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| Unit 1 | Corrosion Science |
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| Introduction to Solid State and its types |
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1) INTRODUCTION: Solids are the substances characterized by definite shape, definite volume, non compressibility, very slow diffusion, rigidity and mechanical strength.

☺ The atoms, ions, molecules in solids are closely packed and are held tightly by strong forces of attraction. Due to this, a substantial restriction is imposed on their movement.

☺ The atoms, ions, molecules or the constituent particles are fixed to definite positions of equilibrium within the solid crystal.

☺ The Engineering Materials are divided into different categories based on their physical and chemical properties.

2) TYPES OF SOLIDS: Solid materials are classified according to the regularity of the atoms, ions or the constituent particles are arranged in them.

☺ They are of two types: a) Crystalline solids and b) Amorphous solids.

3) CRYSTALLINE SOLIDS: These exist in well defined crystalline forms, with their atoms, ions or molecules arranged in a certain geometrical pattern, throughout the three dimensional network of the crystal. Thus in crystalline solids, there is long range order in their structures.

Examples: Sodium chloride, Sulphur, sugar, Diamond, all the metals etc.

4) AMORPHOUS SOLIDS: In these, the arrangement of the constituent particles or the structural units present in them is random. As they don't have regular arrangement, they do not have long range order in their structures.

☺ In fact amorphous solids (meaning without form) can be considered to be super cooled liquids which are characterized by short range order.

☺ However amorphous solids possess rigidity, stiffness which is because of their very high viscosities. So, in amorphous solids, the constituent particles remain at their fixed positions.

5) GENERAL PROPERTIES OF CRYSTALLINE SOLIDS:

- They have regular orderly arrangement of structural units in definite geometrical forms.
- They possess sharp (definite, fixed) melting points.
- Their physical properties (like Elasticity, tensile strength, refractive index, conductivity etc) are different along different directions. Such substances are called anisotropic substances. In short Crystalline substances are Anisotropic.
- They have crystal symmetry.
- When Crystalline solids are cut with sharp edged tool, it gets easily cut along certain planes (Cleavage Plane). The Cleavage planes are inclined to each other at certain angles.
- They are solids in true sense and possess definite shape and volume.
- Their X-ray pictures (diffraction patterns) show orderly arranged pattern of spots in their structures. Examples: Diamond, Quartz, Sodium chloride etc.

- 6) GENERAL PROPERTIES OF AMORPHOUS SOLIDS: They have following properties ...
- They have completely random arrangement of the structural units in them.
 - They do not have sharp (fixed) melting points, rather they have melting range of temperatures. A type of a wax melts in the region from 60°C to 80°C . They become soft on heating and start flowing.
 - They are isotropic in nature. Their physical properties (such as refractive index, tensile strength, elasticity, conductivity etc) are same along all the directions.
 - Due to this reason they can be given or converted into desired shapes with tools. e.g. Wood.
 - Amorphous substances have do not have any symmetry.
 - They are not true solids, but are considered to be super-cooled liquids.
 - They are non-rigid without any definite shape and volume.
 - X-ray pictures (Diffraction patterns) show concentric rings.
- Examples:- Rubber, Glass, Plastics etc.

7) DIFFERENTIATE BETWEEN AMORPHOUS SOLIDS AND CRYSTALLINE SOLIDS.

| AMORPHOUS SOLIDS | CRYSTALLINE SOLIDS |
|--|--|
| <ol style="list-style-type: none"> Their structural Units are randomly arranged. They do not have sharp melting points. They are <u>isotropic*</u> in nature. i.e. Their properties like tensile strength, refractive index, conductivity, elasticity etc are same along all the directions. When Amorphous substances are cut by a sharp-edged tool (like knife), irregular fracture is developed. Amorphous solids do not have Symmetry. They are not true solids but are super-cooled liquids. They are non-rigid. Many of them do not have definite shape and volume. X-ray pictures of these solids show concentric rings. <u>Examples:-</u> Rubbers, Glass, Plastics etc. <p>Q) <u>Isotropic*</u> = (Substances having same or similar properties in all directions are called "Isotropic substances").</p> | <ol style="list-style-type: none"> Their structural Units are orderly arranged in definite geometrical forms. They have sharp melting points. They are <u>anisotropic*</u> in nature. i.e. Their properties like tensile strength, refractive index, conductivity, elasticity etc are different along different directions. When Crystalline solid is cut with a sharp-edge tool (like knife), it gets cut along an inclined plane (Cleavage plane). Crystalline solids have Crystal Symmetry. They are solids in true sense. They are rigid and have definite shape and volume. X-ray pictures show orderly diffraction pattern. <u>Examples:-</u> Diamond, Quartz, NaCl etc. <p>Q) <u>Anisotropic*</u> = (Substances having different values for certain properties in different directions are called "Anisotropic substances").</p> |

- 8) CLASSIFICATION OF CRYSTALLINE SOLIDS: Crystalline solids are Classified on the basis of the types of Bonds present in them. They are mainly classified into:

a) Ionic Solids, b) Covalent Solids, c) Molecular Solids & d) Metallic Solids.

- 9) IONIC SOLIDS: Ionic substances contain ionic bonds between their constituent particles (ions). They contain positively (+ve) and negatively charged (-ve) ions arranged between

oppositely charged ions. The binding forces are Coulombic forces of attraction which are called Ionic Bonds.

- ☺ Ionic Bonds are non-directional in nature.
- ☺ Electropositive metals lose electron/s to form +ve ions & Electronegative elements gain electrons to form -ve ions. The oppositely charged ions combine by electrostatic forces of attraction to form ionic bonds.
- ☺ When proper number of positive and negative ions are brought together, these ions arrange themselves in a typical geometrical pattern to form Ionic Solids.
- ☺ During formation of crystals of Ionic solids, energy is released. As a result a stable ionic bond is formed.
- ☺ The energy released during formation of ionic solids is called Lattice Energy.
- ☺ Lattice Energy is defined as: "The quantity of heat energy liberated when appropriate number of oppositely charged ions in gaseous state are brought together from infinite distance to form 1 gm mole of an ionic solid substance".
- ☺ Lattice Energy is a measure of the strength of Ionic Bond. Higher is the value of Lattice Energy with negative (-ve) sign, stronger is the bond.
- ☺ Lattice Energy can be theoretically calculated on the basis of electrical charges, sizes and the type of arrangement of ions in its crystal using following equation:-

$$U = \frac{e^2 \cdot z^2 \cdot N_0 \cdot A}{r} \left(1 - \frac{1}{n}\right)$$

Where, e = electrical charge on an electron,

z = common factor of valences of the two ions,

n = Empirical number 10,

r = distance between the nuclei of oppositely charged ions,

A = Madelung constant

☺ In practice, Lattice Energy of Ionic Solids is obtained by using the energy values involved in formation of Ionic Solid with the help of Hess' Law. This is called Born-Haber Cycle/ method.

☺ Principle of the method is : "In a cyclic process, the Net change in the energy is always zero".

10) BORN-HABER CYCLE FOR NaCl(s):-

☺ Formation Enthalpy of NaCl(s), can be given by following equation: $\text{Na}(s) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{NaCl}(s)$. The above process takes place in following steps:-

- a) Sublimation:- $\text{Na}(s) \xrightarrow{\Delta} \text{Na}(g)$; S; (Value known)
- b) Ionisation:- $\text{Na}(g) \rightarrow \text{Na}^+(g) + e^-$; I; (Value known)
- c) Dissociation Energy:- $\frac{1}{2} \text{Cl}_2(g) \rightarrow 2 \text{Cl}(g)$; D/2; (Value known)
- d) Electron Affinity:- $\text{Cl}(g) + e^- \rightarrow \text{Cl}^-(g)$; -A; (Value known)
- e) Lattice Energy:- $\text{Na}^+(g) + \text{Cl}^-(g) \rightarrow \text{NaCl}(s)$; -U. (VALUE NOT KNOWN)

Net Reaction by adding all above a), b), c), d) e) is nothing but Formation Enthalpy equation given in the beginning of this Topic. $\text{Na}(s) + \frac{1}{2} \text{Cl}_2(g) \rightarrow \text{NaCl}(s)$. -Q (value known)

According to Hess' Law [-Q = S + I + D/2 + (-A) + (-U)]

- ☺ Knowing all other values, Lattice Energy can be found out by using Born-Haber Cycle.
- ☺ Lattice Energy must be negative (-ve) with higher value to have strong Ionic Bond.

11) CHARACTERISTICS OF IONIC SOLIDS:- Ionic Solids show following properties ...

- a) Due to strong electro-static force of attraction between oppositely charged ions ionic crystal possesses:- i) high Lattice Energy, ii) Brittleness & iii) high melting and boiling points.
- b) Ionic Solids are soluble in Polar Solvents having high di-electric constant (such as water, alcohol etc) since Polar solvents provide sufficient energy to separate the ions from the crystal. However they are insoluble in solvents like Carbon tetrachloride, benzene etc. This is in accordance with principle "Like dissolves like".
- c) Ionic solids possess extremely small vapour pressure at room temperature due to their very large binding energies.
- d) Ionic Solids are insulators in solid state as all the ions in solid have definite places and cannot move in the crystal structure.
- ☺ However in their liquid (molten or fused) state or in their aqueous solutions, they are good conductors of electricity. This is because, their ions can move easily under the influence of applied electric field.
- e) Metals from Group I and II (which are highly electropositive) have a tendency to combine with non-metals from Group VI and VII (which are highly electronegative) to form Ionic Bonds. Examples:- NaCl (sodium chloride), LiF (Lithium fluoride), CaO (Calcium oxide) etc.

12) EXPLAIN COVALENT SOLIDS AND GIVE THEIR CHARACTERISTICS.

