Water Treatment

(*Types of hardness-Units, Alkalinity of water and its significance, Softening methods and Numerical problems based on these methods; Membrane-based processes; Dissolved Oxygen, Problems with Boiler feed water and its treatments.)*

Lecture-1

1.0 Introduction

Water is nature's most wonderful, abundant and useful compound. Without food, human can survive for a number of days, but without water one cannot survive. And with good reason – without water, we'd be nothing. Just dust. It's a tremendously valuable resource, yet one we waste and pollute abnormally. It's a finite resource; we only have what we have. And although there is about 332,500,000 cubic miles of it on earth – only one-hundredth of one percent of the world's water is readily available for human use. We really need to learn how to show it some respect. Which is where World Water Day comes in? March 22 is celebrated as World Water Day.

Even though water deserves celebration every day, we'll take this occasion to give a shout-out to this incredible compound that gives us life and sustains the planet around us. So with that in mind, consider the following facts – some wondrous, some disturbing, all eye-opening.

Some facts about water are 1. The average human body is made of 50 to 65 percent water.

2. Newborn babies have even more, ringing in at 78 percent water.

3. Water covers 70.9 percent of the planet's surface.

4. Ninety-seven percent of the water on Earth is salt water; the water found in the Earth's lakes, rivers, streams, ponds, swamps, etcetera accounts for only 0.3 percent of the world's fresh water. The rest is trapped in glaciers or is in the ground.

5. There is more water in the atmosphere than in all of our rivers combined.

6. a lot can live in one drop of water. There can be a lot going on in a single drop of ocean water. It will most likely have millions (yes, millions!) of bacteria and viruses. And it could also have fish eggs, baby crabs, plankton, or even small worms.

Water is not only essential for the lives of animals and planets, but also occupies a unique position in industries. In industries, water is used for steam generation, as coolants in power & chemical plants, in steel, paper, textiles, etc. Have a look on some facts about volume of water use in some of the industries: 1. it takes 924 gallons of water to produce 2.2 pounds of rice. 2. It takes 2.6 gallons of water to make a sheet of paper. 3. It takes 2,641 gallons of water to make a

This study material is availabe on SIT ASSAN BETA

pair of jeans. 4. It takes 6.3 gallons of water to make 17 ounces of plastic. 5. It takes 39,090 gallons of water to manufacture a new car.

2.0 Impurities in water

Once water has fallen on the earth as rain, it will either start to penetrate the soil, remain on the surface in puddles, or run off into rivers or lakes - depending largely on the type of rock strata found immediately below the earth's surface. Therefore, the main source of impurities is the mineral and organic constituents which make up the upper layers of the earth's crust, and which are dissolved or held in suspension by the water. Surface waters are especially prone to seasonal changes in quality caused mainly by varying levels of organic contaminants. For instance, during the autumn and winter months, dead leaves and decaying plants release large quantities of organic matter into streams, lakes and reservoirs.

Water has been called both 'the matrix of life' and 'the universal solvent'. So in addition to providing a life-support system for a broad range of living organisms, it can dissolve virtually every chemical compound, though not necessarily to a detectable degree. It normally contains < 500 mg/l total dissolved solids TDS - equivalent to a purity of 99.95%. Even so, minute quantities of impurities can have a profound effect on industrial and laboratory processes - hence the need for purification.

The impurities present in raw waters can be classified as follows:

A. **Dissolved impurities:** It is of three types: (**1).** *Inorganic salts* (due to presence of dissolved salts like carbonates, bicarbonates, nitrates, chlorides and sulphates of calcium (Ca), magnesium (Mg), iron (Fe),sodium (Na), etc. (**2).** *Organic matters* (due to presence of humic and fulvic Acids, pesticides, detergents, etc.) (3) *Dissolved gases* (includes O_2, CO_2). Dissolved impurities causes corrosion in boilers and imparts hardness to water.

B. **Suspended impurities:** It is of three types: (1) *Organic* (includes vegetable & animal matters, industrial & domestic by-products, oil globules, etc.); (2) *Inorganic* (includes clay/silica/sand particles); (3) *Colloidal (*organic and inorganic)- includes finely divided silica, clay, sand, products from organic wastes, etc. Such impurities impart tirbidity, colour and odour to water.

C. **Living Matters:** It is of two types: (1) *Micro-organisms* (include bacteria, fungi, protozoa, and algae); (2) *Macro-organisms* (includes fish, worm, larvae, shrimps, etc.). Living matters brings health related issues upon consumptions.

3.0 Sources of impurities:

Following are the sources of impurities in water:

A. Gases like O_2, CO_2, etc. are picked up from the atmosphere by rain water.
B. Decomposition of plant and animal remains introduce organic impurities in water.
C. Water takes inorganic impurities when it comes in contact with ground, soil or rocks.
D. Suspended/living matters impurities are also introduced in water when it comes in contact with sewage or industrial waste.

4.0 Specification of water for different uses

This study material is availabe on SIT ASSAN BETA

It is not true that water with same condition will be use in all kinds of industries or purposes. Specifications of water for various industries are different. Few examples are discussed below:

A. ***Boilers in steel industries*** require water of no hardness, dissolved gases, alkaline and acidic masses.

B. ***Paper industries*** need water free from silica, turbidity, alkalinity, hardness, etc.

C. ***Textile industries*** require water of nearly zero hardness and no organic matter content.

D. ***Beverage industries*** need water free from alkaline constituents.

E. ***Sugar industries*** demand water free from salts like sulphates, nitrates, etc.

F. ***Pharmaceutical industries*** need ultra pure water free from pathogenic bacteria.

N.B.: As per the BIS 2012 (Bureau of Indian Standard), we require drinking water of following specifications:

1. pH value-6.5-8.5; 2. Total dissolved solid-500 mg/l; 3. Ca- 75 mg/l; 4. Chloride- 250 mg/l; 5. Fluoride- 1.0 mg/l; 6. Iron-0.3 mg/L; 7. Total hardness- 200 mg/l; 8. Arsenic-0.01 mg/l; 9. Lead-0.01 mg/l; Mercury-0.001 mg/l; cyanide- 0.05 mg/l; 10. Colour-colourless; 11. Pathogenic micro-organisms- nil per 100 ml water.

5.0 Hardness of water

Hardness in water is a characteristic by virtue of which it prevents lathering/foaming of soap solution. It is also defined as the soap consuming capacity of water. Higher is the hardness of water larger is the consumption of soap. Hardness is due to presence of dissolved salts of calcium (Ca), magnesium (Mg) and other heavy metals like iron (Fe), manganese (Mn), aluminum (Al). In other words hardness in water is due to bicarbonate (HCO_3^-), chloride (Cl^-), sulphate (SO_4^{3-}), and nitrate (NO_3^-) of Ca, Mg, Fe, Mn, Al, etc.

Salts like $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, $FeSO_4$, $Al_2(SO_4)_3$, $MnSO_4$, etc. are responsible of hardness of water. **The major contributor towards hardness is Ca and Mg-salts.

N.B.: Chemical constituents like $NaHCO_3$, $CaCO_3$, NaCl, KCl, K_2SO_4, Na_2SO_4, $NaNO_3$, KNO_3, Fe_2O_3, etc. are treated as ***non-hardness constituents***.

Soap consuming tendency of hard water (Why is hard water consumes more soap?)

Soaps are sodium (Na) or potassium (K) salt of higher fatty acids (e.g.; Stearic acid $C_{17}C_{35}COOH$, oleic acid $C_{17}C_{33}COOH$, palmitic acid $C_{15}C_{31}COOH$). For example, $C_{17}C_{35}COONa$ (Sodium stearate).

A sample of hard water (let say contains hardness constituent as $CaCl_2$) when treated with soap does not produce enough lather, but on the other hand forms a white scum or precipitate.

This study material is availabe on SIT ASSAN BETA

The precipitation process continues till all the hardness constituents are removed as white scum. After this, soap generates enough foam with water. The chemical reactions involved during this process are as follows:

1. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2$ → $(C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
2. Soap + water → Produce enough foam

Hard Water and Soft Water

The water which does not produce lather with soap solution readily, but forms a white curd is called hard water. In fact any cations which produce soft precipitate with soap solution will contribute to hardness. Examples include Ca^{+2}, Mg^{+2}, etc. On the other hand, water which lathers easily on shaking with soap solution is called soft water. Soft water is free from dissolved Ca and Mg-salts. The difference between the two is summarized in the following table-1.

Sl. No.	**Hard Water**	**Soft Water**
1	Water which does not produce lather with soap solution, but forms a white curd, is called "Hard Water".	Water which readily form foam on shaking with soap solution, is called "Soft Water".
2	It contains dissolved Ca and Mg-salts.	It does not contain dissolved Ca and Mg-salts.
3	Cleansing quality of soap is depressed and a lot of soap is wasted during washing and bathing.	Cleansing quality of soap is not depressed and a little amount of soap is wasted during washing and bathing.
4	B. Pt. of water is elevated.	Water boils at 104 ^{0}C.
5	Hair and skin becomes hard and dull.	Hair and skin becomes soft.
6	No **Plumbo-solvency** occurs	**Plumbo-solvency** occurs
7	Hardness > 50 ppm	**Hardness** < 50 ppm

***A residual hardness of about 85 ppm as $CaCO_3$ equivalent is needed for drinking purposes.

Plumbosolvency: **Plumbosolvency** is the ability of a solvent like water to dissolve lead (Pb latin name-Plumbus). Soft water is a plumbo-solvent. Permissible limit of Pb in water is 0.05 ppm.

- ✓ **Why water should not be soft for drinking purposes?**
  The reason is that soft water is plumo-solvent and helps in dissolution of Pb as per the following reaction: $\mathbf{2Pb + 2H_2O + O_2 \rightarrow 2Pb(OH)_2}$
  N.B: The solubility of Pb in water is diminished in the presence of HCO_3^- (i.e., in hard water)
  Also mineral like Ca are needed by us for strengthening our bone and developing teeth.

Q. 1. What is plumbo-solvency?

This study material is availabe on SIT ASSAN BETA

Ans: **Plumbosolvency** is the ability of a solvent like water to dissolve lead (Pb: latin name-Plumbus).

Q. 2. Give reason that hard water is not a plumbo-solvent.

Ans. As the solubility of Pb (plumbus) in water is diminished in the presence of HCO_3^- (i.e., in hard water), it provides a protective layer on the surface of the pipe.

Q. 3. Give reason that hard water consumes a lot of soap.

Ans. A sample of hard water (let say contains hardness constituent as $CaCl_2$) when treated with soap does not produce enough lather, but on the other hand forms a *white scum or precipitate*. The precipitation process continues till all the hardness constituents are removed as white scum. After this, soap generates enough foam with water. The chemical reactions involved during this process are as follows:

3. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2$ → $(C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
4. Soap + water → Produce enough foam

Q. 4. Write the chemical reactions involved when hard water reacts with soap.

Ans. The chemical reactions involved during this process are as follows:

1. $2C_{17}C_{35}COONa$ (soap) + $CaCl_2$ → $(C_{17}C_{35}COO)_2Ca$ (*Calcium Stearate, White scum*) + 2NaCl
2. Soap + water → Produce enough foam

Table-2 *Advantages and disadvantages of hard water*

Advantages	***Disadvantages***
1. Taste of water is better than soft water	*1. It produces white precipitate with soap solution. Thus, the washed clothes look dull.*
2. Dissolved Ca-salts helps in producing strong teeth and healthy bones in children	*2. Causes boiler corrosion.*
3. Not a plumbo-solvent	*3. Increases B. Pt. of water.*

Q. 5. Mention some advantages of hard water. (Refer the above table-2)

Q. 6. Mention some disadvantages of hard water. (Refer the above table-2)

This study material is availabe on SIT ASSAN BETA

Lecture-2 of Water Treatment

Types of Hardness

It is of two types: (1) Temporary Hardness and (2) Permanent Hardness

1. *Temporary Hardness:* It is caused by the presence of dissolved bicarbonates (HCO_3^-) of Ca and Mg, heavy metals like Al, Mn and carbonates of Fe. The salts responsible are $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, etc. These salts are thermally unstable and undergo thermal decomposition to form insoluble substance as follows;
   a. $Ca(HCO_3)_2 \rightarrow CaCO_3$ (ppt.) + H_2O + CO_2
   b. $Mg(HCO_3)_2 \rightarrow Mg(OH)_2$ (ppt.) + $2CO_2$

So, temporary hardness can be removed by boiling. It is otherwise known as *carbonate or alkaline hardness*.

2. *Permanent Hardness:* It is caused by the presence of chloride (Cl^-), nitrates (NO_3^-), sulphates (SO_4^{2-}) of Ca, Mg, Fe, Al, Mn, etc. The salts responsible are $CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$, $MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, $Al_2(SO_4)_3$, $FeSO_4$, etc. These salts are thermally stable as present in ionic form in water. So, they can't be remove by heating but removed by softening methods. It is also known as *non-carbonate or non-alkaline hardness*.

Total Hardness

All the hardness causing salts contribute towards total hardness. So, total hardness is the sum of temporary and permanent hardness.

Q. 7. Which of the following salt is a non-hardness constituent?

$MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$, $Al_2(SO_4)_3$, $NaHCO_3$

Ans. $NaHCO_3$

Q. 8. Which of the following salts are hardness constituents?

$CaCl_2$, $Ca(NO_3)_2$, K_2SO_4, Na_2SO_4, $NaNO_3$, KNO_3, Fe_2O_3

Ans. $CaCl_2$ and $Ca(NO_3)_2$

5.2 Degree of Hardness

As $CaCO_3$ is insoluble in water, it does not contribute towards hardness of water. But, hardness of water is expressed in terms of equivalent amount of $CaCO_3$ due to following reasons:

A. Ease in calculation as its molecular weight is 100.

This study material is availabe on SIT ASSAN BETA

B. It is the most insoluble salt that can be precipitated during water treatment.

Equivalent of $CaCO_3$ = (S, strength of hardness substance in mg/L) x [100/ (2 x M/n-factor)]

Where, M = Molar mass of hardness substance.

N.B.: n-factor of all Ca and Mg-salts are 2. For aluminum sulphate, it is 6.

- ✓ All hardness and non-hardness constituents can be expressed as **Equivalent of $CaCO_3$**

Q. 9. Give reason that $CaCO_3$ is used to express hardness of water.

Ans. The hardness of water is expressed in terms of equivalent amount of $CaCO_3$ due to following reasons:

A. Ease in calculation as its molecular weight is 100.
B. It is the most insoluble salt that can be precipitated during water treatment.

Q. 10. What happens when hard water containing temporary hardness constituents are boiled for some time?

Ans. Temporary hardness constituents like $Ca(HCO_3)_2$ $Mg(HCO_3)_2$ are thermally unstable and undergo thermal decomposition to form insoluble substances like $CaCO_3$ & $Mg(OH)_2$ as follows;

c. $Ca(HCO_3)_2 \rightarrow CaCO_3$ (ppt.) + H_2O + CO_2
d. $Mg(HCO_3)_2 \rightarrow Mg(OH)_2$ (ppt.) + $2CO_2$

Example-1 Express the following constituents as $CaCO_3$ eq.: (1) 162 mg/L of $Ca(HCO_3)_2$, (2) 111 mg/L of $CaCl_2$, and (3) 117 mg/L NaCl, Given: At mass: Ca = 40, C = 12, O = 16, H = 1, Na = 23, Cl = 35.5

Solution: (1) $Ca(HCO_3)_2$ as $CaCO_3$ eq. = 162 x 100/162 = 100 mg/l, here n-factor = 2

(2) $CaCl_2$ as $CaCO_3$ eq. = 111 x 100/111= 100 mg/l, here n-factor = 2

(3) NaCl as $CaCO_3$ eq. = 117 x 100/2 x 58.5 = 100 mg/l, **here n-factor = 1**

Example-2

A water sample contains 136 mg/L of $CaSO_4$. Calculate the hardness as equivalent amount of $CaCO_3$. (At mass of Ca = 40, S = 32, O = 16)

Solution: Equivalent of $CaCO_3$ = 136 x [100/(2 x 136/2) = 100 ppm

Example-3 How many gram of $MgSO_4$ dissolved per litre gives 200 ppm of hardness as equivalent amount of $CaCO_3$. (At mass: Mg = 24, S = 32, O = 16)

This study material is availabe on SIT ASSAN BETA

Solution: Equivalent of $CaCO_3$ = (S, strength of hardness substance in mg/L) x [100/ (2 x M/n-factor)]

So, (S, strength of hardness substance in mg/L) = Equivalent of $CaCO_3$/ [100/ (2 x M/n-factor)]

Or S = 200/[100/(120)] = 240 mg/L = 0.24 g/L

5.3 Units of hardness and their inter-relations

Hardness can be expressed by the four units.

1. Parts per million (ppm): It is the 1 part of $CaCO_3$ equivalent hardness per 10^6 parts of water.
2. Millligrams per litre (mg/L): It is the no of mg of $CaCO_3$ equivalent hardness present per litre of water.
3. Degree French (^{0}Fr): It is the 1 part of $CaCO_3$ equivalent hardness per 10^5 parts of water.
4. Clarke's degree (^{0}Cl): It is the part of $CaCO_3$ equivalent hardness per 70,000 parts of water.

Relationships between various units of Hardness

5. We know that, 1 ppm = 1 part per 10^6 parts of water
   1 ^{0}Fr = 1 part per 10^5 parts of water,
   And 1 ^{0}Cl = 1 part per 70, 000 parts of water
   So, 1 part = 10^6 ppm = 10^5 ^{0}Fr = 70,000 ^{0}Cl
   Or, 10^6 ppm = 10^5 ^{0}Fr = 70,000 ^{0}Cl
   Divide all by 10^6, so that **1 ppm = 0.1 ^{0}Fr = 0.07 ^{0}Cl = 1 mg/L**

Q. 11. Show that 1 ppm = 1 mg/L

Answer: 1 mg/L means 1 mg of $CaCO_3$ eq. hardness in 1L of water

= 1 mg of $CaCO_3$ eq. hardness in 10^6 mg of water ***(as for water, 1 L = 1 Kg = 1000 g = 1000,000 mg = 10^6 mg)

= 1 part of $CaCO_3$ equivalent hardness per 10^6 parts of water = 1 ppm (Proved)

This study material is availabe on SIT ASSAN BETA

Example-4 A sample of water on analysis was found to contain the following impurities:

Impurity	$Ca(HCO_3)_2$	$Mg(HCO_3)_2$	$MgSO_4$	$CaSO_4$	K_2SO_4
Quantity (mg/L)	4	6	8	10	10
Mol Wt.	162	146	120	136	134

Calculate the temporary, permanent, and total hardness of water in ppm, ^{0}Fr and ^{0}Cl.

Solution:

Impurity	**Quantity (mg/L)**	**n-factor**	**Mol. Wt.**	**$CaCO_3$ eq. in mg/L**
$Ca(HCO_3)_2$	4	2	162	4 x (100/162)= 2.47
$Mg(HCO_3)_2$	6	2	146	6 x (100/146)= 4.11
$MgSO_4$	8	2	120	8 x (100/120)= 8.33
$CaSO_4$	10	2	136	10 x (100/136)= 5.88

N.B.: K_2SO_4 is a non-hardness constituent.

(i) **Temporary Hardness (due to bicarbonates of Ca and Mg) =** 2.47 + 4.11 = 6.58 ppm = 6.58 x 0.1 ^{0}Fr = 0.658 ^{0}Fr = 6. 58 x 0.07 ^{0}Cl = 0.46 ^{0}Cl

(ii) **Permanent hardness (due to sulphates of Ca and Mg) =** 5.88 + 8.33 = 14.21 ppm = 1.421 **^{0}Cl** = 0.995 ^{0}Cl

(iii) **Total hardness =** 6.58 + 14.21 = 20.79 ppm = 2.079 ^{0}Fr = 0.9947 ^{0}Cl

Example-5

A sample of water on analysis was found to contain the following impurities:

Impurity	$Mg(HCO_3)_2$	$CaSO_4$	$MgCl_2$	$CaCl_2$	NaCl
Quantity (mg/L)	16.2	27.2	9.5	22.2	10
Mol Wt.	162	136	95	111	58.5

Calculate the temporary, permanent, and total hardness of water in ppm, ^{0}Fr and ^{0}Cl.

This study material is availabe on SIT ASSAN BETA

Solution:

Impurity	Quantity (mg/L)	n-factor	Mol. Wt.	$CaCO_3$ eq. in mg/L
$Mg(HCO_3)_2$	16.2	2	162	16.2 x (100/162)= 10
$CaSO_4$	27.2	2	136	27.2 x (100/136)= 20
$MgCl_2$	9.5	2	95	9.5 x (100/95)= 10
$CaCl_2$	22.2	2	111	22.2 x (100/111)= 20

N.B.: NaCl is a non-hardness constituent.

(i) **Temporary Hardness (due to** $Mg(HCO_3)_2$**) = 10 mg/L = 10** ppm = 10 x 0.1 ^{0}Fr = 1.0 ^{0}Fr = 10 x 0.07 ^{0}Cl = 0.7 ^{0}Cl

(ii) **Permanent hardness (due to** $CaSO_4$, $MgCl_2$, $CaCl_2$ **) =** 20 + 10 + 20 = 50 mg/L = 50 ppm = 5.0 ^{0}**F** = 3.5 ^{0}Cl

(iii) **Total hardness =** 10 + 50 = 60 ppm = 6 ^{0}Fr = 4.2 ^{0}Cl

This study material is availabe on SIT ASSAN BETA

Lecture-3

6.0 Water Quality Parameters

Water quality parameters include chemical, physical, and biological properties. Parameters that are frequently monitored for water quality include hardness, acidity, alkalinity, temperature, dissolved oxygen, pH, conductivity, turbidity, colour, odour, etc.

1. **Hardness:** (already discussed)
2. **Alkalinity: It is a measure of the ability of water to neutralize the acids.**
3. **Dissolved oxygen: It is the mass of the oxygen gas present, in milligrams per liter of water. Oxygen is more easily dissolved in cold water.**
4. **Acidity:** Acidity of water is its quantitative capacity to react with a strong base.
5. **Temperature:** Water Temperature is a controlling factor for aquatic life: it controls the rate of metabolic activities, reproductive activities and therefore, life cycles.
6. **pH:** pH is an important limiting chemical factor for aquatic life. If the water in a stream is too acidic or basic, the H+ or OH- ion activity may disrupt aquatic organisms biochemical reactions by either harming or killing the stream organisms.
7. **Conductivity:** It is a measure of how well water can pass an electrical current (i.e., it is a measure of a solution's ability to conduct electricity). It is an indirect measure of the presence of inorganic dissolved solids such as chloride, nitrate, sulfate, phosphate, sodium, magnesium, calcium, iron and aluminum.
8. **Turbidity:** Turbidity is a measure of the cloudiness of water. Cloudiness is caused by suspended solids (mainly soil particles) and plankton (microscopic plants and animals) that are suspended in the water column.
9. **Colour:** It is due to the presence of natural organic matter (humic substance giving the yellow color. The color may also be caused by certain industrial waste and by some metallic complexes.
10. **Odour:** It is often due to dissolved organic impurities, such as phenols, chlorophenols, sewage component.

Alkalinity

It is a measure of the ability of water to neutralize the acids.

Any substances which can cause an increase in the hydroxide ion concentration [OH^-] upon dissociation or due to hydrolysis or due to decomposition contribute towards alkalinity of water. Alkalinity is due to presence of ions like CO_3^{2-}, OH^-, HCO_3^- in the water. So, presence of constituents like NaOH, Na_2CO_3 and $NaHCO_3$ in water makes the water alkaline as per the following reactions:

1. $NaOH \rightarrow Na^+ + OH^-$ (Dissociation)
2. $Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$ (Hydrolysis)
3. $NaHCO_3 \rightarrow NaOH + CO_2$ (Thermal decomposition)

N.B.: Alkalinity in water is due to only $CO_3^{2-}/OH^-/HCO_3^-$ or due to OH^- and CO_3^{2-} together or due to CO_3^{2-} and HCO_3^- together. But, the possibility of OH^- and HCO_3^- together in water is ruled out. (Why?)

This study material is availabe on SIT ASSAN BETA

*** Because they combine to form CO_3^{2-} in water as per the following reaction:

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$ (or $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$)

Drawbacks of highly alkaline water

Some of the drawbacks are: 1. It causes alkaline corrosion in boiler known as caustic embrittlement.
2. It may leads to deposition of precipitates in boiler tubes and pipes.
3. Not fit for human consumption for a longer period of time.

Q. Which of the following combination is ruled out and why?

A. OH^- and CO_3^{2-}
B. CO_3^{2-} and HCO_3^-
C. OH^- and HCO_3^-

Ans. **C.** Because they combine to form CO_3^{2-} in water as per the following reaction:

$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$ (or $NaOH + NaHCO_3 \rightarrow Na_2CO_3 + H_2O$)

Dissolved Oxygen (DO)

It is the most usual corrosion causing factor in boilers. DO react with the iron (Fe) of boiler in presence of water to form rust (Ferric oxide).

Chemical reaction:

$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$ (ferrous form is unstable)

$Fe(OH)_2$ oxidizes in presence of oxygen to form Ferric oxide ($Fe_2O_3 . xH_2O$).

Removal of DO: (1) By heating

(2) By addition of dilute solution of Hydrazine (NH_2-NH_2 or N_2H_4), Sodium sulphite Na_2SO_3 and sodium sulphide Na_2S

1. $O_2 + N_2H_4 \rightarrow N_2 + 2H_2O$
2. $O_2 + 2Na_2SO_3 \rightarrow 2Na_2SO_4$
3. $2O_2 + Na_2S \rightarrow Na_2SO_4$

Q. How to remove DO by adding hydrazine to water?

Ans. $O_2 + N_2H_4 \rightarrow N_2 + 2H_2O$

6.1 Boiler feed water

This study material is availabe on SIT ASSAN BETA

Lot of water is used in boilers of steel industries for generation of steam. But, water with specific characteristics is fit for feeding into it.

A boiler feed water should have the following characteristics:

a. Total hardness should be either 0 or less than 2 ppm.
b. Alkalinity should be less than 1 ppm.
c. Should be free from acidic masses
d. Should be free from dissolved gases like oxygen and carbon dioxide

6.2 Common problems in boiler

The common problems which were arising in boiler due to feeding of hard/alkaline/acidic water are as follows:

A. Formation of soft and hard precipitates known as **sludges and scales**, respectively
B. Boiler Corrosion

Q. What should be the characteristics of boiler feed water?

Ans. ***A boiler feed water should have the following characteristics:***

e. Total hardness should be either 0 or less than 2 ppm.
f. Alkalinity should be less than 1 ppm.
g. Should be free from acidic masses
h. Should be free from dissolved gases like oxygen and carbon dioxide

Boiler Corrosion

It is the decay or loss of boiler body material (usually made of iron) either due to chemical or electrochemical reactions with its environment.

Causes of boiler corrosion:

1. Presence of dissolved O_2 in water
2. Presence of dissolved CO_2 in water
3. Presence of alkaline masses in water (e.g. NaOH)
4. Presence of acidic masses in water (e.g. HCl)
5. Presence hardness causing substance like $MgCl_2$ in water ($MgCl_2 + H_2O \rightarrow Mg(OH)_2$ (ppt.) + 2 HCl)

Disadvantages:

1. Reduces the life of boiler
2. Causes leakages at joints
3. Increases the cost of repair & maintenance

This study material is availabe on SIT ASSAN BETA

Q. What is boiler corrosion? Mention some of its limitations.

Ans. Boiler corrosion is the decay or loss of boiler body material (usually made of iron) either due to chemical or electrochemical reactions with its environment.

Disadvantages:

1. Reduces the life of boiler
2. Causes leakages at joints
3. Increases the cost of repair & maintenance

This study material is availabe on SIT ASSAN BETA

Lecture-4

7.0 Softening of hard water

Since hard water is unsuitable for domestic as well as industrial use, it is advisable to remove or reduce the amount of hardness causing salts from the water. *The process by which we remove or reduce the hardness of water is termed as "**softening**" of water.* The hardness causing salts can be removed or its amount can be reduced from the water by the two ways:

A. External Treatment, and
B. Internal treatment

External Treatment: It is carried out before its entry into the boiler. This treatment prevents boiler problems. Hence, it's a preventive method. The various external treatment or water softening methods are: *(A) Lime-Soda Process; (B) Zeolite process; an (C) Ion-exchange resin process.*

Internal treatment: It is carried inside the boiler after the external treatment by addition of chemicals. It is a corrective method to remove those salts which were not completely removed by external treatment. The various internal treatments are: *(A) Colloidal conditioning; (B) Phosphate conditioning; (C) Carbonate conditioning; (D) Calgon conditioning; (E) EDTA conditioning, etc.*

Fig.1. Types of water treatment

Q. *Differentiate between External and Internal Treatment of water.*

Sl. No.	***Internal Treatment***	***External Treatment***
1	It is carried out in the boiler itself.	It is carried out outside the boiler, before water enters the boiler.
2	It is a corrective method	It is a preventive method
3	It includes: (A) Colloidal conditioning; (B) Phosphate conditioning; (C) Carbonate	It includes: (A) Lime-Soda Process; (B) Zeolite process; an (C) Ion-

This study material is availabe on SIT ASSAN BETA

	conditioning; (D) Calgon conditioning, etc.	exchange resin process.

Q. Define softening with a suitable example.

Ans. The process by which we remove or reduce the hardness of water is termed as "softening" of water. Example:- Lime-Soda process

7.1 External Treatment of Water Softening

(A) Lime (L)-Soda (S) Softening Process

Basic Principle: The basic principle of this process is to convert all the soluble hardness causing constituents into insoluble masses (known as precipitates) by addition of calculated amount of lime **$Ca(OH)_2$** and soda **Na_2CO_3** to the hard water. The precipitates [$CaCO_3$ and $Mg(OH)_2$] are then removed by sedimentation (a settling process) and filtration.

Types of L-S process: Based on the working temperature of the softener, it is of two types.

(1) Cold L-S Process, and (2) Hot L-S Process

Cold L-S Process: In this process calculated amount of chemicals (L & S) are added to the water at room temperature (RT).

But, at RT, the precipitates formed are very fine and do not settle down easily under the force of gravity and can easily pass through the filter too. So, in order to avoid such situation a small amount of **coagulants** like potash alum [$K_2SO_4.Al_2(SO_4)_3.24H_2O$], Aluminium sulfate $Al_2(SO_4)_3$, or sodium aluminate $NaAlO_2$ are added to the water along with L & S. Thus coagulant helps in converting fine particles to coarse particles. This process provides water with a residual hardness of 50-60 ppm.

Hard water + L + S + Coagulant → precipitate + soften water

1. $CaCl_2$ (hard water) + Na_2CO_3 (soda) → $CaCO_3$ (ppt) + 2 NaCl
2. $MgCl_2$ + $Ca(OH)_2$ (lime)+ Na_2CO_3 (soda) → $Mg(OH)_2$ (ppt) + $CaCO_3$ (ppt) + 2 NaCl

Working process: Hard water and calculated amount of lime, soda and coagulant are fed from the top of the softener fitted with a paddle stirrer at RT (see Figure). Vigorous stirring ensures continuous mixing and softening takes place. The soften water rising up passes through a wood-fibre filter whereby traces of sludge are removed. The precipitates settle down at the bottom by the time the softened water reaches the outlet. Coarse precipitates are settled down and relatively

This study material is availabe on SIT ASSAN BETA

finer one is retained by the wood filter. The precipitates are periodically removed through the sludge outlet.

Limitations of cold L-S process: Some of the limitations are: (1) Residual hardness is high (50-60 ppm), so not fit for boiler operation; (2) As it operates at RT, softening capacity is low; (3) Dissolved gases are not removed; (4) Relatively more chemicals are needed (coagulant is required)

Fig. 2. Cold L-S softening method

Hot L-S Process: In this process water is treated with calculated amount of lime and soda at a temperature of 90-100 ^{0}C.

Working process: Raw water, chemicals and steam are thoroughly mixed in a reaction tank maintained at ~100 ^{0}C using steam. The sludge formed after reaction is settled down in a conical *sedimentation vessel*. Then water passed through a ***sand filter*** to obtain clear and soften water with a residual hardness 15-30 ppm.

Advantages of Hot L-S process over cold process:

1. Process is faster, 2. Good softening capacity, 3. No coagulant is required, 4. Relatively less amount of chemicals are needed, 5. Dissolved gases are also removed, 6. Pathogenic bacteria are also killed, 7. Residual hardness is relatively low

Limitations of L-S process: Some limitations are: (1) It requires careful operation and skilled supervision for economical and efficient softening. (2) Sludge disposal is a problem, (3) Softened water has high concentration of soluble salts like sodium sulfate, NaCl, etc. and has high residual hardness. So, not fit for boiler operation.

