Electro Chemistry Part-III

Nernst Equation, Batteries Corrosion, Passivity

I: Nernst equation

Nernst equation gives the dependence of the electrode potential on the concentration of ion with which the electrode is reversible. This equation holds good for reversible electrodes.

a) For metal electrodes, the half-cell reaction is

$$M^{n+} + ne^- \leftrightharpoons M$$

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[M]}{[M^{n+}]} \quad \text{Or} \quad E = E^0 + \frac{0.059}{n} \log C$$

b) For non - metal electrodes, the half cell reaction is $\quad A + ne^- \leftrightharpoons A^{n-}$

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[A^{n-}]}{[A]} \quad \text{Or} \quad E = E^0 - \frac{0.059}{n} \log C$$

For H electrode $E = -0.059 \, pH$

c) Concentration cell is galvanic cell in which both the electrodes are of same type but the electrolytes have different concentration.

$Cu|CuSO_4 \, (C_1) \, || \, CuSO_4 \, (C_2)|Cu$

The cell potential of the concentration cell can be calculated by

$$E_{cell} = \frac{2.303RT}{nF} \log \frac{C_2}{C_1}$$

At 298K, $E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$

d) When the cell reaction is in equilibrium, the cell EMF (E) is zero. So the Nernst Equation is

$$E^0 = \frac{2.303RT}{nF} \log K_c \text{ (or) } E^0 = \frac{0.0591}{n} \log K_c$$

e) **For Hydrogen Electrode:** $2H^+ + 2e^- \rightarrow H_2{}_{(P\,atm.)}$, $E_{RP} = E_{RP}^0 - \frac{0.059}{n} \log \frac{P_{H_2}}{\left[H^+\right]^2}$

f) For Electrode Concentration Cells

The two electrodes of different concentration are dipped in the same solution of electrolyte.

Eg1 $Pt, H_{2(P_1)} / H^+ / H_{2(P_2)}, Pt$, $E_{cell} = \frac{0.059}{n} \log \frac{P_1}{P_2}$

Eg2 $Pt, Cl_{2(P_1)} / Cl^- / Cl_{2(P_2)}, Pt$, $E_{cell} = \frac{0.059}{n} \log \frac{P_2}{P_1}$

g) Emf of cell= $E^\circ{}_{cell} - \frac{0.059}{n} \log \frac{[products]}{[reactats]}$

II: Cell potential – Gibbs Energy:

 I. The change in free energy is represented by ΔG.

II. For spontaneous reaction, ΔG will have negative value ($\Delta G = -ve$)

III. Electrical work done in one second = Electrical potential $\times$ total charge passed.

IV. To obtain maximum work from a galvanic cell, the charge has to be passed reversibly.

V. The reversible work done by a galvanic cell = decrease in its free energy.

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

VI. When no current is drawn from the cell the EMF of the cell is E, the amount of charge passed is nF(n = no of electrons and F = Faraday) then $\Delta G = -nFE$

VII. If the activity of reacting species is unity, then $E = E^0$, then we can have

$\Delta G^0 = -nFE^0$

From standard free energy, the equilibrium constant can be calculated

$$\Delta G^0 = -RT \ln k_C \quad \text{or} \quad \Delta G^0 = -2.303 RT \log K_c$$

VIII: If two half cell reactions having electrode potential E_1^0 and E_2^0 are combined to give a third half cell reaction having an electrode potential E_3^0 then

$$\Delta G_3^0 = \Delta G_1^0 + \Delta G_2^0$$

i.e $\quad -n_3 F E_3^0 = -n_1 F E_1^0 - n_2 F E_2^0 \quad$ or $\quad E_3^0 = \dfrac{n_1 E_1^0 + n_2 E_2^0}{n_3}$

* If number of electrons involved are equal then $E_3^0 = E_1^0 + E_2^0$

III. Some Commercial Cells and Batteries

i) The electrochemical cells can be used to generate electricity.

ii) The word battery is used for two (or) more galvanic cells generally connected in series.

iii) There are two types of commercial cells:

(a) Primary cells:-

i) It is an electrochemical cell which acts as a source of electrical energy without being previously charged up by an electric current from an external source of current.

ii) In which electrode reactions cannot be   reversed by external source.

iii) These are not chargeable.

iv) Examples of this type is dry cell (or) Leclanche cell, voltaic cell.

