

Chapter 4

ELECTROCHEMISTRY

Lecture/Lession Plan -3

ELECTROCHEMISTRY

4.1 Electrochemical cell

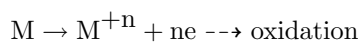
Chemical reaction can take place by passing electrical energy under suitable condition. This is commonly known as electrolysis. The device, where this transformation may take place is known as electrolytic cell.

In case of reverse electrolysis, spontaneous chemical reaction generates electrical energy and the device where this phenomenon happens is known as electrochemical cell or galvanic cell. An example of electrochemical cell is Daniel cell. In this section we will discuss details of electrochemical cells and how some physical parameters of a solution can be determined from from it.

4.2 Redox reaction

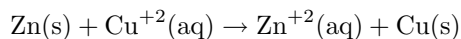
If in a chemical reaction oxidation and reduction happens simultaneously, then the reaction is known as redox reaction. In this section we will emphasize on that type of oxidation-reduction reaction which happens by electron transfer only.

Generally loss of electron is known as oxidation and gain of electron by another species is known as reduction.

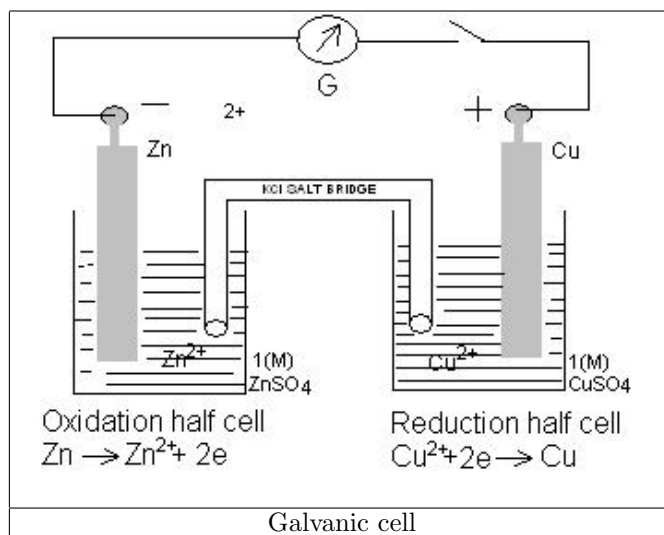


If a zinc rod is dipped in a blue coloured copper sulphate solution, metallic zinc will be oxidised by losing electron and zinc cation will come into solution whereas copper cation will be reduced by accepting electron to brown coloured metallic copper and will be deposited on zinc rod. Thus with time we will notice the disappearance of blue colour of the solution and overgrowth of brown copper

on zinc rod. This oxidation-reduction (redox) can be expressed as-



The above stated reaction and the principle can be used to form a galvanic cell which is known as Daniel Cell.



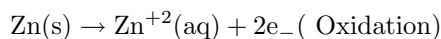
A zinc rod is dipped in a zinc sulphate solution and a copper rod is dipped in a copper sulphate solution separately. Now if we connect the two rod by an external circuit and an ammeter is placed in parallel to the circuit.

4.2.1 Salt bridge

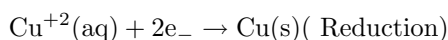
Two end of an inverted U-tube is dipped into two beaker containing solution. Both end of the U-tube is plugged by cotton or wool so that any direct contact of electrolyte solution and the salt inside salt bridge can be avoided. This U-tube is known as salt bridge and is filled with electrolyte like KCl, KNO₃ or NH₄NO₃ etc.

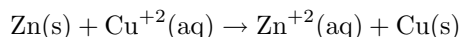
As soon as the external circuit is completed, a flow of electricity will be observed as deflection in ammeter will be noticed. This is due to the flow of electron from zinc rod to copper rod. These rods are termed as electrodes; the zinc rod will be called as ANODE and the copper will be called as CATHODE. As the electron flows from zinc (Anode) to copper (Cathode), the zinc rod must be rich of electron and there must be demand for electron at copper rod. This indicate that electron loss reaction (oxidation) is happening at anode and electron consumption reaction (reduction) is happening at cathode. The chemical reaction that is responsible for the generation of electricity will be like this-

At ANODE



At CATHODE





As the negative charged electron flows from zinc rod (anode) to copper rod (cathode), conventionally the current will flow in opposite direction.