Ans:- Co-valent solids consists of an array of atoms that share electrons with neighbouring atoms in such a way, that they form strong Covalent Bonds between them.

- ☺ Usually atoms of the same elements or the elements having less difference in their electronegativities combine with each other to form such compounds.
- ☺ Formation of a co-valent bond between the two neighboring atoms can be explained by Valence Bond Theory.
- ☺ The co-valent bonds can be formed by overlapping of pure or hybridized orbitals.

CHARACTERISTICS OF CO-VALENT SOLIDS:-

- i) Co-valent bonds are strong and directional nature, so co-valent solids possess fairly high melting and boiling points.
- ii) They are Hard in nature due to strong & directional nature of co-valent bonds in them.
- iii) They are mostly non-polar in nature and so are insoluble in water.
- iv) They are soluble in non-polar or organic solvents.
- v) In certain cases they exhibit the property of space isomerism, since they have fixed bond lengths.
- ☺ Examples:- SiC (Silicon Carbide), Diamond (C), Graphite (C), Silicon dioxide (SiO_2), Zinc Sulphide (ZnS), Silver Iodide (AgI) etc.

13) EXPLAIN MOLECULAR SOLIDS AND GIVE THEIR CHARACTERISTICS.

ANS:- Molecular solids involve weak Van Der Waal's forces or secondary forces of attraction between different molecules. These forces have very short range and attract all discrete species (like atoms, ions, molecules) when they are very close (approx up to 5°A).

Thus Molecular Crystals consists of a symmetrically arranged discrete molecules bound by Van-Der Wall's forces of attraction.

CHARACTERISTICS OF MOLECULAR SOLIDS:- They exhibit following characteristics:-

- a) Due to presence of weak intermolecular of attraction, they are soft and volatile and possess low melting and boiling points. They liquefy and solidify at very low temperatures.
- b) The molecules are electrically neutral & all the electrons in them are localized.
- c) They are insulators of electricity.
- d) Their melting and boiling points go on increasing with the increase in their molecular masses. In fact they (mp, bp or magnitude of these forces) are directly proportional to the no. of electrons present in valance shell & At Nos of the atoms in them. For Example :- Boiling Point of I_2 (Mol mass = 253) > Br_2 (Mol mass = 159.8) > Cl_2 (Mol mass 76.9) > F_2 (Mol mass = 28.0) > H_2 (Mol mass = 2.016)
- e) Other Examples of other Molecular Solids:- $CO_2(s)$, $H_2(s)$, $N_2(s)$ etc.

14) METALLIC SOLIDS & THEIR CHARACTERISTICS.

- ☺ The structure of Metallic Solids can be explained by Electron Sea Model.
- ☺ According to this the positively charged metal ions are dipped in the sea of electrons. They are all held together by the electrostatic forces of attractions between them.
- ☺ They can form different types of crystal structures. (HCP, BCC, FCC etc)

CHARACTERISTICS OF METALLIC SOLIDS:-

- a) They have high melting and boiling points.
 - b) They are good conductors of heat and electricity.
 - c) They have High Tensile Strength.
 - d) They are Lustrous, possess reflectivity and exhibit different colours.
 - e) They malleable and ductile in nature.
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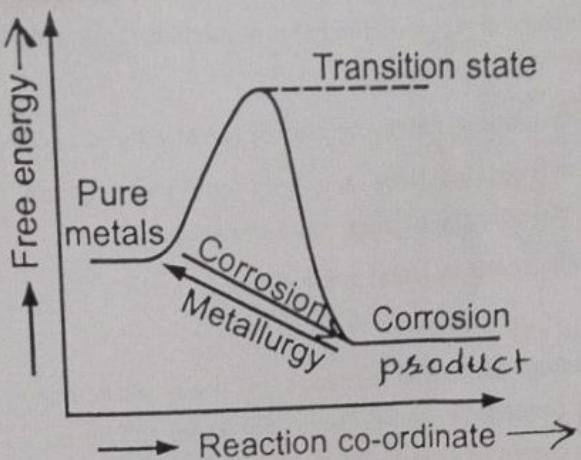
Corrosion Science

15) CORROSION.

- ☺ The unintentional and undesired destruction of a metal chemical or electro-chemical reactions, starting at the surface of a metal is called Corrosion of a metal.
- ☺ During corrosion formation of an undesired or unwanted compound takes place at its surface. The corrosion products formed are most commonly oxides or sulphates, sulphides, nitrates etc.

MAJORITY OF THE METALS HAVE A TENDENCY TO UNDERGO CORROSION:- In nature almost all the metals (except Au, Pt etc) occur in their combined state such as Oxides, Sulphates, Sulphides, Chlorides etc. These naturally occurring compounds of the metals are called Minerals or Ores.

- ☺ In order to obtain pure metals from the minerals or ores, one needs to carry out many Physical and Chemical processes. This science of obtaining a pure metal from its ore is called Metallurgy.



- ☺ The reason for metals undergoing corrosion naturally can be well understood with the help of Thermodynamics.
- ☺ In Nature, every system has a natural tendency to go to the lower state of Free Energy.
- ☺ In nature, we get metals in the form of their combined states (compounds) which are at the lower state, than pure metals.
- ☺ Therefore, metals undergo corrosion in order to decrease their Free Energy, spontaneously.
- ☺ From above diagram, there is a lowering of Gibb's Free Energy, when a metal undergoes corrosion to form some undesirable compound (corrosion product).

Q 17) WHAT IS CORROSION? GIVE ITS MAIN TYPES.

ANS:- Definition: The unintentional and undesired destruction of a metal chemical or electrochemical reactions, starting at the surface of a metal is called Corrosion of a metal.

- ☺ It is the result of the chemical reaction between the surface atoms of the metal and the gases present in the atmosphere under changing climatic conditions.
- ☺ Corrosion of a metal is mainly of two types. They are ...

- a) Dry or Direct Chemical Corrosion and b) Wet or Electro-chemical corrosion.

Q18) NAME THE GASES WHICH USUALLY CAUSE DRY OR DIRECT CHEMICAL CORROSION.

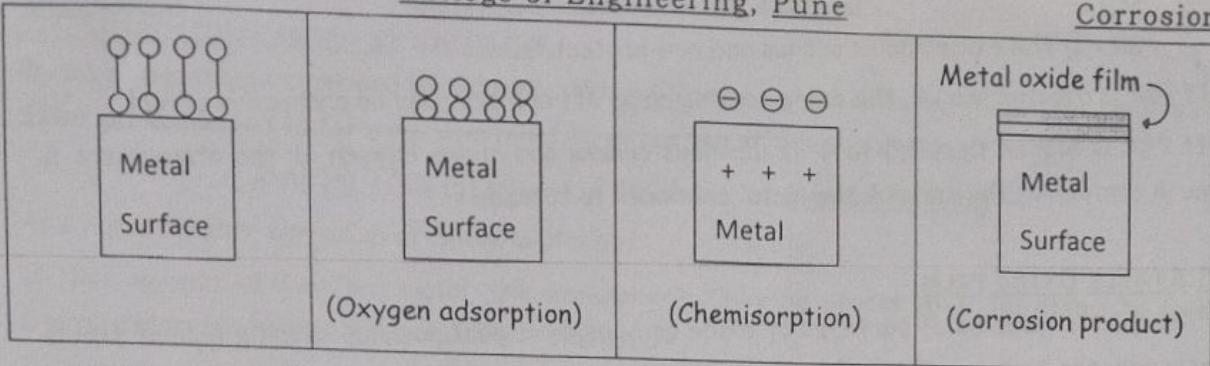
ANS:- The gases like Oxygen (in majority of the cases), Chlorine, Hydrogen, SO_2 , SO_3 , oxides of Nitrogen etc are usually responsible for the Dry or Direct Chemical Corrosion.

Q 19) EXPLAIN CORROSION DUE TO OXYGEN (OR) OXIDATIVE CORROSION.

ANS:- Oxygen present in the atmosphere, reacts with the surface atoms of the metals to form respective metal oxide (which is unwanted). Due to this a film of metal oxide is formed on the metallic surface. The extent of corrosion depends upon the nature of the metal oxide formed on its surface.

☺ Mechanism of Oxidative Corrosion: This mainly takes place in following steps.

- i) Physisorption of O_2 :- Due to Van Der Wall's forces of attraction, O_2 molecules get adsorbed on the surface of the metal. This is a surface phenomenon.
- ii) Chemisorption of O_2 molecule:- The oxygen is an electro-negative element and the metals are electro-positive in nature. Therefore, electrons get transferred from metal atoms to oxygen and formation of oxide ions takes place. The electrons required for the ion formation are taken from the metallic surface atoms. $\text{O}_2(\text{g}) + 4 \text{e}^- \longrightarrow 2 \text{O}^{2-}$. As a result, a chemical bond is formed between metal atoms/ions and oxide ions. This chemisorption continues till uni-molecular layer of metal oxide is formed on the metal surface completely.
- iii) The metal cations combine with oxide ions to form metal oxide. In this way, metal oxide is formed on the metallic surface.



- ☺ The thickness of the metal oxide film formed is usually less than $300 \text{ } \text{\AA}$.
- ☺ If the thickness of the metal oxide film is greater than $300 \text{ } \text{\AA}$, it is called Scale.
- iv) Above reactions can be represented as under:-
- a) $2 \text{M} \longrightarrow 2 \text{M}^{+n} + 2n\text{e}^-$. (Oxidation)
- b) $n/2 \text{O}_2 + 2n\text{e}^- \longrightarrow n\text{O}^{2-}$. (Reduction)

20) THE TYPES OF OXIDE FILMS FORMED ON THE METALS SURFACE DUE TO CORROSION.

The types or the nature of the oxide film formed on the metallic surface are:-

- a) Stable Oxide film,
- b) Unstable Oxide film
- c) Porous Oxide film and
- d) Volatile Oxide film.

