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Internal Assessment Test 1 – July 2022

Sub:	Engineering Chemistry				Sub Code:	21CHE22	Branch:	CSE, ISE, Mech & Civil		
Date:	09-07-2022	Duration:	90 min's	Max Marks:	50	Sem / Sec:	II / A to G		OBE	
Question no. 1 is COMPULSORY and answer any THREE FULL Questions from the rest.								MARKS		
								CO	RBT	
1 (a)	Define free energy. Derive the Nernst equation for single electrode potential.				[7]	CO1	L3			
	(b) Define metallic corrosion? Illustrate electrochemical theory of corrosion taking rusting of iron as an example.				[7]	CO1	L3			
2 (a)	Define ion selective electrode. Discuss the construction and working principle of glass electrode with a neat sketch.				[6]	CO1	L2			
	(b) An Electrochemical cell consists of a zinc electrode dipped in 0.25 M Zn(NO ₃) ₂ and silver electrode dipped in 0.1 M AgNO ₃ . Represent the cell and write the half cell and net cell reactions. Also, calculate the emf. of the cell at 40 °C. Given, std reduction potential of Zn & Ag are -0.76 V and 0.80V respectively.				[6]	CO1	L4			
3 (a)	Describe the construction and working of saturated calomel electrode with a neat sketch.				[6]	CO1	L2			
	(b) A cell is constructed by coupling Cu electrode dipped in 0.4 M CuSO ₄ and Ni electrode dipped in 0.04 M NiSO ₄ . Write the cell representation, cell reaction & calculate emf of the cell at 298K, given SRPs of Cu and Ni as 0.34 & -0.25 v respectively.				[6]	CO1	L4			

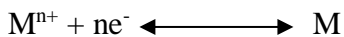
4 (a)	Discuss primary, secondary and reserve batteries with examples.				[6]	CO1	L2		
	(b) Illustrate the construction, working mechanism and applications of Li-ion batteries with a neat sketch.				[6]	CO1	L3		
5(a)	Explain in detail about direct recycling method for recycling of lithium- ion battery.				[6]	CO1	L2		
	(b) Explain the following process in detail with suitable diagram and reactions i) Differential metal corrosion ii) Pitting Corrosion.				[6]	CO2	L3		
6 (a)	Explain the role of following factors on the rate of corrosion. (i) Ratio of anodic and cathodic areas (ii) pH				[6]	CO2	L3		
	(b) What is Corrosion penetration rate? A piece of corroded plate was found in the submerged ocean vessel. It was estimated that the original area of the plate was 8.2 inch ² and that approximately 2.9 kg had corroded away during the submersion for a period of 12 years. Calculate CPR in terms of mpy and mm/y. Given density of iron = 7.9 g/cm ³ , K (mpy)= 534, K(mm/y)= 87.6.				[6]	CO2	L4		
7 (a)	What is galvanization? Describe the galvanization process in detail.				[6]	CO2	L2		
	(b) Define metal finishing. Mention (any five) technological importance of metal finishing.				[6]	CO2	L1		

(Chief Course Instructor)

Answer 1a. Free energy refers to the amount of internal energy of a thermodynamic system that is available to perform work

Derivation of Nernst equation for single electrode potential:

Consider an electrode assembly undergoing a reversible reaction.



For above reaction the equilibrium constant is $K_c = \frac{[M]}{[M^{n+}]}$.

The equilibrium constant (Kc) is related to change in free energy by Vant Hoff equation as follows

$$\Delta G = \Delta G^{\circ} + RT \ln K_c \dots \dots \dots (1)$$

According to thermodynamics, for any reversible system the decrease in free energy (- ΔG) represents maximum amount of work that can be obtained from a chemical reaction.

$$-\Delta G = W_{\max} \dots \dots \dots (2)$$

$$W_{\max} = n \times F \times E \dots \dots \dots (3)$$

n = moles of electrons, F = Cmol⁻¹, E = JC⁻¹ Equating equations (2) & (3)

$$-\Delta G = n \times F \times E \text{ or}$$

$$\Delta G = - n \times F \times E$$

Under standard conditions, when concentrations of all species is unity, standard free energy change is given by equation

$$\Delta G^{\circ} = - n \times F \times E^{\circ}$$

Where ΔG^o = Change in free energy under standard conditions, E^o is a constant called standard electrode potential.

