Module-3

Electrochemistry Nernst Equation and application, relation of EMF with thermodynamic functions (ΔH, ΔF and Δ S). Lead storage battery. Corrosion; causes, effects and its prevention. Phase Rule and its application to water system.

Contents

1.Electrochemistry

Electrochemistry is a branch of chemistry which deals with interconversion of electrical energy to chemical energy and vice versa. For ex: i) In a battery, chemical energy is converted to electrical energy ii) In electroplating / electrolysis electrical energy is converted to chemical energy. Substances that allow electric current to pass through them are known as conductors. For ex: the metals, graphite, fused salts, aqueous solution of acids, bases & salts. While insulator or non-conductor is a substance which does not allow electric current to pass through it. For ex: wood, plastic.

1.1. Electrode Potential: When a metal is kept in a solution of its own ions, the metal acquires either negative or positive charge with respect to the solution. So, a definite potential difference is developed between the metal and the solution. This potential difference is known as electrode potential**.** For example, when a plate of zinc is placed in a solution having zinc ions (Zn^{2+}), it becomes negatively charged with respect to solution and thus a potential difference is set up between zinc plate and the solution. This potential difference is termed the electrode potential of zinc. Similarly, when copper is placed in a solution having copper ions (Cu^{2+}), it becomes positively charged with respect to solution. A potential difference is set up between the copper plate and the solution. The potential difference thus developed is termed as electrode potential of copper. The potential difference is established due to the formation of electrical double layer known as Helmholtz double layer.

Osmosis is the diffusion solvent molecule through a semipermeable membrane, when a semipermeable membrane separates a solution from a solvent, then only solvent molecules can flow through the semipermeable membrane. During osmosis a pressure is developed on SPM which is known as osmotic pressure.
Solution pressure is a measure of the tendency of molecules or atoms to cross a bounding surface between phases and to enter into a **solution**.

The osmotic pressure of a solution is the pressure difference needed to stop the flow of solvent across a semipermeable membrane. The osmotic pressure of a solution is proportional to the molar concentration of the solute particles in solution. If the solution pressure is greater than the osmotic pressure, the tendency of the metal to lose ions predominates. A potential difference is therefore set up with the metal left with negative charge with respect to the solution. So the positive ions will enter the liquid and the metal negatively charged with respect to solution. The formation of double layer prevents the further expulsion of ions from the metal, and thus there is rapidly established a state of equilibrium with a definite potential difference, termed as electrode potential.
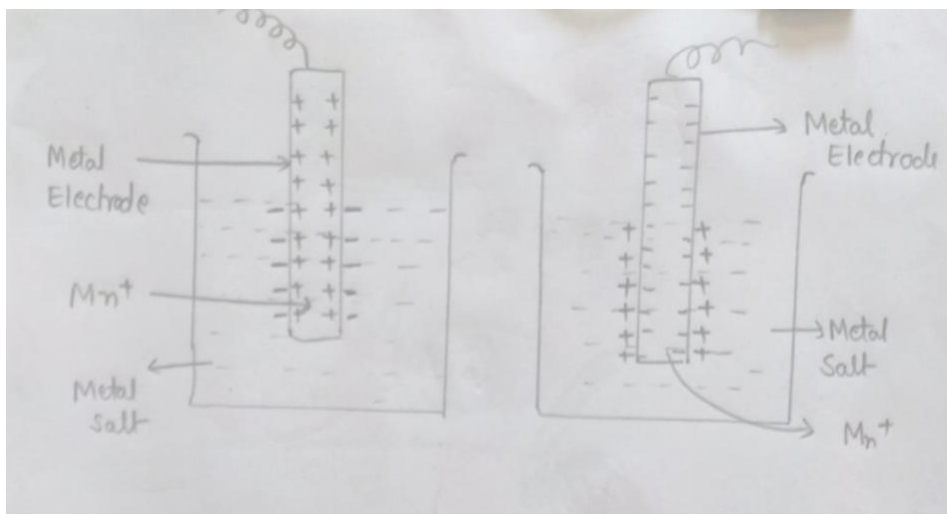
Figure: Representation of positive and negative electrode potential

Following two changes occur when a metal rod is dipped in its salt solution

Oxidation: Metal ions goes from the electrode into solution leaving an excess of electrons and thus a negative charge on the electrode.

The conversion of metal atoms into metal ions by the attractive force of polar water molecules.

$$M \rightarrow M^{n+} + ne^- \qquad \qquad \dots\dots\dots\dots\dots(1)$$
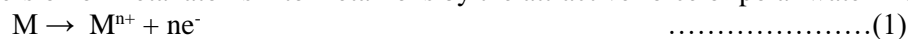
The metal ions go into the solution and the electrons remain on the metal making it negatively charged. The tendency of the metal to change into ions is known as electrolytic solution pressure.

Reduction: Metal ions in solution gain electrons from the electrode leaving a positive charge on the electrode. Metal ions start depositing on the metal outer surface leading to a positive charge on the metal.

$$M^{n+} + ne^- \rightarrow M \qquad \qquad \dots\dots\dots\dots\dots(2)$$

In the starting, both these changes occur with different speeds but soon an equilibrium is established.

$$M \rightleftharpoons M^{n+} + ne^- \qquad \qquad \dots\dots\dots\dots\dots(3)$$

In practice, one effect is greater than the other,

If first effect is greater than the second, the metal acquires a negative charge with respect to solution and

If the second effect is greater than the first, it acquires positive charge with respect to solution, thus in both the cases a potential difference is build up.

The magnitude of the electrode potential of a metal is a measure of its relative tendency to lose or gain electrons.

Depending on the nature of the metal electrode to lose or gain electrons, the electrode potential may be of two types:

1.1.2. Oxidation potential: When electrode is negatively charged with respect to the solution than it is known as anode. Oxidation occurs at anode.

$$M \rightarrow M^{n+} + ne^- \qquad \qquad \qquad …………………(4)$$

1.1.3. Reduction potential: When electrode is positively charged with respect to solution than it is known as cathode. Reduction occurs at cathode.

$$M^{n+} + ne^- \rightarrow M \qquad \qquad \qquad …………………(5)$$

1.2. Standard Electrode Potential

To find out the electrode potentials of different electrodes, it is necessary to specify the concentration of the ions which is present in solution.

The potential difference developed between metal electrode and the solution of its ions at molarity (1M) concentration at 25°C (298 K) is called standard electrode potential. According to the IUPAC convention, the reduction potential alone be called as the electrode potential (E^O), i.e., the given value of electrode potential be regarded as reduction potential unless it is specifically mentioned that it is oxidation potential.

Standard reduction potential of an electrode means that reduction reaction is taking place at the electrode. If the reaction is reversed and written as oxidation reaction, the numerical value of electrode potential will remain same, but the sign of standard potential will have to be reversed.

1.3. Reference Electrode (Standard Hydrogen Electrode / SHE)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip and coated with platinum black (to adsorb hydrogen gas). A platinum wire is surrounded by the platinum strip and sealed in a glass tube as to contact the outer circuit through mercury. The platinum strip and glass tube are surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a few holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution having H^+ ion concentration 1 M. Pure hydrogen gas is circulated at 1 atmospheric pressure.

A part of the gas is adsorbed and the rest escapes through holes. This gives an equilibrium between the adsorbed hydrogen and hydrogen ions in the solution.

$$H_2 \rightleftharpoons 2H^+ + 2e^- \qquad \qquad \qquad …………………(1)$$

The temperature of the cell is maintained at 25^0C. By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.00 Volt.

The hydrogen electrode thus obtained forms one of two half-cells of a voltaic cell. When this half-cell relates to any other half-cell, a voltaic cell is constituted. The hydrogen electrode can act as cathode or anode with respect to another electrode.
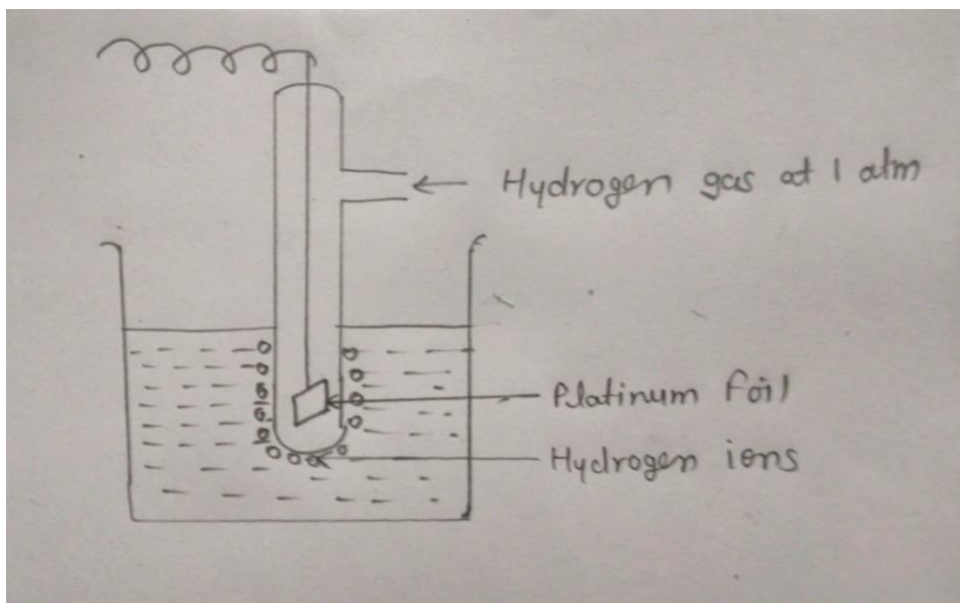
Figure: Standard Hydrogen Electrode

1.4.Electrochemical series: When elements are arranged in increasing order (downwards) of their standard electrode potentials that arrangement is called as electrochemical series.

Metal ion	Standard Reduction Potential (eV).
$Li^+ + e^- \rightarrow Li$	-3.05
$K^+ + e^- \rightarrow K$	-2.93
$Ca^+ + 2e^- \rightarrow Ca$	-2.90
$Na^+ + e^- \rightarrow Na$	-2.71
$Mg^+ + 2e^- \rightarrow Mg$	-2.37
$Al^{+3} + 3 e^- \rightarrow Al$	-1.66
$Zn^{+2} + 2e^- \rightarrow Zn$	-0.76
$Cr^{+3} + 3e^- \rightarrow Cr$	-0.74
$Ni^{+2} + 2 e^- \rightarrow Ni$	-0.23
$Sn^{+2} + 2 e^- \rightarrow Sn$	-0.14
$Pb^{+2} + 2e^- \rightarrow Pb$	-0.73
$Fe^{+3} + 3e^- \rightarrow Fe$	-0.04
$H^+ + e^- \rightarrow ½ H$	0.00
$Cu^{+2} + 2 e^- \rightarrow cu$	+0.34
$Ag^+ + e^- \rightarrow Ag$	+0.80
$Pb^{+4} + 4 e^- \rightarrow Pb$	+0.86
$Au^+ + e- \rightarrow Au$	+1.69
$½ F_2 + e^- \rightarrow F^-$	+2.87

Features of electrochemical series:
- In electrochemical series a metal with high reduction potential has a higher tendency to undergo reduction.

- A metal having low reduction potential tend to oxidize more easily.

For example standard reduction potential of F_2 / F^- is the highest, so F_2 is easily reduced to F^-.
and standard reduction potential of Li^+ / Li is least, so Li^+ is reduced with great difficulty to Li.

- In electrochemical series the metals which are placed on top displace the metals below them from their salt solution. For example: Zn will displace Cu from the solution of Cu^{2+}

$$Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu.$$

- For spontaneous reaction EMF should be positive.
- If EMF is negative value then the reaction is non-spontaneous.
-

1.5.Cell Potential

The cell potential is the measure of the potential difference between the two half cells in an electrochemical cell. The potential difference is caused by the ability of electrons to flow from one half cell to the other.