21) PILLING-BEDWORTH RATIO (PBR).

- ☺ The ratio of the volume of the oxide film formed on the metal surface to the volume of the metal involved in the formation of that oxide is called Pilling-Bedworth Ratio.

$$\text{Pilling - Bedworth Ratio (PBR)} = \frac{\text{Volume of the metal oxide formed}}{\text{Volume of the metal involved in the formation of that oxide}}$$

- ☺ The value of PBR can predict the nature of the oxide film formed.
- ☺ Following table gives idea about the PBR values and the nature of the oxide film formed.

| PBR > 1 (Examples) | PBR < 1 (Examples) |
|--|--|
| In such cases, the oxide film formed is stable, non-porous and protective. | In such cases, the oxide film formed is porous and non-protective in nature. |
| i) $\text{Al}_2\text{O}_3 : \text{Al} = 1.28$ | i) $\text{Na}_2\text{O} : \text{Na} = 0.57$ |
| ii) $\text{Ag}_2\text{O} : \text{Ag} = 1.59$ | ii) $\text{CaO} : \text{Ca} = 0.64$ |
| iii) $\text{NiO} : \text{Ni} = 1.65$ | iii) $\text{MgO} : \text{Mg} = 0.81$ |
| iv) $\text{CuO} : \text{Cu} = 1.68$ | |
| v) $\text{FeO} : \text{Fe} = 1.77$ | |
| vi) $\text{Cr}_2\text{O}_3 : \text{Cr} = 2.07$ | |
| vii) $\text{Fe}_2\text{O}_3 : \text{Fe} = 2.14$ | |

- ☺ If, $\text{PBR} > 1$, the oxide film is Stable, Protective and non-porous.

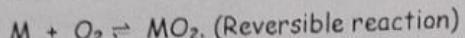
- ⌚ If PBR < 1, The oxide film is porous and non-protective.
- ⌚ If PBR is greater than 2, the oxide coating chips off and provides no protective effect.
- ⌚ If PBR is higher than 3.5 to 4, it develops cracks and allows oxygen of the atmosphere to come in contact of the metal & the metal continues to corrode

22) STABLE OXIDE FILM.

- ⌚ This film is made up of particles of oxide and has a compact packing. Such a type of film is tightly adhered to the surface of the metal.
- ⌚ In this the volume of the oxide film formed is greater than 1. i.e. its PBR > 1.
- ⌚ Such a type of film protects the metal from further corrosion & acts as a protective layer.
- ⌚ Usually the metals like Al, Sn, Cr, Cu etc.

23) UNSTABLE OXIDE FILM.

- ⌚ This type of film is observed on the surface of Noble metals like Ag, Au, Pt etc.
- In this case the oxidation of the metal is a reversible process. As soon as oxide of the metal is formed, it decomposes into respective metal and oxygen spontaneously.



- ⌚ Therefore, even if corrosion takes place the metal oxide due to its reversible nature gives back the metal. As a result the metal doesn't undergo corrosion.

24) POROUS OXIDE FILM.

- ⌚ This type of film is observed on the surface of Alkali and Alkaline earth metals. Some of the transition group elements such as iron also show this type of film.
- ⌚ The film formed in such cases is porous so that oxygen from the air diffuses through the film or cracks and come in contact with the metal surface.
- ⌚ The process continues till the metal is completely corroded.
- ⌚ It is usually found to take place in the cases in which PBR values are less than 1. (or much higher) Examples:- Na, K, Li, Ca, Fe etc.

25) VOLATILE OXIDE FILM.

- ⌚ In such cases the oxide formed is volatile in nature. As a result, oxide film is formed on the metal surface, it evaporates and the new metal surface gets exposed to the atmosphere. This process continues till all the metal gets exhausted.

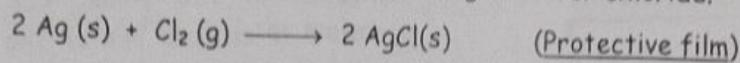
Example:- Molybdenum (Mo). In this, Mo gets oxidized to MoO_3 which is volatile in nature.

26) CORROSION CAUSED BY GASES OTHER THAN OXYGEN

- ⌚ Other gases like H_2 , CO_2 , H_2S , Cl_2 , SO_2 , SO_3 , NO_x (different Oxides of Nitrogen) also cause corrosion of the metals.
- ⌚ The degree of Corrosion due to these gases depends upon affinity of the metal and the gas, as well as protective nature of the film formed by the corrosion product.

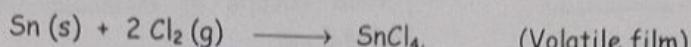
27) CORROSION CAUSED BY CHLORINE.

☺ Silver metal gets corroded by chlorine. When Chlorine reacts with Ag, the surface atoms of Silver get converted to form a protective film or coating of Silver chloride.



As a result further corrosion of Silver is stopped.

☺ But, in case of Tin (Sn) metal, the atmospheric Chlorine reacts with Tin atoms to form Stannic chloride which is highly volatile in the nature.



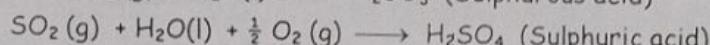
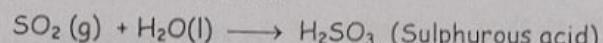
Because of its volatile nature, the SnCl_4 formed gets evaporated as soon as formed, leaving behind new Sn atoms undergo corrosion.

28) CORROSION CAUSED BY GASES LIKE HYDROGEN SULPHIDE, OXIDES OF SULPHUR, OXIDES OF NITROGEN

☺ In petroleum industry, due to burning of fossil fuels, large amount of H_2S is produced.

a) Corrosion due to Hydrogen sulphide:- This Hydrogen sulphide at higher temperatures corrode Iron, steel etc as under. $\text{Fe} + \text{H}_2\text{S(g)} \xrightarrow{(\Delta)} \text{FeS} + \text{H}_2\text{g(g)}$.

b) Corrosion due to oxides of Sulphur:- Due to burning of fossil fuels, large quantities of oxides of Sulphur like SO_2 are released in the atmosphere. These oxides create atmospheric pollution. These gases are cause of Acid rains.



In presence of these acids, the many metals & metallic equipments undergo corrosion.

c) Nitrogen in the atmosphere reacts with oxygen during lightning (which produces high temp) in rainy season. The chain of following reactions lead to formation of Nitric acid which is also highly corrosive to the metals & equipments.

- i) $\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \xrightarrow{(1210 \text{ to } 1700^\circ\text{C})} 2 \text{NO(g)}$,
- ii) $2 \text{NO(g)} + \text{O}_2(\text{g}) \xrightarrow{(1100^\circ\text{C})} 2 \text{NO}_2(\text{g})$,
- iii) $\text{NO}_2(\text{g}) + \text{O}_3(\text{g}) \longrightarrow \text{NO}_3 + \text{O}_2(\text{g})$,
- iv) $\text{NO}_2(\text{g}) + \text{iNO}_3(\text{g}) \longrightarrow \text{N}_2\text{O}_5$
- v) $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \longrightarrow 2 \text{HNO}_3$.

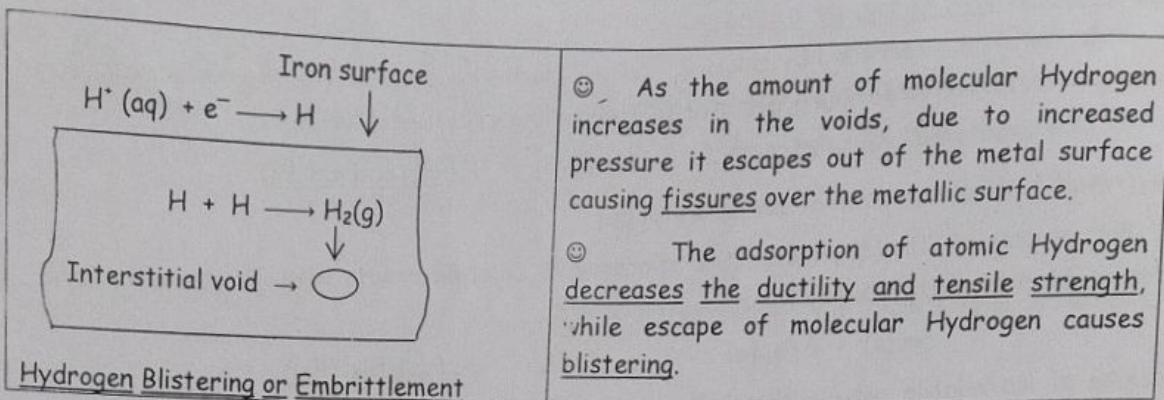
In this way, oxides of Sulphur and Nitrogen can lead to corrosive atmosphere.

29) CORROSION CAUSED BY HYDROGEN GAS. (OR) HYDROGEN EMBRITTLEMENT
(OR) HYDROGEN BLISTERING.

☺ Attack of Hydrogen on metal surface at Low Temperature is called "Hydrogen Embrittlement" or "Hydrogen Blistering". It can also cause "De-Carburisation".

☺ Under specific conditions, as a result of the chemical or electro-chemical action, atomic Hydrogen is formed. For example:- Aq solution of H_2S reacts with surface atoms of Fe to form atomic Hydrogen. $\text{Fe(s)} + \text{H}_2\text{S(aq)} \longrightarrow \text{FeS(s)} + 2 \text{H(g)}$.

☺ These atoms of H, diffuse through the surface of Iron & get accumulated in the Interstitial Voids. Here, such H atoms combine to form molecular Hydrogen. $\text{H} + \text{H} \longrightarrow \text{H}_2\text{g(g)}$.