This study material is availabe on SIT ASSAN BETA

Fig. 3. Hot L-S process

Q. Differentiate between Cold and Hot L-S process.

Sl. No.	***Cold L-S process***	***Hot L-S process***
1	*Performed at RT*	*Performed at ~100 ^0C*
2	*Slow process*	*Fast process*
3	*Coagulant is needed*	*Coagulant is not needed*
4	*Filtration is not easy*	*Filtration is easy as viscosity decreases at high temperature*
5	*Residual hardness is 60 ppm*	*Residual hardness is 15-30 ppm*
6	*Dissolved gases are not removed*	*Dissolved gases are removed*
7	*Low softening capacity*	*High softening capacity*
8	*Bacteria are not killed*	*Bacteria are killed*

Q. What is a coagulant? Give an example.

Ans. Coagulant is a substance which converts the finer ppt. into coarser one. Example:-Potash Alum

Q. What is coagulation? Give an example of a coagulation reaction

Ans. Coagulation is a process of converting finer ppt. into coarse ppt. by adding a coagulant.

$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow Al(OH)_3$ (gelatinous ppt.) $+ 3CaSO_4 + 6CO_2$

This study material is availabe on SIT ASSAN BETA

Q. What is the basic principle of L-S process?

Ans. The basic principle of this process is to convert all the soluble hardness causing constituents into insoluble masses (known as precipitates) by addition of calculated amount of lime **$Ca(OH)_2$** and soda **Na_2CO_3** to the hard water. The precipitates [$CaCO_3$ and $Mg(OH)_2$] are then removed by sedimentation (a settling process) and filtration. This softening process proceeds via precipitation reaction.

Q. Mention some advantages of Hot L-S process over cold process.

Ans: Some of the advantages of hot L-S process are:

1. Process is faster
2. Good softening capacity
3. No coagulant is required
4. Relatively less amount of chemicals are needed
5. Dissolved gases are also removed
6. Pathogenic bacteria are also killed
7. Residual hardness is relatively low

This study material is availabe on SIT ASSAN BETA

Lecture-5 & 6

7.2 Calculation of Lime-Soda requirement

Points to be remembered:

1. Substances like NaCl, Na_2SO_4, $NaNO_3$, KCl, K_2SO_4, KNO_3, SiO_2, Fe_2O_3, etc. do not consume any L & S. So, these should not be taken into consideration for calculating the L & S requirements.
2. All the substances should be converted into their respective $CaCO_3$ equivalent.
3. Ca-hardness precipitated as $CaCO_3$ and Mg-hardness as $Mg(OH)_2$

Chemicals requirement for Temporary hardness constituents:

A. $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ -------- needs 1 mole of L (1L)

B. (i) $Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow \mathbf{Ca(HCO_3)_2} + Mg(OH)_2$ ----- 1L
(ii) $\mathbf{Ca(HCO_3)_2} + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ ----- 1L

1L + 1L = 2 L

Or by combining eq. (i) and (ii) we get
$Mg(HCO_3)_2 + 2Ca(OH)_2 \rightarrow 2CaCO_3 + Mg(OH)_2 + 2\,H_2O$ --- 2L

✓ *1 mole of $Ca(HCO_3)_2$ needs 1 mole of Lime whereas 1 mole of $Mg(HCO_3)_2$ needs 2 moles of Lime.*

Chemicals requirement for Permanent hardness constituents:

A. ***Calcium permanent hardness*** *(*$CaCl_2$, $Ca(NO_3)_2$, $CaSO_4$)

(i) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaCl$ ------- needs 1 mole of Soda (1S)

(ii) $Ca(NO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaNO_3$ ----- needs 1 mole of Soda (1S)

(iii) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ----- needs 1 mole of Soda (1S)

✓ ***** *All Calcium permanent hardness constituents* [$CaCl_2$, $CaSO_4$, $Ca(NO_3)_2$] *need only 1-mole of Soda (1S)*

B. ***Magnesium permanent hardness*** *(*$MgCl_2$, $Mg(NO_3)_2$, $MgSO_4$)

(i) $MgCl_2 + Ca(OH)_2 + \rightarrow Mg(OH)_2 + CaCl_2$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of CaCl2. For its removal we need 1 mole of Soda*
$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\,NaCl$ ------- needs 1 mole of Soda (1S)

✓ **So, 1 mole of *Magnesium permanent hardness needs 1 mole of lime and 1 mole of Soda* (1L + 1S).**

Chemicals requirement for coagulants* ($FeSO_4$, $Al_2(SO_4)_3$)*:

(i) $FeSO_4 + Ca(OH)_2 + \rightarrow Fe(OH)_2 + CaSO_4$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of* $CaSO_4$. *Its removal needed 1 mole of Soda*

This study material is availabe on SIT ASSAN BETA

$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ------- needs 1 mole of Soda (1S)

- ✓ ***So,*** $FeSO_4$ ***needs 1 mole of lime and 1 mole of Soda*** **(1L + 1S).**

(ii) $2Al_2(SO_4)_3 + 3Ca(OH)_2 + \rightarrow 2Al(OH)_3 + 3CaSO_4$ – 3 moles of Lime (3L)

$3CaSO_4 + 3Na_2CO_3 \rightarrow 3CaCO_3 + 3Na_2SO_4$ ------- needs 3 mole of Soda (3S)

- ✓ ***So,*** $Al_2(SO_4)_3$ ***needs 3 mole of lime and 3 mole of Soda*** **(3L + 3S).**

Q.1 Give reason that 1 mole of *$Ca(HCO_3)_2$ needs 1 mole of Lime whereas 1 mole of $Mg(HCO_3)_2$ needs 2 moles of Lime. (write chemical reactions)*

Ans.

A. $Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ -------- needs 1 mole of L (1L)

B. (i) $Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow$ **$Ca(HCO_3)_2$** $+ Mg(OH)_2$ ----- 1L

(ii) **$Ca(HCO_3)_2$** $+ Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_2O$ ----- 1L

1L + 1L = 2 L

Q. 2. Give reason that *Calcium permanent hardness constituents need only 1- mole of Soda (1S).*

Ans.

(i) $CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaCl$ ------- needs 1 mole of Soda (1S)

(ii) $Ca(NO_3)_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaNO_3$ ----- needs 1 mole of Soda (1S)

(iii) $CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4$ ----- needs 1 mole of Soda (1S)

Q.3. Give reason that 1 mole of *Magnesium permanent hardness needs 1 mole of lime and 1 mole of Soda* (1L + 1S).

Ans.

(i) $MgCl_2 + Ca(OH)_2 + \rightarrow Mg(OH)_2 + CaCl_2$ ------- needs 1 mole of Lime (1L) *but releasing 1 mole of CaCl2. For its removal we need 1 mole of Soda*

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2\ NaCl$ ------- needs 1 mole of Soda (1S)

Q.4. Give reason that lime is not consumed by $CaCl_2$ or any calcium-permanent hadness constituents.

Ans. $CaCl_2 + Ca(OH)_2 \rightarrow CaCl_2 + Ca(OH)_2$

See the above reaction, there is no change in reactant and product side. It means there is no reaction between these two constituents.

7.3 Solved numerical on Lime-soda requirements

Example-1 A sample of water on analysis has been found to contain 100 mg/L of $Ca(HCO_3)_2$ and 200 mg/L of Na_2SO_4. Calculate the amount of lime and soda required for softening of 10,000 litres of hard water. (At. mass: Na = 23, Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

This study material is availabe on SIT ASSAN BETA

Solution: Na_2SO_4 does not consume chemicals like lime and soda.

N.B: if purity of lime and soda is not mention then take % purity = 100

$Ca(HCO_3)_2$ as $CaCO_3$ eq. = 100 x (100/162) = 61.72 mg/L

$Ca(HCO_3)_2$ require only 1L (**no soda requirement**, that is soda amount = 0)

So, lime required for softening of 10,000 L of hard water = 74/100($Ca(HCO_3)_2$ $CaCO_3$ eq.) x V x (100/% purity of lime)

= (74/100) x 61.72 mg/L x 10,000 L x 100/100 (here purity of lime 100%)

= 456728 mg = 456.728 g (Ans.)

Example-2 A sample of water on analysis has been found to contain 150 mg/L of $Ca(HCO_3)_2$ and 100 mg/L of Na_2SO_4. Calculate the amount of lime and soda required for softening of 15,000 litres of hard water after boiling the water for 20 min. (At. mass: Na = 23, Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

Solution: As boiling removes $Ca(HCO_3)_2$, lime and soda required will be zero.

Example-3 A sample of water on analysis has been found to contain 150 mg/L of $Ca(HCO_3)_2$ and 100 mg/L of $CaSO_4$. Calculate the amount of lime and soda required for softening of 15,000 litres of hard water after boiling the water for 20 min. (At. mass: Ca = 40, H =1, C = 12, O =16, S = 32 g/mol)

Solution: Boiling will remove the $Ca(HCO_3)_2$. So only $CaSO_4$ will be remain in the hard water after boiling.

$CaSO_4$ consumes only soda (Mol .mass = 136 g)

$CaSO_4$ as $CaCO_3$ eq. = 100 x (100/136) = 73.52 mg/L

Soda required = 106/100 ($CaSO_4$ as $CaCO_3$ eq.) x V x (100/%purity of soda)

= 106/100 x 73.52 x 15,000 x 100/100 (purity of soda is 100%)

= 1168968 mg = 1.168968 Kg (take 1 mg = 10^{-6} Kg)

Lime reqd. = 0

Example-4 Calculate the amount of Lime and soda needed for the softening of 10,000 litres of hard water having 10 mg/l of $MgSO_4$. (Given: % purity of lime = 90 and % purity of soda = 95; At. mass of Mg =24, S = 32 and O = 16))

Solution: We know that all magnesium permanent hardness consumes both lime and soda

This study material is availabe on SIT ASSAN BETA

$MgSO_4$ as $CaCO_3$ eq. = 10 x 100/120 = 8.33 mg/L or ppm

(i) **Lime reqd.** = 74/100 ($MgSO_4$ as $CaCO_3$ eq.) x Vol. of hard water x (100/% purity)
= (74/100) x 8.33 mg/L x 10,000 L x (100/90) = 6851.85 mg = 6.851 g

(ii) **Soda Reqd.** = 106/100 ($MgSO_4$ as $CaCO_3$ eq.) x Vol. of hard water x (100/% purity)
= (106/100) x 8.33 mg/L x 10,000 L x (100/95) = 9298.24 mg = 9.298 g

Example-5 Calculate the amount of Lime and soda needed for the softening of 50,000 litres of hard water having $Mg(HCO_3)_2$ = 144 ppm, $Ca(HCO_3)_2$ = 25 ppm, $MgCl_2$ = 95 ppm, $CaCl_2$ = 111 ppm, Fe_2O_3 = 25 ppm, and Na_2SO_4 = 15 ppm.

Solution:

As Fe_2O_3 and Na_2SO_4 are non-hardness constituents, they do not consume Lime (L) and Soda (S)

Constituents	Strength (ppm or mg/L)	Mol. Mass	Chemical Need	$CaCO_3$ eq. (mg/L)
$Mg(HCO_3)_2$	144	146	2L	144 x (100/146) =98.6
$Ca(HCO_3)_2$	25	162	1L	25 x (100/162) =15.4
$MgCl_2$	95	95	L + S	95 x (100/95) =100
$CaCl_2$	111	111	S	111 x (100/111) =100

**n-factor = 2 for all the salts

Remember that Lime is reqd. by $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, and $MgCl_2$

(i) **Lime reqd.** = 74/100 [(2 x $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (74/100) x [2 x 98.6 + 15.4 + 100] mg/L x 50,000 L x (100/100)
= 11566200 mg = 11566200 x 10^{-6} Kg = 11.5666 Kg

Soda is reqd. by only $CaCl_2$ and $MgCl_2$

(ii) **Soda reqd.** = 106/100 [($CaCl_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)
= (106/100) x [100 + 100] mg/L x 50,000 L x (100/100)
= 10600000 mg = 10600000 x 10^{-6} Kg = 10.6 Kg

This study material is availabe on SIT ASSAN BETA

Example-6 A water sample contains $Mg(HCO_3)_2$ = 73 ppm, $Ca(HCO_3)_2$ = 81 ppm, $MgCl_2$ = 95 ppm, $CaSO_4$ = 68 ppm, and Na_2SO_4 = 30 ppm. Calculate the cost of chemicals for softening of 20,000 litres of hard water, if purity of lime is 95% and that of soda is 90%. The costs per 1 Kg of lime and soda are Rs. 75 and Rs. 1200, respectively.

Solution: As Na_2SO_4 is a non-hardness constituent, it does not consume Lime (L) and Soda (S)

Constituents	Strength (ppm or mg/L)	Mol. Mass	Chemical Need	$CaCO_3$ eq. (mg/L)
$Mg(HCO_3)_2$	73	146	2L	73 x (100/146) =50
$Ca(HCO_3)_2$	81	162	1L	81 x (100/162) =50
$MgCl_2$	95	95	L + S	95 x (100/95) =100
$CaSO_4$	68	136	S	68 x (100/136) =50

Lime is reqd. by $Mg(HCO_3)_2$, $Ca(HCO_3)_2$, and $MgCl_2$

(i) **Lime reqd.** = 74/100 [(2 x $Mg(HCO_3)_2$ + $Ca(HCO_3)_2$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)

= (74/100) x [(2 x 50) + 50 + 100] mg/L x 20,000 L x (100/95)

= 3894736.842 mg = 3894736.842 x 10^{-6} Kg = 3.894 Kg

Cost of lime = 3.894 x 75 = Rs. 292.05

Soda is reqd. by only $MgCl_2$ and $CaSO_4$

(i) **Soda reqd.** = 106/100 [($CaSO_4$ + $MgCl_2$); all as $CaCO_3$ eq.] x Vol. of hard water x (100/% purity)

= (106/100) x [50 + 100] mg/L x 20,000 L x (100/90)

= 3533333.333 mg = 3533333.333 x 10^{-6} Kg = 3.533 Kg

Cost of soda = 3.533 x 1200 = Rs. 4239.6

Now, total cost of chemicals (cost of lime + cost of soda) = Rs. 292.05 + Rs. 4239.6 = **Rs. 4,531.65**

This study material is availabe on SIT ASSAN BETA

Example-6 Find the hardness of water if water containing 100 mg/L of $Ca(HCO_3)_2$, 200 mg/L of $Mg(HCO_3)_2$ and 250 mg/L NaCl is boiled for 15 minute.

Ans. Hardness = 0, as Temporary hardness is removed by boiling. NaCl is non-hardness mass.

Example-7 A water sample contains 150 mg/L of **$Ca(HCO_3)_2$**, 111 mg/L of $CaCl_2$, 12 mg/L of $MgSO_4$, and 250 mg/L of Na_2SO_4. Find the temporary, permanent and total hardness of water after boiling for 10 minute.

Ans. (i) **$Ca(HCO_3)_2$ can be removed by boiling. So, temp. Hardness = 0**

Na_2SO_4 is a non-hardness mass.

Here, Permanent hardness is due to presence of dissolved $CaCl_2$ and $MgSO_4$ in water.

So, at first we have to express these hardness constituents as $CaCO_3$ eq.

$CaCl_2$ as $CaCO_3$ eq. = (111 x 100/111) = 111 mg/L; Molar mass of $CaCl_2$ = 111, n-factor = 2

$MgSO_4$ as $CaCO_3$ eq. = (12 x 100/120) = 10 mg/L; Molar mass of $MgSO_4$ = 120, n-factor = 2

(ii) So, **Perm. Hardness** = 100 + 10 = 110 mg/l = 110 ppm = 11 ^{0}Fr = 7.7 ^{0}Cl.

(iii) **Total hardness** = temp + perm. = 0 + 110 = 110 mg/l = 110 ppm = 11 ^{0}Fr = 7.7 ^{0}Cl.

This study material is availabe on SIT ASSAN BETA

Lecture-7 & 8

Zeolite as a softner

What are zeolites?

Zeolites are naturally occurring hydrated sodium alumino silicate minerals. They are capable of exchanging reversibly its sodium ions (Na^+) for hardness causing ions (e.g., Ca^{2+}, Mg^{2+}, etc.) in water. This ion-exchange property makes them a suitable candidate for softening process.

The chemical representation of zeolites are $Na_2O.Al_2O_3.xSiO_2.yH_2O$, where x = 2-10 & y = 2-6. It is mentioned as Na_2Ze.

Zeolite is derived from the *Greek* word *Zein* + *Lithos*, meaning "*boiling Stone"*. If heated strongly, zeolite melts with bubbling moisture, which look like as if a stone is boiling. The term zeolite was coined by Swedish Geologist Axel Cronsted in 1756. Zeolite has open structure with many cavities or pores. This porous structure permits free movement of water molecules and ions.

Zeolites are of two types: (1) *Natural zeolites:* They are relatively less porous, more durable and amorphous in nature. Example: $Na_2O.Al_2O_3.4SiO_2.2H_2O$; (2) *Synthetic/artificial* zeolites: They are made in the laboratories of industries. Such zeolites are relatively more porous and less durable, but *having large ion exchange capability per unit weight*. They are prepared by heating together sodium carbonate Na_2CO_3, alumina Al_2O_3 and silica SiO_2 in a muffle furnace maintained at about 1000 ^{0}C. Artificial zeolites are also called as **Permutit**.

Q. Give reason that artificial zeolites are preferred over natural one for the softening of hard water.

Answer: As the artificial is more porous *it has large ion exchange capability per unit weight* than natural one.

Zeolite Softening Process

Softening of Hard water is done in a **Zeolite softener**. The hard water is passed/percolated at a specified rate through a bed of zeolites fixed in a cylindrical stainless steel softener so that hardness causing ions (Ca^{+2}, Mg^{+2}, etc.) are retained by the zeolite bed and outgoing water contains sodium ions (Na^+). The reaction taking place during the softening process is mentioned as below:

$$Na_2Ze + CaCl_2 \rightarrow CaZe + 2NaCl$$

$$Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2\ NaHCO_3$$

This study material is availabe on SIT ASSAN BETA

$$Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2\ NaHCO_3$$

From the above reaction we learnt that with the progress of softening process more and more Na_2Ze are converting into CaZe/MgZe and the sodium salt concentration is increasing in the outgoing water. In other words, the Na^+ ion content responsible for ion exchange is decreasing with time. So, after some time the zeolite (Na_2Ze) is completely converted into calcium and magnesium zeolite of no ion exchange capability. It means after some time it ceases to soften water and zeolite is said to be gets exhausted. At this stage, the feeding of hard water to the softener is temporarily stopped and regeneration is done for the exhausted zeolite.

Regeneration of exhausted zeolite: It is done by treating with a concentrated (10%) NaCl solution (known as *Brine solution*). The reaction taking places during the regeneration process are:

$$CaZe + 2NaCl \rightarrow Na_2Ze \text{ (reclaimed zeolite)} + CaCl_2 \quad \text{(washings)}$$

$$MgZe + 2\ NaCl \rightarrow Na_2Ze + MgCl_2$$

The washings are led to the drain and the regenerated zeolite bed is used for softening process.

Fig. Zeolite softener

Q. Give reason that sodium chloride is preferred for regeneration exhausted zeolite.

Answer: It is of low cost and the products of regeneration (washings) are highly soluble so that can be easily rinsed out from the zeolite bed.

Limitations of zeolite process:

This study material is availabe on SIT ASSAN BETA

1. Turbid water clogs the pores of the zeolite and thereby making it inactive.
2. Water containing ions like Mn^{2+} and Fe^{2+} are firmly stick to the zeolite bed so very difficult to be regenerated.
3. Acidic water destroys the zeolite bed.
4. Hot water tends to dissolve the zeolite bed.
5. Water softened by this process contains salts like $NaHCO_3$ causes boiler corrosion.
6. Higher cost of the plant is also a limiting factor.

Q. Turbid water should not be softened by zeolite process. Give reason

Ans. Turbid water clogs the pores of the zeolite and thereby making it inactive

Q. How to soften turbid hard water using a zeolite softener?

Ans. At first suspended matter must be removed by coagulation before it is fed into the softener.

Q. **Acidic water should not be softened by zeolite process. Give reason**

Ans. Acidic water destroys the zeolite bed.

Q. How to soften acidic hard water using a zeolite softener?

Ans. Acidic water must be neutralized with soda in advance before feeding into zeolite bed.

Q. How to regenerate an exhausted zeolite bed?

Ans. It is done by treating with a concentrated (10%) NaCl solution (known as *Brine solution*). The reaction taking places during the regeneration process are:

$$CaZe + 2NaCl \rightarrow Na_2Ze \text{ (reclaimed zeolite)} + CaCl_2 \quad \text{(washings)}$$

$$MgZe + 2\ NaCl \rightarrow Na_2Ze + MgCl_2$$

Q. Water softened by zeolite softener is not fit for boiler. Give reason.

Ans. It contains salt like $NaHCO_3$ which undergoes decomposition under boiler condition to form NaOH, a caustic mass.

$$NaHCO_3 \rightarrow NaOH + CO_2$$

The caustic mass makes the water alkaline and leads to alkaline boiler corrosion called as ***Caustic Embrittlement*.**

Q. Water should be free from ions like Mn^{2+} and Fe^{2+} before fed into the boiler. Give reason.

This study material is availabe on SIT ASSAN BETA

Ans. Water containing ions like Mn^{2+} and Fe^{2+} are firmly stick to the zeolite bed so very difficult to be regenerated.

Advantages of Zeolite process

1. The residual hardness is about 10 ppm whereas in L-S process it lays between 15-60 ppm.
2. Equipment used is compact and occupies less space.
3. It is clean in use. No sludge formation occurs during the process.
4. Less skilled people can operate as well as maintain easily.
5. Less time is needed for softening as compared to L-S process.

Comparison between Zeolite and L-S process

Sl. No.	Zeolite process	L-S process
1.	Produces water of residual hardness of 10-15 ppm	Produces water of residual hardness lays between 15-60 ppm
2.	Based on ion exchange principle	Based on precipitation principle
3.	Softened water contain large amount of sodium salts	Treated water contains lesser % of Na-salts
4	Capital cost is higher	Capital cost is lower
5	Not suitable for treating acidic and turbid water	No such limitation
6	Equipment occupies less space	Occupies more space
7	No sludge formation	Sludge formation occurs
8	Dissolved gases are not removed	They are removed in hot L-S process
9	No bacteria are killed	They are killed in hot L-S process
10	Treated water contains large amount of $NaHCO_3$	Free from $NaHCO_3$
11	Less skill is required to operate it	Skilled operate can operate it successfully

Solved Numerical

Example-1 The hardness of 10,000 liters of a sample of water was removed by passing it through a zeolite softener. The Exhausted zeolite needed 200 liters of NaCl solution containing 150 g/L of NaCl for regeneration. Find the harness of water.

Solution:

This study material is availabe on SIT ASSAN BETA

Method-1

Strength of NaCl = 150 g/L

It means, 1L solution contains 150 g of NaCl

So, 200 L will contains = 150 x 200 = 30, 000 g = 30,000 x 1000 mg of NaCl

NaCl as $CaCO_3$ eq = 30,000,000 x (100/2x58.5) **[eq wt of NaCl = 58.5]**

= 25641000 mg

Now, 10,000 L of water = 25641,000 mg eq of $CaCO_3$

- ⇨ 1 L of water = (25641,000/10,000) = 2564.1 mg/l or ppm.

Method-2

We know that $S_1V_1 = S_2V_2$

That is S_{NaCl} x V_{NaCl} = S_{water} x V_{water}, Here S = strength and V = Volume

So, 150 x 200 = S_{water} x 10,000

- ⇨ S_{water} = (150 g/Lx 200 L)/10,000 L= 3 g/L = 3000 mg/L

In terms $CaCO_3$ eq, hardness = 3000 x 100/(2 x 58.5) = 2564 ppm. **[eq wt of NaCl = 58.5]**

Example-2 An exhausted zeolite softener was regenerated by passing 150 L of NaCl solution having a strength of 150 g/L of NaCl. Find the total volume of water that can be softened by this zeolite softener, if the hardness of water is 500 ppm.

Solution:

Method 1

Strength of NaCl = 150 g/L

It means, 1L solution contains 150 g of NaCl

So, 150 L will contains = 150 x 150 = 22500 g = 22500 x 1000 mg of NaCl

NaCl as $CaCO_3$ eq. = 22500,000 x (100/2x58.5), eq wt of NaCl = 58.5

= 1.932 x 10^7 mg $CaCO_3$ eq.

Hardness is given as 500 ppm = 500 mg/l

So, it means 500 mg in 1L

This study material is availabe on SIT ASSAN BETA

Then, 1 mg in 1/500 L

Now, 1.932×10^7 mg in = (1/500) x 1.932×10^7 = 38461 L (Ans.)

Method 2

$S_{NaCl} \times V_{NaCl} = S_{water} \times V_{water}$, Here S = strength and V = Volume

- **(150,000 mg/L x 100/117) as $CaCO_3$ eq. x 150 L = 500 mg/L as $CaCO_3$ eq. x** V_{water}
- V_{water} = 38641 L

This study material is availabe on SIT ASSAN BETA

Lecture-9 and 10

Polymeric Material (Resin) as a Softner

What is a Resin?

Resin is a macromolecule i.e., organic polymer. It may be thermoplastic or thermosetting. For example, Epoxy resin, Bakelite, Urea-formaldehyde resin, etc.

Ion-exchange Resins: They are insoluble, cross-linked organic polymers with a porous structure attached with some functional groups (FG) like –OH, $-SO_3H$, -COOH, $-NH_2$, etc. responsible for reversibly exchange with ions (e.g., Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}, etc.) present in hard water.

Types of Ion-exchange resins: Depending on the nature of FG attached to the polymer, they are of two types: (1) Cation exchange resin, and (2) Anion exchange resin

Cation exchange resins: They are mainly styrene-divinyl benzene copolymers containing sulphonic acid ($-SO_3H$) or carboxylic acid (-COOH) FG. The acidic FG having hydrogen ions ($-H^+$) are *exchange with cations* like Ca^{2+}, Mg^{2+} etc. present in the hard water. It means these hardness causing cations are retained by the resin.

Some commercial cation exchange resins are **Amberlite IR-120 and Dowex-50**.

Anion exchange resins: They are mainly styrene-divinyl benzene or amine-formaldehyde copolymers containing basic FG like amino or quaternary ammonium or quaternary phosphonium. As such they are of no use. To act as an *anion exchange resin*, it is treated with dil. NaOH solution to introduce –OH group into it. This basic group –OH is capable of *exchange with anions* of water. It means these anions are retained by it after passing through it.

Some commercial anion exchangers are **Amberlite IR-400 and Dowex-3**.

Softening of hard water using polymeric ion-exchangers

An ion-exchanger consists of two vertical columns: (1) cation exchange and (2) anion exchange.

The hard water is first passed through the cation exchange column so that all cations are removed from it and equivalent amount of H^+-ions are released from the column to water. Let us represent the cation exchange resin as **Res-H^+.** Here the loosly bound H+ ions are capable of exchanging with cations like Ca^{2+} and Mg^{2+}.

$$2Res\text{-}H^+ + Ca^{2+} \text{ (Cation of hard water)} \rightarrow (Res)_2Ca + 2H^+$$

$$2Res\text{-}^-H^+ + Mg^{2+} \text{ (Cation of hard water)} \rightarrow (Res)_2Mg + 2H^+$$

This study material is availabe on SIT ASSAN BETA

After passing through the first column, the water is passed through anion exchange column to remove all the anions like Cl^-, NO_3^-, SO_4^{2-}, etc. present in the water and an equivalent amount of –OH- ions are released from the column to the water. Let us represent this resin as **Res-OH$^+$.**

$$\text{Res-OH}^- + \text{Cl}^- \text{ (anion of hard water)} \rightarrow \text{Res-Cl} + \text{OH}^-$$

$$\text{Res-OH}^- + \text{NO}_3^- \text{ (anion of hard water)} \rightarrow \text{Res-NO}_3 + \text{OH}^-$$

Now the outgoing water is free from all ions so it is ion-free or *deioinized* water. This water also called as *de-mineralized* water. This water is free from any acidic or alkaline masses. Finally the ion-free water is passed through a *de-gasifier* maintained at about 100 ^{0}C to remove dissolved gases like O_2, CO_2, etc.

Regeneration of ion exchange resins

After working for some time, the ion-exchange resins lost their ion-exchange capacity and are said to be exhausted.

The exhausted cation exchange resin column can be regenerated by passing a solution of dil. HCl or H_2SO_4.

$$(\text{Res})_2\text{Ca (exhausted cation exchange resin)} + 2\text{H}^+ \text{ (from HCl)} \rightarrow 2\text{Res-H}^+ + \text{Ca}^{2+}$$

The exhausted anion exchange resin column can be regenerated by passing a solution of dil NaOH or KOH.

$$\text{Res-Cl (exhausted anion exchange resin)} + \text{OH}^- \text{ (from NaOH)} \rightarrow \text{Res-OH}^- + \text{Cl}^-$$

The regenerated resins are then used again for softening.

Fig. Polymeric ion-exchanger

This study material is availabe on SIT ASSAN BETA

Advantages:

1. This process can be used for softening highly acidic and alkaline waters.
2. Residual hardness lies between 0-2 ppm.
3. De-gasifier removes dissolved gases like O_2
4. Water is germ free

Limitations:

1. It is an expensive process
2. Turbid water causes problem
3. Water is not fit for human consumption. (we need minerals like Ca)

Q. 1 What is the use of a de-gasifier in ion-exchange resin softener? (2 mark)

Ans. It is a device used to remove unwanted dissolved gases like O_2, CO_2, etc from the soften water.

Q. 2 Differentiate between soft water and de-mineralized/de-ionised water (3 mark)

Sl. No.	**Soft Water**	**De-mineralized Water**
1	We called water as soft when its hardness <= **50 ppm**	Hardness lays between 0-2 ppm
2	Used for domestic use	Not recommended as such for drinking purpose
3	Obtain using L-S or zeolite process	Made by distillation or resin process
4	Not suitable for boiler	Fit for boiler operation

Q 3. Mention some advantages of resin process. (2 mark)

1. **Ans.** This process can be used for softening highly acidic and alkaline waters.
2. Residual hardness lies between 0-2 ppm.
3. De-gasifier removes dissolved gases
4. Water is germ free

Q. 4. Mention some limitations of resin process. (2 mark)

Ans.

1. It is an expensive process
2. Turbid water causes problem
3. Water is not fit for human consumption. (we need minerals like Ca)

This study material is availabe on SIT ASSAN BETA

Q.5 How to regenerate an exhausted cation-exchange resin? (2 mark)

Ans. The exhausted cation exchange resin column can be regenerated by passing a solution of dil HCl or H_2SO_4.

$$(Res)_2Ca \text{ (exhausted resin)} + 2H^+ \text{ (from HCl)} \rightarrow 2Res\text{-}H^+ + Ca^{2+}$$

Q.6 How to regenerate an exhausted anion-exchange resin? (2 mark)

Ans. The exhausted anion exchange resin column can be regenerated by passing a solution of dil NaOH or KOH.

$$Res\text{-}Cl \text{ (exhausted resin)} + OH^- \text{ (from NaOH)} \rightarrow Res\text{-}OH^- + Cl^-$$

Long Question

Q1. Discuss the ion-exchange resin process with a suitable softner diagram. (7 mark)

This study material is availabe on SIT ASSAN BETA

Module -2.

CORROSION SCIENCE

Syllabus:

Definition and scope of corrosion, Dry and wet corrosion; Direct chemical corrosion, Electrochemical corrosion and its mechanisms; Types of electrochemical corrosion, (differential aeration, galvanic, concentration cell); Typical Electrochemical corrosion like Pitting, Inter-granular, Soil, Waterline; Factors affecting corrosion, Protection of corrosion.

Course Outcome: Utilize the knowledge of electrochemistry and corrosion science in preventing engineering equipments from corrosion.

Objectives:

- **To know about the basic nature of corrosion and its processes**
- **To identify types of corrosion**
- **To recognize the various factors affecting corrosion**
- **To understand about the various protective measures against corrosion**

Lecture-1

1.0 Introduction

We use a wide collection of engineering materials such as plastic, rubbers, composites, ceramics, metals & alloys, etc. in many modern technologies for various applications like constructions, automobiles, aerospace, and bio-medicals in our day-to-day life. The choice of a particular material for an appropriate application under a specific condition is the sole responsibility of the design engineer. Whenever a design engineer choose a metal for any application, he/she

This study material is availabe on SIT ASSAN BETA

consider the various properties of materials like mechanical, physical, chemical, etc. But, it is also true that a construction engineer gives importance to mechanical and physical properties of a metal and completely ignores the chemical properties, i.e., *effect of interaction of a metal with its environment.* For example, in construction we usually concentrate on the mechanical strength of metallic rods and normally ignore its chemical reactivity towards the environment. However, the interaction of metals & alloys with its environment plays an important role in selection and hence the performance of materials for any purposes. So, effective use of any constructional materials depends on mechanical, physical and chemical properties of materials.

For example, lead (Pb) pipes are not used for plumbo-solvent water (soft water) as concentration of Pb beyond 0.05 ppm is highly toxic and galvanized iron containers are not used for storing food stuff as zinc salts obtained via chemical interaction are toxic to human beings.