- It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. So it is necessary to join the electrode with other electrode whose potential is known. This electrode is termed as reference electrode. The EMF of the resulting cell is measured experimentally.
- The EMF of the cell is equal to the sum of potentials on the two electrodes.
-
- E.M.F. of the cell = $E_{Anode} + E_{Cathode}$ = Oxidation potential of anode + Reduction potential of cathode
- It is not possible to measure the absolute value of the single electrode potential directly. Only the difference in potential between two electrodes can be measured experimentally. It is, therefore, necessary to couple the electrode with another electrode whose potential is known. This electrode is termed as reference electrode. The EMF of the resulting cell is measured experimentally.
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1.6.Electrochemical cell: The devices which convert chemical energy to electrical energy & electrical energy into chemical energy are known as electrochemical cells they contain two electrodes in contact with an electrolyte, they are mainly of two types.

1.6.1.Galvanic cells: It is an electrochemical cell in which the free energy of chemical reaction is converted into electrical energy i.e. electricity is produced from a spontaneous chemical reaction. Example: voltaic cell or Daniel cell

1.6.2.Electrolytic cell: It is an electrochemical cell in which external electrical energy is used to carry out a non- spontaneous chemical reaction. Examples of electrolysis are the decomposition of water into hydrogen and oxygen, and bauxite into aluminium and other chemicals.

Cell representation: An electrochemical cell or galvanic cell is obtained by coupling two half cells. For example, Daniel cell obtained by coupling Zn half-cell and copper half-cell through a salt bridge

$$Zn \mid ZnSO_4 \ (aq) \parallel CuSO_4(aq) \mid Cu$$
$$\text{(anode)} \qquad \text{(cathode)}$$
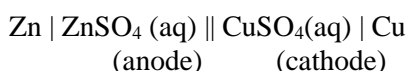
[$\parallel$] double lines represents salt bridge When reduction potentials of electrodes are known then the emf of the cell is represented as

$E = E^0 - 2.303 \times RT/ nF \log c$

$E = E^0 - 0.0591$ n log c
E cell = E cathode - E anode
E cell = EMF of the cell.
E cathode = Reduction potential of cathode.
E anode = Reduction potential of anode.
+ve value of E_{cell} indicates, the cell reactions feasible
-ve value of E_{cell} indicates, that the cell reaction is not feasible. In such case electrodes are to be reversed in order to bring about the chemical reaction.

1.7. Galvanic cell : Daniel cell is an example of galvanic cell. It consists of Zn rod and Cu rod; Zn rod is dipped in $ZnSO_4$ solution and Cu rod dipped in $CuSO_4$ solution. Each electrode in its electrolytic solution is known as half-cell. The two solutions are connected by U shaped tube known as salt bridge. Thus two electrolytic solutions are in contact with each other. A salt bridge is a U- shaped tube containing concentrated solution of an inert electrolyte like KCl, KNO_3, K_2SO_4 in order to complete the circuit.

Application of salt bridge:
- Salt bridge prevents the mechanical flow of solution from one-half cell to another.
- It minimizes the liquid-liquid junction potential (Potential arises between two solutions when they are in contact).
- To maintain the electron neutrality.

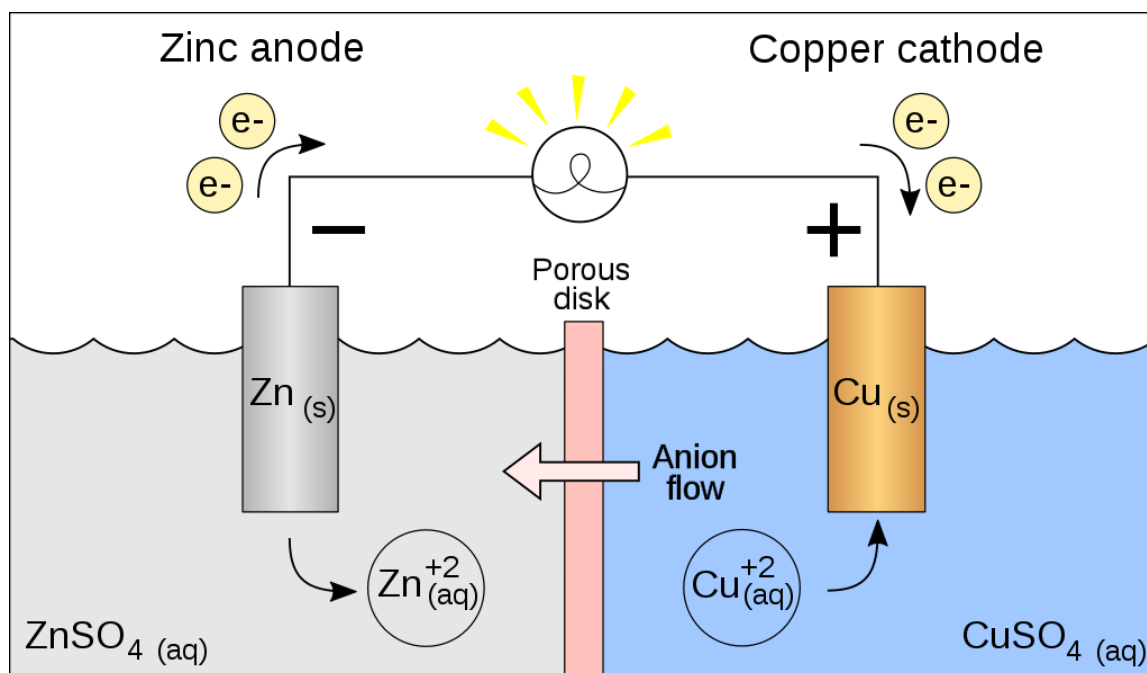Cell reactions: The electrode reactions of Daniel Cell are :

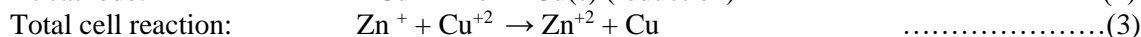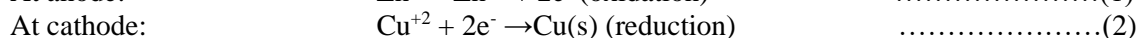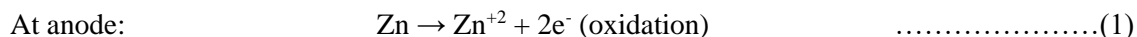|		
At anode:	$Zn \rightarrow Zn^{+2} + 2e^-$ (oxidation)	…………………(1)
At cathode:	$Cu^{+2} + 2e^- \rightarrow Cu(s)$ (reduction)	…………………(2)
Total cell reaction:	$Zn^+ + Cu^{+2} \rightarrow Zn^{+2} + Cu$	………………….(3)

Figure: Galvanic cell

1.8. Difference between Galvanic and Electrolytic cell

S. No.	Galvanic cells	Electrolytic cells
1.	convert chemical energy to electrical energy	Convert an electrical energy to chemical energy
2.	The anode is negative terminal while cathode is positive terminal	The anode is positive terminal while cathode is negative terminal
3.	Galvanic cell has no battery, it is for spontaneous reactions	Electrolytic cell has a battery to act as a source of energy for non-spontaneous reactions to occur.
4.	Salt bridge is required.	Salt bridge is not required.

1.9. Nernst Equation

The Nernst equation provides a relation between the cell potential of an electrochemical cell, the standard cell potential, temperature, and the reaction quotient. Even under non-standard conditions, the cell potentials of electrochemical cells can be determined with the help of the Nernst equation.

The Nernst equation is often used to calculate the cell potential of an electrochemical cell at any given temperature, pressure, and reactant concentration. The equation was introduced by a German chemist Walther Hermann Nernst.

Nernst equation is an equation relating the capacity of an atom/ion to take up one or more electrons (reduction potential) measured at any conditions to that measured at standard conditions (standard reduction potentials) of 298K and one molar or one atmospheric pressure.

Nernst Equation for Single Electrode Potential

$$M^{n+} + ne^- \rightarrow M \qquad\qquad\qquad …………………(1)$$

$$E_{cell} = E^0 - [RT/nF] \ln Q \qquad\qquad\qquad …………………(2)$$

Where,

- E_{cell} = cell potential of the cell
- $E°$ = cell potential under standard conditions
- R = universal gas constant
- T = temperature
- n = number of electrons transferred in the redox reaction
- F = Faraday constant

- Q = reaction quotient

The calculation of single electrode reduction potential (E_{red}) from the standard single electrode reduction potential ($E°_{red}$) for an atom/ion is given by the Nernst equation.

For a reduction reaction, Nernst equation for a single electrode reduction potential for a reduction reaction $M^{n+} + ne^- \rightarrow nM$ is;

$$E_{red} = E\ M^{n+}/M = E°Mn+/M - [2.303RT/nF]\ log\ [1/[M^{n+}]] \qquad\qquad ....(3)$$

Where,

- R is the gas constant = 8.314 J/K Mole
- T = absolute temperature,
- n = number of mole of electron involved,
- F = 96487 ($\approx$96500) coulomb/mole = charged carried by one mole of electrons.
- $[M^{n+}]$ = active mass of the ions. For simplicity, it may be taken as equal to the molar concentration of the salt.

Nernst Equation at 25°C

For measurements carried out 298K, the Nernst equation can be expressed as follows.

$$E = E^0 - 0.0592/n\ log_{10}\ Q \qquad\qquad ....(4)$$

Therefore, as per the Nernst equation, the overall potential of an electrochemical cell is dependent on the reaction quotient.

Derivation of Nernst Equation

Consider a metal in contact with its own salt aqueous solution. Reactions of metal losing an electron to become an ion and the ion gaining electron to return to the atomic state are equally feasible and are in an equilibrium state.

$$M^{n+} + ne^- \rightarrow nM \qquad\qquad ....(5)$$

In the reduction reaction, 'n' moles of an electron is taken up by the ion against a reduction potential of $E_{red.}$

1. The *Nernst Equation* is derived from the Gibbs free energy **under standard conditions**.
$$E° = E°\ reduction - E°\ oxidation \qquad\qquad ....(6)$$
ΔG is also related to E under general conditions
$$\Delta G = -nFE \qquad\qquad ....(7)$$
- n is the number of electrons transferred in the reaction (from balanced reaction),
- F is the Faraday constant (96,500 C/mol), and
- E is potential difference.

2. Change in the free energy at standard conditions of 298K and one molar /one atmospheric pressure conditions is $\Delta G°$. From the above relation, it can be written that

$$\Delta G° = -nFE°_{red} \qquad\qquad ....(8)$$

Where,

$E°_{red}$ is the reduction potential measured at standard conditions.

3. During the reaction, concentration keeps changing and the potential also will decrease with the rate of reaction.

To get the maximum work or maximum free energy change, the concentrations have to be maintained the same. This is possible only by carrying out the reaction under a reversible equilibrium condition.

For a reversible equilibrium reaction, vant Hoff isotherm says:

$$\Delta G = \Delta G° + RT \ln K \qquad\qquad\qquad\qquad\text{…………………(9)}$$

Where,

- K is the equilibrium constant
- $K = \text{Product/Reactant} = [M]^n/[M]^{n+}$
- R is the Gas constant = 8 .314J/K mole
- T is the temperature in Kelvin scale.