I. Dry cell or Leclanche cell

Dry cell consists of a zinc container which acts as anode and graphite as cathode rod surrounded by powdered manganese dioxide and carbon. The Zinc electrode is in contact with paste of ammonium chloride and zinc chloride. The paste, $C+MnO_2$ and $NH_4Cl + ZnCl_2$ are separated by a porous sheet. The zinc vessel is surrounded by card board. The zinc vessel is sealed with pitch .The following reactions occur in dry cell,.

Anode reaction: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
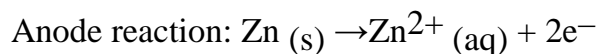
Cathode reaction: $MnO_2(s) + NH_4^+{}_{(aq)} + e^- \rightarrow MnO(OH) + NH_3$

(Or) $MnO_2 + H_2O + e \rightarrow MnO(OH) + OH^-$

Zn is reductant & MnO_2 is oxidant and acts as depolarizer.

The secondary reactions taking place in dry cell are

$NH_4Cl + OH^- \rightarrow NH_3 + Cl^- + H_2O$, $Zn^{+2} + 2NH_3 + 2Cl^- \rightarrow ZnCl_2.2NH_3$

Ammonia produced in the reaction forms a complex, $[Zn(NH_3)_4]^{2+}$ .The potential of the cell is nearly 1.5V.

II. Mercury cell

It is used for low current devices

Anode: ZnHg

Cathode: paste of HgO & Carbon

Electrolyte: paste of KOH & ZnO

Anode reaction, $ZnHg + 2OH^- \rightarrow ZnO_{(s)} + H_2O + Hg_{(l)} + 2e^-$

Cathode reaction, $HgO + H_2O + 2e^- \rightarrow Hg_{(l)} + 2OH^-$

Zn is reductant and HgO is oxidant

Overall cell reaction is $Zn + HgO_{(s)} \rightarrow ZnO_{(s)} + Hg_{(l)}$

Overall reaction does not involve any ion.

Cell potential remains constant during its life. Cell potential – 1.35 volt.

(b) Secondary cells:-

i) Electrical energy from an external source is first converted into chemical energy
(Electrolysis) and when the source is removed then the cell is made to operate in the
reverse direction.

ii) Secondary cells are those which can be   rechargeable and used again and again.

iii) These are designed to convert the energy from combustion of fuel such asH_2. CO,
CH_4 etc directly into electrical energy.

iv) The common examples are hydrogen-oxygen fuel cell, Hydrocarbon fuel cell Ni-Cd
cell, Lead accumulator, Li-ion battery.

v) Acid storage cell is Lead accumulator and Alkali storage cell is Edison Battery

Lead storage battery": It is used in automobiles & invertors.

Anode: Lead grids of filled with spongy lead

Cathode: Lead grids of filled with PbO_2

Cathode & anode are arranged alternately .Cathode and anode are separated by thin fiber

       glass sheets

Electrolyte: 38% (by weight) solution of H_2SO_4

Anode reaction, $Pb + SO_4{}^{2-}{}_{(aq \rightarrow)} \quad PbSO_4{}_{(s)} + 2e^-$

Cathode reaction, $PbO_2 + SO_4{}^{2-}{}_{(aq)} + 4H^+ + 2e^- \rightarrow PbSO_4{}_{(s)} + 2H_2O{}_{(l)}$

    Overall cell reaction,

    $Pb_{(s)} + PbO_2{}_{(s)} + 2H_2SO_4{}_{(aq)} \rightarrow 2PbSO_4{}_{(s)} + 2H_2O{}_{(l)}$

During working of cell, H_2SO_4 is used up (during discharge)

During charging of battery, cell reactions a reversed. i.e., $PbSO_4$ on anode is converted

to $Pb_{(s)}$ and $PbSO_4$ on cathode is converted to $PbO_2{}_{(s)}$

At anode - $PbSO_4{}_{(s)} + 2H_2O_{(l)} \rightarrow PbO_2{}_{(s)} + SO_4{}^{-2}{}_{(aq)} + 4H^+{}_{(aq)} + 2e^-$

At cathode $PbSO_4{}_{(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4{}^{-2}{}_{(aq)}$

    Lead sulphate accumulated at cathode and anode is converted into lead and lead dioxide respectively. Charging and discharging of lead storage battery is known as double sulphation. The voltage increases with the concentration of electrolyte. The voltage varies from 1.88V

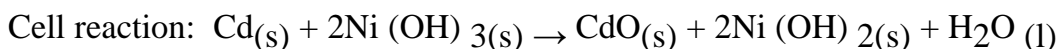(5% H_2SO_4) to 2.15V (40% H_2SO_4).