This lesson largely confined to interaction of metal with its environment, factors affecting such interaction and various way to control their interaction.

1.1 What is Corrosion?

Corrosion is "any process of loss of metallic materials from its surface through an undesirable chemical or electrochemical attack by its environment". It is a naturally occurring process, i.e., a thermodynamically feasible process for which $\Delta G < 0$.

N.B.: Corrosion always starts from its surface because surface is active due to presence of unsatisfied valency forces known as *active sites*.

Examples of corrosion: (1) R*usting of iron:*

Fe (substrate) + O_2 (environment) + H_2O (electrolyte) → Fe_2O_3. xH_2O (rust)

This study material is availabe on SIT ASSAN BETA

Fig. 1. Rusting of iron pipe

(2) *Tarnishing of silver:*

$$2Ag + H_2S \rightarrow Ag_2S \text{ (black layer on the Ag-surface)} + H_2$$

Fig. Tarnished silver articles

(3) *Greenish layer on copper articles:*

$$2Cu + CO_2 + H_2O + O_2 \rightarrow CuCO_3 + Cu(OH)_2$$

(Green layer; basic copper carbonate)

This study material is availabe on SIT ASSAN BETA

Fig. Green layer on the surface of a copper strip

1.2 Why corrosion occurs in metal?

We know that metals are extracted from their ores (i.e., combined form of metals) by the expense of huge amount of energy. It means that ores are energetically stable than pure metal. In other words, isolated pure metals are lies in excited state (a higher energy state) than their corresponding ores. For example, as pure Ca metal has a higher energy than its combined state, it prefers to lies in a lower energy & higher stability state, i.e., $CaCO_3$. So, when metals (possessing higher energy) are exposed to various environments (such as gases, moisture, liquids, etc.) during their uses, they interact with environment chemically or electrochemically cause loss of metal from its surface in the combined form (lower energy state). So in conclusion, the stability matter. We term such interaction as corrosion. *If we people prefer to be in calm & cool lower energy state, then why not materials?*

Fe (higher energy unstable state) + O_2 + H_2O → Fe_2O_3. xH_2O (lower energy stable state) + energy; ΔG is negative

In the above reaction, the rust (Fe_2O_3. xH_2O) formed is thermodynamically more stable than the pure iron metal.

In general, corrosion leads to loss in many useful properties like mechanical strength, luster, ductility, conductivity, etc. of the pure metal.

This study material is availabe on SIT ASSAN BETA

1.3 Consequences of corrosion

Corrosion is a big problem. It is a costly process in terms of costly to repair, costly in terms of contaminated product, in terms of environmental damage, and costly in terms of human safety. For example, the worldwide annual direct cost involved due to metallic corrosion is **2.2 trillion US dollar**. This amount can be reduced by 25-30 % by employing suitable corrosion prevention methods. The various effects of corrosion are as follows:

A. *Production related consequences are*:

(i) Decrease in production rate
(ii) Increase in maintenance cost (repair/replace) resulting in an increase in the overall production cost
(iii) Loss in some important properties of metals

B. Health related consequences are:

(i) Contamination of foods
(ii) Leakage of toxic gases, liquids from the cylinder/pipes
(iii) Contamination of drinking water (water pollution)
(iv) Contamination of medicines
(v) Infection caused by rusted iron articles

C. Safety related consequences are:

(i) Sudden collapse of bridges, buildings results in loss of life/resources
(ii) Unpredicted failure of machineries/ machineries parts

So, by adopting suitable protection measures one can reduce this cost considerably. One can also check the rate of corrosion to a great extent by *regular inspection and maintenance of equipments*. For example, some equipment requires regular repainting and occasional inspection but equipment used in power plants, processing plants, aircraft, marine, etc. needed extensive maintenance schedules.

N.B.: Corrosion is not always unwanted. It is wanted in various processes like electroplating, surface finishing/smoothening, in research for sample preparation, etc.

Q.1 Mention some health related issues with corrosion.

Ans. Some of the health related issues due to corrosion are:

(i) Contamination of foods

This study material is availabe on SIT ASSAN BETA

(ii) Leakage of toxic gases, liquids from the cylinder/pipes
(iii) Contamination of drinking water (water pollution)
(iv) Contamination of medicines
(v) Infection caused by rusted iron articles

Q.2 **Mention some production related consequences with corrosion.**

Ans. *Production related consequences are*:

(i) Decrease in production rate
(ii) Increase in maintenance cost (repair/replace) resulting in an increase in the overall production cost
(iii) Loss in some important properties of metals

Q.3 **Mention some safety related outcomes with corrosion.**

Ans.

(i) Sudden collapse of bridges, buildings results in loss of life/resources
(ii) Unpredicted failure of machines/ machineries parts

1.4 Types of corrosion

Corrosion affects the metal in various ways that depends on the nature metal itself and the nature of the immediate environment. One can classify corrosion in various ways which are as follows:

(A) Nature of the environment: Based on the nature of the environment, corrosion is classified as (i) *dry corrosion and (ii) wet corrosion*.

(i) Dry corrosion/Chemical corrosion: This class of corrosion occurs mainly by direct chemical action of the environment (oxygen, hydrogen sulphide, sulphur oxide, chlorine, anhydrous inorganic liquids, etc.) on the surface of the metal. It occurs usually in absence of moisture and at high temperature. Example includes oxidation corrosion, chlorination, sulphidation, liquid metal corrosion, etc.

$$2Fe + 3/2O_2 \rightarrow Fe_2O_3 \text{ (oxidation)}$$
$$Sn + 2Cl_2 \rightarrow SnCl_4 \text{ (chlorination)}$$
$$2Ag + H_2S \rightarrow Ag_2S + H_2 \text{ (sulphidation)}$$

(ii) Wet/Electrochemical corrosion: This class of corrosion occurs when a metal comes in contact with a conducting liquid or when two different metals

This study material is availabe on SIT ASSAN BETA

or alloys are either immersed or dipped partially in a solution. It occurs via formation of electrochemical cells in presence of moisture. It is otherwise known as *aqueous corrosion*. Wet corrosion is more common than dry corrosion. Examples are rusting of iron in an aqueous medium, Galvanic corrosion, etc.

(B) Nature/spreading of corrosion: Based on the nature of corrosion, it is classified as *(i) non-localized (uniform) localized and (ii) localized (non-uniform).*

(i) *Non-localized (uniform) corrosion:* The surface of the metal corrodes away at the same rate. It occurs in absence of moisture and at high temperature on homogeneous/heterogeneous surface.

Examples: Oxidation of metals, tarnishing of silver, etc.

(ii) *Localized (non-uniform) corrosion:* In this type some areas are corrode away at rapid rates than other. Usually occurs in presence of moisture or electrolyte via formation of many tiny electrochemical cells only on heterogeneous surface. The localized corrosion may be *microscopic* or *macroscopic*.

Examples: Galvanic corrosion, Pitting, crevice corrosion, and waterline corrosion are macroscopic corrosion and stress corrosion, season cracking, and dezincification are microscopic corrosion.

Q.4 Differentiate between chemical and electrochemical corrosion.

Chemical/ Dry Corrosion	Electrochemical/Wet Corrosion
It occurs in dry or non-aqueous medium (in absence of moisture)	It occurs in wet condition or in presence of moisture
It occurs via direct chemical attack	It occurs via formation of electrochemical cells
It is uniform in nature (non localized)	It is not uniform. Localized in nature
It is a slow process	It is a fast process
It occurs on both homogeneous and hetero generous surfaces	It occurs only on heterogeneous surfaces
Corrosion product accumulates at the place of corrosion	Corrosion occurs at anode but product accumulated near the cathode
Example: Oxidation	Example: rusting of iron in an aqueous medium

This study material is availabe on SIT ASSAN BETA

Lecture-2

1.5 Chemical or Dry Corrosion:

Dry corrosion of metals occurs in non-aqueous solution and in non-humid (dry) atmosphere. It occurs due to direct chemical interaction between the surfaces of metal and corrosive environment like atmospheric gases (e.g., O_2, H_2S, Cl_2, etc.) or anhydrous liquid like HCl, H_2SO_4, etc.

Most common type of dry corrosion is **Oxidation Corrosion.**

Oxidation Corrosion: It occurs when a reactive metal is exposed to O_2 in absence of moisture. Upon oxidation a thin layer of oxide formed on the surface of metal

(i) $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
(ii) $Ca + 1/2O_2 \rightarrow CaO$
(iii) $Mg + 1/2O_2 \rightarrow MgO$

1.5.1 Nature of Oxide layer

A thin layer of oxide formed on the surface of metal can be non-porous, porous, unstable or volatile.

(i) ***Non-porous oxide layer*:** It is stable, impervious and tightly sticks on the surface. It acts as a protective coating and prevents further corrosion.
Example: Metals like Cu, Al, and Cr forms protective oxide layer such as CuO, Al_2O_3, Cr_2O_3, respectively.

(ii) ***Unstable oxide layer:*** Such layer is formed by gold (Au) and platinum (Pt). As oxide layer decomposes back to metal and oxygen, Au and Pt do not undergo oxidation corrosion.
Example: $4Au + 3O_2 \rightarrow 2Au_2O_3$

(iii) **Volatile oxide layer:** The moment it is formed it gets volatilized and the metal surface is again gets exposed for further attack leading to continuous and rapid corrosion.
Example: $2Mo + 3O_2 \rightarrow 2MoO_3$ Molybdenum oxide (volatile oxide layer)

This study material is availabe on SIT ASSAN BETA

$2V + 2.5O_2 \rightarrow V_2O_5$ Vanadium oxide (volatile oxide layer)

- ✓ *This is the reason why Molybdenum and Vanadium undergo rapid corrosion in oxygen atmosphere.*

(iv) ***Porous oxide layer*:** Due to porous nature, oxygen attacks the metal through pores and corrosion continues till the entire metal is converted into metal oxide.

Metals like Fe, Ca, Mg, K, etc. form porous oxide layer.

Q.5 Define oxidation corrosion with a suitable example.

Ans. It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2. $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

Q.6. How many types of oxide layer can be formed on the surface of metal?

Ans. **Four type** (Porous, non-porous, unstable, Volatile)

Q.7. Which type of oxide results in rapid and continuous corrosion?

Ans. Volatile

Q.8 Name a metal which can form a volatile oxide layer (mention reaction).

Ans. Molybdenum (Mo); $2Mo + 3O_2 \rightarrow 2MoO_3$

Q.9 Name two metals which form porous oxide layer.

Ans. Na, K

Q.9 Name two metals which form non-porous oxide layer.

Ans. Al and Cr

Q.9 Name two metals which form unstable oxide layer.

Ans. Au and Pt

Q 10. Corrosion resistance of iron can be significantly improved by alloying with aluminum. Justify it.

This study material is availabe on SIT ASSAN BETA

Ans. The improved corrosion resistance of iron upon alloying with Al is that alloying element forms a protective layer of Al_2O_3 on the surface of host metal.

Q 10. Corrosion resistance of iron can be significantly improved by alloying with chromium. Justify it.

Ans. The improved corrosion resistance of iron upon alloying with Cr is that alloying element forms a protective layer of Cr_2O_3 on the surface of host metal.

Q 11. Stainless steel maintains its luster for a longer period of time. Give reason.

Ans. Stainless steel is an alloy of iron with alloying elements like Al, Cr, etc. These alloying elements upon exposure to oxygen form a protective layer of Al_2O_3/Cr_2O_3 on the surface of it to prevent formation of rust.

1.5.2 Piling-Bedworth Rule (PBR)

PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

According to this rule, smaller is the specific volume ratio; greater is the rate of oxidation corrosion, because oxide films will be porous.

[N.B: **Specific Volume Ratio SVR = (Volume of metal oxide formed/Volume of metal)]**

In general, If,

- SVR $\geq$ 1; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.)
- SVR >>>1; Oxide layer is non protective in nature (usually > 2), example, Fe_2O_3

Q. 12. What is PBR?

Ans. PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

This study material is availabe on SIT ASSAN BETA

According to this rule, smaller is the specific volume ratio; greater is the rate of oxidation corrosion, because oxide films will be porous.

Q 13. What is specific volume ratio (SVR). Mention its significance.

Ans. Specific Volume Ratio SVR = (Volume of metal oxide formed/Volume of metal consumed)]

In general, If,

- SVR $\geq$ 1; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.)
- SVR >>>1; Oxide layer is non protective in nature (usually > 2), example, Fe_2O_3

1.5.3 Mechanism of Oxidation Corrosion

The various steeps involved are as follows:

Step-1 Metal gets oxidized to generate metal ions and electrons.

$$Mg \rightarrow Mg^{2+} + 2e$$

Step-2 Electrons so released by Mg is captured by atmospheric O_2 and forms oxide anion (O^{2-})

$$\frac{1}{2} O_2 + 2e \rightarrow O^{2-}$$

Step-3 The metal ions and O^{2-} are moved towards metal-atmosphere interface and form metal oxide (MgO) at the point of meeting.

$$Mg^{2+} + O^{2-} \rightarrow MgO \text{ (formed at the surface)}$$

This study material is availabe on SIT ASSAN BETA

Fig. Mechanism of oxidation corrosion

Here, MgO is a porous layer, so further oxidation occurs till whole metal is converted into oxide.

But in case of Al, it forms a protective layer of Al_2O_3 and hence it resists further oxidation process.

Q. 14. Define oxidation corrosion. Discuss its mechanism.

Ans. It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2. $Mg + 1/2O_2 \rightarrow MgO$

For mechanism, refer section 1.5.3

This study material is availabe on SIT ASSAN BETA

Lecture-2

1.5 Chemical or Dry Corrosion:

Dry corrosion of metals occurs in non-aqueous solution and in non-humid (dry) atmosphere. It occurs due to direct chemical interaction between the surfaces of metal and corrosive environment like atmospheric gases (e.g., O_2, H_2S, Cl_2, etc.) or anhydrous liquid like HCl, H_2SO_4, etc.

Most common type of dry corrosion is **Oxidation Corrosion.**

Oxidation Corrosion: It occurs when a reactive metal is exposed to O_2 in absence of moisture. Upon oxidation a thin layer of oxide formed on the surface of metal

(i) $4Fe + 3O_2 \rightarrow 2Fe_2O_3$
(ii) $Ca + 1/2O_2 \rightarrow CaO$
(iii) $Mg + 1/2O_2 \rightarrow MgO$

1.5.1 Nature of Oxide layer

A thin layer of oxide formed on the surface of metal can be non-porous, porous, unstable or volatile.

(i) ***Non-porous oxide layer*:** It is stable, impervious and tightly sticks on the surface. It acts as a protective coating and prevents further corrosion.
Example: Metals like Cu, Al, and Cr forms protective oxide layer such as CuO, Al_2O_3, Cr_2O_3, respectively.

(ii) ***Unstable oxide layer:*** Such layer is formed by gold (Au) and platinum (Pt). As oxide layer decomposes back to metal and oxygen, Au and Pt do not undergo oxidation corrosion.
Example: $4Au + 3O_2 \rightarrow 2Au_2O_3$

(iii) **Volatile oxide layer:** The moment it is formed it gets volatilized and the metal surface is again gets exposed for further attack leading to continuous and rapid corrosion.
Example: $2Mo + 3O_2 \rightarrow 2MoO_3$ Molybdenum oxide (volatile oxide layer)

This study material is availabe on SIT ASSAN BETA

$2V + 2.5O_2 \rightarrow V_2O_5$ Vanadium oxide (volatile oxide layer)

- ✓ *This is the reason why Molybdenum and Vanadium undergo rapid corrosion in oxygen atmosphere.*

(iv) ***Porous oxide layer*:** Due to porous nature, oxygen attacks the metal through pores and corrosion continues till the entire metal is converted into metal oxide.

Metals like Fe, Ca, Mg, K, etc. form porous oxide layer.

Q.5 Define oxidation corrosion with a suitable example.

Ans. It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2. $4Fe + 3O_2 \rightarrow 2Fe_2O_3$

Q.6. How many types of oxide layer can be formed on the surface of metal?

Ans. **Four type** (Porous, non-porous, unstable, Volatile)

Q.7. Which type of oxide results in rapid and continuous corrosion?

Ans. Volatile

Q.8 Name a metal which can form a volatile oxide layer (mention reaction).

Ans. Molybdenum (Mo); $2Mo + 3O_2 \rightarrow 2MoO_3$

Q.9 Name two metals which form porous oxide layer.

Ans. Na, K

Q.9 Name two metals which form non-porous oxide layer.

Ans. Al and Cr

Q.9 Name two metals which form unstable oxide layer.

Ans. Au and Pt

Q 10. Corrosion resistance of iron can be significantly improved by alloying with aluminum. Justify it.

This study material is availabe on SIT ASSAN BETA

Ans. The improved corrosion resistance of iron upon alloying with Al is that alloying element forms a protective layer of Al_2O_3 on the surface of host metal.

Q 10. Corrosion resistance of iron can be significantly improved by alloying with chromium. Justify it.

Ans. The improved corrosion resistance of iron upon alloying with Cr is that alloying element forms a protective layer of Cr_2O_3 on the surface of host metal.

Q 11. Stainless steel maintains its luster for a longer period of time. Give reason.

Ans. Stainless steel is an alloy of iron with alloying elements like Al, Cr, etc. These alloying elements upon exposure to oxygen form a protective layer of Al_2O_3/Cr_2O_3 on the surface of it to prevent formation of rust.

1.5.2 Piling-Bedworth Rule (PBR)

PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

According to this rule, smaller is the specific volume ratio; greater is the rate of oxidation corrosion, because oxide films will be porous.

[N.B: **Specific Volume Ratio SVR = (Volume of metal oxide formed/Volume of metal)]**

In general, If,

- SVR $\geq$ 1; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.)
- SVR >>>1; Oxide layer is non protective in nature (usually > 2), example, Fe_2O_3

Q. 12. What is PBR?

Ans. PBR gives information about protective or non-protective nature of oxide layer formed on the surface of a metal.

This study material is availabe on SIT ASSAN BETA

According to this rule, smaller is the specific volume ratio; greater is the rate of oxidation corrosion, because oxide films will be porous.

Q 13. What is specific volume ratio (SVR). Mention its significance.

Ans. Specific Volume Ratio SVR = (Volume of metal oxide formed/Volume of metal)]

In general, If,

- SVR ≥ 1; oxide layer is non-porous, hence protective in nature (Example: Al_2O_3, CuO, Cr_2O_3, etc)
- SVR< 1; Oxide layer is non protective in nature as it may not fully cover the metal surface (Example, CaO, MgO, K_2O, Na_2O, etc.)
- SVR >>>1; Oxide layer is non protective in nature (usually > 2), example, Fe_2O_3

1.5.3 Mechanism of Oxidation Corrosion

The various steeps involved are as follows:

Step-1 Metal gets oxidized to generate metal ions and electrons.

$$Mg \rightarrow Mg^{2+} + 2e$$

Step-2 Electrons so released by Mg is captured by atmospheric O_2 and forms oxide anion (O^{2-})

$$\frac{1}{2} O_2 + 2e \rightarrow O^{2-}$$

Step-3 The metal ions and O^{2-} are moved towards metal-atmosphere interface and form metal oxide (MgO) at the point of meeting.

$$Mg^{2+} + O^{2-} \rightarrow MgO \text{ (formed at the surface)}$$

This study material is availabe on SIT ASSAN BETA

Fig. Mechanism of oxidation corrosion

Here, MgO is a porous layer, so further oxidation occurs till whole metal is converted into oxide.

But in case of Al, it forms a protective layer of Al_2O_3 and hence it resists further oxidation process.

Q. 14. Define oxidation corrosion. Discuss its mechanism.

Ans. It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O_2. $Mg + 1/2O_2 \rightarrow MgO$

For mechanism, refer section 1.5.3

This study material is availabe on SIT ASSAN BETA

Lecture-3

1.6 Electrochemical or Wet corrosion:

Wet corrosion of metals occurs in aqueous solution and in humid atmosphere through formation of a large number of minute electrochemical cells. The mechanism of corrosion can be explained by *electrochemical theory*. It involves anodic dissolution (oxidation) of metal and cathodic reduction of oxidants (e.g. oxygen) present in the solution/electrolyte.

1.6.1 Electrochemical theory of wet corrosion:

According to this theory, the various steps involved in wet corrosion are as follows:

Step 1: Formation of anodic and cathodic areas

Step 2: Oxidation at anodic areas results in liberation of electrons and generation of metallic ions, for example Fe^{2+} from metal Fe

Step 3: Generation of non-metallic anions like hydroxyl anion (OH^-) by absorption of electrons (e^-) by oxidants like O_2

Step 4: Formation of corrosion product near cathode

Depending on the nature of the corrosive environment, the reaction occurs at the cathode (cathodic reaction) proceeds with (i) absorption of oxygen or (ii) hydrogen evolution

1.6.2 Mechanism of wet corrosion

A. Oxygen absorption mechanism:

Rusting of iron (Fe) in *a neutral aqueous medium* of electrolyte (such as NaCl) with dissolved oxygen or oxygen in the atmosphere follows oxygen absorption mechanism.

Let us consider that an iron piece is exposed to a humid environment that is not acidic in nature. Also assume that a small piece of metal with lower oxidation

This study material is availabe on SIT ASSAN BETA

potential (relative to Fe) is sat on its surface. Under this situation, pure iron with higher oxidation potential acts as anode and undergoes corrosion/rusting.

Fig. 2. Mechanism of wet corrosion by oxygen absorption.

The mechanism of rusting of iron piece in neutral medium involves the following steps:

(i) Oxidation of 'Fe' results in formation of metallic ion (Fe^{2+}) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ ------ (oxidation)

(ii) The liberated electrons are captured by the oxidants (O^2) at the cathode to form non-metallic ions (OH^-)

At Cathode: $1/2O_2$ (oxidant) + $H_2O + 2e^- \rightarrow 2OH^-$ ----- (reduction)

(O_2 absorption occurs)

(iii) The cations Fe^{2+} and anions OH^- liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide $Fe(OH)_2$. As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ($Fe_2O_3.xH_2O$) or ferric hydroxide $Fe(OH)_3$-a brownish product (called rust) and deposited near the cathode.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3$ or $Fe_2O_3.xH_2O$ (in pr. of excess O_2)

This study material is availabe on SIT ASSAN BETA

N.B.: In limited oxygen environment, ferrous hydroxide converted into a blackish oxide Fe_3O_4 (Ferrous ferric oxide, $FeO.Fe_2O_3$)

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe_3O_4$ (limited supply of O_2)

Factors affecting the rate of rusting: The various factors are:

a. Amount of dissolved oxygen
b. Presence of acid and electrolytes
c. Deposition of rust on its surface
d. Potential difference between iron and the metal sat on its surface

B. Hydrogen evolution mechanism:

Rusting of iron (Fe) *in an acidic medium* (such as HCl) follows hydrogen evolution mechanism.

Let us consider that an iron piece is exposed to an acidic environment. Also assume that a small piece of metal with lower oxidation potential (relative to Fe) is sat on its surface. Under this situation, pure iron acts as anode and undergoes corrosion/rusting.

Fig. 3. Mechanism of wet corrosion by hydrogen evolution.

The mechanism of rusting of iron piece in an acidic environment involves the following steps:

(i) Oxidation of 'Fe' results in formation of metallic ion (Fe^{2+}) and generation of electrons at anode of the electrochemical cell. The ions go

This study material is availabe on SIT ASSAN BETA

into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

At Anode: $Fe \rightarrow Fe^{2+} + 2e^{-}$ (oxidation)

(ii) At the cathode, the liberated electrons are captured by the hydrogen ions (H^{+}-ions) to form H-atoms and later form H_2 molecules. The H_2 molecules combine with dissolved oxygen forms water.

At Cathode: $4H^{+} + 4e^{-} \rightarrow 4H\ (2H_2\uparrow)$ (Reduction)

(H_2 evolution occurs)

$2H_2 + O_2 \rightarrow 2H_2O$

Therefore, the net cathodic reaction is: $4H^{+} + 4e^{-} + O_2 \rightarrow 2H_2O$

(iii) As the ferrous ions are unstable, they are oxidized by atmospheric oxygen to form rust as per the following reactions.

$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^{+}$

$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3.\ xH_2O$ (rust)

Long Questions

Q.1. Define wet corrosion. Discuss the mechanism of rusting of iron in a neutral or alkaline medium.

Ans. Wet corrosion of metals occurs in aqueous solution and humid atmosphere through formation of a large number of minute electrochemical cells.

Mechanism of rusting of iron: refer section 1.6.2 A

Q.2. Discuss the mechanism of rusting of iron in an acidic medium.

Ans. refer section 1.6.2 B

Short type answer

Q.1 Mention the factors affecting rusting of iron.

Ans. The various factors are:

1. Amount of dissolved oxygen
2. Presence of acid and electrolytes
3. Deposition of rust on its surface

This study material is availabe on SIT ASSAN BETA

4. Potential difference between iron and the metal sat on its surface

Q.2 Write the chemical reaction which occurs at cathode during rusting of iron in a neutral medium.

Ans. $1/2O_2 + H_2O + 2e^- \rightarrow 2OH^-$

Medium type Answer

According to this theory, the various steps involved in wet corrosion are as follows:

Step 1: Formation of anodic and cathodic areas

Step 2: Oxidation at anodic areas results in liberation of electrons and generation of metallic ions, for example Fe^{2+} from metal Fe

Step 3: Generation of non-metallic anions like hydroxyl anion (OH^-) by absorption of electrons (e^-) by oxidants like O_2

Step 4: Formation of corrosion product near cathode

Depending on the nature of the corrosive environment, the reaction occurs at the cathode (cathodic reaction) proceeds with (i) absorption of oxygen or (ii) hydrogen evolution

Q.1 Discuss the electrochemical theory of wet corrosion.

Ans. Refer 1.6.1

This study material is availabe on SIT ASSAN BETA

Lecture-4 and 5

1.7 Electrochemical and Galvanic Series

Electrochemical or EMF series is obtained when metals are arranged as per their increasing standard reduction potential. The metals located at the top of the series are considered the most active, with the highest level of negative electrochemical potential. The metal that can be found at the bottom is the most noble and contains the highest amount of positive electrochemical potential.

It is observed that some metals like aluminum (Al) exhibits more noble (passive) behavior towards corrosion. But, this quality is going against what predicted by the electrochemical or EMF series. As per the EMF series, the standard oxidation potential of 'Al' is higher than that of 'Fe', but Fe suffers from corrosion whereas 'Al' resists it. So, scientist thought of another series which could provide real and useful information about the corrosion of metals and alloys in a particular environment. This series is known as "*Galvanic Series*".

Galvanic series is a list of metals and alloys which are arranged in a specific sequence as per their relative corrosion potential in a specific environment (usually sea water). In this series, there is no place for non-metals like chlorine, fluorine, etc.

Galvanic Series: (*Corrosion tendency decreases for Top to down*)

Fig. 3. Galvanic series of some metals and alloys in sea water.

This study material is availabe on SIT ASSAN BETA

Q. What is Galvanic series? What is its use?

Ans. Galvanic series is a list of metals and alloys which are arranged in a specific sequence as per their relative corrosion potential in a specific environment (usually sea water). It is useful for studying the corrosion of metals and alloys.

1.7.1 *Differentiate between EMF series and Galvanic series (medium type-3 marks)*

Sl. No.	*EMF series*	*Galvanic series*
1	It is a list of metals and non-metals which are arranged in a specific sequence as per their relative standard Ox. Potential/Red. Potential.	It is a list of metals and alloys which are arranged in a specific sequence as per their relative corrosion potential in a specific environment (usually sea water).
2	The position of metals and non-metals are fixed in the series.	The position of metals and alloys are not fixed in the series. Position may change by changing the environment.
3	No place for alloys	No place for non-metals
4	It predicts the relative displacement tendencies.	It is useful for studying the corrosion of metals and alloys.

1.8 Some typical electrochemical/wet corrosion

In general, wet corrosion is more common than the dry corrosion. Rusting of iron in a neutral/alkaline/acidic environment is belongs to this class of corrosion. Some of the typical wet corrosions are: *(1) Galvanic corrosion, (2) Waterline corrosion; (3) Pitting; (4) Caustic Embrittlement; (5) Soil corrosion, (6) Microbial corrosion, etc.*

1.8.1 Galvanic Corrosion/Differential Metal Corrosion/Bimetallic Corrosion

Galvanic corrosion occurs when two different metals or alloys are in contact are immersed in a conducting medium. Here, the metal with higher standard oxidation potential acts as anode and undergoes dissolution/corrosion. When two different metals are joined together, they form a Galvanic couple. Some examples of Galvanic couples are: Zn and Cu; Fe and Cu, Zn and Ag, etc. This corrosion is

This study material is availabe on SIT ASSAN BETA

otherwise known as *differential/bimetallic corrosion* as two different metals are used.

In Zn and Cu Galvanic couple, Zn with higher standard oxidation potential (+ 0.76 V) than Cu (-0.34 V) acts as anode and here Cu acts as cathode.

In order to discuss on the mechanism of corrosion, let us consider that a Zn-Cu couple is exposed to a neutral humid environment.

Fig. 4. Mechanism of Galvanic Corrosion.

Mechanism:

(i) Zn undergoes oxidation: $Zn \rightarrow Zn^{2+} + 2e$

(ii) Oxidant (O_2) in the atmosphere accepts these electrons to form anions

$1/2O_2$ (oxidant) + $H_2O + 2e^- \rightarrow 2OH^-$ (reduction)

(iii) Corrosion product forms by combination of cations and anions

$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$

Factors affecting Galvanic Corrosion:

The various factors are enlisted as below:

1. Position of metals in the Galvanic series: The more apart the metals are from each other in the series, the greater is the corrosion.
2. Distance effect: Corrosion is highest at the junction and rate decreases progressively with distance from the interface.

This study material is availabe on SIT ASSAN BETA

3. Area effect: If anodic area will be much smaller than cathodic area then rapid corrosion will be occur.

Control of Galvanic corrosion: It can be minimized by:

a. By avoiding direct contact
b. By choosing two metals close to one other in the Galvanic series
c. By proper designing (By keeping anodic area much larger than cathode)
d. By putting an insulating layer between two metals

✓ **Some examples of Galvanic corrosion**

1. Steel screws in Brass marine hardware (steel-anode)
2. Lead-antimony solder around copper wire (tin-anode)
3. A steel propeller shaft in Bronze bearings (steel-anode)
4. Steel or iron pipe connected to copper plumbing (steel-anode)

Q. Iron corrodes faster than Aluminium even though Fe is placed below Al in the EMF series. Give reason

Ans. It is because Al forms a protective oxide of Al_2O_3 on its where as Fe forms a porous Fe_2O_3 layer.

Q. What is Galvanic corrosion? How to control it? *Short answer*

Ans. Galvanic corrosion occurs when two different metals or alloys are in contact are immersed in a conducting medium. Here, the metal with higher standard oxidation potential acts as anode and undergoes dissolution/corrosion.

Control of Galvanic corrosion: It can be minimized by:

a. By avoiding direct contact
b. By choosing two metals close to one other in the Galvanic series
c. By proper designing (By keeping anodic area much larger than cathode)
d. By putting an insulating layer between two metals

Q. Mention factors affecting the rate of Galvanic corrosion. *Short answer*

Ans. The various factors are enlisted as below:

This study material is availabe on SIT ASSAN BETA

1. Position of metals in the Galvanic series: The more apart the metals are from each other in the series, the greater is the corrosion.
2. Distance effect: Corrosion is highest at the junction and rate decreases progressively with distance from the interface.
3. Area effect: If anodic area will be much smaller than cathodic area then rapid corrosion will be occur.

Long type

Q. Discuss the mechanism of Galvanic corrosion with a specific example. Mention the factors affecting its rate.

Ans. See section 1.8.1

Q. Impure metal corrodes faster than pure metal under identical conditions. Give reason.

Ans. Impurities in metal results in heterogeneity. Hence, it causes formation of a large number of small electrochemical cells and corrosion occurs at anodic part.

Q. A steel or iron screw in a brass marine hardware corrodes. Give reason.

Ans. This is due to Galvanic corrosion. Here, steel or iron screw acts as anode due to their higher standard oxidation potential.

Q. Where the wet corrosion takes place?

Ans. It always takes place at anode. At, anode loss of electron takes place.

Q. A piece of impure and pure zinc are placed in a salt solution. Which will corrode faster?

Ans. Impure one. As impurities leads to formation of Galvanic cells.

Q. Small anodic area results in intense corrosion. Give reason.

Ans. This is due to area effect. If anodic area will be very small than cathodic area then the huge demand of electrons by cathode can only be fulfilled by small anode by undergoing rapid dissolution. Rapid dissolution means rapid corrosion.

Here (Cathodic area/Anodic area) >>1.

This study material is availabe on SIT ASSAN BETA

Q. A copper equipment should not possess a small steel bolt. Give reason.

Ans. Here bolt will act as anode and (Cathodic area/Anodic area) >>1. So, rapid dissolution or rapid corrosion of bolt (anode) will occur.