4. Substituting for free energy changes in Vant Hoff equation,

$$- nFE_{red} = - nFE°_{red} + RT \ln [M]/[M^{n+}] \qquad\qquad\text{…………………(10)}$$

$$- nFE_{red} = - nFE°_{red} + 2.303\ RT \log [M]^n/[M^{n+}] \qquad\text{…………………(11)}$$

Dividing both sides by $- nF$,

$$E_{red} = E°_{red} - 2.303\ (RT/nF) \log [M]^n/[M^{n+}] \qquad\text{…………………(12)}$$

Applications of Nernst equation
1. To study the effect of electrolytes concentration on electrode potential.
2. It can be used to calculate the cell potential.
3. To calculate the cell potential.
4. To find out the EMF of a solution

1.10. Relation of EMF with thermodynamic functions (ΔH, ΔF and ΔS)

Gibbs free energy which is also known as Gibbs function or Gibbs energy or free enthalpy is a quantity used to measure the maximum work done in a thermodynamic system when the temperature and pressure are constant. Gibbs free energy is denoted as G.

Gibbs Free Energy Equation

The electrical energy produced by a Galvanic cell is given by the product of its EMF and quantity of electricity. The net work performed by a reaction is as follows:

Net electrical work done = QE   …………….…..(1)

Workdone = coulombs X volt = Joule

E=Electromotive force

Q=quantity of electricity

According to Faradey's laws

$$Q = nF \qquad\qquad \text{……….………..….(2)}$$

Q= quantity of electricity

N= number of electrons

F=96500 coulombs

By putting value of equation 2 in equation 1

Net work done = nFE   ……….…..……. (3)

Gibbs and Helmoltz was pointed that the electrical energy of a reversible cell is given by the free energy decreases.

As electrical energy produced by the cell = nFE

Hence $-\Delta G = nFE$ …………………(4)

ΔG= free energy change of the reaction

If the substance involved in standard states i.e. at 298K and 1 atmosphere pressue, then

$$-\Delta G^o = nFE^o \qquad\qquad \text{…………….....(5)}$$

ΔG = negative, the reaction is spontaneous

ΔG = positive, the reaction is non-spontaneous

$\Delta G = 0$, the reaction is at equilibrium

Enthalpy and e.m.f. of cell

Enthalpy: When a process occurs at constant pressure, the heat evolved (either released or absorbed) is equal to the change in enthalpy. The change in free energy, ΔG, is equal to the sum of the enthalpy plus the product of the temperature and entropy of the system.

Entropy: A measure of the unavailable energy in a closed thermodynamic system that is also usually considered to be a measure of the system's disorder, that is a property of the system's state, and that varies directly with any reversible change in heat in the system and inversely with the temperature of the system

The enthalpy is given by

$$\Delta H = \Delta G + T\Delta S \qquad\qquad \text{………..…..(6)}$$

According to Gibbs –Helmholtz equation

$$-\Delta G = -\Delta H - T \left[\frac{\partial(-\Delta G)}{\partial T}\right]_P \qquad\qquad \text{………..…..(7)}$$

ΔH = decrease in enthalpy of the cell at constant pressure

Substituting the value of ΔG from equation (4)

$$nFE = -\Delta H - T \left[\frac{\partial(-nFE)}{\partial T}\right]_P \qquad \text{................(8)}$$

$$nFE = -\Delta H + T\, nF \left[\frac{\partial E}{\partial T}\right]_P \qquad \text{................(9)}$$

$$E = -\frac{\Delta H}{nF} + T \left[\frac{\partial E)}{\partial T}\right]_P \qquad \text{.............. (10)}$$

Where n, F are constant and $\left[\frac{\partial E)}{\partial T}\right]_P$ is temperature coefficient of the cell.

$$\Delta G = \Delta H - nF\, T \left[\frac{\partial(E)}{\partial T}\right]_P \qquad \text{........,...... (11)}$$

$$\Delta G = \Delta H - T\, \Delta S \qquad \text{.............. (12)}$$

$$\Delta S = nF \left[\frac{\partial(E)}{\partial T}\right]_P \qquad \text{................(13)}$$

ΔS = Change in entropy
F= 1 Faraday =96500 coulombs
(∂ E / ∂ T)$_P$= Temperature coefficient

- Temperature coefficient = 0 (Electrical energy = enthalpy)
- Temperature coefficient = positive value, the e.m.f. of the cell increases with temperature (Electrical energy > enthalpy)
- Temperature coefficient = negative value, the e.m.f. of the cell decreases with temperature (Electrical energy < enthalpy)

1.11. Batteries: Battery can be defined as a device which contains two or more electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage. They are mainly of 2 types.

1.11.1.Primary Battery: The battery in which the cell reaction is not reversible i.e, when the cell reaction is completed or all the reactants are exhausted, then no more electricity is produced and the battery becomes dead. Primary battery can't be recharged. Example: Silver oxide, Alkaline & carbon zinc.

1.11.2.Secondary batteries: The battery in which the cell reaction can be reversed by passing direct electric current in opposite direction. Thus a secondary battery may be used through a large number of cycles of discharging and charging. Example: nickel-cadmium (NiCd), lead acid, and lithium ion **batteries**.

1.12. Lead – acid Battery

Construction
Anode : sponge metallic lead
Cathode : Lead dioxide
Electrolyte: dil. H_2SO_4
 A number of lead plates (- ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel. The lead plates are fit in between lead dioxide plates various plates are separated from adjacent plates by insulators like wood strips, rubber or glass fibre. The entire combination is immersed in approximately 20 – 21 % dil. H_2SO_4 of density 1.2 to 1.3.
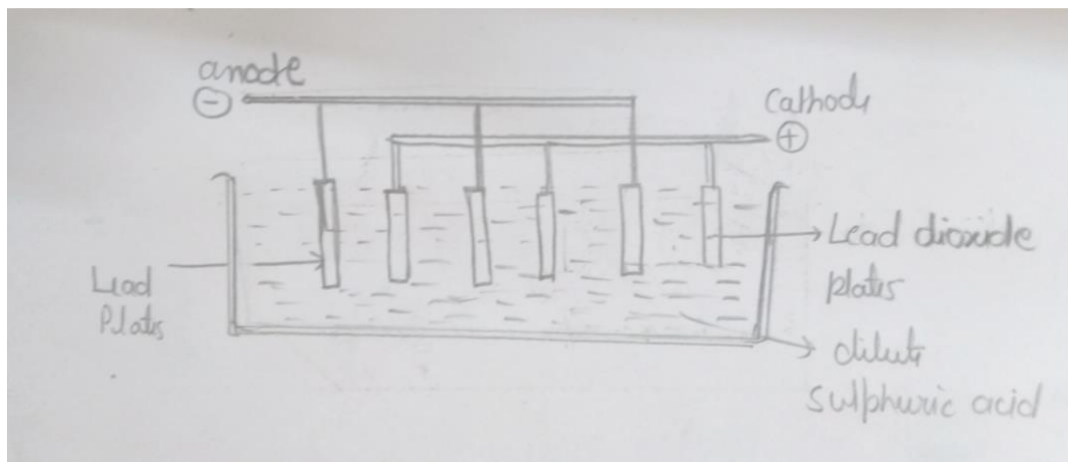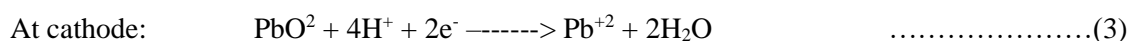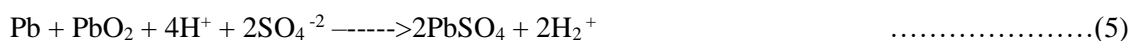
Figure Lead storage battery

Discharging: - when the strong cell is operating as voltaic cell, it is said to be discharging, he lead electrode loses es which flow through the wire. Thus at anode oxidation of lead takes place

At anode :   Pb --------> Pb^{+2} + 2e   …………………(1)
Then it combines with SO_4^{-2} ions

Pb^{+2} + SO_4^{-2} -------> $PbSO_4$ …………………(2)
The electrons flow to the cathode. Here PbO_2 gains electrons and undergoes reduction from +4 to +2 and thus combines with SO_4^{-2} .
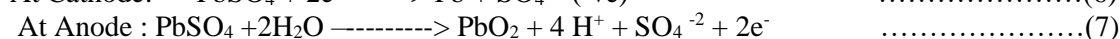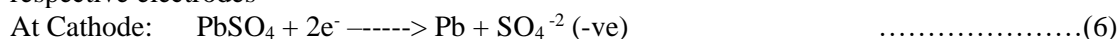
At cathode: PbO^2 + $4H^+$ + $2e^-$ -------> Pb^{+2} + $2H_2O$ ………………….(3)
 Pb^{+2} + SO_4^{-2} ---------> $PbSO_4$ ↓   …………………(4)
So, the net reactions during use is

Pb + PbO_2 + $4H^+$ + $2SO_4^{-2}$ ------>$2PbSO_4$ + $2H_2^+$ …………………(5)

Energy used in automobiles is a combination of six cells in series to form a battery with an e.m.f of 12 volts. (each cell is about 2 volts).

Charging: - When both anode and cathode become concert with $PbSO_4$,the cell stops to function as voltaic cell to recharge it, the reactions taking place during charging are reversed by passing an external e.m.f. greater than 2 volts from a generation and following reactions take place at the respective electrodes
At Cathode: $PbSO_4$ + $2e^-$ ------> Pb + SO_4^{-2} (-ve)   …………………(6)
 At Anode : $PbSO_4$ +$2H_2O$ ----------> PbO_2 + 4 H^+ + SO_4^{-2} + $2e^-$ …………………(7)

The Net reaction during charging is:

$2PbSO_4 + 2H_2O + energy \text{——-------->} PbO_2 + 4H+ + 2SO_4^{-2} + Pb$ …………………(8)

During charging, the lead acid strong cell acts as electrolytic cell. During discharging, concentration of H_2SO_4 decreases while during charging, its concentration increases.
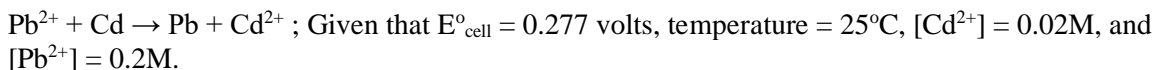
Applications: Automobile and construction equipment, stand by backup systems.

Advantages: Low cost, ability to perform well in high and low temperatures.

Disadvantages: They have low cycle life, a quick self-discharge and low energy densities.

Question and answer

Q.1. What is the Cell Potential of the electrochemical cell in Which the cell reaction is:

$Pb^{2+} + Cd \rightarrow Pb + Cd^{2+}$; Given that $E^o_{cell} = 0.277$ volts, temperature $= 25^oC$, $[Cd^{2+}] = 0.02M$, and $[Pb^{2+}] = 0.2M$.

Ans. Since the temperature is equal to 25^oC, the Nernst equation can be written as follows;

$E_{cell} = E^0_{cell} - (0.0592/n) \log_{10}Q$

Here, two moles of electrons are transferred in the reaction. Therefore, n = 2. The reaction quotient (Q) is given by $[Cd^{2+}]/[Pb^{2+}] = (0.02M)/(0.2M) = 0.1$.

The equation can now be rewritten as:

$E_{cell} = 0.277 - (0.0592/2) \times \log_{10}(0.1) = 0.277 - (0.0296)(-1) = 0.3066$ Volts

Thus, the cell potential of this electrochemical cell at a temperature of 25^oC is 0.3066 volts.

Q.2 The Cu^{2+} ion concentration in a copper-silver electrochemical cell is 0.1M. If $E^o (Ag^+/Ag) = 0.8V$, $E^o(Cu^{2+}/Cu) = 0.34V$, and Cell potential (at 25^oC) = 0.422V, find the silver ion concentration.

Ans. The Silver electrode acts as a cathode whereas the copper electrode serves as the anode. This is because the standard electrode potential of the silver electrode is greater than that of the copper electrode. The standard electrode potential of the cell can now be calculated, as shown below.

