}_{102} 6d^{10}_{112} 7p^6_{118}$

Figure 6 - Aufbau procedure based on energy levels diagram of many-electron atoms

Problem 6.

Calculate the number of unpaired electron in $_{24}Cr$

Solution - $_{24}Cr \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \mathbf{4s^1}, \mathbf{3d^5}$

So, in $_{24}Cr$ 6 e- s are unpaired.

Problem 7.

Calculate the number of unpaired electron in Cr^{+3}

Solution - $Cr^{+3} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \mathbf{4s^0}, \mathbf{3d^3}$

So, in Cr^{+3} 3 e- s are unpaired.

THE PAULI EXCLUSION P

The Pauli exclusion principle (Wolfga
states that no two electrons in the same atom c
all four of their quantum numbers. What this
two electrons can occupy the same orbital, a
same orbital must have opposite spins. (The
suggests that only two electrons with opposit
orbital! Stated another way, **no two electrons**
numbers *n, l, m and s* in the same atom. Pa
be stated in some other ways, but the idea is
room to accommodate electrons. A state acce
spins.

Because an electron spins, it creates
be oriented in one of two directions. For two
the spins must be opposite to each other; th
These substances are not attracted to m
diamagnetic. Atoms with more electrons t
another contain unpaired electrons. These su
to magnets and are said to be **paramagneti**

In applying these rule, You should r
an **energy state.** Pauli exclusion principle a
Aufbau process, which is figuring out the
elements.

HUND'S RUL

Hund's rule suggests that elect
separate orbitals of subshells. This rule g
to different states in each sub-shell of the a
electrons fill each and all orbitals in the
with opposite spins.

Hund's rule states that :

1. Every orbital in a sublevel is singly occu
   occupied.
2. All of the electrons in singly occupie
   maximize total spin).

It has been observed that half filled and full
aquaire extra stability due to their symme

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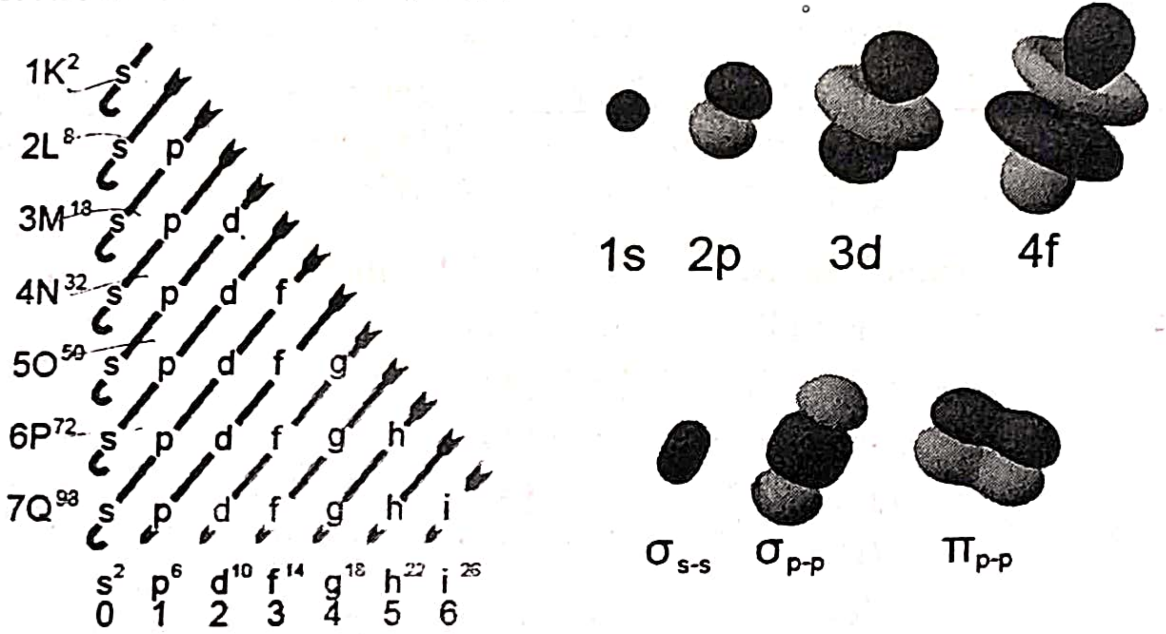