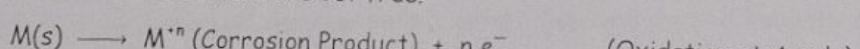
- ☺ As the amount of molecular Hydrogen increases in the voids, due to increased pressure it escapes out of the metal surface causing fissures over the metallic surface.
- ☺ The adsorption of atomic Hydrogen decreases the ductility and tensile strength, while escape of molecular Hydrogen causes blistering.

- **De-Carburisation**:- It is a type of Corrosion taking place due to the attack of Hydrogen gas on metals at High Temperature.
- ☺ Streams of hot gases coming out of Refineries, Cracking processes etc contain certain amount of gaseous Hydrogen.
- ☺ This Hydrogen gets adsorbed into metallic voids and then dissociates to form atomic Hydrogen. The atomic Hydrogen thus formed reacts with Carbon present in the steel, to form Methane (CH_4), at High Temperature. $\text{C}(\text{s}) + 4 \text{H}(\text{g}) \xrightarrow{\text{High Temp}} \text{CH}_4(\text{g})$.
- ☺ As a result, the Carbon in the steel decreases. Thus the process of removal of carbon of Carbide from the steel by the action of Hydrogen gas at high temperature is called "De-Carburisation".
- ☺ Due to "De-Carburisation", mechanical strength of the steel decreases.

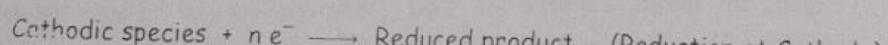
Wet or Electro-chemical or Immersion Corrosion

30) ELECTRO-CHEMICAL CORROSION AND ITS TYPES.

- ☺ Electrochemical Corrosion can be defined as :- "The corrosion caused by exposure of a metal in contact with an electrolytic solution" (which can be water, acid, base or a salt solution) the formation of an Electrochemical Cell or a Galvanic Cell takes place.
- ☺ Due to formation of Electrochemical or Galvanic cells, different Anodic and Cathodic areas are formed.
- ☺ The corrosion always takes place at Anodic areas which undergoes oxidation. At anode, the atom/s get oxidized and electrons are set free.



- ☺ Cathodic areas always undergo Reduction. The electrons released at Anode are accepted by Cathodes to form the reduced product.



- ☺ Depending upon the nature of the corrosive environment (type of electrolyte), it can be classified into following types:-
- a) Hydrogen Evolution Mechanism or b) Oxygen Absorption mechanism.

31) WET (ELECTROCHEMICAL) CORROSION BY HYDROGEN EVOLUTION MECHANISM.

☺ Wet (Electrochemical) Corrosion by Hydrogen Evolution mechanism takes place usually in rainy season, when there is more moisture in the air. During this season, there is a possibility of presence of H⁺ ions on the surface of the metal.

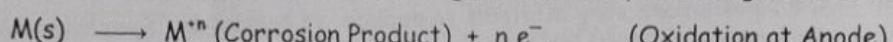
☺ The acidic gases like CO₂, SO₂ etc dissolve in the moisture present on the metallic surface give rise to H⁺ ions due to dissociation.

☺ The surface metal atoms act as Anodes & the region where H⁺ ions are present act as Cathodes.

☺ All the metals which are above "H" in Electro-Chemical series undergo this type of corrosion.

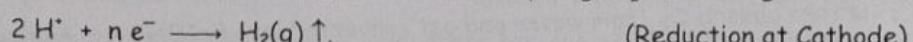
☺ Following Reactions take place during this:-

At Anode :- The metal atoms acting as Anode/s get oxidized by releasing some electrons.



The released electrons travel on the surface of the metal and reach the places where H⁺ ions are available.

At Cathode :- The region where H⁺ ions are present act as Cathodes. Here, The H⁺ ions accept the released electrons at Anode and get reduced to Hydrogen gas, which gets evolved.

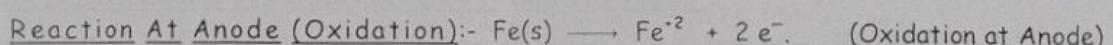


☺ As Hydrogen gas is evolved in this, it is called "Hydrogen Evolution Mechanism".

32) ELECTROCHEMICAL (WET) CORROSION BY OXYGEN ABSORPTION MECHANISM.

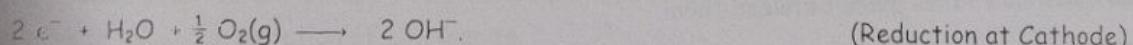
☺ Wet (Electrochemical) Corrosion by this mechanism/method, usually takes place when the metal is exposed to neutral H₂O or a neutral salt (NaCl) solution.

➢ When metal is exposed to neutral water :- Rusting/Corrosion of iron takes place in this way when it is in contact with or immersed in the neutral water. During this Fe atoms act as Anodes.



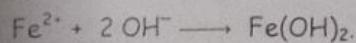
The released electrons flow towards the region where water is available. These regions where water is available act as Cathodes.

Reaction At Cathode (Reduction):- Here, the water molecules and the dissolved oxygen in it, accept these electrons and get reduced to hydroxyl (OH⁻) ions.



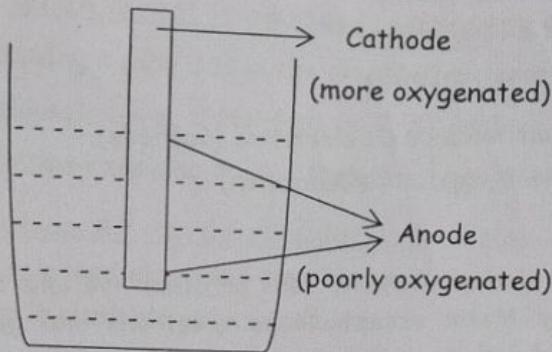
☺ It should be noted that, corrosion (Fe → Fe²⁺) takes place at Anode and OH⁻ ions are formed at Cathode. The Fe²⁺ ions being smaller in size, diffuse faster and go towards OH⁻ ions.

☺ The Fe²⁺ ions formed at Anode combine with these OH⁻ ions to form Fe(OH)₂.



The Fe(OH)₂ molecules further absorb O₂ from water and get converted into Fe(OH)₃ as under:- 2 Fe(OH)₂ + H₂O + $\frac{1}{2}$ O₂(g) → 2 Fe(OH)₃. (Yellow Rust, a corrosion product) The Corrosion product is formed at Cathode.

☺ As dissolved O₂ gas is absorbed in this mechanism, it is called "Oxygen Absorption Mechanism".



- ☺ Consider a Zinc rod dipped partially into aq solution of $ZnCl_2$.
- ☺ The area of the Zn rod which immersed under $ZnCl_2(aq)$, gets less supply of oxygen (which is due to dissolved oxygen only) and the area of the Zn rod which is at the boundary surface and above in the air gets more oxygen supply.

(DIFFERENTIAL AERATION CORROSION)

- ☺ This creates two regions on the Zn surface of varying concentration of oxygen. Due to this, a small potential difference is set up between two regions. This results in the formation of a Concentration Cell.
- ☺ As shown in the diagram, when a Zn rod is immersed into $ZnCl_2(aq)$ solution, the part of the Zn rod which is immersed gets less Oxygen supply and behaves as an Anode.
- ☺ The part of the Zn rod at the boundary surface and above in the air gets enough oxygen supply and acts as a Cathode.
- ☺ Reaction At Anode :- $Zn(s) \longrightarrow Zn^{2+} + 2 e^-$. (Oxidation)
- These electrons travel towards Cathodic region.
- ☺ Reaction At Cathode :- $2 e^- + H_2O + \frac{1}{2} O_2(g) \longrightarrow 2 OH^-(aq)$. (Reduction)
- ☺ Thus the Metal (Zinc) in the Anodic region gets corroded.
- ☺ Example:- i) A drop of a water or a salt solution on a metal surface, can lead to this type of corrosion.

36) "Crevice Corrosion".

- ☺ "Corrosion occurring within Crevices* & other shielded areas of metal surface exposed to corrosive medium like:- dirt, sand particles, other solids, water, presence of some electrolyte etc is called Crevice Corrosion".

[Crevice* :- The meaning of Crevice is a fracture or a fissure or a crack as it develops on the surface of a rock, bone etc. In this topic we can consider a Crevice to be a narrow fissure or a fracture developed on the metal surface.]

- ☺ It is a Wet Corrosion and a type of Concentration Cell corrosion.

Illustration:- The inner part of the Crevice is less oxygenated and therefore, acts as an Anode. While outer part is more oxygenated and so behaves as a Cathode. As a result, following reactions take place:-

- ☺ Reaction At Anode :- $M(s) \longrightarrow M^{2+} + 2 e^-$. (Oxidation)

These electrons travel and towards Cathodic region.

- ☺ Reaction At Cathode :- $2 e^- + H_2O + \frac{1}{2} O_2(g) \longrightarrow 2 OH^-(aq)$. (Reduction)

The M^{2+} ions formed at Anode and combine with OH^- ions to form $M(OH)_2$, a corrosion product.

- ☺ Thus the Metal in the Anodic region gets corroded.

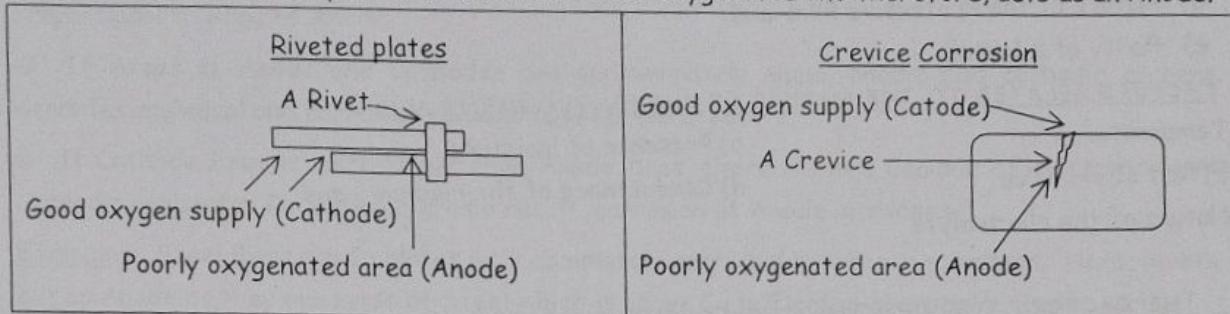
- ☺ Crevice Corrosion is intense in the medium containing Chloride ions.