$E^o_{cell} = E^o_{cathode} - E^o_{anode} = 0.8V - 0.34V = 0.46V$

Since the charge on the copper ion is +2 and the charge on the silver ion is +1, the balanced cell reaction is:

$2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$
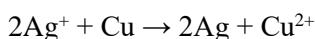
Since two electrons are transferred in the cell reaction, n = 2. Now, the Nernst equation for this electrochemical cell can be written as follows.

$E_{cell} = E^0_{cell} - (0.0592/2) \times \log(0.1/[Ag^+]^2)$

$0.422V = 0.46 - 0.0296 \times (-1 - 2\log[Ag^+])$

Therefore, $-2\log[Ag^+] = 1.283 + 1 = 2.283$

Or, $\log[Ag^+] = -1.141$

$[Ag^+] = antilog(-1.141) = \textbf{0.0722 M}$

Q.3. The standard electrode potential of zinc ions is 0.76V. What will be the potential of a 2M solution at 300K?

Ans. The Nernst equation for the given conditions can be written as follows;

$EM^{n+}/M = E^o – [(2.303RT)/nF] \times \log 1/[Mn^+]$

Here,

- $E° = 0.76V$
- $n = 2$
- $F = 96500$ C/mole
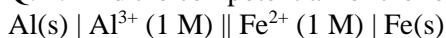- $[Mn^+] = 2$ M
- $R = 8.314$ J/K mole
- $T = 300$ K

Substituting the given values in Nernst equation we get,

$EZn^{2+}/Zn = 0.76 – [(2.303 \times 8.314 \times 300)/(2 \times 96500)] \times \log 1/2 = 0.76 – [0.0298 \times (-0.301)]$
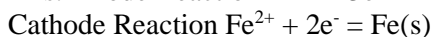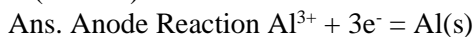
$= 0.76 + 0.009 = \mathbf{0.769V}$

Therefore, the potential of a 2M solution at 300K is 0.769V.

Q. 4. Find the cell potential for the following:
$Al(s) | Al^{3+} (1 M) \| Fe^{2+} (1 M) | Fe(s)$
$E (Al^{3+}/Al) = -1.706$ volt
$E (Fe^{3+}/Fe) = -0.409$ volt
Ans. Anode Reaction $Al^{3+} + 3e^- = Al(s)$
Cathode Reaction $Fe^{2+} + 2e^- = Fe(s)$
Ecell = E cathode – Eanode
Ecell = -0.409 - (- 1.706)
Ecell= 1.297 volt

Q.5. Calculate the equilibrium constant at 298K for the reaction taking place between $CuSO_4$ and Al. Given $E° = 2V$.

Ans. $2Al + 3 Cu^{2+} \rightarrow 2Al^{3+} + 3Cu$

$Al \rightarrow Al^{3+} + 3e^-$] x 2

$Cu^{2+} + 2e^- \rightarrow 2Cu$] x 3
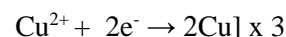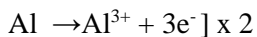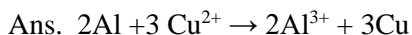
So number of electrons (n) = 6

$\log K_c = 6 \times 2/0.0591$

$\log Kc = 203.39$

$Kc = Antilog\ 203.39$

Q.6. The EMF of the cell at 15ºC is 0.67531 Volt and temperature coefficient is 0.00065 Vdegree[-1.] Calculate the value of ΔG, ΔS and ΔH, If the process is carried out reversibly.

$Cd/CdCl_2.2H_2O// AgCl_{(s)}/Ag$

Ans. $Cd + 2AgCl \leftrightarrow CdCl_2 + 2Ag$

$\Delta G = - n F E$ cell

$\Delta G = -2 \times 96500 \ C \times 0.67531 \ V$

$\Delta G = - 130.335 \ KJ$

$\Delta S = 2 \times 96500 \times 0.00065$

$= 125.45 \ JK^{-1}$

$\Delta H = \Delta G + T\Delta S$

$\Delta H = -130.335 + 288K \times 125.45 \ JK^{-1} \times 10^{-3} \ KJ$

$\Delta H = 166.465 \ KJ$

Q. 7 For galvanic cell, emf is 1.018 K. its temperature coefficient = - 4 X10^{-5} VK^{-1}. Calculate ΔG, ΔS and ΔH for the cell.

Ans. $\Delta G = - n F E$

$= -2 \times 96500 \ C \times 1.018 \ V$

$= -1.964 \times 10^5 \ J$

$\Delta S = nF \left[\frac{\partial (E)}{\partial T}\right]_P$
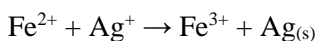
$= 2 \times 96500 \ C \times - 4 \times 10^{-5} \ VK^{-1}$

$= -7.72 \ JK^{-1}$

$\Delta H = - nFE + T \ nF \left[\frac{\partial E}{\partial T}\right]_P$

$= 2 \times 96500 \ C \times 1.018 \ V + [193 \ K \times 2 \times 96500 \ C \times (- 4 \times 10^{-5} \ VK^{-1})]$

$= -1.99 \times 10^5 \ J$

Q. 8. Calculate the standard free energy change of the cell reaction.

$Fe^{2+} + Ag^+ \rightarrow Fe^{3+} + Ag_{(s)}$

Given: $E^o \ (Fe^{3+}/Fe^{2+}) = 0.77$ volt
 $E^o \ (Ag^+/Ag) = 0.80$ volt
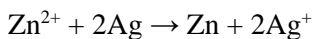Ans. E^ocell = E °cathode $-$ E°anode
        =0.80-(0.77)
        =0.03V

$\Delta G = nFE^o$
        $= -1 \times 96500 \times 0.03$
        $= -2895 \ K$

Q.9. Predict whether the reaction is feasible or not.

$Zn^{2+} + 2Ag \rightarrow Zn + 2Ag^+$

Ans. The half cell reaction

$$2 \text{ Ag} \rightarrow 2 \text{ Ag}^+ + 2e^- \quad E^o = 0.80V$$

$$Zn^{2+} + 2e^- \rightarrow Zn \qquad E^o = -0.763 \text{ V}$$
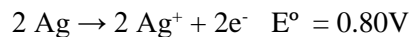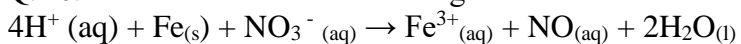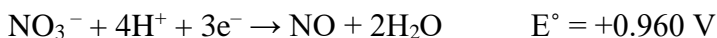
$$E^o\text{cell} = E°\text{cathode} - E°\text{anode}$$

$$= -0.763 - 0.80$$
$$= -1.563V$$

Since E°cell is negative, the reaction is not feasible.

Q. 10. . What is E° for the following balanced reaction?

$$4H^+ \text{ (aq)} + Fe_{(s)} + NO_3^-{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + NO_{(aq)} + 2H_2O_{(l)}$$

Standard Reduction Potential

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \qquad E° = +0.960 \text{ V}$$
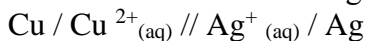$$Fe^{3+} + 3e^- \rightarrow Fe \qquad\qquad\qquad E° = +0.771 \text{ V}$$

Ans. For the above reaction

$$E°\text{cell} = E°\text{cathode} - E°\text{anode}$$

$$= 0.960 - 0.771$$
$$= 1.89 \text{ V}$$

Q. 11. Given the electrochemical reaction shown, if the standard reduction potential of $Ag^+ \rightarrow Ag$ is +0.80 V, and the standard reduction potential of $Cu^{2+} \rightarrow Cu$ is +0.34V, what is E° for the following?
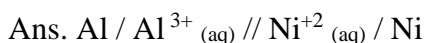
$$Cu / Cu^{2+}{}_{(aq)} // Ag^+{}_{(aq)} / Ag$$

Ans. For the cell

$$E°\text{cell} = E°\text{cathode} - E°\text{anode}$$

$$= 0.80 - 0.34$$
$$= 0.46 \text{ V}$$

Q.12 Given the electrochemical reaction shown, if the standard reduction potential of $Ni^{+2} \rightarrow Ni$ is -0.26 V, and the standard reduction potential of $Al^{3+} \rightarrow Al$ is -1.66V, what is E° for the following?

$$Al / Al^{3+}{}_{(aq)} // Ni^{+2}{}_{(aq)} / Ni$$

Ans. $Al / Al^{3+}{}_{(aq)} // Ni^{+2}{}_{(aq)} / Ni$
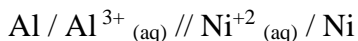
For above cell

$$E°\text{cell} = E°\text{cathode} - E°\text{anode}$$

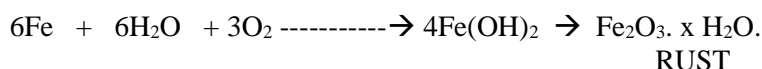$$= -0.26 - (-1.66)$$
$$= 1.4 \text{ V}$$

University Question:

Q.1. What is salt bridge? Mention its function in an electrochemical cell.

Q.2. Give reactions of lead storage cell when it behaves like galvanic cell.

Q.3. Describe the construction and working of Galvanic cell. Calculate the EMF of the following cell and also write the cell reactions. Zn | Zn2 + (0.001M) || Ag + (0.1M) | Ag The standard potential of Ag/Ag + half-cell is +0.80 V and Zn/Zn2+ is -0.76V

Q.4. Principle and working of Galvanic cell.

Q.5. What is Nernst equation? The emf of a cell measured by means of a hydrogen electrode against a saturated calomel electrode at 298K is 0.4188 V. If the pressure of the H_2 (g) was maintained at 1atm, calculate the pH of the unknown solution, given potential of reference calomel electrode is 0.2415 V.

E resources:

1. https://nptel.ac.in/courses/104/106/104106105/
2. https://www.khanacademy.org/science/chemistry/oxidation-reduction/batter-galvanic-voltaic-cell/v/galvanic-cell-voltaic-cell
3. https://www.youtube.com/watch?v=JYO20y4uDmE
4. https://www.khanacademy.org/test-prep/mcat/physical-processes/intro-electrochemistry-mcat/v/nerst-equation-edited
5. https://www.khanacademy.org/science/chemistry/oxidation-reduction/cell-potentials-under-nonstandard-conditions/v/using-the-nernst-equation
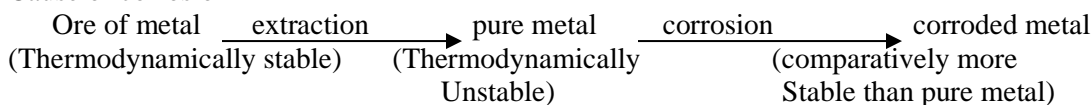6. https://www.youtube.com/watch?v=H6Vctvdkq-s

2. CORROSION

Corrosion is a chemical or electrochemical attack of environment on metal which results in the loss of its metallic properties and it gets destructed. eg. - rusting of corrosion.

$$6Fe + 6H_2O + 3O_2 \text{-----------} \rightarrow 4Fe(OH)_2 \rightarrow Fe_2O_3. \, x \, H_2O.$$
$$\text{RUST}$$

** CROMIUM AND GOLD DO NOT UNDERGO CORROSION.

Cause of corrosion

Ore of metal   extraction   pure metal   corrosion   corroded metal
(Thermodynamically stable)   (Thermodynamically   (comparatively more
                    Unstable)   Stable than pure metal)

2.1.Types of corrosion-

2.1.1.Dry Corrosion/Chemical Corrosion. When metal gets corroded in the absence of any conducting medium then it is k/as dry corrosion.

2.1.2.Wet Corrosion/ Electrochemical Corrosion / Immersed Corrosion. When metal gets corroded in the presence of any conducting medium then it is k/as dry corrosion.