$1s^{2}_{2}2s^{2}_{4}2p^{6}_{10}3s^{2}_{12}3p^{6}_{18}4s^{2}_{20}3d^{10}_{30}4p^{6}_{36}5s^{2}_{38}4d^{10}_{48}5p^{6}_{54}6s^{2}_{56}4f^{14}_{70}5d^{10}_{80}6p^{6}_{86}7s^{2}_{88}5f^{14}_{102}6d^{10}_{112}7p^{6}_{118}$

Figure 6 - Aufbau procedure based on energy levels diagram of many-electron atoms

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So, in ${}_{24}Cr$ 6 e- s are unpaired.

Problem 7.

Calculate the number of unpaired electron in Cr^{+3}

Solution - $Cr^{+3} \rightarrow 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \mathbf{4s^0, 3d^3}$

So, in Cr^{+3} 3 e- s are unpaired.

CHEMICAL BONDING

Chemical bonding is the heart of understanding chemistry. Atom does not have free existence therefore, atoms of approximately all substances found in combined state. Charge less particle formed by the combination of atoms is called molecule. The relative attraction between atoms present in molecules is called chemical bond. **A chemical bond is a lasting attraction between atoms that enables the formation of chemical compounds.** The bond may result from the electrostatic force of attraction between atoms with opposite charges, or through the sharing of electrons as in the covalent bonds.

THEORIES OF CHEMICAL BONDING

In 1916, G. N. Lewis proposed that a chemical bond forms by the interaction of two shared bonding electrons, with the representation of molecules as Lewis structures. In 1927 the Heitler–London theory was formulated which for the first time enabled the calculation of bonding properties of the hydrogen molecule H_2 based on quantum mechanical considerations. In 1931 Linus Pauling was published landmark paper on chemical bonding, name of this theory is **Valence Bond Theory (VBT).** In 1932 F.Hund and R.S.Mulliken developed a theory for chemical bonding named as **Molecular orbital theory (MOT).** In this book we are focusing on VBT and MOT.

VALENCE BOND THEORY (VBT) - According to this theory a covalent bond is formed between two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron. This theory focuses on the concepts of electronic configuration, atomic orbitals (and their overlapping) and the hybridization of these atomic orbitals. Chemical bonds are formed from the overlapping of atomic orbitals wherein the electrons are localized in the corresponding bond region.

The valence bond theory also goes on to explain the electronic structure of the molecules formed by this overlapping of atomic orbitals. It also emphasizes that the nucleus of one atom in a molecule is attracted to the electrons of the other atoms. The chemical bonding of two hydrogen atoms as per the valence bond theory is illustrated below.

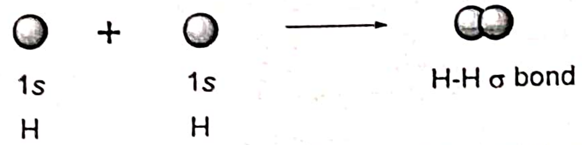

Figure 7. Formation of Sigma Bonds between Two Atoms–Valence Bond Theory (VBT)

Postulates of Valence Bond Theory

1. The overlapping of two half-filled valence orbitals of two different atoms results in the formation of the covalent bond. The overlapping causes the electron density between two bonded atoms to increase. This gives the property of stability to the molecule.
2. In case the atomic orbitals possess more than one unpaired electron, more than one bond can be formed and electrons paired in the valence shell cannot take part in such a bond formation.
3. A covalent bond is directional. Such a bond is also parallel to the region of overlapping atomic orbitals.
4. Based on the pattern of overlapping, there are two types of covalent bonds: sigma bond (σ) and a pi bond (“). The covalent bond formed by sidewise overlapping of atomic orbitals is known as pi bond whereas the bond formed by overlapping of atomic orbital along the inter nucleus axis.is known as a sigma bond.