Q. Why does a steel pipe in a large copper tank is undergoes rapid corrosion?

Ans. Steel is anodic to copper, i.e., steel pipe will act as anode. Again the steel pipe is much smaller than the tank. That is here (Cathodic area/Anodic area) >>1. So, rapid corrosion will occur in steel pipe.

Q. In a structure, two dissimilar metals should not allow to come in contact with each other. Give reason.

Ans. If they will contact, Galvanic corrosion will occur at metal with higher standard oxidation potential.

Q. Rusting of iron is quicker in saline water than in ordinary water. Give reason.

Ans. The presence of NaCl in saline water leads to increased conductivity of water layer in contact with the iron surface, thereby corrosion current increases and rusting is speeded up.

Numerical

How much rust ($Fe_2O_3.3H_2O$) will be formed when 10 kg of iron (Fe) have completely rusted away? (At. mass: Fe = 56, H =1, O =16)

Ans. Mol. Mass of rust ($Fe_2O_3.3H_2O$) = 214 g

Here, rust contains 2 Fe-atoms.

So, 214g of rust contains 2 x 56 = 112 g Fe

Or, 112 g Fe produces 214 g rust

Then, 10 kg = 10,000g of Fe will form = (214/112) x 10,000 = 19107 g = 19.1 kg.

This study material is availabe on SIT ASSAN BETA

1.8.2 Differential aeration corrosion

It is an electrochemical corrosion which occurs when a portion of metal is exposed to different air or oxygen concentration than the rest part. This difference in air or O_2 concentration causes a difference in standard oxidation potential between the two areas. Here, the poorly aerated/oxygenated part acts as anode and undergoes corrosion.

In order to study the mechanism of corrosion, let us consider that a metal (say Iron) is partially immersed in a dilute solution of NaCl (electrolyte). The metallic part which is not immersed in the electrolyte is strongly aerated whereas the part inside the electrolyte is poorly aerated. So, a difference in potential thus developed causes the flow of electron from anode to cathode. The poorly aerated part will acts as anode and suffers from metallic dissolution.

Mechanism:

(i) $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) $1/2O_2$ (oxidant) + $H_2O + 2e^- \rightarrow 2OH^-$ (reduction)

(iii) $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow \underbrace{Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O}_{\text{(rust)}}$ (In pr. of excess O_2)

Fig. 5. Mechanism of differential aeration corrosion.

The two most common differential aeration corrosion is:

A. *Water-line corrosion*

This study material is availabe on SIT ASSAN BETA

B. *Pitting*

Q. What is the chemical formula of rust?

Ans. $Fe(OH)_3$ or $Fe_2O_3.xH_2O$

Q. What is differential aeration corrosion? Give an example.

Ans. It is an electrochemical corrosion which occurs when a portion of metal is exposed to different air or oxygen concentration than the rest part. Here, the poorly aerated/oxygenated part acts as anode and undergoes corrosion.

The two most common differential aeration corrosion is:

A. *Water-line corrosion*
B. *Pitting*

Q. A pure metal rod half-immersed vertically in water starts corroding at the bottom. Give reason.

Ans. This is due to differential aeration corrosion. The rod above the waterline is more strongly aerated and acts as cathode. On the other hand the lower part of the rod immersed in water is less-aerated and acts as anode and suffers from corrosion.

Q. Why does part of an iron nail inside the wooden structure undergoes corrosion easily?

Ans. The part of the nail inside the wood is not exposed to the atmosphere. So, it is very poorly oxygenated part as compared to the remainder part. So, nail inside the wood acts as anode and suffers from corrosion. It is differential aeration corrosion.

Water-line corrosion

It is a *differential aeration corrosion or oxygen concentration cell corrosion* wherein corrosion occurs just below the waterline when a steel tank is half-filled with water. Here, as the part just below the water-line is poorly aerated/oxygenated acts as anode and undergoes oxidation to form metallic ions. The part above the water-line has more access to air or oxygen acts as cathode.

Mechanism:

This study material is availabe on SIT ASSAN BETA

(i) $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) $1/2O_2$ (oxidant) + $H_2O + 2e^- \rightarrow 2OH^-$ (reduction)

(iii) $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow \underbrace{Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O}_{\text{(rust)}}$ (In pr. of excess O_2)

Fig. 6. Mechanism of water-line corrosion.

N.B.: ***Oxygen concentration cell corrosion:*** It is an electrochemical corrosion occurs when the metal surface is exposed varying concentration of air or oxygen. Here, metallic part exposed to less oxygen acts as anode and undergoes dissolution.

Pitting Corrosion

It is a highly localized differential aeration corrosion which proceeds at a rapid rate to form "pits" or cavities on the surface of the metal. Under the following situations pits are formed on the metallic surface:

1. When impurities like sand, dust, scale, etc. sat on the surface
2. When there is any breakage of protective oxide film at a localized area

Let us consider that a dust particle is sitting on the surface of an iron metal and the metal is exposed to a neutral humid atmosphere. The rusting of iron will occur as per the following steps:

(i) **At Anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) **At Cathode:** $1/2O_2$ (oxidant) + $H_2O + 2e^- \rightarrow 2OH^-$ (reduction)
(O_2 absorption occurs)

This study material is availabe on SIT ASSAN BETA

(iii) **Rust formation:** The cations Fe^{2+} and anions OH^- liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide $Fe(OH)_2$. As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ($Fe_2O_3.xH_2O$) or ferric hydroxide $Fe(OH)_3$-a brownish product (called rust) and deposited near the cathode.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O \text{ (in pr. of excess } O_2)$$

Fig. 7. Mechanism of pitting corrosion.

This study material is availabe on SIT ASSAN BETA

Lecture-6

Pitting Corrosion

It is a highly localized differential aeration corrosion which proceeds at a rapid rate to form "pits" or cavities on the surface of the metal. Under the following situations pits are formed on the metallic surface:

1. When impurities like sand, dust, scale, etc. sat on the surface
2. When there is any breakage of protective oxide film at a localized area

Let us consider that a dust particle is sitting on the surface of an iron metal and the metal is exposed to a neutral humid atmosphere. The rusting of iron will occur as per the following steps:

(i) **At Anode:** $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

(ii) **At Cathode:** $1/2O_2$ (oxidant) + $H_2O + 2e^- \rightarrow 2OH^-$ (reduction)
(O_2 absorption occurs)

(iii) **Rust formation:** The cations Fe^{2+} and anions OH^- liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide $Fe(OH)_2$. As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ($Fe_2O_3.xH_2O$) or ferric hydroxide $Fe(OH)_3$-a brownish product (called rust) and deposited near the cathode.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \text{ or } Fe_2O_3.xH_2O \text{ (in pr. of excess } O_2)$$

This study material is availabe on SIT ASSAN BETA

Q. Iron corrodes faster under drops of salt solution. Give reason.

Ans. This is due to differential aeration corrosion. As part of iron covered by drop is poorly oxygenated part, it acts as anode and undergoes rapid corrosion.

Q. Corrosion of water filled steel tanks occurs below water line. Give reason.

Ans. This is due to differential aeration corrosion. Here, as the part just below the water-line is poorly aerated/oxygenated acts as anode and undergoes oxidation to form metallic ions. The part above the water-line has more access to air or oxygen acts as cathode.

Q. Why wire mesh is corrodes faster at joints?

Ans. The joints of wire mesh are stressed due to welding, so becomes anode and undergoes corrosion.

Q. Why deposition of extraneous matter like dirt, sand, dust, etc. on the surface of metal for a long period is unwanted?

Ans. This causes differential aeration corrosion. Deposition of matter on the surfaces restricts the access of O_2 below it; thereby it becomes anode and undergoes localized corrosion.

Q. Why should nickel plated iron articles be free from pores and pin holes?

Ans. Here, Iron acts as anode and Nickel acts as cathode. Presence of pores in Ni-plated articles exposes the anodic Fe-metal to the atmosphere at these points. So, galvanic cell is form and intense localized corrosion occurs.

Soil Corrosion:

Soil corrosion is a concentration cell corrosion which occurs due to differential oxygen concentration. Buried pipelines are suffered from this. For example, let us consider that iron (Fe) pipelines are passing through clay-based soil and then through sand-based soil. Since clay is less aerated than sand, iron pipe passing through clay-based soil will act as anode and suffers from corrosion.

This study material is availabe on SIT ASSAN BETA

Mechanism: At Anode: $Fe \rightarrow Fe^{2+} + 2e^{-}$------- (oxidation)

At Cathode: $1/2O_2$ (oxidant) + $H_2O + 2e^{-} \rightarrow 2OH^{-}$ ---- (reduction)

Net reaction: $Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3$ or $Fe_2O_3.xH_2O$

Inter-granular Corrosion

It is an electrochemical corrosion in which corrosion occurs at the grain boundaries. In a particular corroding medium, the grain boundaries contain material with higher oxidation potential than the grains. So, grain boundaries acts as anode and suffers from corrosion. It is otherwise known as *inter-crystalline* corrosion.

Inter-granular corrosion usually occurs in alloys in specific environments. For example, in stainless steel SS (an alloy of Fe, Cr, Al, etc.) deposition of chromium carbide at grain boundaries results in depletion of Cr adjacent to it. Chromium carbides can be precipitated if the stainless steel is worked at the temperature range 550–850°C, for example during heat treatment or welding. If the temperature lies in the critical range for too long, chromium carbides will start to form in the grain boundaries, which then become susceptible to inter-granular corrosion. The area adjacent to the grain boundaries becomes depleted in chromium (the chromium reacts with carbon and forms carbides) and this zone, therefore, becomes less resistant to inter-granular corrosion. The depleted in Cr region acts as anode and results in corrosion along the grain boundaries. Inter-granular corrosion results in sudden failure of material.

This study material is availabe on SIT ASSAN BETA

Fig. Inter-granular corrosion in SS-steel

Control methods:

Materials with good resistance to inter-granular corrosion are steel grades with low carbon content (0.03 % C) and Ti/Nb-stabilized steels.

Q. What is inter-granular corrosion? Discuss it with a suitable example.

Q. Soil corrosion is differential aeration corrosion. Justify it.

This study material is availabe on SIT ASSAN BETA

Lecture-7

1.9 Factors affecting rate and extent of corrosion

As we know that corrosion occurs due to interaction between metal and its surrounding environment. So, any factor that has the ability to change either the nature of the metal or the nature of the environment or both is definitely going to alter the rate & extent of corrosion.

So, let us list first how the rate of corrosion depends on the nature of metal.

- ***Nature of the metal:***

(i) ***Particle size (grain size) of metal:*** Smaller is the particle size; larger is the rate of anodic dissolution. If particle size of the metal will be smaller then, the rate of anodic dissolution will be faster.

(ii) ***Residual stress in the metal:*** Stressed part acts as anode and undergoes corrosion in a corrosive environment. So, between a bent iron wire and a straight wire, the rate of corrosion will be faster in case of bent wire with stressed part (anode).

(iii) ***Purity of metal:*** Lesser is the % purity; greater is the rate of corrosion. For example, between a 99 % pure Zn and 60 % pure Zn, rate of corrosion will be more in case of later.

(iv) ***Nature of the oxide film:*** The smaller is the specific volume ratio (i.e., the ratio of volume of metal oxide to the volume of metal); greater is the oxidation/dry corrosion. Porous and volatile oxide layer causes rapid dry corrosion.

(v) ***Position of the metals and alloys in the EMF or Galvanic series*:** Grater is the difference in their position, faster is the rate of Galvanic corrosion.

(vi) ***Size of the anode*:** Smaller is the size of the anode; greater is the rate of corrosion. If cathodic area will be large, then it will demand more electrons from the small anode for reduction reaction to happen. So, in order to fulfill the huge demand of electrons by the cathode, anode will undergo rapid dissolution (i.e., loss of electrons) process. Hence, this causes rapid corrosion at anodic part.

This study material is availabe on SIT ASSAN BETA

(vii) ***Passive nature of metal*:** Some metals like Al, Cr, Ni, Co, etc. resist corrosion as they form protective oxide layer on their surface. The exhibition of improved corrosion resistance than expected from their position in the Galvanic series owing to the formation of protective oxide layer is known as *Passivity*.

(viii) ***Solubility of corrosion products*:** Larger is the solubility of the product in the medium; greater is the rate of corrosion. For example, Pb undergoes corrosion at smaller rate in H_2SO_4 medium. The reason is that when Pb reacts with H_2SO_4, it forms a product $PbSO_4$ that is insoluble in the medium itself. This product gets coated over the metal and resists further dissolution process.

(ix) ***Volatility of corrosion products*:** Volatile corrosion products result in rapid and continuous corrosion. Molybdenum (Mo) metal suffers from rapid oxidation corrosion as the product MoO_3 is volatile in nature and it volatizes leaving the underlying metal surface for further oxidation corrosion.

➢ ***Nature of the environment***

(i) ***Temperature:*** The rate of corrosion increases with rise in temperature (T) due to the following reasons (i) Decrease in concentration of dissolved oxygen with rise in T; (ii) Increase in rate of anodic dissolution; and (iii) Increase in rate of evolution of H_2 gas at cathode.

(ii) ***% Humidity:*** In general, greater is the % humidity in the atmosphere, the larger is the rate of corrosion. The reason is that moisture dissolves many gases like O_2, H_2S, SO_2, etc. and salt like NaCl to supply the electrolyte needed for setting up of electrochemical cell.

(iii) ***pH of the medium:*** Rate of corrosion is more in acidic media than in *alkaline or neutral medium. For example, rate of corrosion of Fe is faster* in a medium with pH = 4 and slower when pH = 11.

(iv) ***Conductance of the medium:*** Greater is the conductivity of the electrolytic medium; larger is the rate of corrosion. For example, the rate of corrosion of buried iron pipe is greater in clayey and mineralized soil than that of dry sandy soil. The reason is that clayey and mineralized soil is more conducing due to presence of ions than that of dry sandy soil.

This study material is availabe on SIT ASSAN BETA

(v) ***Formation of O_2 concentration cell:*** O_2 concentration cell is developed when a metal is exposed to differential aeration. The poorly oxygenated part acts as anode and undergoes corrosion.

For example, part of an iron nail inside a wooden structure suffers from this class of corrosion. As the part inside the wood has less access to oxygen, acts as anode and undertake corrosion.

(vi) ***Presence of impurities in the atmosphere:*** Rate of corrosion is more in industrial areas and coastal belt. The reason for is that presence of gases like H_2S, SO_2, CO_2 and fumes of acids like H_2SO_4 and HCl in industrial areas makes the environment more conducting near the surface of the metal. Similarly, in sea areas presence of NaCl in the atmosphere makes the environment a good electrolyte and hence, a more conducting medium.

(vii) ***Presence of suspended particles in the atmosphere:*** Presence of suspended particles like NaCl, $(NH_4)_2SO_4$, activated charcoal, etc. in the atmosphere has the ability to absorb moisture and providing a good conducting medium near the surface of metal.

2.0 Control of corrosion

As corrosion occurs in various forms and affected by numerous factors, the science behind control or prevention corrosion is highly complex. According to the requirements, different corrosion control methods are adopted by various industries to tackle unsafe effects and negative result of corrosion. Corrosion leads to water pollution. For example corroded pipelines, containers, etc. contaminates the drinking water and poses problem not only to the environment but also to the mankind. So, efficient preventive measures should be employed to check the detrimental effect of corrosion.

As corrosion is occurs due to interaction between metal and environment, one can check the rate of corrosion either by modifying the properties of metal or by modifying the environment. Accordingly, control methods are classified into two parts:

A. ***Corrosion control by modification of the environment:*** In this type, metals are protected by two ways: (1) by the removal of corrosion

This study material is availabe on SIT ASSAN BETA

causing substances; and (2) by the use of substances (known as *inhibitors*) which can reduce the rate of cathodic/anodic reaction.

B. ***Corrosion control by modification of the properties of metal:*** The various methods applied to modify the properties of metal are:

1. Use of Protective coatings
2. Electrochemical or cathodic protection
3. By selection of suitable metal and proper designing of structures
4. By alloying

Corrosion Inhibitors

Corrosion inhibitors are chemical substances which are added in small amount (0.1 %) to the corrosion medium to prevent or slow down the oxidation or reduction reactions on the surface of the metal. Inhibitors do their job by providing a protective layer on the metal surfaces.

Inhibitors are of two types; (1) Inorganic, and (2) Organic

Inorganic Inhibitors: It includes chromates, phosphates, molybdates, zinc, polyphosphates, etc. They are mainly used in boilers, fractional distillation plant, cooling towers, etc.

Inorganic inhibitors are classified as (a) Anodic, and (b) Cathodic

Anodic Inhibitors: Chemical substances which inhibits the anodic (oxidation) reaction. Example includes molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), chromates ($Cr_2O_7^{2-}$), silicates (SiO_3^{2-}), etc. These anions react with metallic ions to produce insoluble precipitates. Insoluble substances so obtained are then get adsorbed on the surface of metal and hence slow down the rate of anodic reaction.

$$Cr_2O_7^{2-} + Fe^{2+} + H_2O \rightarrow Cr_2O_3 + Fe_2O_3 + 2OH^-$$

Cathodic Inhibitors: Chemical substances which inhibits the cathodic (reduction) reaction. Example includes $ZnSO_4$, $MgSO_4$, Na_2SO_3 and $Ca(HCO_3)_2$. $ZnSO_4$, $MgSO_4$, and $Ca(HCO_3)_2$ slow down the anodic reaction by forming a layer of $Zn(OH)_2$, $Mg(OH)_2$, $CaCO_3$ on the metallic surface. Na_2SO_3 inhibits by removing dissolved oxygen ($Na_2SO_3 + 1/2O_2 \rightarrow Na_2SO_4$).

This study material is availabe on SIT ASSAN BETA

Organic Inhibitors: It includes amines (RNH_2), mercaptans (R-SH), substituted urea, and thioureas, amides ($R\text{-}CONH_2$), Imidazoline, etc. These substances adsorbed on the surface of metal and acts as protective coating. They attach to the surface by chemisorptions and physical adsorption.

This study material is availabe on SIT ASSAN BETA

Q & A on Factors affecting corrosion

Q. Aluminium is not attacked by conc. HNO_3 but Iron gets rapidly corroded even by dil. HNO_3. Justify this statement.

Ans. In Conc. HNO_3, Al gets oxidized and forms a protective layer of Al_2O_3 on its surface.

Q. Give reason that Stainless steel (SS) exhibits high corrosion resistance in HNO_3 solution over a wide range of concentrations.

Ans. Because Cr present in SS forms a protective layer of Cr_2O_3 on its surface upon oxidation by HNO_3.

Q. What is meant by the term Passivity?

Ans. Passivity or passivation is a phenomenon by which a metal or alloy exhibit high corrosion resistance due to formation of a highly protective film on its surface.

Q. A 55 % purity Zn suffers from rapid corrosion as compared to 99.9 % Zn. Give reason.

Ans. Greater is the % impurity of a metal, faster is the rate of corrosion due to formation a large number of electrochemical cells.

Q. Corrosion of Zn can be minimized by increasing the ph to 11. Give reason.

Ans. At pH =11, Zn forms $Zn(OH)_2$ ppt. and gets adsorbed on the surface of Zn to resist further dissolution.

Q. Corrosion of metals occurs at a faster rate in clayey and mineralized soil. Give reason.

Ans. Conductivity of clayey and mineralized soil is more than sandy soil.

Q. Which gases in the atmosphere are likely to accelerate the rusting of iron?

Ans. CO_2, SO_2, SO_3, NO_2, etc.

This study material is availabe on SIT ASSAN BETA

Q. Rate of metallic corrosion increases with increase in temperature. Give reason.

Ans. Corrosion rate increases with temperature due to increase in the rate of diffusion of ions.

Q. What are the factors which affects the rate of corrosion? (5 marks)

Ans. Refer above (section 1.9)

This study material is availabe on SIT ASSAN BETA

Lecture-9

2.0 Control of corrosion

As corrosion occurs in various forms and affected by numerous factors, the science behind control or prevention corrosion is highly complex. According to the requirements, different corrosion control methods are adopted by various industries to tackle unsafe effects and negative result of corrosion. Corrosion leads to water pollution. For example corroded pipelines, containers, etc. contaminates the drinking water and poses problem not only to the environment but also to the mankind. So, efficient preventive measures should be employed to check the detrimental effect of corrosion.

As corrosion is occurs due to interaction between metal and environment, one can check the rate of corrosion either by modifying the properties of metal or by modifying the environment. Accordingly, control methods are classified into two parts:

A. *Corrosion control by modification of the environment:* In this type, metals are protected by two ways: (1) by the removal of corrosion causing substances / corrosion stimulants; and (2) by the use of substances (known as *inhibitors*) which can reduce the rate of cathodic/anodic reaction.

B. *Corrosion control by modification of the properties of metal:* The various methods applied to modify the properties of metal are:

1. Use of Protective coatings
2. Electrochemical or cathodic protection
3. By selection of suitable metal and proper designing of structures
4. By alloying

A. Corrosion control by modification of the environment

1. Removal of corrosion causing substances / corrosion stimulants

- Corrosion due to DO can be prevented by its removal by addition of reducing substance like hydrazine
- To prevent corrosion due to acids, they are neutralized with lime

This study material is availabe on SIT ASSAN BETA

- To prevent corrosion due to alkalis, they are neutralized with acids
- To prevent corrosion due to salts, they are removed by ion-exchange methods.
- To prevent corrosion due to moisture, they are removed by dehumidification using silica gel.

2. Using Corrosion Inhibitors

Corrosion inhibitors are chemical substances which are added in small amount (0.1 %) to the corrosion medium to prevent or slow down the oxidation or reduction reactions on the surface of the metal. Inhibitors do their job by providing a protective layer on the metal surfaces.

Inhibitors are of two types; (1) Inorganic, and (2) Organic

Inorganic Inhibitors: It includes chromates, phosphates, molybdates, zinc, polyphosphates, etc. They are mainly used in boilers, fractional distillation plant, cooling towers, etc.

Inorganic inhibitors are classified as (a) Anodic, and (b) Cathodic

Anodic Inhibitors: Chemical substances which inhibit the anodic (oxidation) reaction are called *Anodic Inhibitors.* Example includes molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), chromates ($Cr_2O_7^{2-}$), silicates (SiO_3^{2-}), etc. These anions react with metallic ions to produce insoluble precipitates. Insoluble substances so obtained are then get adsorbed on the surface of metal and hence slow down the rate of anodic reaction.

Cathodic Inhibitors: Chemical substances which inhibit the cathodic (reduction) reaction are called *Cathodic Inhibitors*. Example includes $ZnSO_4$, $MgSO_4$, Na_2SO_3 and $Ca(HCO_3)_2$. $ZnSO_4$, $MgSO_4$, and $Ca(HCO_3)_2$ slow down the anodic reaction by forming a layer of $Zn(OH)_2$, $Mg(OH)_2$, $CaCO_3$ on the metallic surface. Na_2SO_3 inhibits by removing dissolved oxygen ($Na_2SO_3 + 1/2O_2 \rightarrow Na_2SO_4$).

Organic Inhibitors: It includes amines (RNH_2), mercaptans (R-SH), substituted urea, and thioureas, amides ($R\text{-}CONH_2$), Imidazoline, etc. These substances adsorbed on the surface of metal and acts as protective coating. They attach to the surface by *chemisorptions* and *physical adsorption*.

This study material is availabe on SIT ASSAN BETA

Q. How to control rate of corrosion removing corrosion stimulants from the environment? (5 marks)

Ans. Some of the methods of removal of corrosion stimulants are as follows:

- Corrosion due to DO can be prevented by its removal by addition of reducing substance like hydrazine
- To prevent corrosion due to acids, they are neutralized with lime
- To prevent corrosion due to alkalis, they are neutralized with acids
- To prevent corrosion due to salts, they are removed by ion-exchange methods.
- To prevent corrosion due to moisture, they are removed by dehumidification using silica gel.

Q. What is an inhibitor?

Ans. It is a chemical substance which when added to the environment slows down the corrosion reaction. Example- molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), $ZnSO_4$

Q. Define anodic inhibitor with an example.

Ans. Those Chemical substances which inhibit the anodic (oxidation) reaction are called as anodic inhibitor. For example molybdates (MoO_4^{2-})

Q. Define cathodic inhibitor with an example.

Ans. Those Chemical substances which inhibit the anodic (oxidation) reaction are called as anodic inhibitor.

Q. What is an organic inhibitor?

Ans. It is an organic substance which decreases the rate of corrosion. For example: Thiourea

B. *Corrosion control by modification of the properties of metal*

1. Alloying: Corrosion resistance of most metals is increased by alloying them with suitable elements like Al, Cr, etc. Chromium is the best alloying metal for iron.

This study material is availabe on SIT ASSAN BETA

2. Protective Coatings

In this route a thin layer of material (e.g.; metal, non-metal, polymer, etc.) is applied on the surface of another material which is to be protected from corrosion by various techniques such as spraying, hot dipping, electroplating, etc. In general there are two types of protective/surface coating:

1. Metallic coating (includes coating of Zn, Sn, etc. on iron)
2. Non-metallic coating: It is again classified as organic (e.g. paints, polymer, etc.) and inorganic coating (e.g. phosphate, chromate, cement coating, etc.)

A good coating material should have the following characteristics:

a. Coating should be non-porous, non-volatile, and continuous
b. Coating should be hard
c. Coating should be able to withstand direct attack of environment

Metallic Coatings

The materials in construction (iron and steel) are suffers from corrosion in acidic and alkaline environment. Construction materials should have high mechanical strength, high corrosion resistance and low cost. In order to make materials resistant against corrosion, their surfaces are coated with metals like, zinc, tin, copper, chromium, etc.

Depending on the nature of coating material, metallic coating is classified into two categories:

A. Anodic or Sacrificial Coatings, and
B. Cathodic or Barrier Coatings

Anodic or Sacrificial Coatings: In this method, an active or more anodic metal is coated over the base metal which is to be protected from corrosion. For example, iron (Fe) is protected from corrosion by applying a coat of Al, Cd, or Zn. Here, active metal (Al, Cd, or Zn) protect the base Fe-metal sacrificially.

Galvanization: The process of coating of Zn-metal over the iron is known as Galvanization. It is an anodic coating. It can be done by spraying or hot dipping. Zn is active and acts as anode as its standard oxidation potential (0.76 V) is higher

This study material is availabe on SIT ASSAN BETA

than that of Fe (0.44 V). Galvanization protects the iron by the following two ways:

(i) By providing a non-porous, non-volatile continuous oxide layer (ZnO) on the surface of iron, and
(ii) By sacrificially (i.e, Zn acts as anode and undergoes dissolution)

Fig. 10. Anodic coating (Galvanization of Iron)

So, *Galvanization* is a double protection route. As Zn is more anodic, it protects the underlying metal sacrificially when the protective oxide layer breaks at some point of time by the environment.

Cathodic or Barrier coating: In this method, a passive or less anodic metal is coated over the base metal which is to be protected from corrosion. For example, iron (Fe) the base metal is protected from corrosion by applying a coat of passive metals like Sn, Pb, or Ni. Here, less active or passive metal (Sn, Pb, or Ni) protect the more active base Fe-metal only by developing a protective oxide layer.

*** Remember that any breakage in the coating layer results in rapid corrosion. This happens because metal exposed at the breakage point acts as anode which has relatively very small area. When anodic area is much smaller than the cathodic area, rapid corrosion like pitting occurs on the surface.

Tinning: The process of coating of tin (Sn)-metal over the iron is known as Tinning. Sn is less active and acts as cathode as its standard oxidation potential (0.14 V) is lower than that of Fe (0.44 V). So, here base metal is more active than the coating metal. The coat metal protects the underlying metal Fe only by forming

This study material is availabe on SIT ASSAN BETA

an impervious oxide layer of tin oxide (SnO_2). Any damage on this layer results in pitting or formation of cavity on the surface of iron. So, a lot of care should be taken to tin plated iron can otherwise leads to rapid corrosion. Tinning is a single protection method.

Fig. 11. Cathodic coating (Tinning of Iron)

Distinguish between Galvanization and Tinning

Sl. No.	Galvanization	Tinning
1	A process of covering the surface of iron by a layer of zinc (Zn)	A process of covering the surface of iron by a layer of tin (Sn)
2	Zinc protects the iron by both sacrificially and formation of protective oxide layer	Tin protects the iron only by formation of protective oxide layer
3	Double protection route	Single protection route
4	Galvanized iron (GI) containers are not safe to store foodstuffs as food acids reacts with Zn to form toxic masses. Always there is a chance of food poising.	Tin coated container is safe to store foodstuffs. No food poisoning occurs.

Q. Why are Galvanized utensils not used?

Ans. Zn of Galvanized utensils gets dissolved in dilute food acids and forms highly toxic compounds may lead to food poisoning.

Q. Why are tinned utensils used for storing foodstuffs?

This study material is availabe on SIT ASSAN BETA

Ans. Tin is non-toxic in nature and not dissolved in dilute food acids.

Q. Zn-coated iron article is protected from rusting even when the coating is scratched. Explain it.

Ans. Zn is anodic to Fe, so when the ZnO film is scratched, Zn is preferentially attacked by the corrosive environment to form $Zn(OH)_2$ corrosion product and Fe is protected.

Q. Name two metals used for anodic coating.

Ans. Zn, Al

Q. Name two metals used for cathodic coating.

Ans. Sn, Pb

3. Proper designing

Some of design principles are as follows:

A. Avoid contact of dissimilar metals in presence of a corrosive environment
B. Keep the anodic area much larger than cathodic area
C. Anodic metal should not be painted or coated
D. Sharp corners, edges, etc. should be avoided (i.e., avoid L, T, V shaped profiles in constructions)

This study material is availabe on SIT ASSAN BETA

4. Cathodic or Eletrochemical Protection

It is a technique applied to reduce corrosion of underground metallic structures by forcing it to behave like a cathode. There are two types of cathodic protection:

A. *Sacrificial Protection*
B. *Impressed current method*

Sacrificial Protection

We know that wet/electrochemical corrosion occurs via formation of separate anode and cathode. The existence of potential difference between anode and cathode causes loss of electron (oxidation) at anode. So, without cathodic protection, active metal suffers from corrosion. If a more active metal is connected via an insulated Cu-wire to a metallic structure which is undergoing corrosion then corrosion occurs at more active metal and the metallic structure can be protected. As the more active metal is sacrificed in the process of protecting the metallic structure, it is known as *sacrificial anode*. Examples of sacrificial anode are Zn, Mg, Al, and their alloys.

Sacrificial cathodic protection methods are widely used for the protection of relatively small structures like underground pipelines, storage tanks, etc.

Fig. Sacrificial protection of buried water pipe.

This study material is availabe on SIT ASSAN BETA

Impressed current cathodic protection

In this protection method, current from an external source such as battery is applied to the metallic structure to neutralize the corrosion current. This is done to forcing the metallic structure (anode) to behave as cathode and hence protected. **(Actually during corrosion, current passes from anode to cathode, so to nullify it, current is applied in the opposite direction) In this process materials such as graphite, high silica iron, stainless steel, etc. are acts as anode. The anode is surrounded by a conducting medium (back fill) to have an electrical contact between itself and the surrounding soil. This method is applied in various relatively bigger structures like ship, transmission line towers, tanks, etc.

Fig. Impressed current cathodic protection

Q. Give reason that Zinc is used as sacrificial anode for protection of iron from rusting.

Ans. As std. oxidation potential of Zn is more than Fe, corrosion will be takes place at Zn and iron will be protected.

Q. Sharp corners should be avoided in any structural design. Give reason.

Ans. As sharp corners region are poorly oxygenated part acts as anode and undergoes differential aeration corrosion.

Q. What is cathodic protection? Give an example.

This study material is availabe on SIT ASSAN BETA

Ans. It is a corrosion control technique applied to reduce corrosion of underground metallic structures by forcing it to behave like a cathode. Example: sacrificial cathodic protection.

Q. What is impressed current cathodic protection?

Ans. It is a corrosion control method in which a battery is connected to the metallic structure in order to cancel out the corrosion current.

Q. What is sacrificial anode? Give an example.

Ans. It is a metal with higher standard oxidation potential than the metal which is to be protected from corrosion. For example for iron, Zn is acts as sacrificial anode.

Q. How is cathodic protection of iron is different from Galvanization?

Ans. In cathodic [protection, the iron structure is made cathode by connecting it with a metal with higher std. Ox. Pot. Like Zn, Mg, etc. On the other hand, Galvanization is coating of Zn-metal on the surface of Iron.

Q. Ship hull is connected to Zn-rod. Give reason.

Ans. Here Zn acts as sacrificial anode and protects the ship from corrosion.