2.2.Differences between Wet and Dry corrosion

	Dry corrosion	**Wet corrosion**
1	It occurs in dry condition.	It occurs in wet condition.
2	If the corrosion takes place due to direct chemical attack (in the absence of moisture), corrosion is known as dry corrosion.	If the corrosion takes place due to electrochemical attack in presence of moisture or a conducting medium, corrosion is known as wet corrosion.
3	Explained by chemical mechanism.	Explained by electrochemical mechanism.
4	It occurs on both heterogeneous and homogeneous surfaces.	It occurs only on heterogeneous metal surfaces.
5	Corrosion is uniform.	Corrosion is not uniform.
6	It is a slow process.	It is a fast process.
7	Corrosion products accumulate at the place where corrosion occurs.	Corrosion take place at anode but products accumulate near the cathode.

2.3.Factors influencing corrosion

2.3.1.Nature of metal: Extent of corrosion depends upon the position of the metal in galvanic series. When two metals are in electrical contact in presence of an electrolyte, the metal higher up in galvanic series becomes anodic and suffers corrosion.

2.3.2.Purity of metal: The rate of corrosion increases with the extent of impurities. Impurities accelerated the corrosion due to the formation of minutes electrochemical cells because of heterogeneity caused by them.

2.3.3.Physical state of the metal: The physical state of metal such as orientation of grains, grain structures, localized stresses, scratches etc., highly influences the rate of corrosion.

2.3.4.Nature of the oxide film: In aerated atmosphere, almost all the metals get covered with an oxide film. If the specific volume of the metal oxide film formed is lesser than the volume of the metal atom, then the film will be porous. The porosity will easily allow oxygen to diffuse into metal and causes further corrosion.

2.3.5.Area effect: If the area of cathode is large as compared to anode then the corrosion of the anode is rapid and severe. This is because; when the cathodic area is large it will demand more electrons, which can be only supply by anodic area, so very rapid corrosion occurs.

2.3.6.Solubility of the products of corrosions: If the corrosion product is soluble in the corroding medium then corrosion proceeds at a faster rate.

2.4.Difference between electrochemical and Galvanic Series

S. No.	Electrochemical Series	Galvanic Series
1.	The arrangement of metals and non-metals in increasing order of their standard reduction potential is known as electrochemical Galvanic Series.	The arrangement of metals and alloys in decreasing order of their corroding tendency in an unpolluted sea water is known Galvanic Series
2.	It contains metals and nonmetals.	It contains metal and alloy
3	It is an ideal series	It is a practical series
4	This series is based upon electrode potential.	This series is based on actual corrosion rate
5	Position of a given metal is fixed in series.	Position of a given metal in series may change.
6	It gives no idea about the position of alloys	It gives clear idea about the position of alloys
7	It gives information about the displacement tendencies.	It gives information about the relative corrosion tendencies.

2.5.Wet Corrosion / Electrochemical Corrosion / Immersed Corrosion- This type of
corrosion takes place-
1. When a conducting liquid is in contact with a metal.
2. When two dissimilar metals, immersed partially in conducting medium, are connected to each other.

Mechanism of wet corrosion / electrochemical theory of corrosion –This theory involves-

(a) oxidation of metal at anode resulting in the formation of metallic ions

$$M \longrightarrow M^{n+} + ne^- \text{ (oxidation)}$$

(b) At cathode, e- liberated from anode are consumed through reduction reaction by-

2.5.1. Evolution of hydrogen gas

2.5.2. Absorption of oxygen gas

Depending upon the nature of corrosive environment.

2.5.1 Evolution of Hydrogen (corrosion in acidic medium)-when the metals which are positioned above the hydrogen in electrochemical series, are kept in acidic medium (like HCl) then they get corroded with evolution of hydrogen. So this is displacement of H^+ from acidic solution by metal.
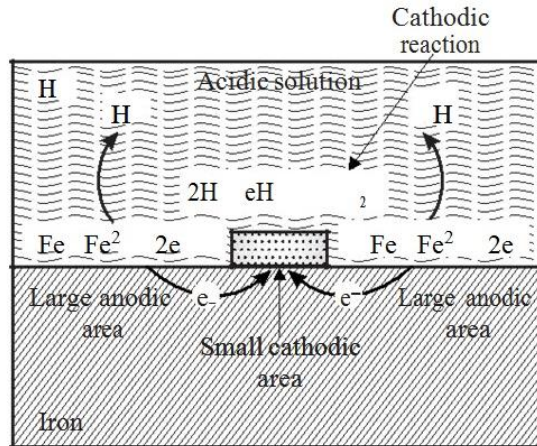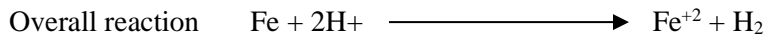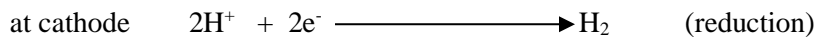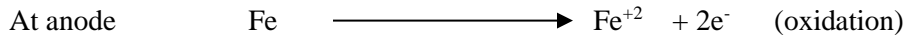

Fig: Evolution of Hydrogen

Reaction

At anode $Fe \longrightarrow Fe^{+2} + 2e^-$ (oxidation)

at cathode $2H^+ + 2e^- \longrightarrow H_2$ (reduction)

_____

Overall reaction $Fe + 2H+ \longrightarrow Fe^{+2} + H_2$

2.5.2. Oxygen absorption mechanism/rusting of iron in alkaline or neutral medium- Usually metals are covered with a metal oxide layer. Suppose this metal is exposed to alkaline or neutral atmosphere (i.e. it has dissolved oxygen) and small portion of the oxide layer gets scratched then bare surface of metal comes in contact with environment and work as anode whereas remaining part works as cathode.
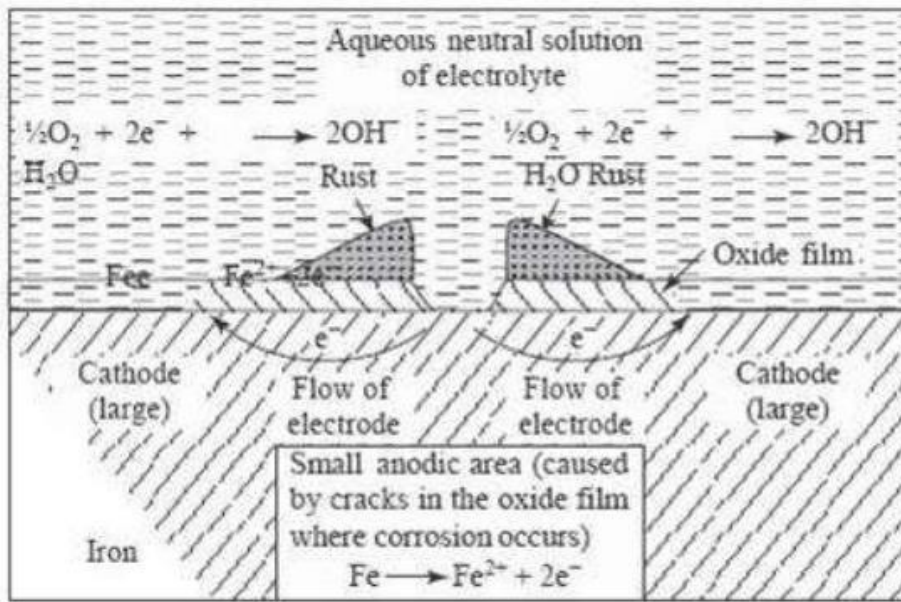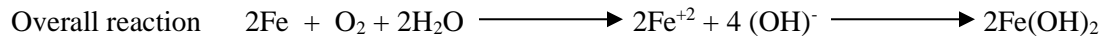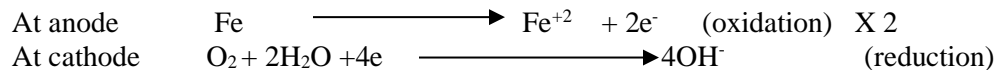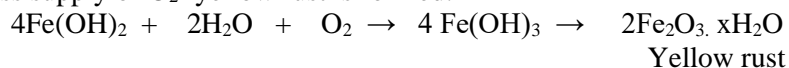
Fig: Oxygen absorption mechanism

At anode   Fe $\longrightarrow$ Fe^{+2} $+ 2e^-$ (oxidation) X 2
At cathode $O_2 + 2H_2O + 4e$ $\longrightarrow$ $4OH^-$ (reduction)

_____

Overall reaction $2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{+2} + 4\,(OH)^- \longrightarrow 2Fe(OH)_2$
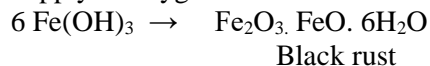
Now depending on the availability of oxygen in environment, two types of corrosion products are formed.

in excess supply of O_2- yellow rust is formed.
$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4\,Fe(OH)_3 \rightarrow 2Fe_2O_3.\,xH_2O$$
Yellow rust

in limited supply of oxygen- black rust is formed.
$$6\,Fe(OH)_3 \rightarrow Fe_2O_3.\,FeO.\,6H_2O$$
Black rust

2.6.Different types of corrosion- there are many types of corrosion.

2.6.1.Galvanic corrosion/ differential metal corrosion - when two metals ,with large difference in reduction potential, are in contact then one metal acts as anode whereas second metal acts as cathode. the anode metal starts to get oxidized and releases electron which is accepted by cathode and it gets reduced.
Eg. Zn-Cu Galvanic cell.
That is why bolts and nuts made up of same metal are preferred in practice.

2.6.2.Pitting corrosion – when the corrosion results in the formation of small pits then it is called as pitting corrosion. It takes place due to a small anodic and large cathodic area.

Corrosion extent α cathodic area / anodic area.

Suppose, a small drop of conducting liquid is kept on metal rod. Then the dropped are (having less concentration of dissolved O_2) acts as anode and starts to get corroded. As cathodic area (high concentration of atm. O_2) is very large, its high demand of e- for reduction is to be supplied by small anodic area. So there is a very fast oxidation which results in a deep pit.
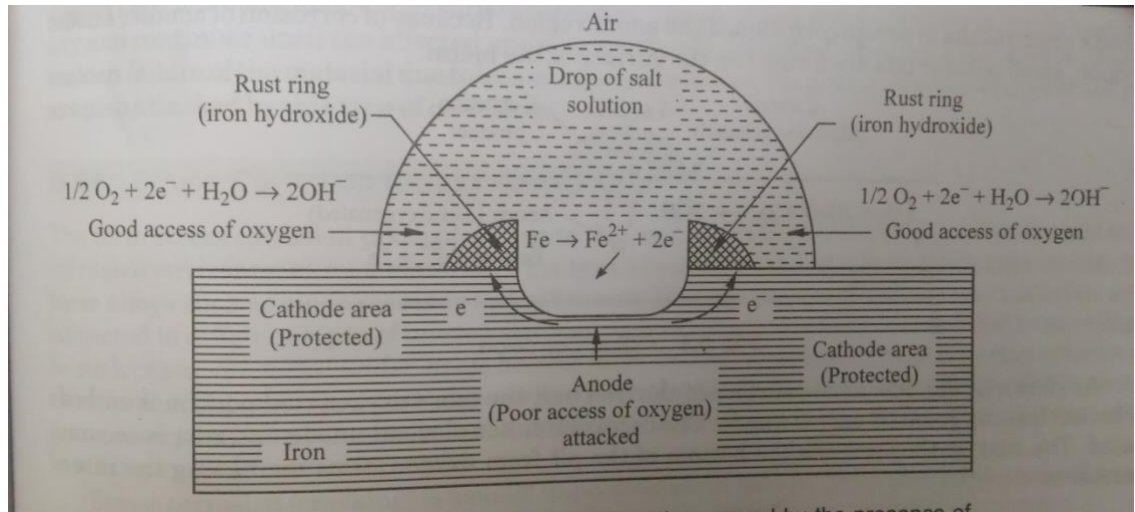
Fig. Pitting Corrosion

2.6.3.Concentration Cell Corrosion/ Deferential Aeration Corrosion- when a metal rod is partially immersed in a electrolytic solution and partially exposed to atmosphere,, then it results in the formation of concentration cell. The immersed part (poor oxygenated area) becomes anode and undergoes oxidation.