VBT illustrated by the figures as below -

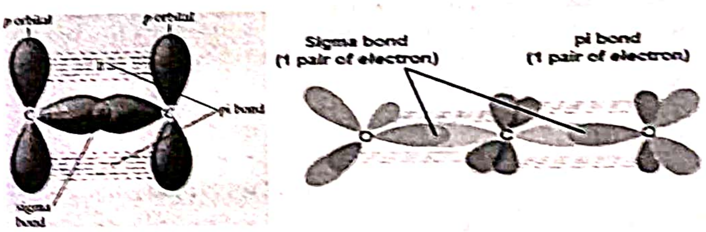

Figure 8. Formation of Sigma and Pi Bonds – Valence Bond Theory (VBT)

It can be noted that sigma bonds involve the head-to-head overlapping of atomic orbitals whereas pi bonds involve parallel overlapping.

hydrogen atom bound to another electronegative atom. Hydrogen bonds are responsible for the properties of water and many biological molecules.

In other words Hydrogen Bonding may be defined as "A weak bond between two molecules resulting from an electrostatic attraction between a proton in one molecule and an electronegative atom in the other". It is represented by dotted line (…….). whereas covalent bond represented by dash (—). Hydrogen bond is established by the attraction force between hydrogen and a highly electro negative atoms, hence it can be considered as a ionic bond. Its bond energy is around 50- 100Kcal/ mol while bond length is larger than a covalent bond.

Example – HF, H_2O, C_2H_5OH

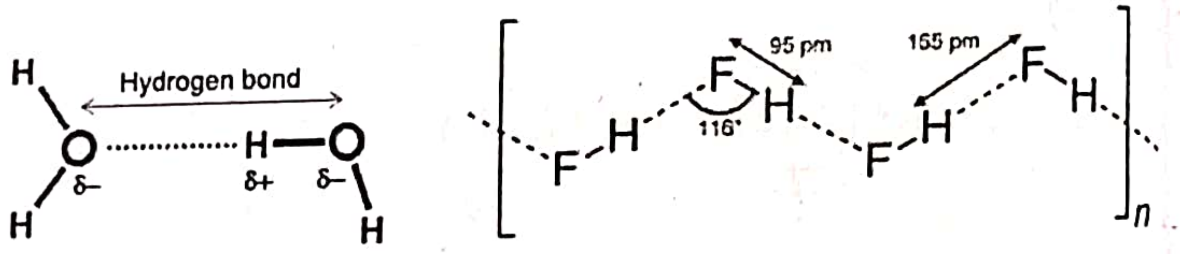

Figure 16 . Example of H_2O and HF

Hydrogen bonds can be classified into two types; a. Intermolecular hydrogen bond and b. Intramolecular hydrogen bond.

a. Intermolecular hydrogen bond

This occurs when the hydrogen bonding is in between H-atom of one molecule and an atom of the electronegative element of another molecule. **For example (i) hydrogen bond between the molecules of hydrogen fluoride. (ii) hydrogen bond in alcohol or water molecules.**

Intermolecular hydrogen bond results into association of molecules. Hence, it usually increases the melting point, boiling point, viscosity, surface tension, solubility, etc.

b. Intramolecular hydrogen bond

This bond is formed between the hydrogen atom and an atom of the electronegative element (F,O,N) , of the same molecule .Intramolecular hydrogen bond results in the cyclization of the molecules and prevents their association. Consequently, the effect of this bond on the physical properties is negligible. For example, intramolecular hydrogen bonds are present in molecules such as o-nitrophenol, o-nitrobenzoic acid, etc.

UNIT 2

CO-2 Use relevant water treatment method to solve industri problems.

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a. Water Treatment - Hardness, Types of Hardness, Determinati of hardness , using EDTA method Hard water, Boiler Problem Boiler corrosion, caustic embrittlement, priming and foamin scales and sludge, Water softening: lime soda process a. Hot lim soda process b. Cold lime soda process, Zeolite process, io exchange process a. Cation exchange b. Anion exchange Municip Water Treatment, Sedimentation, Coagulation, Filtratio Sterilization, BOD & COD

b. Polymer - Classification of polymer, Types of rubber : Natur and, synthetic, processing of natural rubber. Synthetic rubbe Properties and applications of Buna-N, Thiokol, Neoprene.

Session Outcomes

SO2. 1 Perform water softening for the industrial hard water.

SO2. 2 Use the relevant water treatment method for municipal water.