Therefore by substituting values of ΔG, ΔG^o and Kc in equation (1), we get

$$-nFE = -nFE^{\circ} + RT \ln \frac{[M]}{[M^{n+}]}$$

$$-nFE = -nFE^{\circ} + RT \ln [M] - RT \ln [M^{n+}]$$

Dividing whole equation by -nF

$$\frac{-nFE}{-nF} = \frac{-nFE^{\circ}}{-nF} + \frac{RT \ln [M]}{-nF} - \frac{RT \ln [M^{n+}]}{-nF}$$

$$E = E^{\circ} - \frac{RT \ln [M]}{nF} + \frac{RT \ln [M^{n+}]}{nF}$$

Under standard condition [M] = 1,

$$E = E^{\circ} + \frac{RT}{nF} \ln [M^{n+}]$$

$$nF$$

Converting natural log to base 10, we get

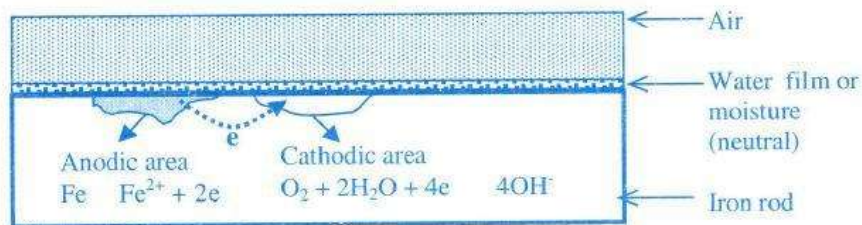
$$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}]$$

Substituting the values for R (8.314 JK⁻¹mol⁻¹), F (96500 Cmol⁻¹) and T (298K)

$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}]$$

Answer 1b. Destruction of metal surface in surrounding environment due to chemical or electrochemical reaction is known as corrosion. eg rusting of iron

Electrochemical theory of corrosion:



(i) According to electrochemical theory, corrosion of metals takes place due to the formation of minute galvanic cells over the surface of metal. Thus anodic and cathodic regions are formed on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.

(ii) At the anodic region oxidation reaction takes place and the metal gets converted into its ions by liberating electrons. Consequently, metal undergoes corrosion at the anodic region.



(iii) The electrons flow from the anodic to cathodic area and at the cathodic region, reduction takes place. Since metal cannot be reduced further, metal atoms at the cathodic region are unaffected by the cathodic reaction. Some constituents of the corrosion medium take part in the cathodic reaction. There are three possible ways in which the reduction can take place.

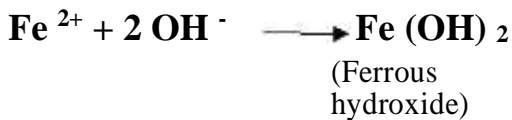
- If the solution is aerated and almost neutral,
 - $O_2 + H_2O + 2e^- \longrightarrow 2OH^-$
- If the solution is deaerated and almost neutral:



- If the solution is deaerated and acidic:



(iv) Corrosion of iron produced Fe^{2+} ions and OH^- ions at the anode and cathode sites respectively. These ions diffuse towards each other and produce insoluble $\text{Fe}(\text{OH})_2$.



(v) In an oxidizing environment, it is oxidized to ferric oxide and the rust is hydrated ferric oxide.



Answer 2a. Ion selective electrodes selectively respond to a specific ion in a mixture and potential developed is a function of concentration of that ion in the solution. Eg. Glass electrode.