Function of salt bridge: Salt bridge mainly helps in maintaining the electrical neutrality of both the electrolytic solution used in a Daniel cell. When the redox reaction happens in a Daniel cell, from anode metallic zinc is converted to zinc cation and comes to solution hence the solution is enriching with positive charge. To neutralize this positive charge, negative charged ions like chloride anion etc comes out from the salt bridge and goes into anode solution. Similarly, at cathode positively charged cations are reduced and hence the electrolyte solution have a shortening of positive charge. To neutralize this, salt bridge provide the cations like potassium cation etc.

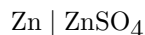
4.3 General way to represent an electrochemical cell

Generally ANODE is represented at left hand side and CATHODE is represented at right hand side and both side is separated by salt bridge. Anode is represented by writing the metallic electrode first followed by a single bar vertically and then the electrolyte solution. For cathode, the electrolyte solution is written first followed by the vertical bar and the metallic electrode. The physical states of both the electrolytic solution and the electrode written in first bracket sometimes. Now in between cathode and anode a double vertical bar placed as a symbol for salt bridge. Thus the above Daniel cell be represented as-



where the first part is anode and the second part is cathode.

Anode:



and Cathode:



Sometimes a single electrolyte solution and two electrode used in a galvanic cell. In that case to represent the cell, no vertical bar is used for salt bridge and the cell is represented as-



4.4 EMF of Cell

In a general galvanic cell electron flow from anode to cathode; this implies that the anode is rich of electron and cathode have a demand for electron. In very crude science greater the difference of electron density in between this two electrode, higher will be the potential difference between the two half cell. This potential difference basically controls the flow of electricity in a galvanic cell circuit. The difference in potential between two electrode is known as electromotive force (EMF). Now, as in anode oxidation takes place so potential of anode is known as oxidation potential. Similarly the

potential of cathode is known as reduction potential. Electromotive force (EMF) of a cell will be defined as a force which drives the negatively charged electrons from anode to cathode and hence the electricity flow from cathode to anode.

Standard EMF or Potential (E^0): Standard EMF or standard potential of a cell is defined as the EMF of an electrode when all the component of the cell are in standard state, i.e., solutes are at 1M concentration, gaseous components are in 1 atm pressure, solid components are at their pure state and temperature of the system is at 25°C. EMF of a cell is generally expressed as E_{cell} . The EMF of a cell will be the sum of the two electrode potential;

$$E_{\text{cell}} = E_{\text{anode}}(\text{oxidation}) + E_{\text{cathode}}(\text{reduction})$$

where E_{anode} is the oxidation potential of anode and E_{cathode} is the reduction potential of cathode. Now, conventionally cell emf can be written in reduction format, i.e., both the cathode and anode emf should be expressed in reduction form. The cathode was already in reduction format and hence we need to change the anode expression from oxidation format to a reduction format. Generally a change in sign will do this job.

$$E_{\text{cell}} = E_{\text{cathode}}(\text{reduction}) - E_{\text{anode}}(\text{reduction})$$

Thermodynamic significance of EMF: As both emf (E) of a cell and Gibbs free energy (ΔG) related to spontaneity of a chemical reaction, hence both can be correlated by an equation-

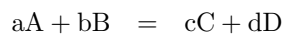
$$\Delta G = -nFE$$

where n is the number of electron involve in the reaction and F denotes Faraday (96500 coulomb/mole). As both n and F is positive valued for a chemical reaction, then EMF (E) of a reaction must be positive for spontaneity of the chemical reaction as in that case ΔG will be negative. So, for a spontaneous chemical reaction E must be positive and for a non-spontaneous reaction E will be negative. For an equilibrium reaction E will be zero.