Long Questions

1. **What is cathodic protection? Discuss the sacrificial cathodic protection with a suitable example.**
2. **Discuss Galvanization and tinning process with a suitable example.**
3. **What is cathodic protection? Discuss the impressed current cathodic protection with a suitable example.**

This study material is availabe on SIT ASSAN BETA

Energy Science

(Fuels & Combustion; Batteries)

Contents: Types of fuels, Calorific value, Determination of Calorific value, Combustion and its calculations, Solid fuel: Coal analysis (Proximate and ultimate analysis), Liquid fuels: IC engine fuel, concept of knocking, antiknocking, octane No and cetane No, Fractional Distillation of petroleum, Cracking of heavy oils; Elementary ideas on some gaseous fuels (Natural gas, Water gas, Producer gas, LPG) (Synthesis is excluded), Battery technology – Fundamentals of primary & Secondary cells, Rechargeable batteries: Lead acid storage battery, Lithium ion battery, Fuel cells: principles, applications. Elementary idea on Photo-voltaics.

Course Outcome: Classify various fuels based on combustion parameters and understand the working principle of various batteries.

Lecture-1

1.0 Introduction

In recent years our dependency on energy has enhanced a lot as a result of the increase in the standard of living and rapid technological advancement. The various types of fuels like liquid, solid and gaseous fuels are available for firing in boilers, furnaces and other combustion equipments. The selection of right type of fuel depends on various factors such as availability, storage, handling, pollution and landed cost of fuel. The knowledge of the fuel properties helps in selecting the right fuel for the right purpose and efficient use of the fuel.

Process industries, businesses, homes, and transportation systems have vast heat requirements that are also satisfied by *combustion* reactions. The energy usually comes from the fuels like petroleum, coal and natural gas known as *Fossil fuel*. Since these sources of energy will never last forever hence their proper utilization is the main concern these days.

** *Combustion* is the conversion of a substance called a *fuel* into chemical compounds known as *products of combustion* by combination with an *oxidizer*.

This study material is availabe on SIT ASSAN BETA

The combustion process is an *exothermic* chemical reaction, i.e., a reaction that releases energy as it occurs.

** Fossil fuel: They are formed by the decay of vegetable and animal matter over many thousands of years under conditions of high pressure and temperature and with a deficiency or absence of oxygen.

2.0Fuel and its classification

A fuel can be defined as *any combustible substance which during combustion gives large amount of industrially and/or domestically useful heat.* The heat evolved by burning of fuels is used for heating purposes, in locomotive engines, in internal combustion engine, etc. We use coal as a reducing agent in metallurgical industry. Examples of some fuels are coal, coke, LPG, CNG, petrol, diesel, etc.

Classification of fuels:

1. **Based on their occurrence:** Fuels are classified as A. *natural or primary* and B. *artificial or secondary* fuels.
   A. Natural fuels: They are found in nature as such. Examples are coal, wood, petroleum and natural gas.
   B. Artificial fuels: They are prepared from primary fuels. Examples are coke, petrol, diesel, coal gas, etc.
2. **Based on their physical state of aggregation:** Fuels are classified as solid, liquid and gaseous.
   Solid fuels: Coal, coke, wood
   Liquid fuels: Petroleum, petrol diesel, kerosene
   Gaseous fuel: CNG, LPG, coal gas, biogas

3.0Calorific Value (CV) or Heat value

The CV is the total quantity of heat liberated from combustion of a unit mass or unit volume of the fuel in air or oxygen. So, it is the measurement of produced heat or energy. It is measured either as Gross Calorific Value (GCV) or Net Calorific Value (NCV). The difference being the latent heat of condensation of the water vapour produced during the combustion process.

Units of calorific value:

For solid fuels: cal/g; Kcal/Kg
For liquid or gaseous fuels: Kcal/m^3

This study material is availabe on SIT ASSAN BETA

Gross calorific value (GCV): Gross calorific value (GCV) assumes all vapour ($H_2O_{(g)}$) produced during the combustion process is fully condensed. So, *it is total amount of heat liberated when unit mass or unit volume of the fuel has been burnt completely and products of combustion (CO_2 & H_2O) are cooled to RT.* It is also called as Higher Calorific Value (HCV).

Net calorific value (NCV): Net calorific value assumes the water leaves with the combustion products without fully being condensed. So, So, *it is total amount of heat liberated when unit mass or unit volume of the fuel has been burnt completely and products of combustion (CO_2 & H_2O) are allowed to escape.* It is also called as Lower Calorific Value (LCV).

Fuels should be compared based on the NCV.

Relationship between GCV and NCV:

NCV = HCV- Latent heat of water vapour formed

= HCV – 0.09H x 587; where H = % H in the fuel.

So, for a fuel without H-content, NCV = HCV

Calorific value can be determined using a Bomb Calorimeter.

4.0 Theoretical calculation of Calorific value by Dulong's Formula:

Assumption: Calorific value of a fuel is the sum of the calorific values due to all the components (C,H, S) present in the fuel. It is also assumed that if oxygen is present in the fuel then it is present in the combined form with hydrogen as H_2O.

The GCV of the component C, H, and S are 8080,34500, and 2240 cal/g, respectively.

GCV = 1/100[8080C + 34500(H-O/8) + 2240S] in cal/g

Where, C = % Carbon in the fuel; H = % Hydrogen in the fuel, and %S= % Sulphur in the fuel

Solved Examples:

Example-1 Calculate the GCV and NCV of a coal sample having the following composition: C = 80%, H=7%, O=3%, S=3.5%, N=2.1% and ash=4.4% as per proximate analysis.

This study material is availabe on SIT ASSAN BETA

Solution: N and ash are non-combustible matter, not take part in calculation process

GCV = 1/100[8080C + 34500(H-O/8) + 2240S]

= 1/100[8080x80 + 34500(7-3/8) + 2240 x 3.5] = 8828 cal/g

NCV = HCV – 0.09H x 587 = 8828-0.09x7x587 = 8458 cal/g.

Example-2 Calculate the HCV and LCV of a coal sample having the following composition: C = 75%, H=5.2%, O=12.1%, N=3.2% and ash=4.5%

Solution: N and ash are non-combustible matter

GCV = 1/100[8080C + 34500(H-O/8) + 2240S]

= 1/100[8080 x 75 + 34500(5.2-12.1/8) + 2240 x 0] = 7332.2 cal/g

NCV = HCV – 0.09H x 587 = 8828-0.09x5.2x587 = 7057.5 cal/g.

5.0Characteristics of a good fuel

A good fuel should have the following characteristics:

1. It should have High Calorific Value.
2. It should have moderate ignition temperature.
3. It should have low moisture content.
4. It should have low non-combustible matter content.
5. It should have moderate rate of combustion.
6. It should have low cost.
7. It should be easy to transport.
8. It should not emit harmful products.
9. It should have low volatile matter content.

Q. 1. Define calorific value.

Ans. The CV is the total quantity of heat liberated from combustion of a unit mass or unit volume of the fuel in air or oxygen.

Q. 2. 5 Kg of a solid fuel generates 55,000 Kcal of heat. Find its calorific value (CV).

Ans: CV = 55,000/5 = 11,000 Kcal/Kg

This study material is availabe on SIT ASSAN BETA

Q.3 When 100 m^3 gaseous fuels like LPG undergoes combustion, it generates 110,000 Kcal of heat. Find its CV.

Ans. CV = 110,000/100 = 1100 Kcal/m^3

Q.4 Mention the condition for which HCV will be same as LCV?

Ans. When % H = 0 in a fuel then HCV = LCV

Q. 5. Mention some characteristics of good fuel. (Medium type, 3 marks)

Ans. Refer section 5.0

Q.6.A good fuel should contain very less amount of moisture. Give reason.

Ans. During burning, moisture takes some of the liberated heat in the form of latent heat of vapourization. Therefore, it lowers the effective CV of fuel.

Q. 7 . Distinguish between GCV and NCV.

Ans. Refer section 3.0

Q8. What is meant by Ignition temperature?

Ans. The lowest temperature at which the fuel must be pre-heated so that it starts burning smoothly.

Q. 9. Why should an ideal fuel have moderate ignition temperature?

Ans. Low ignition temperature can cause fire hazards and involves danger in fuel storage and transport; while high ignition temperature causes difficulty in starting ignition of fuel. Hence, an ideal fuel should have moderate ignition temperature.

This study material is availabe on SIT ASSAN BETA

Corrosion Inhibitors

Corrosion inhibitors are chemical substances which are added in small amount (0.1 %) to the corrosion medium to prevent or slow down the oxidation or reduction reactions on the surface of the metal. Inhibitors do their job by providing a protective layer on the metal surfaces.

Inhibitors are of two types; (1) Inorganic, and (2) Organic

Inorganic Inhibitors: It includes chromates, phosphates, molybdates, zinc, polyphosphates, etc. They are mainly used in boilers, fractional distillation plant, cooling towers, etc.

Inorganic inhibitors are classified as (a) Anodic, and (b) Cathodic

Anodic Inhibitors: Chemical substances which inhibit the anodic (oxidation) reaction are called *Anodic Inhibitors.* Example includes molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), chromates ($Cr_2O_7^{2-}$), silicates (SiO_3^{2-}), etc. These anions react with metallic ions to produce insoluble precipitates. Insoluble substances so obtained are then get adsorbed on the surface of metal and hence slow down the rate of anodic reaction.

Cathodic Inhibitors: Chemical substances which inhibit the cathodic (reduction) reaction are called *Cathodic Inhibitors*. Example includes $ZnSO_4$, $MgSO_4$, Na_2SO_3 and $Ca(HCO_3)_2$. $ZnSO_4$, $MgSO_4$, and $Ca(HCO_3)_2$ slow down the cathodic reaction by forming a layer of $Zn(OH)_2$, $Mg(OH)_2$, $CaCO_3$ on the metallic surface. Na_2SO_3 inhibits by removing dissolved oxygen ($Na_2SO_3 + 1/2O_2 \rightarrow Na_2SO_4$).

Organic Inhibitors: It includes amines (RNH_2), mercaptans (R-SH), substituted urea, and thioureas, amides ($R\text{-}CONH_2$), Imidazoline, etc. These substances adsorbed on the surface of metal and acts as protective coating. They attach to the surface by *chemisorptions* and *physical adsorption*.

Q. What is an inhibitor?

Ans. It is a chemical substance which when added to the environment slows down the corrosion reaction (i.e., redox reaction). Examples- molybdates (MoO_4^{2-}), phosphates (PO_4^{3-}), $ZnSO_4$

This study material is availabe on SIT ASSAN BETA

Q. Define anodic inhibitor with an example.

Ans. Those chemical substances which inhibit the anodic (or oxidation) reaction are called as anodic inhibitor. For example molybdates (MoO_4^{2-})

Q. Define cathodic inhibitor with an example.

Ans. Those chemical substances which inhibit the cathodic (or reduction) reaction are called as cathodic inhibitor. Example: $ZnSO_4$

Q. What is an organic inhibitor?

Ans. It is an organic substance which decreases the rate of corrosion.

Example: Thiourea

Q. Differentiate between anodic and cathodic inhibitor.

Ans.

Anodic Inhibitor	Cathodic Inhibitor
Substances which inhibit the anodic (or oxidation) reaction are called as anodic inhibitors.	Substances which inhibit the cathodic (or reduction) reaction are called as anodic inhibitors.
Example: molybdates (MoO_4^{2-}), phosphates (PO_4^{3-})	Example: $ZnSO_4$, $MgSO_4$

This study material is availabe on SIT ASSAN BETA

Long Questions from Water Treatment

1. **What is the basic principle of L-S softening process? Discuss the cold L-S process with a schematic softener diagram.**
2. **What is the basic principle of L-S softening process? Discuss the hot L-S process with a schematic softener diagram.**
3. **What are zeolites? Discuss the zeolite softening process with a schematic softener diagram.**
4. **What is a resin? Discuss the resin softening process with a schematic softener diagram.**
5. **Differentiate between L-S and Zeolite softening process.**
6. **Numericals to calculate Temp., Perm. And Total hardness.**
7. **Numericals on finding L-S requirement**
8. **Numericals from zeolite softening**

Long Questions from Corrosion

1. What is oxidation corrosion? Discuss its mechanism.
2. Define wet corrosion. Discuss the mechanism of rusting of iron in an alkaline medium.
3. Define wet corrosion. Discuss the mechanism of rusting of iron in an acidic medium.
4. Write short notes: Galvanic Corrosion and Waterline corrosion.

This study material is availabe on SIT ASSAN BETA

5. How the following factors affect the rate of corrosion: pH, Nature of metal, Moisture, conductivity, Position of metal.
6. What is cathodic protection? Discuss the sacrificial cathodic protection with a schematic diagram.
7. Discuss Galvanisation and tinning with suitable diagrams.

This study material is availabe on SIT ASSAN BETA

Lecture-4

7. Solid Fuels

Solid fuel refers to various forms of solid material that can be burnt to release energy, providing heat and light through the process of combustion. Solid fuels have been used throughout human history to create fire and it is still in extensive use all over the world in the present day.

They are of two types: 1. *Natural (wood, coal)* and 2. *Artificial (coke, paddy straw, corn, etc.)*.

Characteristics of a good solid fuel:

1. High calorific value, 2. Low moisture content, 3. Low cost, 4. Low sulphur content, 5. Low ash content, 6. Low volatile matter content, etc.

Advantages of solid fuels: 1. They are easy to transport; 2. Easy to store; 3. Low cost; 4. Possess moderate ignition temperature.

Disadvantages of solid fuels: 1. Ash content is high, 2. Thermal efficiency is low, 3. Burn with clinker formation, 4. Calorific value is lower as compared to liquid fuels, 5. Causes lot of air pollution

7.1 Coal and its analysis

Coal is a fossil fuel. It is a highly carbonaceous matter that has been formed as result of anaerobic microbial decomposition of cellulosic materials of plants under high temperature and pressure condition. Coal is classified into three major types namely anthracite, bituminous, and lignite. Anthracite is the highest rank coal with calorific value ~8700 cal/g. The common coals used in Indian industry are bituminous.

Selection of coal: For the selection of coal for different uses, the following factors are taken into consideration:

1. Calorific value should be high.
2. Moisture content should be low.

This study material is availabe on SIT ASSAN BETA

3. Ash content should be low.
4. Calorific intensity should be high.
5. S and P content should be low.

7.2 Analysis of coal

There are two methods: (A) ultimate analysis and (B) proximate analysis. **The proximate analysis determines only the fixed carbon, volatile matter, moisture and ash percentages whereas the ultimate analysis determines all coal component elements, solid or gaseous.** The ultimate analysis is determined in a properly equipped laboratory by a skilled chemist.

A. Proximate Analysis: The proximate analysis determines only the fixed carbon, volatile matter, moisture and ash percentages using simple apparatus.

1. **Measurement of Moisture**

Determination of moisture is carried out by placing a sample of powdered raw coal of size 200-micron size in an uncovered crucible and it is placed in the oven kept at 108±2 °C. Then the sample is cooled to room temperature and weighed again. The loss in weight represents moisture.

% moisture = (loss in wt/wt of coal) x 100

Suppose we have taken 1 g of coal and after the removal of moisture its weight is 0.95g. Then % moisture = (1-0.95/1) x 100 = 5 %

2. **Measurement of Volatile Matter (VM)**

After the removal of moisture, dried sample of coal is then covered with a lid is placed in an electric furnace maintained at 900 °C. The crucible is taken out after 10 min of heating. The sample is cooled and weighed. Loss in weight is reported as VM.

% VM = (loss in wt due to removal of VM/wt. of coal) x 100

3. **Measurement of Ash**

The cover from the crucible used in the last test is removed and the crucible is heated in a furnace maintained at 750 ^{0}C until all the carbon is burned. The residue is weighed, which is the incombustible ash.

% ash = (wt. of ash/wt. of coal) x 100

4. **Fixed Carbon**

In actual practice, Fixed Carbon or FC derived by subtracting from 100 the value of moisture, volatile matter and ash.

% FC = 100 - % (Moisture + VM + ash)

This study material is availabe on SIT ASSAN BETA

Significance of Various Parameters in Proximate Analysis

(a) Fixed carbon:

Fixed carbon is the solid fuel left in the furnace after volatile matter is distilled off. It consists mostly of carbon but also contains some hydrogen, oxygen, sulphur and nitrogen not driven off with the gases. Fixed carbon gives a rough estimate of heating value or calorific value of coal.

(b) Volatile Matter:

Volatile matters are the methane, hydrocarbons, hydrogen and carbon monoxide, and incombustible gases like carbon dioxide and nitrogen found in coal. Thus the volatile matter is an index of the gaseous fuels present. Typical range of volatile matter is 20 to 35%.

Volatile Matter

• Proportionately increases flame length, and helps in easier ignition of coal. But higher % is unwanted because it decreases the CV.

(c) Ash Content:

Ash is an impurity that will not burn. Typical range is 5 to 40%

Ash

- Reduces handling and burning capacity
- Increases handling costs
- Affects combustion efficiency
- Causes clinkering
- Reduces Calorific value

(d) Moisture Content:

Since it replaces combustible matter, it decreases the heat content per kg of coal. Typical range is 0.5 to 10%

Moisture

• Increases heat loss, due to evaporation

Q. What should be the characteristics of an ideal solid fuel?

Q. What is proximate analysis of coal? Mention its significance. (Long question)

This study material is availabe on SIT ASSAN BETA

L-5 and 6

Ultimate Analysis: The ultimate analysis indicates the various elemental chemical constituents such as Carbon C, Hydrogen H, Oxygen O, Sulphur S, Nitrogen N, etc. It is useful in determining the quantity of air required for combustion and the volume and composition of the combustion gases. Typical ultimate analyses of various coals are given in the **Table 1**.

TABLE 1 TYPICAL ULTIMATE ANALYSIS OF COALS

Parameter	Indian Coal, %	Indonesian Coal, %
Moisture	5.98	9.43
Mineral Matter (1.1 × Ash)	38.63	13.99
Carbon	41.11	58.96
Hydrogen	2.76	4.16
Nitrogen	1.22	1.02
Sulphur	0.41	0.56
Oxygen	9.89	11.88

Importance of Ultimate Analysis:

1. **% C and % H:** Greater the % of C & H, better is the coal in quality and calorific value. However, higher % H indicates large content of VM in the sample.

2. **% N:** As N has no calorific value; its presence in the coal is unwanted. So, a good quality of coal should have no or very less % of N.

3. **% S:** It should be small. It generates harmful SO_2 & SO_3 gas on combustion. For metallurgical industries it is undesirable because it combines with Fe and makes it brittle. So, a good quality of coal should have no or very less % of S.

4. **% Ash**: It is determined as per the procedure of proximate analysis. So, a good quality of coal should have very less % of ash.

5. **% O:** Oxygen content decreases the calorific value of the coal. High O-content in the fuel means high content of moisture in it. Usually an increase in 1% O-

This study material is availabe on SIT ASSAN BETA

content decreases the calorific value by about 1.7%. So, a good quality of coal should have very less % of O.

$$\% \ O = 100 - \% \text{ of } (C + H + N + S + ash)$$

Q. Why ultimate analysis of the coal should be carried out?

Ans. Because it is helpful in: 1. Classification of coals, 2. in determining the quantity of air required for combustion and the volume & composition of the combustion gases.

8. Liquid Fuels

They are of two types: 1. Natural (Petroleum) and 2. Artificial (petrol, diesel, furnace oil, etc.).

Advantages of liquid fuels

1. They possess higher CV per unit mass than solid fuels.
2. They burn without forming dust, ash, clinkers, etc.
3. They are easy to transport through pipelines.
4. They can be used in internal combustion (IC) engine.
5. They require less furnace space for combustion.

Disadvantages of liquid fuels

1. The cost of liquid fuel is relatively much higher than solid fuels.
2. Storage cost is high.
3. Greater risk of fire hazards.

8.1 Petroleum-A Natural liquid fuel

It is a primary liquid fuel (a fossil fuel). It is dark greenish-brown viscous oil found deep in Earth's crust. The word petroleum is derived from Latin word *Petra = rock* and *oleum = oil*. It is otherwise known as *rock oil, mineral oil or crude oil*.

This study material is availabe on SIT ASSAN BETA

It is the main source of many secondary fules like petrol, diesel, kerosene, etc., and petrochemicals (e.g, alkanes, alkenes, benzene, etc.).

Petroleum is a complex mixture of paraffinic, olefinic and aromatic hydrocarbons with small quantities of organic compounds of O, N, and S. The average composition of petroleum is: C =80-87%, H = 11-15%, S = 0.1-3.5%, O = 0.1-0.9%, N = 0.4-0.9%.

Refining of Petroleum:

Petroleum mined from the oil well contains many unwanted substances. As such it is of no use. Its purification and fractionations is needed. *Petroleum refining or Oil refining* is an industrial process in which crude oil is extracted from the ground and transformed and refined into useful products like Liquefied Petroleum Gas (LPG), petrol, diesel, kerosene, asphalt base, jet fuel, gasoline, heating oil, fuel oils etc.

The process of refining involves the following stages:

1. ***Separation of water (Cottrell's process):*** The oil is separated from water by allowing it to flow between two highly charged electrodes. The colloidal water-droplets coalesce to form large drops, which separate out from the oil.

2. ***Removal of sulphur compounds:*** They are removed by treating the oil with copper oxide. The reaction results in the formation of copper sulphide (CuS) in solid form which can be removed by filtration.

3. ***Fractional Distillation:***

After the removal of water and S-compounds, the crude oil is heated about 400 0C in a furnace. The hot vapours are then passed up a fractionating column. As the vapours go up, they become gradually cooler and fractional condensation takes place at different heights of column. Higher boiling fractions condense first while lower boiling fractions condenses later.

This study material is availabe on SIT ASSAN BETA

Fig. Fractional distillation of crude petroleum

N.B.: The fractions at the top of the fractionating column have lower boiling points than the fractions at the bottom.

The *three important secondary liquid fuels* obtained are:

1. **Gasoline or petrol:** It contains hydrocarbons from pentane to octane (C_5-C_8). This fraction is obtained between 80-150 ^{0}C. *Its calorific value is about 11,250 cal/gm.*
2. **Kerosene:** It contains higher hydrocarbons (C_{10}-C_{16}). This fraction is obtained between 150-200 ^{0}C. *Its calorific value is about 11,100 cal/gm.*

3. **Diesel:** It contains higher hydrocarbons (C_{15}-C_{18}). This fraction is obtained between 250-300 ^{0}C. *Its calorific value is about 11,000 cal/gm.*

This study material is availabe on SIT ASSAN BETA

S.No.	Fraction's Name	Boiling temperature	Approx. composition in terms of hydrocarbon containing C atoms	Applications
1.	Uncondensed gas. (Refinery gas)	<30° C	C_1 to C_4 (such as ethane, propane, isobutane) Lower Hydrocarbons	Used as domestic industrial fuel under the name L.P.G. (liquefied petroleum gas).
2.	Petroleum ether.	30° to 70° C	$C_5 - C_7$	Used as a solvent.
3.	Gasoline or petrol or motor spirit.	40 to 120° C	$C_5 - C_9$ (calorific value = 11,250 kcal/kg)	Used as fuel for IC engines, solvent and in dry cleaning.
4.	Naphtha or solvent spirit.	120 to 180° C	$C_9 - C_{10}$	As solvent for paints and varnishes and in dry cleaning.
5.	Kerosene oil.	180 to 250° C	$C_{10} - C_{16}$ (calorific value = 11,000 kcal/kg)	As an illuminant jet engine fuel and for preparing laboratory gas.
6.	Diesel oil or fuel oil or gas oil.	250 to 320° C	$C_{10} - C_{18}$ (calorific value = 11,000 kcal/kg)	used as diesel engine fuel.
7.	Heavy oil.	320 to 400° C	$C_{17} - C_{30}$	For getting gasoline by cracking.
	This on refractionation gives :			
(i)	Lubricating oil.			As lubricants
(ii)	Petroleum jelly.(Vaseline)			In cosmetics and medicines.
(iii)	Grease.			As lubricant.
(iv)	Paraffin wax.			In candles, boot polishes, wax paper, tarapaulin cloth, etc.
8.	Residue may be either :	> 400° C	C_{30} and above	used for Waterproofing of roofs and road making.
(i)	Asphalt.			
(ii)	or Petroleum coke.			As a fuel and in moulding arc light rods.

This study material is availabe on SIT ASSAN BETA

Lecture-2 ,3

5.0 Combustion Calculation

✓ *Important points*

1. Substances always combine in definite proportions and these proportions are determined by the mol. masses of the substances involved and the products formed.

   $$C + O_2 \rightarrow CO_2$$

   Here, 12 g of C combines with 32g of oxygen to form 44g of carbon dioxide
   (Mass proportion ratio 12:32:44)
   For gaseous fuel hydrogen, $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O(g)$, 1 vol. of hydrogen combines with ½ vol. of oxygen to form 1 vol of water.

2. 22.4 L of any gas at STP (0 ^{0}C and 1 atm.) has a mass equal to its 1 mol. Thus, 22.4 L of O_2 gas at STP will have a mass of 32g. 22.4 L of Air at STP will have a mass of 28.92 g.

3. Mol. Mass of air is taken as 28.92 g/mol.

4. Air contains 21% of oxygen by volume and 23% by mass. This means 100 g of air contain 23 g of oxygen and 100 L of air contains 21 L of oxygen.

Most Commonly involved combustion Reactions:

1. $\mathbf{H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O(g)}$
2. $\mathbf{C + O_2 \rightarrow CO_2}$
3. $\mathbf{S + O_2 \rightarrow SO_2}$
4. $\mathbf{CO + 1/2O_2 \rightarrow CO}$
5. $\mathbf{CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}}$
6. $\mathbf{C_2H_{6(g)} + 7/2O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}}$
7. $\mathbf{C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(g)}}$
8. $\mathbf{C_2H_{2(g)} + 5/2O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(g)}}$

Solved Examples:

A. For Solid fuels

Example-1 *Calculate the weight and volume of air required for the combustion of 5 kg of coke.*

Solution: **Weight of air required:**

$$C\ (coke) + O_2 \rightarrow CO_2$$

12g of C required 32g of oxygen
5000 g of C will need = 32/12 x 5000 = 13333.33 g of O_2

Air reqd. = (100/23) x 13333.33 = **57971 g**

Volume of air required:

We know that 28.92 g of air occupies volume 22.4 L
57971 g will occupy = (22.4/28.94) x 57971 g = **44870.43 L**

This study material is availabe on SIT ASSAN BETA

Example-2 ***A sample of coal was found to have the following percentage composition: C = 80 %, H =7%, O=5 %, N=3 %, S =2 % and rest is ash. Calculate the minimum air required for complete combustion of 1 kg of coal.***

Solution: Reactions:

1. $C + O_2 \rightarrow CO_2$ (here, 12 g of C needs 32g of O_2)
   12g 32g
2. $H_2 + 1/2O_2 \rightarrow H_2O$ (here 2 g of hydrogen needs 16 g of oxygen)
   2g 16g
3. $S + O_2 \rightarrow SO_2$ (here, 32 g of C needs 32g of O_2)
   32g 32g

As per the data given: 1kg = 1000g of coal contains 800g C, 70g H,50g O, 30g N, 20g S, and 30g ash. (*N and ash are non-combustible matter*)

So, air needed = wt of [C x (32/12) + H x (16/2) + S x (32/32) – O] x 100/23
= [(800 x 32/12) + 70 x (16/2) + 20 x 1 – 50] x 100/23= (2133.33 + 560 + 20 – 50) x 100/23
= 2663.33 x 100/23 =11,579.69 g = **11.57 kg**

Example-3 ***A coal sample was found to have the following % composition: C = 75%, H=5.2%, O=12.1%, N=3.2% and ash=4.5%.***

(i) ***Calculate the weight of air required for complete combustion of 1 kg of coal.***
(ii) ***Find volume of air needed for it.***
*(iii)****Find HCV and NCV.***

Solution:

As per the data given: 1kg = 1000g of coal contains 750 g C, 52g H,121 g O, 32g N, and 32 g ash. (*N and ash are non-combustible matter*)

As no S in the sample, % S = 0

(i). So, wt of air needed = wt of [C x (32/12) + H x (16/2) + S x (32/32) – O] x 100/23
= [(750 x 32/12) + 52 x (16/2)– 121] x 100/23 = (2000 + 416– 121) x 100/23
= 2295 x 100/23 =**9978 g = 9.978 kg**

(ii) Volume of air:
We know that 28.92 g air occupies 22.4 L
9978 g of air will occupy = (22.4/28.92) x 9978 L = 7728.46 L

(ii) **GCV** = 1/100[8080C + 34500(H-O/8) + 2240S]
= 1/100[8080 x 75 + 34500(5.2-12.1/8) + 2240 x 0] = **7332.2 cal/g**
NCV = HCV – 0.09H x 587 = 8828-0.09x5.2x587 = **7057.5 cal/g.**

Example-4
A coal sample gave the following analysis: C = 66 %, H = 4 %, O = 7 %, N = 2 %, S = 3 %, moisture = 8 % and ash = 10 %. Determine the amount of air needed if 1 Kg of coal is burnt with 25% excess air.

Ans. As per the data given: 1kg = 1000g of coal contains 660 g C, 40g H,70 g O, 20g N, 30 g S, 80 g moisture and 100 g ash. (*N , moisture and ash are non-combustible matter*)

This study material is availabe on SIT ASSAN BETA

Air needed = = wt of [C x (32/12) + H x (16/2) + S x (32/32) – O] x 100/23 x 125/100
= [(660 x 32/12) + 40 x (16/2) + 30 x (32/32) – 70] x 100/23 x 125/100
= (1760 + 320 + 30 – 70) x 100/23 x 125/100 = 11,086.956 g

B. For gaseous fuels

Example-1 ***Calculate the volume of air needed for the complete combustion of 100 L of hydrogen gas.***

Solution: Combustion rxn: $H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$
1 vol ½ vol

It means, 1 L of hydrogen needs ½ L of oxygen
So, 100 L needs = 50 L O_2
Vol of air needed = vol of Oxygen x (100/21) = 50 x 100/21 = **238.095 L**

Example-2 ***A gaseous fuel has the following composition by volume: CH_4 = 70 %, CO_2 = 20 % and N_2 = 10 %. Find the volume of air required for the complete combustion of 1 m^3 of this fuel.***

Solution: CO_2 and N_2 gas are non-combustible. 1 m^3 of gas contains 0.7 m^3 CH_4

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$$

Here, 1 vol.of methane gas needs 2 vol of oxygen
Then, 0.7 m^3 CH_4 needs = 2 x 0.7 = 1.4 m^3 O_2
Vol of air needed for 1 m^3 of gas = 1.4 x 100/21 = **6.66 m^3**

Example-3 ***A gaseous fuel has the following composition by volume: CH_4 = 70 %, H_2 = 20 % CO_2 = 5% and N_2 = 5 %. Find the volume of air required if 1 m^3 of this fuel is burnt with 40% excess air.***

Solution: **:** 1 m^3 of gas contains 0.7 m^3 CH_4, 0.2 m^3 H_2, 0.05 m^3 CO_2 *and* 0.05 m^3 N_2. *Here,* CO_2 and N_2 gas are non-combustible.

Combustion equation	Volume of Oxygen needed
$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$	0.7 x 2 = 1.4 m^3
$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$	0.2 x ½ = 0.1 m^3
	Total Vol. of O_2 = 1.4 + 0.1 = 1.5 m^3

Vol. of air needed = Vol of O_2 x 100/21 x 140/100 = 1.5 x 100/21 x 140/100 = 10 m^3 = 10 x 10^3 L = 10^4 L

Example-4 ***A gaseous fuel has the following composition by volume: CH_4 = 80 %, H_2 = 5 %, O_2 = 10 % and N_2 = 5 %. Find the volume and weight of air required if 1 m^3 of this fuel is completely burnt.***

Solution: Solution: 1 m^3 of gas contains 0.8 m^3 CH_4, 0.05 m^3 H_2, *0.1 m^3 O2, and* 0.05 m^3 N_2. *Here,* N_2 gas is non-combustible.

This study material is availabe on SIT ASSAN BETA

Combustion equation	Volume of Oxygen needed
$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$	0.8 x 2 = 1.6 m^3
$H_{2(g)} + 1/2O_{2(g)} \rightarrow H_2O_{(g)}$	0.05 x ½ = 0.025 m^3
	Total Vol. of O_2 = 1.4 + 0.025 = 1.625 m^3 **Fuel contains O_2 = 0.1 m^3** **So, net O_2 needed = 1.625-0.1 = 1.525 m3**

Vol. of air needed = Vol of O_2 x 100/21 x 140/100 = 1.525 x 100/21 = 7.261 m^3 = 7.261 x 10^3 L

Wt. of air needed:

We know that 22.4 L of air weigh 28.92 g

So, 7.261 x 10^3 L will weigh = (28.92/22.4) x 7.261 x 10^3 = 9.374 x 10^3 g = 9.374 Kg.

Preared by Dr. Manoranjan Behera
Silicon Institute of Technology, BBSR

This study material is availabe on SIT ASSAN BETA

10. Battery

Battery is an electrochemical cell or a group of two or more cells connected in series which converts chemical energy into electrical energy. Examples: Nickel-Cadmium Ni-Cd cell; Lead-acid storage cell, Laclanche (Zn-C) cell, Li-ion battery, etc.