SO2. 3 Differentiate Natural and Synthetic Rubbers

2 (A) WATER TREATMENT

HARDNESS OF WATER

Hardness of water is that characteristics **"which prevents latheri of soap"**. Hardness is the soap consuming capacity of water sample. Thi is due to presence of certain salts of Ca^{++}, Mg^{++} and other heavy metal ion like Al^{+++}, Fe^{++} and Mn^{++} dissolved in water.

Water which does not produces lather with soap are termed as har water. On the other hand soft water readily produces lather when mixe with a little quantity of soap

Example :- Chemical reaction of soap (Sodium stearate) with hadrnes producing salts like calcium chloride and Magnesium sulphat are shown as follows-

$$\underset{\text{Sodium stearate (soap)}}{2C_{17}H_{35}COONa} + \underset{\text{Hardness}}{CaCl_2} \rightarrow \underset{\text{calcium stearate (Insoluble)}}{(C_{17}H_{35}COO)_2Ca} + 2NaCl$$

$$\underset{\text{(soap)}}{2C_{17}H_{35}COONa} + \underset{\text{Hardness}}{MgSO_4} \rightarrow \underset{\text{Magnesium stearate (Insoluble)}}{(C_{17}H_{35}COO)_2Mg} + Na_2SO_4$$

The water are commercially classified on the basis of degree of hardness as Table below-

Table 1. Range of hardness in the water

Hardness	Name of the water
0-70 mg/liter	Soft water
70-150 mg/liter	Moderate hard water
150-300 mg/liter	Hard water
300 mg/liter and above	Very hard water

TYPES OF HARDNESS –

Hardness can be divided in to two types

(A) **Temporary Hardness/ Carbonate / Alkaline Hardness** – Temporary hardness is caused by the presence of dissolved bicarbonates of Ca and Mg and other heavy metal ions. It can be removed by boiling of water. Example of hardness producing ions are - $\mathbf{Ca(HCO_3)_2}$ and $\mathbf{Mg(HCO_3)_2}$.

(B) **Permanent Hardness / Non Carbonate / Non alkaline Hardness** - Permanent hardness is caused by the presence of dissolved chlorides and sulphates of Ca and Mg and other heavy metal ions. It can not be removed by boiling of water. For removal process softening methods are required. Example of hardness producing ions are $\mathbf{CaCl_2}$, $\mathbf{MgCl_2}$, $\mathbf{CaSO_4}$, $\mathbf{FeSO_4}$, $\mathbf{Al_2(SO_4)_3}$.

Table 2. Difference between Temporary Hardness and Permane
Hardness

Temporary Hardness	Permanent Hardness
(i) It is caused by the presence of dissolved bicarbonates of Calcium, Magnesium and other heavy metals.	(i) It is caused by the presence of soluble chlorides and sulphates of Calcium, Magnesium, and other heavy metals
(ii) Salts which are responsible for temporary hardness are – $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$	(ii) Salts which are responsible for permanent hardness are – $CaCl_2$, $MgCl_2$, $CaSO_4$, $FeSO_4$, $Al_2(SO_4)_3$
(iii) It can be removing by simple boiling of water.	(iii) It can't be removed by simply boiling of water.
(iv) Bicarbonates are decomposed and are converted into insoluble carbonates or hydroxides, which precipitate and settle down at the bottom of the vessel. $Mg(HCO_3)_2 \xrightarrow{Heat} Mg(OH)_2\downarrow + 2CO + CO_2\uparrow$	(iv) Softening methods are required for removal of hardness.
(v) It is also known as carbonate or Alkaline hardness.	(v) It is also known as non carbonate or non alkaline hardness.