When oxygen supply gets finished (gets depleted) no further reduction oxygen takes place.

Example:- A riveted* plate section (riveting of a metal & iron or steel) undergoes Crevice corrosion. [A Rivete* :- It is a metal pin passing through the holes in the two or more metal plates which are to be held together or joined. Usually all the metallic buttons of a Jeans are riveted.]

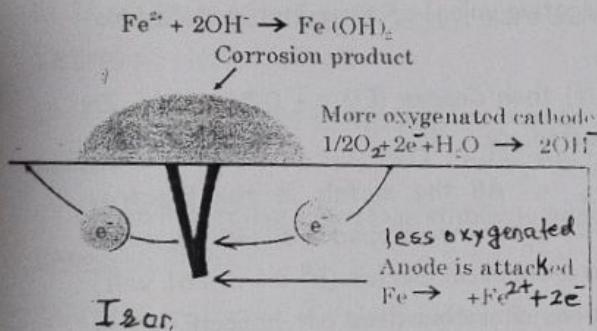
It is a Wet Corrosion and a type of Concentration Cell corrosion.

Illustration:- The inner part of the Crevice is less oxygenated and therefore, acts as an Anode.



37) "Pitting Corrosion".

(A Pit is a hole or a depression or a cavity, in this case, on the metallic surface)



PITTING CORROSION: "Corrosion caused by the development of pit/s on the surface of a metal is called Pitting Corrosion".

Pitting corrosion is extremely localized attack resulting in the formation of cavities or holes around which metal is relatively unattacked.

Pits usually grow downward from the horizontal surface of the metal.

Due to formation of pit/s, the protective layer breaks down at those places. As a result, the metallic atoms in that region get exposed to atmosphere, act as Anodes and undergo corrosion.

The protected part (where pitting doesn't take place, act as Cathode).

Due to relatively very small Anodic region (pits), the rate of corrosion also increases.

Reaction At Anode :- $M(s) \longrightarrow M^{2+} + 2 e^-$. (Oxidation)

These electrons travel and towards Cathodic region.

Reaction At Cathode :- $2 e^- + H_2O + \frac{1}{2} O_2(g) \longrightarrow 2 OH^-(aq)$. (Reduction)

The M^{2+} ions formed at Anode and combine with OH^- ions to form $M(OH)_2$, a corrosion product.

This type of corrosion accelerates in presence of chloride ions other electrolytes which might get accumulated in those pits.

Example:- Corrosion of stainless steel by sulphuric acid or containing ferric chloride.

FACTORS AFFECTING RATE OF CORROSION

38) Factors affecting/influencing the corrosion rate & their Classification.

The Corrosion Rate mainly depends upon following factors:-

- A) Factors related to the nature of the metal.
 - B) Factors related to nature of the environment and
 - C) Factors related to nature of the corrosion product.
- ☺ FACTORS RELATED TO THE NATURE OF THE METAL ARE FURTHER CLASSIFIED INTO :-
- a) Position of the Metal in the Electro-Chemical or Galvanic series,
 - b) Hydrogen Overvoltage or Overpotential,
 - c) Relative Areas of Anode and Cathodes,
 - d) Nature of the Protective Film and
 - e) Purity of a Metal.
- ☺ FACTORS RELATED TO THE NATURE OF THE ENVIRONMENT ARE:-
- a) Temperature,
 - b) Presence of moisture,
 - c) Effect of pH value,
 - d) Conductance of the medium and
 - e) Nature of the electrolyte.

39) THE FACTORS INFLUENCING THE CORROSION RATE WHICH ARE RELATED TO THE NATURE OF THE METAL THEY ARE:-

a) POSITION OF THE METAL IN THE ELECTRO-CHEMICAL OR GALVANIC SERIES:-
 Higher is the position (i.e. higher is the magnitude of negative value) of the metal in Electro-Chemical or Galvanic Series, faster it corrodes.

Example:- Zinc is higher in position ($E^0 = -0.761$ volt) than Copper ($E^0 = +0.34$ volt). Zn corrodes faster than Copper when placed in the same electrolyte.

b) HYDROGEN OVERVOLTAGE OR OVERPOTENTIAL :- All the metals in the Electro-Chemical Series, which are above Hydrogen should liberate H_2 gas when dipped in dil HCl solution.
 ☺ For example Zinc which is above Hydrogen in Electro-Chemical Series ($E^0 = -0.761$ volt) should liberate H_2 gas when placed in dilute HCl solution. But this does not happen. It is observed that, when extra potential of + 0.70 volt is applied, liberation of H_2 gas is observed practically. i.e. H_2 is evolved at ($-0.761 + 0.70 = -0.061$ volt)

☺ "This potential difference between the potential at which liberation of H_2 gas is observed and the Theoretical Potential is called Hydrogen Overvoltage or Over-potential".

☺ Following table give the idea about the Overpotential of different metals.

| Metal | Theoretical value at which H_2 gas should evolve (E^0) (volt) | Extra/over potential needed (volt) | Potential at which H_2 is practically evolved |
|----------|---|------------------------------------|---|
| Platinum | + 1.20 v | + 0.12 v | 1.32 v |
| Silver | + 0.797 v | + 0.29 v | 0.817 v |
| Copper | + 0.337 | + 0.25 v | 1.097 v |
| Hydrogen | 0.00 v | ----- | ----- |
| Lead | - 0.13 v | + 0.60 v | 0.47 v |
| Tin | - 0.14 v | + 0.50 v | 0.36 v |
| Nickel | - 0.23 v | + 0.25 v | 0.02 v |
| Iron | - 0.44 v | + 0.27 v | - 0.71 v |
| Zinc | - 0.761 v | + 0.70 v | - 0.061 v |

☺ In general it is found that, higher is the value of over-potential, less is the corrosion tendency of a metal.

c) RELATIVE AREAS OF ANODE AND CATHODES:- Corrosion of a metal mainly depends upon the relative areas of Anode and Cathodes.

☺ It can be given by following equation:- Rate of Corrosion $\propto \frac{\text{Area of Cathode}}{\text{Area of Anode}}$

In other words, Corrosion Rate is directly proportional to area of Cathode and is inversely proportional to Area of Anode.

☺ If Areas of Anode and Cathodes are approximately equal, anodic and cathodic current densities are equal and corrosion does not get accelerated.

☺ If Cathode Area is much larger than Anode Area, there is more demand of electrons from Cathodic region for Reduction and as a result, corrosion at Anode increases.

Example:- Steel Rivets in Cu plates gets completely corroded in corrosive medium. Here, Rivets act as Anode as they are made of Steel which is above Cu in Electro-chemical/Galvanic series.

d) NATURE OF THE PROTECTIVE FILM:- Depending the nature of the protective film, the corrosion stops or continues.

☺ If the Protective Film is Porous, more oxygen diffuses & corrosion continues.

Examples:- Na_2O , Li_2O etc.

☺ If the Protective is non-porous, oxygen cannot diffuse and corrosion decreases to a large extent. Examples:- PbSO_4 , FeO , Fe_2O_3 , Al_2O_3 etc.

☺ If the Protective Film is un-stable, it decomposes back to Metal and corrosion continues.

Example:- PtO_2 .

☺ If the Protective is Volatile, it evaporates as soon as it is formed and corrosion continues.

Example:- MoO_3 .

[Also Refer Q21 for more details on this.]

e) PURITY OF A METAL:- Pure metals resist corrosion than impure metals.

| ☺ Presence of impurities accumulated in certain areas or regions of a metal can cause potential difference and so are the sources of corrosion. Following table gives the idea about the Rate of corrosion of a metal and presence of impurities. | Purity of Zinc metal | Relative Corrosion Rate |
|---|----------------------|-------------------------|
| | 99.999% | 1 |
| | 99.99% | 2650 |
| | 99.95% | 5000 |

40) THE FACTORS INFLUENCING THE CORROSION RATE WHICH ARE RELATED TO THE NATURE OF THE ENVIRONMENT:- Factors affecting corrosion, which depend on the Environment are discussed below.

A) TEMPERATURE:- Rates of almost all chemical reactions increase with the increase in the temperature. In the same way Rate of Corrosion also increases with the rise in temperature in corrosive environment.

☺ This is due to increase in the mobility of the reacting ions.

Example:- Steel corrodes faster in boiling sulphuric acid than in cooler.

B) PRESENCE OF MOISTURE:- In general, Corrosion Rate increases with increasing moisture in the atmosphere. Moisture provides oxygen and other gases provide electrolyte, which helps in accelerating the setting up of Electro-Chemical of Galvanic Cells.

C) EFFECT OF pH VALUE OF THE ELECTROLYTE :- Generally it can be said that,

- ☺ Acidic environment ($\text{pH} < 7$) is more Corrosive than Alkaline environment ($\text{pH} > 7$).
- ☺ Zinc gets corroded in Acidic medium but undergoes less corrosion between pH 10 to 11.
- ☺ Many metals are easily attacked by Acids but not by Alkalies.
- ☺ Iron undergoes corrosion in highly alkaline range of $\text{pH} = 12$ to 14, causing Caustic Embrittlement. [Later on discussed in Pourbaix Diagram.]