Nickel - Cadmium cell: It has longer life than lead storage battery but more expensive. In this

    Anode – Cd (s)

    Cathode – Ni $(OH)_3{}_{(s)}$

    Electrolyte – Moist NaOH (or) KOH

Cell potential 1.4 volt

Cell reaction: $Cd_{(s)} + 2Ni\,(OH)_{3(s)} \rightarrow CdO_{(s)} + 2Ni\,(OH)_{2(s)} + H_2O_{(l)}$

Cd – reductant & Ni (OH)$_3$– oxidant

IV: Fuel Cells

Fuel Cells are Galvanic cells that convert energy of combustion of fuels like hydrogen, methane, and methanol etc., directly into electrical energy are called fuel cells.

1. Fuel cells may be liquid fuel cells (or) gas fuel cells.

  i. In liquid fuel cells $CH_3OH, C_2H_5OH, HCHO, N_2H_4$ are used as fuels.

 ii. In gas fuel cells - H_2. CO, CH_4 etc are used as fuels.

2. Fuel cells i) working below 100°C are low temperature cells.

 ii) Working between 100-250°C are medium temperature cells.

iii) Working above 500°C are high temperature cells.

3. H_2O_2, HNO_3, air, O_2 etc. are used as oxidants.

4. Pt, Porous PVC, PTFE coated with Ag are used as electrodes.

5. In biochemical cells organic compounds disintegrated by micro organisms.

These are in use now a day.

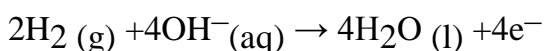a) H_2 -O_2 FUEL CELL: [The cell used to supply electrical power in the Apollo space program].

Electrodes**:** Porous carbon electrodes with catalysts like finely divided platinum or palladium.

Electrolytes: H_2 and O_2 are bubbled through concentrated aqueous NaOH solution.

Cathode Reaction:

$O_{2\,(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-_{(aq)}$

Anode Reaction,

$2H_{2\,(g)} + 4OH^-_{(aq)} \rightarrow 4H_2O_{(l)} + 4e^-$
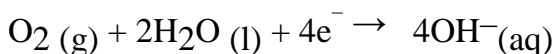
Overall reaction – $2H_2 (g) + O_2 (g) \rightarrow 2H_2O (l)$

The cell runs continuously as long as reactants are supplied. Efficiency of fuel cell is about 70% and

Fuel cells are pollution free

General representation of fuel cell: Fuel/electrode/ electrolyte/ electrode / oxidant.

b) Hydrocarbon-Oxygen Fuel Cell

Hydrocarbons are burned in oxygen at high temperature to get large amount of electrical energy.

Air freed from impurities (or) pure oxygen is oxidant.

Aq. KOH is used as electrolyte.

Pt electrodes are used.

H_3PO_4 is used as electrolyte if hydrocarbon is burned. It is because the obtained CO_2 in combustion is absorbed by Aq . KOH.

V. Corrosion

The natural tendency of conversion of a metal into its mineral compound form an interaction with the environment (Polluted air, water, associated other Metals etc) is known as corrosion.

Ex : Iron converts itself into its oxide (Fe_2O_3- haematite),Copper converts itself into its carbonate ($CaCO_3.Cu(OH)_2$ - Malachite),Silver converts itself into its sulphide (Ag_2S - horn silver).

*Corrosion in case of iron is known as rusting and in case of silver is known as tarnishing.

Mechanism

In corrosion, a metal is oxidised by loss of electrons to oxygen and formation of oxides.
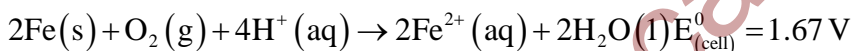
Corrosion of iron (commonly known as rusting) occurs in presence of water and air. At a particular spot (figure given above) of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction.

Anode: $2Fe(s) \rightarrow 2Fe^{2+} + 4e^- \quad E^0_{(Fe^{2+}/Fe)} = -0.44V$
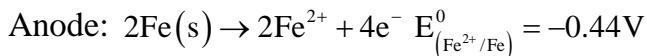
Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+, which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere. This spot behaves as cathode with the reaction.