4.5 Nernst equation

The Nernst equation represents a relationship between cell potential and the concentration of the reactant and product present in that chemical cell.

Let us consider a chemical reaction-



where a mole A reacts with b mole B and gives c mole C and d mole D as product. Now change in Gibbs free energy of this chemical reaction can be written as-

$$\Delta G = \Delta G^0 + RT \ln Q$$

where Q is known as reaction quotient which is very similar to equilibrium constant (K) and ΔG^0 is called as standard change of Gibbs free energy.

Where Q can be expressed as-

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

As we know that-

$$\begin{aligned}\Delta G &= -nFE \\ \Delta G^0 &= -nFE^0 \\ -nFE &= -nFE^0 + RT\ln Q \\ E &= E^0 - \frac{RT}{nF}\ln Q \\ E &= E^0 - \frac{0.0591}{n}\log Q\end{aligned}$$

This is Nernst equation which shows how emf of a cell changes with the change of concentration of both reactant and product.

4.6 Single Electrode Potential

The standard potential of a galvanic cell can be expressed as-

$$\begin{aligned}E_{\text{cell}}^0 &= E_{\text{cathode/reduction}}^0 + E_{\text{anode/oxidation}}^0 \\ E_{\text{cell}}^0 &= E_{\text{cathode/reduction}}^0 - E_{\text{anode/reduction}}^0\end{aligned}$$

Where $E_{\text{cathode/reduction}}^0$ is the standard reduction potential of the cathode half cell and $E_{\text{anode/oxidation}}^0$ is the standard oxidation potential of the anode half cell. The standard potential of any half cell or any one electrode can not be determined directly. We can only measure the difference in emf between two electrode by constructing cell. In this case if we can use one standard electrode or reference electrode whose standard potential is zero, then we can measure the difference or the the standard potential of the other half cell.

Standard hydrogen electrode can solve this problem as the standard potential of hydrogen electrode is zero. This electrode can be formed by immersing a platinum wire (electrode) in a acid solution of strength 1(M). Interesting point is that this hydrogen electrode can serve either as cathode or anode depending upon the nature of other half cell electrode.

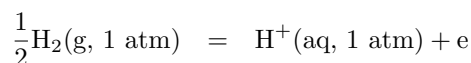
As anode: The hydrogen electrode can be used as anode and in that case pure H_2 gas is passed into solution and it is oxides to hydrogen ion (cation) by releasing electron at Pt electrode. In this case, the other half cell will act as cathode and electron will be transported from hydrogen electrode to cathode where selective reduction will happen. Any half cell electrode whose standard reduction potential is positive can serve as cathode with hydrogen electrode as anode to complete a full electrochemical cell where spontaneous chemical reaction will generate electrical energy.

As cathode: Similarly, the hydrogen electrode can be used as cathode and in that case H^+ ion will be reduced to hydrogen gas by accepting electron. In this case, the other half cell will act as anode and electron will be transported to hydrogen electrode from anode where selective oxidation will happen. Any half cell electrode whose standard reduction potential is negative can serve as anode with hydrogen electrode as cathode to complete a full electrochemical cell where spontaneous chemical reaction will generate electrical energy.

Standard hydrogen electrode (SHE) can be expressed as-



Anode half cell reaction:



The reverse will be for cathode half cell reaction. Now for both cases the electrode potential will be 0 V at 25°C.

4.7 Determination of standard half cell reduction potential of an unknown electrode half cell

Let us consider to determine the $\text{M}^{+n} | \text{M}$ half cell standard reduction potential. In this case we will make a electrochemical cell with this half cell with a standard hydrogen electrode. If by the completion of external circuit, hydrogen gas bubbling is observed at hydrogen electrode then hydrogen electrode is acting as cathode. If we observed that hydrogen gas is consumed at hydrogen electrode, then hydrogen electrode is acting as anode.