D) CONDUCTANCE OF THE MEDIUM:- Many times, stray current is leaked from an electric circuit and flows through metallic structure into the earth.

- ☺ The points at which current leaves the metallic surface act as Anode and it gets dissolved due to corrosion.
- ☺ Such corrosion is found to be taking place faster in moist soil containing moisture and other electrolytes. The moisture present in the soil increases conductance of the medium and as a result, underground corrosion of a metal increases.

E) NATURE OF THE ELECTROLYTE:- The electrolyte itself is a source of potential difference. The solution potential of a metal depends on the type of the ions and their concentrations in the solution. So, change in the concentration of electrolyte will change the electrode potential difference and in turn will affect the corrosion of a metal.

- ☺ For example:- i) Crevice corrosion is intense in presence of chloride ions.
ii) Stray current corrosion is more in the moist soil containing dissolved electrolytes.

41) EXPLAIN THE FACTORS AFFECTING CORROSION RELATED TO THE CORROSION PRODUCTS.

- ☺ Factors affecting corrosion, which depend on the nature of the corrosion product are:-
- i) The corrosion product forms a protective barrier either around Anode or Cathode or in the region between Anode and Cathode. As a result, corrosion rate decreases.
- ii) Even if, the Anode and Cathode regions are far away, the corrosion rate does not get affected.

42) PASSIVITY OF THE METALS.

- ☺ [Passivity means to become un-reactive or to remain unchanged]
- ☺ Passivity is defined as "The phenomenon in which a metal or an Alloy exhibits outstanding higher corrosion resistance than its position in the Electro-chemical or Galvanic Series".
- ☺ Passivity is a result of formation of a very thin but protective invisible film on the surface of the metal or an alloy, which makes metal or alloy more Noble or less reactive.
- ☺ The uni-molecular layer of oxide or some other compound of a metal is formed on its surface, which is self-repairing.

☺ Examples:- i) Titanium, Aluminium, stainless steel alloys which contain Chromium are passive in oxidizing environment.

- ii) Lead when immersed in conc H_2SO_4 , develop a film of $PbSO_4$, which makes the Lead passive.
- iii) Aluminium when comes in conc HNO_3 develops a layer of Al_2O_3 which makes it passive.
[But in dilute HNO_3 rapid corrosion of a metal is observed]
- iv) Similarly, a piece of iron/steel dissolves in dilute HNO_3 (i.e. gets corroded) but, in concentrated HNO_3 , it gets oxidized & a thin protective oxide layer is formed over its surface. This phenomenon is called "Passivation".

43) THE POURBAIX DIAGRAM AND ITS USES.

- ☺ A diagrammatic system showing the effect of both Potential and pH has been evolved by Pourbaix. That is called Pourbaix Diagrams.
- ☺ Pourbaix diagrams show the effect of pH on the Electrode Potential of the electrodes.
- ☺ Redox potentials are useful in predicting corrosion behavior of metals.
- ☺ The electrode potentials of a system in which the electrolytic concentration is not 1M, can be calculated by using Nernst equation.

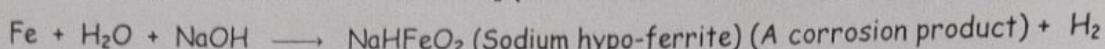
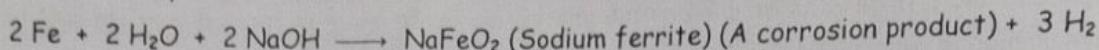
$$E = E^0 + \frac{R \cdot T}{n \cdot F} \log \frac{[\text{Oxidised Species}]}{[\text{Reduced Species}]} = E^0 + \frac{0.092}{n \cdot F} \log \frac{[\text{Oxidised species}]}{[\text{Reduced species}]}$$

Where, E = Half cell potential of an electrode, E^0 = Standard Half Cell potential of an electrode, F = Faraday's constant & n = number of electrons getting exchanged in the rxn.

- ☺ Following is a Pourbaix diagram for Fe-H₂O system.
- ☺ Different metals/Alloys have different diagrams.
- ☺ E-pH Diagram for Fe-H₂O system, Potential is on Y-axis and pH values are on X-axis.
 - ☺ Let us imagine a vertical line on Y-Axis at pH = 7 and a horizontal line on X-Axis at 0.0 volt.
 - ☺ In the region from the bottom up to potential = - 0.6 v, Fe exists in most pure state. The corrosion cannot take place in this region. Thus it can be said that, in Region enclosed in A,B,C,D,E & F corrosion does not take place. This is due to Cathodic Protection/Passivity.
 - ☺ In the region below pH 7 and above potential = - 0.6 volt, the corrosion starts. In this region Fe^{2+} exists. If the potential is increased further, rapid corrosion takes place.
- ☺ If the potential is increased further, Ferric Hydroxide is formed as a corrosion product. When pH is below 4, Ferric Oxide (Fe_2O_3) is formed and if the pH above 4, Ferric hydroxide ($Fe(OH)_3$) is formed.

☺ The Region enclosed in B,C,H & I is called "Region of Stability" or "Stable Region" Here, formation of Fe(OH)_2 takes place which forms a dense protective film over Iron surface and prevents it further corrosion.

☺ In the region: C, D, G & H, where, pH is very high (12 to 14) and electrolyte is highly Alkaline, Fe undergoes "Caustic Embrittlement". In this Formation of Ferrite ion (FeO_2^-) or hypo-ferrite ion (HPO_2^-) takes place as under:-



☺ USEFULNESS OF THE POURBIAX DIAGRAMS:- With help of Pourbax diagram:-

- It is possible to predict spontaneous direction of a reaction.
- Composition of the corrosion product can be estimated or predicted.
- The needed Environmental changes by which, corrosion can be prevented or reduced can also be predicted.

CORROSION AND CONTROL

- ☺ It is necessary to learn about Corrosion prevention and its control.
- ☺ We know that, the extent or corrosion or rate of corrosion depends upon following main factors:-
- a) Nature of the Metal,
- b) Nature of the Environment and
- c) Design of the specimen under study.
- ☺ It is practically impossible to stop or avoid corrosion entirely. But its rate can be decreased.
- ☺ Rate of corrosion can be decreased to a large extent by following methods:-
- i) Anodic Protection:- In this, the reaction taking at Anode is retarded/avoided.
- ii) Cathodic Protection:- In this, the reaction taking at Cathode is retarded/avoided.
- iii) By formation of an Alloy,
- iv) Coating the metal by other metal.
 - i) If other metal is more reactive than base metal, it is called Anodic Coating.
 - ii) If other metal is less reactive than base metal, it is called Cathodic Coating.
- v) Conditioning of Corrosive Environment which mainly includes:-
- i) Removal of oxygen from the electrolyte,
- ii) Modification in the pH value of electrolyte, use of inhibitors,
- iii) Change in the temperature,
- vi) By electrically isolating the material using insulators,
- vii) By choosing metals which are close to each other in electro-chemical series.
- viii) By Metal Cladding, in which the base metal (to be protected) is firmly bonded/sandwiched between thin sheets of other metal etc.

CATHODIC AND ANODIC PROTECTION

45) CATHODIC PROTECTION.- "When a Metal or an alloy is forced to behave as a Cathode by using some method, it is called Cathodic Protector".

☺ Cathodic Protection is done by one of the two methods:-

- i) By External DC Power supply which is also called "Impressed current Method" or
- ii) By appropriate Galvanic coupling which is also called "Sacrificial Anode Method".

46) ANODIC PROTECTION:- "When a protective film of metal compound (usually oxide) is formed on the metal or alloy surface by externally applying DC anodic current to the metal or an alloy".

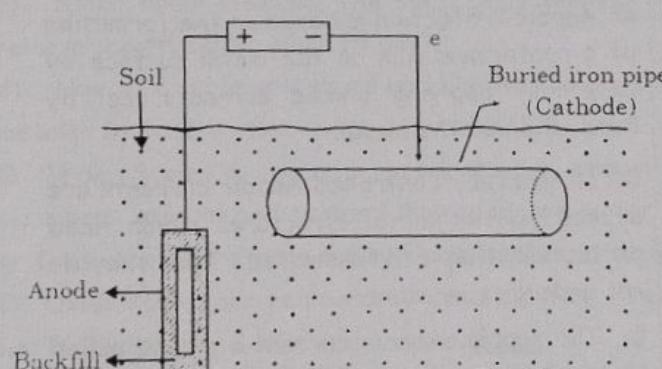
47) CATHODIC PROTECTION BY IMPRESSED CURRENT METHOD".

☺ "When a Metal or an alloy is forced to behave as a Cathode by using some method, it is called Cathodic Protection".

☺ The science of Cathodic Protection was first developed by Sir Humphry Davy in 1924. During those days, the body of War ships used to be made of Copper. The outer copper body of those ships was protected from corrosion by sea water by using Iron Anodes.

☺ CATHODIC PROTECTION BY IMPRESSED CURRENT METHOD:- It is also called, Cathodic protection by external power supply.

☺ In this method, external DC power supply is connected to underground pipe or a tank which is to be protected.



Impressed current cathodic Protection

☺ The negative (-ve) terminal of the DC source, is connected to the tank and Positive (+ve) end is connected to a Graphite electrode, which is then immersed into the corroding medium/ground.

☺ The Anode is surrounded by backfill which consists of Gypsum or bentonite (An Absorbent Clay) to improve electrical contact between Anode and surrounding soil.

☺ The current from the Anode passes through the electrolyte and Corrosion of Cathode is suppressed.

☺ This method is economical, where electric power is cheap.

47) CATHODIC PROTECTION BY "SACRIFICIAL ANODE METHOD".

CATHODIC PROTECTION:- "When a Metal or an alloy is forced to behave as a Cathode by using some method, it is called Cathodic Protection".