Concentration cell corrosion

At anode   Zn $\longrightarrow$ Zn^{+2} + $2e^-$ (oxidation)

Whereas exposed area (high oxygenated area) acts as cathode and undergoes reduction of O_2.

At cathode $O_2 + H_2O$ $\longrightarrow$ OH^- (reduction)

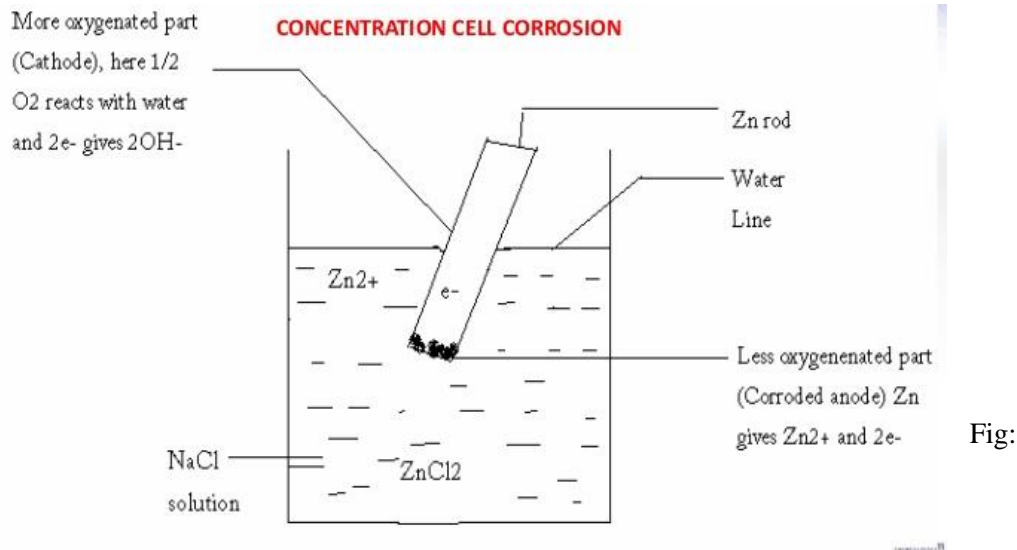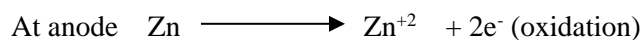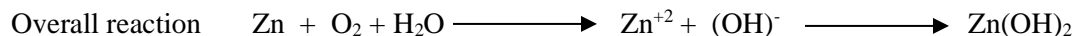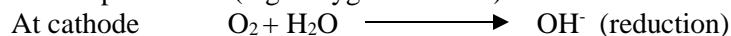Overall reaction $Zn + O_2 + H_2O \longrightarrow Zn^{+2} + (OH)^- \longrightarrow Zn(OH)_2$

2.7.Prevention of corrosion- there are many methods of prevention from corrosion which are given below –

2.7.1.Cathodic protection(Electrochemical protection)- it is based on the principle that the metal to be protected is forced to behave as a cathode. It is done by either of one way-

2.7.1.1.Sacrificial Cathodic Protection-- In this method, the metal which is to be protected is connected with a more reactive (more anodic) metal. So the more active metal will behave as anode and the metal to be protected starts to behave as cathode. All corrosion is concentrated on more active metal, not on the metal to be protected. As the more active metal is sacrificed in the process to save the metal from corrosion, hence it is called as sacrificial cathodic protection. The sacrificial metal is replaced after consumed completely. eg .Burried Water pipe lines are connected with Mg, Al etc. rods.

oxidation:
$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$

reduction:
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
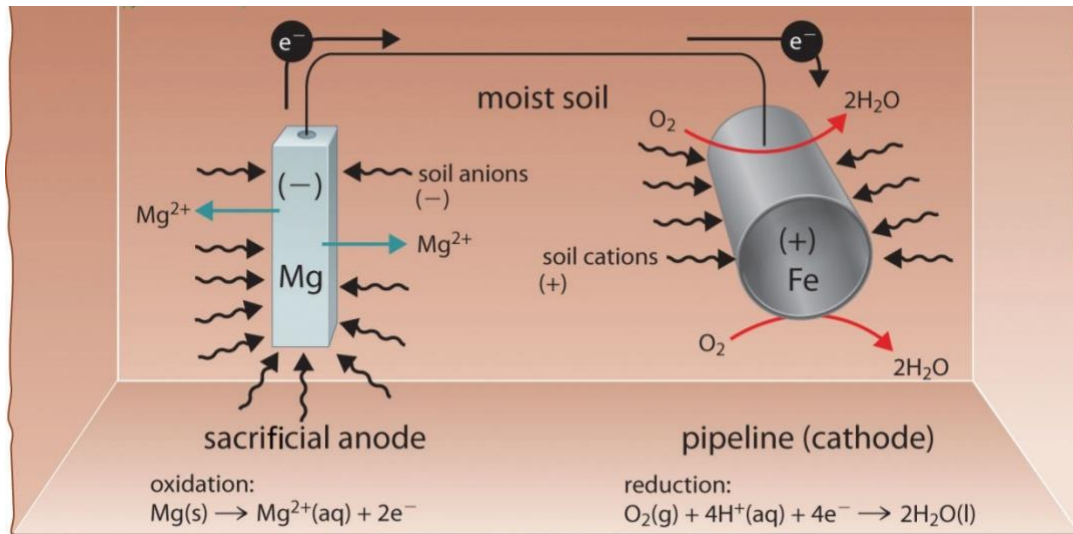
Fig: sacrificial cathodic protection

2.7.1.2. Impressed current cathodic protection-In this method the a current from an external sources is impressed (applied in opposite direction) to nullify the corrosion current. This is done to convert the corroding metal from anode to cathode. Once the metal becomes cathode, it is protected from corrosion.

Fig: Impressed cathodic protection

2.7.2 Coating- Coating means any physical, continuous barrier b/w metal and corrosive environment which prevents their direct interactions.

There are three types of coating.
2.7.2.1. Metallic coating.
2. 7.2.2. Organic coating.
2.7.2.3. Inorganic coating.

2.7.2.1. Metallic Coating- It means coating of metal on base metal (metal to be protected). It is done in two ways-

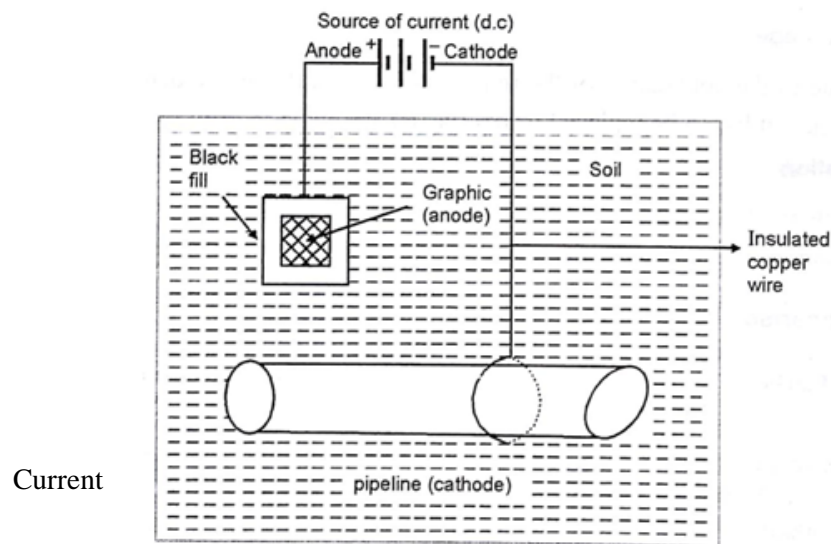| Anodic coating/sacrificial coating	Cathodic coating/Noble coating.
1. In this metallic coating, the coating of more reactive metal (having high oxidation potential) is done on base metal.	1. In this metallic coating, the coating of noble metal (having very low oxidation potential) is done on base metal.
2. In anodic coating, base metal is protected but anodic coating metal undergoes corrosion sacrificially.	2.In noble coating, base metal is protected and coating metal also does not undergo corrosion
3. It is effective even if it gets broken/scratched	3. It is not effective, if it gets broken/scratched.
4. eg. Zn,Al coating on steel.	4. eg.coating of Sn on Fe.

2.7.2.2. Organic Coating-In this coating, a barrier of organic compounds are formed.eg - paints, varnishes, plastics on metal.

2.7.2.3. Inorganic Coating - In the inorganic coating, inorganic compounds converts the surface of metal into non metallic layer which prevents further corrosion.

2.7.3. Use of Inhibitors:- Inhibitors are the chemicals which prevents or slow the rate of corrosion.
Cathodic inhibitor-It inhibits the cathodic reaction by consuming H^+.eg. Urea .
Anodic inhibitors—These inhibitors reacts with ion on anode and form a layer or ppt on metal which prevents further corrosion. eg. – Alkalies, chromates, phosphates etc.

2. 7.4.Modification of Environment-
i. Moisture can be removed by increasing the storing temperature, by using silica. Al_2O_3 etc.
ii. Acid can be removed by addition of lime.
i. Excess O_2 can be removed by mechanical (deaeration) or chemical (NH_2NH_2).
iv. Salts can be removed by filtration.

2.7.5. By using pure metal- Impurity in metal causes heterogeneity which decreases corrosion resistance of metal,
2. 7.6. Using metal alloys- corrosion is also avoided by using alloys. Eg. Cr is alloyed into iron or steel by electroplating.
2. 7.7. Proper designing-important designing principles are-
- Avoid the contact of two dissimilar metals with a large difference of reduction potential.
- In galvanic cells, use large anodic area as compare to cathodic area.
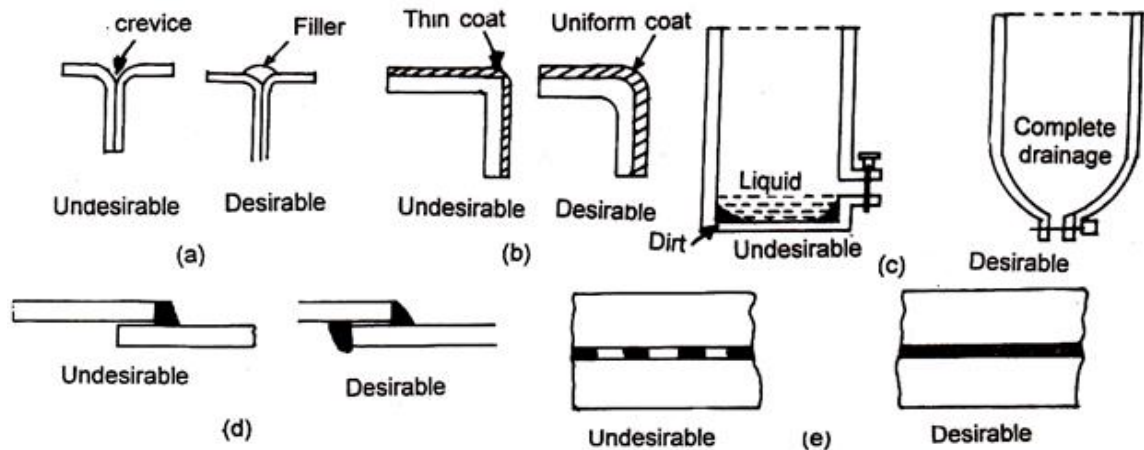- Proper drainage of water (avoid sharp edges).