Glass Electrode:

Construction: The glass electrode consist of glass tube, the bottom of the glass tube is glass bulb covered with glass membrane made up of special glass of low melting point and high electrical conductivity ($\text{SiO}_2, \text{Na}_2\text{O}, \text{Al}_2\text{O}_3$ etc., and it allows only H^+ ions). Glass bulb consists of 0.1 N HCl (Assume concentration is C_1) and Ag/AgCl electrode, which serves as internal reference electrode .

Working: The glass electrode is dipped into any solution containing H^+ ions then glass electrode develops potential called as glass electrode potential. It is represented as E_G .

Then, $E_G = E_b + E_{\text{Ag/AgCl}} + E_{\text{assy}} \dots\dots\dots (1)$

Where, E_b = Boundary potential, $E_{\text{Ag/AgCl}}$ = Potential due to Ag/AgCl and E_{assy} = asymmetric potential

Boundary potential (E_b); It is a potential developed across the glass membrane when concentration of the solution inside and outside the glass membrane are different.

Mathematically it is represented as, $E_b = E_1 - E_2$

Where, E_1 = Potential due to H^+ present inside the bulb (Unknown solution)

E_2 = Potential due to H^+ present in outside solution (Unknown solution)

According to Nernst equation

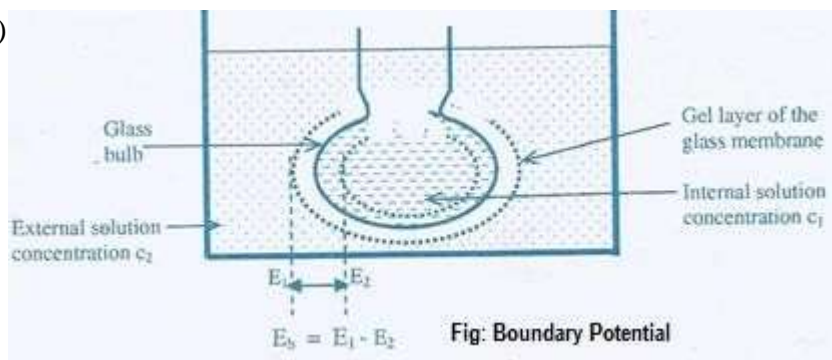
$$= E^\circ + \frac{0.0591}{n} \log C_2 - (E^\circ - \frac{0.0591}{n} \log C_1)$$

$$= \frac{0.0591}{n} \log C_2 - \frac{0.0591}{n} \log C_1$$

Where, $C_1 = 0.1 \text{ M}$ and $n = 1 (\text{H}^+)$

$$= \frac{0.0591}{n} \log C_2 - K \text{ or}$$

$$= K + \frac{0.0591}{n} \log C_2$$



Glass selects only H⁺ ions ignoring other ions.

Hence $C_2 = H^+$

$E_b = K + 0.0591 \log [H^+]$, Where, $\log [H^+] = -pH$

Hence $E_b = K - 0.0591pH$ -----(2)

Substituting eqn (2) in (1)

$E_G = K - 0.0591pH + E_{Ag/AgCl} + E_{assy}$

$E_G = E^{\circ}_G - 0.0591pH$

Answer 2b.

$Zn(s)/Zn(NO_3)_2(0.25M)//AgNO_3(0.1M)/Ag$

$Zn \rightarrow Zn^{2+} (0.25M) + 2e^-$

$[Ag^+ (0.1M) + e^- \rightarrow Ag(s)] \times 2$

The Nernst equation is: $E_{cell} = E^{\circ}_{cell} + \frac{2.303 \times R \times T}{nF} \log \frac{[Ag^+]^2}{[Zn^{2+}]}$

$$E_{cell} = \{0.80 - (-0.76)\} + \frac{2.303 \times 8.31 \times 313}{2 \times 96500} \log \frac{[0.1 \times 0.1]}{[0.25]}$$

$$E_{cell} = 1.56 + 0.0310 (-1.3979)$$

$$E_{cell} = 1.517 \text{ V}$$

Ans 3a. Reference Electrodes:

The electrodes whose potentials is known and constant and they are used to determine the potential of another unknown electrode are known as reference electrodes.