☺ In this method, the metallic structure (pipe or tank etc) to be protected from corrosion is made to act as Cathode by electrically connecting it with other metal which is more reactive or has a higher negative potential.

◎ The Anodic metal gets corroded while, the Cathodic metal structure gets protection from corrosion.

◎ Examples:-

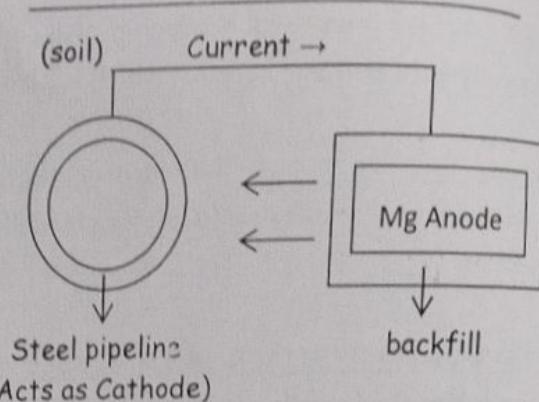
a) If a steel pipe-line or a steel tank is to be protected from corrosion, it is connected to Magnesium metal which acts as Anode with respective steel, being more reactive.

b) In a domestic water heater, the steel tank in which water gets stored & heated, needs protection from corrosion. Therefore, a Magnesium rod is inserted in it tank which acts as Anode and forces Steel tank to behave as Cathode.

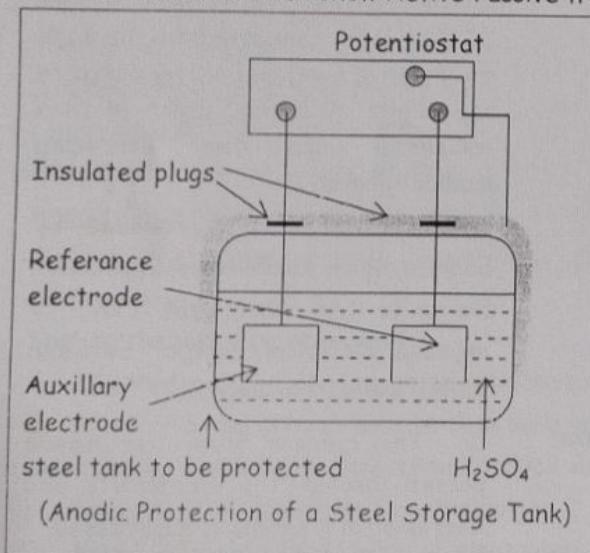
◎ Selection of Anodic material is based on engineering and economic considerations.

◎ The examples of the materials/metal used as Sacrificial Anodes are:- Magnesium, Steel, Graphite, Silicon, Iron, Zinc, Graphite etc. Amongst all of them most widely used is Mg.

◎ Its installation cost is very low but, operational cost is very high.



48) ANODIC PROTECTION:- This method of protection of a metal or an alloy is possible only for those metals which show Active-Passive transition or behavior.



◎ Anodic Protection is based on the formation of a protective film on the metal surface by externally applying anodic currents. i.e. by Passivation of the metal.

◎ If carefully controlled Anodic currents are applied to the metal structures which need protection, they are Passivated. Thus they do not undergo corrosion.

◎ The supply, Anodic current a device called "Potentiostat" is used. The potentiostat maintains the metal at a constant potential with respect to Reference electrode.

◎ Out of the Three terminals of the Potentiostat,

One is connected to the metal to be protected (tank, pipe etc). Other one to Auxiliary Cathode (Platinum) and the third one is connected to Reference electrode (Calomel Electrode).

The Potentiostat maintains a constant potential between the metal structure (to be protected) and Reference electrode.

◎ Anodic Protection is applicable only to those metals or Alloys which show Active-Passive behavior.

◎ It requires low current and is applicable in extremely corrosive environment also.

◎ Its installation cost is very high but operational cost is low.

PROTECTIVE COATINGS

- ☺ The surface of Engineering Materials (metals) can be protected by covering it with metallic, organic or inorganic materials.
- ☺ The coating material should possess following properties:-
- a) It should provide a satisfactory barrier between the metal and environment.
- b) The coating should impart mechanical properties, thermal insulating properties and oxidation resistance to the protected surface of the metal.
- c) The effectiveness of these coatings depends upon their thickness, type of the environment and the required degree of protection.
- d) Coatings can also give decorative appearance to the metal.

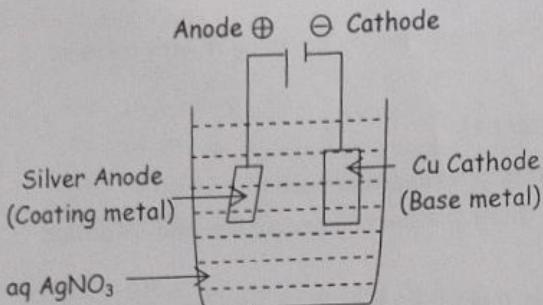
49) SURFACE TREATMENT TO BE GIVEN TO A METAL BEFORE COATING.

- ☺ Before application of any protective coating, the surface of the metal should be cleaned so that excellent surface adhesion is obtained.
- ☺ Method of Surface Treatment before Coating:- It is done in following order:-
- a) First, organic fatty substances, Fats, oils etc are removed by cleaning it by some Organic Solvent like Naptha, Toluene, Xylene, Actone etc.
- b) Metal surface is then cleaned by steam & hot water containing wetting agents like alkalies.
- c) After alkali cleaning, the surface is washed by water and then by 1% Chromic acid to remove the traces of alkali (if any).
- d) Now, the surface is dried and Oxides, Scales and any other corrosion product formed over metallic surface is removed by Mechanical Cleaning.
- ☺ Oxide, Scales & corrosion products are removed by using bristle brush, detergent, knife scrappers, grinder and cutter followed by hot water.
- ☺ Loose scales are removed by flame heating and mechanical brushing.
- ☺ Oxide scales are removed by sand blasting. During sand blasting, the mixture of sand and hot air under pressure is used as a blast.
- ☺ For complete removal of scales, metals are immersed in various pickling solutions. Acid pickling is more convenient method for removal of scales than mechanical cleaning and sand blasting.
- ☺ The type of the pickling solution to be used depends upon the type of the scales to be removed. e.g. Plain carbon steel is pickled by warm & dilute H_2SO_4 , then cold HCl with inhibitor and finally with alkaline solution of Na_2CO_3 or lime.

50) PROCESS OF ELECTROPLATING METHOD FOR PROTECTING A METAL.

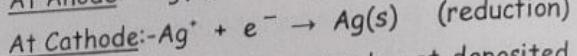
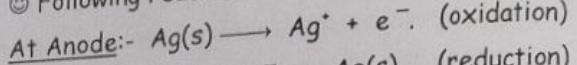
- ☺ The metal to be protected is called a Base Metal and the metal to be coated on the base metal is called Plating metal.
- ☺ In this method, the Base metal to be coated by other metal is made to act as a Cathode.
- ☺ The plating metal (metal whose coating is to be done) is made to act as an Anode.
- ☺ The electrolyte used is a solution of a salt of the coating metal.

Illustration:- If a Cu article is to be coated by Silver, then the Copper article is used as a Cathode and a Silver rod/plate is used as an Anode. The electrolyte used is aq AgNO_3 .



④ DC type of Electric current is passed through the electrolyte and electrodes as shown in the diagram.

④ Following reactions take place.



④ Thus Ag atoms from Anode get deposited on Copper Cathode and Silver plating is done.

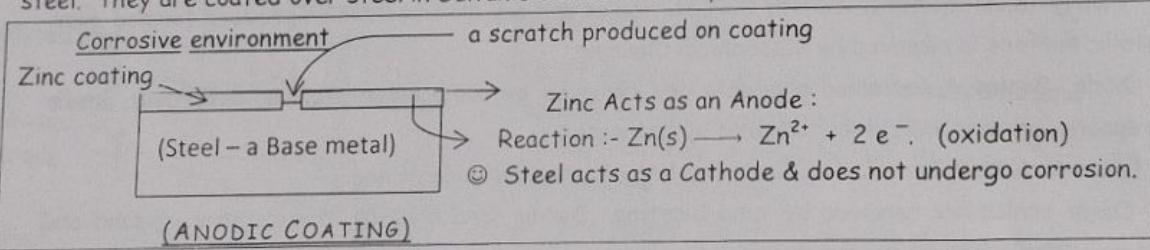
- ④ Electroplating is one of the most important methods of applying metallic coatings.
- ④ With this method, the plating of base metals by coating of Zinc, Nickel, Tin, Iron, Copper are frequently used.
- ④ Sometimes, Plating by Gold, Silver, Platinum is also done.

51) THE DIFFERENT TYPES OF METALLIC COATINGS.

④ Depending upon the position of the Coating Metal in the electro-chemical series, with respect to the Base metal, the coatings are divided into two types:-

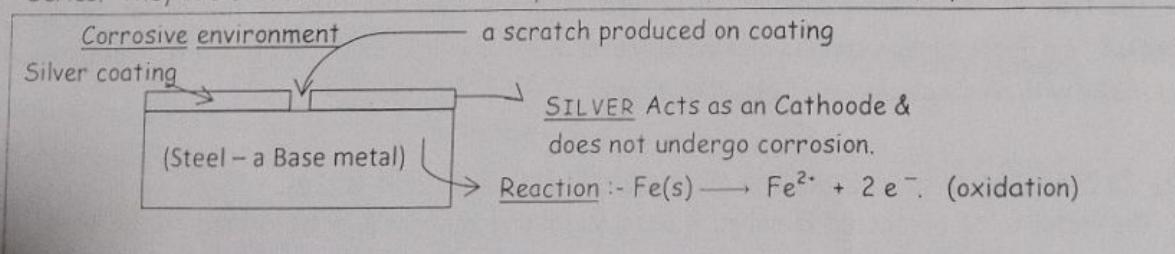
a) Anodic Coating and b) Cathodic Coating.

a) ANODIC COATINGS:- In Anodic Coatings, the Coating Metals are Anodic with respect to the Base Metal. For example:- Aluminium, Zinc, Cadmium have higher electrode potential than steel. They are coated over steel in Galvanic Series. So they are used to coat steel Anodically.



b) CATHODIC COATING :- In this, the Coating Metals are Cathodic with respect to the Base Metal. i.e. Coating metals are more noble metals with respect to base metals.