Fig: Corrosion prevention by proper design

Question and answer

Q.1. Iron corrodes faster than aluminium, even though iron is placed below aluminium in the electrochemical series. Why?

Ans.: When aluminium is exposed to environment, it forms a non-porous protective oxide film of Al_2O_3. This oxide film of aluminium surface does not permit corrosion to occur. So, aluminium is not corroded easily.

Q.2. Rusting of iron is quicker in saline water than in ordinary water. Why?

Ans. Saline water contains common salt, sodium chloride, which leads conductivity of water. When saline water comes in contact with iron, corrosion current increases and rusting of iron takes place rapidly.

Q.3. How does rain effects on corrosion?

Ans. Rain may have following important effects on corrosion:

i.   It may remove corrosion product as in the case on nickel.

ii.   Its presence may develop a product having protective quantities as in the case of copper.

iii.   The rate of attack may be increased as a result of break down or removal of an otherwise protective coating.

Q.4. Why does corrosion occur in steel pipe connected to copper plumbing?

Ans. Steel is an alloy of iron, which is higher in the electrochemical series. So, it forms the anode. Hence, iron undergoes oxidation and gets corroded when steel pipe is connected to copper plumbing is exposed to a corroding environment.

Q.5. What do you mean by galvanic corrosion?

Ans. When two dissimilar metals such as zinc and copper are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series, i.e. zinc in the present case, undergoes corrosion and the type of corrosion is called galvanic corrosion. For example, corrosion in steel pipe connected to copper plumbing.

Q.6. Why does corrosion of water filled steel tanks occur below the waterline?

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Ans. The areas of steel tank above the water line is more oxygenated and acts as cathode, whereas the areas below water line is not exposed to air and act as anode. Thus, the anodic area below water line undergoes oxidation and gets corroded. This is called differential aeration corrosion.

Q.7. What is meant by term passivity?
Ans. Passivity is the phenomenon in which a metal or an alloy shows high corrosion resistance due to formation of highly protective and very thin surface film, which is about 0.0004 mm thick. This film is insoluble, non-porous, and self-healing in nature. The metal such as Ti, Cr, Al, etc. and a wide verity stainless steel alloys containing Cr show high corrosion resistance due to formation of protective oxide film of these metals easily. Any damage to this film is automatically repaired in oxidizing environments. In reducing environment, the passive metals become chemically active and undergo corrosion.

Q.8. How does waterline corrosion ships prevented?
Ans.: One of the most effective ways to prevent and control ship corrosion is to apply coatings to parts that are most susceptible to corrosion, such as the hull. This area of the ship sits below the waterline, so it experiences more exposure to damaging salts and minerals. Waterline corrosion is prevented by painting the sides of ships by special antifouling paints such as cuprous oxide (or other copper compounds).

Q.9. What do you mean by the terms galvanization and tinning?
Ans.: Coating of zinc on iron by hot dipping is called galvanization and coating of tin on iron is called tinning.

Q.10. Why does part of a nail inside the wood undergo corrosion easily?
Ans.: The part of nail inside the wood is not exposed to atmospheric condition and becomes deoxygenated thereby behaves as anode. So, due to differential aeration, the part of nail inside the wood acting as anode, undergoes oxidation and gets corroded.

Q.11. A copper equipment should not possess a small steel bolt. Why?
Ans. Steel contains iron, which is more anodic than copper. So, steel bolt acts as anode and gets corroded. The copper equipment acts as cathode and is protected. Since anodic area is very small, so it is completely corroded in the due course of time and action of bolt gets finished.

Q.12. What are inhibitors? Explain about anodic and cathodic inhibitors.
Ans. Inhibitors are substances which when added in small quantity to the aqueous medium, decreases the rate of corrosion of the metal. They may be organic or inorganic small molecules that dissolve in the corroding medium but don't form any protective film or scale either in cathodic or anodic area. Anodic inhibitors are generally salts react with metal ions to form insoluble compounds. They form a thin film on the anodic surface and prevent further corrosion. Examples of anodic inhibitors include silicates, phosphates, chromates of alkali and transition metals.
Cathodic inhibitors: In acidic medium, corrosion takes place due to cathodic reaction, where hydrogen is liberated. $H+ + 2e- \rightarrow H_2$ Thus, corrosion at anode can be controlled by (a) decreasing the evaluation of hydrogen at the cathode, (b) Increasing the over voltage of hydrogen at the anode The evaluation of hydrogen can be controlled by addition of organic inhibitors such as amines, heavy metal soaps, substituted ureas and thioureas. Antimony and arsenic oxides or salts such as meta arsenate are also used as inhibitors. In neutral solutions, the cathodic reactions is due to absorption of oxygen and formed OH ions.
$H_2O + 1/2O_2 + 2e- \rightarrow 2OH-$
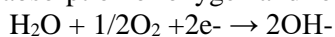
This can be eliminated by adding reducing agents such as sodium sulphite (Na_2SO_3) or deaeration. Diffusion to the cathodic areas can be retarded by adding inhibitors like Zn, Ni or Mg salts to the corroding medium.

Q.13. Why Al is less corroded than Fe instead having higher position in electrochemical series?
Ans. Passivity of metal:- Passivity of metal is the process in which a metal or alloy exhibits a much higher corrosion resistance power than expected from its poison in electrochemical series. Passivity is due o the formation of a highly protective and very thin layer on the surface of metal or on the alloy, which makes it more noble. The process of formation of this layer is known as passivation and it is particular in nature for an environment in other type of environment it behaves according the position in electrochemical series. eg. Al is less corroded than Fe instead having higher position in electrochemical series due the formation of a very stable aluminum oxide layer.

University Question:
Q.1. Analyze why does part of a nail inside the wood undergoes corrosion easily?
Q.2. Describe electrochemical theory of corrosion. Briefly explain sacrificial anodic protection and impressed current cathodic protection.
Q.3.Discuss rusting of iron by Hydrogen evolution and Oxygen absorption mechanism Briefly explain sacrificial anodic protection and impressed current cathodic protection.
Q.4. Why does part of a nail inside the wood undergoes corrosion easily?

E resources:

1. https://www.youtube.com/watch?v=m8t4btjJd5Y
2. https://www.youtube.com/watch?v=q3c-ig5G3bA
3. https://www.youtube.com/watch?v=W6URLa36eNg
4. https://www.youtube.com/watch?v=UpfG3HqhcWg

3. PHASE RULE

Phase Rule

Given by Williard Gibbs

Statement Phase rule states that "If the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action but are influenced only by temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases (P) by the following phase rule equation :

F+P = C + 2

3.1.Phase (P)

A phase is defined as "an homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces" Example:

3.1.1. Liquid phase: The number of liquid phase depends on the number of liquids present and their miscibility.

If two liquids are immiscible, they will form two separate liquid phases. Example: benzene and water

If two liquids are miscible they will form one liquid phase only. Example: alcohol and water

3.1.2. Solid phase: Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it. Example: Many forms of Sulphur can exist together, but these are all separate phases.

3.1.3. Gaseous phase: Since a gaseous mixture is thoroughly miscible in all proportions, it will form one phase only. Example: a mixture of N_2 and H_2 forms one phase only.

3. 1.4. A solution of a substance in a solvent consists of one phase only, e.g. glucose solution.

3.1.5. A heterogeneous mixture like:

$$CaCO_3 \text{ (s) } \leftrightarrow CaO \text{ (s) } + CO_2 \text{ (g)} \qquad \qquad \text{………………….(1)}$$

It consists of three phases (i.e., two solids and one gaseous).

3. 1.6. In the equilibrium reaction:

$$Fe(s) + H_2O(g) \leftrightarrow FeO(s) + H_2(g) \qquad \qquad \text{…………………(2)}$$

There are two solid phases, Fe and FeO and one gaseous phase consisting of $H_2O(g)$ and $H_2(g)$. Thus three phases exists in equilibrium.

3. 1.7. Water consists of three phases:

Ice (s)↔ Water (l) ↔Water vapour (g) …………………(3)

3.2.Component (C)

Component is defined as "the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation".

Example :

3.2.1. In the water system,

Ice (s)↔ Water (l) ↔Water vapour (g) …………………(4)

The chemical component of all the three phases is H_2O and therefore it is one component system.

3. 2.2. Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition of all phases is S. Thus is an one component system.

3.2.3. A system of saturated solution of NaCl consists of two component system.

3.2.4. In the thermal decomposition of $CaCO_3$,

 $CaCO_3$ (s)↔ CaO (s) + CO_2 (g) …………………(4)

The composition of each of the three phases can be expressed in terms of at least any two of the independent variable constituents, $CaCO_3$, CaO and CO_2. Composition of each of the three phases can be expressed in terms of any two constituents, $CaCO_3$ and CaO and CO_2 as shown below:

If $CaCO_3$ and CaO constituents

Phase	Component
$CaCO_3$ (s)	$CaCO_3$ (s) + 0CaO (s)
CaO (s)	0$CaCO_3$ (s) + CaO (s)
CO_2 (g)	$CaCO_3$ (s) - CaO (s)

If $CaCO_3$ and CO_2 constituents

Phase	Component

$CaCO_3$ (s)	$CaCO_3$ (s) + $0CO_2$(g)
CaO (s)	$CaCO_3$ (s) - $0CO_2$(g)
CO_2 (g)	$0CaCO_3$ (s) +CO_2(g)

If CaO and CO_2 constituents

Phase	Component
$CaCO_3$ (s)	CaO(s) + CO_2(g)
CaO (s)	CaO(s) + $0CO_2$(g)
CO_2 (g)	$0CaO$(s) + CO_2(g)

Thus in all cases, only two components are required to express the composition of each phases. Hence it is a two component system.

3.2.5. In the dissociation of NH_4Cl, the following equilibrium occurs:

NH_4Cl (s) $\leftrightarrow$ NH_3 (g) + HCl (g)　　　　　　　　　　…………………(5)
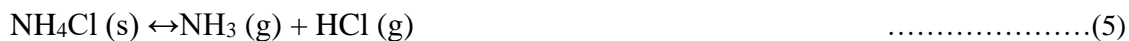
In close system consists of two phase namely solid NH_4Cl and the gaseous mixture containing NH_3+HCl. When NH_3 and HCl are present in equivalent quantities the composition of both the phases can be represented by the same chemical compound NH_4Cl and hence the system will be a one component system.

However in open system if NH_3 or HCl is in excess, the system becomes two component system because decomposition of NH_4Cl would not give the correct composition of the gas phase. Hence NH_3 or HCl would be required to specify the gas composition. Hence it becomes two component system.

If there are S substances and R relations among them, then the number of components (C) can be calculated as:

C = S-R

3.3. Degree of freedom

Degree of freedom is defined as the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to

define the condition of a system completely. A system having 1, 2, 3 or 0 degrees of freedom is called univariant, bivariant, trivariant and nonvariant respectively.