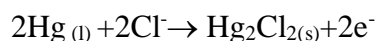
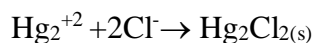
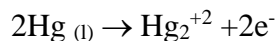
Construction and working of calomel electrodes:

It is a metal-insoluble salt electrode, where metal in contact with its insoluble salt and the solution contains the anion of the salt. Mercury is placed at the bottom of the glass tube above which a paste of mercury and mercurous chloride are present. It is filled on the top with the saturated solution of KCl. A platinum wire sealed into a glass tube is dipped into mercury and used to provide the external electrical contact. Depending on the nature of the other electrode it can either acts as anode or cathode.

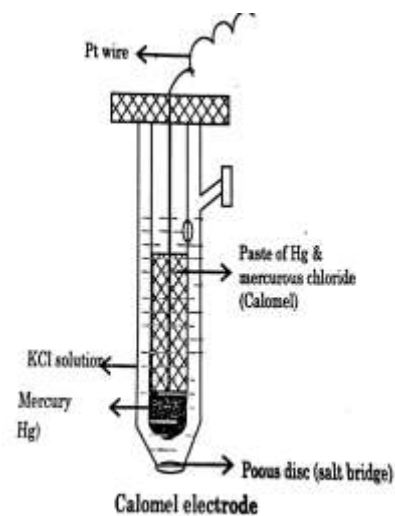
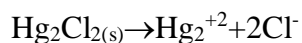
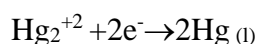
Electrode representation: $Hg_{(s)}/Hg_2Cl_2 \text{ (paste)}; Cl^-$

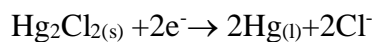
Working:

If the electrode behaves as anode, the electrode reaction is:



If the electrode behaves as cathode, the electrode reaction is:

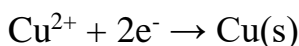
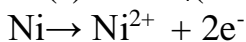




The electrode potential of calomel electrode depends on concentration of chloride ions.
For saturated KCl $E = 0.2422\text{V}$ (called Saturated calomel electrode)

Uses: It is used as a secondary reference electrode in the measurement of single electrode potential. It is the most commonly used reference electrode in all potentiometric determination

Ans 3b.



The Nernst equation is: $E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{2.303 \times R \times T}{nF} \log \frac{[\text{Cu}^{2+}]}{[\text{Ni}^{2+}]}$

$$E_{\text{cell}} = \{0.34 - (-0.25)\} + \frac{2.303 \times 8.31 \times 298}{2 \times 96500} \log \frac{[0.4]}{[0.04]}$$

$$E_{\text{cell}} = 0.59 + 0.0295 (1)$$

$$E_{\text{cell}} = 0.6195 \text{ V}$$

Ans 4a.

1. **Primary batteries:** In primary batteries, the net cell reaction is not completely reversible and hence these are not rechargeable.

For example: Zn – MnO₂, Li-MnO₂ batteries etc.

2. **Secondary batteries:** In secondary batteries, the net cell reaction is completely reversible and hence these are rechargeable.

For example: Lead storage battery, Ni – Cd battery etc.

3. **Reserve batteries:** One of the key components i.e. electrolyte, in reserve batteries is incorporated into the battery when required. When one of the key components is separated from remainder, chemical reaction between cell components (self discharge) is prevented and battery can be stored for a long period of time.

For example: Mg-AgCl, Mg-CuCl, Zinc – Silver oxide reserve batteries, etc.