For example:- Gold, Copper, Nickel Silver have lower electrode potential than steel in Galvanic Series. They are coated over steel. So they are used to coat steel Cathodically.



- ④ Only pore free & continuous coatings can give protection to the base metal. If pores or a scratch is present on the base metal, it undergoes corrosion. The coating remains intact.

52) DIFFERENTIATION BETWEEN ANODIC AND CATHODIC COATINGS.

| Anodic Coatings / (Sacrificial Coatings) | Cathodic Coatings |
|--|---|
| <p>1) In this the Coating Metal acts as Anode & the Base metal (metal to be protected) acts as Cathode. It is also called <u>Sacrificial Coating</u>.</p> <p>2) The coating metal lies higher in the Electrochemical or Galvanic Series compared to the base metal (which is to be protected).</p> <p>3) The Coat metal acts as Anode & undergoes corrosion and the base metal gets protected, if any Galvanic cell formation takes place due to a scratch or bend or stress etc.</p> <p>4) This type of coating is preferred over Cathodic coating.</p> <p>5) <u>Example:-</u> i) Zinc coating over Steel. (It is Galvanized iron or steel)</p> | <p>1) In this the Coating Metal acts as Cathode & the Base metal (which is to be protected) acts as Anode.</p> <p>2) The coating metal lies lower in the Electrochemical or Galvanic Series compared to the base metal (which is to be protected).</p> <p>3) The Coat metal acts as a Cathode & so does not undergoes corrosion and the base metal gets corroded, if any Galvanic cell formation takes place due to a scratch or bend or stress etc.</p> <p>4) This type of coating is not preferred over Anodic coating.</p> <p>5) <u>Example:-</u> i) Tin coating over Steel. (It is called Tinned Steel or Iron)</p> |

EXERCISE QUESTIONS FOR PRACTICE

- 1) Define Corrosion.
- 2) Explain how corrosion and Metallurgy are opposite processes.
- 3) Explain giving examples, Dry Corrosion.
- 4) Write a short note on:- Hydrogen Embrittlement or Hydrogen Blistering.
- 5) What is Atmospheric corrosion? Explain giving different examples with reactions.
- 6) Explain corrosion due to following gases:- a) O₂, b) Cl₂, c) SO₂, d) diff. oxides of Nitrogen.
- 7) What is Wet corrosion? State its types.
- 8) Discuss mechanism of corrosion of a metal due to oxygen.
- 9) Name the different types of Oxide films than can be formed on the metallic surface as a corrosion product.
- 10) Write a short note on "Pilling-Bedworth Ratio".
- 11) Write a short note on "Stable Oxide Films", giving suitable examples with their PBR values.
- 12) Write a short note on "Un-Stable Oxide Films", giving examples with their PBR values.
- 13) Write a short note on "Porous Oxide Films", giving suitable examples with their PBR values.
- 14) Write a short note on "Volatile Oxide Films". Give an example.
- 15) What is electrochemical corrosion? Explain its mechanism by Hydrogen evolution method.
- 16) What is Wet Corrosion? Explain its mechanism by Oxygen absorption method.
- 17) Distinguish between: Hydrogen Evolution and Oxygen Absorption Mechanisms of corrosion.
- 18) Explain Galvanic Corrosion giving an example.
- 19) What is Concentration Cell Corrosion? State its different types.

- 20) What is Concentration Cell Corrosion? Explain Differential aeration corrosion giving suitable illustration with the diagram and reactions involved in it.
- 21) Write a short note on:- Pitting and Crevice corrosion.
Explain the mechanism with the diagram and reactions taking place in it.
- 22) Discuss the Factors affecting the Rate of corrosion, which depend upon the Nature of the metal.
- 23) Discuss the Factors affecting the Rate of corrosion, which are related to the Nature of the environment.
- 24) Write a short note on "Passivity". Explain giving some examples.
- 25) Name the metals which usually undergo the formation of Stable Oxide Films.
- 26) Which metals have a tendency to form Porous oxide film? Why?
- 27) Explain giving reaction/s the corrosion due to hydrogen sulphide gas.
- 28) What is Pourbaix diagram? Explain in detail, what information can be obtained from it with the help of a well labeled diagram.
- 29) What are the characteristics features of a good protective coating? How is it superior to other methods for corrosion control?
- 30) Explain Chemisorption.
- 31) Enlist the types of oxide films formed due to corrosion and explain any two of them.
- 32) Why a metal doesn't get affected by an unstable film?
- 33) Explain corrosion due to Nitrogen and its compounds.
- 34) What is Hydrogen Embrittlement? Explain in details its process.
- 35) What is Electro-chemical cell? Give their types.
- 36) Explain Galvanic Cell with the cell reactions and a well labeled diagram.
- 37) What is standard electrode potential? Give its equation and meaning of each term used in it.
- 38) Explain Nernst equation giving the meanings of the terms in it.
- 39) What is electro-chemical series? Give its applications.
- 40) What is Galvanic Series? Give its applications.
- 41) How Galvanic Series is advantageous over Electro-chemical series?
- 42) What is Hydrogen overpotential? How it is related to corrosion tendency of a metal?
- 43) Explain with diagram, Immersion Corrosion.
- 44) What is Differential Aeration process? What it leads to?
- 45) How the position of a metal in the Galvanic Series affects its rate of corrosion?
- 46) Give the relation between Galvanic corrosion and the relative areas of Anode and cathode.
- 47) How purity of a metal affects Corrosion? Explain giving example.
- 48) Differentiate between Galvanization and Tinning.
- 49) Why the rusting of iron is faster in saline water than in pure water?
- 50) Describe in detail, how the Cathodic Protection works? Which of the following metal/s can prevent iron from rusting Cathodically? Mg, Zn, Cu, Pb. Why?
- 51) A steel can be protected by coating it with Zinc. Explain in detail how it prevents corrosion?
- 52) A buried iron pipe-line is protected by Magnesium bars which are connected by a copper wire. Answer following:-
- a) What acts as Anode?
 - b) What acts as a Cathode?
 - c) Give the reaction at Anode
 - d) Give the reaction at Cathode.

- 53) Give the principles of Anodic Protection.
 54) What is Cathodic Protection? Under which conditions, is this protection more useful?
 55) Describe the process of Electroplating giving a well labeled diagram & the reactions.
 56) Explain Cathodic Protection by Impressed current method.
 57) Explain Cathodic Protection by Sacrificial method.
 58) Explain Anodic Protection.
 59) Explain the treatment given to the metal surface before any coating.
 60) What are types of Metal Coatings? Describe them in detail.
 61) Differentiate between Anodic and Cathodic Metal Coatings.
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PRACTICE NUMERICALS BASED ON PBR

1) Aluminium undergoes oxidation to form its oxide Al_2O_3 on its surface. If its Pilling-Bedworth ratio (PBR) is = 2.754, calculate density of Al_2O_3 .

Given:- density of Aluminium = 2.70 gm/cc, At wts:- Al = 27, O = 16 gms/mole.

Comment on the nature of oxide film formed. Would it be protective or not? Why?

(Ans:- density of Al_2O_3 = 1.8518 gm/cc. It will be non-porous & protective as PBR > 1.)

2) Calculate PBR for oxide of Magnesium. Predict its protective nature.

Given:- At wts :- Mg = 24, O = 16 gm/mole each. Densities of Mg and MgO are 1.74 & 3.65 gms/cc respectively.

(Ans:- PBR = 0.8191. As PBR < 1, the film is porous and non-protective.)

3) $2 \text{Ca(s)} + \text{O}_2\text{(g)} \longrightarrow 2 \text{CaO(s)}$. Predict the nature of CaO film with the help of following information. At wts:- Ca = 40, O = 16 gms/mole each. Density of Ca & CaO are 1.55 & 3.40 gms/cc respectively. (Ans:- PBR = 0.6382. As PBR < 1, the film is protective and porous.)

4) (COEP - Nov 2014) Calculate the Pilling-Bedworth Ratio obtained from the (4)

following information. Reaction :- $\text{Fe(s)} \longrightarrow \text{FeO(s)}$. Density of oxide = 5.70 gm/cc,
Density of metal = 7.87 gm/cc. At wts:- Fe = 55.8 gm/mole and O = 16 gm/mole.

Also state whether the film is protective or non-protective.

(Ans:- PBR = 1.776. As PBR > 1, the film is non-porous & protective.)

QUESTIONS ASKED IN PREVIOUS END SEMESTER EXAMINATION (ESE) OF COEPNOVEMBER - 2014

- 1) Small anodic areas result into intense corrosion. Give reason. (1)
- 2) Oxygen free water is used in boilers for steam generation. Give reason. (1)
- 3) Differentiate between Cathodic and Anodic Coatings. (2)
- 4) Discuss how the nature of the metal affects corrosion. (2)
- 5) Discuss Pourbaix (E - pH) diagram for Fe. (3)
- 6) Write a short note on "Potentiostatic Anodic Protection" used to protect chemical reactors from corrosion. (3)
- 7) Discuss mechanism of "Wet Corrosion" giving reactions involved. (3)
- 8) Calculate the Pilling-Bedworth Ratio obtained from the following information. (4)