If hydrogen electrode acts as cathode, then-

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{H}^+|\text{H}_2}^0 - E_{\text{M}^{+n}|\text{M}}^0 \\ E_{\text{cell}}^0 &= 0 - E_{\text{M}^{+n}|\text{M}}^0 \\ E_{\text{M}^{+n}|\text{M}}^0 &= - E_{\text{cell}}^0 \end{aligned}$$

If hydrogen electrode acts as anode, then-

$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{M}^{+n}|\text{M}}^0 - E_{\text{H}^+|\text{H}_2}^0 \\ E_{\text{cell}}^0 &= E_{\text{M}^{+n}|\text{M}}^0 - 0 \\ E_{\text{M}^{+n}|\text{M}}^0 &= E_{\text{cell}}^0 \end{aligned}$$

A list of standard reduction potential of some half cell electrode is given here from higher positive value to lower value. The value of standard reduction potential indicates the tendency of a species of higher oxidation state to go to a lower oxidation (reduction) state. If two half cell electrode combine and form a electrochemical cell, that electrode will act as cathode preferentially with relatively higher standard reduction potential. Now if we look the standard reduction potential of these two electrode-

$$\begin{aligned} E_{\text{Cu}^{+2}|\text{Cu}}^0 &= +0.34\text{V} \\ E_{\text{Zn}^{+2}|\text{Zn}}^0 &= -0.76\text{V} \end{aligned}$$

This value indicates that Cu^{+2} will preferentially reduced to metallic Cu at cathode and at anode Zn will be oxidised to Zn^{+2} as standard reduction potential value of copper system is higher than zinc system. Point to mention that if we use silver system instead of copper system, then Ag^+ preferentially reduced to silver at cathode and Cu will be oxidised to Cu^{+2} at anode as standard

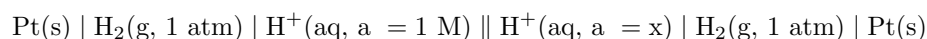
reduction potential value of silver system is higher than copper system.

$$E_{\text{Ag}^+|\text{Ag}}^0 = +0.80\text{V}$$

4.8 Application of Nernst Equation

4.8.1 Measure of pH of a solution by using hydrogen electrode and standard hydrogen electrode:

An electrochemical cell can be constructed by using standard hydrogen electrode (SHE) ($a=1$; acid strength is 1M) and a hydrogen electrode ($a=x$; acid strength is unknown).

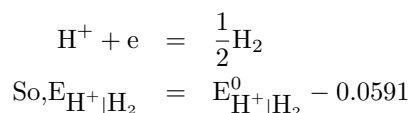


Here the standard hydrogen electrode acts as anode and hydrogen electrode acts as cathode. The half cell potential value of standard hydrogen electrode is zero.

The cell potential of the above cell can be expressed as-

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ E_{\text{cell}} &= E_{\text{H}^+|\text{H}_2} - E_{\text{SHE}} \\ E_{\text{cell}} &= E_{\text{H}^+|\text{H}_2} - 0 \\ E_{\text{cell}} &= E_{\text{H}^+|\text{H}_2} \end{aligned}$$

Now the half cell reaction at cathode is-



So, the Nernst equation for above half cell will be-

$$\begin{aligned} E_{\text{H}^+|\text{H}_2} &= E_{\text{H}^+|\text{H}_2}^0 - \frac{0.0591}{1} \log \frac{[\text{H}_2]^{\frac{1}{2}}}{[\text{H}^+]} \\ E_{\text{H}^+|\text{H}_2} &= 0 - 0.0591 \log \frac{1}{[\text{H}^+]} \\ E_{\text{H}^+|\text{H}_2} &= -0.0591 \text{pH} \end{aligned}$$

Replacing this value in above equation-

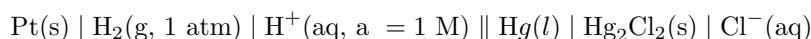
$$\begin{aligned} E_{\text{cell}} &= -0.0591 \text{pH} \\ \text{pH} &= \frac{E_{\text{cell}}}{-0.0591} \end{aligned}$$

Thus pH of a solution can be determined from observed value of an properly constructed electrochemical cell.