Characteristics of a good commercial battery

A good commercial battery should have:

- ✓ Low cost
- ✓ Light in weight
- ✓ Small in size (i.e., portability)
- ✓ High energy efficiency
- ✓ High cycle life
- ✓ Long shelf life
- ✓ Excellent tolerance to variation of temp., vibration, moisture, EM wave, etc.

Types of batteries

In general, there are two types of batteries are available in the market:

1. Primary or non-rechargeable battery
2. Secondary or rechargeable battery

Primary Battery: Here, cell reaction (i.e., a redox reaction) is not reversible. It is also known as dry cell. Example: Laclanche cell

Secondary Battery

Here, cell reaction can be reversed during charging by the supply of an external source. It is also known as reversible cell. Example: Lad-acid storage cell

10.1 Lead-Acid Storage Cell-a rechargeable battery

- ✓ It is a secondary cell which can operate both as a electrochemical cell and as a electrolytic cell. It is also known as lead-acid accumulator.
- ✓ It has the ability to supply electrical energy during discharging (i.e., acts as electrochemical cell).

This study material is availabe on SIT ASSAN BETA

- ✓ Also, it has the ability to receive electrical energy during charging (i.e., acts as electrolytic cell)
- ✓ It can store a lot of charge and provide high current for short periods of time.
- ✓ The lead acid battery is packed in a thick rubber or plastic case to prevent leakage of the corrosive sulphuric acid.

Construction

Like any electrochemical cell, it consists of **an anode, a cathode and an electrolyte**. Here, porous lead (Pb) acts as anode, lead coated with lead oxide (PbO_2) acts as cathode and 20% H_2SO_4 (density ~1.2 g/cc) acts as electrolyte. In general, a storage cell consists of at least six numbers of such cells connected in series to provide a output voltage of ~12V.

Working

Its working consists of two processes: **A.** Discharging, and **B.** Charging

This study material is availabe on SIT ASSAN BETA

Discharging: It is said to be discharging when the battery is used for supplying electrical energy. So, it acts as an electrochemical cell. The following reactions were occurring during discharging.

Chemical reactions for discharging:

Anode (Oxidation): $Pb + SO_4^{2-} \rightarrow PbSO_4\ (s) + 2e$ ---------- (1)

(Here, Pb(0) is oxidized to Pb^{2+})

Cathode (Reduction): $PbO_2 + 4H^+ + SO_4^{2-} + 2e \rightarrow PbSO_4\ (s) + 2H_2O$ -------- (2)

(Here, Pb^{4+} is reduced to Pb^{2+})

Net cell reaction during discharging (a redox reaction): (1) + (2)

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4\ (s) + 2H_2O + Energy$

Or $\mathbf{Pb + PbO_2} + 2H_2SO_4 \rightarrow \mathbf{2PbSO_{4\ (s)}} + 2H_2O + Energy$

- ✓ In the discharged state, both the positive and negative plates become lead(II) sulfate ($PbSO_4$). The electrolyte loses much of its dissolved sulfuric acid and becomes primarily water.

Charging:

During discharging, it acts as electrolytic cell. During discharging, the lead (Pb) of the anode and lead dioxide (PbO_2) of the cathode are covered with lead sulphate ($PbSO_4$).This causes the cell stop working after discharging for some period of time. For further use, it needs to be recharged by passing an external source greater than 2 Volt. This external source causes reversing the cell reactions taking place during discharging.

The following reactions were occurring during discharging.

Chemical reactions for charging:

Anode (Oxidation): $PbSO_4\ (s) + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e$ -------- (1)

(Here, Pb^{2+} is reduced to Pb^{4+})

Cathode (Reduction):

This study material is availabe on SIT ASSAN BETA

$$PbSO_4\,(s) + 2e \rightarrow Pb + SO_4^{2-} \text{ ---------- (2)}$$

(Here, Pb^{2+} is reduced to Pb(0))

Net cell reaction during charging (a redox reaction): (1) + (2)

$$2PbSO_4\,(s) + 2H_2O + \text{Energy} \rightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$$

Or $$2PbSO_4\,(s) + 2H_2O + \textbf{External source} \rightarrow Pb + PbO_2 + 2H_2SO_4$$

*** Notice how the charging reaction is the exact opposite of the discharge reaction.

N.B.: During charging

- ✓ The anodic reaction of discharging becomes cathodic reaction but in reverse order.
- ✓ The cathodic reaction of discharging becomes anodic reaction but in reverse order.

Applications: This cell is used in electrical vehicles, hospitals, trucks, buses, telephone exchange, inverter, UPS, etc.

Limitations:

- ✓ Excessive charging may damage the electrodes
- ✓ Excessive charging may leads to explosion of battery
- ✓ Lead metal is toxic in nature
- ✓ In cold weather, there is a decrease in output voltage.

Q. Write the chemical reactions occur during the discharging.

Q. Write the chemical reactions occur during the charging.

Q. What is an accumulator?

Q. Mention some limitations of lead-acid storage battery.

Q. What do you mean by charging?

Q. What do you mean by discharging?

Q. Briefly discuss the construction and working of lead-acid storage cell. (7 marks)

This study material is availabe on SIT ASSAN BETA

Lecture-7

8.2 Fuels for Internal Combustion (IC) Engines

We use petrol and diesel in IC engines. In an IC engine, a mixture of fuel and air is ignited in a cylinder, either by means of a spark (Spark-ignition engine, e.g., petrol engine) or by compressing the air & fuel mixture (compression-ignition engine, e.g., diesel engine) and the gases evolved under high pressure push the piston down, thus providing the power stroke.

In a 4-stroke engine, following four strokes complete their working cycle:

1. **Suction stroke:** A mixture of air and fuel vapour is drawn into the cylinder.
2. **Compression stroke:** The piston compresses the mixture
3. **Power stroke/Ignition stroke:** The mixture is ignited by an electric spark. The hot products of combustion increase the pressure and push the piston down, providing an output power.
4. **Exhaust stroke:** The piston ascends and expels the exhaust gases from the cylinder.

8.3 Some important terms

Knocking and anti-knocking

The efficiency of an IC engine depends on a factor called compression ratio (CR).

Compression ratio: It is defined as the ratio of gaseous volume (V_1) in the cylinder at the end of the suction-stroke to the volume (V_2) at the end of compression-stroke of the piston.

$$\text{As } V_1 > V_2 \Rightarrow CR = (V_1/V_2) > 1$$

CR indicates the extent of compression of fuel-air mixture by the piston.

This study material is availabe on SIT ASSAN BETA

With increase in CR, efficiency of IC engine also increases but after critical CR, the tendency to knock also increases. The CR at which fuel tends to knock is called critical CR.

Knocking: It is a metallic sound emitted from the cylinder due to abnormal type of combustion of fuel-air mixture.

Consequences of knocking:

Knocking is unwanted due to following reasons:

1. It decreases the power output
2. Results in mechanical damage of the cylinder part

Factors affecting knocking: Some of the factors are:

1. Design of the engine
2. Running condition
3. Chemical structure of the fuel hydrocarbons (HCs)

How chemical structure affects knocking?

Knocking tendency decreases in the order-

n-alkanes; mono-substituted alkanes; cycloalkanes; alkenes; poly-substituted alakanes; aromatics

Aromatic HCs have higher anti-knocking properties than paraffins and olefins.

Anti-knocking substance:

The substance which can reduce the knocking property is aknown as anti-knocking substance. For example Tetra Ethyl Lead (TEL) $(C_2H5)_4Pb$, Diethyl Telluride $(C_2H5)_2Te$ are most commonly used anti-knocking substance. These substances are

This study material is availabe on SIT ASSAN BETA

added to fuel to check knocking in IC engines. During combustion, TEL gives rise to Pb and PbO. These particles are act as free-radical chain inhibitors. As knocking proceeds via a free radical chain reaction, these inhibitors arrest the propagation of the explosive chain reaction.

N.B.: As Pb and PbO deposition decreases the life of IC engine, they must be removed from it. This can be done by adding ethylene dibromide along with TEL to the fuel.

(Pb, PbO) + $C_2H_4Br_2$ → $PbBr_2$, as $PbBr_2$ is volatile in nature it escapes into the atmosphere through the exhaust pipe (Silencer).

Petrol and Diesel engine fuel

Petrol engine fuel

In a petrol engine, the fuel is burnt by a spark obtained by a spark-plug. Petrol engine fuel contains mainly constituents like **branched alkanes, aromatics**, etc. Usually consists of less % of straight chain HCs. The quality of a petrol fuel is determined by its **Octane number**.

Octane Number

The resistance offered by a petrol or gasoline to knocking cannot be defined in absolute terms. It is generally expressed on an arbitrary scale, known as Octane rating proposed by Graham Edgar in 1926. It has been found that n-heptane knocks very badly and iso-octane gives very little knocking.

Fuel	Octane Number	Characteristics
n-heptane (C_7H_{16})	0	Knocks severely
Iso-octane (2,2,4-	100	High Resistance to

This study material is availabe on SIT ASSAN BETA

trimethyl pentane)		knocking

As knocking increases, octane number decreases.

Definition: *Octane number* is the % of iso-octane present in the mixture of n-heptane & iso-octane which has the same knocking characteristics as the gasoline sample, under the same set of conditions.

In this way, a "**90-octane**" number fuel is one which has the same knocking characteristics as a 90:10 mixture of iso-octane and n-heptane.

Diesel engine fuel

In the diesel engine, air is first drawn into the cylinder and compressed to a pressure of about 500 psi Pascal per square inch (34 atm). This compression is accompanied by a rise in temperature to about 500 ^{0}C towards the end of compression stroke, diesel is injected in the form of finely-divided spray into the hot air in the cylinder. The oil absorbs the heat from the air and it ignites spontaneously as it attains the ignition temperature. This rises the temperature and pressure. The piston is pushed by expanding gases in the power stroke.

So, in a diesel engine the fuel is exploded not by a spark, but by the application of heat and pressure.

N.B.: The combustion of fuel in a diesel engine is not instantaneous; the interval between the start of fuel injection and its ignition is called "*Ignition Delay*". Ignition delay is due to the time taken for the vaporization of the individual droplets and rising of the vapors to its ignition temperature. Ignition delay is relatively short for paraffinic fuel, than olefinic, napthalenic and aromatic fuels. Ignition delay is the main cause of knocking in a diesel engine.

Cetane Number

This study material is availabe on SIT ASSAN BETA

The suitability of diesel engine is determined by its "Cetane Value". Cetane number of a fuel is primarily depends on: (1) *Nature* and (2) *Composition of its HCs*. In the following series the cetane number decreases from left to right.

n-alkanes > cycloalkanes > alkenes > branched alkanes > aromatics

- As Ignition delay increases from left to right
- Knocking increases from left to right
- So, Cetane number decreases from left to right

Definition of cetane number: It is the % of hexadecane (cetane) in a mixture of hexadecane & 2-methyl naphthalene which have the same ignition characteristics as the diesel fuel sample under the same set of conditions.

In this way, a "**90-cetane**" number fuel is one which has the same knocking characteristics as a 90:10 mixture of hexadecane and 2-methyl napthalene.

Q.1 Define the term knocking. How to avoid knocking in IC engines?

Q. 2. A small amount of ethylene di-bromide is added to the gasoline along with TEL. Give reason.

Q. 3. Define the term Octane number.

Q. 4. Define Cetane number.

Q.5 Gasoline containing TEL is used in IC engine. Give reason.

This study material is availabe on SIT ASSAN BETA

Lecture-8

8.4 Cracking of Heavy oils

Cracking is defined as the decomposition of heavy oils with high molecular weight HCs into light oil of lower molecular weight HCs in absence of air.

$C_{10}H_{22}$ decane (Heavy oil) → C_5H_{10} (pentene) + C_5H_{12} (pentane)

Objectives of cracking:

1. To fulfill the high demand for gasoline
2. To prepare good quality gasoline

Types of cracking

It is of two types: (1) *Thermal*, and (2) *Catalytic* cracking

Thermal cracking

When the heavy oils are subjected to high temperature (475-650 ^{0}C) and pressure (10-70 atm.) in absence of catalyst, it is called as thermal cracking. Here, the bigger HC molecule breaks down to give smaller molecules of the paraffins, oleifins and some hydrogen. $C_{12}H_{24} \rightarrow H_2 + C_4H_{10} + C_4H_8 + C_4H_4$

Catalytic cracking

When the heavy oils are subjected to lower temperature (400-450 ^{0}C) and pressure (1-2 atm.) in presence of a suitable catalyst, it is called as catalytic cracking. In short, it is written as **cat cracking**. The various catalyst used are aluminium silicate $Al_2(SiO_3)_3$, alumina Al_2O_3, Pt/Rh, etc. Better quality with good quantity of gasoline is produced by this method.

This study material is availabe on SIT ASSAN BETA

8.4.1 Advantages of catalytic cracking over thermal cracking

1. The yield of petrol is higher.
2. The quality of petrol produced is better
3. Petrol possess better anti-knocking characteristic as it contain a higher amount of aromatics HCs
4. Petrol contain a lesser amount of undesirable sulphur compounds
5. Low pressure is needed
6. Cracking process can be easily controlled, so desired products can be obtained
7. % of gum forming compounds (i.e., unsaturated HCs) are very low
8. Production cost is very low as it occurs at low T and P

Q. Define thermal cracking with a suitable example.

Q. Petrol obtained by catalytic cracking is better than thermal cracking process. Give reason.

Ans. Refer above (section 8.4.1)

Q. What is cat cracking?

Ans. When the heavy oils are subjected to lower temperature (400-450 ^{0}C) and pressure (1-2 atm.) in presence of a suitable catalyst, it is called as catalytic cracking or cat cracking.

Q. What is straight-run petrol?

Ans. The petrol obtained by fractional distillation of petroleum is known as straight-run petrol.

Q. Mention the name of two catalysts used in catalytic cracking.

Ans. Aluminium silicate $Al_2(SiO_3)_3$ and alumina Al_2O_3

Q. What is synthetic petrol?

Ans. The petrol obtained by cracking of heavy oils are call synthetic petrol.

9. Gaseous fuels

This study material is availabe on SIT ASSAN BETA

They are of two types: 1. Natural (Natural gas) and 2. Artificial (LPG, water gas, producer gas, biogas, etc.).

Advantages of gaseous fuels:

1. They can be conveyed easily through pipelines to actual place of need
2. They can be lighted at moment's notice
3. They have relatively high calorific value
4. They can burn without any smoke and are ash free.
5. They are free from solid and liquid impurities.
6. Complete combustion without pollution is possible
7. They can be used in IC engines

Disadvantages:

1. Very large and special storage tanks are needed for them.
2. They are highly inflammable, so chances of fire hazards are high in their use.
3. They are relatively costlier than solid fuels.

9.1 Some gaseous fuels

A. Liquefied Petroleum Gas (LPG)

- LPG is a secondary gaseous fuel.
- It is obtained as a by-product during the cracking of heavy oils. It consists of smaller HCs like butane, iso-butane, propane, butylenes, etc. with little or no propylene and ethane.
- Its calorific value is about 27,800 Kcal/m^3.
- The larges use of LPG is as a domestic fuel.
- It is also used as motor fuel.

B. Natural gas

- Natural gas is a fossil fuel or primary fuel.
- It is formed as a result of anaerobic bacterial decomposition of buried plant and animal matters in presence of high T and P.
- Its calorific value varies from 12,000-14,000 Kcal/m^3.

This study material is availabe on SIT ASSAN BETA

- The average composition is: CH_4 = 70-90 %, C_2H_6 = 5-10%, H_2 = 3%, CO + CO_2 = rest.
- It mainly contains methane CH_4 gas.
- It is used as raw material for the manufacture of carbon black- filler for rubber.
- It is used as raw material for the manufacture of H_2 gas.
- It is used for domestic as well as industrial heating.

C. Producer gas

- It is a secondary fuel obtained from coal or coke.
- It is a mixture of CO & H_2 associated with *large % of non-combustible gases N_2 & CO_2.*
- Its calorific value is about 1300 Kcal/m^3.
- The average composition is: CO = 22-30%; H_2 = 8-12%; N_2 = 52-55%, and CO_2 = 3%.
- So, mainly contains **CO and N_2** gas.
- It is used for heating open-hearth furnace in steel & glass industries.
- It is used as reducing agent in metallurgical industry.

D. Water gas

- It is a secondary fuel obtained from coal or coke.
- It is a mixture of CO & H_2 associated *with little % of non-combustible gases N_2 & CO_2.*
- Its calorific value is about 2800 Kcal/m^3.
- The average composition is: H_2 = 51%; CO = 41%; N_2 = 4%, and CO_2 = 4%.
- So, mainly contains **CO and H_2** gas.
- **It is used as a source of H_2.**
- It is used for heating open-hearth furnace in steel & glass industries.
- It is used as reducing agent in metallurgical industry.

Q. Mention some uses of LPG.

Q. Mention the main constituent present in CNG.

This study material is availabe on SIT ASSAN BETA

Ans. Methane

Q. Water gas has higher calorific value than producer gas. Give reason.

Ans. Water gas contains 92 % combustible gases (CO + H2) whereas producer gas contains (30-42%).

Q. Which of the following gas possess highest calorific value? LPG, CNG, water gas, producer gas

Ans. LPG

Q. Write a short note on CNG. (3 marks)

Ans.

- Compressed Natural Gas (CNG) is a fossil fuel or primary fuel.
- It is formed as a result of anaerobic bacterial decomposition of buried plant and animal matters in presence of high T and P.
- Its calorific value varies from 12,000-14,000 Kcal/m^3.
- The average composition is: CH_4 = 70-90 %, C_2H_6 = 5-10%, H_2 = 3%, CO + CO_2 = rest.
- It mainly contains methane CH_4 gas.
- It is used as raw material for the manufacture of carbon black- filler for rubber.
- It is used as raw material for the manufacture of H_2 gas.
- It is used for domestic as well as industrial heating.

This study material is availabe on SIT ASSAN BETA

Fuel cell

- A fuel cell can be defined as an electrochemical cell that generates electrical energy from fuel via an electrochemical reaction.
- These cells require a continuous input of fuel and an oxidizing agent (generally oxygen) in order to continue the reactions that generate the electricity.
- Fuel cells can produce electricity continuously for as long as fuel and oxygen are supplied.
- A fuel cell is similar to electrochemical cells, which consist of a cathode, an anode, and an electrolyte that allows ions.
- The first fuel cells were invented by Sir William Grove in 1838. The first commercial use of fuel cells came more than a century later following the invention of the hydrogen–oxygen fuel cell by Francis Thomas Bacon in 1932. The alkaline fuel cell, also known as the Bacon fuel cell after its inventor, has been used in NASA space programs since the mid-1960s to generate power for satellites and space capsules.

Examples: H_2-O_2 fuel cell, propane-O_2 fuel cell, methanol-O_2 fuel cell, etc.

10.3 Hydrogen-Oxygen (H_2-O_2) fuel cell

- *Alkaline fuel cell or Hydrogen-oxygen fuel cell* was designed and first demonstrated publicly by *Francis Thomas Bacon* in 1959. It was used as a primary source of electrical energy in the Apollo space program.
- The cell consists of two inert porous carbon electrodes impregnated with a suitable catalyst such as Pt, Ag, etc. Here, catalyst is used to increase the rate of reaction.
- The space between the two electrodes is filled with a concentrated solution of KOH or NaOH which serves as an electrolyte.
- H_2 gas and O_2 gas are bubbled into the electrolyte through the porous carbon electrodes. Thus the overall reaction involves the combination of hydrogen gas and oxygen gas to form water.
- The cell runs continuously until the reactant's supply is exhausted. They do not store chemical energy.

This study material is availabe on SIT ASSAN BETA

- This type of cell operates efficiently in the temperature range 343–413 K (70-140 ^{0}C) and provides a potential of about 1.0 V.
- Efficiency is about 70%.

The following chemical reactions are occurring during its working process:

Anode: $2H_{2(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e$ -------- (1)

Cathode: $O_{2(g)} + 4e + 2H_2O_{(l)} \rightarrow 4OH^-_{(aq)}$ --------- (2)

Net cell reaction: (Eq. 1. + Eq. 2) $2H_{2(g)} + O_{2(g)} \rightarrow 2\ H_2O_{(l)} + 1.23$ V

- One such cell can generate power of about 1 V, far from enough to power a vehicle.
- In actual practice, a large number of such cells are stacked together in series to make a battery**. Cell output ranges from 300 W to 5000 W.**

Fig. H_2-O_2 fuel cell

Advantages:

- Energy conversion is high (75-80%).
- Produces water of potable quality.
- Noise and thermal pollution are low.
- Used in space applications and remote areas.
- Saves fossil fuels.

This study material is availabe on SIT ASSAN BETA

Limitations:

- High cost
- Pure hydrogen is also costly.
- Finding a suitable catalyst for electrode is a tough task.
- H_2 and O_2 cylinder to be carried along with the battery.

Applications: Some of the applications are listed below:

- Fuel cell electric vehicles, or FCEVs, use clean fuels and are therefore more eco-friendly than internal combustion engine-based vehicles.
- They have been used to power many space expeditions including the Apollo space program.
- Generally, the by-product produced from these cells is pure water.
- The portability of some fuel cells is extremely useful in some military applications.
- These electrochemical cells can also be used to power several electronic devices.
- Used in military vehicles, aircrafts, etc.
- Fuel cells are also used as primary or backup sources of electricity in many remote areas.

Q. What is a fuel cell? Give an example.

Ans. A fuel cell can be defined as an electrochemical cell that generates electrical energy from fuel via an electrochemical reaction. Example: H_2-O_2 fuel cell

Q. Mention some limitations of a fuel cell.

Q. Mention some advantages of a fuel cell.

Q. Write the chemical reactions involved during the working of a H_2-O_2 fuel cell.

Q. Discuss the construction and working of a H_2-O_2 fuel cell. (7 marks)

This study material is availabe on SIT ASSAN BETA

Module - 6
NANO CHEMISTRY

- Nanochemistry deals with the study of synthesis, characterization and applications of nanomaterials.

Q.1 What is nanomaterials? Give some examples.

Ans. Nanomaterials are those substances whole length or diameter or thickness lies between 1 - 100 nm.

Here, $1\ nm = 10^{-9}\ m$.

Examples:- Fullerene (diameter is ~ 1 nm)
Gold nanoparticles ~ 50 nm

- In general, nanomaterials exhibits improved physical, chemical, optical,

This study material is available on SIT ASSAN BETA
Scanned with Cam

medicinal, thermal catalytic properties than bulk materials.

for example,

(1) A drop of water (d ~ 5 nm) boils at 95.9 °C compared to a large quantity of water.

(2) Antibacterial properties increases in the nano-range

(3) Adhesive property increases in the nano-range

(4) Catalytic activity increases by decreasing size

(5) Thermal property improves on decreasing size

This study material is available on SIT ASSAN BETA
Scanned with Cam

Q.2 Give reason that nanomaterials shows better properties than bulk materials.

Ans:- It is due to the large surface area to volume ratio.

For a spherical particle

$$\frac{\text{Surface Area}}{\text{Volume}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$

spherical particle

r = radius of particle

$\Rightarrow$ the ratio $\uparrow$ as r $\downarrow$ i.e size decreases.

Synthesis of Nanomaterials

In general, nanomaterials (NMs) are synthesised by two approaches:

This study material is available on SIT ASSAN BETA
Scanned with Cam

1. Top-down approach
and
2. Bottom-up approach

Q.3 What is Top-down method? Give an example.

Ans) It is a solid state process in which large particles (in the range of mm or μm) are converted into nanomaterials by mechanical processes like crushing, grinding, Ball milling, etc.

(Fig.)

Example:- High energy ball milling

Q.4 Mention some limitations of Top-down approach.

This study material is available on SIT ASSAN BETA
Scanned with Cam

Ans:- (i) Not Suitable for large scale production

(ii) time consuming process

(iii) Synthesized NMs contains defects

(iv) NMs obtained are not of uniform size

Q.5 What is Bottom-up approach? mention some of its advantages.

Ans:- It is a process by which NMs are obtained by atom-by-atom or molecule-by-molecule or cluster-by-cluster combination.

Examples:- Sol-gel process chemical reduction, combustion, chemical vapour deposition, microwave

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

Synthesis, etc.

Advantages :-

(i) Relatively a fast process
(ii) Develops particles of uniform size & shape
(iii) Develops particles of excellent quality & of good quantity
(iv) Environmental friendly process
(v) Usually NPs are free from any imperfections

Green Synthesis of NPs

Q.6 What is green synthesis? Give an example.

Ans: Green synthesis is a

This study material is available on SIT ASSAN BETA
Scanned with Cam

bottom-up approach where non-toxic safe reagents which are eco-friendly are used for the synthesis of NMs.

Example:- Eco-friendly reagents are plant extracts i.e extracts of leaves, fruits, barks, flowers, etc.

Q.7 Mention some advantages of green synthesis.

Ans) (i) Minimises generation of waste

(ii) uses non-toxic reagents

(iii) fast process

(iv) produces NMs of uniform size, shapes & distributions

(v) low cost process

(vi) Plant extract contains both reducing agent & capping agent.

Teacher's Signature .....
This study material is availabe on SIT ASSAN BETA
Scanned with Cam

Synthesis of nanoparticles (NPs)

Q.8 Mention the raw materials needed to develop NPs.

Ans Three important raw materials needed are:

(i) Precursor salt:- It is a salt from which NPs can be obtained.
For example,

Precursor salts
- $AgNO_3$ → gives Ag-NPs
- $AuCl_3$ → " Au-NPs
- $Zn(NO_3)_2$ → " ZnO-NPs
- $CuSO_4$ → " Cu_2O-NPs

(ii) Reducing Agent:- It reduces the metallic cations of precursor salt to Atomic

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

form.

for example,

$$Ag^{+} + e \xrightarrow{Red^{n}} \underset{(Ag\text{-atom})}{\overset{\text{ox-state}}{Ag^{(0)}}}$$

many Ag-atoms combine to form Ag-NPs

examples:- Citric Acid, Hydrazine (N_2H_4), Plant extract (fr. of Phenols, Alkaloids, etc.)

(iii) Stabilizing / Capping agent:-

It stops agglomeration and growth of NPs.

examples:- Poly vinyl Alcohol, Surfactants, Plant extracts, etc.

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

Q.9 What is a Capping agent? Give an example.

Ans:- A Capping agent is a substance which when added to the precursor salt solution checks agglomeration of NPs.

example:- ~~Citric Acid~~ Poly vinyl Alcohol

Q.10 Name a precursor salt used to synthesize Silver nanoparticles.

Ans:- $AgNO_3$ (Silver Nitrate)

Q.11 Give an example of a reducing agent used in synthesis of NMs.

Ans:- Citric Acid

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

÷ Long Questions ÷

Q.1) Discuss the Synthesis characterisations and applications of Gold nanoparticles (NPs).

Answer

① Synthesis of Gold (Au) NPs

(i) Preparation of Plant extract:

Take 10 g of Papaya leaves and cut into small pieces. The cut pieces are taken in a 200 ml beaker containing 100 ml of distilled water. Place the beaker on a hot magnetic stirrer and boil it for 30 minutes. Then cool it and filter it to get the aqueous extract solution.

(ii) Preparation of Precursor salt solution:

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

Take 10 mg of gold salt $HAuCl_4$ and dissolve it in 10 ml of water to get the aqueous solution.

(iii) Preparation of Au-NPs :-

Take 10 ml of aqueous plant extract solution in a 50 ml beaker and place it on a magnetic stirrer maintained at 50 °C. Add 1 ml of gold solution into dropwise using a micro-pipette. The solution turned pink indicating development of Au-NPs.

$$HAuCl_4 (Au^{+3}) + 3e^- \longrightarrow Au$$

(2) Characterisation of NPs :

The developed Au-NPs

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

were characterised using UV-Visible spectrophotometer and x-ray diffractometer.

(i) UV-Visible Analysis :-

A broad absorption band at 550 nm shows formation of Au-NPs. This band is known as surface plasmon resonance band (SPR-band).

SPR-band results from the resonant oscillations of free electrons of metal atoms.

This study material is available on SIT ASSAN BETA
Scanned with Cam

(ii) X-ray diffraction (XRD) Study

XRD study helps us in knowing the crystalline nature, crystal type and crystallite size of Au-NPs.

In the XRD-pattern, a peak at $2\theta = 38.16^0$ corresponds to (111) plane shows formation of FCC Au-NPs.

Crystallite size can be calculated using the Debye-Scherrer equation:

$$\text{Crystallite size } (d) = \frac{0.94\lambda}{\beta \cos\theta}$$

where, $\lambda = 1.54\ A^0$

θ = Diffraction angle in radians

β = full width at half maximum (FWHM)

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

Applications of Au-NPs:

1. In drug delivery system
2. As a catalyst
3. As bio-sensor
4. Antibacterial & anti-fungal agent
5. In photodynamic Therapy
6. In cosmetics
7. In water treatment, etc.

This study material is available on SIT ASSAN BETA
Scanned with Cam

Q.2 Discuss the synthesis, characterisations & applications of Silver (Ag) NPs.

Ans. Silver NPs can be synthesised using a bio-reduction process.

(A) Synthesis:

(i) Preparation of plant extract

Take 10 g of neem leaves in a 200 ml beaker. Add 100 mL of distilled water to it and placed on a hot magnetic stirrer maintained at 100°C for 30 min. Cool the beaker and filter it to get clear aqueous plant extract.

(ii) Preparation of $AgNO_3$ soln:-

This study material is available on SIT ASSAN BETA
Scanned with Cam

Take 10 mg of $AgNO_3$ salt and dissolve it in 5 ml of distilled water.

(iii) Development of Ag NPs :-

Take 10 ml of extract soln in a 50 mL beaker. placed it on a hot magnetic stirrer maintained at 40°C. Under hot stirring condition add 1 ml of $AgNO_3$ soln to the beaker. The colour suddenly changed to yellowish brown indicating formation of Ag-NPs.

$$Ag^+ (AgNO_3) + e^- \xrightarrow{Red^n} Ag$$

(B) Characterizations :- The sample was characterised using UV-Vis spectrophotometer and X-ray diffractometer.

This study material is available on SIT ASSAN BETA
Scanned with Cam

(i) UV-Visible Study:

In the absorption spectrum a broad band near 420 nm known as SPR-band shows formation of Ag-NPs.

(ii) XRD Study:-

XRD study helps us in knowing:

(a) Lattice type

(b) Crystallite size, and

(c) Crystalline nature of Ag-NPs

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

In the XRD-pattern an intense peak at 38° corresponds to (111) plane of fcc-type Ag-NPs. The crystallite size can be find using Debye-Scherrer eqn -

$$d = \frac{0.94\lambda}{\beta \cos\theta}$$

(c) Applications :- Some applications are :

1. In cosmetics
2. As antibacterial agent
3. In water treatment
4. In food packaging
5. As bio-sensors
6. As catalyst
7. In coatings
8. In textile industries

This study material is available on SIT ASSAN BETA
Scanned with Cam

Q.3 Discuss the synthesis characterisations and applications of Cuprous oxide (Cu_2O) NPs.

Ans:- (A) Synthesis of NPs:-

To synthesize Cu_2O NPs, first prepare the plant extract, then prepare the salt soln and mix the two solution under hot condition.

i) Preparation of Plant extract:- Take 20g of Arka leaves. Cut into pieces and take in a 500 ml beaker. Add 200 ml of water and boil it for 30 min. Cool the beaker and filter it.

(ii) Preparation of Precursor salt solution:- prepare 1M solution of Copper Sulphate by dissolving ~~in~~ suitable

This study material is available on SIT ASSAN BETA
Scanned with Cam

amount of $CuSO_4.5H_2O$ blue crystals in required volume of water.

(iii) Development of Cu_2O NPs :-

Take 10 ml of plant extract in a 50 ml beaker and then placed on a magnetic stirrer maintained at 70°C. Then add 2 ml of $CuSO_4$ soln to it in a drop wise manner. Add few drops of hydrazine soln to it. till the colour changed to reddish brown suspension from blue. The reddish brown particles are Cu_2O NPs.

(B) Characterisations of NPs :-

The Cu_2O NPs were characterised by UV-VIS Spectrophotometer and X-ray diffractometer.

This study material is available on SIT ASSAN BETA
Scanned with Cam

(i) UV-Visible Study:-

On the absorption spectrum a broad band (SPR band) found near 470 nm suggests formation of Cu_2O - NPs.

(ii) XRD Study:-

Characteristics XRD peaks found at 36.8° and 42.3° corresponds to (111) and (200) crystal plane suggests formation of Cu_2O-NPs.

This study material is available on SIT ASSAN BETA
Scanned with Cam

Formation Mechanism :-

$CuSO_4 - 5H_2O \xrightarrow{Hyd.} Cu(OH)_2$

$Cu(OH)_2 \xrightarrow{Heat} Cu_2O$ - NPs

(C) Applications :-

1. As Photo-Catalyst
2. In Water Treatment
3. As Anti-bacterial Agent
4. In Solar cells
5. In magnetic Storage devices

This study material is available on SIT ASSAN BETA
Scanned with Cam

Q.4 Discuss on Synthesis, characterisations and applications of Zinc Oxide (ZnO) nanoparticles.