Consider the water system,

Ice (s)↔ Water (l) ↔Water vapour (g)
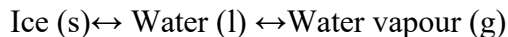
The three phases can be in equilibrium only at particular temperature and pressure. Therefore, when all the three phases are present in equilibrium, then no condition needs to be specified. The system is therefore zero variant or invariant or has no degree of freedom

3.4. Applications of Phase rule to one component system (water system)

Ice (s)↔ Water (l) ↔Water vapour (g)
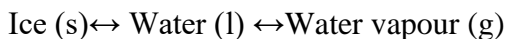
Since water exists in three possible phases such as solid, liquid and vapour, there are three forms of equilibria : Liquid – vapour , solid -vapour and solid- liquid i.e.,

Liquid↔ Vapour

Solid↔ Vapour

Solid ↔Liquid
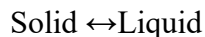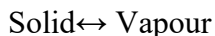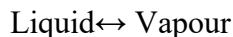
Each equilibrium involves two phases. The nature of these phases which exist in equilibrium at any time depends on the conditions of temperature and pressure. These conditions have been determined and summarized in the pressure-temperature diagram in which pressure is treated as independent variable and is plotted along y – axis whereas temperature is plotted along x axis.
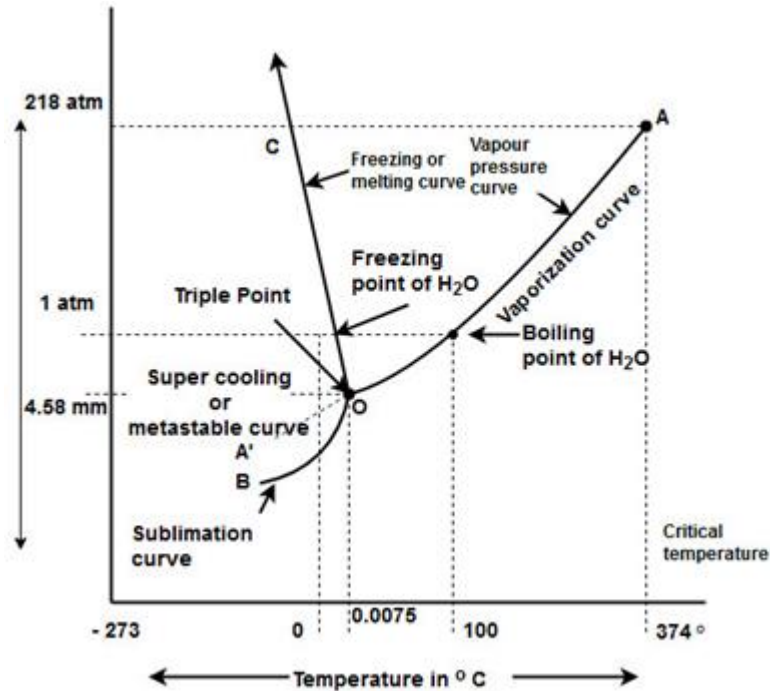
Figure: Water Phase diagram

3.4.1. CURVES

Curve OA The curve OA is called vapourization curve, it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist

Water $\leftrightarrow$ Water vapour

The degree of freedom of the system is one, i.e, univariant. Thus applying phase rule equation,

$F = C - P + 2 = 1 - 2 + 2 ; F = 1$

This equilibrium (i.e, line OA) will extend upto the critical temperature (374^0C). Beyond the critical temperature the equilibrium will disappear only water vapour will exist.

Curve OB The curve OB is called sublimation curve of ice, it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.

Ice $\leftrightarrow$ Vapour

The degree of freedom of the system is one, i.e., univariant. This is predicted by the phase rule.

$F = C - P + 2 ; F = 1 - 2 + 2 ; F = 1$

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This equilibrium line will extend upto the absolute zero (-273^0C) where no vapour can be present and only ice will exist.

Curve OC The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.

Ice$\leftrightarrow$ Water

The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure. The degree of freedom of the system is one. i.e., univariant.

 Curve OB (Metastable equilibrium) The curve OB is called vapour pressure curve of the super-cool water or metastable equilibrium. Where the following equilibrium will exist.

Super-cool water $\leftrightarrow$Vapour

Sometimes water can be cooled below 0^0C without the formation of ice, this water is called super-cooled water. Supercooled water is unstable and it can be converted into solid by 'seeding' or by slight disturbance.

3.4.2. POINT

Triple point (Point 'O') At triple point all the three phases namely ice, water and vapour coexist. Thus the value of P is 3. Applying phase rule equation, the degree of freedom at this point is zero. It means that three phases can coexist in equilibrium only at a definite temperature and pressure. The values are 0.0075^0C and 4.58 mm Hg respectively. At this triple point, neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases.

3.4.3. AREAS

Area BOC represents the solid ice, which is thermodynamically most stable states under these condition. Area AOC represent the liquid water phase, similarly AOB represent gas vapour phase. Area AOC, BOC , AOB represents water, ice and vapour respectively. In order to define the system at any point in the areas, it is essential to specify both temperature and pressure. The degree of freedom of the system is two. i.e.,Bivariant. This is predicted by the phase rule

$F = C - P + 2; F = 1 - 1 +2 ; F = 2$

S. No.	Equilibrium	Phase	C	F=C+2-P	Remarks

1.	Area				
	(i)Left of COB	Ice	1	2 (Bivariant)	P and T can be varied
	(ii)Above of COA	Water	1	2 (Bivariant)	P and T can be varied
	(iii) Right of AOB	vapour	1	2 (Bivariant)	P and T can be varied
2.	Curve				
	(i) curve OC ice ↔water Freezing or melting curve	2	1	1(monovariant)	P or T can be varied
	(ii)curve OA Water↔ Vapour Vaporization curve	2	1	1(monovariant)	P or T can be varied
	(iii) curve OB ice↔ Vapour sublimation curve	2	1	1(monovariant)	P or T can be varied
	(iv) curve OA' Supercooled water↔ Vapour Metastable curve	2	1	1(monovariant)	P or T can be varied
3.	Point O Triple point	3	1	0 (nonvariant)	$T=0.0075^0C$ and $P=4.58$ mm Hg

Ice (s)↔ Water (l) ↔Water vapour (g)				

3.5. Advantage of phase rule

3.5.1.It provides a simple method of classifying equilibrium states of a system such as phases, components and degree of freedom.

3.5.2.It indicates that different systems having the same number of degree of freedom behave in like manner.

3.5.3.It explains the behavior of system when allowed to change in the variables such as pressue, temperature and concentration.

3.5.4.It is applicable to physical as well as chemical equilibria.

3.6. Limitations of phase rule

3.6.1.As the phase rules is applicable to heterogeneous systems in equilibrium, it is therefore of no use for such systems which are slow in reaching the state of equilibrium.

3.6.2. As the phase rule is applicable to a single equilibrium state, it never tells about the number of other equilibrium possible in the system.

3.6.3. All the phases are required to be present under the same temperature, pressure and gravitational forces.

3.6.4. Solids or liquid phase should not be in finely divided form, otherwise vapour pressure may differ from the normal values.

Question with solutions

Q.1. What is Gibbs phase rule for general system?
Ans. The Gibbs phase rule $F+P = C+2$ gives the relationship between the number of phases and components c in a given alloy under equilibrium conditions at constant pressure, where F is the number of thermodynamic degrees of freedom in the system.

Q.2. What is the difference between phase and component?
Ans. A phase is a form of matter that is homogeneous in chemical composition and physical state. The number of components (C) is the number of chemically independent constituents of the system, i.e. the minimum number of independent species necessary to define the composition of all phases of the system.

Q.3. Why is the triple point of water important?
Ans. It is also important to note that the triple point of water correlates with the pressure necessary for liquid water to exist. Because ice is less dense than liquid water, ice frozen at pressures below the triple point will sublime directly into water vapor.

Q.4. What is Triple Point explain with example?
Ans. In thermodynamics, the triple point of a substance is the temperature and pressure at which the three phases (gas, liquid, and solid) of that substance coexist in thermodynamic equilibrium.

Q.4. Why does the phase diagram of water have a negative slope?
Ans. Unlike carbon dioxide and most other substances, the phase diagram of water shows a negative slope for the boundary line between the liquid and solid state. This difference has to do with that fact that water actually expands as it goes from the liquid state to the solid state.

Q.5. Can you have a quadruple point in one component system?
Ans. Quadruple point is not possible in one component system.

$$F+P=C+2$$
$$F+4=1+2 \quad (P=4 \text{ for quadruple point})$$
$$F = -1 \text{ (it is not possible)}$$

Q. 6.What is a critical point on a phase diagram?
Ans.   In a phase diagram, the critical point or critical state is the point at which two phases of a substance initially become indistinguishable from one another. The critical point is the end point of a phase equilibrium curve, defined by a critical pressure T_p and critical temperature P_c
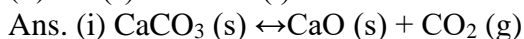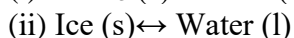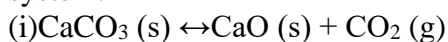
Q.7. What is a supercritical point?
Ans. When a compound is subjected to a pressure and a temperature higher than its critical point, the fluid is said to be "supercritical". In the supercritical region, the fluid exhibits particular proporties and has an intermediate behavior between that of a liquid and a gas.

Q. 8. Can a substance have more than one triple point?
Ans. It is physically impossible for more than three phases to coexist at any combination of temperature and pressure, but in principle there can be more than one triple point in a phase diagram.
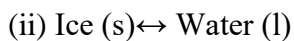
Q.9. Predict the number of phases, component and degree of freedom in following system:
(i)$CaCO_3$ (s) $\leftrightarrow$CaO (s) + CO_2 (g)
(ii) Ice (s)$\leftrightarrow$ Water (l)
Ans. (i) $CaCO_3$ (s) $\leftrightarrow$CaO (s) + CO_2 (g)
No. of phases 3 [$CaCO_3$ (s), CaO (s) and CO_2 (g)]
Number of Component =2
Degree of freed om=C+2-P =2+2-3=1

(ii) Ice (s)$\leftrightarrow$ Water (l)
No. of phases 2 [Ice (s) and Water (l)]

Number of Component =1
Degree of freedom=C+2-P =1+2-2=1

Q.10. Calculate the number of phases and components in sulphur system.

$Ss \leftrightarrow Sm \leftrightarrow S_l \leftrightarrow Sv$

Ans. Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour.

No. of phases = 4

Number of Component =1

Q.11. Calculate the number of components KCl-NaCl-H_2O System.

Ans. KCl-NaCl-H_2O System consist of six species

KCl, NaCl, H_2O, K^+, Na^+ and Cl^- system, so S=6

Independent equilibrium reactions are two, so R=2

$NaCl \leftrightarrow Na^+ + Cl^-$

$KCl \leftrightarrow K^+ + Cl^-$

Hence C = S - (R+1)   for electrolyte solution

Component C = 6-(2+1)

Number of Component = 3

Q.12. Calculate the number of components KCl-NaBr-H_2O System.

Ans. KCl-NaBr-H_2O System consist of nine species

KCl, NaBr, KBr, NaCl, H_2O, K^+, Na^+ , Br - and Cl^- system, so S=9

Independent equilibrium reactions are four, so R=4

$KCl \leftrightarrow K^+ + Cl^-$

$NaBr \leftrightarrow Na^+ + Br^-$

$K^+ + Br^- \leftrightarrow KBr$

$Na^+ + Cl^- \leftrightarrow NaCl$

Hence C = S - (R+1)   for electrolyte solution

Component C = 9-(4+1)

Number of Component = 4

University Questions:

Q.1. Predict the number of phases in saturated NaCl system?

Q.2. Using phase rule outline the salient features of the phase diagram of water system highlighting the name of system (areas, curves and points), phase in equilibrium and degree of freedom in each case.

Q.3. Calculate the no. of P, C and F in the following systems-

i.$NH_4Cl(S\rightarrow) NH_3$ (g) + HCl (g) (open system)

ii.$NH_4Cl(S) \rightarrow NH_3$ (g) + HCl (g) (closed system)

e resources

1. https://www.khanacademy.org/science/chemistry/states-of-matter-and-intermolecular-forces/states-of-matter/v/phase-diagrams
2. https://www.youtube.com/watch?v=NqXIfsxy9yU
3. https://www.youtube.com/watch?v=lrosz8N-9tA
4. https://nptel.ac.in/courses/113/104/113104068/