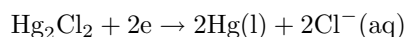
Measure of pH of a solution by using standard hydrogen electrode and a calomel electrode:

Calomel electrode is a half cell electrode which can be used as a reference electrode. In combination of calomel electrode and another unknown electrode, the potential of the later can be calculated from observed cell potential value. Calomel electrode can be constructed by using mercury, mercurous chloride, and KCl solution in a glass tube. As depicted in the picture, mercury (Hg) is taken in the glass tube and on top of this a paste of mercury and mercurous chloride (Hg_2Cl_2) is placed. Finally a known concentration of KCl solution placed on top of the paste in such a way that no mixing happens. A Pt wire is attached to mercury layer only which is connected to electrical circuit.

An electrochemical cell can be constructed by using standard hydrogen electrode as anode and calomel electrode as cathode-



The cathode half cell reaction for calomel electrode will be-



We can express the cell potential for this half cell by using Nernst equation-

$$\begin{aligned} E_{\text{Hg}_2\text{Cl}_2|\text{Hg}} &= E_{\text{Hg}_2\text{Cl}_2|\text{Hg}}^0 - \frac{0.0591}{2} \log[\text{Cl}^-]^2 \\ E_{\text{Hg}_2\text{Cl}_2|\text{Hg}} &= 0.27 - 0.0591 \log[\text{Cl}^-]; (E_{\text{Hg}_2\text{Cl}_2|\text{Hg}}^0 = 0.27\text{V}) \end{aligned}$$

From the above equation we can say that the value of calomel half cell potential depends on chloride ion concentration. If we can fix the concentration of KCl or the chloride ion concentration of a calomel electrode, the half cell potential can be determined. In reality three varieties of calomel electrode available depending upon KCl concentration.

Now, the cell potential of this electrochemical cell can be expressed as-

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ E_{\text{cell}} &= E_{\text{Hg}_2\text{Cl}_2|\text{Hg}} - E_{\text{H}^+|\text{H}_2} \\ E_{\text{cell}} &= E_{\text{Hg}_2\text{Cl}_2|\text{Hg}} - (-0.00591\text{pH}) \\ E_{\text{cell}} &= E_{\text{H}^+|\text{H}_2} + 0.0591\text{pH} \\ \text{pH} &= \frac{E_{\text{cell}} - E_{\text{Hg}_2\text{Cl}_2|\text{Hg}}}{0.0591} \text{ [at 298K]} \end{aligned}$$

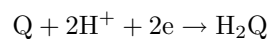
The value of proper calomel electrode potential is available in literature depending upon chloride ion concentration and the observed value for cell potential can be determined from experiment. Hence we can calculate the pH of a acidic solution.

4.9 Quinhydrone electrode

It is a redox electrode where oxidation and reduction happens on organic substrate quinone and hydroquinone. An equimolar solution of quinone and hydroquinone is used here and the platinum

wire of the calomel electrode is attached to it.

The Nernst equation for this half cell reaction will be like-



$$E_{Q|H_2Q} = E_{Q|H_2Q}^0 - \frac{0.0591}{2} \log \frac{[H_2Q]}{[Q][H^+]^2}$$

$$E_{Q|H_2Q} = E_{Q|H_2Q}^0 - \frac{0.0591}{2} \log [H^+]^2$$

$$E_{Q|H_2Q} = E_{Q|H_2Q}^0 + \frac{0.0591}{2} \log [H^+]^2$$

$$E_{Q|H_2Q} = E_{Q|H_2Q}^0 + 0.0591 \log [H^+]$$

$$E_{Q|H_2Q} = E_{Q|H_2Q}^0 - 0.0591 \text{pH}$$

$$\text{pH} = \frac{E_{Q|H_2Q}^0 - E_{Q|H_2Q}}{0.0591}$$

Thus pH can be determined by using quinhydrone electrode.