Cathode: $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(1), E^0_{H^+/O_2/H_2O} = 1.23V$
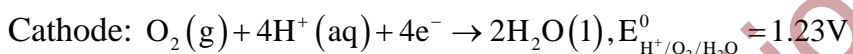
The overall reaction being:

$$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(1) E^0_{(cell)} = 1.67\,V$$

The ferrous ions are further oxidised by atmospheric oxygen to ferric ions which come out as rust in the form of hydrated ferric oxide, i.e $Fe_2O_3.x\,H_2O$

The process of corrosion may be chemical (or) electro chemical in nature

The anodic dissolution of a metal under the conditions of corrosion is known as electrochemical corrosion $M \rightarrow M^{n+} + ne^-$

Corrosion occurs if the environmental conditions of the metal favour the formation of an voltaic cell with the metal acting as anode

Electro - chemical corrosion is basically of two types

1) Hydrogen evolution type

2) Differential oxygenation type

1. Hydrogen Evolution Type

i. This type of corrosion is exhibited by metals which can displace H_2 gas from aqueous solution.

ii.   This happens if the electrode potential of the metal under the conditions of corrosion

is more negative than that of the hydrogen electode under the given conditions.

iii. The hydrogen electrode potential depends on the nature of the metal used as the Cathode and the P^H of the solution. It is almost zero (0V) in 1M acid solution, if the cathode metal is platinised platinum (Black Platinum)

It is about 0.8 V if the cathode metal is Hg

For other Metals the value lies in between these two values (0 to 0.8V)

This type of corrosion depends upon

1) The P^H of the medium

2) Chemical nature of the metal undergoing corrosion

Eg. Pure zinc does not corrode in salt solutions but in the presence of Cu as impurity Zn corrodes.

Zn corrodes in 2M acid but not in neutral salt solution

2. Differential oxygenation corrosion

I. This type of corrosion occurs if O_2 concentration is not uniformly distributed on the surface of the metal

II. Corrosion of the metal generally occurs at the point where O_2 concentration is less

III. The portion of the metal with access to high concentration of O_2 functions as cathode and with access to low concentration of O_2 functions as anode. Hence, the metal with differential oxygenation acts as a galvanic cell

Ex: When an iron rod is immersed in NaCl solution the immersed part is corroded due to less oxygenation of the surface of the metal.

Factors that promote electrochemical corrosion

i. The nature of the impurity metal with which the metal under consideration is associated

For Ex: Cu favours corrosion of Zn. because Zn is more anodic than copper

Zn disfavours corrosion of 'Fe' (Galvanization)

ii. The concentration of O_2 in contact with the surface of the metal

For Ex: Metal rod half immersed in aqueous salt solution gets corroded at the surface not exposed to O_2, i.e., the immersed part of the Metal gets easily corroded

iii. Highly conducting solutions favour rapid corrosion

Prevention of Corrosion

The main principle underlying the methods of prevention of corrosion is to separate the metal (or) isolate the metal from the environment is achieved by different ways. They are

(a) Painting

(b) Alloying (galvanisation)

(c) To prevent as far as possible the contact of the metal surface with good electrical conducting media

(d) Covering by some chemicals like bisphenol.

(e) Cover the surface by other metals (Sn, Zn etc) that are inert (or) react to save the object.

(f) Sacrificial electrode of another metal (like Mg, Zn, etc) which corrodes itself but saves the object.

VI: Passivity

The phenomenon of a metal reaching a stage of non-reactive state in its reaction with concentrated acids may be called passivity.

Iron group of metals and some other transition metals are rendered passive with concentrated acids.

Passivity of a metal can be classified into following three types.

i. Chemical passivity

Non - reactivity of metals after initial reaction with conc HNO_3 is called chemical passivity

Eg: If iron is dipped in conc HNO_3 it is attacked for some time and after becomes inactive.

Passive iron don't dissolve in dil HNO_3 and iron don't displace Ag from $AgNO_3$

Co, Ni, Cr can also become passive. Air can also cause passivity to Fe, Cr, Mo, and W&V

ii. Mechanical Passivity

In some cases dissolution of metal stops due to visible oxide film formation, this is mechanical passivity

Eg: PbO_2 on Pb

Fe, Co, Ni, Mn also exhibits this type of passivity

iii. Electrochemical passivity:

Metal with more -ve SRP functions as anode in cell

Generally Fe, Ni, Co functions as anode. They dissolve as $M \rightarrow M^{+n} + ne^-$

At particular stage anode stops dissolving due to formation of invisible metal oxide film, this phenomenon is called electro - chemical passivity.