DEGREE OF HARDNESS

Hardness of water is expressed as **equivalent of calcium carbonat** **($CaCO_3$)**. The reason for choosing $CaCO_3$ as standard for reporting hardnes of water is the

- **Ease in calculations as its molecular weight of $CaCO_3$ is exactly 10**
- **It is most insoluble salt that can be precipitated in water treatmen**

$$\textbf{Equivalent of } CaCO_3 = \frac{\text{Mass of hardness – producing substance} \times 50}{\text{Chemical equivalent of hardness – producing substanc}}$$

Multiplication factors for different salt are tabulated

Table 3 . Multiplication factors for different salt

Dissolved salt	Molar mass	Chemical equivalent	Multiplication factor for converting into equivalents of $CaCO_3$
$Ca(HCO_3)_2$	162	81	100/162
$Mg(HCO_3)_2$	146	73	100/146
$CaSO_4$	136	68	100/136
$MgSO_4$	120	60	100/120
$CaCl_2$	111	55.5	100/111
$MgCl_2$	95	47.5	100/95
$CaCO_3$	100	50	100/100
$MgCO_3$	84	42	100/84
CO_2	44	22	100/44
$Mg(NO_3)_2$	148	74	100/148
HCO_3^-	61	61	100/122
OH^-	17	17	100/34
CO_3^{-2}	60	30	100/60
$NaAlO_2$	82	82	100/164
$Al_2(SO_4)_3$	342	57	100/114
$FeSO_4.7H_2O$	278	139	100/278
H^-	1	1	100/2

UNIT OF HARDNESS

(A) Parts per million (ppm)
(B) Milligrams per litre (mg/L)
(C) Degree Clark (°Cl)
(D) Degree French (°Fr)

(A) **Parts per million (ppm)** – It is defined as the number of parts of $CaCO_3$ equivalent hardness per 10^6 parts of water.

1ppm = 1 part of $CaCO_3$ equivalent hardness in 106 parts of water.

(B) **Milligrams per litre (mg/L)** – It is defined as the number of milligrams of $CaCO_3$ persent in one litre of water.

1 Mg/L = 1 mg of $CaCO_3$ equivalent hardness per litre of water.

1mg/L = 1 ppm

(C) **Degree Clark (°Cl)** - It is defined as the parts of $CaCO_3$ equivalent hardness per 70,000 parts of water. Or, It is the number of grains of $CaCO_3$ equivalent hardness for a gallon of water.

1 °Cl = 1 part of $CaCO_3$ per 70,000 parts of water

(D) **Degree French) (°Fr)** – It is defined as the parts of $CaCO_3$ equivalent hardness per 10^5 parts of water.

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$$3CaCl_2 + 2Na_3SO_4 \rightarrow Ca_3(PO_4)_2 + 6NaCl$$

(i) NaH_2PO_4 - Sodium dihydrogen phosphate (acidic)

(ii) Na_2HPO_4 - Disodium hydrogen phosphate (weak alkaline)

(iii) Na_3PO_4 - Tri sodium phospate (alkaline)

The use of salt depends upon the alkalinity of boiler feed wat
Calcium precipitated at pH value between 9.5 – 10.5.

(3) **Carbonate Conditioning** – In lower pressure boiler scale formati can be avoided by adding sodium carbonate.

$$CaSO_4 + Na_2CO \rightarrow CaCO_3 + Na_2SO_4$$

$CaCO_3$ is loose sludge which can be removed by blow down operatio

(4) **Calgon Conditioning** – By adding calgon (Sodium hexa me phosphate $(NaPO_4)_6$ in boiler water. It forms soluble complex with C ion.

$$Na_2[Na_4(PO_4)_6] \Leftrightarrow 2Na + [Na_4P_6O_{18}]^{2-}$$

$$2CaSO_4 + [Na_4P_6O_{16}] \rightarrow \underset{\text{soluble complexion}}{[Ca_2P_6O_{18}]^{2-}} + 2Na_2SO_4$$

(5) **Treatment with sodium aluminate $(NaAlO_2)$:-** $NaAlO_2$ ge hydrolyzed yielding NaOH and a gelatinous precipitate of aluminu hydroxide.

$$NaAlO_2 + 2H_2O \rightarrow NaOH + \underset{(ppt)}{Al(OH)_3} \downarrow$$

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2 \downarrow + 2NaCl$$

The ppt of $Mg(OH)_2$ plus $Al(OH)_3$ produced inside the boil entraps finely suspended and colloidal impurities, including oil drops a silica.

CORROSION OF BOILER METAL

Boiler corrosion is a decay of boiler material by a chemical a attac by its environment. Main reasons for the boiler corrosion are -

(a) **Dissolved Oxygen** – Water usually contains above 8 ml of dissolv oxygen per liter. Dissolved oxygen in presence of high temperatur attacks boiler material with the formation of rust.