Ans:- (A) Synthesis:

(i) Preparation of Plant extract:- 20 gm of Hibiscus leaves was boiled in a beaker containing 200 ml of water for 30 minutes. Then cooled the beaker and filter it to get the extract.

(ii) Preparation of Salt Solution:-

Take 10 mg of $Zn(NO_3)_2$ salt and dissolve it in 20 ml of water to prepare salt soln.

(iii) Development of ZnO-NPs:-

Take 20 ml of extract

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

in a 100 ml beaker and placed on a hot magnetic stirrer maintained at 90°C. Then add 2 ml of $Zn(NO_3)_2$ soln to the hot soln. Now add 1 ml of NaOH soln to it. White precipitates of ZnO was collected at the bottom of the beaker. Filter it and collect the powder.

(B) Characterisations:

(i) UV-visible study:-

A broad SPR-band at 370 nm shows the formation of ZnO-NPs.

This study material is available on SIT ASSAN BETA
Scanned with Cam

(ii) XRD - Study :- XRD - Pattern shows 2θ - values at 31.77°, 34.4° and 36.2° corresponds to (100), (002) and (101) planes of ZnO-nps.

Formation mechanism :-

$$Zn(NO_3)_2 \xrightarrow{Hyd.} Zn(OH)_2$$

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO \text{ (NPs)}$$

Applications :-

1. In sensing applications
2. In cosmetics
3. In coatings
4. As UV - filtering Agent
5. As anti-bacterial agent

Teacher's Signature .....

This study material is availabe on SIT ASSAN BETA
Scanned with Cam

* Basic principle of UV-visible spectroscopy:

When the molecule absorbs UV visible light, its electrons get promoted from the ground state to the higher energy state only if energy of incident light is equal to the energy difference between ground state (E_1) and higher energy state (E_2).

i.e Energy of light (E_{photon})

$$= \frac{hc}{\lambda} = E_2 - E_1 = \Delta E$$

$\uparrow\downarrow \rightarrow$ Paired

$S = 2S+1$

$= 0+1 = 1$

(Singlet)

When electrons are paired, it is called singlet state

When parallel it is called triplet state.

This study material is availabe on SIT ASSAN BETA

* Types of Selection Rules

Selection rules are the restrictions imposed on the various types of electronic transitions in a molecule.

(1) Spin rule:- It states that singlet to singlet transition is allowed and singlet to triplet transitions are forbidden or not allowed.

i.e $\boxed{\Delta S = 0}$ (Changes in spin multiplicity is forbidden)

change in spin quantum number is zero.

(2) Symmetry Rule: Laporte Rule

The electronic transitions between orbitals of ~~different~~ same symmetry do not occur i.e not allowed or forbidden.

orbital Rule

$\boxed{\Delta l = \pm 1}$

$n \rightarrow \pi^*$, $\sigma \rightarrow \pi^*$ ~~forbidden~~ (not allowed tr.)

$\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ allowed

This study material is availabe on SIT ASSAN BETA

* Absorption Spectrum:

It is a graph of wavelength (λ) vs Absorbance (A).

A vs λ

An absorption spectrum may contains one band or more than one band.

Absorption band:- It results from coalescence of a large number of closely spaced electronic vibrational & rotational transitions.

Each band is characterised by two parameters.

(i) λ_{max} (Wavelength maximum)

(ii) ϵ_{max} (Molar extinction maximum)

$$\epsilon_{max} = \frac{A_{max}}{c \cdot l}$$

$$A_{max} = \epsilon_{max} \cdot c \cdot l$$

This study material is availabe on SIT ASSAN BETA

(Imp) In general, absorption bands are broad in nature.
It is because each electronic transition is accompanied by a large number of vibrational and rotational transitions. These transitions are so closely spaced that their closeness results in band.

Imp (*) Types of Electronic Transitions

According to the molecular orbital theory, when a molecule is excited by the absorption of UV or visible light, its valence shell electrons are promoted from bonding to an antibonding orbital.

The antibonding orbital of σ & π is σ* and π*, respectively.

n is known as non-bonding orbital.

This study material is availabe on SIT ASSAN BETA

According to the Selection rule the four types of electronic transitions occur in a molecule are:

(A) $\sigma \rightarrow \sigma^*$

(B) $n \rightarrow \sigma^*$

(C) $\pi \rightarrow \pi^*$

(D) $n \rightarrow \pi^*$

Fig:- Electronic Transitions

$n \rightarrow \pi^*$, & $\pi \rightarrow \pi^*$ ⇒

This study material is availabe on SIT ASSAN BETA

The energy required for various transitions obey the following order:

$$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$$

Let us now discuss on the various transitions involved in UV-visible spectroscopy.

(A) $\sigma \rightarrow \sigma^*$ transition:-

It is a high energy process. Since σ-bonds are very strong. So, such transitions require light of very short wavelengths than 200 nm. ($\lambda \sim 125$ nm)

This transition found in molecules having σ-bond.

Examples:- CH_4,

C_3H_8, C_5H_{12}, Cyclohexane, etc.
(All saturated hydrocarbons)

This study material is availabe on SIT ASSAN BETA

(B) $n \rightarrow \sigma^*$ transition:- This type of transition takes place in saturated compounds containing non-bonding (n) electrons. Such transitions also needed light of short λ i.e $\lambda < 250$ nm. (150 - 250 nm)
Compounds undergoing this type of transition are

→ halides (R–X), $CH_3-\ddot{\underset{\cdot\cdot}{Cl}}$, $CH_3\ddot{\underset{\cdot\cdot}{F}}$

(x → non-bonding electron)

→ Alcohols: $CH_3-\ddot{\underset{\cdot\cdot}{O}}H$, $C_2H_5\ddot{\underset{\cdot\cdot}{O}}H$

→ Ethers: $CH_3-\ddot{\underset{\cdot\cdot}{O}}-CH_3$

→ Aldehydes: $CH_3-\overset{\cdot\cdot O \cdot\cdot}{\overset{\|}{C}}-H$

→ Ketones: $CH_3-\overset{\cdot\cdot O \cdot\cdot}{\overset{\|}{C}}-CH_3$

→ Amines: $CH_3-\ddot{N}H_2$

* $n \rightarrow \sigma^*$ transition require relatively less energy than $\sigma \rightarrow \sigma^*$.

This study material is availabe on SIT ASSAN BETA

(C) $\pi \rightarrow \pi^*$ transition: This type of transition occurs in compound with double and triple bonds.

Examples:- , $CH_2=CH_2$, $CH\equiv CH$, $R-\overset{O}{\overset{\|}{C}}-R$, $R-\overset{O}{\overset{\|}{C}}H$, $R-C\equiv N$, $C_6H_5-N=N-C_6H_5$, etc.

Such transition requires absorption of light of $\lambda > 200nm$. (200-300 nm)

(D) $n \rightarrow \pi^*$ transition:- This type of transition found in molecule having both double/triple bond and non-bonding electrons. Absorption band of these transition lies in the region 200-300 nm.

Examples:- $CH_3-\overset{O}{\overset{\|}{C}}-H$ $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

This study material is availabe on SIT ASSAN BETA

$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$ (Amide), $R-\overset{O}{\overset{\|}{C}}-OH$

This transition requires comparatively less energy than that required for $\pi \rightarrow \pi^*$ transition

~ x ~

(imp) Example:- Mention the various type of possible transitions found in the following molecules:

O_2, Cl_2, Benzene, Acetone, Aniline, H_2, N_2 etc.

Ans:-

(i) O_2 : $\ddot{O} \underset{\pi}{\overset{\sigma}{=}} \ddot{O}$ → non-bonding electron

All Transitions occur:

$\sigma \rightarrow \sigma^*$, $n \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$

This study material is availabe on SIT ASSAN BETA

(ii) Cl_2 : $\ddot{\underset{\cdot\cdot}{Cl}} \overset{\sigma}{-} \ddot{\underset{\cdot\cdot}{Cl}}$

$\sigma - \sigma^*$, $n \to \sigma^*$

(iii) Benzene

$\sigma \to \sigma^*$
$\pi \to \pi^*$

(iv) Acetone

$CH_3 \overset{\pi}{-} \overset{\sigma}{\overset{\|}{C}} - CH_3$ ($\ddot{O}$)

$\sigma \to \sigma^*$, $n \to \sigma^*$, $\pi \to \pi^*$, $n \to \pi^*$

(v) Aniline

$\sigma \to \sigma^*$, $\pi \to \pi^*$, $n \to \sigma^*$
✓ (no $n \to \pi^*$)

(vi) H_2, $H \overset{\sigma}{-} H$, only $\sigma \to \sigma^*$

(vii) N_2, $\ddot{N} \overset{\sigma}{\underset{\pi}{\equiv}} \ddot{N}$, $\sigma \to \sigma^*$
$\pi \to \pi^*$

(All transitions) $n \to \sigma^*$, $n \to \pi^*$

This study material is availabe on SIT ASSAN BETA

Module-4

Instrumental Techniques

Ultraviolet and Visible Spectroscopy.

Introduction

Spectroscopy deals with the study of interaction between the matter and electromagnetic radiation / light.

Electromagnetic radiation may be UV, visible, Infrared, microwave, radio wave, etc.

The matter may be atom or molecule.

Molecular Spectroscopy:-

It deals with the study of interaction between molecule and light.

Types: (1) U.V - visible or electronic Spectroscopy

This study material is availabe on SIT ASSAN BETA

2) Infrared or Vibrational spectroscopy

3) Microwave or rotational spectroscopy

Electromagnetic Spectrum:

The arrangement of all types of electromagnetic radiation in order of their increasing wavelengths is known as electromagnetic spectrum.

This study material is availabe on SIT ASSAN BETA

Wave Parameters:

Units:-

Wave motion

(i) Wavelength (λ): Distance betwn the two adjacent crests or troughs.

(1 pm = 10^{-12} m)

unit: nm, μm, Å, pm

(ii) Wave number ($\bar{\nu}$):

Reciprocal of λ

$$\bar{\nu} = \frac{1}{\lambda}$$

unit: cm^{-1}

(iii) Frequency (ν):

Number of waves which can pass through a point in one second.

$$\nu \propto \frac{1}{\lambda} \quad \boxed{\nu = \frac{c}{\lambda}}$$

unit: s^{-1} or Hz

This study material is availabe on SIT ASSAN BETA

(iv) Energy :-

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

Unit :- Joule
calorie

$c = 3 \times 10^{8}$ m/s
$= 3 \times 10^{10}$ cm/s

$h = 6.626 \times 10^{-34}$ J.s
Plank's const.

$1 \text{ Å} = 10^{-10}$ m, 1 nm $= 10^{-9}$ m

1 pm $= 10^{-12}$ m

Example - 1 Calculate the energy associated with a light of wavelength 4000 Å.

Ans :-

$$E = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-34} \text{ J.s} \times 3 \times 10^{8} \text{ m/s}}{4000 \times 10^{-10} \text{ m}}$$

$$= 23.878 \times 10^{-19} \text{ J}$$

This study material is availabe on SIT ASSAN BETA

Ultraviolet - Visible Spectroscopy

It deals with study of interaction of molecule with UV-visible light (200 - 800 nm). Absorption of UV-visible light by a molecule involves the promotion of electrons from the ground state to the higher energy state.

This spectroscopy is otherwise known as electronic spectroscopy.

Range of UV-vis spectrum:

This study material is availabe on SIT ASSAN BETA

Absorption Law:

(Beer-Lambert's law)

This law states that: When a beam of monochromatic light is passed through a dilute solution of an absorbing substance, the rate of decrease of light intensity with thickness of absorbing medium is proportional to the intensity of incident light as well as the concentration of the solution.

Mathematically, this law is stated as, $-\frac{dI}{dl} \propto I \cdot C$

$C \rightarrow$ Conc^n of Solution

This study material is availabe on SIT ASSAN BETA

or, $$-\frac{dI}{dl} = KIC \quad (1)$$

K = A Constant

By rearranging eqn (1) and then integration,

We get,

$$\boxed{\log \frac{I_0}{I} = \epsilon \cdot C \cdot l = A}$$

Where,

I_0 = Intensity of incident light

I = Intensity of transmitted light

C = Conc^n of solⁿ in mol/lt or Molarity

l = thickness or pathlength of solution in cm

ϵ = Molar extinction co-efficient ($M^{-1} cm^{-1}$)

A = Absorbance (no unit)

(*) Factors affecting A

(1) C and l

(2) Nature of molecule

(3)

Unit of Absorbance:- Unitless

Unit of ϵ: $M^{-1} cm^{-1}$ or $(mole/lit)^{-1} cm^{-1}$

This study material is availabe on SIT ASSAN BETA

Absorbance :- (A)

It is the logarithmic ratio of I_0 & I. It is a measure of the absorption of light by a sample

$$A = \log\left(\frac{I_0}{I}\right)$$

It gives information about fraction of light absorbed by the absorbing solution.

Transmittance : (T)

$$T = \frac{I}{I_0}$$

unit : no unit

Relationship betw A & T

$$A = \log\left(\frac{I_0}{I}\right) = -\log\left(\frac{I}{I_0}\right)$$

$$= -\log T$$

$$\boxed{A = -\log T}$$

This study material is availabe on SIT ASSAN BETA

or, $\log T = -A$

or $\boxed{T = 10^{-A}}$

Molar Extinction Coefficient (ϵ):

It gives information about strength of electronic transition.

Graph:- $\boxed{A = \epsilon \cdot c \cdot l}$

A vs C is a st. line

Limitations of Beer-Lambert law

(1) This law is not obeyed:
When absorbing solution is fluorescent

This study material is availabe on SIT ASSAN BETA

(2) When absorbing molecules are in equilibrium

(3) When interaction occurs between solute & solvent

(4) When soln is turbid in nature

(5) When conc^n of soln is high

Example-2 2.5×10^{-4} M solution of a substance in a 1 cm length cell at $\lambda_{max} = 295$ nm has absorbance 1.17. Calculate ϵ_{max} for this soln.

Ans:- $A_{max} = \epsilon_{max} \cdot C \cdot l$

This study material is availabe on SIT ASSAN BETA

$$\Rightarrow \epsilon_{max} = \frac{A_{max}}{c \cdot l} = \frac{1.17}{2.5 \times 10^{-4}\, M \times 1\, cm}$$

$$= 0.468 \times 10^{4}\, M^{-1} cm^{-1}$$

Example – 3

An absorbance of 0.7 was reported when a light of $\lambda = 400\,nm$ passed through a solution of concentration 0.1×10^{-2} M. The thickness of the cell was 10 mm. Find A, T and % T.

(given, $\epsilon = 0.5 \times 10^{3}\, M^{-1} cm^{-1}$)

Soln :-

$$A = \epsilon \cdot c \cdot l$$

$$\boxed{10\,mm = 1\,cm}$$

$$= 0.5 \times 10^{3} \times 0.1 \times 10^{-2} \times 1$$

$$= 0.5$$

Now, $A = -\log T$

$$\Rightarrow T = 10^{-A} = 10^{-0.5}$$

$$= 0.3162$$

$A = \log \frac{I_0}{I}$

$= -\log\left(\frac{I}{I_0}\right)$

$\frac{I}{I_0} = T$

Now, $\% T = 0.3162 \times 100$

$$= 31.62$$

WEDNESDAY
This study material is availabe on SIT ASSAN BETA

Example-4 When a light is passed through a solution, the intensity of light has reduced to 50%. Calculate A & T.

Soln:- $A = \log \frac{I_0}{I}$

here, $I = I_0/2$ (50% reduction)

So, $A = \log \frac{I_0}{I_0/2} = \log 2$

$= 0.3020$

now, $T = 10^{-A} = 10^{-0.3020}$

$= 0.4989$

≈ 0.50

$\therefore \% T = 0.50 \times 100$

$= 50\%$

This study material is availabe on SIT ASSAN BETA

Q.1 prove that $A = 2 - \log(\%T)$

Ans: We know that,

$$\%T = 100 \times T$$

Taking log on both sides

$$\log(\%T) = \log(100 \times T)$$

$$= \log 100 + \log T$$

$$= 2 + \log T$$

$$= 2 - A$$

$$\Rightarrow \boxed{A = 2 - \log(\%T)} \text{ (Proved)}$$

(As $A = -\log T$

or $-A = \log T$)

Q.2 What is

This study material is availabe on SIT ASSAN BETA

(1) Radiation of wavelength 280 nm passed through 1.0 mm of a soln that contained an aqueous soln of Amino acid tryptophan at a conc^n of 0.5 mmol L^{-1}. The light intensity is reduced to 54% of its initial value. Calculate the absorbance and 'ε' of tryptophan at 280 nm. What would be the 'T' through a cell of thickness 2.0 mm?

Ans:

$$T = \frac{I}{I_0} = \frac{54}{100} = 0.54$$

i) $A = -\log T = -\log 0.54 = 0.27$

ii) $A = \epsilon . c . l$

$$\epsilon = \frac{A}{c . l} = \frac{0.27}{(0.5 \times 10^{-3} \text{ mol/L}) \times (1 \times 10^{-1} \text{ cm})}$$

$$= 5.3 \times 10^{3} \text{ mol}^{-1} \text{ L cm}^{-1}$$

iii) $T = \frac{I}{I_0} = 10^{-A} = 10^{-\epsilon . c . l}$

This study material is availabe on SIT ASSAN BETA

$= 10^{-0.54} = 0.29$

So, $\boxed{\% T = 29\%}$

So T drops from 54% to 29% by increasing x from 1 mm to 2 mm.

This study material is availabe on SIT ASSAN BETA

* Allowed and forbidden transitions:-

Allowed transitions:- Those transitions which obey selection rules and ϵ_{max} values is greater than 10^4 for them.

Examples:- $\sigma \rightarrow \sigma^*$, $\pi \rightarrow \pi^*$

* Forbidden transitions:-

Such transitions do not obey selection rules and ϵ_{max} values are less than 10^4. ✓ This transitions is of low intensity.

Examples:- $n \rightarrow \pi^*$, $n \rightarrow \sigma^*$

This study material is availabe on SIT ASSAN BETA

Concept of Chromophore & Auxochrome

Chromophore: (Light absorbing species)

Any isolated covalently bonded group (F.G) that shows a characteristic absorption in the UV or the visible region is known as Chromophore.

All those compounds which absorb light in the UV-Vis region are chromophore (200-800 nm)

Examples of Chromophoric group:

C=C (Alkene), —C≡C— (Alkyne), C=O (Carbonyl), C≡N, C=S

R—NO_2 (Nitro), —COOH (Acid),

—N=N— (Azo), —$CONH_2$ (Amide)

—C_6H_5 (Phenyl).

Example: In Toluene C_6H_5—CH_3, which group is a chromophore.

Ans: —C_6H_5 (Phenyl group)

= Functional groups containing multiple bonds called as chromophore

= Multiple bonds are responsible for absorption of light

This study material is availabe on SIT ASSAN BETA

- **Auxochrome** :- (FG with non-bonding electrons does not absorb in UV region)

Any group which does not itself act as a chromophore but whose presence causes a shift in the absorption band towards longer wavelength or red end of the spectrum is known as Auxochrome.

An auxochrome is called colour enhancing group.

Examples :- $-OH$, $-OR$, $-NH_2$, $-NHR$, $-NR_2$, $-SH$, etc.

All these groups contain non-bonding electrons.

As auxochrome contains non-bonding electrons, it helps in extending the conjugation of a chromophore by sharing its non-bonding electrons.

Auxochromic groups do not show absorption band above 200 nm.

In Aniline, , $-NH_2$ group

This study material is availabe on SIT ASSAN BETA

is an auxochrome.

Benzene without any auxochrome shows an absorption band at 255 nm whereas aniline absorbs at higher wavelength (i.e. at 280 nm).

(gnd) Example

Give reason that aniline absorbs at lower wavelength in acidic medium than in non-acidic medium.

Ans: In acidic medium, Aniline forms anilinium ion and electron pair is no longer present on it. So conjugation is removed.

λ_{max} = 280 nm (Aniline) λ_{max} = 254 nm (Anilinium ion)

This study material is availabe on SIT ASSAN BETA

Terminology for Absorption Shifts

Imp *

Absorption and Intensity Shifts :-

There are four types of shifts can occur for an absorption band. It can move right / left or the height can be increase or decrease. These shifts are known as

(i) Bathochromic shift or effect.

(ii) Hypochromic shift

(iii) Hyperchromic shift

(iv) Hypochromic shift

(i) Bathochromic Shift : (Red shift)

It is an effect by which the absorption maximum (λ_{max}) is shifted towards longer wavelength i.e red end.

WEDNESDAY
This study material is availabe on SIT ASSAN BETA

Hence, also known as red shift. It happens due to presence of an auxochrome or by the change of polarity of solvent.

(ii) Hypsochromic or blue shift:-

It is an effect by virtue of which the 'λ_{max}' is shifted towards shorter wavelength i.e blue end.

It may be caused by the removal of conjugation or auxochrome and also by change the solvent.

(iii) Hyperchromic shift:-

It is an effect due to which the height of absorption band increases i.e ϵ_{max} increases. The introduction of an auxochrome usually increases the intensity of band

This study material is availabe on SIT ASSAN BETA

(iv) Hypochromic Shift:- It is an effect due to which ϵ_{max}-value decreases. Removal of conjugation or auxochrome causes this effect.

✓ λ_{max} shifts Right → Batho chromic

✓ λ_{max} shifts left (Hypso chromic)

N.B:-

$\lambda_{max} \uparrow \rightarrow$ Bathochromic shift

$\lambda_{max} \downarrow \rightarrow$ Hypsochromic shift

A ↑ or $\epsilon_{max} \uparrow \rightarrow$ Hyperchromic shift

A ↓ or $\epsilon_{max} \downarrow$ – Hypochromic

This study material is availabe on SIT ASSAN BETA

Support staff
ICT Maintenan

(*) Factors affecting position of Absorption Band

The various factors are:

1. presence of auxochrome
2. Conjugation
3. Steric effect

(1) Presence of an auxochrome:

The effect of the auxochrome is due to its ability to extend conjugation of a chromophore by the sharing of non-bonding electrons. It causes red or Bathochromic shift.

✓ no auxochrome in Benzene

$\lambda_{max} = 255$ nm

$\lambda_{max} = 280$ nm

This study material is availabe on SIT ASSAN BETA

(2) Conjugation: The λ_{max} value is shifted to longer λ (red shift), if two or more chromophoric groups are present in conjugation in a molecule.

For example, ethylene (one double bond) absorbs at 170nm which Butadiene (two double bond in conjugation ($C{=}C-C{=}C$, d.b, d.b) absorbs at higher λ i.e at 217nm.

Due to conjugation the energy difference between π (BMO) and π^* (ABMO) orbital decreases i.e λ increases.

$$\left(E \propto \frac{1}{\lambda},\ E\downarrow \Rightarrow \lambda\uparrow\right)$$

✓ Hexatriene with 3-double bond in conjugation absorbs at 254 nm.

This study material is availabe on SIT ASSAN BETA

→ As no. of conjugated double bond increases, λ_{max} value increases.

imp **Example:**

Give reason that Tomatoes & Carrots are colour in nature.

Ans:- Lycope in tomatoes and β-carotene in carrots contains π - no of conjugated double bonds. So, they absorb in visible region (400 - 800 nm).

Chromophore (colour bonds)

(1) more at 400 nm

(2) other at 800 nm

N.B

Effect of conjugation -

(1) It decreases the energy gap betn HOMO & LUMO (π*)

(2) Hence, less energy (π) is req. for el. transition to occur at longer λ, enough energy, they interact

This study material is availabe on SIT ASSAN BETA

(3) Steric effect :-

As steric effect in a molecule distorts its geometry, it distorts the conjugation. So, it causes blue shift i.e. λ_{max} value decreases.

for example :-

✓ Cis-isomer absorbs at lower wavelength than trans isomer.

cis-1,2-dichloro ethylene	Trans-1,2-dichloroethylene
Here, steric effect occurs	Here no steric effect
⇒ Distortion occurs	⇒ no distortion.
⇒ Conjugation is disturbed	⇒ Conjugation is not disturbed

they intensify colours.

This study material is availabe on SIT ASSAN BETA

Example:- Give reason that cis-cinnamic acid,

absorbs at 268 nm whereas trans-form

absorbs at higher wavelength (272 nm).

Ans:- Reason is same to 1,2-dichloro ethylene

N-B In general, All cis-form absorbs at lower wavelength than trans-form.

This study material is availabe on SIT ASSAN BETA

Applications of UV-Vis Spectroscopy

Some important applications are:

1. Detection of functional groups like Carbonyl, Carboxylic acid, Amine, Amide, etc.
2. Estimation of extent of Conjugation.
3. Differentiate between Conjugated and non-Conjugated Systems
4. Differentiate between cis and trans isomers
5. Finding Concentration of a Coloured Solution
6. Finding the Structure of Vitamin-A and K.
7. Identification of an unknown Compound
8. Detection of impurity

This study material is availabe on SIT ASSAN BETA

: Questions :-

Short questions

(2 marks)

1. State Beer-Lambert's law.
2. Define Absorbance.
3. Define Molar extinction co-efficient.
4. What is the relationship between A and T.

   $(A = -\log T)$

5. Mention the units of A, T and ε.

   A & T → no units

   $\varepsilon = M^{-1} \cdot cm^{-1}$

6. Give reason that A increases as the conc^n of solution increases:

Ans:-

$$A = \varepsilon \cdot c \cdot l$$

$$A \propto c$$

This study material is availabe on SIT ASSAN BETA

As C increases, no of molecules per unit volume increases. So, light is absorbed by large no. of molecules. i.e $A \uparrow$

(7) Mention the type of electronic transitions occurs in C_6H_6 & C_2H_6.

$C_6H_6 \rightarrow \sigma \rightarrow \sigma^*, \pi \rightarrow \pi^*$

$C_2H_6 \rightarrow \sigma \rightarrow \sigma^*$

(8) Mention two important parameters of an absorption band.

(λ_{max} & ϵ_{max})

(9) Absorption band is broad in nature. Wave region.

(10) Why is carrot red in colour?

(11) Mention Spin rule.

$\Delta S = 0$

This study material is availabe on SIT ASSAN BETA

Long Questions (7 marks)

(1) Discuss the various types of electronic transitions occurs in a molecule.

(2) Define chromophore & auxochrome. Discuss the various types of shifts occurs to absorption band.

Medium Questions (3 marks)

(1) Mention various limitations of Beer-Lambert's law.

(2) Mention the various factors that can cause shifting of band.

(3) Write some applications of UV-Vis spectroscopy.

This study material is availabe on SIT ASSAN BETA

Infra-red Spectroscopy

Infra-red (IR) Spectroscopy deals with the study of interaction between molecules and IR light.

IR region:-

Whole IR region lies between 0.8 μm — 200 μm ($1\ \mu m = 10^{-6} m$)

✓ Interms of wave number ($\bar{\nu} = \frac{1}{\lambda}$), it lies between 12,500 – 50 cm^{-1}.

IR Spectroscopic region → 667 – 4000 cm^{-1}
(667 is smallest finger print region)

N.B

$$\text{Wave number } (cm^{-1}) = \frac{1}{\text{Wavelength in cm}}$$

If $\lambda = 2.5\ \mu m$;

$$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{2.5 \times 10^{-6} m}$$

$$= \frac{1}{2.5 \times 10^{-4} cm} = 4000\ cm^{-1}$$

$1\ \mu m = 10^{-6} m = 10^{-4} cm$

$= 10\,000$

This study material is availabe on SIT ASSAN BETA

(*) The ordinary IR region lies between 4000 – 667 cm^{-1} or 2.5 – 15 μm. This is the region useful for scientists.
(f.G region + finger Print Region)

- IR Spectrum :- It is a record of % Transmittance Vs Wavenumber for (Ethyl Alcohol)

(An IR spectrum)

The IR Spectrum is an important record which gives sufficient information about the structure of a compound, presence of functional group and detecting interaction between two molecules.

This study material is availabe on SIT ASSAN BETA

Unlike UV-Spectra, IR Spectrum consists of a large number of absorption bands.

When IR-light is absorbed by a molecule it causes the molecule to vibrate i.e molecular bond undergoes stretching and bending.

So, IR Spectroscopy is otherwise known as Vibrational Spectroscopy.

Principle of IR-Spectroscopy

The absorption of IR-light causes an excitation of molecule from a lower to higher vibrational level.

All the bonds in a molecule are not capable of absorbing IR-light but only those bonds which are accompanied by a change in

This study material is availabe on SIT ASSAN BETA

(*) Cond^n of IR-activity

(*) Dipole moment should change during vibration

(*) Molecule should have permanent dipole moment

dipole moment will absorb the IR-region.

So, dipole moment should change with change in bond distance. $\left(\frac{d\mu}{dx} \neq 0\right)$

μ = dipole moment, dx = change in bond

IR-Active & IR-Inactive molecules:

The vibrational transitions which are accompanied by a change in the dipolemoment of the molecule are called IR-active transitions and molecule is called IR-active molecule.

Example: Vibrational transitions of C=O, N-H, OH etc are IR-active. (Polar molecules)

IR-active molecules:- H_2O, CH_3OH, H-Cl, NH_3, CH_3COCH_3, CH_3NH_2, CH_3CHO, CH_3-O-CH_3, HF, $CHCl_3$, CO, NO, CN, etc

All (Polar molecules) H_2S, C_2H_5OH,

This study material is available on SIT ASSAN BETA

Heterodiatomic (H-Cl, H-F, etc.) molecules ⇒ Always IR active

Homodiatomic molecule ⇒ (ex. O_2, H_2, F_2, etc.) Always IR inactive

On the other hand, the vibrational transitions (modes) which are not accompanied by a change in dipole moment of molecules are not absorb in the IR-region. (IR-inactive mode)

Example: C=C bond in $CH_2=CH_2$, C≡C bond in CH≡CH, CCl_4, H_2, O_2, F_2 etc. (Homonuclear diatomic molecules)

Molecular Vibrations:-

When IR-light is passed through a sample, the vibrational energy of the molecules is increased. This causes two kinds of fundamental vibrations:

1. Stretching vibration
2. Bending vibration

This study material is availabe on SIT ASSAN BETA

(1) Stretching Vibration:

In this type of vibrations the distance between the two atoms increases or decreases but the atoms remain in the same bond axis. (no change in bond angle)

Not during vibration only bond length changes

$$O = C = O \xrightarrow{IR\ light} O = C = O$$

7A° 7A° → 7A° ← 10A° →

In CO_2 molecule

Stretching occurs

Types of Stretching Vibrations

There are two types of stretching vibrations:

(A) Symmetric Stretching:

In this type, the movement of the atoms w.r.t a particular atom in a molecule is in the same direction.

NOT bond angle changes

This study material is availabe on SIT ASSAN BETA

Symmetric mode is IR-inactive.

(B) Asymmetric Stretching:

In these vibrations, one atom approaches the central atom (C-atom) and other departs from it.

Asymmetric mode is IR-active.

(2) Bending Vibrations:

In this type of vibration, Bond angle can change but no change in bond distance.

Bond angle can be changes during vibration

Bending

This study material is availabe on SIT ASSAN BETA

Types of bending vibrations

Bending vibrations are of 4 types.

- (i) **Scissoring**:- Two atoms approach each other
  - * Bond angle changes. No change in the plane of vibrational mode
- (ii) **Rocking**:- movement of atoms takes place in the same direction.
  - No change in bond angle. No change in the plane of vib. mode
- (iii) **Wagging**:- Two atoms move up and down the plane w.r.t central atom.
  - ✓ No change in bond angle. Change in the plane of vibrational mode
- (iv) **Twisting**:- Here one of the atoms moves up the plane while other moves down the plane w.r.t the central atom.
  - ✓ Bond angle changes
  - ✓ Change in the plane of vibrational mode

This study material is availabe on SIT ASSAN BETA

As we know that more energy is required to stretch a spring than to bend it. Thus, stretching absorption of a bond appear at high freq. regions as compared to bending absorptions of the same bond.

i.e As $E \uparrow$, ν (freq) $\uparrow$.

$$\boxed{E = h\nu} = \frac{hc}{\lambda} = hc\bar{\nu}$$

ν = freq.

$\bar{\nu}$ = wave no

λ = wavelength

This study material is availabe on SIT ASSAN BETA

As we know that more energy is required to stretch a spring than to bend it. Thus, Stretching absorption of a bond appear at high frequencies as compared to bending absorptions of the same bond.

i.e As $E \uparrow$, ν (freq) $\uparrow$.

$$E = h\nu = \frac{hc}{\lambda} = hc\bar{\nu}$$

ν = freq.