Ans 4b. This is a rechargeable battery in which Li ions move from the negative electrode to the positive electrode during discharge and back when charging. (Anode and cathode are layered structure and they are able to insert lithium ion into their layer structure reversibly).

Construction

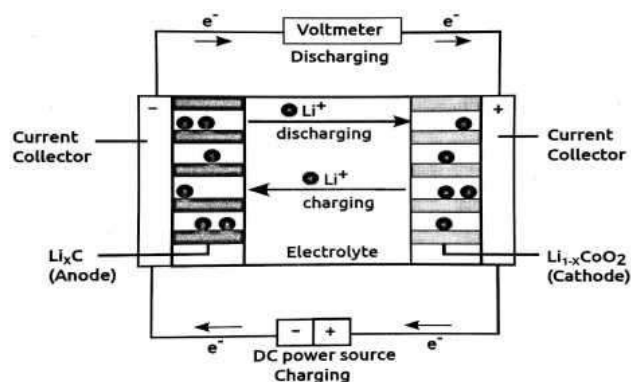
Anode: The negative electrode of a conventional lithium ion cell is made up of graphite C (Lithiated intercalated material, LiC)

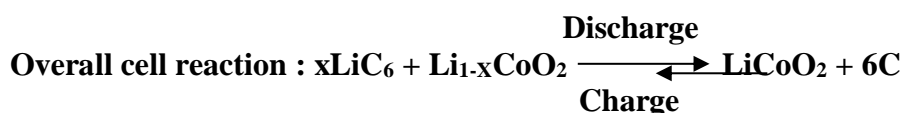
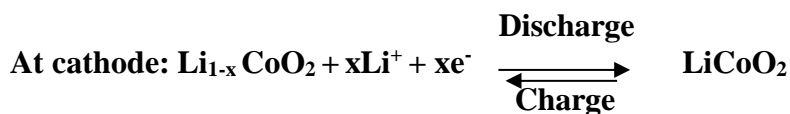
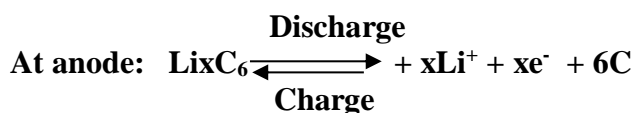
Cathode: It is made up of lithiated transition metal intercalated compound i.e. metal oxide (M = Mn, Co).

Electrolyte: Lithium salt (LiPF₆) in an org solvent or mixture of orgaic carbonates such as ethylene carbonate or diethyl carbonate containing complex of Li-ions.

Working:

In the electrochemical reaction in a Li-ion battery both electrodes allow lithium ions to move in and out of their interiors. When a lithium ion cell is discharging, the positive Li ions moves from the negative electrode and enters the cathode, and when the cell is charging reverse occur.





Electrochemical process is uptake of Li-ions at the anode during charge and their release during discharge. The voltage of LIB is about **3.5-3.7 V**.

Applications:

1. Mobile phones, smartphone, Laptops and tablets, digital cameras camcorders and torches.
2. They are used for energy storage for many electric vehicles.
3. Li-ion batteries are used in telecommunications applications.

Ans (5a) Direct recycling: We define direct recycling as the recovery, regeneration, and reuse of battery components directly without breaking down the chemical structure. It has also been called direct cathode recycling and cathode-to-cathode recycling. The removal of cathode or anode material from the electrode for reconditioning and re-use in a remanufactured LIB is known as direct recycling.

Principle: Mixed metal-oxide cathode materials can be reincorporated into a new cathode electrode with minimal changes to the crystal morphology of the active material.

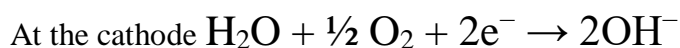
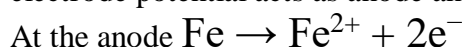
The direct recycling process for cathodes involves following steps.