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 \rightarrow 2[Fe_2O_3 . 2H_2O]$$

Rust.

Removal of dissolved Oxygen- Dissolved oxygen present in water can be removed by chemical method and mechanical de aeration method.

Chemical Method –

Addition of chemicals like sodium sulphite or hydrazine may absorbe the oxygen from water. Sodium sulphite forms precipitate of sodium sulphate and hydrazine will form Nitrogen gas.

a. $2 Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$
sodium sulphite

b. $N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$
Hydrazine

Mechanical de aeration Method –

Water spraying in a perforated plate – fitted in tower, heated from sides and commented to vacuum pump. High temperature low pressure and large exposed surface area reduces the capacity of any kind of gases in water.

(iii) CAUSTIC EMBRITTLEMENT

When water is softened by lime and soda process and is fed into the boiler water it may be likely that some residual Na_2CO_3 is still present in the softened water. Na_2CO_3 decomposes in to NaOH and CO_2 in presence of high temperature and pressure. Presence of NaOH makes the boiler water alkaline or caustic.

Caustic embrittlement is caused because of use of highly alkaline water especially in high pressure boilers.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2?$$

The NaOH containing water flows into the minute hair cracks which always present in the inner side of boiler due to presence of scale and sludges. NaOH migrates in the inner wall of boiler by capillary action. Water get evaporated and the concentration of dissolved caustic soda increases progressively in water.

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So if we let M^{2+} be the total of Ca^{2+} and Mg^{2+} ions in solution then :

$$M^{2+} + H_2EDTA^{2-} \rightarrow MEDTA^{2-} + 2H^+$$

Note that 1 mole of M^{2+} reacts with 1 mole of H_2EDTA^{2-}.

At the equivalence point of the titration :

$$\text{moles } M^{2+} = (\text{moles } Ca^{2+} + \text{moles } Mg^{2+})$$
$$= \text{moles } H_2EDTA^{2-}$$

Experimental determination of hardness of water using EDTA metho

Glass Wares - Burette, Pipette, Conical flask, Beaker

Chemicals - 0.01 M-EDTA, Ammonia buffer solution 2 M NaO solutions

Indicator - Eriochrome black-T,(EBT)

Theory - Presence of Ca^{2+} & Mg^{2+} ions can be determined b titration with EDTA solution using EBT as an indicato

Steps of complex formation

Step 1. Addition of EBT into hard water

EBT + Ca^{2+} / Mg^{2+} → EBT metal complex **(Wine red coloure unstable Complex)**

Step 2. Titration with EDTA in to solution of Step 1

EDTA + Ca^{2+} / Mg^{2+} → EDTA metal complex **(colourless br stable complex)**

Step 3 . Determination of end point

All metal ions of Ca and Mg present in water get utilized. No fre ions of Ca and Mg are present in the water. But we are still addin EDTA into experimental solution. At this point Blue coloure unstable complex of metal –EBT gets break and again solutio become blue colour.

EBT Ca^{2+} / Mg^{2+} complex + EDTA → EDTA metal complex **(colourless) + EBT Free (Blue colour**

- Eriochrom black -T is wine-red in hard water, but turns blue in th presence of free EDTA ions in the solution.
- At pH 10, calcium and magnesium ions form colourless, water solubl complexes with EDTA.

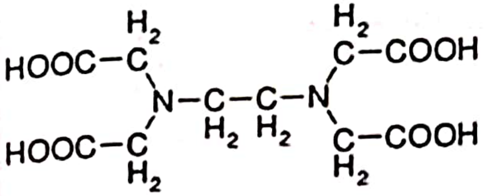

Figure 2 . Structure of EDTA

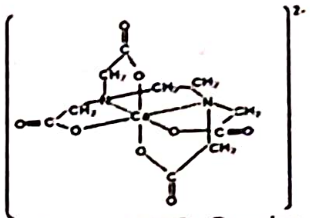

Figure 3 .Metal EDTA Complex

Procedure

1. Measure out 20 ml of tap water into conical flask.
2. Add 10 drops of buffer solution (pH-10).
3. Now add 2-3 drops EBT and titrate with EDTA until the colour of solution changes from wine red to clear blue.
4. Repeat the titration till concordant reading.