$\bar{\nu}$ = wave no

λ = wavelength

This study material is availabe on SIT ASSAN BETA

Vibrational Frequency (ν)

The stretching vibrational frequency of a bond can be calculated using the relationship:

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}}$$

where, K = force constant (it is a measure of bond strength)
unit: gm/s^2 or dyne/cm
μ is reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

(unit = g or kg)

where m_1 = mass of one atom
m_2 = mass of another bonded atom
ν is vibrational freq
(unit = s^{-1} or Hz)

This study material is availabe on SIT ASSAN BETA

Vibrational wavenumber ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c}$$

$$= \frac{\frac{1}{2\pi}\sqrt{\frac{K}{\mu}}}{c}$$

$$\boxed{\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}}$$

unit : cm^{-1}

Factors affecting ν & $\bar{\nu}$:

As $K \uparrow$, $\nu \uparrow$, also $\bar{\nu} \uparrow$

As $\mu \uparrow$, $\nu \downarrow$, also $\bar{\nu} \downarrow$

This study material is availabe on SIT ASSAN BETA

Vibrational frequency (ν)

The stretching vibrational frequency of a bond can be calculated using the relationship:

$$\boxed{\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}}$$

where, K = force constant (it is a measure of bond strength)
unit: gm/s^2 or dyne/cm
μ is reduced mass

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

(unit = g or kg)

where m_1 = mass of one atom (kg or amu)
m_2 = mass of another bonded atom
ν is vibrational freq (unit = s^{-1} or Hz)

1 amu = 1.66×10^{-27} kg

This study material is availabe on SIT ASSAN BETA

Vibrational wavenumber ($\bar{\nu}$)

$$\bar{\nu} = \frac{\nu}{c}$$

(Wave Number)

$$= \frac{\frac{1}{2\pi}\sqrt{\frac{K}{\mu}}}{c}$$

$$\boxed{\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}}$$

unit : cm^{-1}

Factors affecting ν & $\bar{\nu}$:

As, $K \uparrow$, $\nu \uparrow$, also $\bar{\nu} \uparrow$

As $\mu \uparrow$, $\nu \downarrow$, also $\bar{\nu} \downarrow$

This study material is availabe on SIT ASSAN BETA

Durga Prasad Mohanty

Numericals:

(1) Find the reduced mass for C – H bond. given that, $m_C = 12$ amu (in CHy.), $m_H = 1$ amu.

Soln:-

reduced mass $(\mu) = \frac{m_1 m_2}{m_1 + m_2}$

Here, $m_1 = 12$ amu, $m_2 = 1$ amu

$= \frac{12 \times 1}{(12+1)} = 0.9231$ amu.

We know that,

$1 \text{ amu} = 1.664 \times 10^{-24} g$

So, $\mu = 0.9231 \times 1.664 \times 10^{-24} g$

$= 1.536 \times 10^{-24} g$

* Assignment – (1)

Similarly, find reduced mass of C – O bond. given that C = 12 amu & O = 16 amu.

Ans:- $\frac{m_1 m_2}{(m_1+m_2)} \times 1.66 \times 10^{-24} g = 11.41 \times 10^{-24} g$

This study material is availabe on SIT ASSAN BETA

2) Calculate the vibrational frequency and wave number of a C=C bond. Given that $K = 10 \times 10^5$ dyne/cm or (gm/s^2), $C = 12$ amu.

Soln:-

$$\text{Vib. freq}(\nu) = \frac{1}{2\pi}\sqrt{\frac{K}{M}}$$

$$M = \frac{m_1 m_2}{(m_1+m_2)} = \frac{12 \times 12}{(12+12)}$$

$$= 6 \text{ amu} = 6 \times 1.664 \times 10^{-24} g$$

$$= 9.984 \times 10^{-24} g$$

now, i) $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{M}} = \frac{1}{2 \times 3.14}\sqrt{\frac{10 \times 10^5}{9.984 \times 10^{-24}}}$

$$= 5.0395 \times 10^{13} s^{-1}$$

ii) $\bar{\nu} = \frac{\nu}{C} = \frac{5.0398 \times 10^{13} s^{-1}}{3 \times 10^{10} cm/s}$

$$= 1679.83 \text{ cm}^{-1}$$

This study material is availabe on SIT ASSAN BETA

Durga Prasad Mohanty

$1\ dyne = (gm\ cm\ s^{-2})$

Assignment - 2

do yourself Calculate the ν and $\bar{\nu}$ of stretching vibration of C–H bond. Given that, $K = 5 \times 10^5\ gm/s^2\ (dyne/cm)$ and $m_C = 12$ amu & $m_H = 1$ amu)

(3) The vibrational ~~frequency~~ wave number of C–O bond is $3000\ cm^{-1}$. Find the force constant. (Given that $m_C = 12$ & $m_O = 16$ amu).

Sol^n:- $$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \quad \text{—(1)}$$

Squaring eq^n (1), we get

$$(\bar{\nu})^2 = \frac{1}{4\pi^2 c^2} \cdot \frac{K}{\mu}$$

This study material is availabe on SIT ASSAN BETA

$$\Rightarrow \boxed{K = 4\pi^2 c^2 \mu \bar{\nu}^2}$$

$\bar{\nu}$ is given, we have to first find out μ (reduced mass)

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \left(\frac{12 \times 16}{12 + 16}\right) = \frac{192}{28}$$

$$= 6.8571 \text{ amu}$$

$$= 6.8571 \times 1.664 \times 10^{-24} g$$

$$= 11.41 \times 10^{-24} g$$

now, $K = 4\pi^2 c^2 \mu \bar{\nu}^2$

$$= 4 \times (3.14)^2 \times (3 \times 10^{10} \text{ cm/s})^2 \times 11.41 \times 10^{-24} g \times (3150 \text{ cm}^{-1})^2$$

$$= 3644936.366 \text{ gm/s}^2$$

or (dyne/cm)

Assignment :- 3 Find the K of O-H bond. $K = 5.2 \times 10^5$ dyne/cm, given, $\bar{\nu} = 3100 \text{ cm}^{-1}$, $m_O = 16$ amu $m_H = 1$ amu

This study material is availabe on SIT ASSAN BETA

(Imp)

N.B If vibrational freq. is given, K can be find out using eqn. $\boxed{K = 4\pi^2 \mu \nu^2}$

For example,

for C=C bond,

$\nu = 5.0395 \times 10^{13} s^{-1}$

$K = 4\pi^2 \mu \nu^2$

Here, $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{12 \times 12}{12 + 12}$

$= 6 \text{ amu} = 9.964 \times 10^{-24} g$

So, $K = 4\pi^2 \mu \nu^2$

$= 4 \times (3.14)^2 \times (9.964 \times 10^{-24} g) \times (5.0395 \times 10^{13} s^{-1})^2$

$= 10^6 \text{ gm}/s^2$ or dyne/cm

This study material is availabe on SIT ASSAN BETA

Vibrational Energy (E_{vib}):-

The vibrational energy of a chemical bond is quantized and can have the value:

$$\boxed{E_{vib} = \left(v + \frac{1}{2}\right) h\nu} \quad \text{--- (1)}$$

Where, v = vibrational quantum number
$= 0, 1, 2, 3, \ldots$

h = Planck's constant
$(6.626 \times 10^{-34}\ J.s)$

ν = Vib. freq. of the bond.

The energy difference between two vibrational energy levels is

$$\boxed{\Delta E_{vib} = E_2 - E_1 = h\nu} \quad \text{--- (2)}$$

In eqn-(1), if we put $v = 0$, (ground state level)

This study material is availabe on SIT ASSAN BETA

$$\boxed{E_{vib} = \frac{1}{2} h\nu}$$

This is called zero point energy (ZPE)

So, $$\boxed{ZPE = \frac{1}{2} h\nu} \quad \text{--- (3)}$$

Energy difference betn two successive energy levels

(17) $$\Delta E_{vib\,(0\to1)} = E_{vib\,(v=1)} - E_{vib\,(v=0)}$$

$$= \left(1 + \frac{1}{2}\right) h\nu - \frac{1}{2} h\nu$$

$$= \frac{3}{2} h\nu - \frac{1}{2} h\nu = h\nu$$

This study material is availabe on SIT ASSAN BETA

(2) $\Delta E_{vib_{1\to 2}} = E_{vib(v=2)} - E_{vib(v=1)}$

$= \frac{5}{2}h\nu - \frac{3}{2}h\nu$

$= h\nu$

⇒ Two adjacent levels separated by a value $h\nu$.

"All levels are equidistant" or equally spaced.

(3) $\Delta E_{vib_{0\to 2}} = \frac{5}{2}h\nu - \frac{1}{2}h\nu = \frac{4}{2}h\nu = 2h\nu$ (1st overtone)

(4) Selection Rule :-

$$\boxed{\Delta v = \pm 1}$$

+ → for absorption

− → for emission

v = Vibrational quantum number

⇒ $v = 0$ to $v = 1$ transition is allowed whereas $v = 0$ to $v = 2$ is not allowed (here, $\Delta v = \pm 2$)

This study material is available on SIT ASSAN BETA

Durga Prasad Mohanty
Laxmidhar Behera

Numericals

Q.1 Find the vibrational energy for the 1st excited state if vib. freq. is $1000\ s^{-1}$.

Ans:

$$E_{vib} = \left(v + \frac{1}{2}\right) h\nu$$

$$= \left(1 + \frac{1}{2}\right) h\nu$$

$$= \frac{3}{2} \times 6.626 \times 10^{-34}\ J.s \times 1000\ s^{-1}$$

$$= 1.5 \times 6.626 \times 10^{-34} \times 1000\ J$$

$$= 9.939 \times 10^{-31}\ J$$

Q.2 Find zero point energy and spacing between two vibrational levels if vibrational freq is $3 \times 10^{-3}\ s^{-1}$.

Ans: Zero point energy $= \frac{1}{2} h\nu$

$$= \frac{1}{2} \times 6.626 \times 10^{-34}\ Js \times 3 \times 10^{-3}\ s^{-1}$$

$$= 9.939 \times 10^{-37}\ J$$

This study material is availabe on SIT ASSAN BETA

Spacing $= \Delta E = h\nu$

$= 2 \times 9.939 \times 10^{-37}$

$= 19.878 \times 10^{-37}$ J.

imp

Q.3 Find the vibrational freq, vibrational wavno, zero point energy and energy level spacing between two consecutive levels for CO molecule having $K = 1800$ Kg/s^2 (or N/m). At. mass of C = 12 amu, O = 16 amu (or we can write C = 12u & O = 16 u)

Imp

Soln:-

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

K given in Kg/s^2 unit

So, μ (red. mass) to be expressed in Kg.

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \left(\frac{12 \times 16}{12 + 16}\right) \text{amu}$$

This study material is availabe on SIT ASSAN BETA

$\boxed{1\ amu = 1.664 \times 10^{-24}\ g = 1.664 \times 10^{-27}\ kg}$

$= 6.8571\ amu$

$= 6.8571 \times 1.664 \times 10^{-27}\ kg$

$= 11.41 \times 10^{-27}\ kg$

now, i) $\nu = \frac{1}{2\pi}\sqrt{\frac{K}{M}}$

$= \frac{1}{2 \times 3.14}\sqrt{\frac{1800\ kg/s^2}{11.41 \times 10^{-27}\ kg}}$

$= 3.971 \times 10^{14}\ s^{-1}$

ii) $\bar{\nu} = \frac{\nu}{c} = \frac{3.971 \times 10^{14}\ s^{-1}}{3 \times 10^{10}\ cm/s}$

$= 1.3237 \times 10^{4}\ cm^{-1}$

iii) $ZPE = \frac{1}{2} h\nu$

$= \frac{1}{2} \times 6.626 \times 10^{-34}\ J.s \times 1.3237 \times 10^{14}\ s^{-1}$

$= 4.3854 \times 10^{-20}\ J$

iv) vib. energy level spacing $= h\nu = (2 \times ZPE)$

$= 8.77 \times 10^{-20}\ J$

This study material is availabe on SIT ASSAN BETA

Q.4 Calculate the vibrational energy of 1st excited state and force constant of HF molecule if its frequency of oscillation is $4 \times 10^{14}\ s^{-1}$. (At. mass of H = 1u and F = 19u)

Ans:- vibrational energy for 1st excited state ($v = 1$) is

i) $E_{vib} = (v + \frac{1}{2}) h\nu$

$= (1 + \frac{1}{2}) h\nu = \frac{3}{2} h\nu$

$= (1.5 \times 6.626 \times 10^{-34}\ 0.5 \times 4 \times 10^{14}\ s^{-1})$

$= 39.756 \times 10^{-20}\ J$

ii) $K = 4\pi^2 \mu \nu^2$

$= [4 \times 3.14^2 \times 1.58 \times 10^{-24}\ g \times (4 \times 10^{14}\ s^{-1})^2]$

$= \boxed{9.97 \times 10^{4}\ g/s^2}$ Ans

(*) $\mu_{HF} = \frac{m_1 m_2}{m_1 + m_2} = \left(\frac{1 \times 19}{1 + 19}\right)$ amu

$= 0.95 \times 1.664 \times 10^{-24}\ g$

$= 1.58 \times 10^{-24}\ g$

This study material is availabe on SIT ASSAN BETA

Q.5 The vibrational wavenumber of H–Cl bond in HCl molecule is $2900\ cm^{-1}$. Find the vibrational energy for the first excited state and force constant. ($m_H = 1u$, $m_{Cl} = 35.5u$)

Soln:- given that, $\bar{\nu} = 2900\ cm^{-1}$

$$\bar{\nu} = \frac{\nu}{c} \Rightarrow \nu = \bar{\nu} \times c$$

$$= 2900\ cm^{-1} \times 3 \times 10^{10}\ cm/s$$

$$\boxed{\nu = 87 \times 10^{12}\ s^{-1}}$$

now,

i) $$E_{vib} = \left(v + \frac{1}{2}\right) h\nu$$

$v = 1$

$$= \frac{3}{2} h\nu$$

$$= 1.5 \times 6.626 \times 10^{-34}\ J\text{-}s \times 87 \times 10^{12}\ s^{-1}$$

$$= 864.69 \times 10^{-22}\ J$$

This study material is availabe on SIT ASSAN BETA

ii) $K = 4\pi^2 \mu \nu^2$

$= 4 \times 3.14^2 \times 1.6184 \times 10^{-24} g \times (87 \times 10^{12} s^{-1})^2$

$= 483.107 \times 10^3 g/s^2$

$\mu_{H-Cl} = \left(\frac{m_1 m_2}{m_1 + m_2}\right) = \frac{1 \times 35.5}{(1 + 35.5)}$

$= 0.9726$ amu

$= 0.9726 \times 1.66 \times 10^{-24} g$

$= 1.6184 \times 10^{-24} g$

imp

Q.6 The C–H stretching vibration in chloroform ($CHCl_3$) occurs at $3000 cm^{-1}$. Calculate the C–D stretching ~~[illegible]~~ wave no in deutero chloroform ($CDCl_3$).

Soln:- We know that,

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

for C–H bond

$$\bar{\nu}_{C-H} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu_{C-H}}} \quad \text{— (1)}$$

This study material is availabe on SIT ASSAN BETA

for C–D bond

$$\bar{\nu}_{C-D} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu_{C-D}}} \quad \text{— (2)}$$

N-B K is supposed to be same for C–H and C–D bond.

now, from eqn (1) & eqn (2)

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}} \quad \text{— (3)}$$

we have, $\bar{\nu}_{C-H} = 3000\ cm^{-1}$

we have to find out μ_{C-H} & μ_{C-D} first.

$$\mu_{C-H} = \frac{12 \times 1}{(12+1)} = \frac{12}{13} = 0.924$$

$$\mu_{C-D} = \frac{12 \times 2}{(12+2)} = \frac{24}{14} = 1.71u$$

This study material is availabe on SIT ASSAN BETA

from (3),

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = \sqrt{\frac{\mu_{C-H}}{\mu_{C-D}}}$$

$$\Rightarrow \frac{\bar{\nu}_{C-D}}{3000} = \sqrt{\frac{0.92}{1.71}}$$

$$\Rightarrow \bar{\nu}_{C-D} = \sqrt{\frac{0.92}{1.71}} \times 3000$$

$$= 0.73 \times 3000$$

$$= 2190\ cm^{-1} \text{ (Ans).}$$

Finger Print Region:

The region below $\bar{\nu} = 1500\ cm^{-1}$ is rich in many absorptions which are caused due to bending vibrations. This region (500 – 1500 cm^{-1}) is known as finger print region.

This study material is availabe on SIT ASSAN BETA

Some substances containing the same functional group show similar absorption above 1500 cm^{-1} but their absorption positions differ in the finger print region.

This study material is availabe on SIT ASSAN BETA

More Numericals

Q.1) Calculate the force constant and ZPE of CO molecule if the fundamental vibrational wave no ~~frequency~~ is $2140\ cm^{-1}$. (At. mass of $C = 19.9 \times 10^{-27}$ kg & $O = 26.6 \times 10^{-27}$ kg)

Ans. $\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$

$$\Rightarrow \boxed{K = 4\pi^2 c^2 \bar{\nu}^2 \mu}$$

First find out μ

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{(19.9 \times 10^{-27})(26.6 \times 10^{-27} kg)}{(19.9 \times 10^{-27}) + (26.6 \times 10^{-27} kg)}$$

$$= \frac{(19.9) \times (26.6) \times 10^{-54} kg^2}{(19.9 + 26.6) \times 10^{-27} kg}$$

$$= 11.38 \times 10^{-27} kg$$

$$= 11.38 \times 10^{-24} g$$

N.B. Here, at. masses are given in kg so no need to multiply 1.66×10^{-27} kg ~~or~~ 1.66×10^{-24} g

This study material is availabe on SIT ASSAN BETA

i) So, $K = 4 \times 3.14^2 \times (3 \times 10^{10}\ cm/s)^2 \times (2140\ cm^{-1})^2 \times 11.38 \times 10^{-24}\ g$

$= 1.849 \times 10^{6}\ g/s^2$

ii) $ZPE = \frac{1}{2} h\nu = \frac{1}{2} h\bar{\nu} c$

$(\bar{\nu} = \frac{\nu}{c} \Rightarrow \nu = \bar{\nu} c)$

$= \frac{1}{2} \times 6.626 \times 10^{-34}\ J\text{-}s \times 2140\ cm^{-1} \times 3 \times 10^{10}\ cm/s$

$= 21269.46 \times 10^{-24}\ J$

This study material is availabe on SIT ASSAN BETA

Print region.

Number of Fundamental Vibrations:

Polyatomic molecules may exhibit more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the degree of freedom in a molecule.

For a molecule consisting of n number of atoms, total number of degrees of freedom = 3n

This study material is availabe on SIT ASSAN BETA

A molecule of finite dimensions will be made up of rotational, vibrational and translational degrees of freedom.

So,

✓ 3n degrees of freedom = (Translational + Rotational + Vibrational)

⇒ Vibrational degree of freedom = 3n − (Translational + Rotational)

(1)

(A) Linear molecules :-

For a linear molecule of 'n' atoms,

Total degrees of freedom = 3n

Translational " = 3

Rotational " = 2

This study material is availabe on SIT ASSAN BETA

So,
Vibrational degree of freedom $= 3n - (2+3)$
$= \boxed{3n - 5}$

Example :-
Linear molecules,
HCl, CO, CO_2, $CH \equiv CH$, etc.

i) For HCl, $n = 2$
Vib. deg. freedom $= 3n - 5$
$= (3 \times 2) - 5 = 1$

ii) For CO, $n = 2$
Vib. deg. freedom $= 1$

iii) For CO_2, $n = 3$
Vib. deg. of freedom $= 3n - 5$
$= (3 \times 3) - 5 = 9 - 5 = 4$

This study material is availabe on SIT ASSAN BETA

(iv) for C_2H_2, $n = 4$

Vib. deg. freedom $= 3n - 5$

$= (3 \times 4) - 5$

$= 12 - 5 = 7$

(B) Non-linear molecules

Examples: H_2O, SO_2, $CHCl_3$, CH_4, C_6H_6, $POCl_3$, etc.

for a non-linear molecule with n atoms

Total deg. of freedom $= 3n$

Translational " $= 3$

rotational " $= 3$

So,

Vib. deg. of freedom $= 3n - (3+3)$

$= \boxed{3n - 6}$

This study material is availabe on SIT ASSAN BETA

Molecule	n	(Vib. Deg. freedom) (3n − 6)
i) H_2O	3	$(3\times3)-6=3$
ii) SO_2	3	3
iii) $CHCl_3$	5	$(3\times5)-6=9$
iv) CH_4	5	9
v) C_6H_6	12	$(3\times12)-6=30$
vi) $POCl_3$	5	9

(*) Applications of IR-Spectroscopy:

(i) Identification of an organic compound :- from its finger print region

(ii) Structure determination

(iii) Qualitative analysis of functional groups

This study material is availabe on SIT ASSAN BETA

(–OH, –C=O, –$\overset{O}{\overset{\|}{C}}$–H, –COOH, etc.) present in an org. comp.

(iv) In study of chemical reactions

(v) To study interaction between two molecules.

(vi) Detection of impurity in a compound

(vii) To differentiate betw cis & Trans isomers

(viii) Study of Keto-enol Tautomerism.

(ix) Quantitative estimation of an organic mixture

This study material is availabe on SIT ASSAN BETA

Questions & Answers
(IR- Spectroscopy)

Q.1 What is the range of IR-radiation?

Ans: 2.5μ – 15μ or 4000 – 667 cm^{-1}

Q.2 Name the various type of bending vibrations.

Ans: These are scissoring, rocking, wagging & twisting.

Q.3 What do you mean by Finger print region?

(See Notes)

Q.4 What do you mean by fundamental vibrations?

Ans: It corresponds to the first vibrational transition from $v = 0$ to $v = 1$ vibrational energy level.

Q.5 Which of the following diatomic molecules do not absorb in the IR-region or IR-inactive? HCl, N_2, H_2, O_2

This study material is availabe on SIT ASSAN BETA

Ans:- N_2, H_2 & O_2

Q.6 Which of the following molecule is IR-active?
CH_4, CCl_4, F_2, HF

Ans: CH_4 & HF (polar molecules)

Q.7 Cis-1,2-dichloroethene is IR-active whereas trans-form is IR-inactive. Give reason.

Ans:

cis-form has some net dipole moment
Hence, IR-active

Trans-form
Net dipole moment = 0
Hence, IR-inactive

Q.8 What is the selection rule of vibrational spectroscopy?

Ans: $\Delta v = \pm 1$

This study material is availabe on SIT ASSAN BETA

Q.9 Find the vibrational degree of freedom of CO_2 & CH_3Cl.

Ans: i) CO_2, $n = 3$, linear

So, vib. deg. of freedom $= 3n - 5$

$= 3 \times 3 - 5 = 4$

ii) CH_3Cl, $n = 5$, non-linear

vib. deg. of freedom $= 3n - 6$

$= 3 \times 5 - 6 = 9$

Q.10 What is zero point energy?

Ans Energy corresponds to $v = 0$ state

i.e $E_{vib} = \frac{1}{2} h\nu$

This study material is availabe on SIT ASSAN BETA

Q-11 Mention the factors that affects vib. frequency.

Ans

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

Factors are (i) K

(ii) mass of atoms.

Q.12 The C–H wave no of in a compound is observed at 2910 cm^{-1}. Predict the corresponding C–D stretching wave no whose H-atom is replaced by D-deuterium atom.

Ans:

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = 0.73 \simeq \frac{1}{\sqrt{2}}$$

See page-6

So, $\bar{\nu}_{C-D} = 0.73 \times \bar{\nu}_{C-H}$

$= 0.73 \times 2910\ cm^{-1}$

$= 2124\ cm^{-1}$

This study material is availabe on SIT ASSAN BETA

Q.13 Mention the formula to find vib. degrees of freedom of non-linear molecules

A. $3n-6$, n = no. of atoms

Q.14 What is force constant? What is units?

A. Force constant is a measure of bond strength

K of $C \equiv C > C = C > C-C$

Units: g/s^2 or dyne/cm

kg/s^2 or N/m

Q.15 What is the spacing between two consecutive vib. energy levels?

A. $\Delta E_{vib} = h\nu$

This study material is availabe on SIT ASSAN BETA

Q.16 Stretching vibration occurs at higher frequency than bending vibrations. Give reason.

Ans: More energy ($E = h\nu$) is needed to stretch a bond than to bend it.

i.e As $E \uparrow$, $\nu \uparrow$ (freq.)

Q.17 Which form of stretching vibration in CO_2 - molecule is IR - active?

Ans:

Symmetric stretching

Net dipole moment is zero (IR - inactive)

Asymmetric stretching

Here, molecule has some dipole moment (IR - active)

This study material is availabe on SIT ASSAN BETA

$\Rightarrow \boxed{A = 2 - \log(\%T)}$ (As $A = -\log T$)

or $-A = \log T$)

Q.2 What is Isotope effect in IR-spectroscopy?

Ans:- It deals with effect of isotopic mass on the vibrational frequency. As mass increases, vib. freq. decreases.

This study material is availabe on SIT ASSAN BETA

for example,
Isotope of 'H' is Deuterium 'D'
At. mass of 'H' = 1 u & 'D' is 2 u
⇒ If 'H' will be substituted by 'D', its mass will increase by 2-times, so, vib freq. will be decrease by 2-times.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

i.e $\nu \propto \frac{1}{\sqrt{\mu}}$, As $\mu \uparrow$, $\nu \downarrow$

Q.3 Why is methanol is a good solvent for UV but not for IR spectroscopy?

Ans:- The reason is that methanol does not absorb in UV-region but it is absorbs strongly in IR-region (4000 - 667 cm^{-1})

This study material is availabe on SIT ASSAN BETA

Print region.

Number of Fundamental Vibrations:

Polyatomic molecules may exhibit more than one fundamental vibrational absorption bands. The number of these fundamental bands is related to the degree of freedom in a molecule.

For a molecule consisting of n number of atoms, total number of degrees of freedom = 3n

This study material is availabe on SIT ASSAN BETA

A molecule of finite dimensions will be made up of rotational, vibrational and translational degrees of freedom.

So,

✓ 3n degrees of freedom = (Translational + Rotational + Vibrational)

⇒ Vibrational degree of freedom = 3n − (Translational + Rotational)

(1)

(A) Linear molecules :-

For a linear molecule of 'n' atoms,

Total degrees of freedom = 3n

Translational " = 3

Rotational " = 2

This study material is availabe on SIT ASSAN BETA

So,
Vibrational degree of freedom $= 3n - (2+3)$
$= \boxed{3n - 5}$

Example :-
Linear molecules,
HCl, CO, CO_2, $CH \equiv CH$, etc.

i) For HCl, $n = 2$
Vib. deg. freedom $= 3n - 5$
$= (3 \times 2) - 5 = 1$

ii) For CO, $n = 2$
Vib. deg. freedom $= 1$

iii) For CO_2, $n = 3$
Vib. deg. of freedom $= 3n - 5$
$= (3 \times 3) - 5 = 9 - 5 = 4$

This study material is availabe on SIT ASSAN BETA

(iv) for C_2H_2, $n = 4$

Vib. deg. freedom $= 3n - 5$

$= (3 \times 4) - 5$

$= 12 - 5 = 7$

(B) Non-linear molecules

Examples: H_2O, SO_2, $CHCl_3$, CH_4, C_6H_6, $POCl_3$, etc.

for a non-linear molecule with n atoms

Total deg. of freedom $= 3n$

Translational " $= 3$

rotational " $= 3$

So,

Vib. deg. of freedom $= 3n - (3+3)$

$= \boxed{3n - 6}$

This study material is availabe on SIT ASSAN BETA

Molecule	n	(Vib. Deg. freedom) (3n − 6)
i) H_2O	3	$(3\times3)-6=3$
ii) SO_2	3	3
iii) $CHCl_3$	5	$(3\times5)-6=9$
iv) CH_4	5	9
v) C_6H_6	12	$(3\times12)-6=30$
vi) $POCl_3$	5	9

(*) Applications of IR-Spectroscopy:

(i) Identification of an organic compound :- from its finger print region

(ii) Structure determination

(iii) Qualitative analysis of functional groups

This study material is availabe on SIT ASSAN BETA

(–OH, –C=O, –$\overset{O}{\overset{\|}{C}}$–H, –COOH, etc.) present in an org. comp.

(iv) In study of chemical reactions

(v) To study interaction between two molecules.

(vi) Detection of impurity in a compound

(vii) To differentiate betw cis & Trans isomers

(viii) Study of Keto-enol Tautomerism.

(ix) Quantitative estimation of an organic mixture

This study material is availabe on SIT ASSAN BETA

Questions & Answers
(IR- Spectroscopy)

Q.1 What is the range of IR-radiation?

Ans: 2.5μ – 15μ or 4000 – 667 cm^{-1}

Q.2 Name the various type of bending vibrations.

Ans: These are scissoring, rocking, wagging & twisting.

Q.3 What do you mean by Finger print region?

(See Notes)

Q.4 What do you mean by fundamental vibrations?

Ans: It corresponds to the first vibrational transition from $v = 0$ to $v = 1$ vibrational energy level.

Q.5 Which of the following diatomic molecules do not absorb in the IR-region or IR-inactive? HCl, N_2, H_2, O_2

This study material is availabe on SIT ASSAN BETA

Ans:- N_2, H_2 & O_2

Q.6 Which of the following molecule is IR-active?
CH_4, CCl_4, F_2, HF

Ans: CH_4 & HF (polar molecules)

Q.7 Cis-1,2-dichloroethene is IR-active whereas trans-form is IR-inactive. Give reason.

Ans:

cis-form has some net dipole moment
Hence, IR-active

Trans-form
Net dipole moment = 0
Hence, IR-inactive

Q.8 What is the selection rule of vibrational spectroscopy?

Ans: $\Delta v = \pm 1$

This study material is availabe on SIT ASSAN BETA

Q.9 Find the vibrational degree of freedom of CO_2 & CH_3Cl.

Ans: i) CO_2, $n = 3$, linear

So, vib. deg. of freedom $= 3n - 5$

$= 3 \times 3 - 5 = 4$

ii) CH_3Cl, $n = 5$, non-linear

vib. deg. of freedom $= 3n - 6$

$= 3 \times 5 - 6 = 9$

Q.10 What is zero point energy?

Ans Energy corresponds to $v = 0$ state

i.e $E_{vib} = \frac{1}{2} h\nu$

This study material is availabe on SIT ASSAN BETA

Q-11 Mention the factors that affects vib. frequency.

Ans

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

Factors are (i) K

(ii) mass of atoms.

Q.12 The C–H wave no of in a compound is observed at 2910 cm^{-1}. Predict the corresponding C–D stretching wave no whose H-atom is replaced by D-deuterium atom.

Ans:

$$\frac{\bar{\nu}_{C-D}}{\bar{\nu}_{C-H}} = 0.73 \simeq \frac{1}{\sqrt{2}}$$

See page-6

So, $\bar{\nu}_{C-D} = 0.73 \times \bar{\nu}_{C-H}$

$= 0.73 \times 2910\ cm^{-1}$

$= 2124\ cm^{-1}$

This study material is availabe on SIT ASSAN BETA

Q.13 Mention the formula to find vib. degrees of freedom of non-linear molecules

A. $3n-6$, n = no. of atoms

Q.14 What is force constant? What is units?

A. Force constant is a measure of bond strength

K of $C \equiv C > C = C > C-C$

Units: g/s^2 or dyne/cm

kg/s^2 or N/m

Q.15 What is the spacing between two consecutive vib. energy levels?

A. $\Delta E_{vib} = h\nu$

This study material is availabe on SIT ASSAN BETA

Q.16 Stretching vibration occurs at higher frequency than bending vibrations. Give reason.

Ans: More energy ($E = h\nu$) is needed to stretch a bond than to bend it.

i.e As $E \uparrow$, $\nu \uparrow$ (freq.)

Q.17 Which form of stretching vibration in CO_2 - molecule is IR - active?

Ans:

Symmetric stretching

Net dipole moment is zero (IR - inactive)

Asymmetric stretching

Here, molecule has some dipole moment (IR - active)

This study material is availabe on SIT ASSAN BETA

$\Rightarrow \boxed{A = 2 - \log(\%T)}$ (As $A = -\log T$)

or $-A = \log T$)

Q.2 What is Isotope effect in IR-spectroscopy?

Ans:- It deals with effect of isotopic mass on the vibrational frequency. As mass increases, vib. freq. decreases.

This study material is availabe on SIT ASSAN BETA

for example,

Isotope of 'H' is Deuterium 'D'

At. mass of 'H' = 1 u & 'D' is 2 u

⇒ If 'H' will be substituted by 'D' its mass will increase ~~by 2 times~~, so, vib freq. will be decrease too. ~~by 2 times~~.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$$

i.e $\nu \propto \frac{1}{\sqrt{\mu}}$, As $\mu \uparrow$, $\nu \downarrow$

Q.3 Why is methanol is a good solvent for UV but not for IR spectroscopy?

Ans:- The reason is that methanol does not absorb in UV-region but it is absorbs strongly in IR-region (4000 - 667 cm^{-1}).

This study material is availabe on SIT ASSAN BETA