1. Batteries are dismantled to separate metals such as Al and Cu (Current collectors, electrolyte materials like polymers and electrode materials (cells and modules))
2. Electrolyte recovery: Electrolyte is a polymer or organic material, extracted by solvent extraction method.
3. Electrode materials, obtained after dismantling spent batteries, were soaked in N-Methyl-2-pyrrolidone (NMP) before undergoing sonication to separate the current collectors like Al and Cu.
4. Above material is dissolved in acids, metals dissolve in acids and anode material like carbon is floating on the surface and be removed by filtration.
5. Lithium carbonate salt is added to above solution after removing Al and Cu and anode material like carbon, subjected to annealing. This will result in high-cobalt cathodes such as Lithium Cobalt oxide.

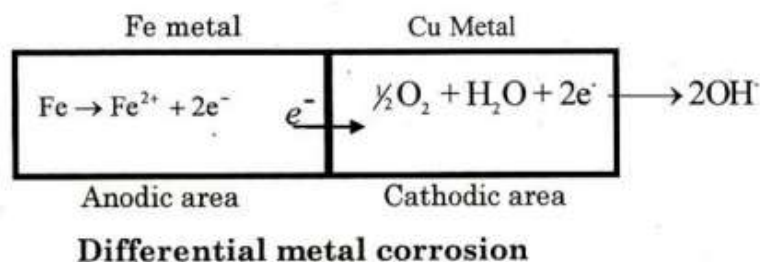
Advantages: Low cost technique, Easy to recover the expensive cathode material and reuse

Ans (5b)

Differential metal corrosion: Galvanic corrosion or differential metal corrosion: This occurs when two dissimilar metals are in contact with each other in a corrosive conductive medium; a potential difference is set up resulting in a galvanic current. The two metals differ in their tendencies to undergo oxidation. The metal with lower electrode potential or more active metal acts as anode and the metal with higher electrode potential acts as cathode. The potential difference is main factor for corrosion to take place. The anodic metal undergoes corrosion whereas cathodic metal gets unattacked. Example: When iron contact with copper iron has lower electrode potential acts as anode and undergo oxidation as,

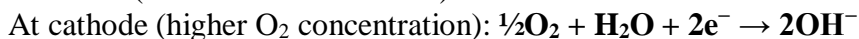
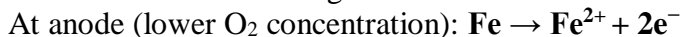


Whereas copper which is having higher electrode potential acts as cathode gets unaffected. The rate of galvanic corrosion depends upon potential difference between anodic and cathodic metals, ratio of anodic and cathodic area and environmental factors and tendency of the metal to undergo passivity etc.

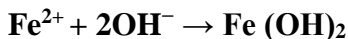


Pitting corrosion:

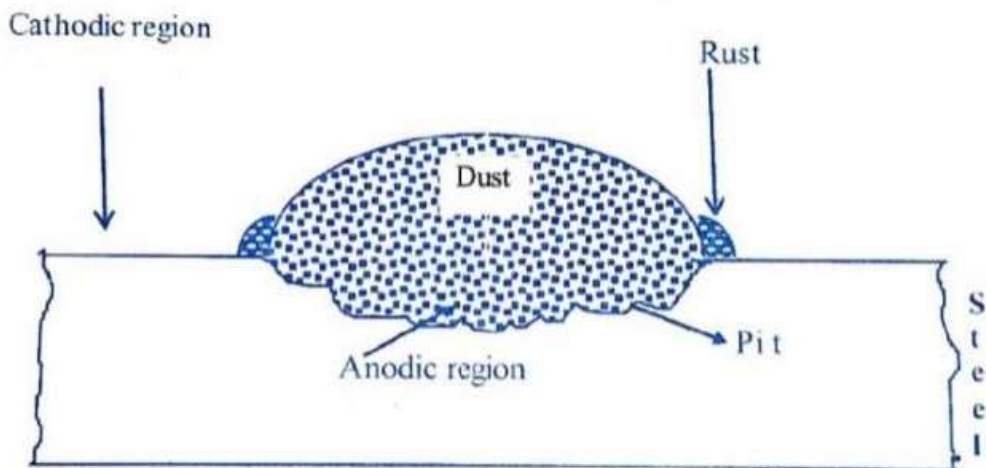
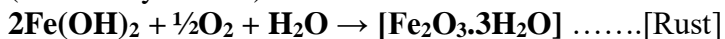
- (i) Pitting corrosion results when small particles of dust/oil droplets get deposited on a steel surface. The portion covered by the dust will be less aerated compared to the exposed surface.
- (ii) The covered portion acts as anode and undergoes corrosion to form pits in the presence of electrolyte and moisture. The remaining part acts as cathode. Once the pit is formed corrosion occurs rapidly because of small anodic area and large cathodic area