Observation Table :

S.No.	Reading of pipette (ml)	Volume of EDTA by Burette (ml)		Final Volume (ml)
		Initial	Final	

Precautions (i) No tinge of reddish blue should remain at the end point.
(ii) The solution should be clear blue.
(iii) Titration should be performed slowly near the end point.

WATER SOFTENING

Removal of hardness from water whether temporary or permanent hardness is done through the process called **softening of water**. It is very essential process because hard water is unsuitable for domestic as well as industrial purposes, During steam generation in industries hard water creates number of boiler problems like scale formation and sludge formation, priming and foaming.

Hardness can be removed by two methods

(1) External Treatment

(2) Internal Treatment

Water can be soften through external treatment are divided as shown –

External Treatment

A) Lime Soda Process
- Cold lime soda Process
- Hot lime soda Process

B) Zeolite Process
- Natural zeolite process
- Synthetic Zeolite process

C) Ion-exchange proc
- Cation exchange resin
- Anion exchange resin

Lime –Soda Process

Principle : The principle involved in this process the solu calcium and magnesium salts in water are chemically converted i insoluble compounds, by adding calculated amount of **lime [$Ca(OH)_2$]** a soda [Na_2CO_3]. **Hardness of Ca and Mg ions present in hard water converted into precipitate of Calcium carbonate [$CaCO_3$]** a **magnesium hydroxide [$Mg(OH)_2$]** respectively. Precipitates are filter and water becomes soft.

a. *COLD LIME –SODA PROCESS*

In this method calculated amount of chemical (lime and soda) a mixed with water at room temperature. The precipitates formed are fine divided, so they do not settle down easily and can't be filtered easily. It essential to add small amounts of Coagulants (like alum, aluminum sulpha sodium aluminate etc.). Coagulants react with hardness and get hydrolyze Gelatinous precipitate of aluminum hydroxide formed and entrapped t fine precipitates as scum. Residual hardness still remains after treatme by cold L-S process is approximately 50 to 60 ppm.

- Raw water and calculated amount of chemicals (lime + soda coagulant) are fed from the top of the inner vertical circular chambe fitted with a vertical rotating shaft varying a number of paddles.
- As the raw water and chemicals flow down, there is a vigorous stirrin and continuous mixing, so softening of water takes place.
- The heavy sludge settled down in the outer chamber by the time an softened water reaches upward.
- The softened water passed through a filter media to ensure complet removal of sludge.
- Filtered soft water finally flows out continuously through the outlet the top.
- Sludge settings at the bottom of the outer chamber are drawn timely.

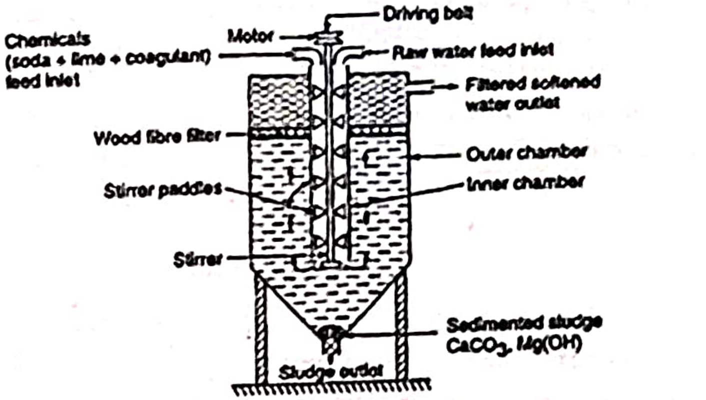

Figure 4 . Cold lime soda process

b. *HOT LIME –SODA PROCESS*

Hot L-S process provides better treatment as compared to cold lime soda process. In this process water is treated with lime and soda at a temperature of 80°C to 100°C water. Rate of softening of water become faster due to more kinetic energy of water molecules. Residual hardness left after treatment is of 15–30 ppm.