Rust formation:



(Ferrous hydroxide)

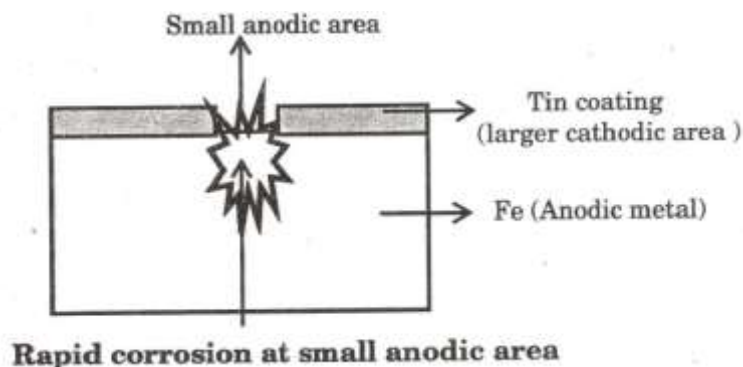


Ans 6a (i) The ratio of anodic and cathodic areas: The rate of corrosion largely depends on the relative size of anode and a cathode.

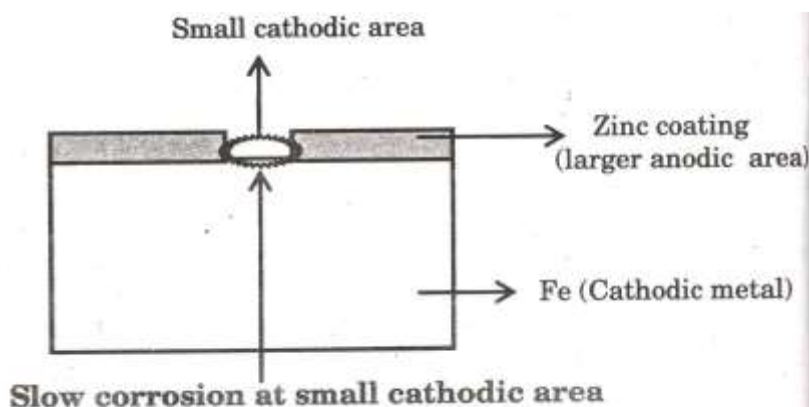
(a) If the metal has a **small anodic and large cathodic area** (i.e; the ratio of anode to cathode is small) then the corrosion is **more intensive and faster in rate**. This is explained as follows

At anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed when the anode is smaller and the cathode region is large, the electrons liberated at the anode are rapidly consumed at the cathode region. This process makes the anodic reaction to take place faster, thus increasing the corrosion rate.

Ex: A broken coating of tin on iron surface, tin is cathodic to iron and the small exposed part of iron acts as an anodic region and the rest of the large tin-coated surface acts as a cathodic region. Because of the small ratio of anodic to cathodic area, the corrosion rate is very high.



(b) If the **cathode is smaller and anode is larger**, the rate of corrosion will be **less**, because the consumption of electrons will be slower and the corrosion reaction as a whole will be slower.



Eg. The broken coating of Zn over Fe, Zn plating on Fe gives an anodic coating to iron (Zn is above Fe in electrochemical series). Thus even if Zn plating peels off at some point, Fe does not get corroded.

(ii) **pH** : In general, the rate of corrosion is high when the nature of the environment is acidic.

(a) If the $\text{pH} < 3$, severe corrosion occurs even in the absence of air due to the continuous evolution of hydrogen at the cathodic region.

(b) If the $\text{pH} > 10$, corrosion of the metal practically ceases, due to the formation of a protecting coating of hydrogen oxide of iron.

Ans (6b) Corrosion Penetration Rate (CPR) is defined in three ways: (1) the speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment, (2) the amount of corrosion lost per year in thickness, (3) the speed at which corrosion spreads to the inner portions of a material.

Corrosion penetrating rate in mpy $CPR = KW/DAT$ Weight loss, $W = 2.9 \times 10^6$ mg Density, $D = 7.9 \text{ g/cm}^3$; Time, $T = 12 \times 24 \times 365$ Area $A = 8.2 \text{ in}^2$ $CPR = \frac{534 \times 2.9 \times 10^6}{7.9 \times 8.2 \times 12 \times 24 \times 365}$ CPR = 227.41 mpy	Corrosion penetrating rate mm/y $CPR = KW/DAT$ Weight loss, $W = 2.9 \times 10^6$ mg Density, $D = 7.9 \text{ g/cm}^3$; Time, $T = 12 \times 24 \times 365$ Area $A = 8.2 \times 6.45 \text{ cm}^2$ $CPR = \frac{87.6 \times 2.9 \times 10^6}{7.9 \times 8.2 \times 6.45 \times 12 \times 24 \times 365}$ CPR = 5.78 mm/y
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Ans (7a)

The process of coating Zn on iron by hot dipping is called galvanizing. It is an example of anodic metal coating. The process of galvanization is carried out as follows,

- (i) The base metal is first treated with organic solvent to remove grease or oil material present on it.
- (ii) It is further treated with dil. H_2SO_4 to remove rust or oxide layer present on it.
- (iii) The metal is then treated with flux of ZnCl_2 and NH_4Cl for better adhesion property.
- (iv) Finally the base metal is dipped into the zinc at $430\text{-}470^\circ\text{C}$.
- (v) The excess zinc is removed from the surface by rolling or wiping etc.

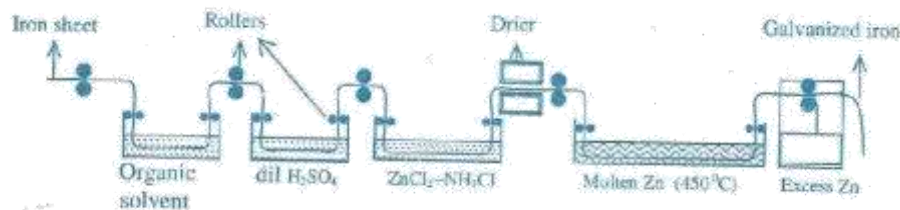


Fig: Galvanisation of Iron

Ans (7b) Definition: Process of surface modification by way of deposition of another metal or metal alloy or polymer or ceramic or oxide layer to bring about intended better surface characteristics is known as metal finishing.

Technological Importance:

Technological significance of metal finishing refers to imparting following different characteristics:

- (i) Better corrosion resistance,
- (ii) Better hardness, strength, wear / abrasion resistance, etc.
- (iii) Better thermal conductance or resistance or reflectance, etc.
- (iv) Better optical reflectance,
- (v) Better electrical conductance or insulation, etc.
- (vi) Building up material or restoration
- (vii) Manufacturing printed circuit boards, capacitors, contacts, etc.
- (viii) Electrotyping (e.g., gramophone records)
- (ix) Electroforming or reforming of articles,
- (x) Electrochemical machining, electropolishing and electrochemical etching, etc.