The softener setup of hot lime soda method consists of **three parts-**

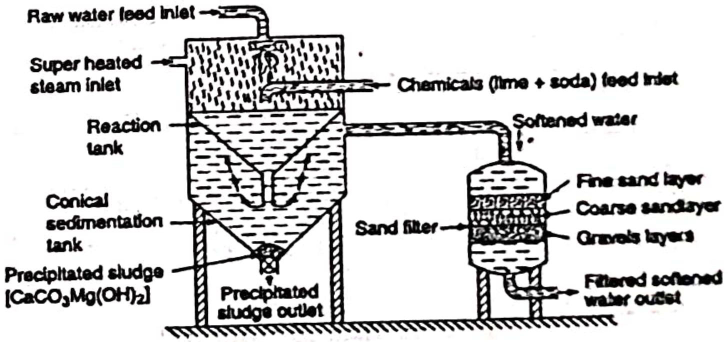

Figure 5 . Hot lime soda process

(a) **Reaction Tank** – The tank has three separate inlet, one each for raw water, chemicals and superheated steam. After their entry they get thoroughly mixed with each other. The reaction starts and get completed in the reaction tank.

(b) **Conical Sedimentation Tank** – from reaction tank the reactants co in this tank and the sludge settles down. Shape of the tank is coni which accelerates the sludge to settle down towards the bottom.

(c) **Sand filter** – It has layer of lime and coarse sand which works as filter and ensure complete removal of the sludge from the softened water.

Processing -

(i) In Hot L-S process reaction proceeds faster.

(ii) No coagulants are needed because sludge and precipitates settle easi

(iii) Some dissolved gases like CO_2 also driven out of the water.

(iv) Viscosity of softened water is lower, so filtration of water becom much easier.

(v) The softening capacity of hot process is many times higher than th of the cold process.

Advantages of Lime –soda Process.

(i) Lime Soda process is very economical.

(ii) It removes not only hardness causing salts but also minerals.

(iii) Due to alkaline nature of treated water, pathogenic bacteria's in wat are reduced.

(iv) Iron and manganese are also removed.

(v) Treated water is alkaline and therefore less corrosive.

Disadvantages of Lime –soda Process.

(i) For efficient and economical softening, careful operation and skille supervision is required.

(ii) Disposal of large amounts of sludge poses a problem.

(iii) Residual hardness present upto 15 ppm, which is not good for boilers

Table 4. Calculation of Lime-Soda Requirement

S. No.	Constituent	Reaction	Need
1.	Permanent hardness of Ca, ($CaCl_2$ and $CaSO_4$)	$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$	S
2.	Permanent hardness of Mg ($MgCl_2$ and $MgSO_4$)	$MgCl_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + CaCl_2$ $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$	L+S
3.	Coagulant $Al_2(SO_4)_3$	$2Al_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$	L+S
4.	Coagulant $FeSO_4$	$FeSO_4 + Ca(OH)_2 \rightarrow Fe(OH)_2\downarrow + CaSO_4$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$	L+S
5.	Free acids H^+HCl and H_2SO_4	$2HCl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O$ $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl$ $H_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O$ $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3\downarrow + Na_2SO_4$	L+S
6.	Temp. Ca $(HCO_3)_2$	$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$	L
7.	Temp. Mg $[Mg(HCO_3)_2]$	$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$	2L
8.	HCO_3^-	$2HCO_3^- + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + H_2O + CO_3^{2-}$	L-S
9.	Dissolved CO_2	$CO_2 + Ca(OH)_2 \rightarrow CaCO_3\downarrow + H_2O$	L
10.	Coagulant $NaAlO_2$	$NaAlO_2 + H_2O \rightarrow Al(OH)_3 + NaOH$	-L

ZEOLITE OR PERMUTIT PROCESS

The word zeolite is derived from two Greek word (zein + lithos) means 'boiling stone'. Natural zeolite are non porous in nature. Chemical structure of sodium zeolite may be represented by $Na_2O.\ Al_2O_3.\ x\ SiO_2.\ Y\ H_2O$. Where $x = 2 - 10$, $Y = 2 - 6$.

Zeolite is hydrated sodium alumino silicate, capable of exchanging reversibly its sodium ions for hardness producing ions in water. Zeolites are also known as permutits. Zeolites are of two types. –

(i) Natural Zeolites

(ii) Synthetic zeoliets